CROSSLINKING KINETICS
IN
FREE-RADICAL COPOLYMERIZATION

By

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CROSSLINKING KINETICS IN FREE-RADICAL COPOLYMERIZATION

To my wife, Yuko
and my parents,
Syoichi and Yoshiko

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ABSTRACT

A new kinetic theory for free radical copolymerization with long chain branching and crosslinking is proposed. This kinetic theory accounts for the history of the generated network structure as well as for all of the important elementary reactions in free radical polymerization. The present theory can be used to make calculations of various important properties such as onset of gelation, weight fraction of sol and gel, number- and weight-average chain length of sol fractions, crosslinking density in sol and gel fractions, etc. Since free radical polymerization is kinetically controlled, each primary polymer molecule experiences a different history of crosslinking and cyclization. The present theory proves the existence and permits the calculation of the crosslinking density distribution, although all statistical models which assume an equilibrium system inevitably employ the assumption that the crosslinking density is the same for all chains. The existence of a crosslinking density distribution with a significant variance is an important feature of the present kinetic theory stating that polymer networks synthesized by free radical polymerization are inherently inhomogeneous on a microscopic scale. This theory reduces to the Flory/Stockmayer theory under Flory's simplifying assumptions and may therefore be considered a general mean-field theory.

The present theory was successfully applied to the copolymerization of methyl methacrylate/ethylene glycol dimethacrylate, and acrylamide/N,N'-methylene-bis-acrylamide. In real systems it was found that the effect of cyclization (intramolecular reactions) and the decreased reactivity of pendant double bonds relative to the monomeric double bonds are important.

This new kinetic theory should assist one to design superior quality network polymer systems and it can also be used to control various polymerization processes. It was found that if branches are formed by chain transfer to polymer the crosslinking density is always higher in continuous stirred tank reactors (CSTR) than in batch reactors, however, this is not true in general for vinyl/divinyl copolymerizations. The variance of the crosslinking density distribution in CSTR's is large due to their broad residence time distributions.

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1. INTRODUCTION

Recently, the polymeric network (gel) has become a very attractive research area combining at the same time fundamental and applied topics of great interest. Especially, the synthesis of network polymers with controlled structure may permit the development of a whole range of useful polymer products. This has been motivated in part by the phenomenal success achieved by superabsorbent polymers, which can absorb as much as 1000-gram of water per gram of polymer, and are currently applied to baby diapers. In a polymer synthesis, a polymer network may be formed if at least one of the components possesses functionality higher than two. The reaction types which lead to network formation may be conveniently divided into three groups.

1) Step-wise polyaddition or polycondensation reactions.
2) The crosslinking of pre-formed polymer chains such as by vulcanization and radiation.
3) Crosslinking chain (co)polymerization, such as free radical copolymerization of vinyl and divinyl monomer.

Since the physical properties of polymeric networks strongly depend on the polymerization kinetics, understanding of the kinetics of network formation is indispensable. As for the modeling of network formation, various models have been proposed since the pioneering work of Flory

[Flory (1941a,b,c),(1942),(1953)] and Stockmayer [Stockmayer (1943), (1944)]. Usually, basic theories have been developed for step-wise polymerization as a simplest mechanism of network formation in which an equilibrium system can be assumed, and these theories have been applied to other mechanisms of network formation with minor modification. Generally, for an f-functional polycondensation system, agreement with data for real systems is quite often satisfactory, however, no theory published prior to this investigation can give satisfactory predictions for a free radical polymerization system, which is of significant commercial interest. This is partly attributed to the characteristic reaction scheme of free radical polymerization, namely, the system is a non-equilibrium one and a crosslinkage is formed only through a polymer radical whose concentration is fairly low and whose life time is very short, and therefore, the existence of other chains of different ages during its growth has significant effects on the kinetics of network formation. In order to build a realistic model for network formation in free radical polymerization, it is necessary for the model to account for these important features.

The main objective of this research is to develop a realistic theory for network formation, which properly accounts for all of the important reactions in free radical polymerization.

1.1. Theoretical Background and Literature Review

In the course of network formation, a polymer molecule of effectively infinite molecular weight may be formed. At this point, termed the gel point, one first observes the visible formation of a gel molecule or insoluble polymer fraction. The gel molecule is insoluble in any solvent even at elevated temperature under conditions where polymer degradation does not occur. Various properties such as viscosity and modulus change abruptly right at the gel point. A simple example is shown in Figure 1.1.1. Gelation should be understood as a critical phenomenon, and possesses similarities with other critical phenomena such as vapour-liquid condensation, nuclear chain reactions, and ferromagnetism.

Network polymers can not be characterized solely by molecular weight distribution and copolymer composition such as the case of linear polymers. Information on network structure, such as crosslinking density, functionality at branching points, chain length distribution between crosslinks, number of elastically ineffective chains, and entanglement involving a pair of internal chains, has a significant effect on the physical and mechanical properties of network polymers. Although new analytical techniques are being developed [Harrison et al. (1985); Andreis, Koenig (1989); Shiga (1989)], a comprehensive characterization of a branched polymer sample is still a formidable task. A schematic example of polymer network synthesized during vinyl/divinyl copolymerization is shown in Figure 1.1.2. There may be many

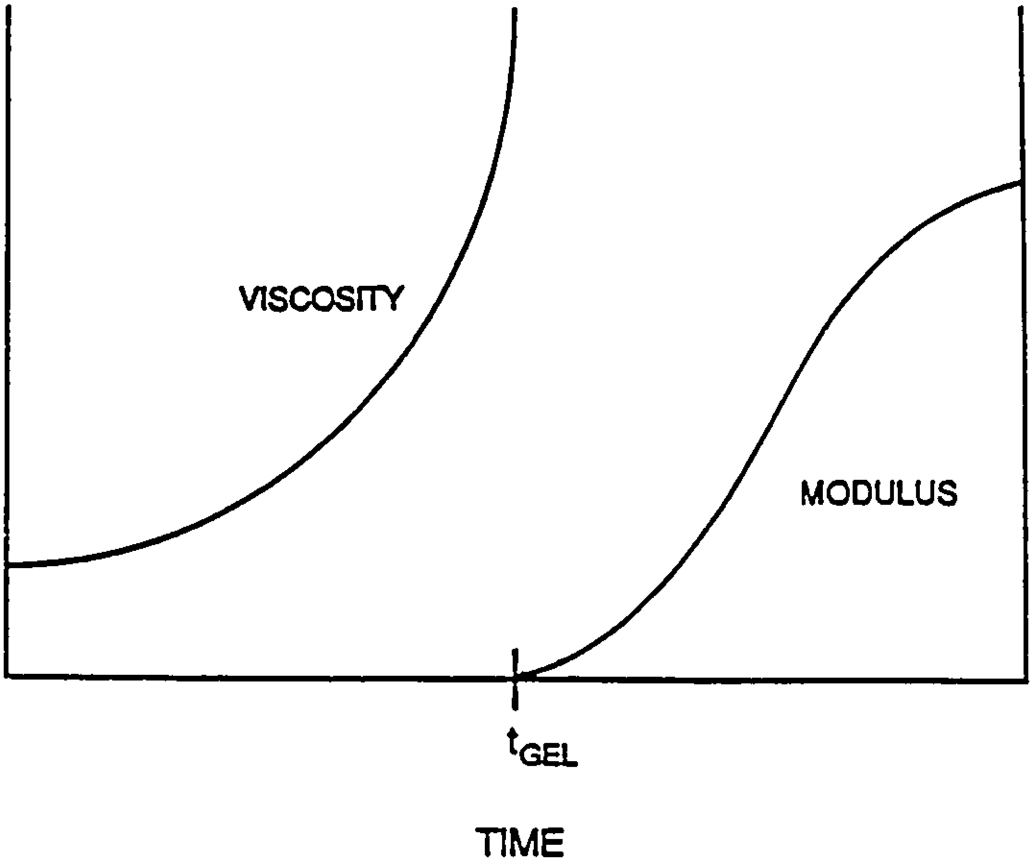


Figure 1.1.1 Viscosity and shear modulus as a function of reaction time. (Taken from [Landin (1985)].)

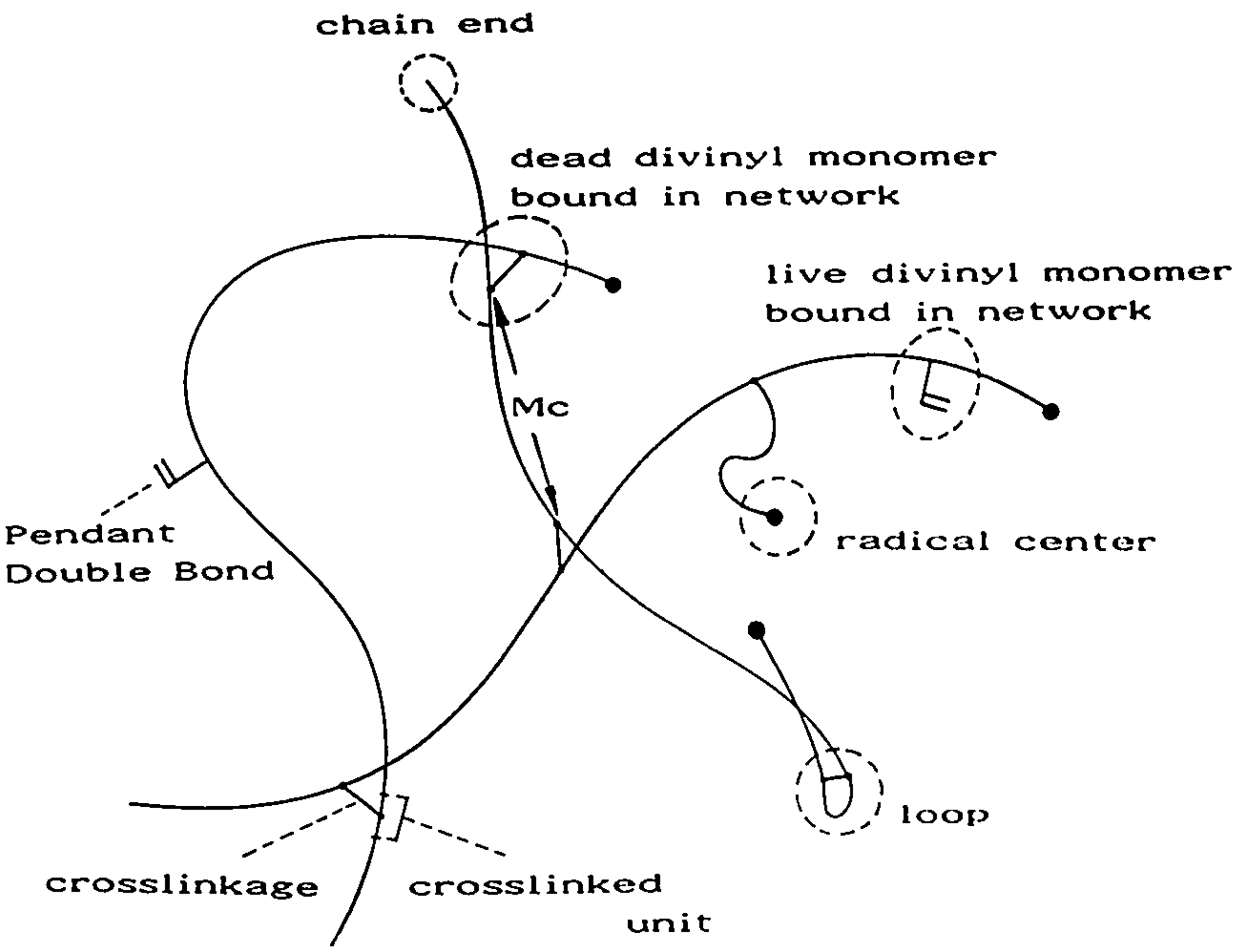


Figure 1.1.2 A schematic drawing of crosslinked polymer networks synthesized by free radical copolymerization of vinyl and divinyl monomer.

radical centers on a network polymer during polymerization since the mobility of chains bound in network polymer is restricted. The live double bonds located on polymer chains are called pendant double bonds. Kinetic behavior of radical centers on polymer chains and that of pendant double bonds are the most important factors which must be considered to understand the kinetics of network formation in free radical polymerization. The number-average molecular weight, M_c, is important from the point of view of the elastic property of a gel molecule. Since crosslinked unit is defined as a unit which bears a tri-branching point, one dead divinyl monomer forms two crosslinked units.

[A] Modeling of Network Formation

It was Carothers [Carothers (1936)] who first derived an equation for the extent of reaction at the gel point. He defined a gel molecule as one with an infinitely large molecular weight. His criterion that gelation occurs when the number average chain length, $\overline{P}_n$, goes to infinity is not acceptable, since polymer molecules larger than $\overline{P}_n$ are always present and will become gel molecules earlier than the hypothetical gel point. However, the concept of "infinitely large molecule", which was still controversial at that time, was fully established by Flory [Flory (1941a,b,c)] using a statistical approach. Various theories have been proposed for network formation since the pioneering work of Flory. The existing theoretical approaches can be divided into three categories, namely, **classical**, **percolation**, and **kinetic** theory. Let us first examine these approaches.

[A-1] Classical Theory

Flory [Flory (1941a,b,c),(1942),(1953)] devised a simple tree-like model. His basic proposal was that the gel point is reached when the expectancy of finding next generation in a particular existing molecule is unity. For the tri-functional monomer units shown in Figure 1.1.3., the conversion of functional groups at the gel point is given by $p_C = 1/(f-1) = 0.5$, where f is the functionality of a monomer unit. His model was a brilliant development and it provides the starting point for most theories of polymeric network formation. A few years later Stockmayer [Stockmayer (1943),(1944)] further developed Flory's idea based on the most probable size distribution. From the beginning Stockmayer emphasized the similarities with other critical phenomena such as vapor-liquid condensation, and these similarities are recently quite often argued especially by physicists as "universality" of critical phenomena. The Flory/Stockmayer model is usually called the classical theory, and enjoys the simplicity of a mean-field theory.

This tree-like concept was generalized by Gordon et al. [Gordon (1962); Gordon, Ross-Murphy (1975)] based on the theory of stochastic branching processes, and recently summarized as a part of Graph Theory [Gordon, Temple (1976); Kuchanov et al. (1988)]. This technique involves abstract mathematics and requires the derivation of the probability generating functions. The method is general but rather difficult to use for real problems. To avoid the use of probability generating functions, other probabilistic methods [Pearson, Graessley

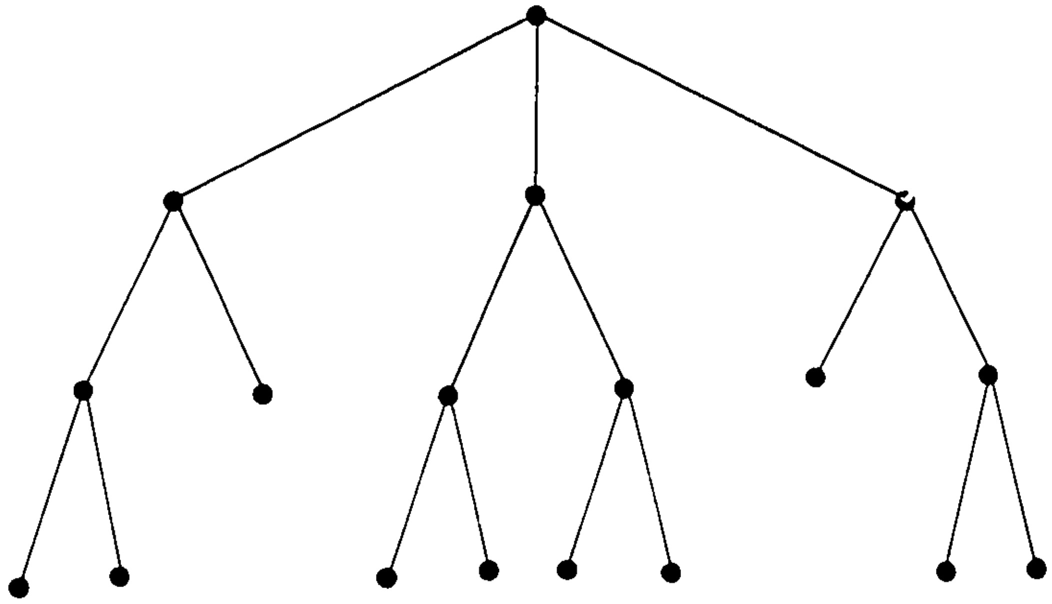


Figure 1.1.3 A schematic drawing of Flory's tree-like model. (functionality, f = 3) This tree-like model is called the Bethe lattice or Cayley tree by physicists.

(1978); Macosko, Miller (1976); Miller, Macosko (1976),(1988); Durand, Bruneau (1982a,b),(1985a,b)] have been developed. Among them the Macosko-Miller model using conditional probabilities is becoming popular due to its simplicity. Although the original Macosko-Miller model could not account for the effect of termination by combination in free radical polymerization [Tobita, Hamielec (1988)], recently it was successfully modified [Dotson et al. (1988)].

All these models are fully equivalent, that is, only the mathematical language is slightly different [Dusek (1984)]. Classical theory has a long history and has proven its power of refinability to accommodate highly system-specific effects especially for polycondensation systems, such as unequal reactivity [Miller, Macosko (1978); Durand, Bruneau (1979a),(1983a)], substitution effect [Gordon, Scantlebury (1966); Gordon, Malcolm (1966); Durand, Bruneau (1979b), (1983b); Miller, Macosko (1980)], cyclization [Kilb (1958); Gordon, Scantlebury (1968); Temple (1972); Stanford et al. (1975), Stepto (1982)].

[A-2] Percolation Theory

All models mentioned above belong to a mean-field theory. On the other hand, the percolation theory [Broadbent, Hammersley (1957); Hammersley (1957); Frisch, Hammersley (1963); Essam (1972); Kirkpatrick (1973); Domb et al. (1980); Stauffer (1985)], which is considered to be equivalent to a non-mean-field theory, has been applied to polymeric gelation [Stauffer et al. (1982); Durand (1986)]. The percolation theory is usually associated with a lattice model to describe network structure. One of the simplest examples in two-dimensional lattices is shown in Figure 1.1.4. In Figure 1.1.4, each bond which has been formed is shown as a short line connecting two monomers though monomers are not shown. In the random (standard) percolation each site of a very large lattice is occupied randomly with probability p, independent of neighbours. One sees some nearly "infinite" molecules in Figure 1.1.4, where "infinite" means that they span the whole sample. Mathematical methods to calculate this threshold exactly are restricted so far to two dimensions [Stauffer (1985)], and therefore, in the practical calculations the Monte Carlo simulation is usually used. It is easy to understand why gelation is a critical phenomenon using the lattice model, namely, at the vicinity of gel point only a few bondings are necessary to form a molecule which spans the whole sample. The percolation models emphasize the universality of critical phenomena and space dimensionality. De Gennes wrote in his book [de Gennes (1979)] that "it took more than 30 years to convince experimentalists that mean-field theory was wrong". However, any non-mean-field theory other than percolation theory has not been proposed yet for polymeric gelation, and present percolation models are far from simulating actual network formation, namely, the bonds are too rigid, the movement of molecules is too suppressed, and necessary chemical rules of bond formation are ignored. The percolation theory is essentially devoted to describe the

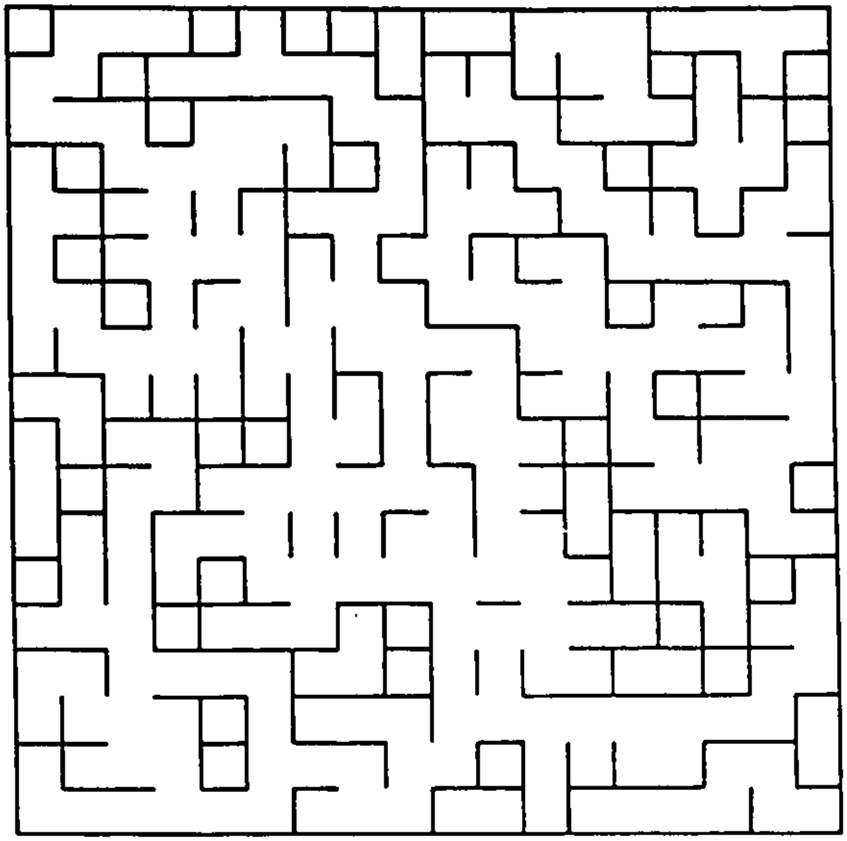


Figure 1.1.4 Example of percolation at the gel point in a square lattice. ($p_c = 0.5$) (Taken from [Stauffer et al. (1982)].)

behavior near the critical threshold p_c (gel point) where the system-specific features are not important, and this simple method is used to determine the critical exponents based on the scaling concepts. However, even in the vicinity of the gel point no clear answer has been found to clarify whether the percolation theory agrees with reality mainly due to experimental difficulties. For instance, for the viscosity a power law $(p_c - p)^{-0.78}$ [Adam et al. (1981)] agrees with the percolation theory, while the elastic shear modulus of gel changes roughly as $(p - p_c)^3$ in some experiments [Adam et al. (1981); Gordon, Torkington (1981)], which agrees better with classical theory. Though the percolation theory emphasizes space dimensionality, Gordon [Gordon (1984)] pointed out that the excluded-volume effect, which seems so important based on intuition, does not have a significant effect. At present it is still considered controversial and unclear which theory is more suitable for polymeric gelation even for the critical change. However, what is really important is not to decide which model is more appropriate but to refine both types of models, and several efforts of refinements for the percolation theory are being done [Herrmann et al. (1983); Leung, Eichinger (1984a,b); Bansil et al. (1984),(1985); Stanley et al. (1985); Balazs et al. (1987); Boots (1988); Simon et al. (1989)].

[A-3] Kinetic Theory

Generally these statistical theories give satisfactory predictions for an f-functional polycondensation systems. However, no theory published prior to this investigation can give satisfactory predictions for a free radical polymerization system. From a theoretical point of view this is not surprising, because the network formation by free radical polymerization is a non-equilibrium system, namely, it is kinetically controlled. Therefore, the application of the conventional statistical models in which an equilibrium system is assumed is only an approximation. (In the models which assume an equilibrium system, the size distribution is calculated anew at each time (or conversion), and these models do not consider the kinetic build up of the system.) In order to include the effect of information stored in the generated structure, kinetic approach is desirable.

The kinetic approach was originally shown in the appendix of Stockmayer's paper [Stockmayer (1943)]. Based on the chemical kinetics, the reaction rate would be proportional to the product of the number of unreacted functional groups in the respective reaction partner. This approach is, essentially, equivalent to Smoluchowski's coagulation equation.

$$(dc_k/dt) = (1/2) \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1} K_{kj} c_j \qquad (1.1.1)$$

where c_s is the time dependent concentration of s-clusters $(s=1,2,3,\ldots,i,j,k,\ldots)$ and K_{ij} is a concentration independent collision kernel which describes the aggregation mechanism. Therefore, the time change in the concentration of molecules of each size is given by an infinite set of differential equations that include kinetic rate constants. This idea has been applied to polymeric systems [Saito (1958),(1972); Inokuchi (1963); Kuchanov, Pismen (1971),(1972); Dusek (1979); Mikes, Dusek (1982); Donoghue, Gibbs (1979); Galina, Szustalewicz (1989)]. The major drawback in these kinetic approaches is that the system of equations are mathematically fairly difficult to solve, although some progress is being made [Kuchanov, Povalotskaya (1982a,b)].

When branched polymers are produced by chain transfer to polymer, an infinite set of differential equations can be solved using the method of moments [Bamford et al. (1953),(1954),(1958); Graessley et al. (1965),(1967); Saito et al. (1969)]. Mikos et al. [Mikos et al. (1986)] applied the method of moments to vinyl/divinyl copolymerization, however, they considered only the first order moment in the pre-gelation period, and therefore, the model fails to predict some of the very important properties such as weight-average chain length of sol and weight fraction of sol, and furthermore, the definition of the gel point was incorrect [Tobita, Hamielec (1989)]. Their failure mainly arises from the fact that the kinetic treatment of copolymerization is very complicated. As is shown in Section 2.1, we applied the pseudo-kinetic rate constant method in order to simplify the kinetic treatment of multicomponent polymerization, and derived general moment equations (Section 2.4).

As was mentioned earlier, application of conventional classical theories to a kinetically controlled system is an approximation, however, modifications to account for the kinetic build up are being done [Landin (1985); Dotson et al. (1988)].

[B] Experimental Observations

In this section let us review the experimental results and consider necessary refinements in order to apply basic theories to an actual network formation by free radical polymerization. For vinyl/divinyl copolymerization, it is well-known that the Flory model functions best at low mole fraction of divinyl monomer, and the error increases with increasing mole fraction of divinyl monomer. Flory assumed the following simplifying assumptions in order to derive his basic equations.

[Flory's Simplifying Assumptions]

1) The reactivities of all types of double bonds are equal.
2) All double bonds react independently of one another.
3) There is no intramolecular reaction in finite molecules.

Unfortunately, none of the above assumptions are fulfilled in a real system. The problems may mainly be attributed to three points, namely, reactivity of pendant double bonds, effect of intramolecular reactions (cyclization), and copolymer composition drift for vinyl/divinyl copolymerizations.

[B-1] Reactivity of Pendant Double Bonds

The first model which accounts for the delay of gel point was proposed by Walling [Walling (1945)]. He assumed pre-gelation branched polymers as discrete masses which are highly swollen by the solvent, and that the diffusion controlled crosslinking reaction delays the gel point. However, his model was shown to be incorrect in a series of papers by Gordon and Roe [Gordon, Roe (1956a,b,c,d)] who found that the termination step, which should depend more strongly on diffusion, is quite often unaffected by diffusion control until after the gel point. Minnema and Staverman [Minnema, Staverman (1958)] on the other hand proposed that the reactivity of pendant double bond decreases due to steric hindrance called "shield effect". It is still unclear whether this "shielding" affects the reactivity of small molecules, however, it may affect the reaction rate of huge molecules with dense core [Dusek (1982)], and at least apparent reactivity of pendant double bonds seems to be decreased [Whitney, Burchard (1980)]. Whether "shielding" is caused by its low mobility or imposed steric hindrance or the inability of macroradicals to propagate inside such a structure, it may be reasonable to assume a decreased reactivity of pendant double bonds in a modeling of network formation. Hild et al. [Okasha et al. (1979); Hild, Rempp (1981); Hild, Okasha (1985a,b,c)] argued that a decreased reactivity of pendant double bonds is the main cause of the delay of gelation. Landin and Macosko [Landin, Macosko (1988)], who measured the number of pendant double bonds by ^{1}H NMR, found that both decreased reactivity of pendant double bonds and intramolecular reactions are responsible for the delay of gel point.

[B-2] Effect of Cyclization

A strong cyclization is characteristic for free radical polymerization which includes divinyl monomer [Dusek (1982)]. The fraction of initially cyclized pendant double bonds is as high as 40% in diallyl phthalate [Simpson et al. (1953)], and even for styrene / p-divinylbenzene the polymer chains are extensively cyclized with the formation of a relatively large number of small rings at low conversions [Soper et al. (1972)]. The fraction of intramolecular cyclization depends strongly on dilution, mole fraction of divinyl monomer, solvent used and to a lesser extent on the length of the crosslinker chain [Bates, Haward (1967); Soper et al. (1972); Ishizu et al. (1986)]. In some cases compact internally cyclized molecules are formed in the early stage of reaction even if phase separation does not occur. These molecules resemble microgel particles with a relatively dense core [Spevacek, Dusek (1980)]. A model for such systems must take into account two steps, namely, the formation of microscopic gel-like particles and interlinking of these particles [Bobalek et al. (1964); Storey (1965); Dusek (1982)].

As for the theoretical treatment of cyclization, several studies have been done for solid polymer [Graessley (1964)], and polycondensation systems [Jacobson, Stockmayer (1950); Kilb (1958);

Gordon (1968); Stepto (1982); Roland, Macosko (1987)]. For free radical polymerization, Dusek and Ilavsky (1975a,b) proposed a model in the context of the theory of stochastic branching [Gordon (1962); Gordon, Ross-Murphy (1975)]. One of the important features of cyclization is that it is controlled not by conventional rate law using average concentrations of functional groups but by conformational statistics of the sequence of bonds.

[B-3] Copolymer Composition

There are complications in the formulation of the copolymer composition equation for vinyl/divinyl copolymerization. If the reactivities of both double bonds on divinyl monomer are the same and independent (the classification of divinyl monomer is shown in Table 2.1.2.), and cyclization does not affect the copolymer composition, the conventional copolymer equation, the Mayo-Lewis equation [Mayo, Lewis (1944)], is valid when monomer concentration is replaced by double bond concentration and by using the reactivity ratios defined with respect to each type of double bond [Gibbs (1964)]. However, in general difficulties arise due to the complicated behavior of pendant double bonds, namely, they may react intermolecularly and intramolecularly, and the reactivity of pendant double bond may not be the same as that for monomeric double bonds. Although various composition equations for vinyl/divinyl copolymerization have been proposed [Roovers, Smets (1963); Gibbs, McHenry (1964); Braun, Brendlein

(1973); Matsumoto et al. (1973); Dusek, Spevacek (1980)], all equations may not be realistic for vinyl/divinyl copolymerization especially with high mole fractions of divinyl monomer. Strictly, in order to know the copolymer composition, it is necessary to know the kinetic behavior of pendant double bonds completely, i.e., a knowledge of reactivity ratios r_1 and r_2 is insufficient to calculate the change in copolymer composition during polymerization. However, usually copolymerization parameters r_1 and r_2 have been obtained without taking into account the monomer consumption by radical centers located on pendant double bonds. Such parameters should be recognized as empirical parameters, and they may not reflect true chemical reactivities, except for the cases in which the mole fraction of divinyl monomer is low enough or at the initial stage of reaction. (More discussion is given in Section 2.1-[B].)

1.2. Scope of Study

The main objective of this research is to build a comprehensive and realistic model for network formation in free radical copolymerization, which should assist one to design superior quality network polymer systems. This work is partly motivated by the increasing use of lightly crosslinked gels such as the super absorbent polymers and gels for gel permeation chromatography (GPC). However, as new fundamental knowledge is elucidated, this work should contribute to the advancement of production technology for whole class of crosslinked polymers which are of significant commercial interest. (It is said that approximately 80% of synthetic polymers used commercially are crosslinked [Andreis, Koenig (1989)].) In building a new model, we wished to account for the important features of free radical polymerization, namely, the system is kinetically controlled and the kinetics involve various elementary reactions.

As was discussed in Section 1.1-[A], there are mainly two trends in the modeling of network formation, namely, classical approaches which belong to a mean-field theory such as classical statistical and kinetic theories, and modern approaches such as percolation theory which is considered to be equivalent to a non-mean-field theory. There is a clear difference between these approaches in the fundamental attitude. The classical approaches aim to predict the whole course of network formation and try to give the criticality of the gelation phenomenon from its circumference, while modern approaches work outwards from a critical singularity. Quite often physicists are more interested in the critical change at the gel point, and they prefer modern approaches. However, from an engineering point of view, what is more important is the whole course of network formation rather than the critical change at the gel point, and to synthesize superior quality network polymer as a final product. Our standpoint, basically, resides in the classical approach, though we use chemical kinetics rather than statistics.

First, in order to simplify the kinetic treatment of a multicomponent polymerization, we developed "the pseudo-kinetic rate constant method" for polymers with long chain branches as well as linear polymers (Section 2.1.). Applying this method, the kinetic treatment of the formation of primary polymer molecules (linear chains) in a multicomponent polymerization reduces to that of a homopolymerization. It was clarified where specific approximations are made and where these approximations are acceptable.

By application of the chemical kinetics for crosslinking reactions, equations not only for the calculation of the overall (average) crosslinking density but also of the "crosslinking density distribution" have been derived (Section 2.2.). In free radical polymerization each primary polymer molecule experiences a different history of crosslinking, and therefore, the crosslinking density of a primary polymer molecule is dependent on its birth time. Conventional models in which an equilibrium system is assumed inevitably employ the assumption that the crosslinking density is the same for all chains, however, this is not true for free radical polymerization. The concept of crosslinking density distribution is completely new, and it has changed one of the limitations of conventional mean-field approaches.

In order to apply a model for network formation to a real system, consideration of cyclization is necessary, although most of the fundamental models neglect this effect. Strict treatment of cyclization for free radical polymerization in a mean-field theory seems to be a formidable task especially at high conversions. We have developed some very simple models for cyclization reactions (Section 2.3.).

To describe various average properties in the pre-gelation period, we have developed a model using the method of moments (Section 2.4.). The model considers all of the important reactions in free radical polymerization, and under special limiting conditions reduces to Flory's theory. It has also been proven that although chain transfer to polymer with termination by disproportionation never causes gelation, if the bimolecular termination reaction includes combination, gelation is predicted to occur under certain conditions.

For the post-gelation period in order to account for the kinetic features of free radical polymerization, Flory's theory for the post-gelation theory has been generalized using the crosslinking density distribution (Section 2.5). This method has given satisfactory predictions for the copolymerization of methyl methacrylate/ethylene glycol dimethacrylate (Section 3.1.).

These kinetic approaches are also applied to the copolymerization of acrylamide/N,N'-methylene-bis-acrylamide in aqueous solution, which is considered to be a highly non-ideal system (Section 3.2.).

As a preliminary attempt to apply these fundamental concepts to polymer reaction engineering, the effect of reactor type (batch, semi-batch, and continuous stirred tank reactor (CSTR)) on the crosslinking density has been investigated (Section 3.3.). It was found that although the CSTR gives higher crosslinking densities than batch reactors when long chain branches are formed by chain transfer to polymer, this is not true in general for vinyl/divinyl copolymerizations.

Finally, the prospect for more realistic models is discussed in Chapter 4, and conclusions are given in Chapter 5.

The fundamental structure of this research is summarized in Figure 1.2.1.

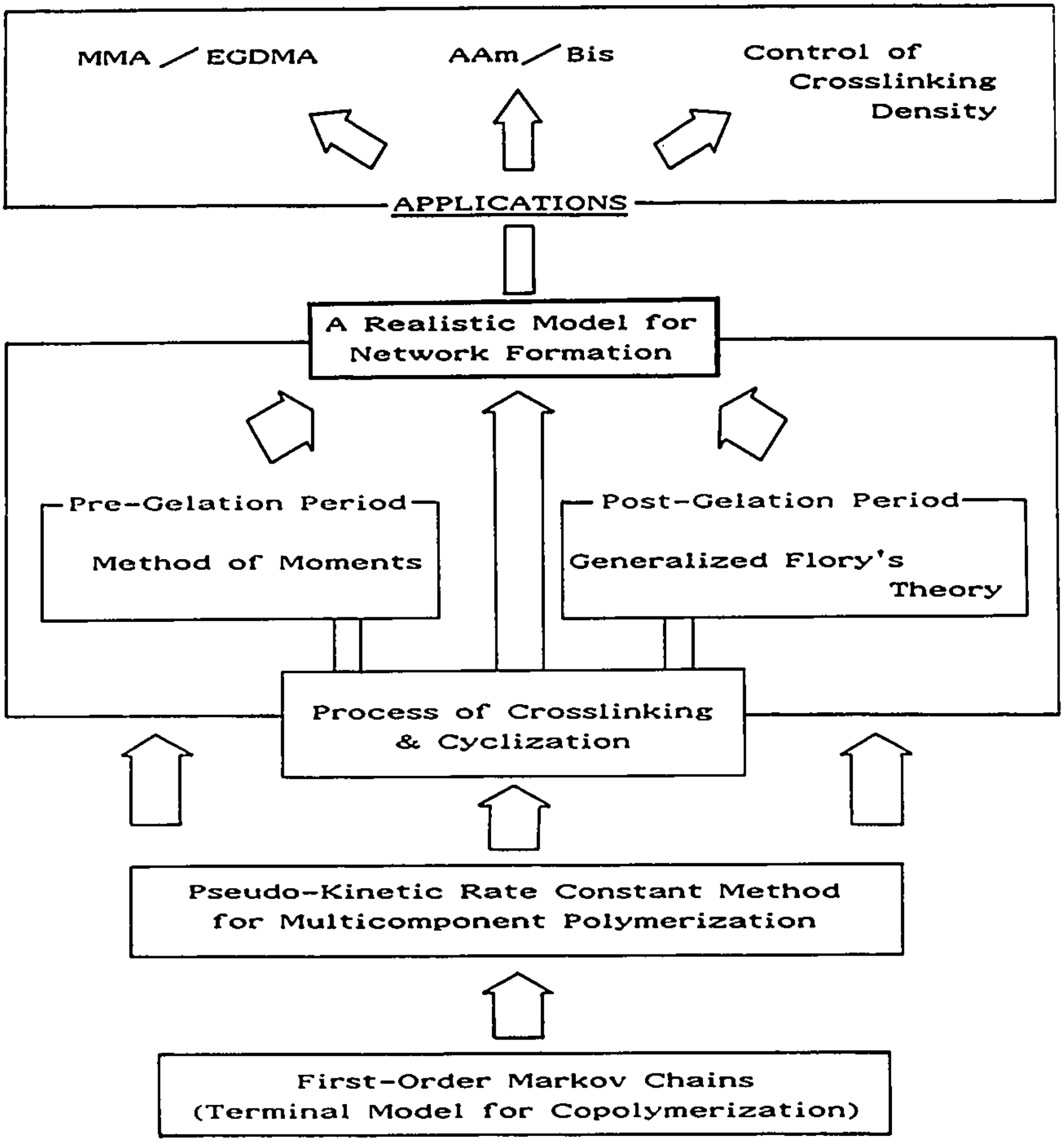


Figure 1.2.1 Fundamental structure of the present research.

2. KINETIC MODEL DEVELOPMENT

2.1. Pseudo-Kinetic Rate Constant Method

[A] Linear Coplymers

The pseudo-kinetic rate constant method for multicomponent polymerization has been applied in some copolymerization studies [Hamielec et al. (1983),(1987); Broadhead et al. (1985)]. However, it is important to make its substance and derivation clear. Here, we clarify where specific approximations are made and where these approximations are acceptable.

Let us consider the copolymerization of monomer M_1 and M_2 assuming the terminal model for copolymerization [Alfrey, Goldfinger (1944a); Mayo, Lewis (1944); Wall (1944)] is applicable. Important elementary reactions are listed in Table 2.1.1. In the table, $R^{\bullet}_{m,n,1}$ and $R^{\bullet}_{m,n,2}$ are polymer radicals with m-units of monomer 1 (M_1) and n-units of monomer 2 (M_2) bound in the polymer chain and active center located on monomer units 1 and 2. $P_{m,n}$ is a polymer molecule with m-units of monomer 1 and n-units of monomer 2. As is shown in Table 2.1.1, a free radical copolymerization involves various elementary reactions, and as the number of components increases kinetic expressions become fairly complicated [Alfrey, Goldfinger (1944b); Odian (1981)]. In order to avoid such complications we use the pseudo-kinetic rate

Table 2.1.1 Elementary reactions for free radical copolymerization

Initiation

$$I \longrightarrow 2R^{\bullet}_{in} \qquad (k_d)$$
$$R^{\bullet}_{in} + M_1 \longrightarrow R^{\bullet}_{1,0,1} \qquad (k_1)$$
$$R^{\bullet}_{in} + M_2 \longrightarrow R^{\bullet}_{0,1,2} \qquad (k_2)$$

Propagation

$$R^{\bullet}_{m,n,1} + M_1 \longrightarrow R^{\bullet}_{m+1,n,1} \qquad (k_{11})$$
$$R^{\bullet}_{m,n,1} + M_2 \longrightarrow R^{\bullet}_{m,n+1,2} \qquad (k_{12})$$
$$R^{\bullet}_{m,n,2} + M_1 \longrightarrow R^{\bullet}_{m+1,n,1} \qquad (k_{21})$$
$$R^{\bullet}_{m,n,2} + M_2 \longrightarrow R^{\bullet}_{m,n+1,2} \qquad (k_{22})$$

Transfer to Monomer

$$R^{\bullet}_{m,n,1} + M_1 \longrightarrow P_{m,n} + R^{\bullet}_{1,0,1} \qquad (k_{f11})$$
$$R^{\bullet}_{m,n,1} + M_2 \longrightarrow P_{m,n} + R^{\bullet}_{0,1,2} \qquad (k_{f12})$$
$$R^{\bullet}_{m,n,2} + M_1 \longrightarrow P_{m,n} + R^{\bullet}_{1,0,1} \qquad (k_{f21})$$
$$R^{\bullet}_{m,n,2} + M_2 \longrightarrow P_{m,n} + R^{\bullet}_{0,1,2} \qquad (k_{f22})$$

Transfer to Small Molecule

$$R^{\bullet}_{m,n,1} + T \longrightarrow P_{m,n} + T^{\bullet} \qquad (k_{fT1})$$
$$R^{\bullet}_{m,n,2} + T \longrightarrow P_{m,n} + T^{\bullet} \qquad (k_{fT2})$$

Termination by Disproportionation

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,1} \longrightarrow P_{m,n} + P_{r,s} \qquad (k_{td11})$$
$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,2} \longrightarrow P_{m,n} + P_{r,s} \qquad (k_{td12})$$
$$R^{\bullet}_{m,n,2} + R^{\bullet}_{r,s,2} \longrightarrow P_{m,n} + P_{r,s} \qquad (k_{td22})$$

Termination by Combination

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,1} \longrightarrow P_{m+r,n+s} \qquad (k_{tc11})$$
$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,2} \longrightarrow P_{m+r,n+s} \qquad (k_{tc12})$$
$$R^{\bullet}_{m,n,2} + R^{\bullet}_{r,s,2} \longrightarrow P_{m+r,n+s} \qquad (k_{tc22})$$

constant method.

Let us consider a simple example. The propagation rate R_p for homopolymerization is given by

$$R_p = k_p\,[R^\bullet][M] \qquad (2.1.1)$$

However, this equation is also applicable for binary copolymerizations if the propagation rate constant k_p is defined as follows.

$$k_p = (k_{11}f_1 + k_{12}f_2)\,\Phi_1^\bullet + (k_{21}f_1 + k_{22}f_2)\,\Phi_2^\bullet \qquad (2.1.2)$$

where $f_1 = [M_1]/[M]$, $f_2 = [M_2]/[M]$, $\Phi_1^\bullet = [R_1^\bullet]/[R^\bullet]$, $\Phi_2^\bullet = [R_2^\bullet]/[R^\bullet]$, $[M]$ is the total monomer concentration ($= [M_1]+[M_2]$), $[R_1^\bullet]$ and $[R_2^\bullet]$ are polymer radical concentrations whose active center is located on monomer unit 1 and 2, and $[R^\bullet]$ is the total polymer radical concentration ($=[R_1^\bullet]+[R_2^\bullet]$).

Equation (2.1.2) shows an example of a pseudo-kinetic rate constant. Applying pseudo-kinetic rate constants, the kinetic treatment of a multicomponent polymerization reduces to that of a homopolymerization. For an N-component system, the pseudo-kinetic rate constants can be defined as follows.

<u>Propagation</u>

$$k_p = \sum_{\substack{i=1\\ j=1}}^{N} k_{ij}\,\Phi_i^\bullet\, f_j \qquad (2.1.3)$$

Transfer to Monomer

$$k_{fm} = \sum_{\substack{i=1\\j=1}}^{N} k_{fij}\,\Phi_i^{\bullet}\,f_j \tag{2.1.4}$$

Transfer to Small Molecule

$$k_{fT} = \sum_{i=1}^{N} k_{fTi}\,\Phi_i^{\bullet} \tag{2.1.5}$$

Termination by Disproportionation

$$k_{td} = \sum_{\substack{i=1\\j=1}}^{N} k_{tdij}\,\Phi_i^{\bullet}\,\Phi_j^{\bullet} \tag{2.1.6}$$

Termination by Combination

$$k_{tc} = \sum_{\substack{i=1\\j=1}}^{N} k_{tcij}\,\Phi_i^{\bullet}\,\Phi_j^{\bullet} \tag{2.1.7}$$

Derivation for these pseudo-kinetic rate constants is shown in Appendix A-1. The fraction of polymer radical of type i, $\Phi_i^{\bullet}$, may be obtained using the stationary-state hypothesis for each type of radical, i.e.,

$$\sum_{j=1}^{N} R_{ji} = \sum_{j=1}^{N} R_{ij} \tag{2.1.8}$$

where R_{ji} is the rate of propagation in which M_i follows M_j.

Even though these pseudo-kinetic rate constants are monomer mole fraction dependent and change with time, this concept facilitates the kinetic treatment greatly.

As shown in Appendix A-2, the pseudo-kinetic rate constant method for linear copolymerization is applicable if the following conditions are satisfied.

1. The terminal model for copolymerization is valid.
2. The number-average chain length is larger than a few hundred.

It is worth noting here that the above conditions are necessary even for the application of the usual copolymer composition equation known as the Mayo-Lewis equation [Mayo, Lewis (1944)], and therefore, this method may be considered quite general. The pseudo-kinetic rate constant method and the Stockmayer bivariate distribution of chain length and composition [Stockmayer (1945); Tosi, Catinella (1970); Stejskal, Kratochvil (1987); Tacx et al. (1988)] are closely related as shown in Appendix B.

The pseudo-kinetic rate constant method and the Stockmayer bivariate distribution are both applicable even when chain length dependent bimolecular termination of polymer radicals is significant if the following ratio,

$$\frac{\text{Probability of growth for polymer radical of type 1 with chain length } r}{\text{Probability of growth for polymer radical of type 2 with chain length } r}$$

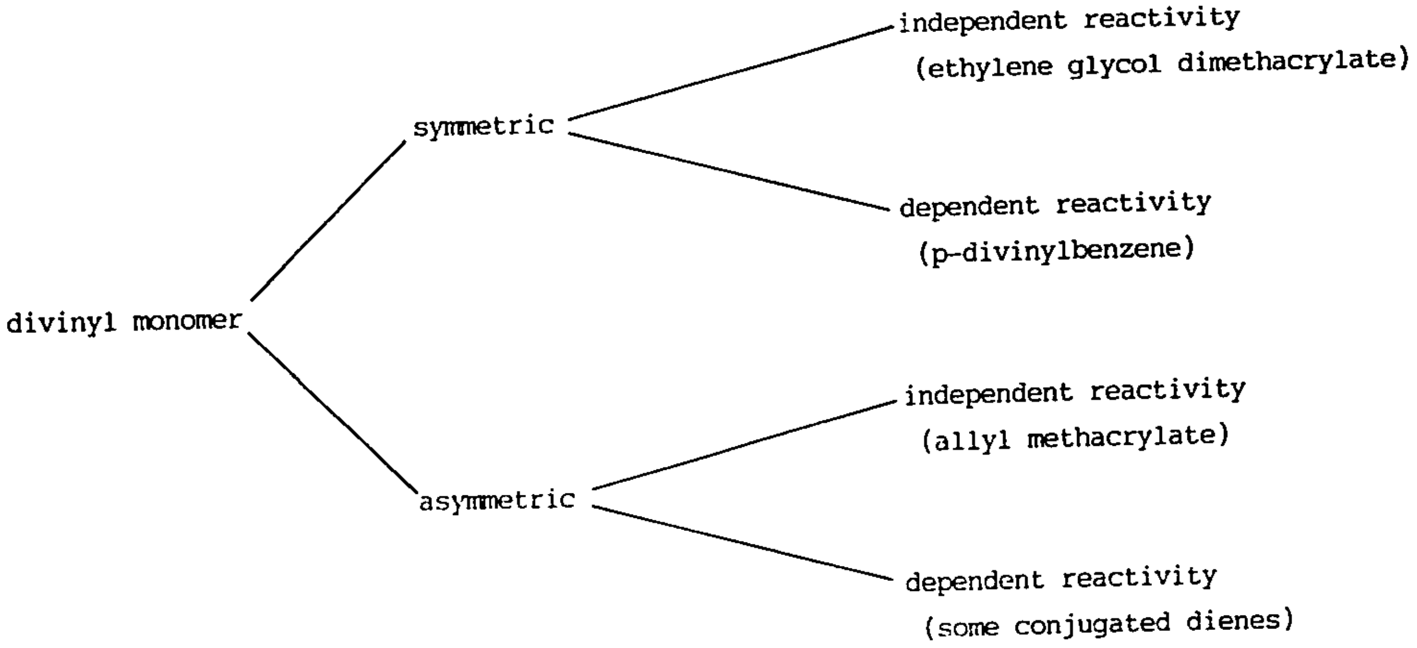
, is independent of chain length (see Appendix B-3). For high polymers this condition is likely to be satisfied, since the above probabilities are both very close to unity.

[B] Non-Linear Copolymer

We now consider the copolymerization of vinyl and divinyl monomer. In divinyl monomer itself the reactivities of two double bonds may be equal (symmetric monomer) or different (asymmetric monomer). Furthermore, the reactivity of the remaining double bonds (pendant double bonds) may change its reactivity after one of the vinyls has reacted. Various types of divinyl monomer can conveniently be classified as shown in Table 2.1.2 [Dusek (1982)]. In order to clarify the theory, we will illustrate cases where the reactivities of both double bonds in a divinyl monomer are equal (symmetric divinyl monomer) such as for the case of ethylene glycol dimethacrylate, N,N'-methylene-bis-acrylamide, and divinylbenzene.

For vinyl/divinyl copolymerization, long chain branches or crosslinkages are formed as is shown in Figure 2.1.1. Even if the reactivities of both double bonds in a divinyl monomer are equal, it is more realistic to consider that the reactivity of pendant double bonds is different from that of double bonds in a divinyl monomer due to physical (shielding effect) and chemical effect (symmetric dependent reactivity such as divinylbenzene). Therefore, at least three types of double bonds and three types of polymer radicals are involved in the polymerization reaction. In order to account for the presence of pendant double bonds (subscript 3 is used to designate the pendant double bonds), the pseudo-kinetic rate constants which were defined by equations (2.1.3)-(2.1.7) should be modified for the copolymerization of

Table 2.1.2 Classification of divinyl monomer (after [Dusek (1982)])



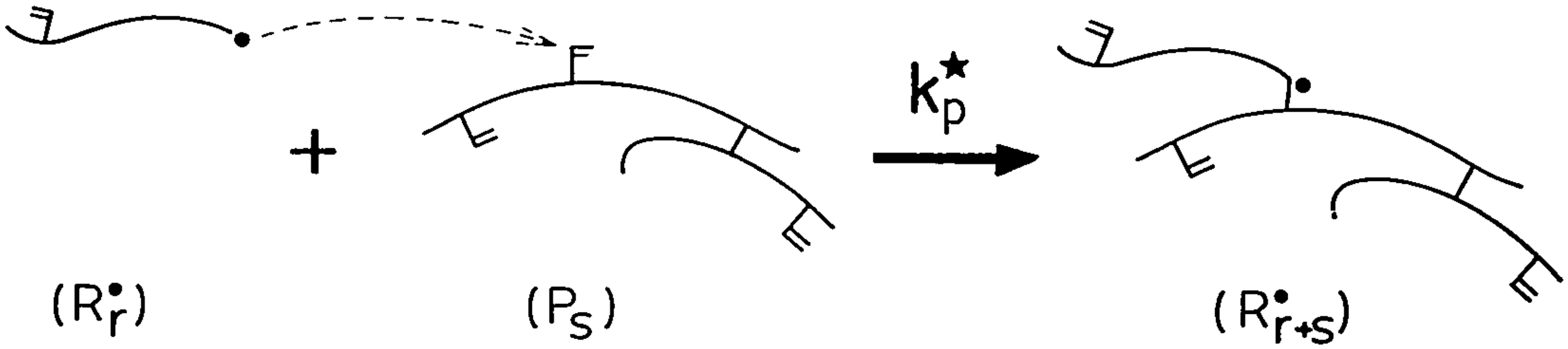


Figure 2.1.1 Reaction with pendant double bonds.

vinyl monomer (M_1) and divinyl monomer (M_2) as follows.

$$k_p=(k_{11}f_1+k_{12}f_2)\,\Phi^\bullet_1+(k_{21}f_1+k_{22}f_2)\,\Phi^\bullet_2+(k_{31}f_1+k_{32}f_2)\,\Phi^\bullet_3 \qquad (2.1.9)$$

$$k_{fm}=(k_{f11}f_1+k_{f12}f_2)\,\Phi^\bullet_1+(k_{f21}f_1+k_{f22}f_2)\,\Phi^\bullet_2+(k_{f31}f_1+k_{f32}f_2)\,\Phi^\bullet_3 \qquad (2.1.10)$$

$$k_{fT}= k_{fT1}\,\Phi^\bullet_1 + k_{fT2}\,\Phi^\bullet_2 + k_{fT3}\,\Phi^\bullet_3 \qquad (2.1.11)$$

$$k_{td}= k_{td11}\,\Phi^{\bullet 2}_1+ k_{td22}\,\Phi^{\bullet 2}_2+ k_{td33}\,\Phi^{\bullet 2}_3+ 2k_{td12}\,\Phi^\bullet_1\,\Phi^\bullet_2+ 2k_{td13}\,\Phi^\bullet_1\,\Phi^\bullet_3 + 2k_{td23}\,\Phi^\bullet_2\,\Phi^\bullet_3 \qquad (2.1.12)$$

$$k_{tc}= k_{tc11}\,\Phi^{\bullet 2}_1+ k_{tc22}\,\Phi^{\bullet 2}_2+ k_{tc33}\,\Phi^{\bullet 2}_3+ 2k_{tc12}\,\Phi^\bullet_1\,\Phi^\bullet_2+ 2k_{tc13}\,\Phi^\bullet_1\,\Phi^\bullet_3 + 2k_{tc23}\,\Phi^\bullet_2\,\Phi^\bullet_3 \qquad (2.1.13)$$

Applying these pseudo-kinetic rate constants, the kinetic treatment of vinyl/divinyl copolymerization reduces to that of a homopolymerization. For example, propagation rate R_p and termination rate R_t are given by

$$R_p = k_p[M][R^\bullet] \qquad (2.1.14)$$

$$R_t = (k_{td} + k_{tc})[R^\bullet]^2 \qquad (2.1.15)$$

where [M] is the total monomer concentration (= $[M_1]+[M_2]$) and $[R^\bullet]$ is the total polymer radical concentration. Obviously, we are not considering special cases where cyclopolymerization of divinyl monomer is significant and it is necessary to account for another type of polymer radical ( $= \Phi_4^\bullet$).

<u>Copolymer Composition</u>: When the monomer consumption by $\Phi_3^\bullet$ is not negligible, a knowledge of the reactivity ratios r_1 and r_2 which are defined with respect to monomer unit is insufficient to calculate the change in copolymer composition during polymerization. Therefore, application of the Mayo-Lewis equation [Mayo, Lewis (1944)]

$$F_2 = (r_2 f_2^2 + f_1 f_2)/(r_2 f_2^2 + 2 f_1 f_2 + r_1 f_1^2) \qquad (2.1.16)$$

or its integrated form, the Meyer-Lowry equation [Meyer, Lowry (1965)]

$$1 - x = (f_1/f_{10})^a \, (f_2/f_{20})^b \, [(f_{10} - d)/(f_1 - d)]^c \qquad (2.1.17)$$

where

$$a = r_2/(1 - r_2) \; , \quad b = r_1/(1 - r_1)$$
$$c = (1 - r_1 r_2)/[(1 - r_1)(1 - r_2)] \; , \quad d = (1 - r_2)/(2 - r_1 - r_2)$$

is not exact, although quite often the copolymerization parameters r_1 and r_2 have been obtained without taking into account the behavior of pendant double bonds. To calculate copolymer composition, one may need to solve the following equations directly.

$$F_2 = \frac{(k_{12}\Phi_1^\bullet + k_{22}\Phi_2^\bullet + k_{32}\Phi_3^\bullet)\, f_2}{(k_{11}\Phi_1^\bullet + k_{21}\Phi_2^\bullet + k_{31}\Phi_3^\bullet)\, f_1 + (k_{12}\Phi_1^\bullet + k_{22}\Phi_2^\bullet + k_{32}\Phi_3^\bullet)\, f_2} \qquad (2.1.18)$$

$$\frac{df_2}{dx} = \frac{f_2 - F_2}{1 - x} \qquad (2.1.19)$$

$$\bar{F}_2 = [f_{20} - f_2\,(1 - x)]/x \qquad (2.1.20)$$

The mole fractions of each radical type $\Phi_1^\bullet$, $\Phi_2^\bullet$, and $\Phi_3^\bullet$ may be obtained applying the stationary-state hypothesis for each type of radical. For example, one may formulate the following equations.

$$k_{12}f_2'\,\Phi_1^\bullet - (k_{21}f_1' + k_{23}f_3')\,\Phi_2^\bullet + k_{32}f_2'\,\Phi_3^\bullet = 0 \qquad (2.1.21)$$

$$(k_{12}f_2' + k_{13}f_3')\,\Phi_1^\bullet - k_{21}f_1'\,\Phi_2^\bullet - k_{31}f_1'\,\Phi_3^\bullet = 0 \qquad (2.1.22)$$

$$\Phi_1^\bullet + \Phi_2^\bullet + \Phi_3^\bullet = 1 \qquad (2.1.23)$$

where f_1', f_2', and f_3' are given by

$$f_1' = f_1(1-x)/[1-x+(\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c)x] \qquad (2.1.24)$$

$$f_2' = f_2(1-x)/[1-x+(\overline{F}_2 - \overline{\rho}_a - \overline{\rho}_c)x] \qquad (2.1.25)$$

$$f_3' = (\overline{F}_2 - \overline{\rho}_a - \overline{\rho}_c)x/[1-x+(\overline{F}_2 - \overline{\rho}_a - \overline{\rho}_c)x] \qquad (2.1.26)$$

where $\overline{F}_2$ is the accumulated mole fraction of divinyl monomer bound in polymer chains, and $\overline{\rho}_a$ and $\overline{\rho}_c$ are the accumulated mole fraction of pendant double bond which has already been consumed by crosslinking reactions and cyclization reactions respectively (later they are called "additional crosslinking density" (Section 2.2) and "cyclization density" (Section 2.3) respectively). It should be noted that k_{13} and k_{23} should be understood as apparent kinetic rate constants, namely, they include the kinetics of cyclization which does not follow the conventional rate law. Details on cyclization will be shown in Section 2.3.

Let us consider the effect of monomer consumption by radical centers located on the pendant double bonds using a simple example. Now assume a system in which the reactivity ratios are given by $r_1= 0.3$ and $r_2= 1.0$. Here, the reactivity ratios are defined with respect to monomer unit, not the number of functional (vinyl) groups. Let us consider the following simplifying conditions.

1) The reactivities of both double bonds on a divinyl monomer are symmetric and independent.

2) Cyclization does not affect the copolymer composition, i.e., cyclization follows the same rate law as crosslinking, and

cyclopolymerization does not occur.

Figure 2.1.3 shows the effect of monomer consumption by $\Phi_3^\bullet$. The broken line shows the case where the monomer consumption by $\Phi_3^\bullet$ is incorrectly neglected.

Considering the above simplifying conditions in more detail, one can show that the Mayo-Lewis equation is valid when monomer concentration is replaced by double bond concentration and by using the reactivity ratios defined with respect to the number of functional (vinyl) groups [Gibbs (1964)]. These reactivity ratios which are defined with respect to the number of vinyl groups (the superscript v is used to designate these reactivity ratios) are related to those defined with respect to monomer units as follows.

$$r_1^v = 2r_1 \qquad (2.1.27)$$

$$r_2^v = r_2/2 \qquad (2.1.28)$$

Therefore, in the above example $r_1^v = 0.6$ and $r_2^v = 0.5$.

However, when the simplifying conditions are not acceptable, one should use equations (2.1.18)-(2.1.26) especially for high mole fractions of divinyl monomer cases and/or at high conversions. Therefore, when one needs to estimate the reactivity ratios in experiments with high mole fraction of divinyl monomer, it may be better to avoid using high conversion data, since one needs to estimate the reactivity of pendant

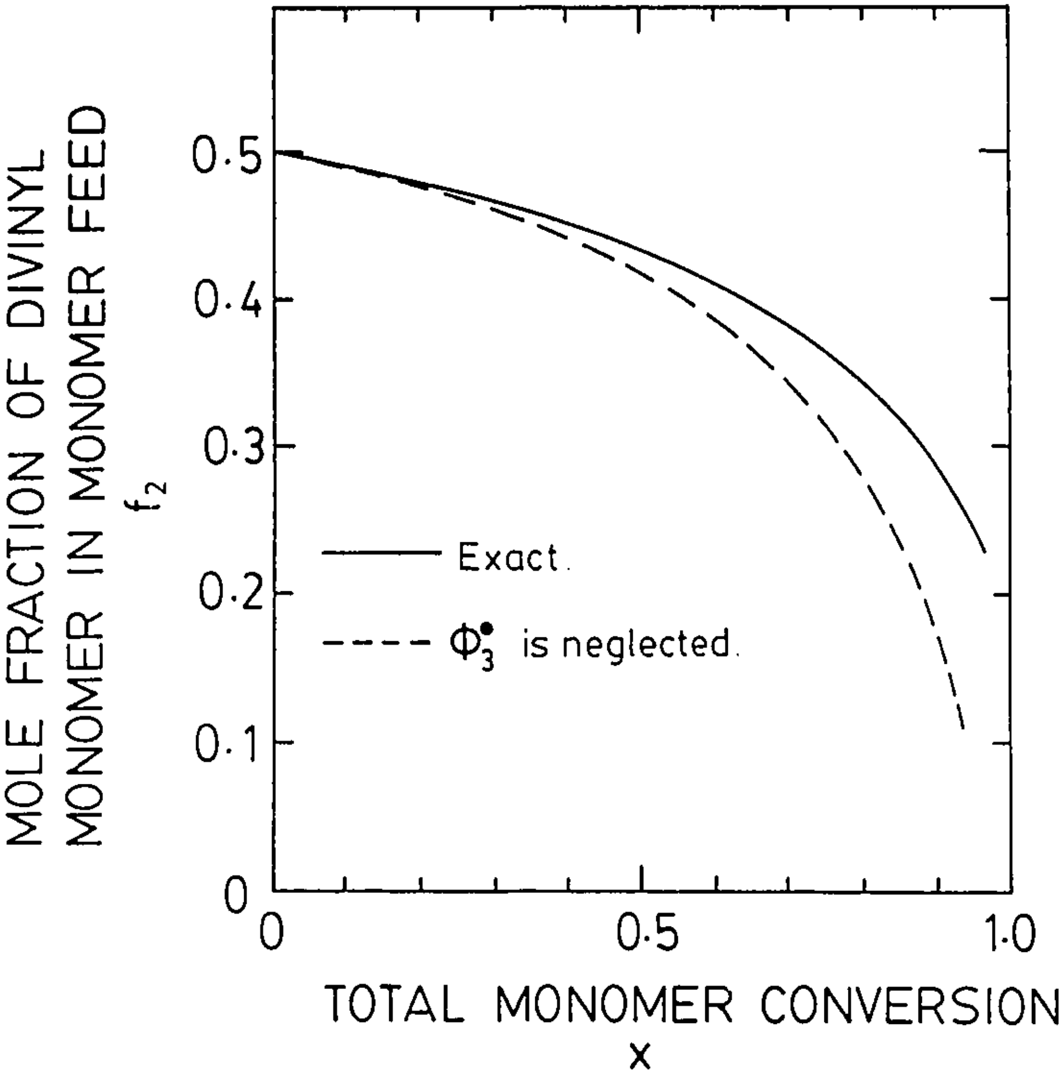


Figure 2.1.2 Compositional drift during vinyl/divinyl copolymerization. ($f_{20} = 0.5$, $r_1 = 0.3$, $r_2 = 1.0$)

double bonds and the degree of cyclization at the same time.

On the other hand, there are cases where monomer consumption by $\Phi_3^\bullet$ is likely negligible. It may be negligible in the pre-gelation period if the effect of cyclization is not too significant, since the number of crosslinkages in the pre-gelation period is very small if the primary chain length is sufficiently large. Another case is when the initial mole fraction of divinyl monomer, f_{20}, is far smaller than unity. For these cases the Mayo-Lewis equation is a reasonable approximation. (Further approximation may be possible for the cases in which very low mole fraction of divinyl monomer, say less than 5×10^{-3}, is used. Details are shown in Appendix C.)

2.2. Kinetics of Crosslinking

[A] Definitions

The primary polymer molecule [Flory (1953)] is used to observe the history of the generated network structure. The primary polymer molecule is a rather imaginary molecule which would exist if all crosslinks connected to it were severed, thus the primary polymer molecule itself is a linear polymer. The crosslinking density ρ^f [Flory (1953)] is used to express the degree of crosslinking of primary polymer molecules. The crosslinking density ρ^f is defined as the fraction of units which are crosslinked.

$$\rho^f = \frac{(\text{number of crosslinked units})}{(\text{total number of units bound in the polymer chain})} \tag{2.2.1}$$

The crosslinked unit is a unit which bears a tri-branching point. Let us consider a simple example shown in Figure 2.2.1. Linear polymer molecule **A** and **B** are primary polymer molecules. The crosslinking densities for each primary polymer molecule are given by $\rho^f{}_A = 1/4$ and $\rho^f{}_B = 1/5$. The overall crosslinking density $\bar{\rho}^f$ is 2/9.

From the point of view of physical properties of a polymer network ρ^f is important. However, once a divinyl monomer unit is bound in the polymer chain, its reactivity may not be the same as that for the monomeric double bonds due to chemical effects and/or steric hindrance

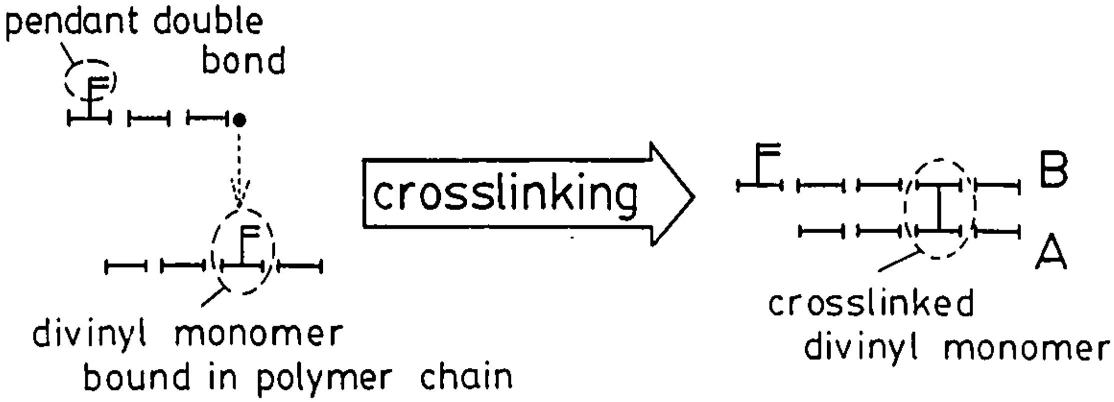


Figure 2.2.1 A simple example of crosslinked polymer formation. The primary polymer molecule **A** consists of four units and has four monomer units, thus $\rho_A^f = 1/4$, and $\rho_A = 1/4$. The primary polymer molecule **B** consists of five units but has four monomer units in it, since one of the units was a pendant double bond on primary polymer molecule **A**, and therefore, $\rho_B^f = 1/5$, and $\rho_B = 1/4$.

known as "shielding effect" [Minnema, Staverman (1958); Landin, Macosko (1988)]. In this case it is important to know which primary polymer molecule the crosslinked divinyl monomer originally belonged to. In order to facilitate the derivation of a mathematical expression for this idea, we define another crosslinking density, ρ , which is defined with respect to the number of monomer units.

$$\rho = \frac{\text{(number of crosslinked units)}}{\text{(total number of } \textbf{monomer units} \text{ bound in the polymer chain)}} \tag{2.2.2}$$

In the simple example shown in Figure 2.2.1, since the crosslinked divinyl monomer was originally bound in the primary polymer molecule **A**, the crosslinking densities for each primary polymer molecule are given by $\rho_A = 1/4$ and $\rho_B = 1/4$. The overall crosslinking density is $\overline{\rho} = 2/8 = 1/4$. When the crosslinking density is far smaller than unity, there is virtually no difference between these two definitions of crosslinking density, however, if high mole fraction of divinyl monomer is used, one needs to carefully distinguish these definitions as has been done in this simple example. The relationship between these two definitions of crosslinking density is shown in Section 2.2.-[B].

Now let us do an exercise. In a primary polymer molecule shown in Figure 2.2.2-(a), what is the maximum crosslinking density of this primary polymer molecule? If your answer is 1/3, it is not correct.

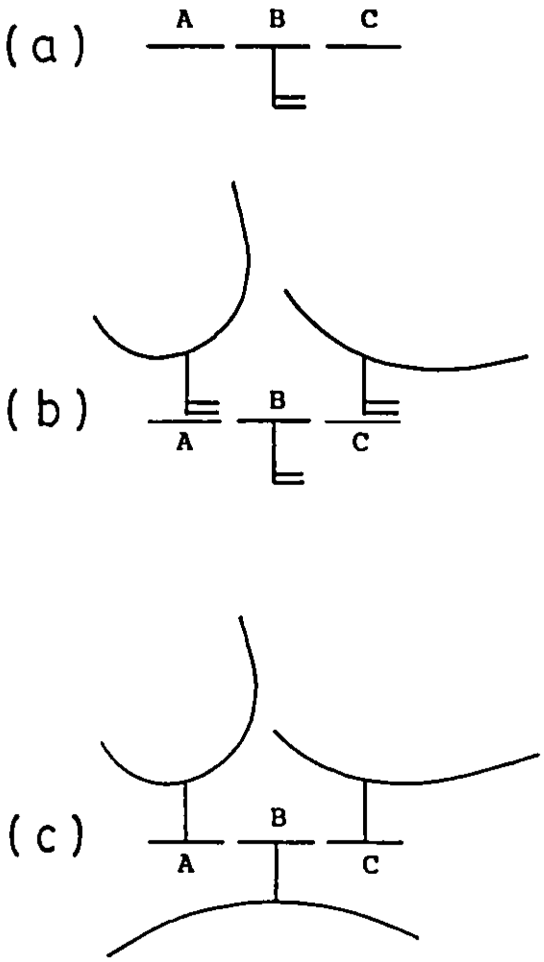


Figure 2.2.2 A remark on the crosslinking density of a primary polymer molecule: (a) A simple example of a primary polymer molecule. (b) A case where unit **A** and **C** have been pendant double bonds of other primary polymer molecules. (c) A possible maximum crosslinking density.

Since the units, **A** and **C**, may have been pendant double bonds of other primary polymer molecules as is shown in Figure 2.2.2-(b). Therefore, the possible maximum crosslinking density is $\rho^f = 1.0$ and $\rho = 3.0$ (see Figure 2.2.2-(c)). In general, the maximum crosslinking density of a primary molecule is $\rho^f = 1.0$ and $\rho = \infty$.

The above question is a rather tricky one, however, one should bear in mind that the maximum crosslinking density of a primary molecule can never be determined from the initial mole fraction of divinyl monomer, f_{20}, although the maximum overall (accumulated) crosslinking density at complete conversion is known from f_{20}.

[B] Crosslinking Density Distribution

Now, let us consider the history of a primary polymer molecule. In free radical copolymerization, each primary polymer molecule experiences a different history of crosslinking, and therefore, the crosslinking densities of primary molecules whose birth time is different may not be the same. Let us assume that the primary polymer molecule **C** shown in Figure 2.2.3 was born at total monomer conversion $x = \theta$. At $x = \psi$, the primary polymer radical **D** adds to a pendant double bond on the primary polymer molecule **C**, which results in a crosslinkage between two primary polymer molecules. In this case from the point of view of primary polymer molecule **D**, this crosslinkage is formed during its growth, so that let us call the density of this type of crosslinking points "instantaneous crosslinking

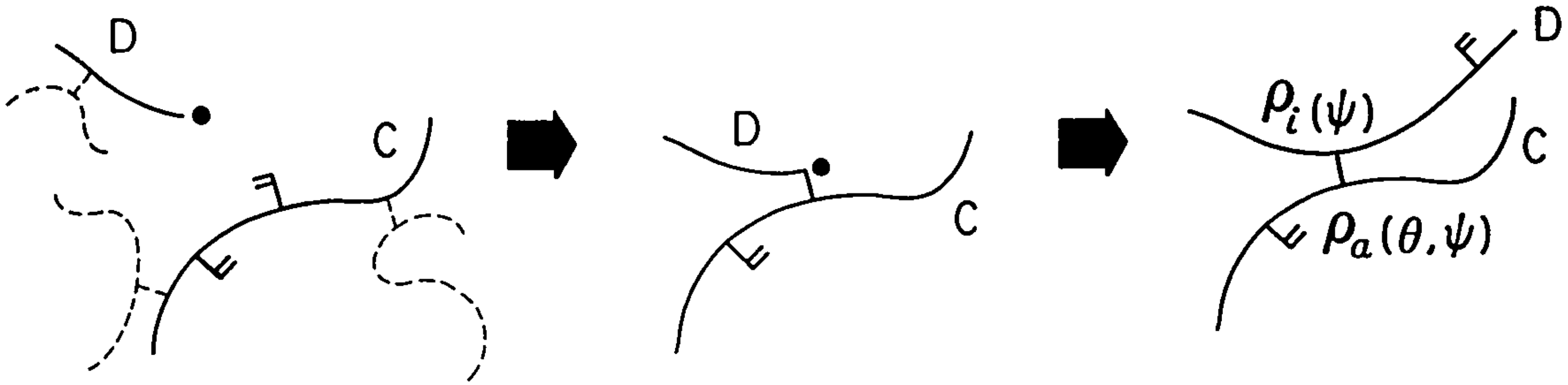


Figure 2.2.3 Schematic drawing of the process of crosslinking.

density", $\rho_i(\psi)$. On the other hand, from the point of view of the primary molecule **C**, the identical crosslinkage is formed but after it was born, so that let us call this type of crosslinking density "additional crosslinking density", $\rho_a(\Theta,\psi)$, i.e., $\rho_a(\Theta,\psi)$ is the additional crosslinking experienced in the conversion interval, Θ to ψ by primary polymer molecules born at conversion Θ. At $x=\psi$, the crosslinking density of the primary polymer molecules which were born at $x=\Theta$ is given by the sum of these two types of crosslinking density.

$$\rho(\Theta,\psi) = \rho_i(\Theta) + \rho_a(\Theta,\psi) \qquad (2.2.3)$$

The concept of Equation (2.2.3) was originally proposed by Flory (1947b) for diene polymers, however, this concept has never been generalized. To calculate the additional crosslinking density, one can formulate the following balance equation assuming a homogeneous system.

$$N_\theta\,[\,\rho_a(\Theta,\psi+\Delta\psi) - \rho_a(\Theta,\psi)\,] = k_p^{*0}\,[F_2(\Theta) - \rho_a(\Theta,\psi) - \rho_c(\Theta,\psi)]\,N_\theta\,[R^\bullet]\,\Delta t \qquad (2.2.4)$$

where N_θ is the total number of monomer units bound in the primary polymer chain born at $x=\Theta$, $F_2(\Theta)$ is the instantaneous mole fraction of divinyl monomer bound in the polymer chain born at $x=\Theta$, $\rho_c(\Theta,\psi)$ is the cyclization density for the primary polymer molecule which was born at $x=\Theta$ (details on cyclization is shown in Section 2.3), and k_p^{*0} is defined by

$$k_p^{*0} = k_{p13}^{*}\,\Phi_1^{\bullet} + k_{p23}^{*}\,\Phi_2^{\bullet} + k_{p33}^{*}\,\Phi_3^{\bullet} \tag{2.2.5}$$

Therefore, the fundamental equation for additional crosslinking density is given by

$$\frac{\partial \rho_a(\Theta,\psi)}{\partial \psi} = \frac{k_p^{*0}\,[\,F_2(\Theta) - \rho_a(\Theta,\psi) - \rho_c(\Theta,\psi)\,]}{k_p\,(\,1-\psi)} \tag{2.2.6}$$

Since all additional crosslinking points need to have thir own partners, namely, instantaneous crosslinking points, the instantaneous crosslinking density is given by the integration over all birth conversions.

$$\begin{aligned} \rho_i(x) &= \int_0^x \frac{\partial \rho_a(\Theta,x)}{\partial x}\,d\Theta \\ &= \frac{k_p^{*0}\,[\,\bar{F}_2(x) - \bar{\rho}_a(x) - \bar{\rho}_c(x)\,]\,x}{k_p\,(\,1-x\,)} \end{aligned} \tag{2.2.7}$$

where all overscript bars are used to designate accumulated values, and for example, $\bar{\rho}_a(x)$ is given by

$$\bar{\rho}_a(x) = \frac{1}{x}\int_0^x \rho_a(\theta,x)\ d\theta \tag{2.2.8}$$

The accumulated crosslinking density, $\bar{\rho}(x)$, which is the average over all polymer chains, is given by

$$\frac{d[x\ \bar{\rho}(x)]}{dx} = \frac{2k_p^{*0}\ [\bar{F}_2(x) - \bar{\rho}_a(x) - \bar{\rho}_c(x)\ ]\ x}{k_p\ (1-x)} \tag{2.2.9}$$

, and $\bar{\rho}(x)$, $\bar{\rho}_a(x)$, and $\bar{\rho}_i(x)$ can be related as follows.

$$\bar{\rho}(x) = \bar{\rho}_a(x) + \bar{\rho}_i(x) = 2\ \bar{\rho}_a(x) = 2\ \bar{\rho}_i(x) \tag{2.2.10}$$

Applying the above equations, it is possible to calculate crosslinking density of primary polymer molecules as a function of the birth conversion θ, namely, primary polymer molecules with different age may not have the same crosslinking density. A hypothetical example of crosslinking density distribution as a function birth conversion is shown in Figure 2.2.4.

Crosslinking densities given above are defined with respect to the number of monomer units, however, from the physical point of view the crosslinking density defined with respect to the number of units, $\rho^f(\theta,\psi)$, may be more important. $\rho^f(\theta,\psi)$ is given by

$$\rho^f(\theta,\psi) = \frac{\rho(\theta,\psi)}{1 + \rho_i(\theta)} \tag{2.2.11}$$

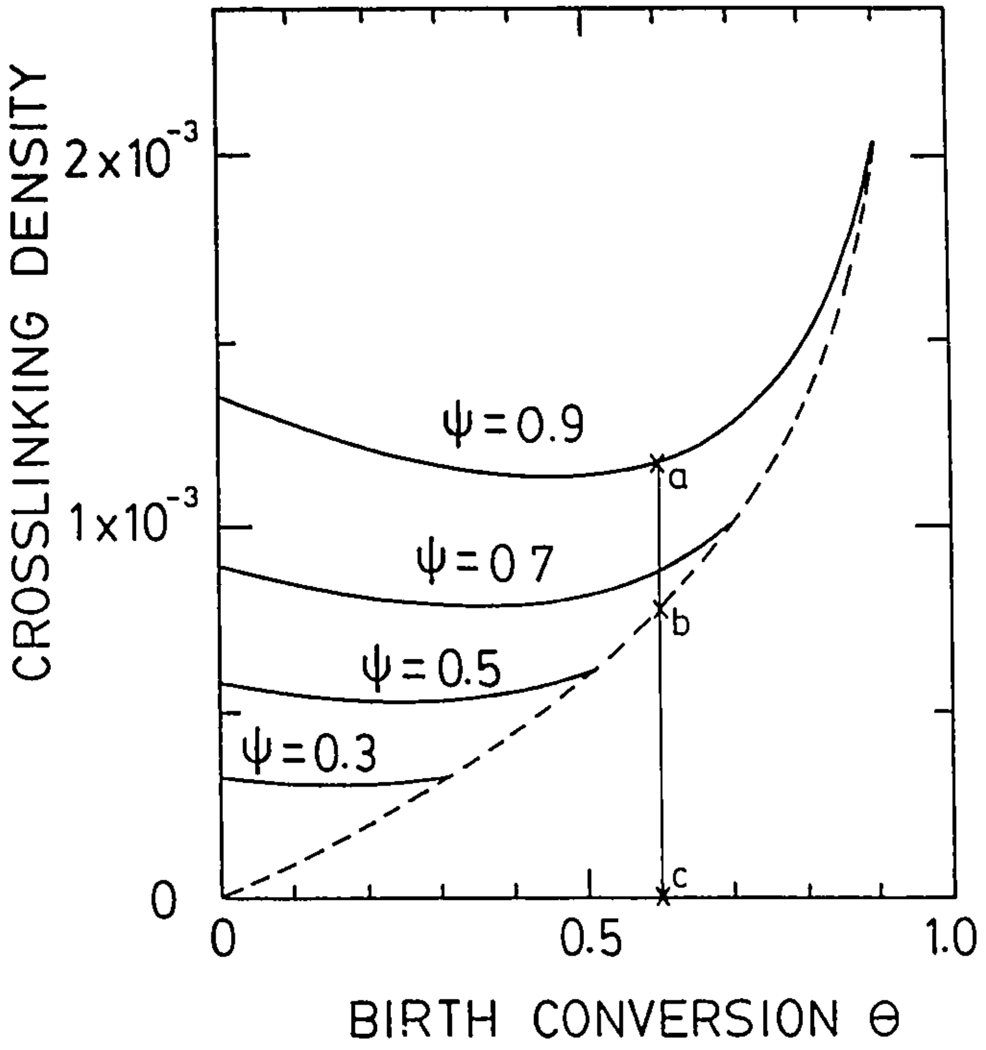


Figure 2.2.4 Crosslinking density distribution: $k_p^{*0}/k_p = 0.5$, $r_1 = 0.5$ $r_2 = 2.0$, $f_{20} = 1 \times 10^{-3}$, $\rho_c = 0$. (——) $\rho(\Theta,\psi) = \rho_i(\Theta) + \rho_a(\Theta,\psi)$, (-----) $\rho_i(\Theta)$. For example, with the present conversion $\psi = 0.9$, the additional crosslinking density for the primary polymer molecules born at conversion $\Theta = 0.6$ is given by $\overline{ab}$, namely, $\overline{ab} = \rho_a(0.6, 0.9)$. $\overline{bc}$ gives instantaneous crosslinking density for primary polymer molecules born at $\Theta = 0.6$, namely, $\overline{bc} = \rho_i(0.6)$, $\overline{ac} = \rho(0.6, 0.9)$.

Figure 2.2.5 shows one of the calculated results. In the calculation, the reactivities of all monomeric double bonds are assumed to be the same, while the reactivity of pendant double bonds is assumed to be one half of the monomeric double bond reactivity. This condition is, basically, the same for that of Figure 2.2.4 except that higher mole fraction of divinyl monomer is used in Figure 2.2.5. The crosslinking density is rather uniform at low conversions (low ψ) , however, it becomes a strong function of birth conversion, θ, at high conversions (high ψ).

As one can easily imagine, if the reactivity of the double bonds in a divinyl monomer is different from that of a vinyl monomer, primary polymer molecules of different age can never have the same crosslinking density. Figure 2.2.6 shows the crosslinking density distribution profile for these cases. In this paper, we use kinetic rate constants and concentrations which are defined with respect to monomer unit, not to the number of vinyl groups. However, in this particular example, the reactivity ratios shown in Figure 2.2.6 are defined with respect to the number of vinyl groups, since it makes it easier to understand the fine features of the system when the reactivity of pendant double bond is the same as that of double bonds in a divinyl monomer and cyclization does not occur. These reactivity ratios are related to those defined with respect to monomer unit by equations (2.1.27) and (2.1.28). Please note that $r_1^V = r_2^V = 1.0$ correspond to $r_1 = 0.5$ and $r_2 = 2.0$ if reactivity ratios are defined with respect to monomer units. As shown

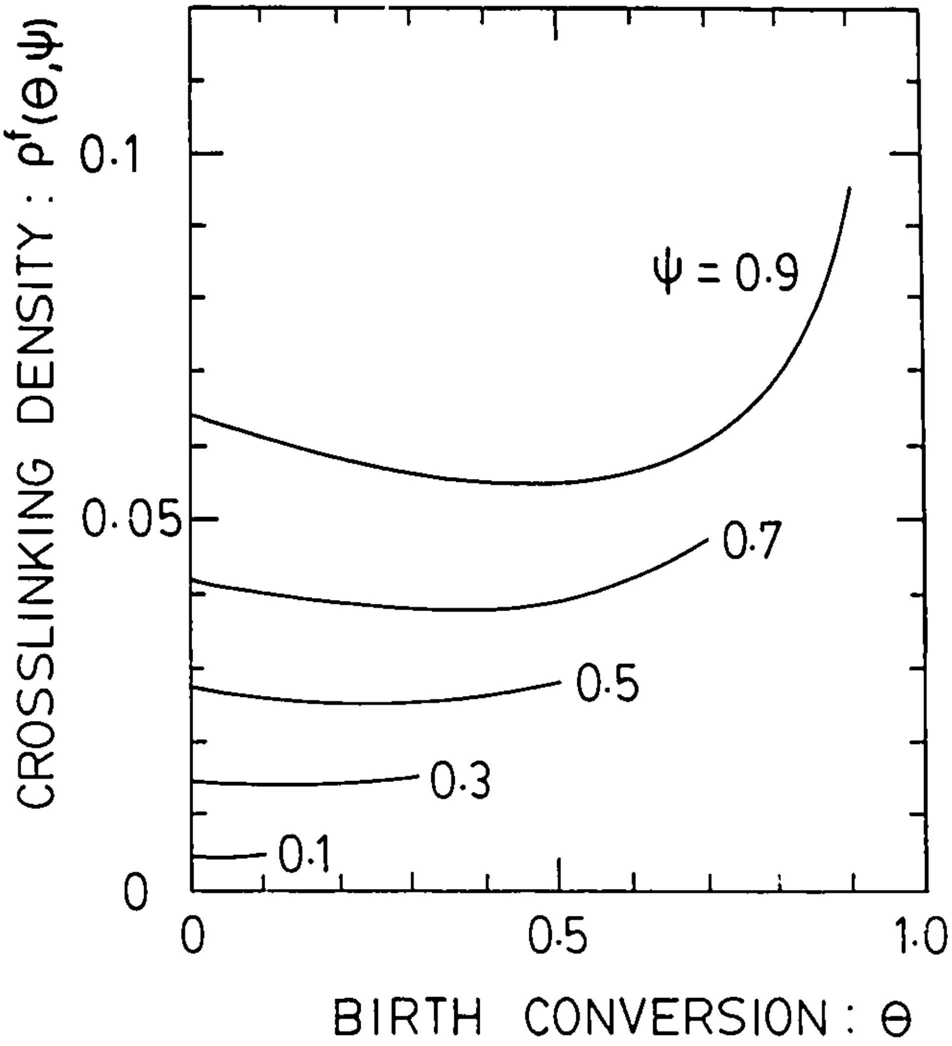


Figure 2.2.5 Crosslinking density distribution (crosslinking density defined with respect to the number of unit). $f_{20} = 0.05$, $\rho_c = 0$, $k_{11} = k_{21} = k_{31} = k_{12}/2 = k_{22}/2 = k_{32}/2$, $k^*_{p13} = k^*_{p23} = k^*_{p33} = k_{11}/2$.

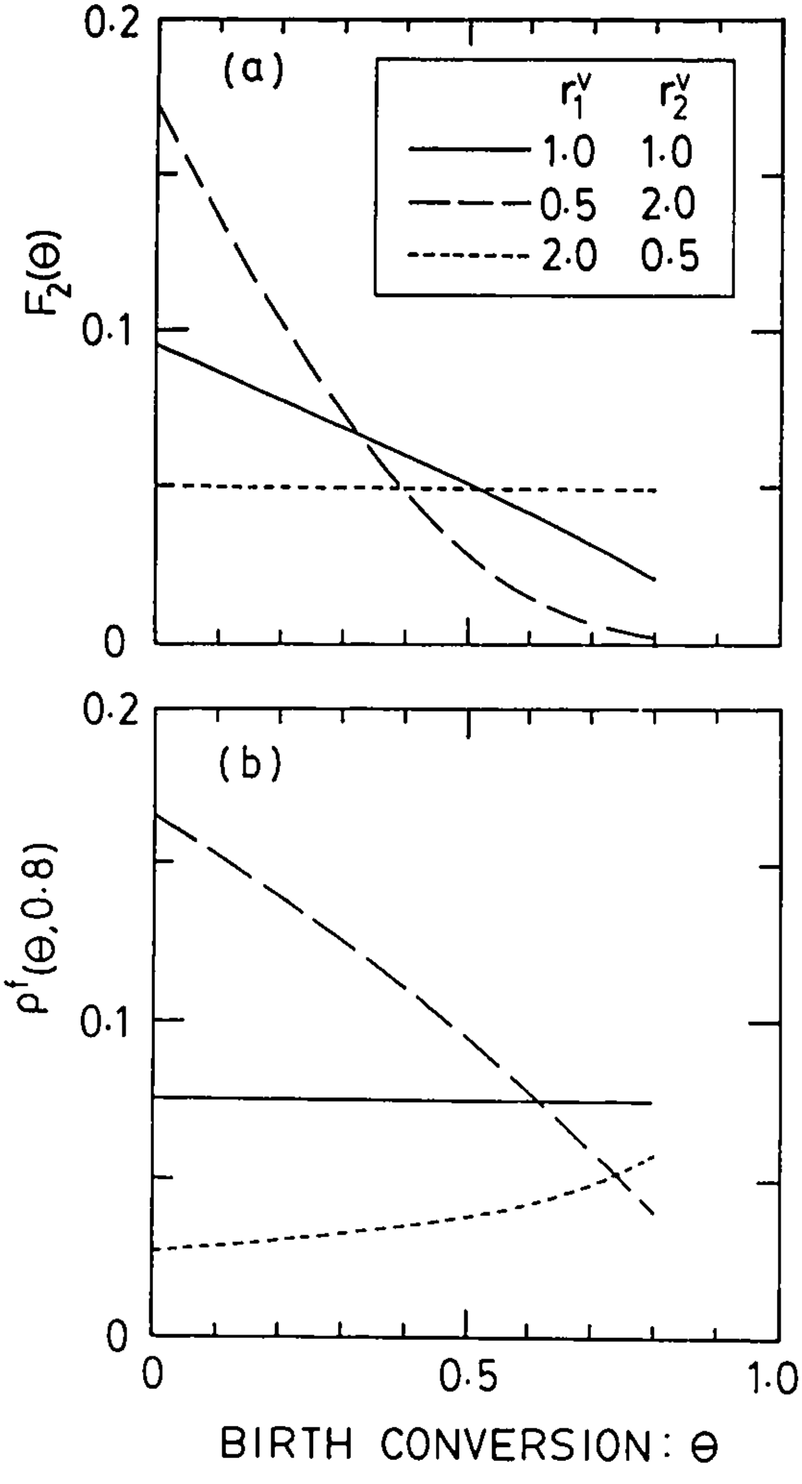


Figure 2.2.6 Effect of monomeric double bond reactivity on (a) compositional drift, and (b) crosslinking density distribution. $\psi = 0.8$, $f_{20} = 0.05$.

in Figure 2.2.6, the variance of the crosslinking density distribution is zero for this case, even though compositional drift of the primary polymer molecules is significant. It is sometimes argued that compositional drift is the cause for the formation of spatially inhomogeneous network structure, however, it is worth noting that "natural" compositional drift is necessary for the formation of a perfectly homogeneous network structure. Since an instantaneous crosslinkage is formed with a divinyl monomer which is bound in another primary polymer molecule, a primary polymer molecule need not possess divinyl monomer units in its backbone to obtain a crosslinkage.

The existence of a crosslinking density distribution is a very important feature of network formation in free radical polymerization. Models for network formation in which an equilibrium system is assumed inevitably employ the assumption that the crosslinking density is the same for all chains. However, this assumption is not strictly valid except under Flory's simplifying assumptions [Flory (1941c)(1953)] which are listed in Section 1.1.-[B] (p.15). For these limiting conditions, all primary polymer molecules possess equal crosslinking density independent of their birth time as it is proven in Appendix D. This is equivalent to stating that there is no difference between the kinetic model which considers the history of the generated network structure and models which assume an equilibrium system. However, in free radical polymerization the following non-ideal effects are important.

1) Differences in the reactivities of monomeric double bonds.

2) Differences in the reactivity of pendant double bonds relative to the monomeric double bonds in a divinyl monomer.

3) Cyclization reactions.

The more significant the above effects are, the larger is the variance of the crosslinking density distribution. Conventionally, it has been argued that there must be a difference between kinetic and equilibrium systems. However, no one has ever stated the difference clearly. The difference has now become clear: The variance of the crosslinking density distribution is exactly zero for equilibrium systems, however, the variance does not have to be zero for kinetic systems. The existence of a crosslinking density distribution shows that polymer networks synthesized by free radical polymerization are inherently not perfectly homogeneous on a microscopic scale. (The existence of a crosslinking density distribution with a large variance does not necessarily imply that a mean-field theory is no longer valid.)

2.3. Kinetics of Cyclization

One of the important features of cyclization is that it is controlled not by the conventional rate law using average concentrations of functional groups, but by conformational statistics of the sequence of bonds. Strict treatment of cyclization for free radical polymerization in a mean-field theory seems to be a formidable task especially at high conversions. Although Dusek and Ilavsky (1975a,b) proposed a model in the context of the theory of stochastic branching, their model is not directly applicable to our kinetic theory. We have developed very simple models for cyclization reactions. These simplified models might be acceptable at this stage in the development of kinetic models for cyclization.

In our formalism, it is convenient to divide the cyclization reactions into two groups, namely, primary and secondary cyclization (see Figure 2.3.1). With primary cyclization the cycle forms within one primary polymer molecule, while with secondary cyclization it is formed between two or more primary polymer molecules. The mathematical importance of the difference between primary and secondary cyclization is that primary cyclization is solely a function of birth time, while secondary cyclization is a function of both birth time and present time.

[A] Primary Cyclization

The use of the "random flight model" for the kinetics of cyclization was originally proposed by Jacobson and Stockmayer

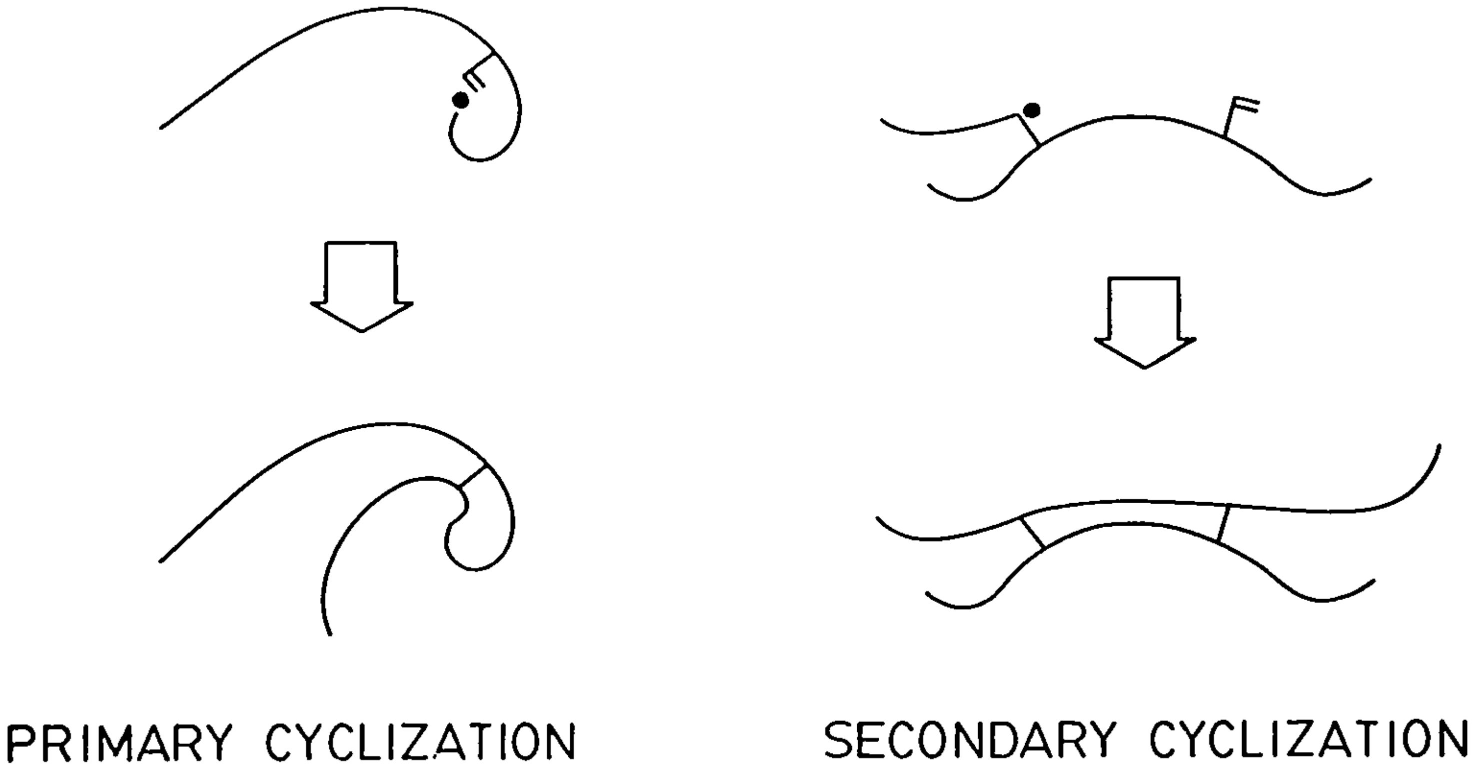


Figure 2.3.1 Classification of cyclization processes.

[Jacobson, Stockmayer (1950)] for a linear polycondensation system. Let us modify this method for primary cyclization. If a radical center on a primary polymer radical is located at the origin of coordinates, the probability that a randomly selected monomer unit bound on the identical primary polymer molecule resides in the volume dV at a distance R is given by

$$W(R)dV = [3/(2\pi l_s^2 n_s)]^{1.5} \exp[-3R^2/(2 n_s l_s^2)] \, dV \qquad (2.3.1)$$

where l_s is the length of a statistical segment and n_s is the number of statistical segments in a chain. In order for the primary cyclization to be formed, R = 0.

$$\begin{aligned} W(0)dV &= [3/(2\pi l_s^2 b)]^{1.5} N^{-1.5} dV \\ &= A N^{-1.5} dV \qquad (2.3.2) \end{aligned}$$

where n_s=bN and N is the number of monomer units, and A is a constant. Equation (2.3.2) shows that smaller cycles have a better chance of formation than larger ones. The probability of forming a cycle for the primary polymer radical with chain length p is given by

$$P_{c,r} = \sum_{N=1}^{p} k'_{cp} F_2 N^{-1.5} \qquad (2.3.3)$$

Therefore, the expectation of the number of cycles formed for a primary polymer molecule with chain length r is given by

$$\begin{aligned} E(n_c) &= \sum_{p=1}^{r} \sum_{N=1}^{p} k'_{c,p} F_2 N^{-1.5} \\ &\cong \int_1^r \int_1^p k'_{c,p} F_2 y^{-1.5} \, dy \, dp \\ &= 2 k'_{c,p} F_2 (r - 2r^{0.5} + 1) \end{aligned} \qquad (2.3.4)$$

The primary cyclization density, ρ_{cp}, is given by

$$\rho_{cp} = E(n_c)/r = 2 k'_{cp} F_2 (1 - 2/r^{0.5} + 1/r) \qquad (2.3.5)$$

As is shown in Figure 2.3.2, the parenthesis of Equation (2.3.5) is approximately constant over a sufficient range of chain length except for oligomeric chain lengths, and therefore, as a first approximation $\rho_{cp}(\Theta)$ is given by

$$\rho_{cp}(\Theta) = k_{cp} F_2(\Theta) \qquad (2.3.6)$$

The overall cyclization density at present conversion, ψ, is therefore given by

$$\bar{\rho}_{cp}(\psi) = k_{cp} \bar{F}_2(\psi) \qquad (2.3.7)$$

Quite often, the reactivity of divinyl monomer is higher than that of

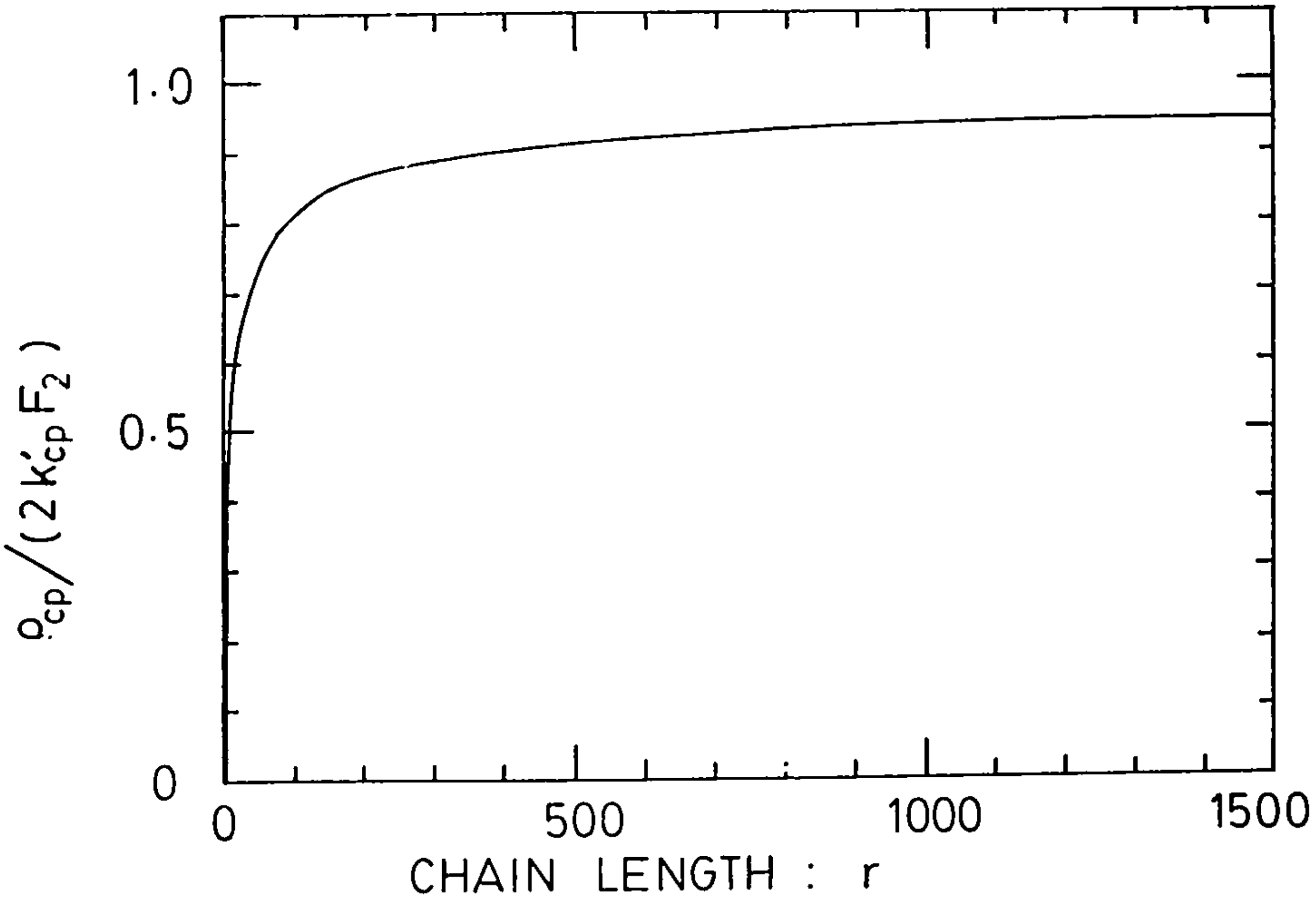


Figure 2.3.2 Effect of chain length on primary cyclization.

(calculated from Equation (2.3.5))

mono-vinyl monomer (since divinyl monomer possesses two double bonds in a monomer unit), so that the primary cyclization density is maximum in the initial stages of reaction.

Equation (2.3.7) shows that the primary cyclization density is proportional to the mole fraction of divinyl monomer bound in the polymer chains, and can also be derived if one assumes that primary cyclization is formed solely with a small number of monomer units. The primary cyclization reaction rate constant, k_{cp}, may be determined by extrapolating the pendant double bond conversion, x_{pd}, to zero monomer conversion, $x=0$, since crosslinkages and secondary cycles do not exist at $x = 0$, although it is unclear whether k_{cp} has a constant value throughout the polymerization. From Equation (2.3.6), if the molecular conformation does not change and primary polymer chain length is large enough, k_{cp} should be independent of monomer composition (f_{20}) and chain length of the primary polymer molecule. Several experimental results showing the effect of the initial mole fraction of divinyl monomer, f_{20}, are summarized in Figure 2.3.3-a and 2.3.3-b. In some cases k_{cp} (= x_{pd}^{0}) appears to be independent of f_{20} as is shown in Figure 2.3.3-a, however, dependence on f_{20} has also been reported (Figure 2.3.3-b). It is worth noting, however, that the results for syrene / ethylene glycol dimethacrylate (EGDMA) at low f_{20} are conflicting depending on who the researchers were (please compare ■ □ and ▼). The problem may partly be caused by inaccuracy of the analytical methods for pendant double bond conversion measurement used

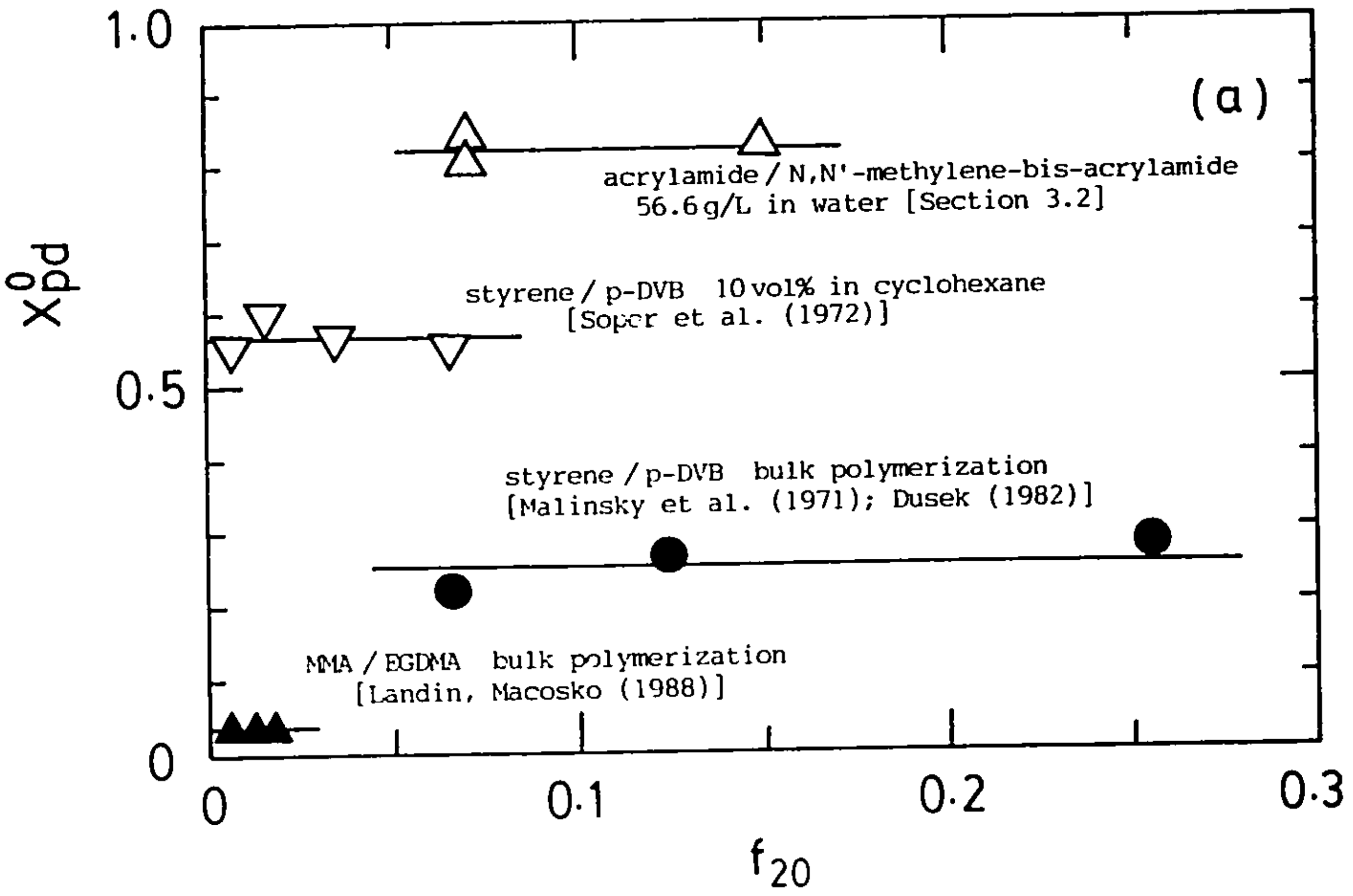


Figure 2.3.3-a Effect of initial mole fraction of divinyl monomer (f_{20}) on primary cyclization.

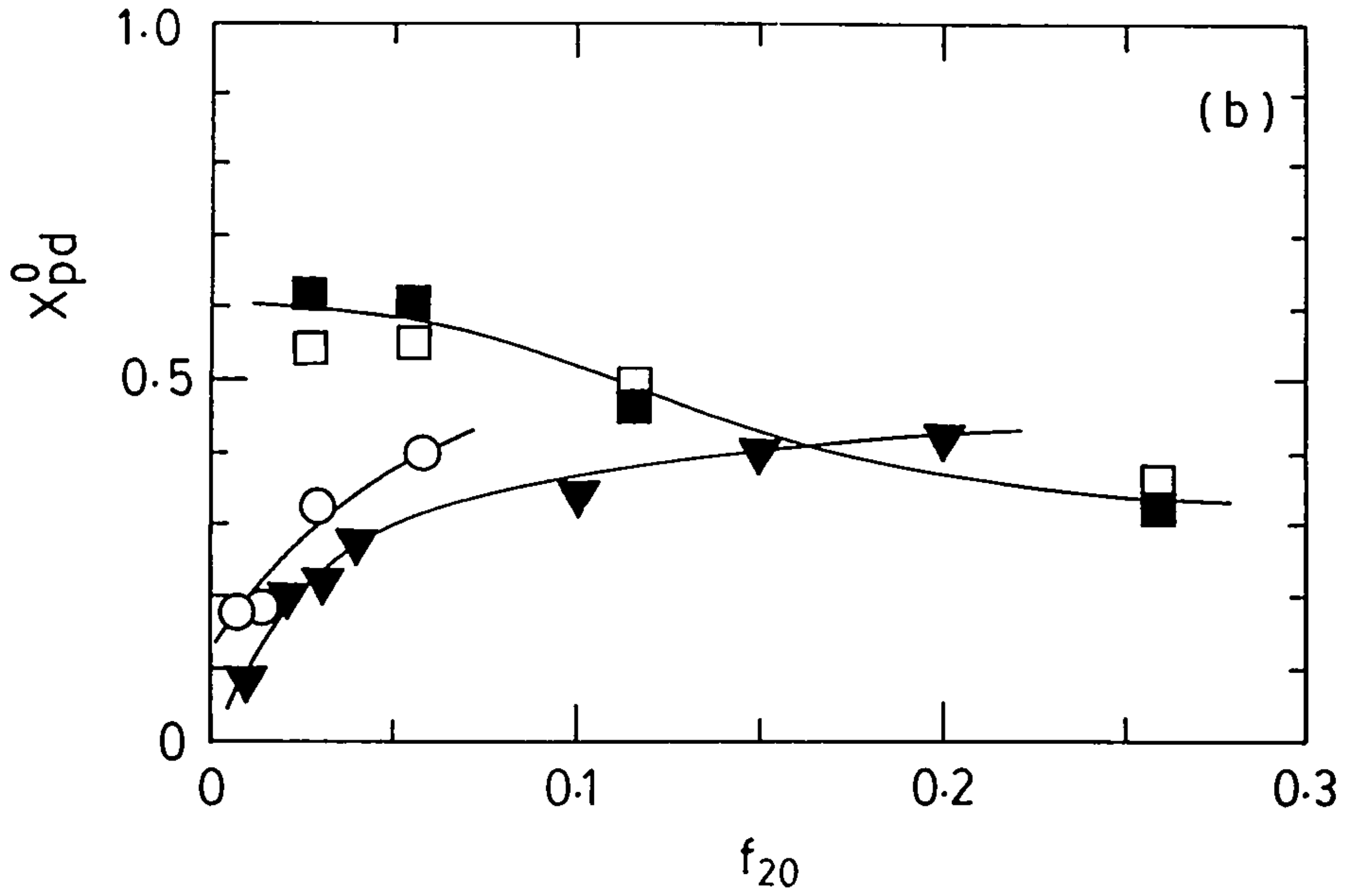


Figure 2.3.3-b Effect of initial mole fraction of divinyl monomer (f_{20}) on primary cyclization.

vrene / p-DVB ○ 15 vol% in toluene [Soper et al. (1972)]
rene / EGDMA ■ bulk polymerization [Dusek, Spevacek (1980)]
□ 60 vol% in toluene [Dusek, Spevacek (1980)]
▼ 15 vol% in toluene [Shah et al. (1978),(1980)]

especially when the amount of divinyl monomer is small. Furthermore, if the molecular conformation changes with addition of divinyl monomer, a dependence on f_{20} is reasonable. Independence of k_{cp} on primary polymer chain length was shown for methyl methacrylate (MMA) / ethylene glycol dimethacrylate (EGDMA) at $f_{20}= 0.0114$ [Landin, Macosko (1988)], and acrylamide / N,N'-methylene-bis-acrylamide at $f_{20}= 0.07$ as is shown in Section 3.2. In general, primary cyclization may be strongly dependent on the flexibility of the chain, on the divinyl monomer type, and on the interaction between polymer and solvent.

[B] Secondary Cyclization

Secondary cyclization can be defined clearly in the pre-gelation period. However, it is ambiguous in the post-gelation period, since from a physical point of view it is impossible to distinguish it from crosslinking. Further complications arise because the crosslinking density given by Equations (2.2.6) and (2.2.7) should also involve intramolecular reactions especially in the post-gelation period. Therefore, secondary cyclization may be recognized as an adjustable parameter or correction factor in order to connect structural properties (such as crosslinking density) to mass properties (such as gel point, average molecular weight of sol fractions, gel/sol ratio).

Although secondary cyclization is also dominated by chain conformational statistics like primary cyclization, it may be convenient to consider the average number of secondary cycles per crosslink, $\eta(\Theta,\Psi)$, since it is necessary to have a crosslinkage in order for secondary cyclization to occur (see Figure 2.3.4). The secondary cyclization of additional type, $\rho_{cs,a}(\theta,\psi)$, and that of instantaneous type, $\rho_{cs,i}(\theta)$, are given by

$$\frac{\partial \rho_{cs,a}(\theta,\psi)}{\partial \psi} = \eta(\theta,\psi) \frac{\partial \rho_{a}(\theta,\psi)}{\partial \psi} \tag{2.3.8}$$

$$\rho_{cs,i}(\theta) = \int_{0}^{\theta} \frac{\partial \rho_{cs,a}(y,\theta)}{\partial \theta} dy \tag{2.3.9}$$

At $x = \psi$, the secondary cyclization density for the primary polymer molecule which was born at $x = \theta$ is given by the sum of these two types of secondary cyclization density.

$$\rho_{cs}(\theta,\psi) = \rho_{cs,i}(\theta) + \rho_{cs,a}(\theta,\psi) \tag{2.3.10}$$

In a real system, $\eta(\theta,\psi)$ should be a very complicated function of the mole fraction of pendant double bonds on the chain, chain length of the primary polymer molecule, molecular conformation, etc. Some simple and perhaps effective approximations might be as follows.

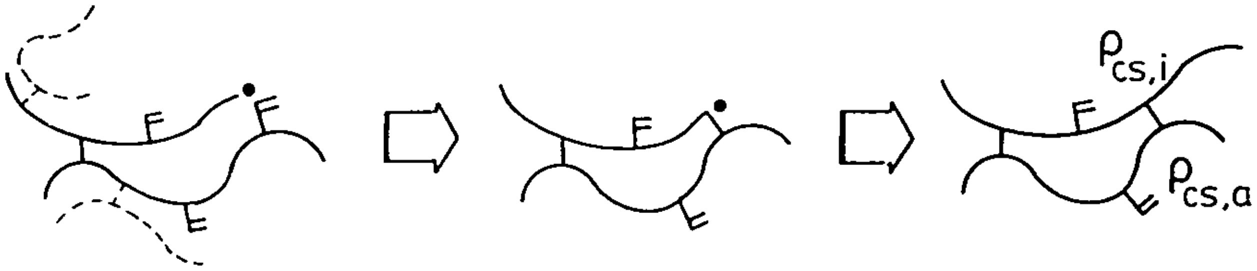


Figure 2.3.4 Process of secondary cyclization.

[zeroth approximation]

$$\eta(\Theta,\psi) = \text{constant}. \qquad (2.3.11)$$

[first approximation]

$$\eta(\Theta,\psi) \propto (\text{average number of pendant double bonds on a primary polymer molecule which was born at } x=\Theta.)$$

$$= k_{cs}\ [F_2(\Theta) - \rho_a(\Theta,\psi) - \rho_{cp}(\Theta) - \rho_{cs,a}(\Theta,\psi)]\ P_{np}(\Theta) \qquad (2.3.12)$$

where $P_{np}(\Theta)$ is the number-average chain length of the primary polymer molecules which were born at $x=\Theta$.

The zeroth approximation seems to be applicable at low conversions ([Landin, Macosko (1988)] and Section 3.2 of this thesis). An example of an application of the first approximation is shown in Section 3.1.

These approximations may not be acceptable for high f_{20} at high monomer conversions where crosslinking reactions become "overall diffusion controlled [Dusek, MacKnight (1988)]". Since a considerable fraction of pendant double bonds is trapped in the polymer network at high monomer conversions, a large number of pendant double bonds remain unreacted even when all monomer molecules have been consumed [Malinsky et al. (1971)]. However, these approximations may be applicable for loose networks.

Based on the elastic properties of gel molecules, it may be reasonable to consider that not only the crosslinkages but also the secondary cyclizations are elastically effective. Let us call the sum of crosslinking density, $\rho(\Theta,\Psi)$, and secondary cyclization, $\rho_{cs}(\Theta,\Psi)$, the "elastic crosslinking density", $\rho_{el.}(\Theta,\psi)$. The "elastic crosslinking density" does not necessarily equal the elastically effective crosslinking density [Flory (1953)], since we do not consider the physical crosslinkages which may be effective in terms of elasticity, and the dangling chains which are not effective.

$$\rho_{el.}(\Theta,\Psi) = \rho(\Theta,\Psi) + \rho_{cs}(\Theta,\Psi) \qquad (2.3.13)$$

In terms of the number of units, the elastic crosslinking density, $\rho^f_{el.}(\Theta,\psi)$, is given by

$$\rho^f_{el}(\Theta,\psi) = \frac{\rho(\Theta,\psi) + \rho_{cs}(\Theta,\psi)}{1 + \rho_i(\Theta) + \rho_{cp}(\Theta) + \rho_{cs,i}(\Theta)} \qquad (2.3.14)$$

Figure 2.3.5 shows the elastic crosslinking density distribution calculated using the same condition as those used in Figure 2.2.5 except for the presence of secondary cyclization ($\eta = 10$). The existence of secondary cyclization changes the profile of the elastic crosslinking density distribution dramatically. A knowledge of the crosslinking density distribution, $\rho(\Theta,\psi)$ (or $\rho^f(\Theta,\psi)$), permits one to calculate the mass properties (such as the onset of gelation, average chain length of the sol fraction, and gel/sol ratio), while the elastic crosslinking

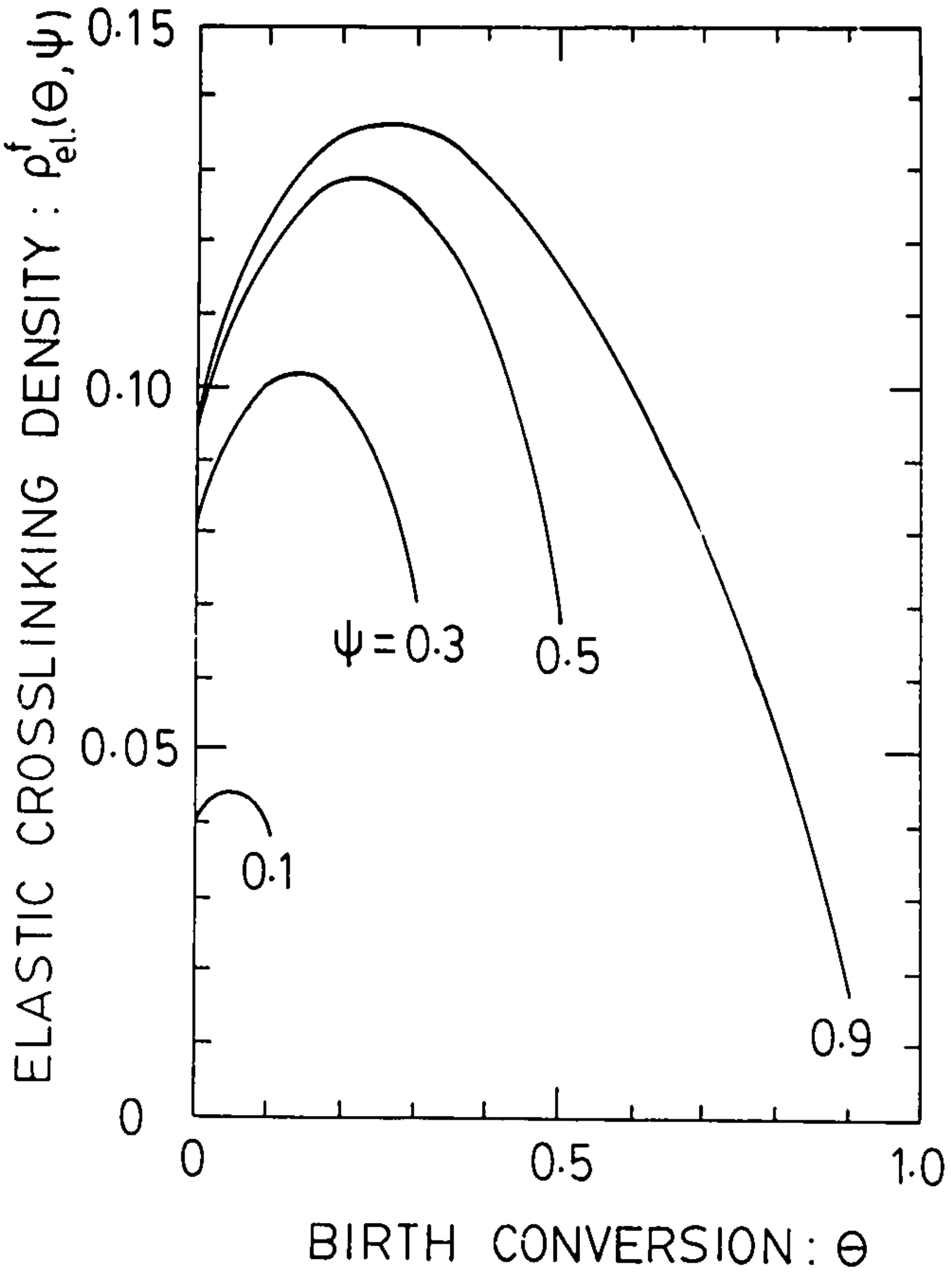


Figure 2.3.5 Elastic crosslinking density distribution.

$k_{11} = k_{21} = k_{31} = k_{12}/2 = k_{22}/2 = k_{32}/2$

$k^{*}_{p13} = k^{*}_{p23} = k^{*}_{p33} = k_{11}/2$, $f_{20} = 0.05$, $\eta = 10.0$

density distribution, $\rho_{e1}(\Theta,\psi)$ (or $\rho^{f}_{e1}(\Theta,\psi)$) is important as a structure property estimator.

2.4. Pre-Gelation Period

[A] Method of Moments

In this section we will show a calculation method for average properties in the pre-gelation period applying the method of moments. Only in this section, is the kinetic treatment of crosslinking different from that used in other sections of this thesis. We are to use a "polymer molecule" which includes crosslinkages as an observing unit, not a primary polymer molecule.

Let us consider the crosslinking reaction which is shown in Figure 2.1.1 (p.32). In this case, the reaction rate between the polymer radical with chain length r and the polymer molecule with chain length s may be given by

$$R_p^*(r,s) = k_p^*(r,s)\ [R^\bullet]\ N_0\ x\ /\ V \qquad (2.4.1)$$

where

$$k_p^*(r,s) = \bar{k}_p^{*0}(r,s)[\bar{F}_2(s) - \bar{\rho}_a(s) - \bar{\rho}_c(s)] \qquad (2.4.2)$$

$$\bar{k}_p^{*0}(r,s) = k_{p13}^*(r,s)\ \Phi_1^\bullet(r) + k_{p23}^*(r,s)\ \Phi_2^\bullet(r) + k_{p33}^*(r,s)\ \Phi_3^\bullet(r) \qquad (2.4.3)$$

N_0 is the initial total number of moles of monomer, and V is the reaction volume. $k_{p13}^*(r,s)$, $k_{p23}^*(r,s)$, and $k_{p33}^*(r,s)$ are the number-average kinetic rate constants for the crosslinking reaction in which polymer radical of type indicated by the first subscript with chain length r reacts with a pendant double bond on polymer molecule with chain length s, $\Phi_1^\bullet(r)$, $\Phi_2^\bullet(r)$, and $\Phi_3^\bullet(r)$ are the mole fraction of polymer radicals of type given by the subscript with chain length r. $\bar{F}_2(s)$, $\bar{\rho}_a(s)$, and $\bar{\rho}_c(s)$ are the accumulated properties of polymer molecules with chain length s. Namely, all terms involved in the pseudo-kinetic rate constant for crosslinking reaction which is given by Equation (2.4.2) are functions of chain length as well as conversion (, thus time). However, at present it is unclear how to derive these functional forms. As a first approximation, it may be reasonable to use the average properties over all chain lengths.

$$k_p^* = \overline{k_p^{*0}(r,s)}[\overline{\bar{F}_2(s)} - \overline{\bar{\rho}_a(s)} - \overline{\bar{\rho}_c(s)}]$$

$$= k_p^{*0}\ [\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c] \qquad (2.4.4)$$

where $k_p^{*0} = k_{p13}^* \Phi_1^\bullet + k_{p23}^* \Phi_2^\bullet + k_{p33}^* \Phi_3^\bullet$

At least, Equation (2.4.4) can be used to give the exact first order moment and overall crosslinking reaction rate R_p^*.

$$R_p^* = k_p^*\ [R^\bullet]\ N_0\ x\ /\ V \qquad (2.4.5)$$

The explicit form of Equation (2.4.5) is the same as that for chain transfer to polymer in homopolymerization, though for the latter case the kinetic rate constant for chain transfer to polymer k_{fp} might be considered constant with time or conversion (it is usually a very slow reaction compared to propagation). The process of chain transfer to polymer which produces tri-branching points is schematically shown in Figure 2.4.1, and the rate of chain transfer to polymer, R_{fp} is given by

$$R_{fp} = k_{fp} \, [R^\bullet] \, N_0 \, x \, / \, V \qquad (2.4.6)$$

Equations (2.4.5) and (2.4.6) are simple equations for which it is possible to apply the method of moments [Bamford, Tompa (1953),(1954); Bamford et al. (1958); Graessley, et al. (1965)].

However, one should bear in mind that the application of k_p^* which is defined by Equation (2.4.4) to calculate second or higher moments is not exact*, though there may not be any problem for the case of chain transfer to polymer in homopolymerization. In order to calculate higher order moments exactly, one must know the chain length dependence of k_p^*. However, if the reactivity of pendant double bonds does not change with chain length, Equation (2.4.4) is applicable for low conversions as shown in Appendix E.

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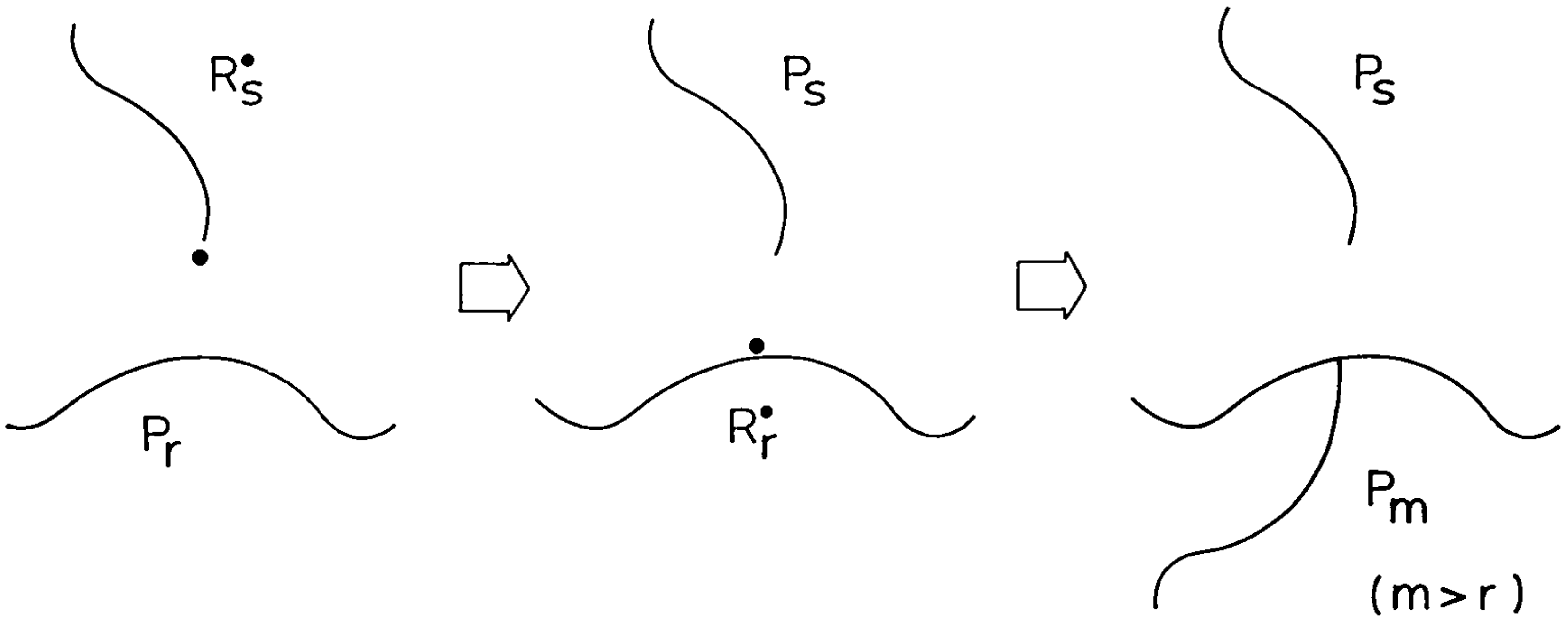
* Use number-average k_p^* for calculation of Q_0 and Q_1, and weight-average k_p^* for calculation of Q_2.



<u>Figure 2.4.1</u> Schematic drawing of the process of chain transfer to polymer.

A tri-branching point is formed by chain transfer to polymer.

In multicomponent polymerization, the pseudo-kinetic rate constant for chain transfer to polymer k_{fp}, is given by

$$k_{fp} = \sum_{\substack{i=1 \\ j=1}}^{N} k_{fpij}\, \Phi^{\bullet}_i\, \bar{F}_j \qquad (2.4.7)$$

where k_{fpij} is the kinetic rate constant of chain transfer to polymer in which a polymer radical of type i abstracts a hydrogen from monomer unit of type j in the polymer chain, and $\bar{F}_j$ is the accumulated mole fraction of monomer M_j bound in the polymer chain. Since chain transfer to polymer is usually a very slow reaction compared to propagation, it may not be necessary to subtract mole fraction of consumed units by the chain transfer reaction. For multicomponent polymerization k_{fp} is not exact for the calculation of higher order moments because of the same reason discussed above.

The i-th moment of the polymer distribution Q_i is given by

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \qquad (2.4.8a)$$

, and that for the polymer radicals Y_i is given by;

$$Y_i = \sum_{r=1}^{\infty} r^i [R^{\bullet}_r] \qquad (2.4.8b)$$

We are to formulate the moment equations using the normalized moments, which are defined as follows.

$$q_i = \frac{V\, Q_i}{V_0\, [M]_0} \qquad (2.4.9)$$

$$y_i = Y_i / Y_0 \qquad (2.4.10)$$

where $[M]_0$ is the initial total monomer concentration, and V_0 is the initial reaction volume.

Invoking the stationary-state hypothesis for radicals, y_i and q_i are given by the following equations (details can be found in Appendix F).

$$y_0 = 1 \qquad (2.4.11)$$

$$y_i = \frac{C_{p(i+1)} + \sum_{j=1}^{i} \binom{i}{j} C^*_{p(j+1)}\, y_{i-j} + \sum_{j=0}^{i-1} \binom{i}{j} y_j}{\tau + \beta + C_{p1}} \qquad (i \geqslant 1) \qquad (2.4.12)$$

$$\frac{dq_0}{dx} = \tau + (\beta/2) - C^*_{p1} \qquad (2.4.13)$$

$$\frac{dq_1}{dx} = 1 \qquad (2.4.14)$$

$$\frac{dq_i}{dx} = \sum_{j=0}^{i-1} \binom{i}{j} y_i + \frac{\beta}{2} \sum_{j=1}^{i-1} \binom{i}{j} y_j\, y_{i-j} + \sum_{j=1}^{i-1} \binom{i}{j} C^*_{p(j+1)}\, y_{i-j} \qquad (i \geqslant 2) \qquad (2.4.15)$$

Initial conditions: $q_1 = q_2 = \cdots\cdots = q_i = 0$ at $x=0$.

where $$C_{pi} = \frac{k_{fp}\, q_i}{k_p(1-x)} \qquad C^*_{pi} = \frac{k^*_p\, q_i}{k_p(1-x)}$$

$$\tau = (R_{td} + R_f)/R_p \quad , \qquad \beta = R_{tc}/R_p \ .$$

R_p; propagation rate.

R_f; rate of chain transfer to monomer and small molecules.

R_{td}; rate of termination by disproportion.

R_{tc}; rate of termination by combination.

The following equations can be used to calculate lower order moments for polymer radicals and polymer molecules.

$$y_1 = \frac{1 + C_{p2} + C^*_{p2}}{\tau + \beta + C_{p1}} \tag{2.4.16}$$

$$y_2 = \frac{1 + C_{p3} + C^*_{p3}}{\tau + \beta + C_{p1}} + \frac{2(1 + C_{p2} + C^*_{p2})(1 + C^*_{p2})}{(\tau + \beta + C_{p1})^2} \tag{2.4.17}$$

$$\frac{dq_2}{dx} = \frac{2(1 + C_{p2} + C^*_{p2})(1 + C^*_{p2})}{\tau + \beta + C_{p1}} + \left[\frac{1 + C_{p2} + C^*_{p2}}{\tau + \beta + C_{p1}}\right]^2 \cdot \beta \tag{2.4.18}$$

$$\frac{dq_3}{dx} = 3\left(\frac{1+C_{p3}+C^*_{p3}}{\tau+\beta+C_{p1}} + \frac{2(1+C_{p2}+C^*_{p2})(1+C^*_{p2})}{(\tau+\beta+C_{p1})^2}\right)\left((1+C^*_{p2}) + \beta\,\frac{1+C_{p2}+C^*_{p2}}{\tau+\beta+C_{p1}}\right)$$

$$+ \frac{3(1+C^*_{p3})(1+C_{p2}+C^*_{p2})}{\tau+\beta+C_{p1}} \qquad (2.4.19)$$

If chain transfer to polymer is negligible, the equations for q_2 and q_3 reduce to the following simple differential equations.

$$\frac{dq_2}{dx} = P_{wp}(1+C^*_{p2})^2 \qquad (2.4.20)$$

$$\frac{dq_3}{dx} = P_{wp}(1+C^*_{p2})[3C^*_{p3} + P_{zp}(1+C^*_{p2})^2] \qquad (2.4.21)$$

where P_{wp} is the instantaneous weight-average chain length of the primary polymer molecules and $P_{wp} = (2\tau + 3\beta)/(\tau+\beta)^2$. P_{zp} is the instantaneous z-average chain length of the primary polymer molecules and $P_{zp} = 6(\tau+2\beta)/[(\tau+\beta)(2\tau+3\beta)]$. Digressing from the subject, it is easy to show that the instantaneous j-th order average chain length of the primary polymer molecules (or linear polymers) P_j is given by

$$P_j = \frac{j}{\tau+\beta} \bullet \frac{2\tau+(j+1)\beta}{2\tau+j\beta} \qquad (2.4.22)$$

For example, P_1 represents the instantaneous number-average chain length for linear polymers (primary polymer molecules are linear), $P_2 = P_{wp}$, and $P_3 = P_{zp}$.

In terms of the moments, the number- and weight-average chain lengths of the accumulated polymer are given by

$$\bar{P}_n = \frac{Q_1+Y_1}{Q_0+Y_0} \qquad (2.4.23)$$

$$\bar{P}_w = \frac{Q_2+Y_2}{Q_1+Y_1} \qquad (2.4.24)$$

When the weight-average chain length $\bar{P}_w$ goes to infinity, the onset of gelation occurs. In practice, however, Q_i is much larger than Y_i except in the very vicinity of the gel point, since the concentration of polymers with radical centers is far smaller than that of polymers as is shown in Figure 2.4.2. Therefore, Equations (2.4.23) and (2.4.24) reduce to the following equations.

$$\bar{P}_n = Q_1/Q_0 = q_1/q_0 \qquad (2.4.25)$$

$$\bar{P}_w = Q_2/Q_1 = q_2/q_1 \qquad (2.4.26)$$

Q_i $(i \geq 2)$ and Y_i $(i \geq 1)$ go to infinity at the same conversion

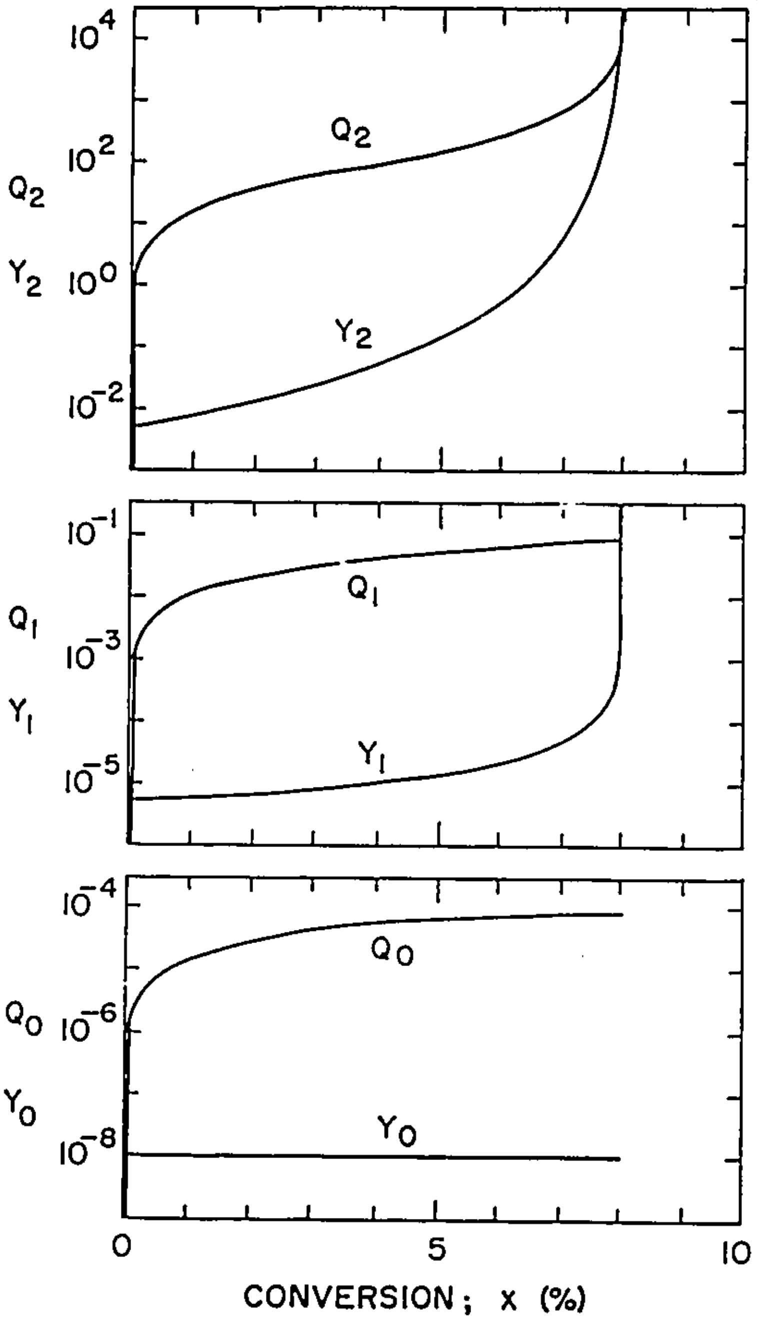


Figure 2.4.2 Comparison of the size of moments for polymers and polymer radicals.
($\tau = \beta = 1 \times 10^{-3}$, $k_p^* / k_p = 1 \times 10^{-2}$, $Y_0 = 1 \times 10^{-8}$, $[M]_0 = 1$)

x_c, while Q_1, Q_0, and Y_0 remain finite at all conversions. In practice, when the second order moment q_2 (or Q_2) goes to infinity, the onset of gelation is predicted to occur.

Similarly, it is possible to calculate the number- and weight-average chain lengths for polymer radicals as follows.

$$\bar{P}_n^{\bullet} = Y_1/Y_0 = y_1 \tag{2.4.27}$$

$$\bar{P}_w^{\bullet} = Y_2/Y_1 = y_2/y_1 \tag{2.4.28}$$

This method is unique in the fact that the difference in the size of polymer molecules with and without radical centers can be shown. An simple example is shown in Figure 2.4.3. The size of polymer radicals is usually larger than that of polymer molecules without radical centers, since the larger polymers have a better chance of being attacked by a polymer radical and becoming a polymer radical. Strictly, this moment method breaks down at the very vicinity of the gel point, since all polymer radicals are assumed to possess only one radical center per polymer molecule. However, the calculation results showing that the number-average chain length of the polymer radicals goes to infinity may be interpreted as follows - the gel molecule is not a dead polymer, but a polymer molecule with many radical centers.

Figure 2.4.4 shows an example of the application of the method of moments derived herein to the copolymerization of styrene and

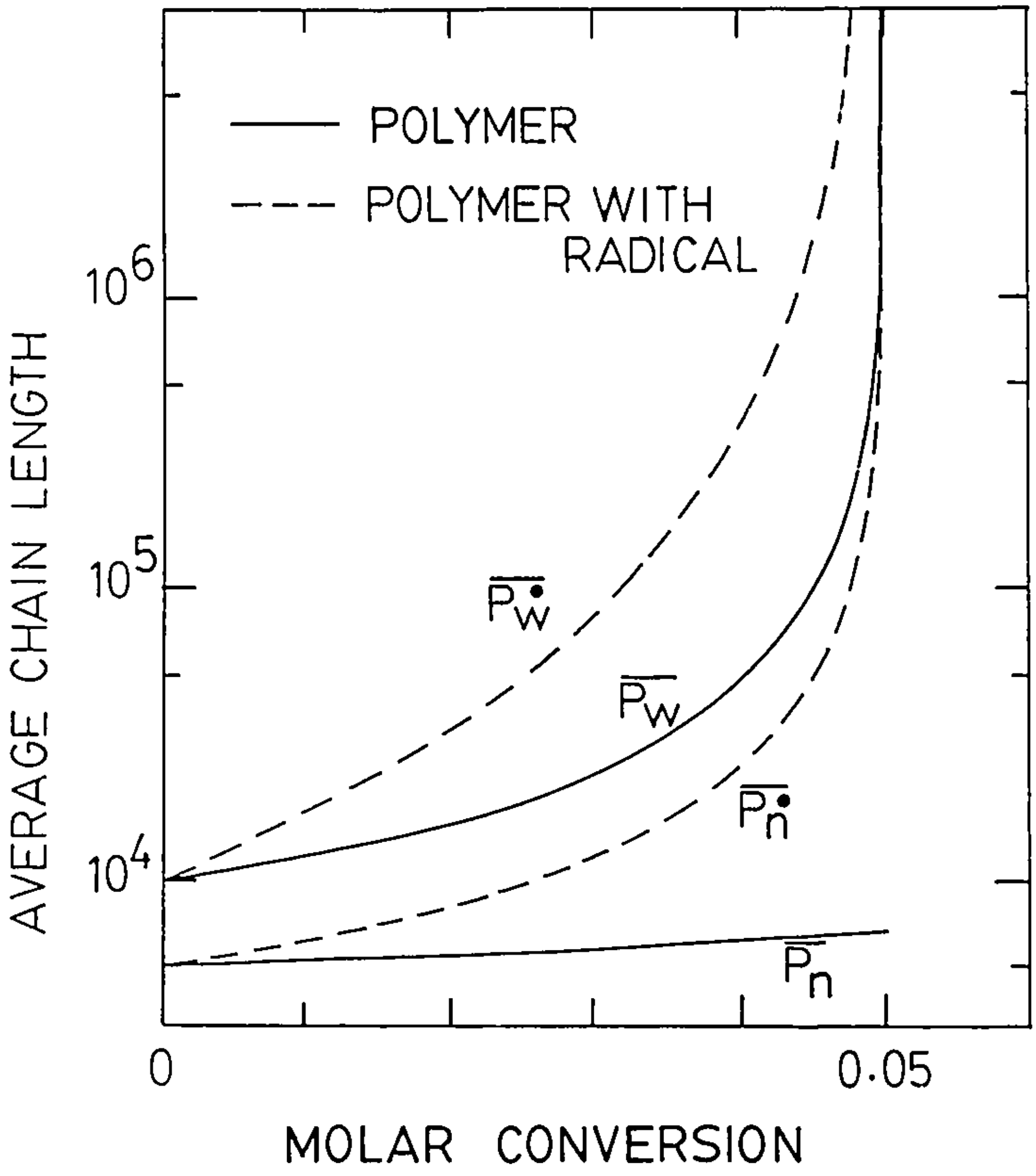


Figure 2.4.3 Average chain length development for polymers with and without radical centers in the pre-gelation period.

$\tau = 2 \times 10^{-4}$, $k_p^* / k_p = 2 \times 10^{-3}$.

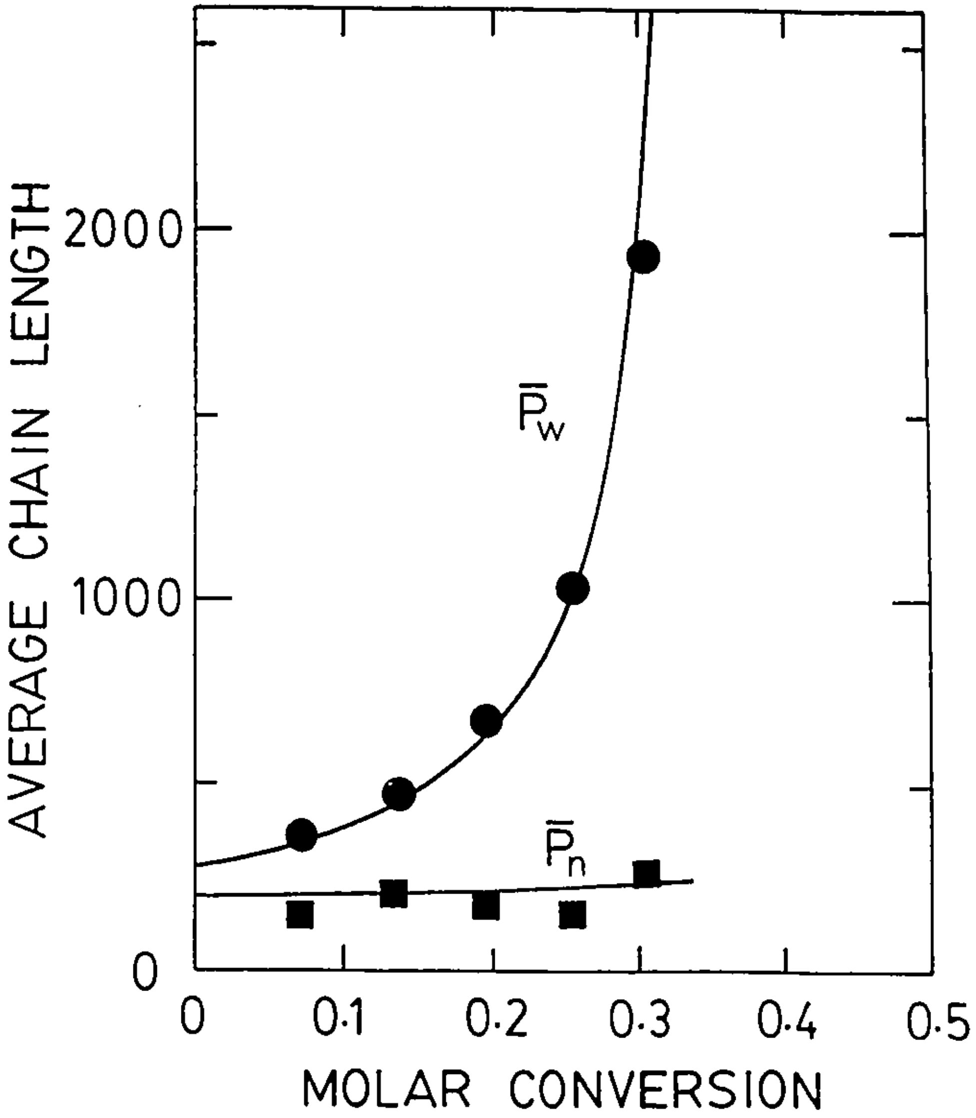


Figure 2.4.4 Average chain length development in the pre-gelation period. (Copolymerization of styrene/m-DVB in benzene at 60°C [Hild, Okasha (1985)]. $f_{20} = 0.0196$, $[M]_0 = 4.08$ mol/L, $[AIBN] = 0.08$ mol/L, $r_1 = 0.44$, $k_d = 8.5 \times 10^{-6}$, $f = 0.614$, $k_p/k_{tc}^{0.5} = 0.0213$, $k_p^*/k_p = 0.255$.

m-divinylbenzene. The experimental data were taken from a paper by Hild and Okasha [Hild, Okasha (1985a)]. The weight-average molecular weight was determined by light scattering, while the number-average molecular weight was determined by gel permeation chromatography (GPC). Although the effect of cyclization is not considered in the calculation, agreement with data seems to be satisfactory. (The calculated gel point deviates from the observed gel point. This may be attributed to the significant intramolecular reactions near the gel point, and the specific diffusion controlled crosslinking reactions as is discussed in Chapter 4.)

Since n-th order moment equation is given, theoretically, it should be possible to calculate the chain length distribution. Bamford and Tompa (1953,1954) calculated the chain length distribution from the moment equations applying Laguerre polynominals. However, this method is, practically, restricted to the initial stage of reaction where the polydispersity (= $\bar{P}_w/\bar{P}_n$) is not large, since the series does not converge rapidly (, although it may not be impossible to calculate). In order to understand how chain length distribution changes during crosslinking polymerization qualitatively, one may resort to the analysis for crosslinking of pre-formed chains (see Appendix G).

[B] Chain Transfer to Polymer

An interesting question about this reaction type is whether chain transfer to polymer can cause gelation or not. Flory (1947b) predicted that chain transfer to polymer would not cause gelation without assistance of other inter-linking processes. In our formalism of the method of moments, the fundamental equation for the second order moment is given by

$$\frac{dq_2}{dx} = \frac{2\,(1+C_{p2})}{\tau+\beta+C_{p1}} + \frac{\beta\,(1+C_{p2})^2}{(\tau+\beta+C_{p1})^2} \qquad (2.4.29)$$

(In the above equation, the terminal double bonds are assumed not to react.) From Equation (2.4.29), it is possible to prove that chain transfer to polymer plus termination by disproportionation can never cause gelation, however, if the bimolecular termination reaction includes combination, gelation is predicted to occur under certain conditions. The proof that an infinitely large molecule cannot be produced by chain transfer to polymer with termination by disproportionation is shown in Appendix H. Figure 2.4.5 and 2.4.6 show some of the calculated results. (Please note that the ordinate of Figure 2.4.6 is plotted in a logarithmic scale.)

Why does termination by combination makes it possible to form a infinitely large molecule while termination by disproportionation cannot? Termination by combination is a process which makes an inter-linking between two polymer radicals as is shown in Figure 2.4.7. The product **P** has, at least from a topological point of view, the same structure as the crosslinking formed by vinyl/divinyl copolymerization, which was shown in Figure 2.1.1 (p.32). There is a clear difference between the molecules produced by chain transfer to polymer with termination by disproportionation.

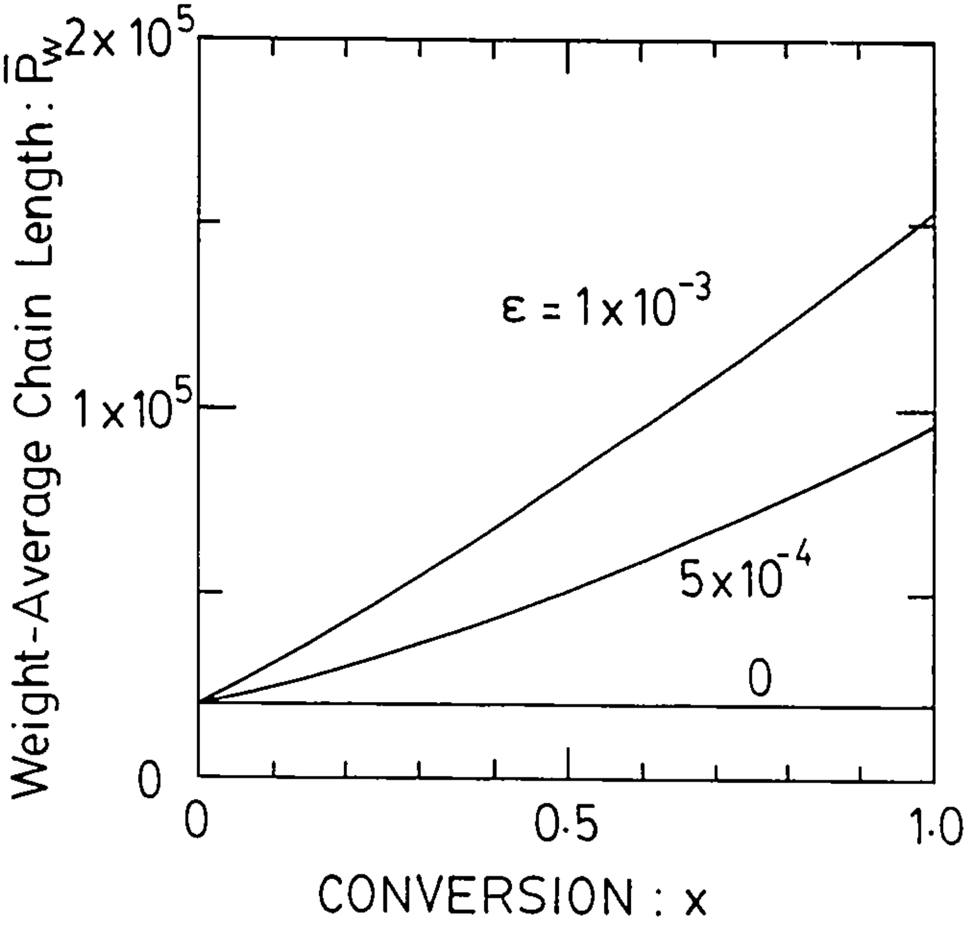


Figure 2.4.5 Weight-average chain length development for chain transfer to polymer with termination by disproportionation. ($\tau = 1.0 \times 10^{-4}$) $\varepsilon = k_{fp}/k_p$.

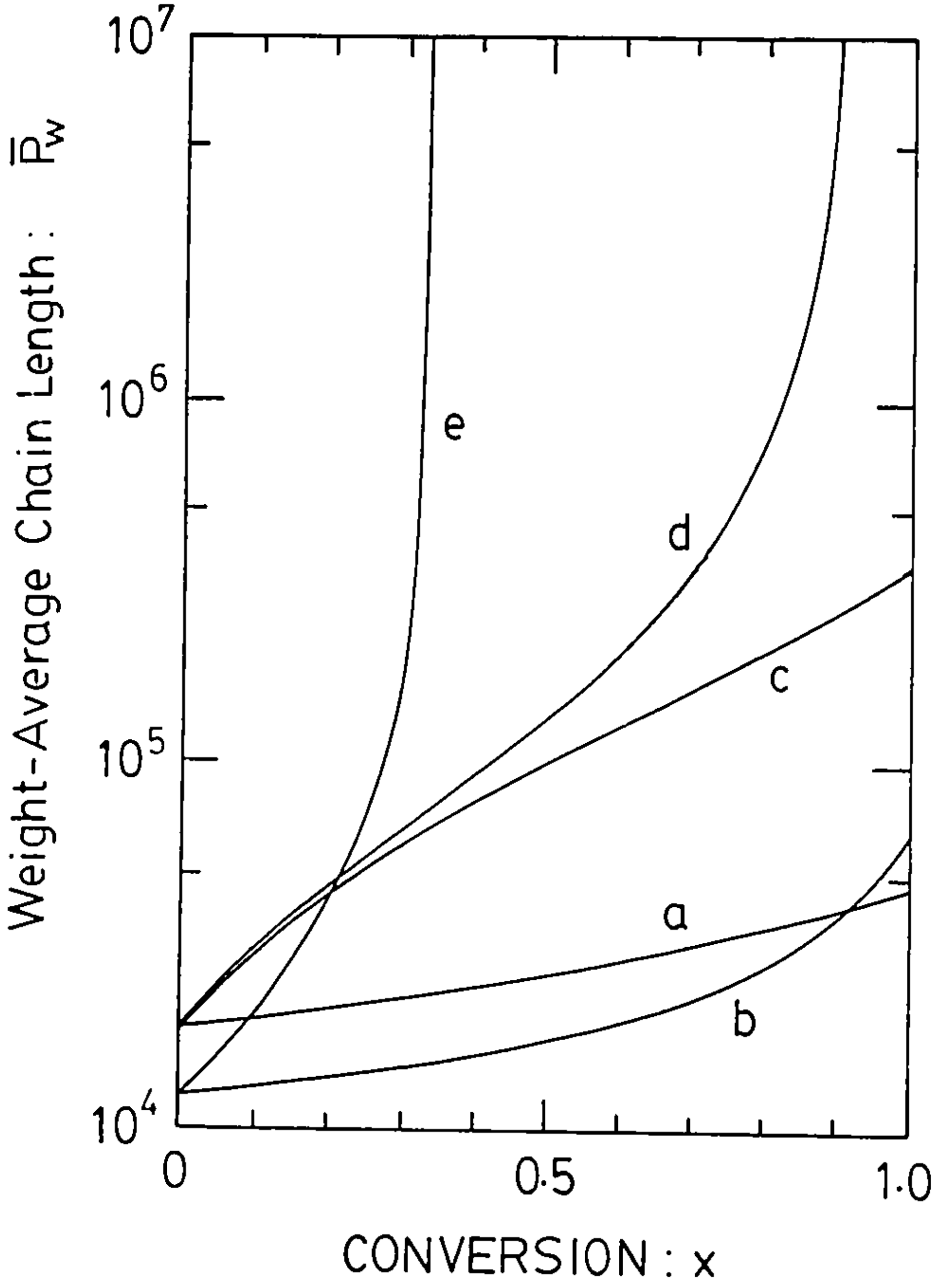


Figure 2.4.6 Weight-average chain length development for chain transfer to polymer with termination by disproportionation and combination.

	a	b	c	d	e
τ	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}
β	1×10^{-5}	1×10^{-4}	5×10^{-6}	1×10^{-5}	1×10^{-4}
k_{fp}/k_p	1×10^{-4}	1×10^{-4}	1×10^{-3}	1×10^{-3}	1×10^{-3}

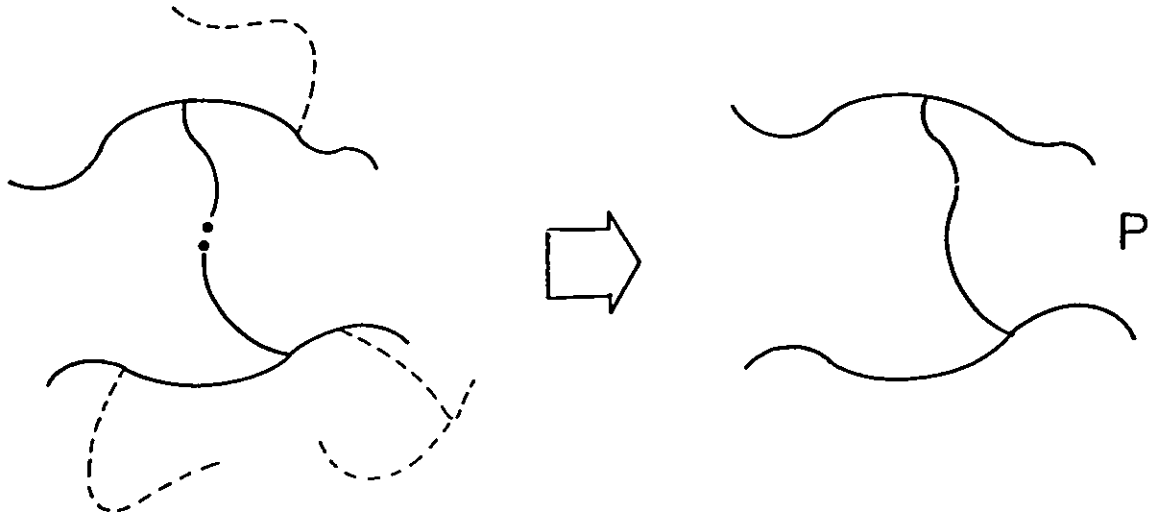


Figure 2.4.7 Chain transfer to polymer with termination by combination.

[C] Comparison with Flory's Theory

Flory's theory assumes an equilibrium system, and therefore, it is not applicable for the cases where the crosslinking density distribution has a significant variance. However, quite often the variance of the crosslinking density distribution is rather small at low conversions, thus the effect of crosslinking density distribution may be negligible for the pre-gelation period. Therefore, Flory's theory may be valid for the pre-gelation period for a wider range of conditions than originally expected. From Flory's theory, the weight-average chain length $\bar{P}_w$ in the pre-gelation period is given by

$$\bar{P}_w(x) = \frac{\bar{P}_{wp}(x)}{1 - \bar{\rho}(x)\ \bar{P}_{wp}(x)} \qquad (2.4.30)$$

where $\bar{P}_{wp}(x)$ is the weight-average chain length of the accumulated primary polymer molecules at conversion x.

Though Flory did not show a general calculation method for the crosslinking density, $\bar{\rho}(x)$, in free radical copolymerization of vinyl and divinyl monomer, it is possible to apply Equation (2.2.9) to calculate crosslinking density of the accumulated polymer and compare Flory's theory with our kinetic theory.

The equivalence has been proven theoretically for two limiting conditions, namely, (a) gelation occurs at very low conversions, and (b) low mole fraction limit of divinyl monomer with Flory's simplifying assumptions (see Appendix I). For other conditions, numerical calculations show that there is, practically, no difference between Equation (2.4.30) and our kinetic approach as is shown in Figure 2.4.8-a,b,c (calculation conditions are shown in Table 2.4.1). From a theoretical point of view, the fundamental concepts for these two models may be different, however, from a practical point of view, it may be concluded that our kinetic model using the method of moments and Flory's theory are equivalent in the pre-gelation period.

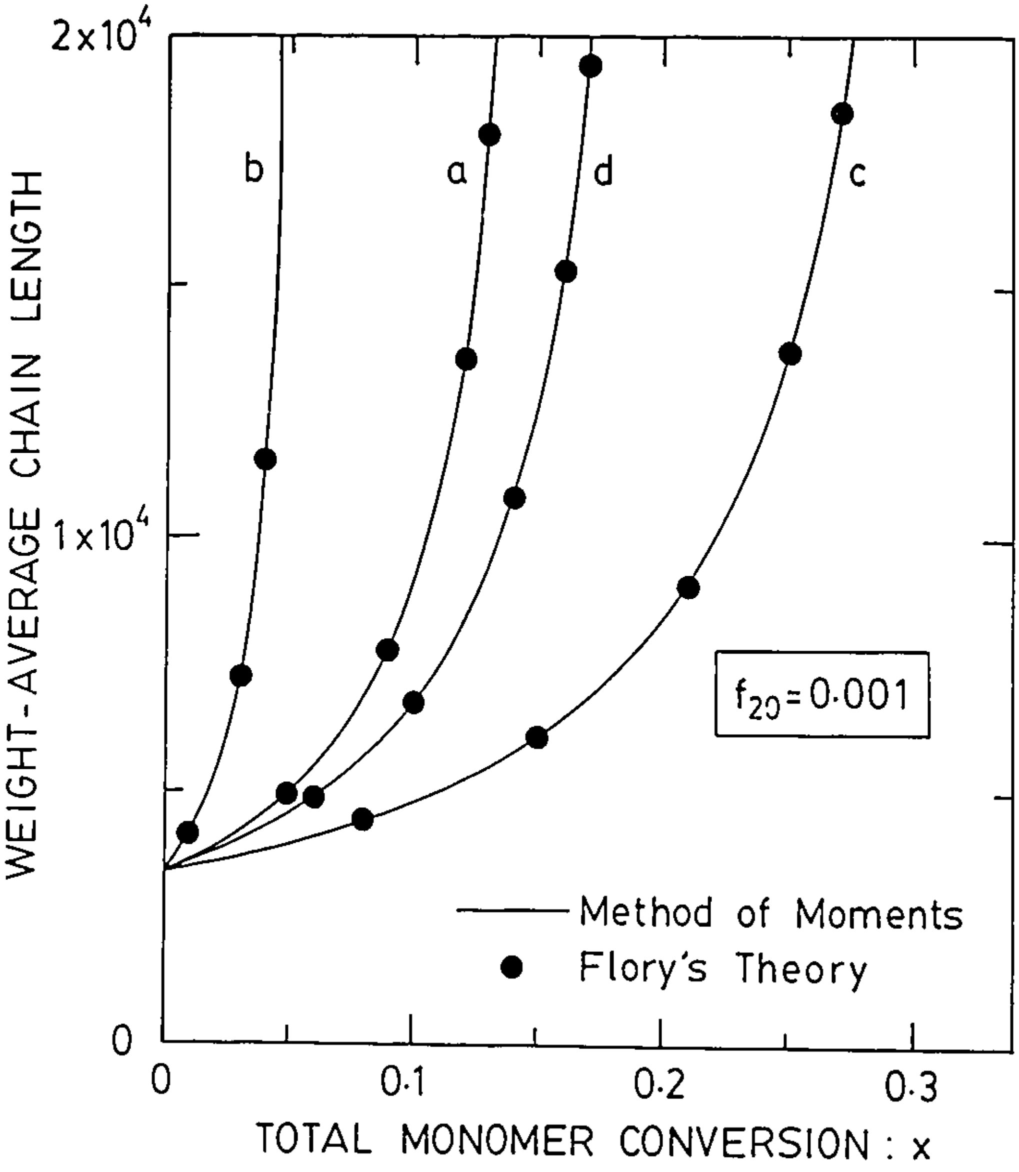


Figure 2.4.8-a Comparison between the method of moments and Flory's theory. $f_{20} = 0.001$

(Kinetic parameters used are shown in Table 2.4.1.)

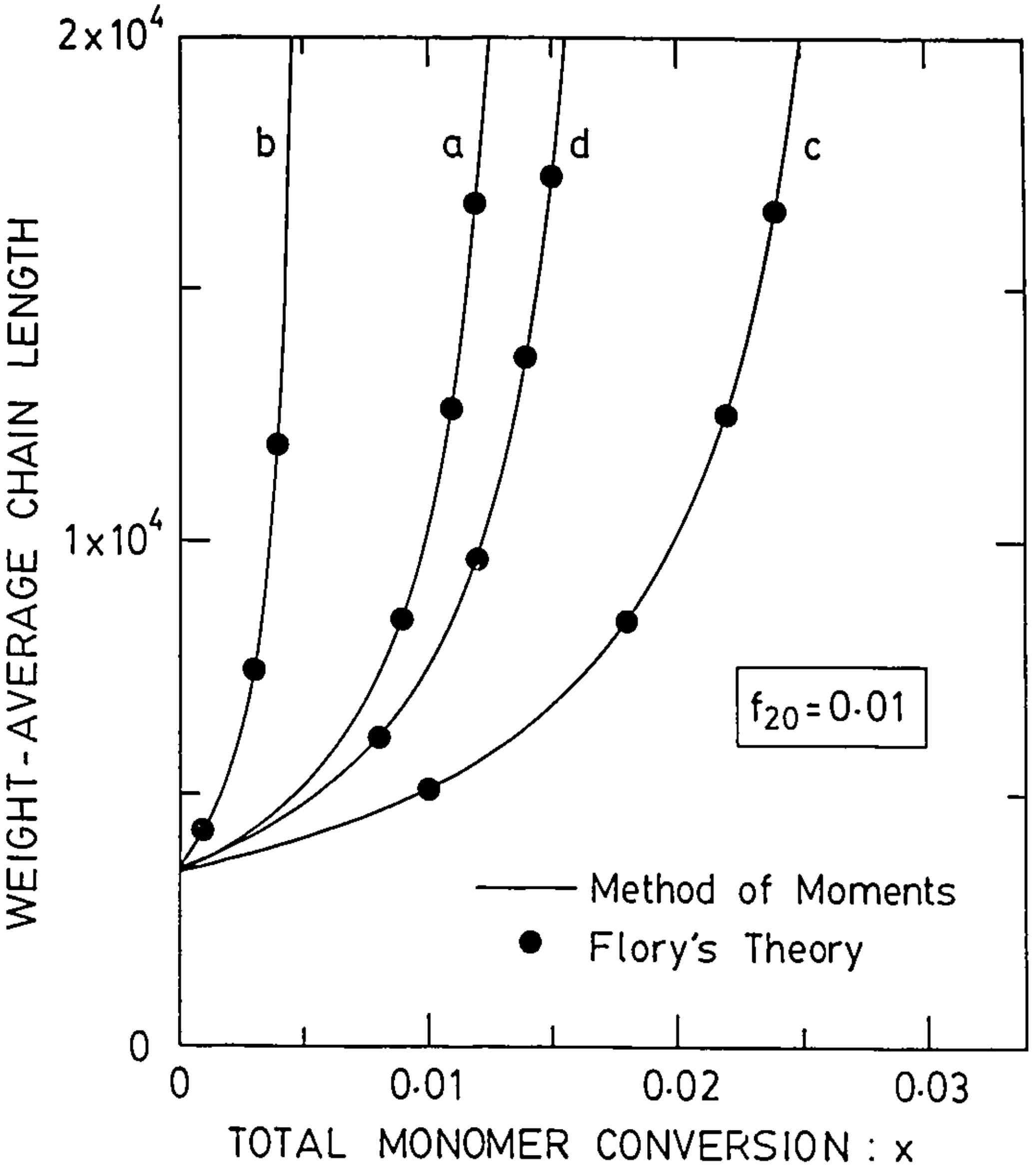


Figure 2.4.8-b Comparison between the method of moments and Flory's theory. $f_{20} = 0.01$

(Kinetic parameters used are shown in Table 2.4.1.)

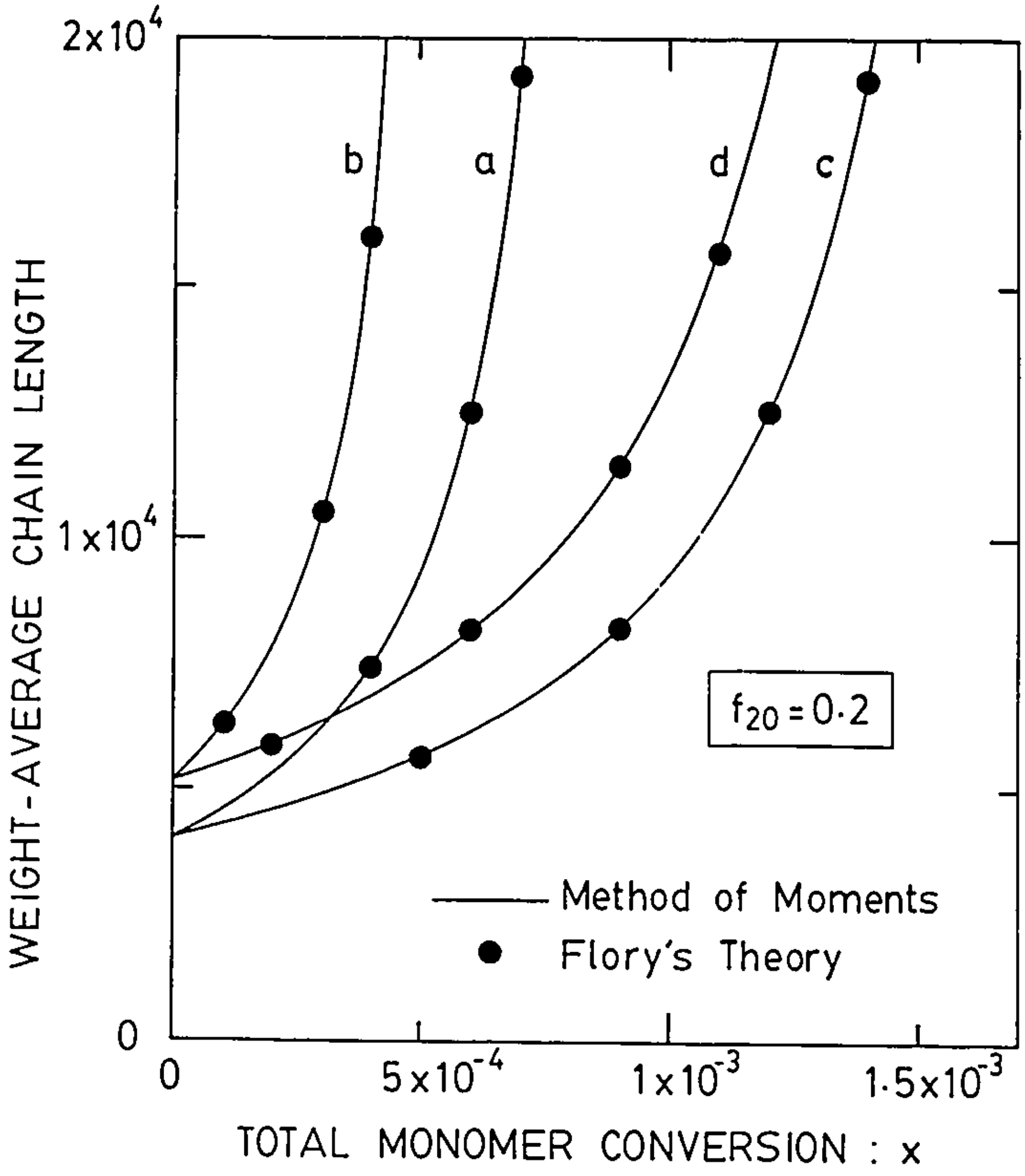


Figure 2.4.8-c Comparison between the method of moments and Flory's theory. $f_{20} = 0.2$

(Kinetic parameters used are shown in Table 2.4.1.)

Table 2.4.1 Calculation conditions for Figure 2.4.8.

$[M]_0 = 9.0$ mol/L , $[I]_0 = 0.02$ mol/L ,

Initiation; $k_d = 5.0 \times 10^{-6}$ sec^{-1} , $f = 1.0$

Termination; $k_{td11} = k_{td12} = k_{td22} = k_{tc11} = k_{tc12} = k_{tc22} = 1.0 \times 10^7$

	a equal reactivity	b unequal reactivity	c decreased reactivity of pendant double bonds	d
k_{11}	300	300	300	300
k_{12}	600	1000	600	1000
k_{21}	300	500	300	500
k_{22}	600	500	600	500
k^*_{p13}	300	500	150	150
k^*_{p23}	300	250	150	150

No cyclization reactions.

(Since the number of crosslinkages in the pre-gelation period is very small, it is reasonable to neglect monomer consumption by just reacted pendant double bonds, $\Phi^{\bullet}_3$.)

2.5. Post-Gelation Period -- A Generalization of Flory's Theory --

The quantitative treatment of the post-gelation period is, in general, much more difficult than that for pre-gelation period. One of the simplest methods is to consider the gel growth (or sol decrease) based on the chemical kinetics using the same pseudo-kinetic rate constant for crosslinking reaction defined by Equation (2.4.4). However, the error associated with the use of Equation (2.4.4) increases as reaction proceeds, i.e., at high conversions (see Appendix E). Furthermore, there are problems concerning the conditions right at the gel point (details are discussed in Appendix J). In this section, Flory's theory for the post-gelation period [Flory (1947a)] is generalized.

Flory's theory of network formation assumes an equilibrium system, and therefore, generalization is necessary in order for it to be applicable to a free radical polymerization system except under Flory's simplifying assumptions (see p.15). For Flory's simplifying assumptions, the variance of the crosslinking density distribution is zero, namely, all primary polymer molecules possess the same crosslinking density independent of their birth time. This is equivalent to stating that there is no difference between kinetic models which consider the history of the generated network structure and the models which assume an equilibrium system. However, Flory's simplifying assumptions are unrealistic for free radical polymerization in the post-gelation period, and therefore, it is necessary to account for the crosslinking density distribution. Applying the concept of crosslinking density distribution as a function of birth conversion, Θ, it is possible to generalize Flory's theory of network formation for the post-gelation period.

For example, let us consider the weight fraction of sol W_s. From the statistical theory by Flory, the weight fraction of sol is given by

$$W_s = \sum_{r=1}^{\infty} w_r^f \, (1-\rho^f W_g)^r \qquad (\rho^f \ll 1) \tag{2.5.1}$$

where W_g is the weight fraction of gel, namely, $W_g = 1-W_s$, and w_r^f is the weight-chain length distribution of the primary polymer molecules which is given by the number of units, not by the number of monomer units. Similarly, the crosslinking density should also be expressed with respect to the number of units. However, from the theoretical point of view, the use of Equation (2.5.1) is restricted to low crosslinking density regions. Therefore, ρ^f and w_r^f can be substituted by ρ and w_r respectively with negligible error. Then, how should Equation (2.5.1) be modified when the crosslinking density is not far smaller than unity? Practically, when the crosslinking density is not far smaller than unity, there is no sol left in the reaction system if the primary polymer chain length is large enough, and Equation (2.5.1) expresses this behavior well. Therefore, from a practical point of view, Equation (2.5.1) can also be applied to high crosslinking density regions, though in these regions Equation (2.5.1) gives $W_s \simeq 0$.

Now, let us generalize Equation (2.5.1) using the crosslinking density distribution. At conversion ψ, the weight fraction of sol for the primary polymer molecules which were born at conversion Θ is given by

$$W_s(\Theta,\psi) = \sum_{r=1}^{\infty} w_r(\Theta)[1-\rho(\Theta,\psi)\ W_g(\Theta,\psi)]^r \qquad (2.5.2)$$

Since the primary polymer molecules are linear polymers, we know the functional form of $w_r(\Theta)$.

$$w_r(\Theta)=(\tau(\Theta)+\beta(\Theta))[\tau(\Theta)+(\beta(\Theta)/2)(\tau(\Theta)+\beta(\Theta))(r-1)]r\Phi^{r+1} \qquad (2.5.3)$$

where $\Phi=1/[1+\tau(\Theta)+\beta(\Theta)]$.

Substituting Equation (2.5.3) into Equation (2.5.2), one obtains

$$W_s(\Theta,\psi) = A\ G_1\ [T + A\ B\ G_1] \qquad (2.5.4)$$

where $T = \tau(\Theta)/[\ \tau(\Theta)+\beta(\Theta)+\rho(\Theta,\psi)\ W_g(\Theta,\psi)]$

$B = \beta(\Theta)/[\ \tau(\Theta)+\beta(\Theta)+\rho(\Theta,\psi)\ W_g(\Theta,\psi)]$

$A = T + B$

$G_1 = 1-\rho(\Theta,\psi)\ W_g(\Theta,\psi)$.

The accumulated sol fraction which can be measured in experiments is found by integration over all birth conversions.

$$\overline{W}_s(\psi) = \frac{1}{\psi}\int_0^{\psi} W_s(\Theta,\psi)\ d\Theta \qquad (2.5.5)$$

Other important properties which were derived by Flory (1947a) can similarly be generalized as follows.

Partition of Crosslinkages between Sol and Gel: The crosslinking density of the sol fraction (ρ^{sol}) and gel fraction (ρ^{gel}) are given by

$$\rho^{sol}(\theta,\psi) = \rho(\theta,\psi)\ W_s(\theta,\psi) \tag{2.5.6}$$

$$\rho^{gel}(\theta,\psi) = \rho(\theta,\psi)\ [1+ W_s(\theta,\psi)] \tag{2.5.7}$$

The crosslinking density of accumulated polymer in each fraction is given by

$$\bar{\rho}^{sol}(\psi) = \frac{1}{\psi\,\overline{W}_s(\psi)}\int_0^{\psi} \rho^{sol}(\theta,\psi)\ W_s(\theta,\psi)\ d\theta \tag{2.5.8}$$

$$\bar{\rho}^{gel}(\psi) = \frac{1}{\psi\,\overline{W}_g(\psi)}\int_0^{\psi} \rho^{gel}(\theta,\psi)\ W_g(\theta,\psi)\ d\theta \tag{2.5.9}$$

The elastic crosslinking density in the sol fraction ($\rho^{sol}_{el.}$) and gel fraction ($\rho^{gel}_{el.}$) may be calculated by substituting $\rho_{el.}(\theta,\psi)$ for $\rho(\theta,\psi)$.

Number- and Weight-Average Chain Length of the Primary Polymer Molecules which Belong to the Sol Fraction: At $x = \psi$, the weight-chain length distribution of the primary polymer molecule, which were born at $x = \Theta$, within the sol fraction is given by

$$w_r^{sol}(\Theta,\psi) = w_r(\Theta)\ G_1^{\,r} \ /\ W_s(\Theta,\psi) \qquad (2.5.10)$$

The number-average chain length of the primary polymer molecules which were born at $x = \Theta$ is given by

$$P_{np}^{sol}(\Theta,\psi) = \frac{1}{\sum_{r=1}^{\infty} [\, w_r^{sol}(\Theta,\psi)/r \,]} \qquad (2.5.11)$$

Substituting Equation (2.5.11) into Equation (2.5.10), one obtains

$$P_{np}^{sol}(\Theta,\psi) = \frac{W_s(\Theta,\psi)}{A G_1\, [\, \tau(\Theta) + (\, \beta(\Theta)/2)\, A\, G_1 \,]} \qquad (2.5.12)$$

The accumulated value up to $x = \psi$ is given by

$$\bar{P}_{np}^{sol}(\psi) = \frac{\psi\ \overline{W}_s(\psi)}{\int_0^{\psi} \frac{W_s(\Theta,\psi)}{P_{np}^{sol}(\Theta,\psi)}\, d\Theta} \qquad (2.5.13)$$

The weight-average chain length of the primary polymer molecules which were born at $x=\Theta$ is given by

$$P_{wp}^{sol}(\Theta,\psi) = \sum_{r=1}^{\infty} r\, w_r^{sol}(\Theta,\psi) \qquad (2.5.14)$$

Substituting Equation (2.5.10) into Equation (2.5.14), one obtains

$$P_{wp}^{sol}(\Theta,\psi) = \frac{\Lambda\ U}{W_s(\Theta,\psi)}[T\ G_2 + \Lambda\ B\ G_1\ G_3] \qquad (2.5.15)$$

where $U = G_1/[\tau(\Theta) + \beta(\Theta) + \rho(\Theta,\psi)\ W_g(\Theta,\psi)]$

$G_2 = 2 - \rho(\Theta,\psi)\ W_g(\Theta,\psi)$

$G_3 = 3 - \rho(\Theta,\psi)\ W_g(\Theta,\psi)$.

The accumulated weight-average chain length of the primary polymer molecules within sol fraction is given by

$$\bar{P}_{wp}^{sol}(\psi) = \frac{1}{\psi \bar{W}_s(\psi)} \int_0^{\psi} P_{wp}^{sol}(\Theta,\psi)\ W_s(\Theta,\psi)\ d\Theta \qquad (2.5.16)$$

<u>Number- and Weight-Average Chain Length of Sol Fraction</u>:

Number-average chain length of the sol fraction is given by

$$\bar{P}_n^{sol}(\psi) = \frac{1}{[\ 1/\bar{P}_{np}^{sol}(\psi)\ ] - [\ \bar{\rho}^{sol}(\psi)\ /2\ ]} \qquad (2.5.17)$$

$\bar{P}_{np}^{sol}(\psi)$ is given by Equation (2.5.13).

The weight-average chain length of the sol fraction is given by

$$\bar{P}_{w}^{sol}(\psi) = \frac{\bar{P}_{wp}^{sol}(\psi)\,[\,1 + \bar{\rho}^{sol}(\psi)\,]}{1 - \bar{\rho}^{sol}(\psi)\,[\,\bar{P}_{wp}^{sol}(\psi) - 1\,]}$$

$$\simeq \frac{\bar{P}_{wp}^{sol}(\psi)}{1 - \bar{\rho}^{sol}(\psi)\,\bar{P}_{wp}^{sol}(\psi)} \qquad (2.5.18)$$

<u>Number-Average Chain Length of the Primary Polymer Molecules which Belong to the Gel Fraction</u>: This property may be useful when one uses the classical equation for swelling derived by Flory (see Equation (3.1.1)).

The weight-chain length distribution of the primary polymer molecules within gel fraction $w_r^{gel}(\theta,\psi)$ is given by

$$w_r^{gel}(\theta,\psi) = [w_r(\theta) - w_r^{sol}(\theta,\psi)\; W_s(\theta,\psi)]/W_g(\theta,\psi)$$

$$= w_r(\theta)\;(1 - G_1{}^{r}) / W_g(\theta,\psi) \qquad (2.5.19)$$

The number-average chain length of the primary polymer molecules which belong to the gel fraction $P_{np}^{gel}(\theta,\psi)$ is given by

$$P_{np}^{gel}(\Theta,\psi) = \frac{1}{\sum_{r=1}^{\infty} w_r^{gel}(\Theta,\psi)/r}$$

$$= \frac{W_g(\Theta,\psi)}{S[\,\tau(\Theta)+(\,\beta(\Theta)/2)\,S\,]} \qquad (2.5.20)$$

where $S= \rho(\Theta,\psi)\ W_g(\Theta,\psi)/[\tau(\Theta)+\ \beta(\Theta)+\ \rho(\Theta,\psi)\ W_g(\Theta,\psi)]$.
The accumulated value $\overline{P}_{np}^{gel}(\psi)$ is given by

$$\overline{P}_{np}^{gel}(\psi) = \frac{\psi\ \overline{W}_g(\psi)}{\int_0^{\psi} \frac{W_g(\Theta,\psi)}{P_{np}^{gel}(\Theta,\psi)}\ d\Theta} \qquad (2.5.21)$$

The generalized Flory's theory shown in this section accounts for the kinetic build up of the network structure through the crosslinking density distribution which is a very important feature in a free radical polymerization system. However, this theory still assumes an imaginary equilibrium among the primary polymer molecules which were born at the same time. Therefore, this theory is an approximate approach and does not fully reflect the kinetic feature of network formation in free radical polymerization.

3. APPLICATIONS

3.1. Copolymerization of Methyl Methacrylate / Ethylene Glycol Dimethacrylate

The copolymerization of methyl methacrylate (MMA) with ethylene glycol dimethacrylate (EGDMA) has been investigated for more than 40 years [Walling (1945); Loshaek et al. (1953),(1955); Gordon, Roe (1956a,b,c,d); Shultz (1958); Hayden, Melville (1960); Horie, et al. (1975); Whitney, Burchard (1980); Landin, Macosko (1988)]. However, comprehensive experimental data on the kinetics of network formation especially for the post-gelation period are not available. In order to test the present theory, an experimental investigation on the kinetics of the bulk free radical copolymerization of MMA and the divinyl monomer, EGDMA, initiated with azobisisobutyronitrile (AIBN) at 70°C covering a wide range of monomer conversions was made.

[A] Experimental

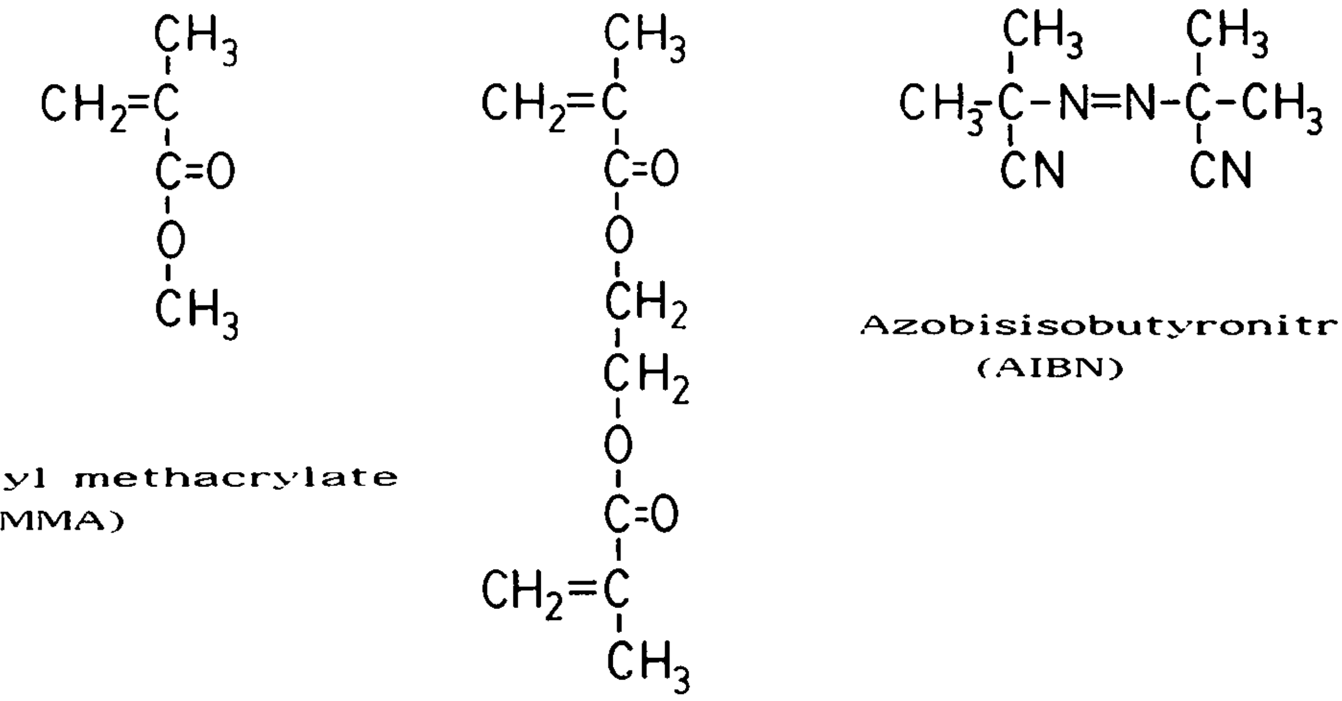
The mono-vinyl monomer, methyl methacrylate (MMA) (Regent grade, Fisher Scientific) was washed with 10% aqueous potassium hydroxide to remove inhibitor (hydroquinone monomethyl ether), followed by several washing with deionized water. After drying successively with anhydrous sodium sulfate and 4 Å molecular sieves, it was distilled under reduced pressure. The middle fraction was collected.

The divinyl monomer, ethylene glycol dimethacrylate (EGDMA) (Aldrich Chemical), was washed similarly to remove inhibitor (hydroquinone), and then distilled under reduced pressure.

The initiator, azobisisobutyronitrile (AIBN) (Eastman Kodak), was recrystallized three times from absolute methanol, followed by drying in vacuum at room temperature. The chemical structures of MMA, EGDMA, and AIBN are shown in Figure 3.1.1.

Monomer solutions were prepared shortly before use by weighing the required amounts of MMA, EGDMA, and AIBN. Each of the pyrex ampoules of 5 mm O.D. was filled with ca. 2g of monomer solution. After degassing by four successive freeze-thaw cycles using liquid nitrogen and a reduced pressure, the ampoules were torch sealed. The polymerization was initiated by immersing the ampoules in an oil bath maintained at 70 °C. The polymerization was stopped by thrusting the ampoules into liquid nitrogen.

The ampoules were broken and the contents were put into a covered flask with acetone and hydroquinone. After being shaken on a shaker for 24 hours, the swollen gel, if present, was concentrated by centrifugation, and then it was extracted by acetone in a Soxhlet extractor with a coarse grade glass thimble for one day. The sol-free gel was dried at 120 °C in a vacuum for one week to constant weight. The sol polymer was precipitated from solution using methanol, and dried at 50 °C in a vacuum oven for two days. Conversions to gel and sol were



Methyl methacrylate
(MMA)

Ethylene glycol
dimethacrylate
(EGDMA)

Azobisisobutyronitrile
(AIBN)

Figure 3.1.1 Structure of MMA, EGDMA, and AIBN.

determined gravimetrically. Typical experimental results are shown in Figure 3.1.2. A gel molecule is formed abruptly right at gel point, x_c, and it grows fairly rapidly in the post gelation period. The gel once formed acts like a great sponge rapidly consuming sol polymer and polymer radicals. The autoacceleration which is known as the "Trommsdorf effect" or "gel effect" is fairly significant. (The experimental data are tabulated in Appendix K.)

In order to estimate the structural properties, swelling experiments were done at room temperature. Usually it took three days to reach an equilibrium state. Typical experimental results are shown in Figure 3.1.3. The swelling ratio, q_m, is the ratio of volume of swollen and unswollen structures. It was assumed that the volume change in mixing of gel and solvent is negligible. Since chloroform gives higher swelling ratios, we decided to use chloroform as the test solvent.

As it is well-known, the swelling behavior of a polymer network can be described by a balance between mixing and elastic free energy [Flory (1953)]. Although sophisticated models for the elastic behavior of polymer networks are being developed [Ronca, Allegra (1975); Flory (1976),(1985); Marrucci (1981); Questel, Mark (1985); Edwards, Vilgis (1986); Adolf (1988)], they are too complex to be applied, and therefore, we used the original Flory's theory [Flory (1953)] to estimate the crosslinking density of a gel molecule. The fundamental equation for swelling used is given by the following equation [Flory (1956); Hwa (1962); Miller (1966)].

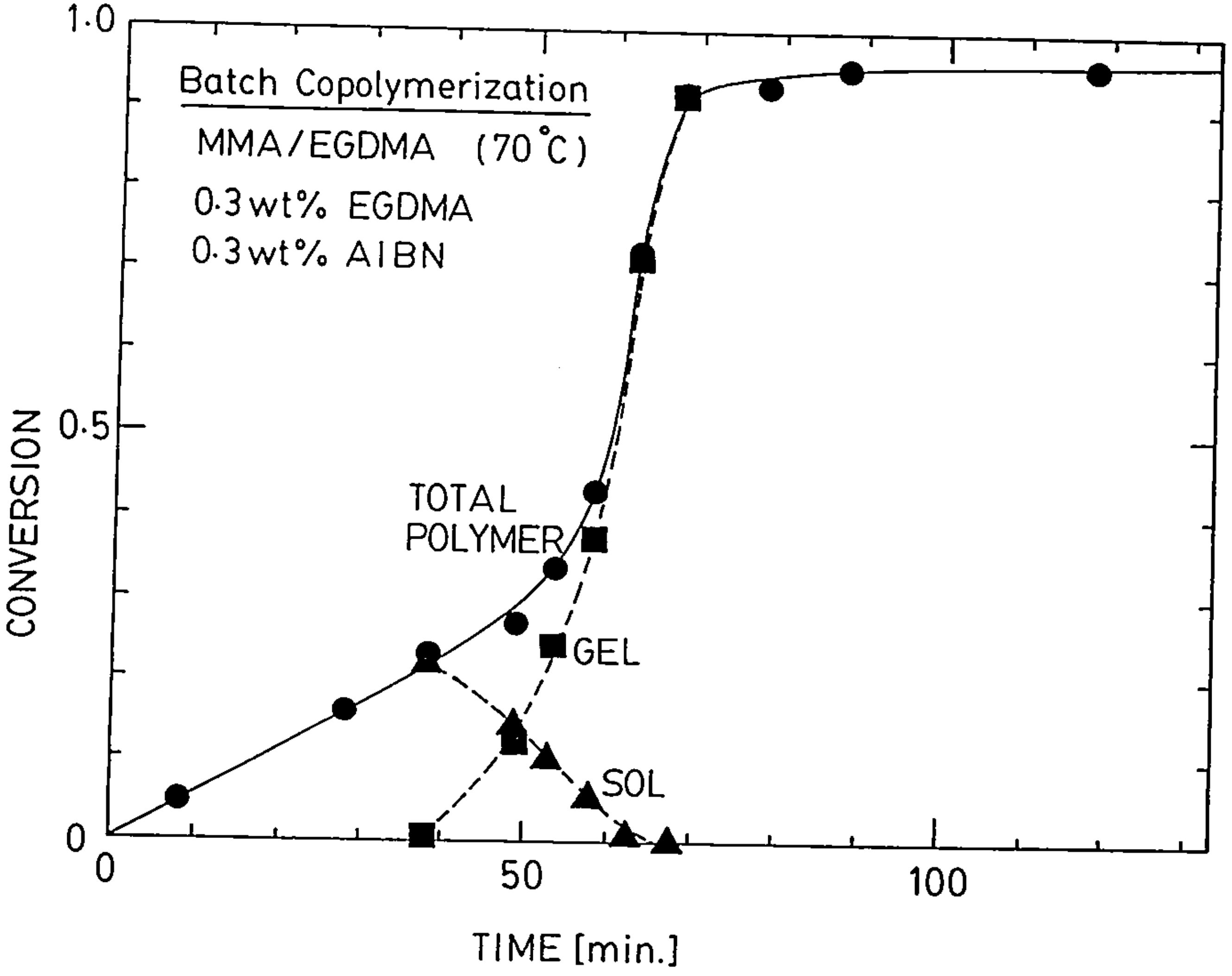


Figure 3.1.2 Bulk copolymerization of MMA and EGDMA.

$f_{20} = 1.52 \times 10^{-3}$

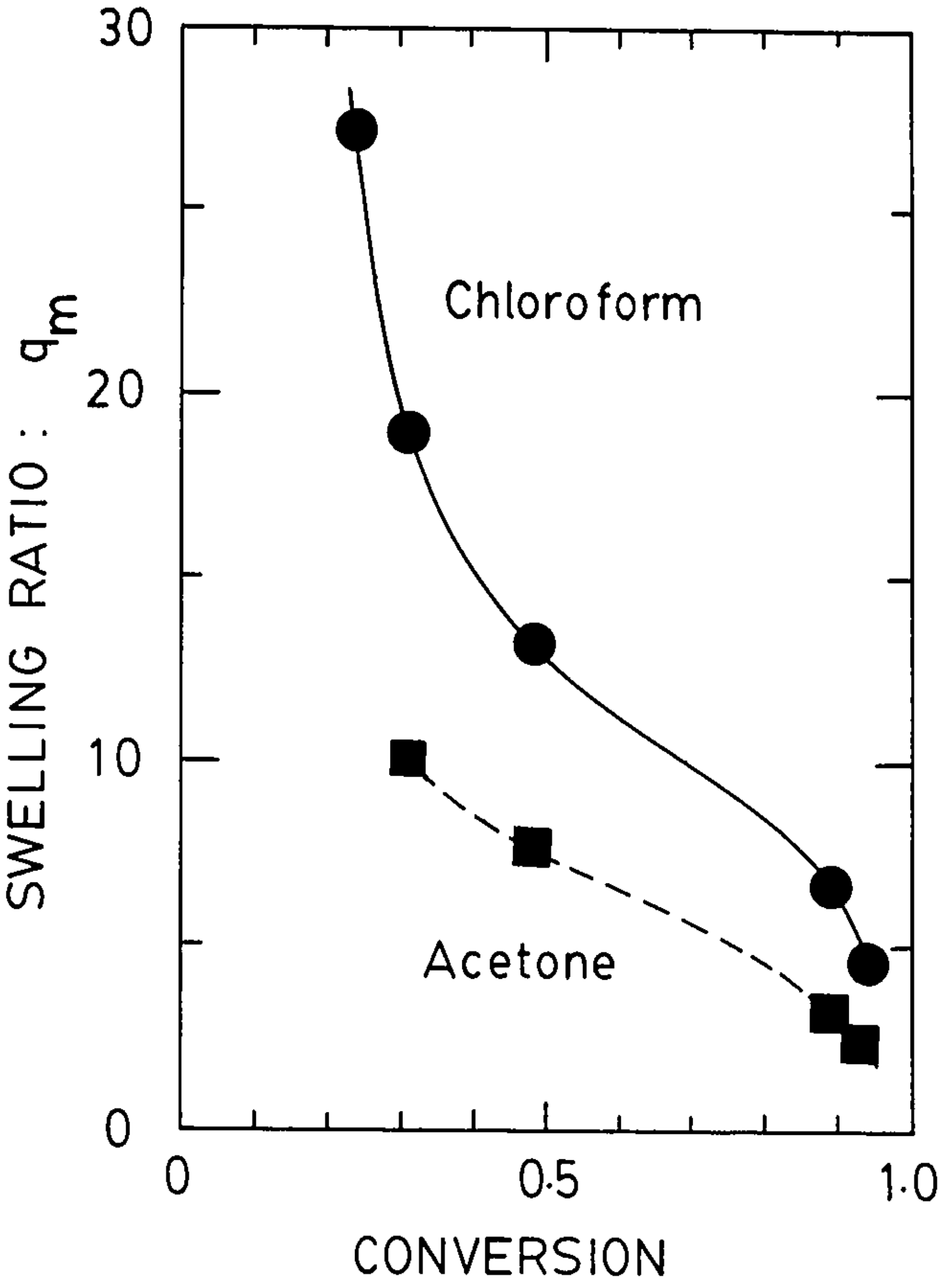


Figure 3.1.3 Swelling experiments for gel molecules in chloroform and acetone at room temperature. Each gel was separated from sol completely. $f_{20} = 5.08 \times 10^{-3}$

$$-[\ \ln(1-v_{2m})+v_{2m}+\chi_1 v_{2m}^2\ ]=g\,(\bar{v}_1\, d_2/M_c)(1-2M_c/M_{np})(\zeta_0^{2/3}\, v_{2m}^{1/3}-v_{2m}/2) \tag{3.1.1}$$

where

v_{2m} ; volume fraction of polymer in the swollen gel at equilibrium. v_{2m} is equal to the reciprocal of swelling ratio , q_m.

χ_1 ; Flory's interaction parameter. For polymethyl methacrylate in chloroform, χ_1 = 0.365 [Patterson (1969)].

$\bar{v}_1$; molar volume of solvent. For chloroform, $\bar{v}_1$= 80.18 cm^3/mol.

d_2 ; density of polymer. For polymethyl methacrylate, d_2= 1.19 g/cm^3.

M_c ; number-average molecular weight between crosslinks.

M_{np} ; number-average molecular weight of the primary polymer molecules which belong to gel fraction. M_{np} can be calculated from Equation (2.5.21).

g is an empirical constant to account for the effect of physical chain entanglement , i.e., the physical crosslinkages. For a gel molecule at high conversions, this effect may be significant, however, at low conversions it may be reasonable to neglect this term since the network structure should be quite loose. Therefore, as a first attempt we used g= 1. ζ_0 is the volume fraction of polymer in the system during the crosslinking procedure, and therefore, when the mole fraction of divinyl monomer f_{20} is far smaller than unity, ζ_0 can be replaced by total monomer conversion x for bulk copolymerization, i.e., ζ_0 = x.

[B] Application of the Present Theory

As is shown in Figure 3.1.4, the autoacceleration is fairly significant in the post-gelation period. This autoacceleration is also significant for homopolymerization of MMA (see Figure 3.1.4), and it can be interpreted as diffusion controlled termination. An increase of radical concentration during autoacceleration period was proven by ESR analysis [Zhu et al. (1989b,c,d)], and significant increase of average chain length has been shown [Balke, Hamielec (1973); Stickler et al. (1984)]. Since the effect of autoacceleration during crosslinking is much more significant than that when linear polymers are being synthesized, it is reasonable to consider that the primary polymer chain length drift in this period is fairly significant. However, at present it is unclear how to estimate the decrease in the termination rate constant theoretically, so that the empirical correlation shown below was applied.

$$k_p/k_t^{0.5} = k_p^0/(k_t^0)^{0.5} = A \qquad (x < Z_2) \qquad (3.1.2a)$$

$$= A \exp[Z_1(x - Z_2)] \qquad (Z_2 < x < Z_4) \qquad (3.1.2b)$$

$$= A \exp[Z_1(x - Z_2) - Z_3(x - Z_4)] \qquad (Z_4 < x) \qquad (3.1.2c)$$

Four adjustable parameters Z_1, Z_2, Z_3, and Z_4 were estimated from time-conversion histories. The initiator efficiency f may decrease

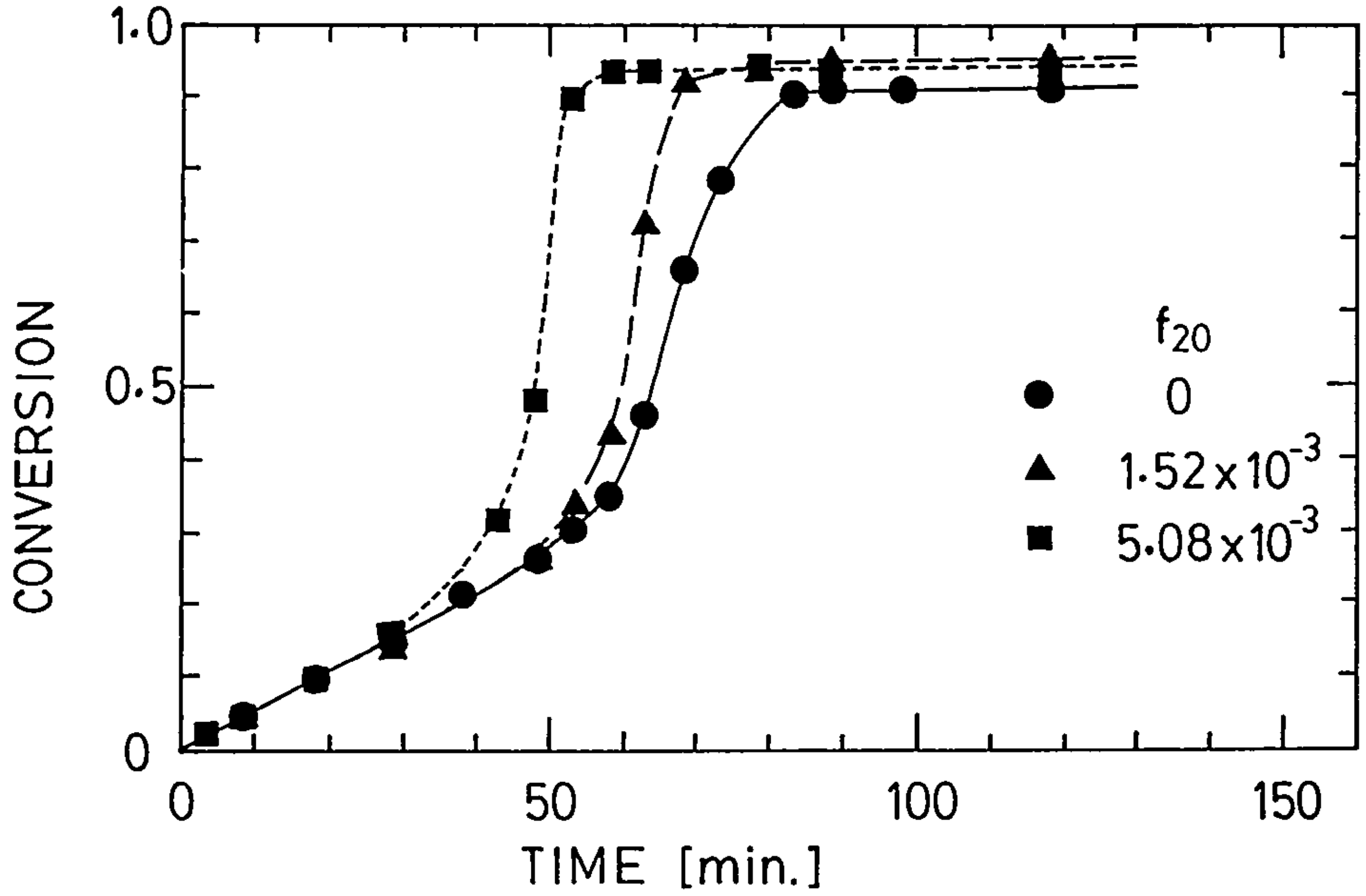


Figure 3.1.4 Conversion-time histories for the copolymerization of MMA/EGDMA at 70°C, and 0.3 wt% AIBN.

at high conversions [Zhu et al. (1989a,b)], however, constant initiator efficiency ($f=0.6$) was used in the calculations. When the initial mole fraction of divinyl monomer (EGDMA) is far smaller than unity ($f_{20} \ll 1$), all pseudo-kinetic rate constants for the formation of primary polymer molecules in a chemically controlled reaction region can be approximated by those for homopolymerization of MMA. Kinetic rate constants used are summarized in Table 3.1.1. Curve fittings to time-conversion histories are shown in Figure 3.1.5-a,b,c.

As is discussed in Section 1.1-[B-3], there are complications in the determination of reactivity ratios for vinyl/divinyl copolymerization, and large variations of reactivity ratios have been reported for various vinyl/divinyl monomer pairs [Frick et al. (1981)]. Although Li et al. [Li et al. (1989)] determined reactivity ratios for MMA/EGDMA, they used the Meyer-Lowry equation [Meyer, Lowry (1965)] for high mole fractions of divinyl monomer (f_{20} = 0.25, 0.5, 0.75) without considering cyclization and monomer consumption by radical centers located on just reacted pendant double bonds, so that their reactivity ratios may not reflect intrinsic reactivities and it may not be able to apply their reactivity ratios to low mole fractions of divinyl monomer cases. For copolymerization of MMA/EGDMA, since the chemical structures of vinyl groups are the same, the reactivity ratios are expected to be r_1= 0.5 and r_2= 2.0. These reactivity ratios were confirmed by several researchers [Whitney, Burchard (1980); Landin, Macosko (1988)] using ^{1}H-NMR to copolymers at low monomer conversions. We, therefore,

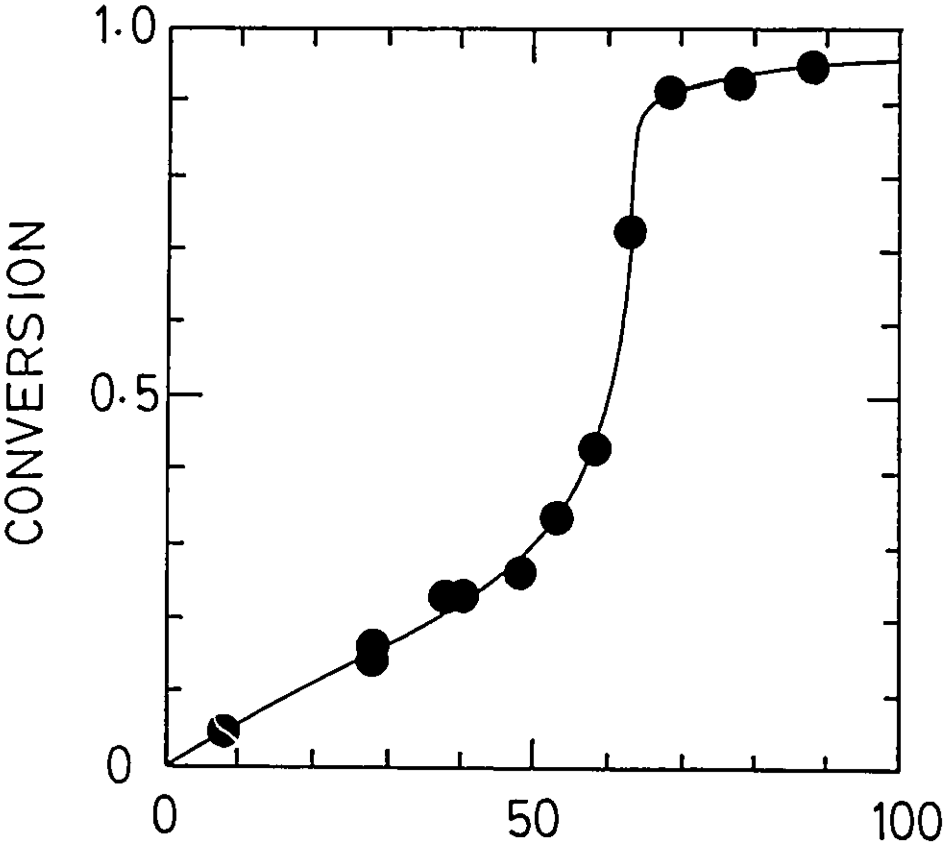


Figure 3.1.5-a Time-conversion data and fitted curve.

$f_{20} = 1.52 \times 10^{-3}$,

$Z_1 = 8.4$, $Z_2 = 0.192$, $Z_3 = 37.0$, $Z_4 = 0.81$.

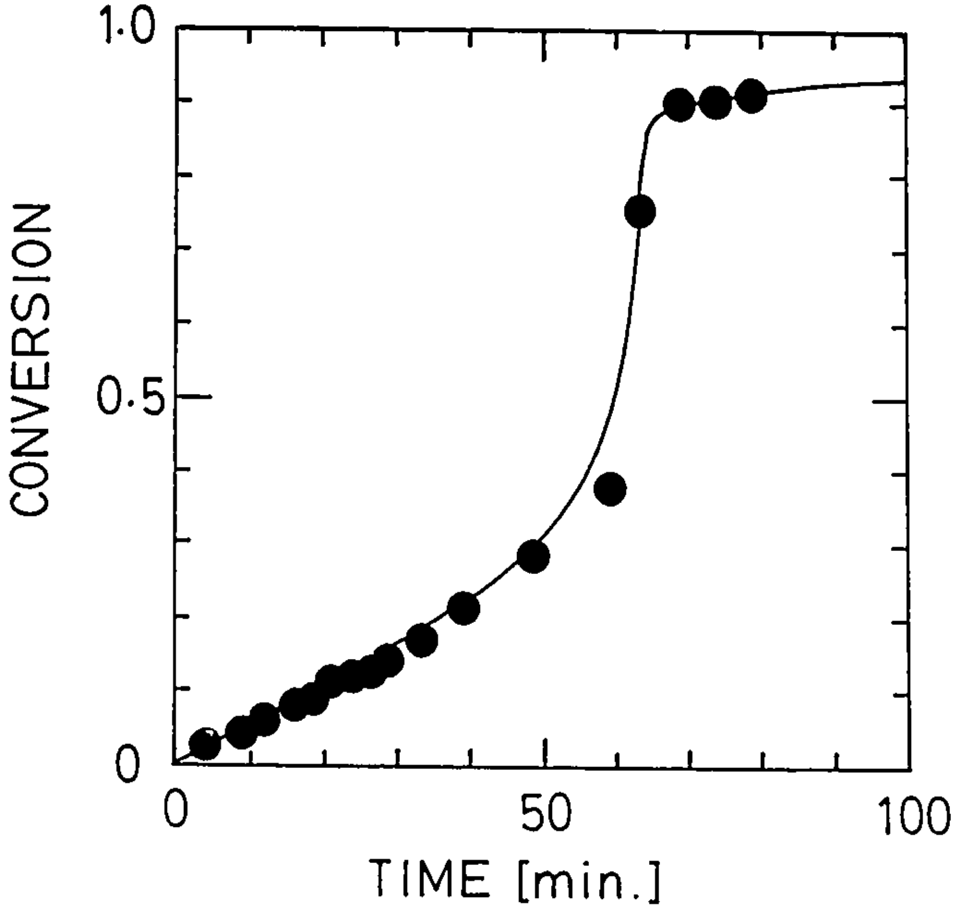


Figure 3.1.5-b Time-conversion data and fitted curve.

$f_{20} = 2.53 \times 10^{-3}$,

$Z_1 = 7.95$, $Z_2 = 0.185$, $Z_3 = 51.0$, $Z_4 = 0.82$.

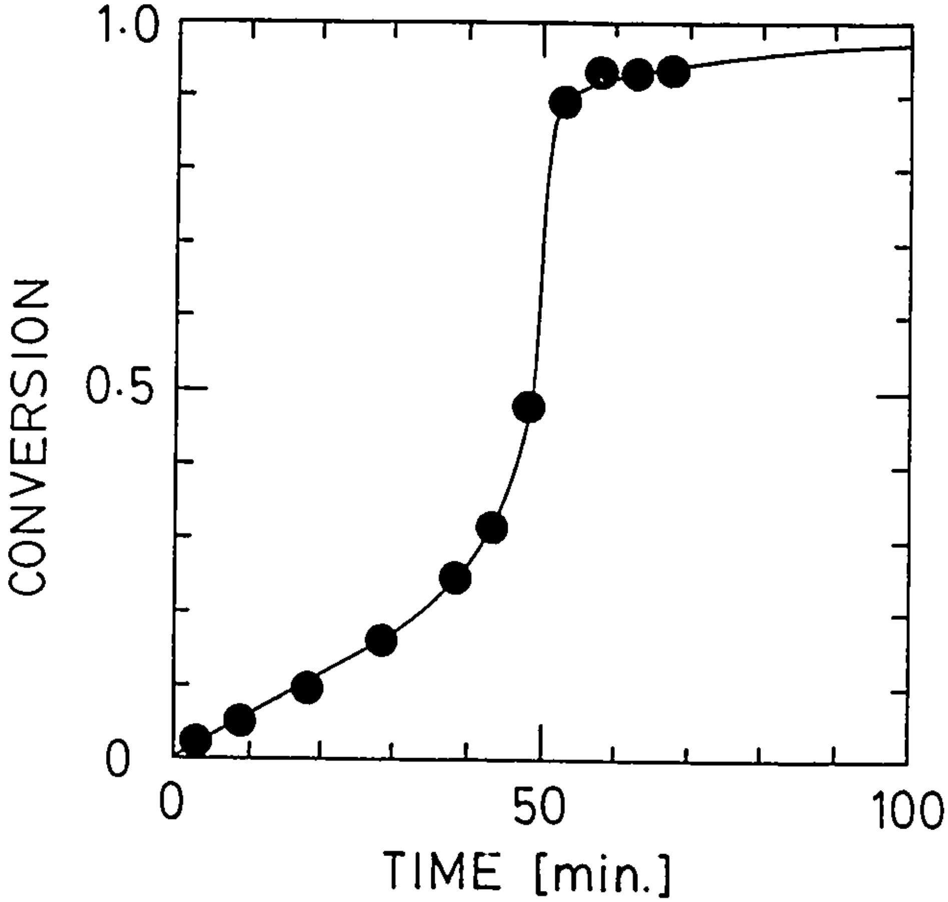


Figure 3.1.5-c Time-conversion data and fitted curve.

$f_{20} = 5.08 \times 10^{-3}$,

$Z_1 = 8.8$, $Z_2 = 0.143$, $Z_3 = 28.0$, $Z_4 = 0.75$.

Table 3.1.1 Kinetic rate constants used for calculations

	reference
[Initiation of AIBN]	
$k_d = 3.4 \times 10^{-5}$ [1/sec]	[Panke et al. (1983)]
$f = 0.6$	[Panke et al. (1983)]
[Polymerization of MMA]	
$k_p^0 / (k_t^0)^{0.5} = 0.129$ [L/mol sec]	[Panke et al. (1983)]
$k_{td} / (k_{td} + k_{tc}) = 0.494$	[Stickler et al. (1984)]

decided to use reactivity ratios, $r_1 = 0.5$ and $r_2 = 2.0$.

As a first approximation, we used the following pseudo-kinetic rate constant for the crosslinking reaction and the effect of cyclization was neglected.

$$k_p^*(\Theta, \Psi) = k_p^{*0} [F_2(\Theta) - \rho_a(\Theta,\Psi)] \qquad (3.1.3)$$

When the mole fraction of EGDMA is far smaller than unity, k_p^{*0} may be considered constant. Figure 3.1.6 shows the comparison of predictions with experimental data. Even with these rough approximations, the calculated results agree with experimental data fairly well. At this stage, since we do not consider the effect of cyclization, we cannot comment on the general tendency of the reactivity of pendant double bonds. However, the apparent reactivity of pendant double bonds seems to decrease as the mole fraction of divinyl monomer, f_{20}, increases, which implies that the deviation from Flory's simplifying assumptions becomes significant for high mole fractions of divinyl monomer.

Next, let us examine the model which includes the effect of cyclization. In order to find the elastic crosslinking density of a gel molecule, swelling experiments were done (see Figure 3.1.3). We estimated the elastic crosslinking density of a gel molecule using Equation 3.1.1. Figures 3.1.7-a,b show the comparison with experimental data. For bulk copolymerization of MMA and EGDMA primary cyclization

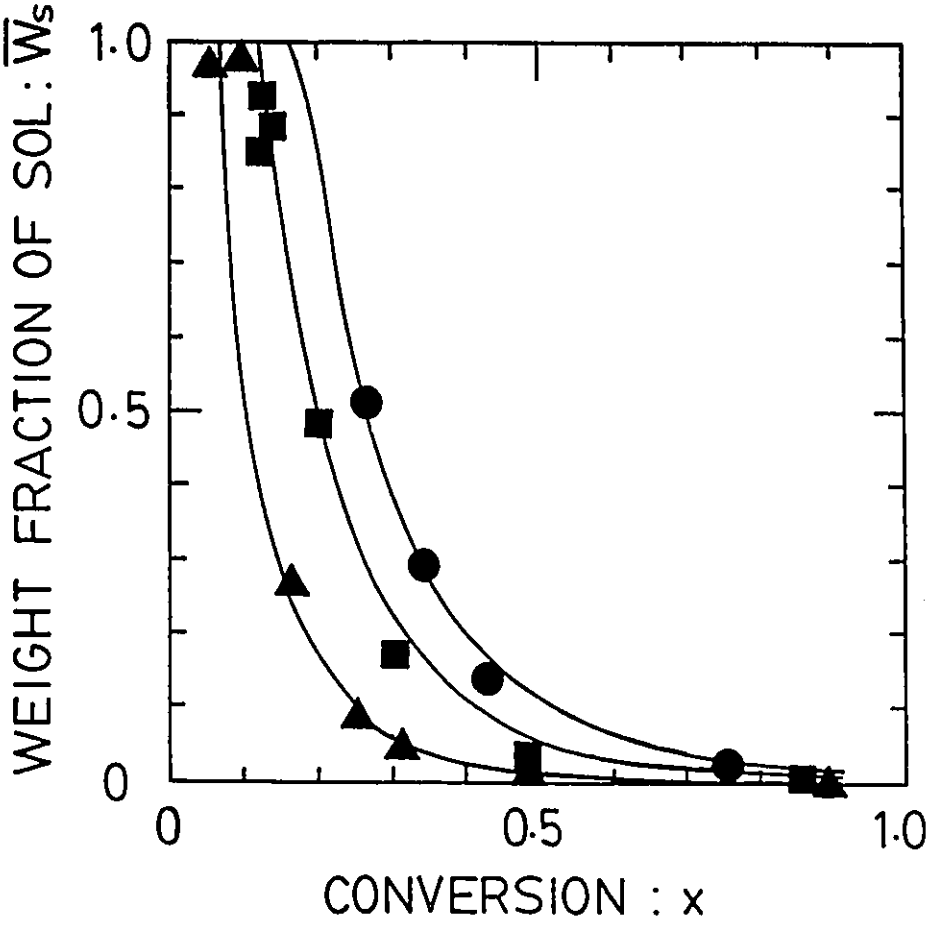


Figure 3.1.6 Weight fraction of sol; comparison with experimental data. (k_p^{*0}/k_p was used as an adjustable parameter.)

	f_{20}	k_p^{*0}/k_p
●	1.52×10^{-3}	0.59
■	2.53×10^{-3}	0.51
▲	5.08×10^{-3}	0.48

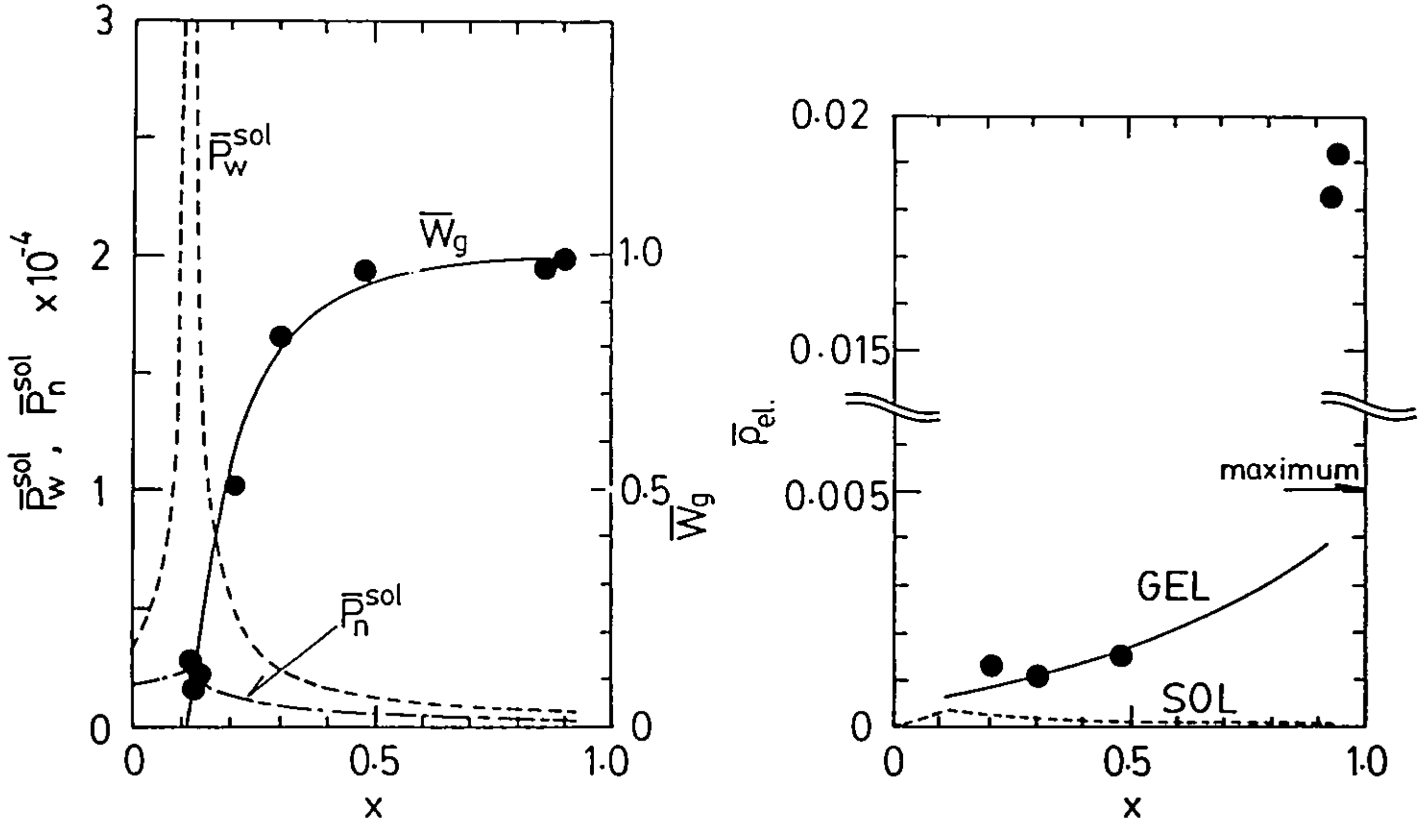


Figure 3.1.7-a Application of the present theory.

● experimental data. $f_{20} = 2.53 \times 10^{-3}$, $k_p^{*0}/k_p = 0.52$, $k_{cs} = 0.02$.

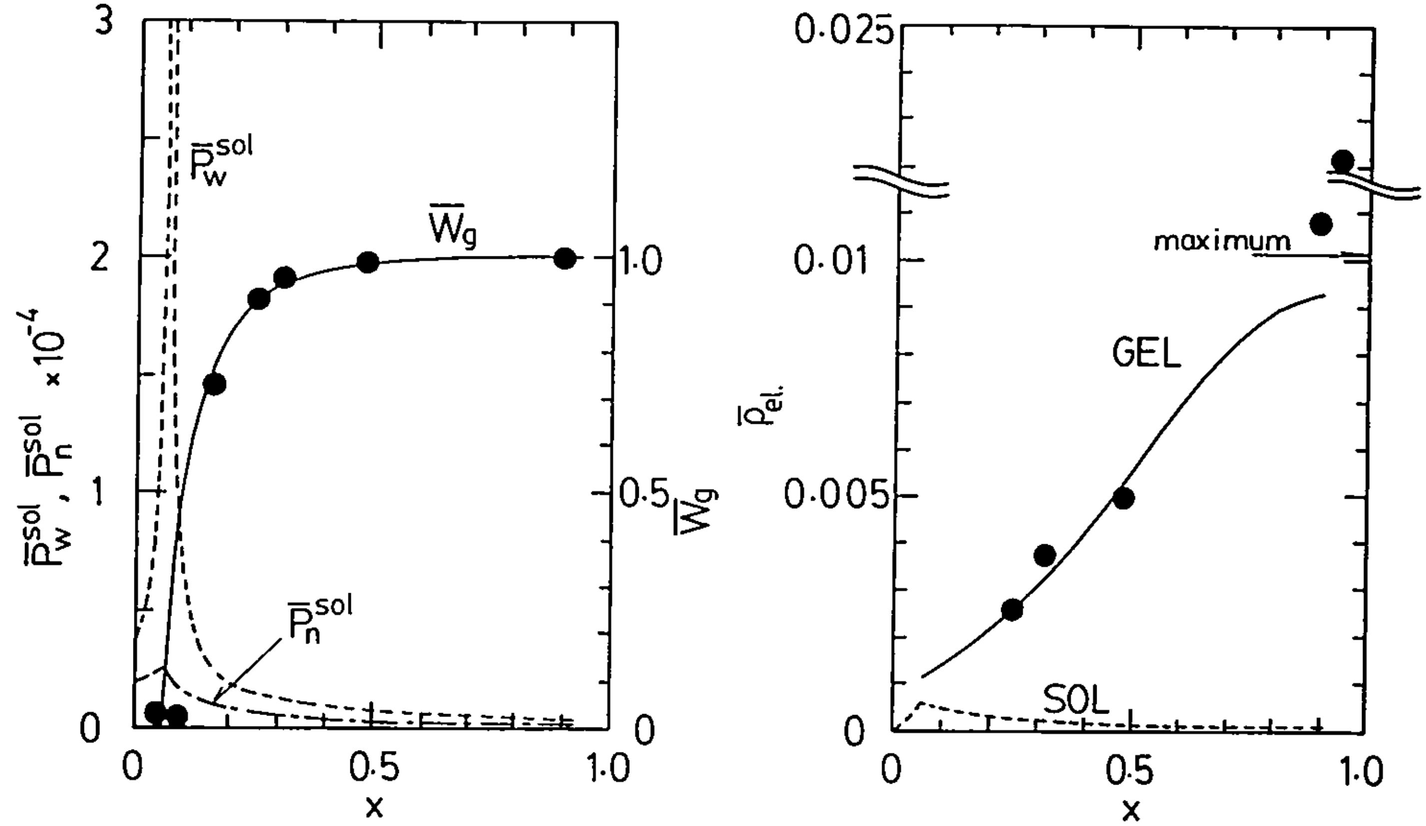


Figure 3.1.7-b Application of the present theory.

● experimental data. $f_{20} = 5.08 \times 10^{-3}$, $k_p^{*0}/k_p = 0.5$, $k_{cs} = 0.06$.

may have a minor effect [Landin, Macosko (1988)], and was neglected in the calculation. For secondary cyclization, the first approximation which was given by Equation (2.3.12) was applied. The maximum crosslinking density at 100% monomer conversion, which can be calculated from initial mole fraction of divinyl monomer, i.e., $2f_{20}$, is indicated by an arrow in Figures 3.1.7-a,b. Thus, the experimental values of crosslinking density at high conversions are clearly too high. This may be caused by the entanglement effect or physical crosslinkages. (Please remember we used g=1 in Equation (3.1.1).) However, for loose gel at low conversions, the agreement with calculations seems satisfactory.

The parameter for the apparent reactivity of pendant double bonds k_p^{*0}/k_p has a significant effect on mass properties such as onset of gelation, gel/sol ratio, and average chain length of sol fraction, while changing k_{cs} changes structural properties of network polymers greatly.

3.2. Copolymerization of Acrylamide / N,N'-methylene-bis-acrylamide

[A] Introduction

It is well-known that the Flory gelation model functions best at low mole fractions of divinyl monomer with the error increasing rapidly with increasing levels of divinyl monomer. The deviation from the Flory model has been attributed to the intramolecular reaction, namely, cyclization, and to decreased reactivity of pendant double bonds. In the bulk copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), it was found that secondary cyclization and the decreased reactivity of pendant double bonds are mainly responsible for the delay of the onset of gelation when the mole fraction of divinyl monomer is small [Landin, Macosko (1988)]. This result is also supported by the present work (Section 3.2), since the present theory gives satisfactory predictions not only mass properties (weight fraction of gel) but also structural properties (crosslinking density) with application of appropriate rate constants for crosslinking reactions and secondary cyclizations. However, it is quite natural to suspect that the relative contribution of these three effects, namely, decreased reactivity of pendant double bonds, primary cyclization, and secondary cyclization, changes with chemical systems used and polymerization conditions.

Polyacrylamide gels are usually synthesized by copolymerization of acrylamide (AAm) and N,N'-methylene-bis-acrylamide (Bis) in aqueous solution, and they have been used in gel permeation chromatography (GPC) and as a stabilizing medium in the zone electrophoresis of proteins and nucleic acids. Both types of application rely strongly on a molecular sieve mechanism, and therefore, a control of network structure is very important. Various studies have shown that polyacrylamide gels are inhomogeneous (swelling equilibrium [Richards, Temple (1971); Hsu et al. (1983)], Permeation [Weiss et al. (1979),(1981)], neutron and light scattering [Geissler et al. (1982); Weiss (1981)], differential scanning calorimetry (DSC) [Gupta, Bansil (1983)], Raman spectroscopy [Gupta, Bansil (1983)], electron microscopy [Hsu, Cohen (1984)], and mechanical measurements [Janas et al. (1980); Baselga et al. (1987)], namely, they possess regions having very different degrees of crosslinking density. Since Flory's idealized model assumes that the crosslinking density is the same for all chains, copolymerization of AAm and Bis may be considered as a highly non-ideal system. In this section, we clarify what kinds of non-ideality govern the copolymerization of AAm and Bis in aqueous solution.

[B] Preliminary Considerations

Process of Crosslinking: Network formation in free radical polymerization is a non-equilibrium process, namely, it is kinetically controlled, and therefore, each primary polymer molecule experiences a different history of crosslinking and cyclization. Based on the chemical kinetics, it is possible to estimate the crosslinking density as a function of its birth time (Section 2.2). The existence of crosslinking density distribution shows that the polymer networks synthesized by free radical polymerization are inherently inhomogeneous on a microscopic scale. The variance of the crosslinking density distribution becomes significant when the following non-ideal effects are important.

1) Differences in the reactivities of monomeric double bonds.
2) Decreased reactivity of pendant double bonds relative to monomeric double bonds.
3) Cyclization reactions.

Recently Baselga et al. [Baselga et al. (1989b)] argued that the differences in the reactivity of monomeric double bonds are responsible for inhomogeneous polyacrylamide networks. They determined the reactivity ratios from the change in copolymer composition during copolymerization, and found that the reactivity ratio of the double bond on acrylamide, $r_1^V=1.14$, and that on N,N'-methylene-bis-acrylamide, $r_2^V=1.7$. Figure 3.2.1 shows the crosslinking density of a primary polymer molecule at total monomer conversion, x=0.8, as a function of monomer conversion when the given primary polymer molecule was born, Θ, namely, $\rho^f(\Theta, 0.8)$ is the crosslinking density at x=0.8 for the primary polymer molecule which was born at $x=\Theta$. As is shown in Figure 3.2.1, the crosslinking density is the same for all primary polymer molecules regardless of their birth time when $r_1^V=r_2^V=1.0$, and as the reactivity ratios, r_1^V and r_2^V, deviate from unity, the crosslinking density can differ appreciably with birth time. However,

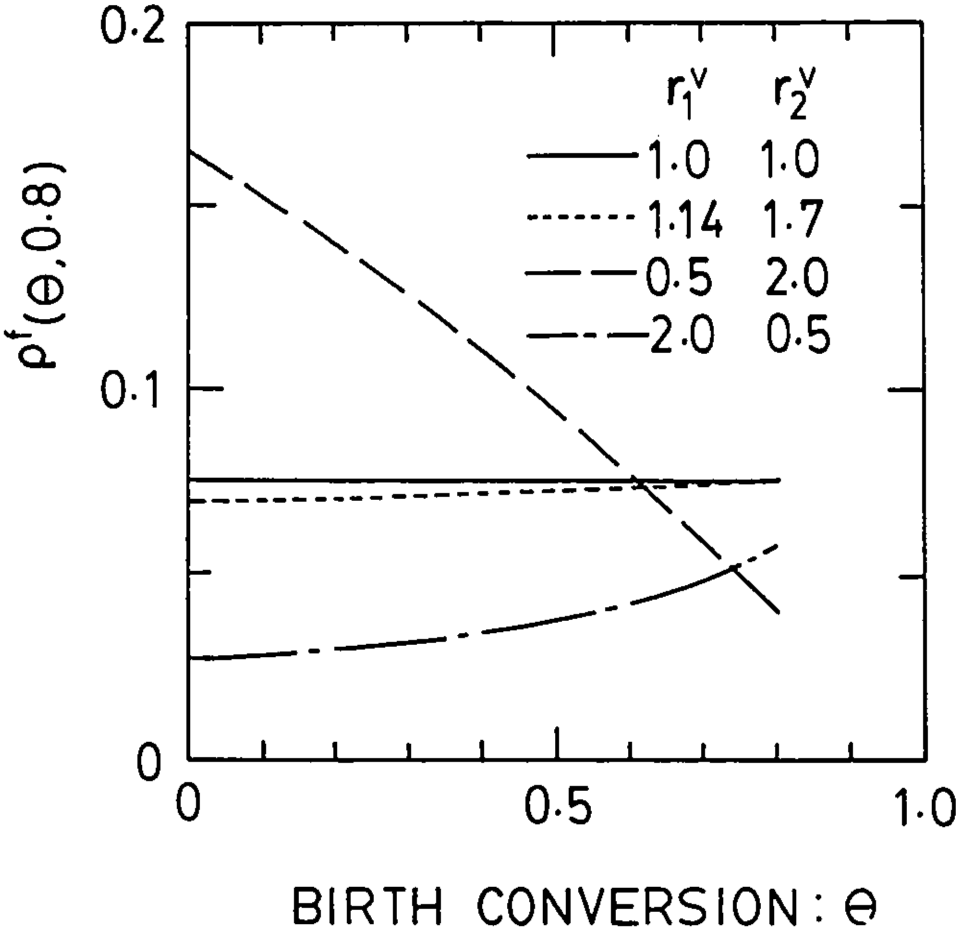


Figure 3.2.1 Effect of monomeric double bond reactivity on the crosslinking density of primary polymer molecules at total monomer conversion, $x = 0.8$. θ is the total monomer conversion at which the given primary polymer molecule was born. Initial mole fraction of divinyl monomer, $f_{20} = 0.05$.

fairly large differences in the reactivities of monomeric double bonds would be necessary to account for the formation of inhomogeneous networks. The reactivity ratios, $r_1^V=1.14$ and $r_2^V=1.7$, clearly do not give a significant range of crosslinking densities and therefore differences in the reactivities of monomeric double bonds for the acrylamide system studied by Baselga et al. cannot explain the existence of inhomogeneous networks.

Process of Cyclization: We use Equation (2.3.6) for primary cyclization, and check the applicability to the AAm/Bis system. For secondary cyclization, we use zeroth approximation (Equation (2.3.11)), namely, we assume the average number of secondary cycles per crosslink, η, constant. With this approximation, the accumulated mole fraction of the pendant double bonds which is consumed by crosslinking and secondary cyclization, $\bar{\rho}_{e1,a}$ $(= \bar{\rho}_a + \bar{\rho}_{cs,a})$, is given by

$$\frac{d(x\,\bar{\rho}_{e1,a})}{dx} = \frac{k_{p,e}^{*0}[(1-k_{cp})\bar{F}_2 - \bar{\rho}_{e1,a}]x}{k_p\,(1-x)} \qquad (3.2.1)$$

where $k_{p,e}^{*0} = (1+\eta)\,k_p^{*0}$.

The pendant double bond conversion, x_{pd}, is given by;

$$\begin{aligned} x_{pd} &= (\bar{\rho}_{e1,a} + \bar{\rho}_{cp})/\bar{F}_2 \\ &= (\bar{\rho}_{e1,a}/\bar{F}_2) + k_{cp} \qquad (3.2.2) \end{aligned}$$

Reactivity Ratios: As discussed earlier, there are problems concerning the copolymer composition equation for vinyl/divinyl copolymerizationn. However, we use the conventional copolymer composition equation, namely, the Mayo-Lewis equation to calculate copolymer composition as a first approximation.

For the copolymerization of AAm and Bis, since the chemical structures of vinyl groups are the same, the reactivity ratios are expected to be $r_1 = 0.5$ and $r_2 = 2.0$. (Please note that since a divinyl monomer possesses two double bonds, the reactivity ratios defined with respect to monomer unit, r_1 and r_2, are related to those defined with respect to double bonds, r_1^V and r_2^V by Equation (2.1.27) and (2.1.28).)

On the other hand, Baselga et al. [Baselga et al. (1989b)] estimated the reactivity ratios by application of the Meyer-Lowry equation to their copolymer composition data, and found that $r_1 = 0.57$ and $r_2 = 3.4$. Unfortunately, they did not mention the confidence intervals for their parameters, so that it is difficult to decide whether their reactivity ratios should be considered different from the expected values. We decided to use reactivity ratios, $r_1 = 0.5$ and $r_2 = 2.0$, for the calculation of copolymer composition based on the following reasons. 1) Baselga et al.'s experimental data could be fit equally well using reactivity ratios, $r_1 = 0.5$ and $r_2 = 2.0$, as is shown in Figure 3.2.2. 2) Especially, for mole fractions of divinyl monomer less than 15 % which we have used for our experiments, there is

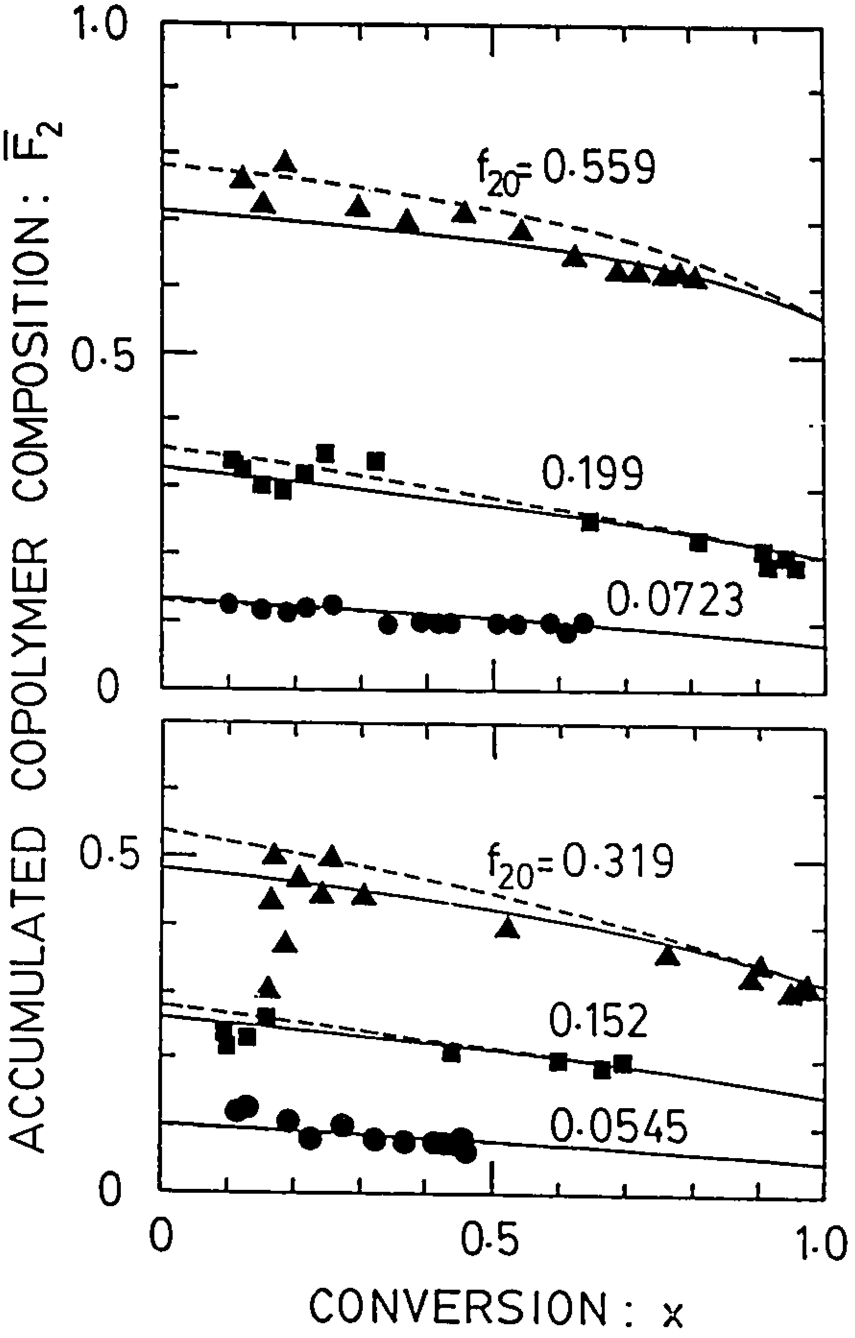


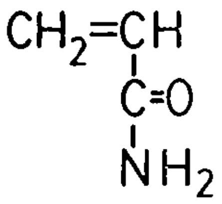
Figure 3.2.2 Calculated and experimental compositional drift of the accumulated AAm/Bis copolymer. Experimental data are taken from [Baselga et al. (1989b)]. Calculated values: ———, $r_1 = 0.5$, $r_2 = 2.0$;
-------, $r_1 = 0.57$, $r_2 = 3.4$.

practically no difference in the calculated copolymer composition using r_1= 0.5, r_2= 2.0 and r_1= 0.57, r_2= 3.4.

[C] Experimental Procedure

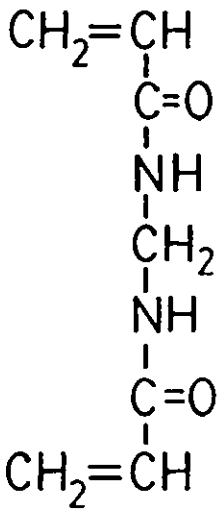
Acrylamide (AAm) and N,N'-methylene-bis-acrylamide (Bis) were high purity Aldrich products (electrophoresis grade). As initiator, the redox system potassium persulfate (PS) / triethanolamine (TEA) was employed. PS was purchased from BDH Chemicals, and TEA was from Fisher Scientific. Structures of AAm, Bis, PS, and TEA are shown in Figure 3.2.3.

AAm, Bis, and TEA were dissolved in ion-exchanged water, and poured into the glass reactor shown in Figure 3.2.4. The glass reactor was kept in a water bath maintained at 25°C. After deaeration by bubbling N_2 for 20 minutes, PS, also dissolved in ion-exchanged water and kept at 25°C with N_2 bubbling, was injected by syringe. From preliminary experiments, more than 10 minutes of N_2 bubbling was necessary for sufficient reproducibility. N_2 bubbling was continued throughout polymerization in order to mix the reactants, i.e., if no mixing was provided, insoluble micro-gel-like particles tended to sediment and gel molecules were formed only in the lower part of the reactor. Since the diameter of the reactor is not small enough, a temperature rise was observed. An example of temperature increase and time-conversion history is shown in Figure 3.2.5. However, the maximum temperature rise was less than 3°C, and the effect on the kinetics is



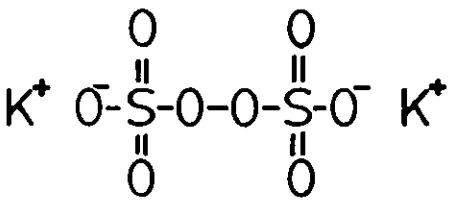
$CH_2=CH-C(=O)-NH_2$

Acrylamide
(AAm)



$CH_2=CH-C(=O)-NH-CH_2-NH-C(=O)-CH=CH_2$

N,N'-methylene-
bis-acrylamide
(Bis)



$K^+ \; {}^-O-S(=O)_2-O-O-S(=O)_2-O^- \; K^+$

Potassium persulfate
(PS)

$N(CH_2CH_2OH)_3$

Triethanolamine
(TEA)

<u>Figure 3.2.3</u> Structures of AAm, Bis, PS, and TEA.

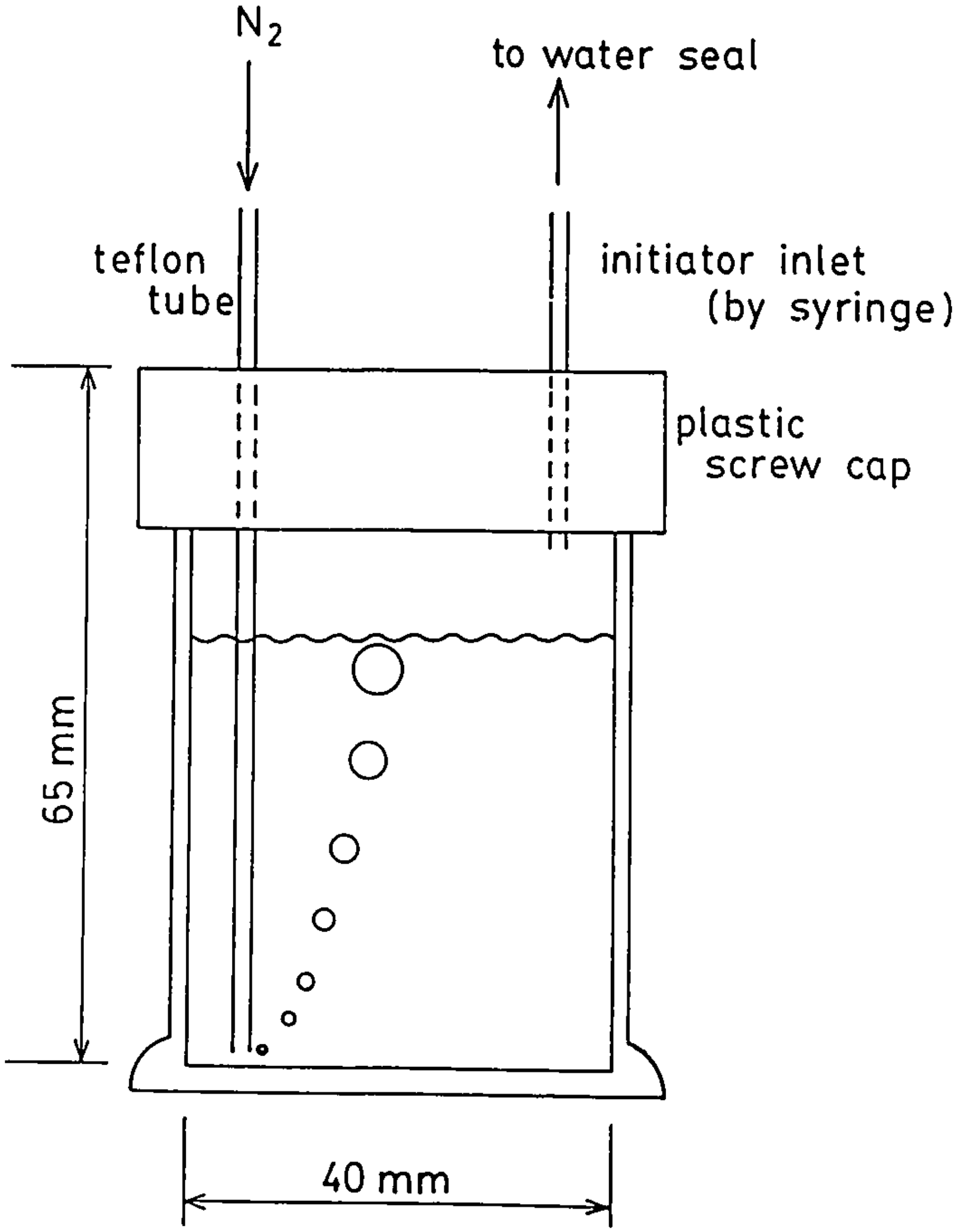


Figure 3.2.4 Schematic drawing of the reactor used for batch polymerization.

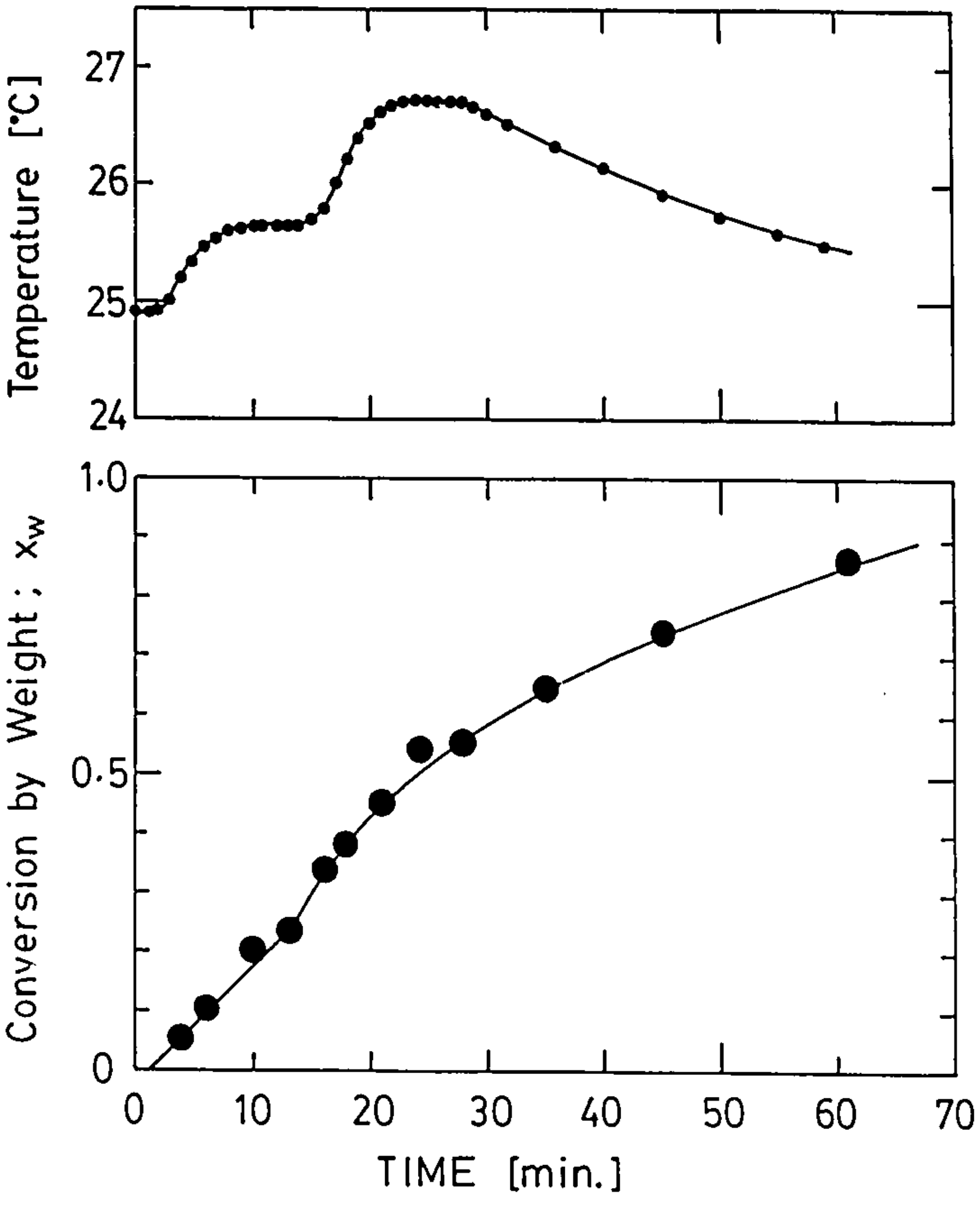


Figure 3.2.5 Conversion and temperature histories during copolymerization for $f_{20} = 0.07$ with 0.094 mol/L of IPA.

considered tolerable.

The polymerization was stopped by adding acetone containing 0.3 wt% of 4-methoxyphenol at a desired time, with complete mixing with the break up of gel molecules if they were present. The polymer was separated by centrifugation, and washed with acetone containing 4-methoxyphenol three times. The washed polymers were dried at 60°C under vacuum for more than three days. Conversion was determined gravimetrically. Complete removal of monomer was checked by liquid chromatography for several samples. Number of pendant double bonds was measured by bromometry (bromate/bromide titration). When the size of ruptured gels was not small enough, they were ground with a mortar and pestle in order to reduce titration time. The end point was determined when the solution remained colorless for more than 15 minutes.

Concentrations used were 56.6 g/L for comonomers. 2.48 $\times 10^{-3}$ mol/L for PS, and 4.23 $\times 10^{-4}$ mol/L for TEA. The weight-average chain length ($\bar{P}_w$) for homopolymer of AAm was measured by low-angle laser light scattering photometry using Chromatix KMX-6 LALLS photometer by application of the one-point method [Hunkeler, Hamielec (1988)]. $\bar{P}_{w,homo} = 1.07 \times 10^5$ was obtained. The measured weight-average chain length agrees well with the calculated value, $\bar{P}^{cal}_{w,homo} = 1.06 \times 10^5$, by the use of kinetic parameters, $k_p/(k_{td})^{0.5} = 4.74$ [L/mol sec]$^{0.5}$, $k_{fm}/k_p = 1.14 \times 10^{-5}$ (both parameters are taken from [Kim, Hamielec (1984)]), and the initial reaction rate measured in experiments ($(dx/dt)_0 = 1.34 \times 10^{-4}$ [sec^{-1}]). When 0.094 mol/L of isopropyl alcohol (IPA) was added as a chain transfer agent, $\bar{P}_{w,homo}$ decreased to 2.83 x10^4.

[D] Polymerization Kinetics

The conversion-time histories for initial mole fraction of divinyl monomer f_{20}= 0.07, and homopolymerization of AAm are shown in Figure 3.2.6. The gel point was assumed to occur when the acceleration in polymerization rate occurred, and more conveniently, it was monitored by measuring the sharp temperature increase in the reactor. The presence of 7 mol% of Bis increases noticeably the overall polymerization rate even in the pre-gelation period. Since the reactivity of Bis is higher than AAm, the increase of reaction rate is understandable, however, such large increase (the ratio of polymerization rate at zero monomer conversion on a weight basis is about 3.5) can not be attributed to the addition of monomer with higher reactivity. This large increase would be better explained by the dramatic increase in radical concentration caused by a large decrease in the bimolecular termination rate of polymer radicals. As it was reported earlier [Bansil, Gupta (1980)], polyacrylamide gels with $f_{20} > 0.02$ become turbid. In our experiments, it was clearly observed that the reaction system becomes turbid right from the start of polymerization, and that these particles tend to sediment if no mixing is used. These insoluble micro-gel-like particles seem to be responsible for the increase in polymerization rate. If all double bonds are equally reactive with no cyclization,

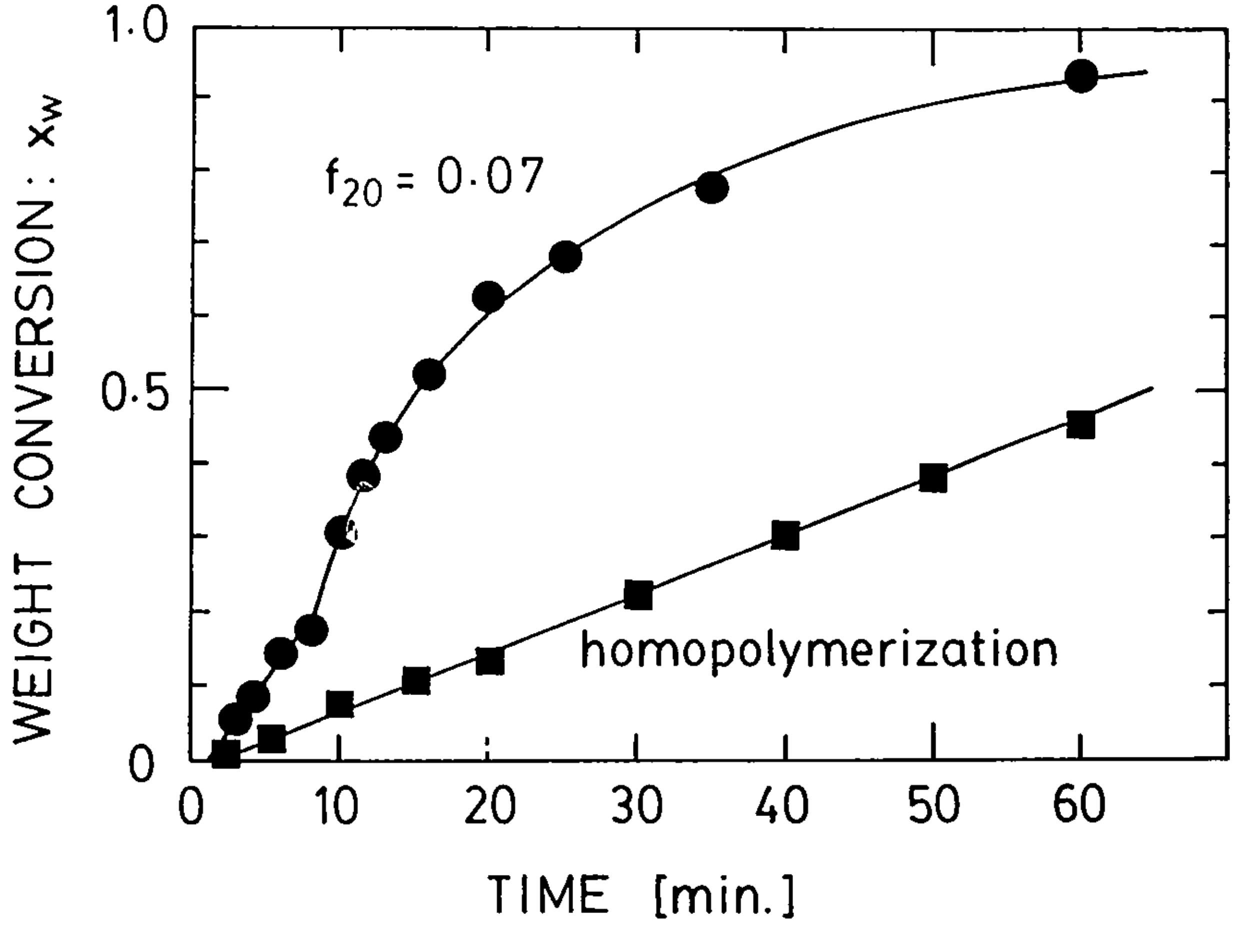


Figure 3.2.6 Conversion-time histories for the copolymerization of AAm/Bis ($f_{20} = 0.07$) and homopolymerization of AAm.

Flory's theory, using $\bar{P}_{wp} = 1.07 \times 10^5$ for the weight-average chain length of the primary polymer molecules, predicts the following double bond conversion (p_c) at the gel point.

$$p_c = (1 + f_{20})/[2\ f_{20}\ \bar{P}_{wp}] = 7.14\ \times 10^{-5} \qquad (3.2.3).$$

It is expected that various non-idealities not accounted for by Flory's model delay the gel point. However, it may be possible to assume that gelation occurs on a microscopic scale at a fairly low conversion, and consequently, insoluble micro-gels are formed. Since the mobility of radical centers located on a micro-gel is restricted, the bimolecular termination rate may decrease considerably. These micro-gels were connected with each other with tie polymer chains, and gelation, on a macroscopic scale, was observed at a weight conversion $x_{cw} \approx 0.2$.

[E] Kinetics of Pendant Double Bond Consumption

The number of pendant double bonds versus monomer conversion was measured for three experimental conditions, namely, f_{20}=0.07, 0.15, and 0.07 with 0.094 mol/L of IPA. The pendant double bond conversion x_{pd} versus monomer conversion is shown in Figure 3.2.7. The lines were calculated using Equation (3.2.1). The parameters used (k_{cp} and $k_{p,e}^{*0}/k_p$) are tabulated in Table 3.2.1. The agreement of calculations with experimental data seems satisfactory at least for conversions less than 50 %. At high conversions, $k_{p,e}^{*0}/k_p$ may decrease because of the

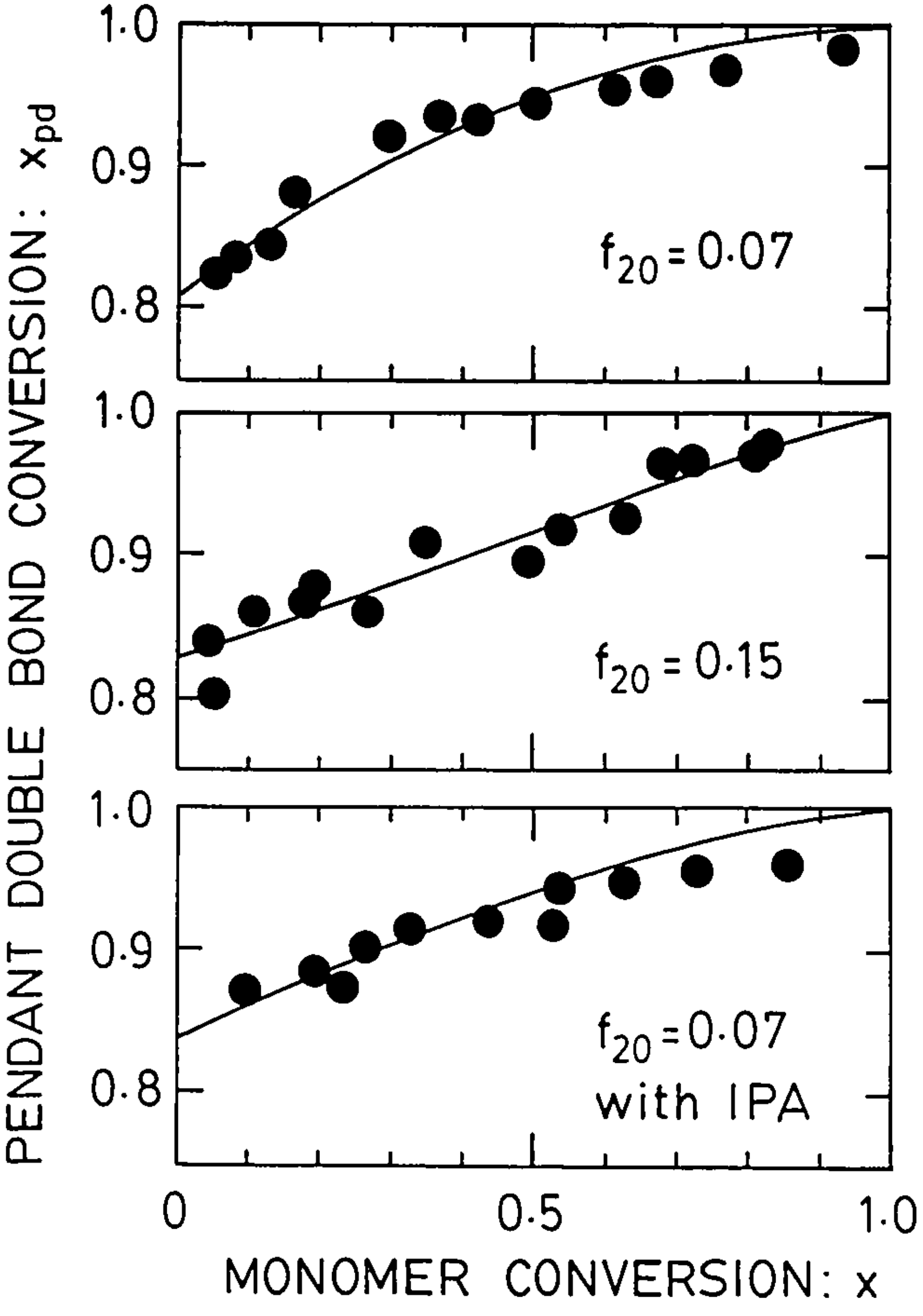


Figure 3.2.7 Pendant double bond conversion (x_{pd}) versus monomer conversion (x) measured by bromate/bromide titration and calculated (————) using Equation (3.2.1) and parameters in Table 3.2.1.

Table 3.2.1 Experimental conditions, gel point, and estimated parameters

Experiment number	f_{20}	[IPA] (mol/L)	k_{cp}	$k^{*0}_{p,e}/k_p$	Gel Point Weight Conv.	x_c Molar Conv.
R1	0.07	0	0.81	3.8	0.20	0.19
R2	0.15	0	0.83	1.9	0.25	0.23
R3	0.07	0.094	0.84	2.7	0.25	0.24

Experiment number	$\bar{\rho}_a(x_c) = 1/(2\bar{P}_{wp})$	$\bar{\rho}_{el,a}(x_c)$	η	k_p^{*0}/k_p
R1	4.67×10^{-6}	7.54×10^{-3}	1.61×10^{3}	2.35×10^{-3}
R2	4.67×10^{-6}	9.24×10^{-3}	1.98×10^{3}	9.60×10^{-4}
R3	1.77×10^{-5}	5.94×10^{-3}	3.35×10^{2}	8.05×10^{-3}

tighter structure of the gel, i.e., trapping of pendant double bonds [Malinsky et al. (1971)].

The intercept at zero monomer conversion in Figure 3.2.7 gives the degree of primary cyclization (= k_{cp}). At least 80 % of the pendant double bonds are found to be consumed by primary cyclization at zero monomer conversion. A simple model for primary cyclization given by Equation (2.3.6) shows that k_{cp} is independent of monomer composition (f_{20}), and the chain length of the primary polymer molecule, if 1) the molecular conformation does not change, and 2) the primary polymer chain length is large enough. The y-intercept of Figure 3.2.7 (= k_{cp}) seems nearly independent of f_{20} and the chain length of primary polymer molecules, and this result supports Equation (2.3.6). (Several experimental results of the effect of the initial mole fraction of divinyl monomer f_{20} on primary cyclization at zero conversion reported are summarized in Figures 2.3.3-a,b.)

Primary cyclization appears to be fairly significant. Lower monomer concentrations are believed to promote the effect of cyclization [Bates, Howard (1967); Semlyen (1976); Dusek (1982)]. (Please note our monomer concentration is less than 6 wt%.) For N,N'-methylene-bis-acrylamide (Bis), even gel-free homopolymerization was reported for a very low monomer concentration with special redox initiator [Gopalan et al. (1982),(1983); Gupta et al. (1987); Rathnasabapathy et al. (1988a,b)], and cyclopolymerization of Bis was proposed. It is unclear whether cyclization formed within one Bis unit is significant or not in our experiments, however, it might contribute somewhat to the high k_{cp} values found.

$k_{p,e}^{*0}/k_p$ shows the apparent reactivity of pendant double bonds including secondary cyclization. An example of elastic crosslinking density distribution change during polymerization for $f_{20}= 0.07$ without IPA is shown in Figure 3.2.8. It may be reasonable to guess that the polymer network is inhomogeneous at least on a microscopic scale.

Estimated values of $k_{p,e}^{*0}/k_p$ are larger than unity, while the observed gel point on a macroscopic scale is much larger than predicted by Equation (3.2.3). This fact implies that the consumption of pendant double bonds by secondary cyclization is much greater than that by crosslinking. Assuming that the weight-average chain length of primary polymer molecules is the same as that for homopolymers of AAm synthesized under the same reaction conditions, it is possible to roughly estimate η and k_p^{*0}/k_p from the observed gel point. These estimates are also shown in Table 3.2 1. When f_{20} is increased, network structure becomes tighter, and therefore, apparent reaction rate for the crosslinking reaction decreases due to steric hindrance. With these high mole fractions of divinyl monomer, insoluble micro-gels are formed. The reaction rate between these micro-gels are likely to decrease, since there are many inaccessible double bonds and radical centers (see Figure 4.0.1 in Chapter 4). A tight structure also increases the effect of secondary cyclization. When the primary polymer

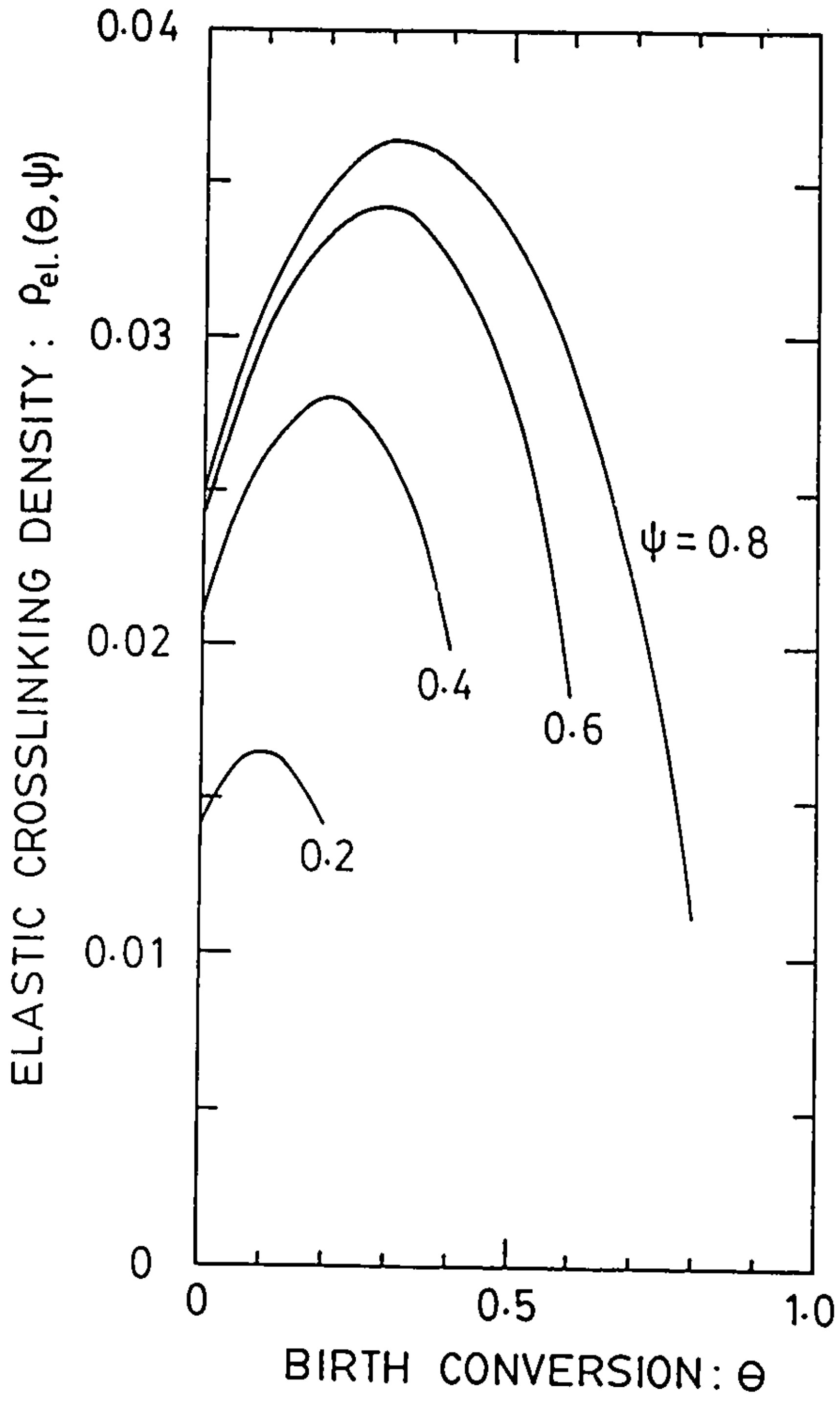


Figure 3.2.8 Change of the calculated elastic crosslinking density distribution profile for $f_{20} = 0.07$ without IPA. At a certain monomer conversion, ψ, the primary polymer molecules with different birth time may bear completely different crosslinking density.

chain length is made smaller using IPA ($\overline{P}_{w,homo}$= 2.83 x10^4), the probability that a growing primary polymer molecule can find two or more pendant double bonds decreases, and therefore, the effect of secondary cyclization decreases. This effect was also reported by Landin and Macosko [Landin, Macosko (1988)] for MMA/EGDMA. Decreased secondary cyclization should reduce the gel tightness, and may contribute to an increase in the apparent reaction rate of crosslinking. Higher mobility of smaller molecules may also increase the apparent reactivity of pendant double bonds.

In free radical polymerization, a crosslinkage is formed only via a polymer radical whose concentration is fairly low and whose life time is very short, and therefore, steric effects caused by the presence of other chains as well as its own chain have a significant effect on the kinetics of network formation. When these physical effects are significant, it would be necessary to regard the apparent crosslinking reaction rate as structure dependent as well as chain length dependent. At least, it seems reasonable to consider that the reaction rate between huge molecules (or micro-gels) decreases as they grow in size and become tighter. Our experimental conditions under which insoluble micro-gels are formed may be rather unusual, however, from the point of view of the mobility of the chains the formation of micro-gels may be a general feature of network formation in free radical polymerization [Spevacek, Dusek (1980)]. The formation mechanism of micro-gels may be as follows. Even if the reaction between huge molecules is hindered sterically, small molecules, which exist in far greater number, can diffuse into these huge molecules. Therefore, the structure of huge molecules may be tighter than that for smaller ones. A tight structure increases the probability of secondary cyclization, and thus it becomes even tighter. A tighter structure further decreases reaction rate between huge molecules. With continual repetition of these processes, micro-gels would be formed.

[F] Non-Idealities at Very Low Mole Fractions of Divinyl Monomer

The steric effects, which are discussed in the previous section, should be weaker when low mole fractions of divinyl monomer are used. However, if k_{cp} is the same even for very low mole fractions of divinyl monomer, the effect of primary cyclization on the consumption of pendant double bonds should remain unchanged, i.e., approximately 80 % of pendant double bonds may still consumed by primary cyclization. Therefore, it may be expected that primary cyclization is the main cause of the delay of the gel point for very low f_{20} at low monomer concentrations. (Please note our monomer concentration is less than 6 wt%). In order to test this hypothesis, experiments with $f_{20}= 1 \times 10^{-4}$ and 2×10^{-4} were done. The conversion-time histories obtained are shown in Figure 3.2.9. Black keys are used to designate the samples in which gel molecules were observed. All gels are clear for these low f_{20}, and micro-gels were not visually observed. The formation of gel molecules was determined, basically, by measuring the fluidity of the reaction mixture. At a desired time the screw cap of the reactor was opened. When a gel molecule is obviously formed, the contents will not flow out

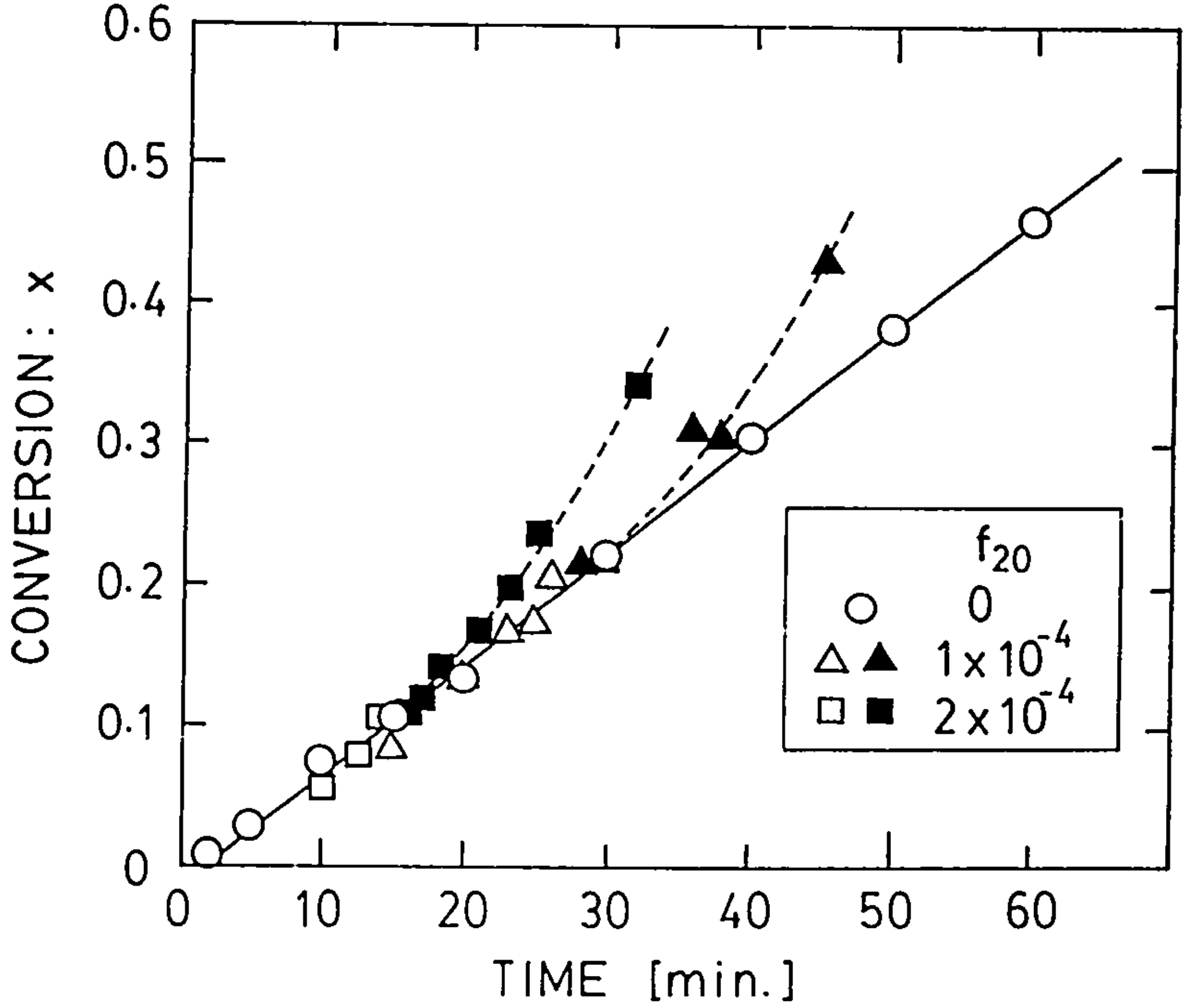


Figure 3.2.9 Conversion-time histories for the polymerization of AAm/Bis, and AAm.

Black keys are used to designate that a gel molecule was visually observed in the system.

of the reactor. In the vicinity of the gel point, the reactor contents were poured into water in which 4-methoxyphenol had been added. After being shaken, the diluted reaction mixture was checked to see whether swollen gel comparable in size to that of the reactor was observed. The gas bubble method [Baselga et al. (1989a)] did not work well for our polymerization conditions since near the gel point, the gel molecule is too flexible and weak to trap a bubble.

If Flory's simplifying assumptions are applicable, gel point, x_c is given by

$$x_c = 1 / (2 f_{20} \bar{P}_{wp}) \qquad (f_{20} \ll 1) \qquad (3.2.4)$$

If primary cyclization is the only cause of the delay of gelation, and Equation (2.3.6) is applicable for primary cyclization, the variance of crosslinking density distribution is zero, therefore, there is no difference between kinetic and equilibrium models. The above equation can be modified to account for primary cyclization reactions as follows.

$$x_c = 1 / [2 f_{20} \bar{P}_{wp} (1 - k_{cp})] \qquad (f_{20} \ll 1) \qquad (3.2.5)$$

It is reasonable to use $\bar{P}_{wp} = 1.07 \times 10^5$, the value for the weight-average primary polymer chain length measured for the homopolymerization of AAm.

The observed and calculated gel points are shown in Table 3.2.2. The value $k_{cp} = 0.79$ agrees fairly well with the results obtained from the measurements of pendant double bond conversions at zero monomer conversion for $f_{20} = 0.07$ and 0.15 ($k_{cp} = 0.81 - 0.84$, see Table 3.2.1).

Table 3.2.2 Observed and calculated gel point (x_c)

f_{20}	Observed	Equation (3.2.4)	Equation (3.2.5) with k_{cp}= 0.79.
1×10^{-4}	0.22	0.047	0.22
2×10^{-4}	0.11	0.023	0.11

It may be reasonable to regard primary cyclization as the main cause of the delay of the onset of gelation for copolymerizations with very low mole fractions of divinyl monomer and low monomer concentrations.

The effects of cyclization (primary and secondary) and steric hindrance on the crosslinking reaction change with polymerization conditions. Up to moderately high mole fractions of divinyl monomer, a general description of these effects may be as follows. At low monomer concentrations, the effect of primary cyclization is important, and secondary cyclization and steric hindrance become significant as the mole fraction of divinyl monomer (f_{20}) increases. At high monomer concentrations, the effect of primary cyclization may be small [Landin, Macosko (1988)], since the probability of finding vinyl groups other than those on its own chain is large. The effects of secondary cyclization and steric hindrance on the crosslinking reaction become significant as f_{20} increases. From these considerations, network defects in polyacrylamide gels may be smallest in the limits of high monomer concentration and very low mole fraction of divinyl monomer. This hypothesis was also proposed by Baselga et al. [Baselga et al. (1987)] who studied the elastic properties of polyacrylamide gels.

The existence of a crosslinking density distribution shows that polymer networks synthesized by free radical polymerization are inherently inhomogeneous on a microscopic scale, and steric hindrance between huge molecules enhances this character and results in the formation of inhomogeneous networks on a macroscopic scale.

3.3. Control of Crosslinking Density

[A] Production of Homogeneous Networks -- Semi-Batch Operation --

When the effect of steric hindrance between huge molecules is significant, the crosslinking reactions are likely to be chain length dependent, and therefore, it would be impossible to prevent the formation of micro-gels, which results in spatially inhomogeneous networks. In such cases, all we could do would be to make the crosslinking densities uniform inside micro-gel particles. However, if the effect of chain length dependence in crosslinking reactions is not strong enough, it may be possible to produce spatially homogeneous networks by application of semi-batch reactors.

Since a gel molecule is an infinitely large molecule, one may need to use the following polymerization processes in order to apply semi-batch reactors with micro-mixing.

1) Dispersion polymerizations such as suspension and emulsion polymerizations.
2) Solution and bulk polymerizations with assistance of very tough mixer such as kneader mixers. In this case, gel molecules are broken into pieces.

The viscosity of a gel molecule is infinitely large, and therefore, various non-idealities in mixing are expected to cause a spatial distribution of monomer and polymer concentrations. However we neglect such distributions, and the reaction system is assumed to be homogeneous.

Fundamental Equations: The monomer balance equations are given by

$$V_0[M]_0 + m - V[M] = n \qquad (3.3.1)$$

$$V_0[M]_0 f_{20} + m_2 - V[M]f_2 = nF_2 \qquad (3.3.2)$$

where V is the reaction volume, [M] is the total molar concentration of comonomers in a reaction system, and subscript 0 is used to designate the initial value. n is the accumulated number of moles of comonomers bound in polymer chains, m is the accumulated number of moles of comonomers fed in the semi-batch period, and m_2 is that for divinyl monomer.

The polymerization rate is given by

$$dn/dt = k_p[R^\bullet][M]V \qquad (3.3.3)$$

The balance equation for additional crosslinking density, ρ_a, is given by

$$N_b[\ \rho_a(b,n+\Delta n) - \rho_a(b,n)] = k_p^{*0}[F_2(b) - \rho_a(b,n) - \rho_c(b,n)][R^\bullet]N_b\,\Delta t \qquad (3.3.4)$$

where b is the accumulated number of moles of comonomers bound in polymer chains when the primary polymer molecule is born, and N_b is the instantaneous number of moles of comonomers bound in polymer chains at n=b.

Therefore, the fundamental equation for additional crosslinking density is given by

$$\frac{\partial \rho_a(b,n)}{\partial n} = k_p^{*0}\,[\,F_2(b) - \rho_a(b,n) - \rho_c(b,n)\,]\,[R^\bullet]\;/\;(\,dn/dt\,)$$

$$= \frac{k_p^{*0}\,[\,F_2(b) - \rho_a(b,n) - \rho_c(b,n)\,]}{k_p\,[M]\,V} \qquad (3.3.5)$$

where k_p^{*0}, k_p, [M], and V are the values at present n.

The instantaneous crosslinking density, $\rho_i(b)$, is given by

$$\rho_i(b) = \int_0^b \frac{\partial \rho_a(y,b)}{\partial b}\,dy$$

$$= \frac{k_p^{*0}\,b}{k_p\,[M]\,V}\,[\,\overline{F}_2(b) - \overline{\rho}_a(b) - \overline{\rho}_c(b)\,] \qquad (3.3.6)$$

where k_p^{*0}, k_p, [M], and V are the values at n = b.

A Policy to Produce Homogeneous Networks

General Considerations: In order to produce polymer networks with uniform crosslinking density, $\rho^f(b,n)$ should be independent of b at a given n.

$$\partial \rho^f(b,n)/\partial b = 0 \qquad (3.3.7)$$

If mole fraction of divinyl monomer in the reaction mixture, f_2, is much smaller than unity, the above equation is practically equivalent to

$$\partial \rho(b,n)/\partial b = 0 \qquad (3.3.8)$$

When the polymerization is continued until all monomer molecules are consumed, it is usually impossible to produce polymers with equal crosslinking densities for all polymer chains. In general, homogeneous networks are produced only at a certain time in a semi-batch period.

Simplified Models for Cyclization: Let us apply very simple models for cyclization reactions which are shown in Section 2.3. Primary cyclization density is given by

$$\rho_{cp}(b) = k_{cp}\ F_2(b) \qquad (3.3.9)$$

For secondary cyclizations, we use zeroth approximation (Equation (2.3.12)), namely, we assume that the number of secondary cycles formed per crosslink, η, is constant.

$$\rho_{cs}(b,n) = \eta\ \rho(b,n) \qquad (3.3.10)$$

By application of Equations (3.3.9) and (3.3.10), the elastic crosslinking density, $\rho_{el.}(b,n)$ (= $\rho(b,n) + \rho_{cs}(b,n)$), is given by

$$\frac{\partial \rho_{el,a}(b,n)}{\partial n} = \frac{k^{*0}_{p,e}\ [(1-k_{cp})\ F_2(b) - \rho_{el,a}(b,n)\ ]}{k_p\ [M]\ V} \qquad (3.3.11)$$

$$\rho_{el,i}(b) = \int_0^b \frac{\partial \rho_{el,a}(y,b)}{\partial b}\ dy$$

$$= \frac{k^{*0}_{p,e}\ b}{k_p\,[M]\ V}\ [(1-k_{cp})\ \bar{F}_2(b) - \bar{\rho}_{el,a}(b)\ ] \qquad (3.3.12)$$

$$\rho_{el.}(b,n) = \rho_{el,i}(b) + \rho_{el,a}(b,n) \qquad (3.3.13)$$

where $k^{*0}_{p,e} = (1+\eta)k^{*0}_p$.

Thus, a necessary condition for homogeneous networks is given by

$$\partial \rho_{el}(b,n)/\partial b = 0 \qquad (f_2 \ll 1) \qquad (3.3.14)$$

<u>A Semi-Batch Policy</u>: Various policies could be used to produce homogeneous networks. A simple policy is given below.

> "Add parts of both monomers to the reactor at t=0, and the use time-varying feed rates for both monomers to maintain $[M]V = n_0$ constant throughout the semi-batch period."

In this policy, Equation (3.3.11) reduces to

$$\frac{\partial \rho_{el,a}(b,n)}{\partial n} = \frac{k_{p,e}^{*0}\,[\,(1 - k_{cp})\,F_2(b) - \rho_{el,a}(b,n)\,]}{k_p\, n_0} \qquad (3.3.15)$$

When $f_2 \ll 1$, $k_{p,e}^{*0}/k_p$ may be consider constant. In this case, the above equation can be solved analytically.

$$\rho_{el,a}(Y,Z) = (\,1 - k_{cp}\,)\,F_2(Y)\,[\,1 - \exp[\,-\frac{k_{p,e}^{*0}}{k_p}\,(\,Z - Y\,)\,]\,] \qquad (3.3.16)$$

where $Y = b/n_0$, and $Z = n/n_0$.

$$\rho_{el,i}(Y) = (k_{p,e}^{*0}/k_p)Y[\,(1-k_{cp})\overline{F}_2(Y) - \overline{\rho}_{el,a}(Y)] \qquad (3.3.17)$$

$$d[Y\ \overline{\rho}_{el,a}(Y)]/dY = (k_{p,e}^{*0}/k_p)[\,(1-k_{cp})\overline{F}_2(Y) - \overline{\rho}_{el,a}(Y)]Y \qquad (3.3.18)$$

Applying the above equations, one can numerically calculate $F_2(Y)$ for a given Z, thus necessary monomer feed composition to produce a homogeneous network can be obtained. One should not forget to check if the calculated $F_2(Y)$ is realizable by adding comonomers keeping [M]V constant.

<u>A Simple Example</u>: Let us consider the following simple case, namely, $f_{20}= 0.01$, $r_1= 0.5$, $k^{*0}_{p,e}/k_p= 2.0$, $k_{cp}= 0.2$. The elastic crosslinking density distribution during polymerization in a batch reactor is shown in Figure 3.3.1. The produced polymer networks possess crosslinking density distributions with large variances.

Necessary conditions to produce polymer networks with uniform crosslinking density at $Z = 2.0$ in a semi-batch reactor are calculated. Copolymer composition, $F_2(Y)$, and compositions of comonomers which flow into the semi-batch reactor $f_{2,f}(Y)$ are shown in Figure 3.3.2. (Please note that in order to keep $[M]V$ constant the flow rate of comonomers changes with polymerization rate, thus time.) The crosslinking density distribution change during semi-batch polymerization is shown in Figure 3.3.3. The crosslinking densities of polymer chains are not equal except at $Z=2.0$.

There would be many problems in a real operation, however, by application of the present theory, at least it would be possible to reduce the heterogeneity in the polymer networks.

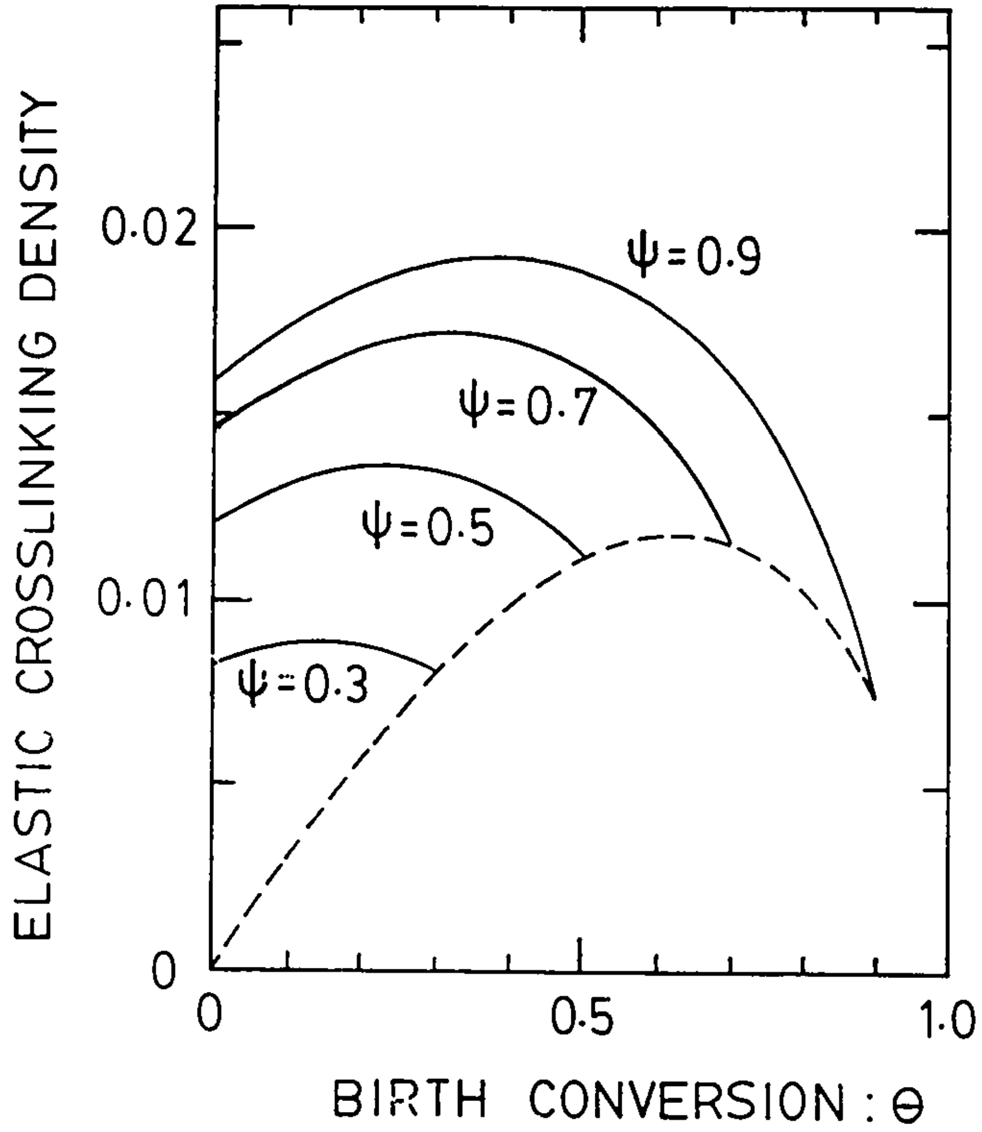


Figure 3.3.1 Crosslinking density distribution change during batch polymerization. $f_{20} = 0.01$, $r_1 = 0.5$, $k^{*0}_{p,e} / k_p = 2.0$, $k_{cp} = 0.2$.

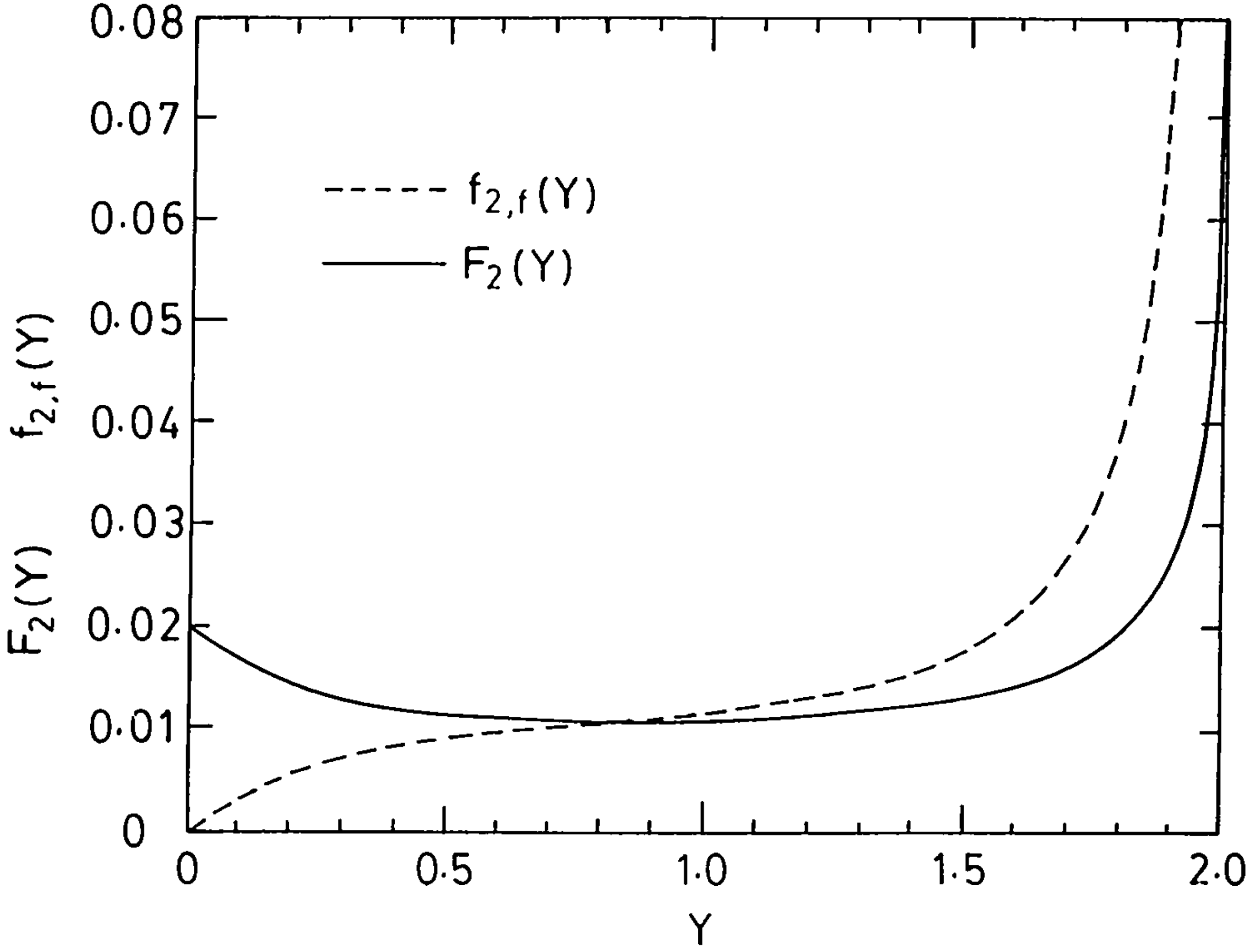


Figure 3.3.2 Copolymer composition change, $F_2(Y)$, and necessary composition of comonomers which flow into the reactor, $f_{2,f}(Y)$, during semi-batch period.

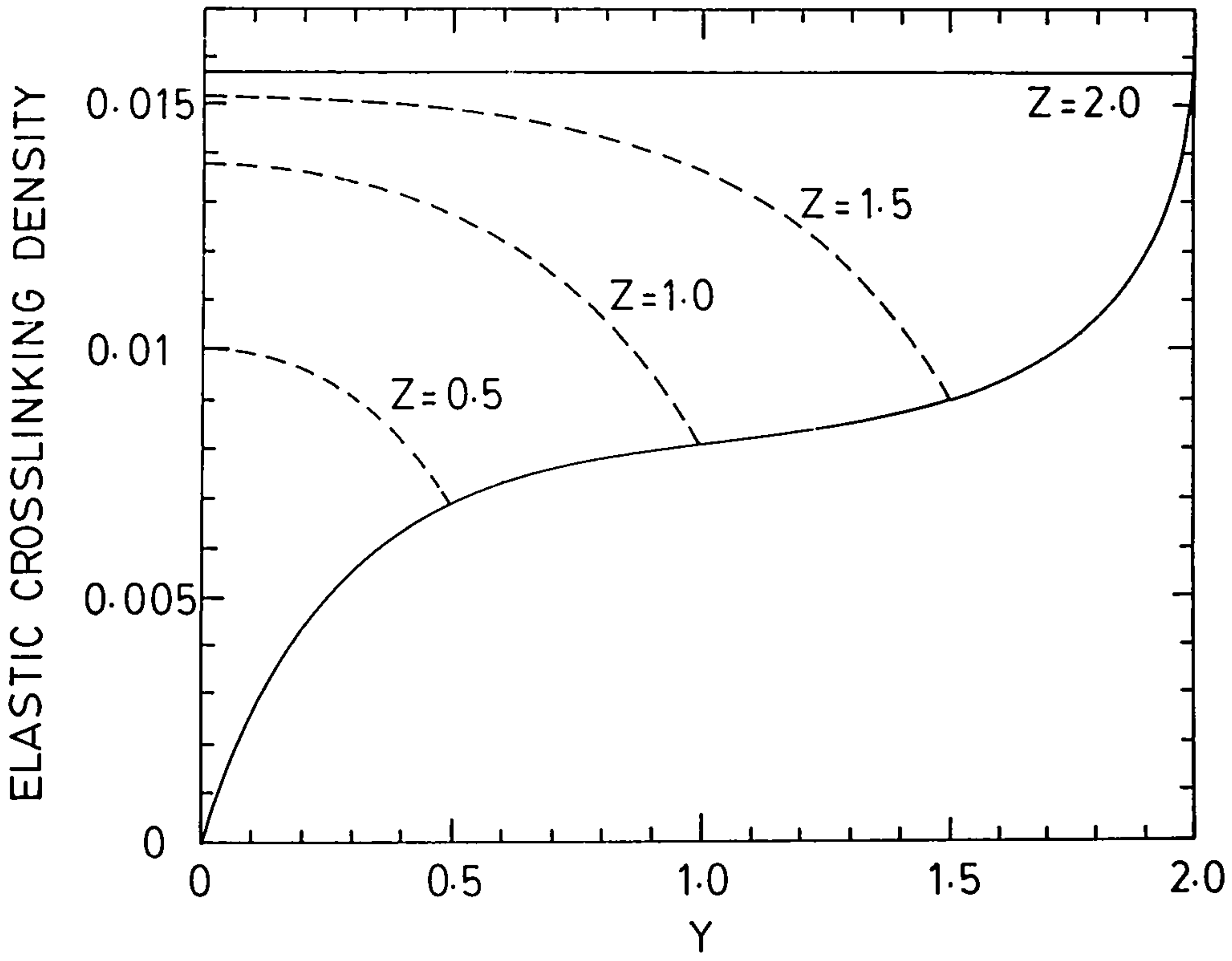


Figure 3.3.3 Crosslinking density distribution change during semi-batch polymerization.

[B] Comparison between Batch Reactors and Continuous Stirred Tank Reactors (CSTR)

It is generally believed that the crosslinking density is higher for polymers synthesized by CSTR than those by batch reactors, since polymers with high concentration exist throughout polymerization in a CSTR. This is true if long chain branches are formed by chain transfer to polymer [Nagasubramanian et al. (1970a,b)], however, this is not always true for vinyl/divinyl copolymerization as is shown in this section. It was found that when the reactivity of double bonds on divinyl monomer is higher than that of vinyl monomer ($r_1 < 0.5$) and/or the effect of secondary cyclization is significant so that $k_{p,e}^{*0}/k_p$ is large, the crosslinking density may be higher for polymers synthesized by batch reactor in a certain conversion range. In a CSTR, the variance of the crosslinking density distribution is large due to the broad residence time distribution, and if the deviation from Flory's simplifying assumptions is small, the variance of the crosslinking density distribution is larger for a CSTR. However, as the effect of non-idealities increases, it may be possible for the variance to be larger with batch reactors.

[B-1] Chain Transfer to Polymer

Let us consider the CSTR shown in Figure 3.3.4. The overall crosslinking density, $\bar{\rho}$, is given by

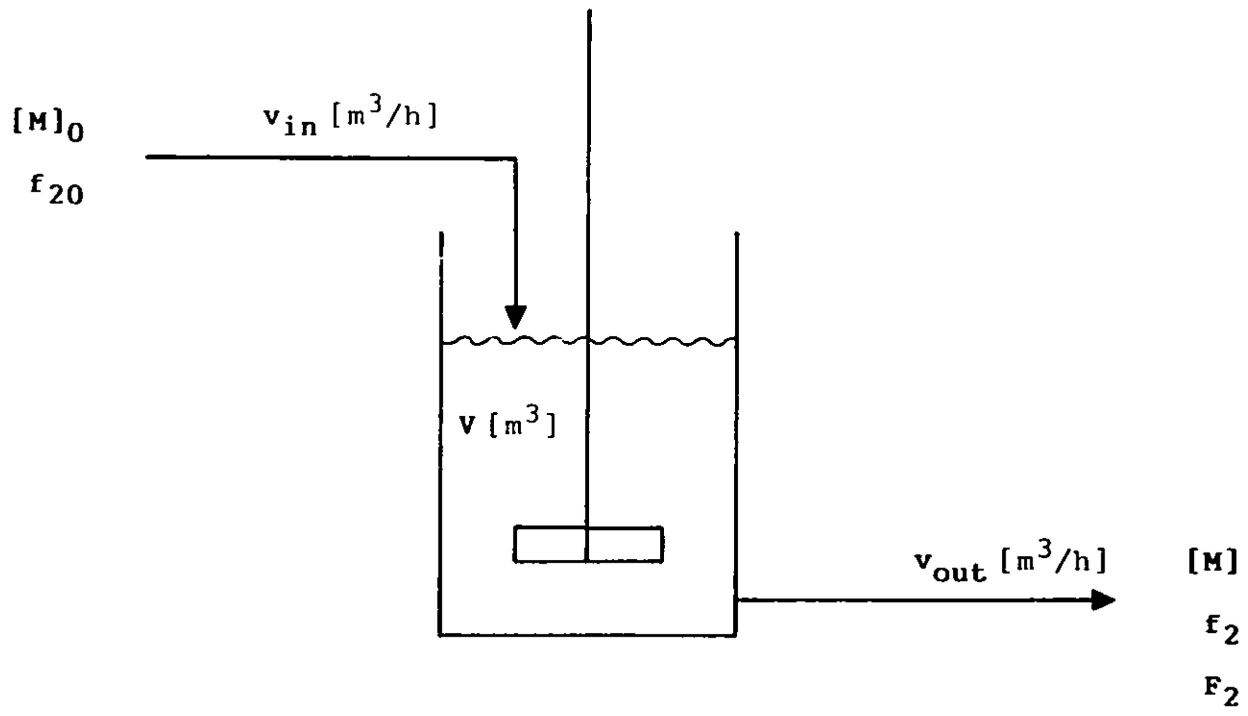


Figure 3.3.4 Schematic drawing of a continuous stirred tank reactor (CSTR).

$$d(VQ_1 \bar{\rho})/dt = k_{fp}Q_1[R\bullet]V - Q_1 \bar{\rho}\, v_{out} \qquad (3.3.19)$$

At steady-state,

$$\bar{\rho} = k_{fp}\,[R\bullet]\,\bar{t} \qquad (3.3.20)$$

where $\bar{t}$ is the mean residence time (= V/v_{out}).

The balance equation for polymer is given by

$$d(VQ_1)/dt = k_p[R\bullet][M]V - Q_1 v_{out} \qquad (3.3.21)$$

At steady-state,

$$[R\bullet] = x/[k_p(1-x)\bar{t}] \qquad (3.3.22)$$

Substituting Equation (3.3.22) into Equation (3.3.20), one obtains

$$\bar{\rho}_{CSTR} = k_{fp}x/[k_p(1-x)] \qquad (3.3.23)$$

For batch reactors, the following equation holds if the volume change during polymerization is neglected.

$$d(x\,\bar{\rho})/dx = k_{fp}x/[k_p(1-x)] \qquad (3.3.24)$$

The above equation can be solved analytically.

$$\bar{\rho}_{Batch} = \frac{k_{fp}}{k_p} \left[(1/x) \ln \frac{1}{1-x} - 1 \right] \qquad (3.3.25)$$

From Equations (3.3.23) and (3.3.25), the ratio, $\bar{\rho}_{Batch}/\bar{\rho}_{CSTR}$, at the same monomer conversion is given by

$$\frac{\bar{\rho}_{Batch}}{\bar{\rho}_{CSTR}} = \frac{(1/x) \ln[1/(1-x)] - 1}{[x/(1-x)]} \qquad (3.3.26)$$

Figure 3.3.5 shows the calculation results using Equation (3.3.26). The ratio is less than 0.5 for all conversions.

[B-2] Vinyl / Divinyl Copolymerizations

Copolymer Composition: For a CSTR a balance equation for divinyl monomer, M_2, is given by

$$d(V[M_2])/dt = v_{in}[M]_0 f_{20} - v_{out}[M] f_2 - v_{out} Q_1 \bar{F}_2 = 0$$

(3.3.27)

If the volume change during polymerization is neglected,

$$f_{20} - (1-x) f_2 - x\bar{F}_2 = 0 \qquad (3.3.28)$$

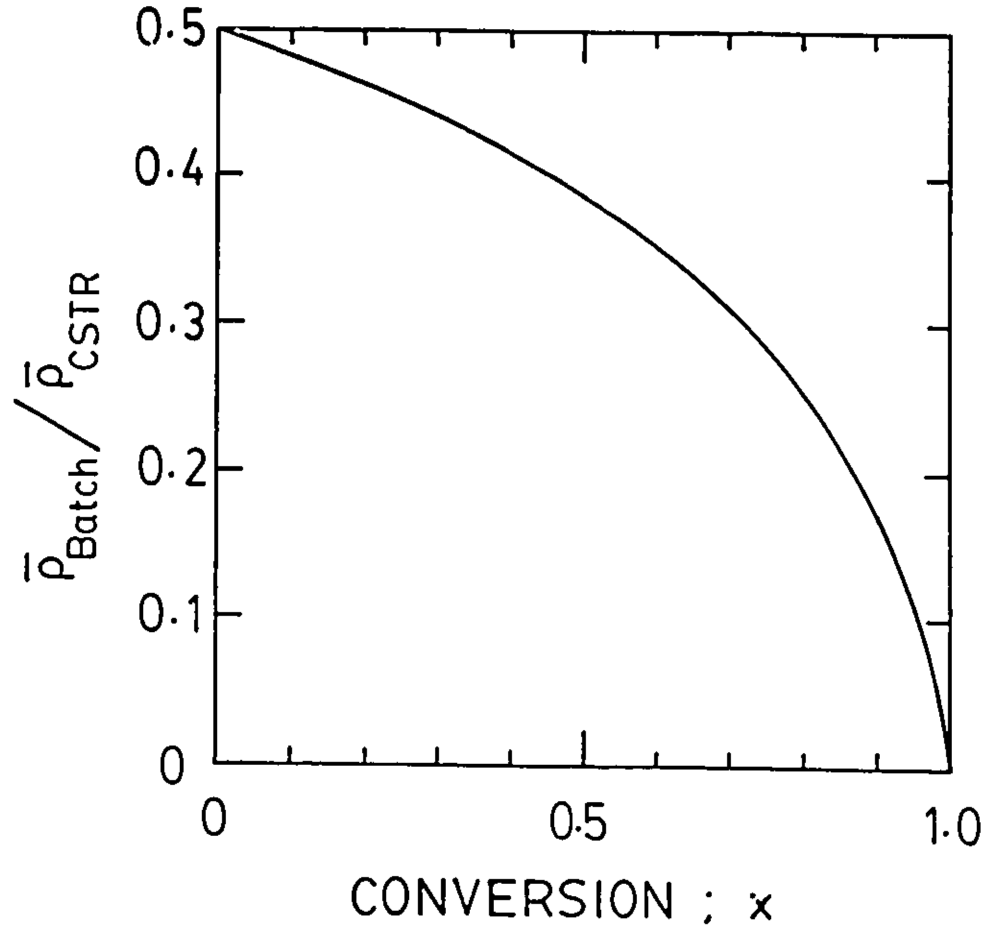


Figure 3.3.5 Effect of reactor type on crosslinking density.

(Chain transfer to polymer.)

Let us assume that copolymer composition is approximated by the Mayo-Lewis equation. Since the accumulated copolymer composition, $\bar{F}_2$, is the same as the instantaneous copolymer composition, F_2, in a CSTR,

$$\bar{F}_2 = F_2 = (r_2 f_2^2 + f_1 f_2)/(r_2 f_2^2 + 2f_1 f_2 + r_1 f_1^2) \tag{3.3.29}$$

Using Equations (3.3.28) and (3.3.29), copolymer compositions for a CSTR are obtainable.

On the other hand, copolymer compositions for batch polymerization may be approximated by the Meyer-Lowry equation. Figure 3.3.6 shows the copolymer composition of accumulated polymers. The mole fractions of monomer with higher reactivity (, in this case divinyl monomer,) bound in the accumulated polymers is higher for batch reactors at the same monomer conversion.

Overall Crosslinking Density: Applying the simple models for cyclization reactions, the balance equation for the elastic crosslinking density, $\bar{\rho}_{el}$, is given by

$$d(VQ_1\ \bar{\rho}_{el})/dt = 2k^{*0}_{p,e}[(1-k_{cp})\bar{F}_2 - \bar{\rho}_{el}/2]Q_1[R^\bullet]V - Q_1\ \bar{\rho}_{el}v_{out} = 0 \tag{3.3.30}$$

Substituting Equation (3.3.22), one obtains

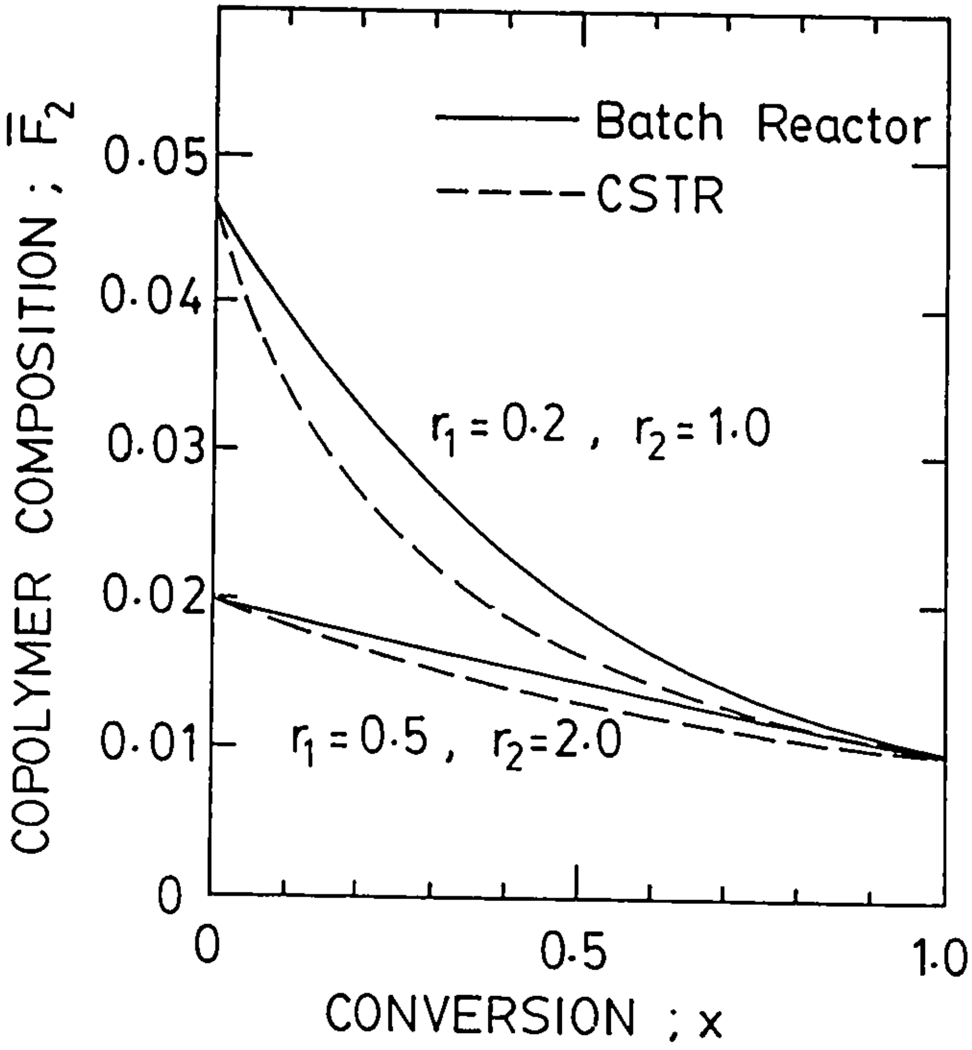


Figure 3.3.6 Accumulated copolymer composition as a function of total monomer conversion in a batch reactor and a CSTR. $f_{20} = 0.01$.

$$\bar{\rho}_{el}^{CSTR} = \frac{2\,(k_{p,e}^{*0}/k_p)(1-k_{cp})\,\bar{F}_2\,x}{(k_{p,e}^{*0}/k_p)\,x + (1-x)} \qquad (3.3.31)$$

For batch reactors, the fundamental equation for overall elastic crosslinking density, $\bar{\rho}_{el}^{Batch}$, is given by

$$\frac{d(x\,\bar{\rho}_{el}^{Batch})}{dx} = 2\,\frac{k_{p,e}^{*0}}{k_p}\bullet\frac{[(1-k_{cp})\,\bar{F}_2 - \bar{\rho}_{el}^{Batch}/2\,]\,x}{(1-x)} \qquad (3.3.32)$$

Before making numerical calculations, let us consider an approximate magnitude of $k_{p,e}^{*0}/k_p$ with respect to the reactivity ratio. If the mole fraction of divinyl monomer is much smaller than unity, $k_p^{*0} \approx k_{p13}^{*}$, and $k_p \approx k_{11}$. Therefore, if the effect of secondary cyclization is small, $k_{p,e}^{*0}/k_p \approx 1/(2r_1)$. As a first approximation, $k_{p,e}^{*0}/k_p$ may have the order of $1/(2r_1)$. For example, if $r_1 = 0.2$, $k_{p,e}^{*0}/k_p = 2.5$ may be an initial guess. Let us call the $k_{p,e}^{*0}/k_p$ value based on the above calculation the "standard" value.

Numerical calculations were done for $f_{20} = 0.01$ and $k_{cp} = 0$. Figure 3.3.7 shows the case in which the reactivity ratios are $r_1 = 0.5$ and $r_2 = 2.0$. If $k_{p,e}^{*0}/k_p$ has a "standard" value, i.e., $k_{p,e}^{*0}/k_p = 1.0$, the crosslinking density is higher for CSTR. However, if $k_{p,e}^{*0}/k_p$ is large due to, for example, secondary cyclization, the crosslinking density may be higher for batch reactors at high

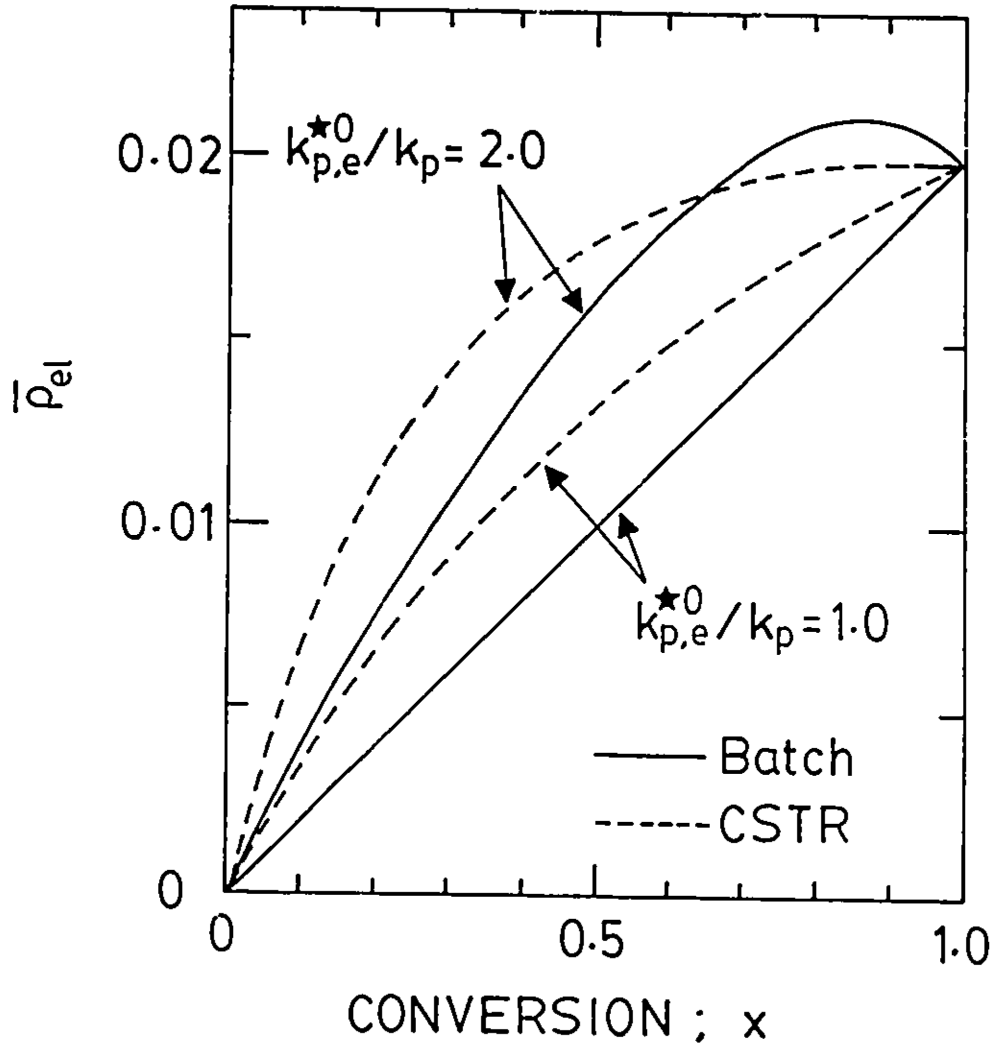


Figure 3.3.7 Crosslinking density as a function of total monomer conversion in the two reactor types. $f_{20} = 0.01$, $r_1 = 0.5$, $r_2 = 2.0$, $k_{cp} = 0$.

conversions.

Figure 3.3.8 shows the case in which the reactivity ratios are $r_1 = 0.2$ and $r_2 = 1.0$. In this case, the reactivity of double bonds with $R_1^{\bullet}$ is higher for those on divinyl monomer. The "standard" value for $k_{p,e}^{*0}/k_p$ may be 2.5, and for this condition crosslinking density is higher for batch reactors at conversions higher than 43%.

It may be concluded that crosslinking density may be higher for batch reactors if the reactivity of double bonds on divinyl monomer is higher that of vinyl monomer ($r_1 < 0.5$) and/or the effect of secondary cyclization is significant so that $k_{p,e}^{*0}/k_p$ is large enough.

Crosslinking Density Distribution: In a CSTR, polymers with different crosslinking densities are produced due to the residence time distribution. This is a clear difference from batch reactors in which it is caused by the difference in the mole fraction of pendant double bonds among primary polymer molecules with different birth time.

The instantaneous crosslinking density as well as the copolymer composition can be considered the same for all primary polymer molecules in a CSTR. Applying the simple models for cyclization reactions, the elastic crosslinking density of instantaneous type, $\rho_{el,i}$, is given by

$$\rho_{el,i} = \frac{k_{p,e}^{*0}\left[(1 - k_{cp})\, F_2 - \bar{\rho}_{el,a}\right] x}{k_p\,(1 - x)} \qquad (3.3.33)$$

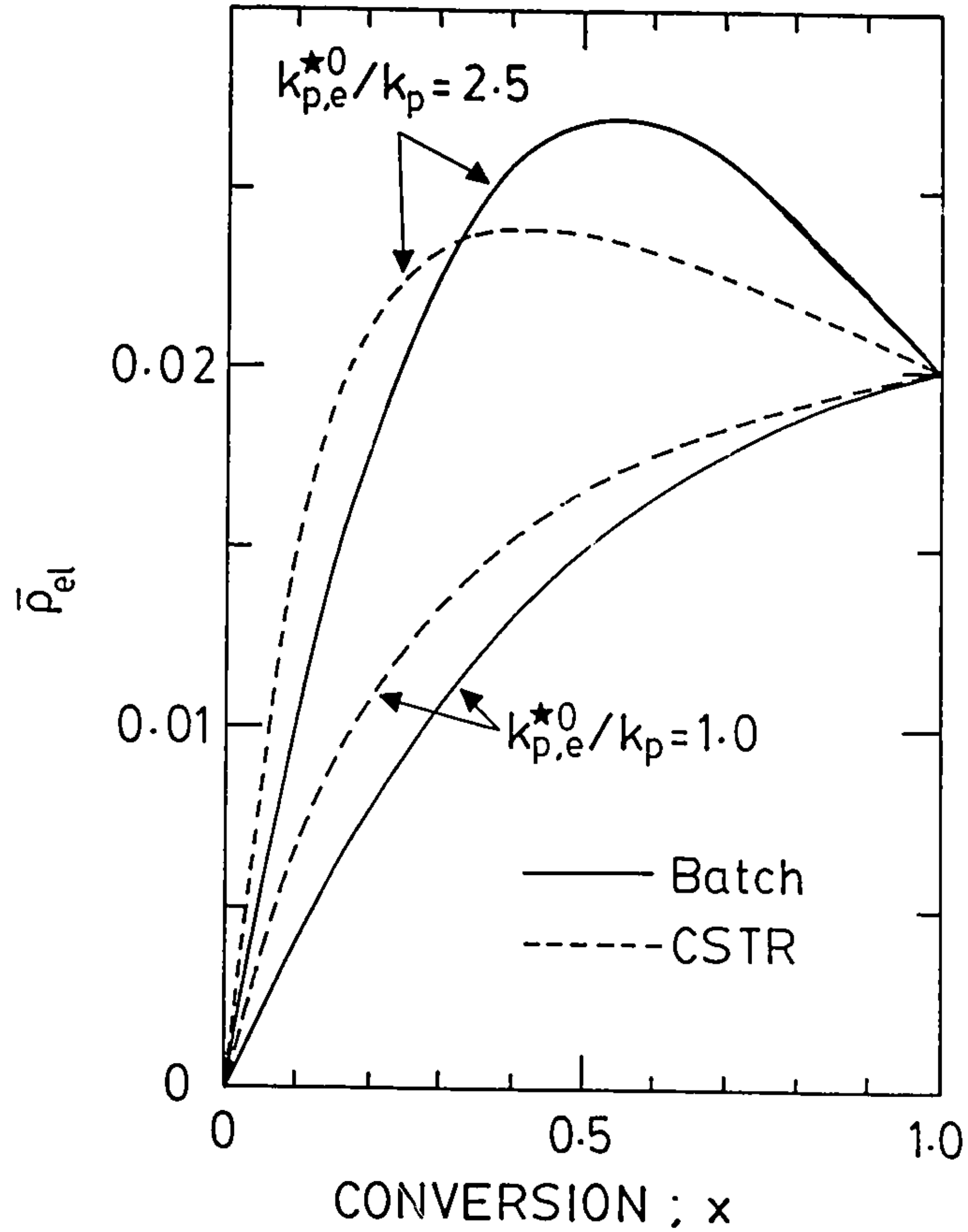


Figure 3.3.8 Crosslinking density as a function of total monomer conversion in the two reactor types. $f_{20} = 0.01$, $r_1 = 0.2$, $r_2 = 1.0$, $k_{cp} = 0$.

Since the total number of additional crosslinks and that of instantaneous crosslinks are equal, i.e., $\bar{\rho}_{e1,i} = \bar{\rho}_{e1,a}$, and $\rho_{e1,i}$ is the same for all primary polymer molecules,

$$\rho_{e1,i} = \frac{(k_{p,e}^{*0}/k_p)(1-k_{cp})F_2\,x}{(k_{p,e}^{*0}/k_p)\,x + (1-x)} \qquad (3.3.34)$$

The additional crosslinking density of the primary molecules whose residence time is t is given by

$$d\,\rho_{e1,a}(t)/dt = k_{p,e}^{*0}[(1-k_{cp})F_2 - \rho_{e1,a}(t)][R^{\bullet}] \qquad (3.3.35)$$

Integration over t = 0 to t gives

$$\rho_{e1,a}(t) = (1-k_{cp})F_2[1-\exp(-k_{p,e}^{*0}[R^{\bullet}]t)] \qquad (3.3.36)$$

Substituting Equation (3.3.22), one obtains

$$\rho_{e1,a}(t) = (1-k_{cp})F_2\left[1-\exp\left(-\frac{k_{p,e}^{*0}}{k_p}\bullet\frac{x}{1-x}\bullet\frac{t}{\bar{t}}\right)\right] \qquad (3.3.37)$$

Since the residence time distribution, F(t/t), is given by

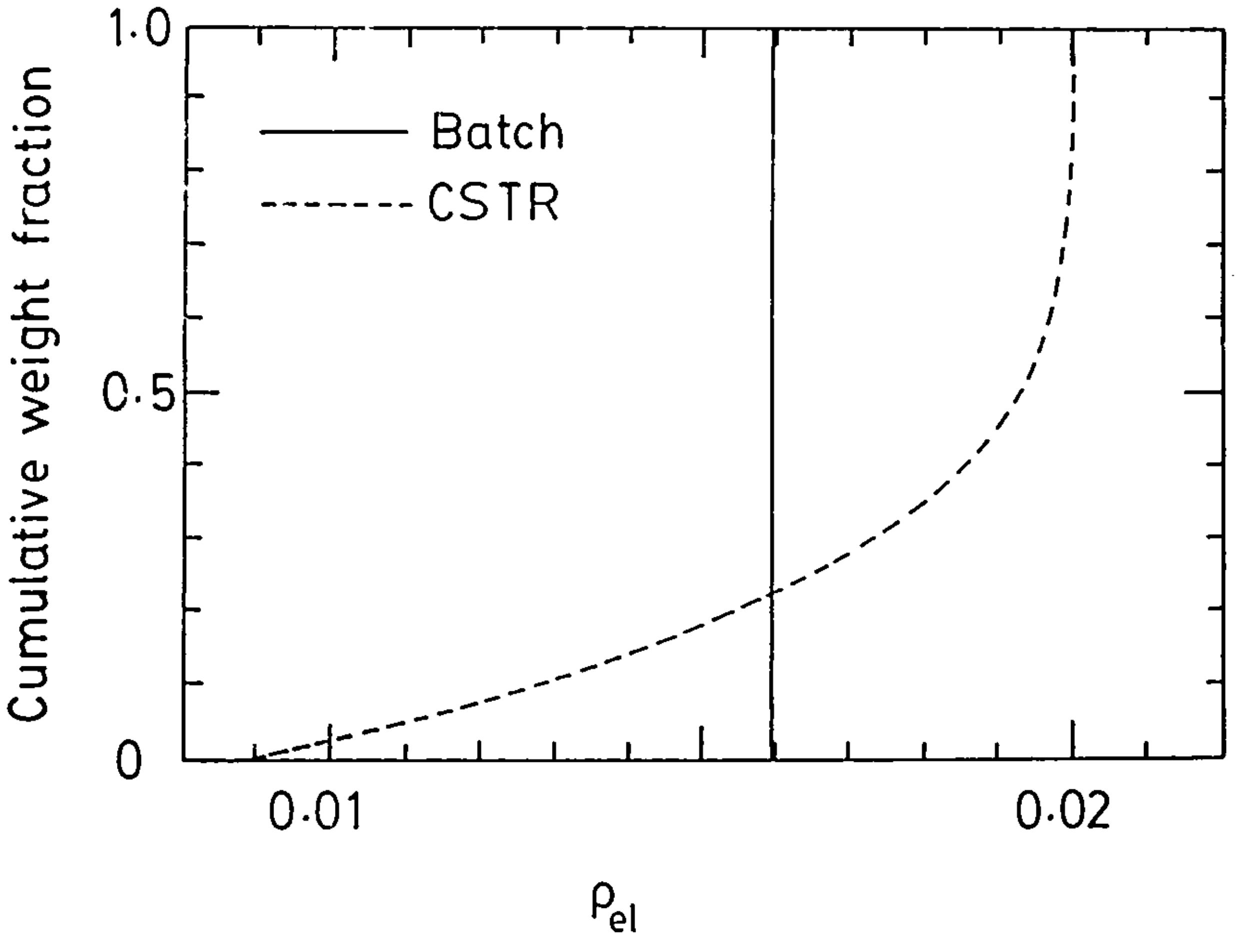
$$F(t/\bar{t}) = 1 - \exp(-t/\bar{t}) \qquad (3.3.38)$$

, one can calculate the crosslinking density distribution using

Equations (3.3.34), (3.3.37), and (3.3.38). (Copolymer compositions, F_2, can be calculated from Equations (3.3.28) and (3.3.29).)

Figure 3.3.9 shows the case in which a perfectly homogeneous network is formed in batch polymerization. Polymers produced by CSTR, however, have crosslinking density distributions with large variances.

Figure 3.3.10 shows the case in which $k^{*0}_{p,e}/k_p = 2.0$ but all other conditions are the same as those of Figure 3.3.9. In this case, the variances are large for both types of reactor. In general, the variance of the crosslinking density distribution is large in a CSTR due to the broad residence time distribution, however, since the cause of broad crosslinking density distributions is completely different for these reactor types as was mentioned earlier, there may be conditions for which the variance of the crosslinking density distribution is larger for batch reactors.



<u>Figure 3.3.9</u> Cumulative weight fraction of the primary polymer molecules whose elastic crosslinking density is smaller than ρ_{el}. $k_p^{*0}/k_p = 1.0$, $r_1 = 0.5$, $r_2 = 2.0$, $f_{20} = 0.01$, $x = 0.8$, $k_{cp} = 0$.

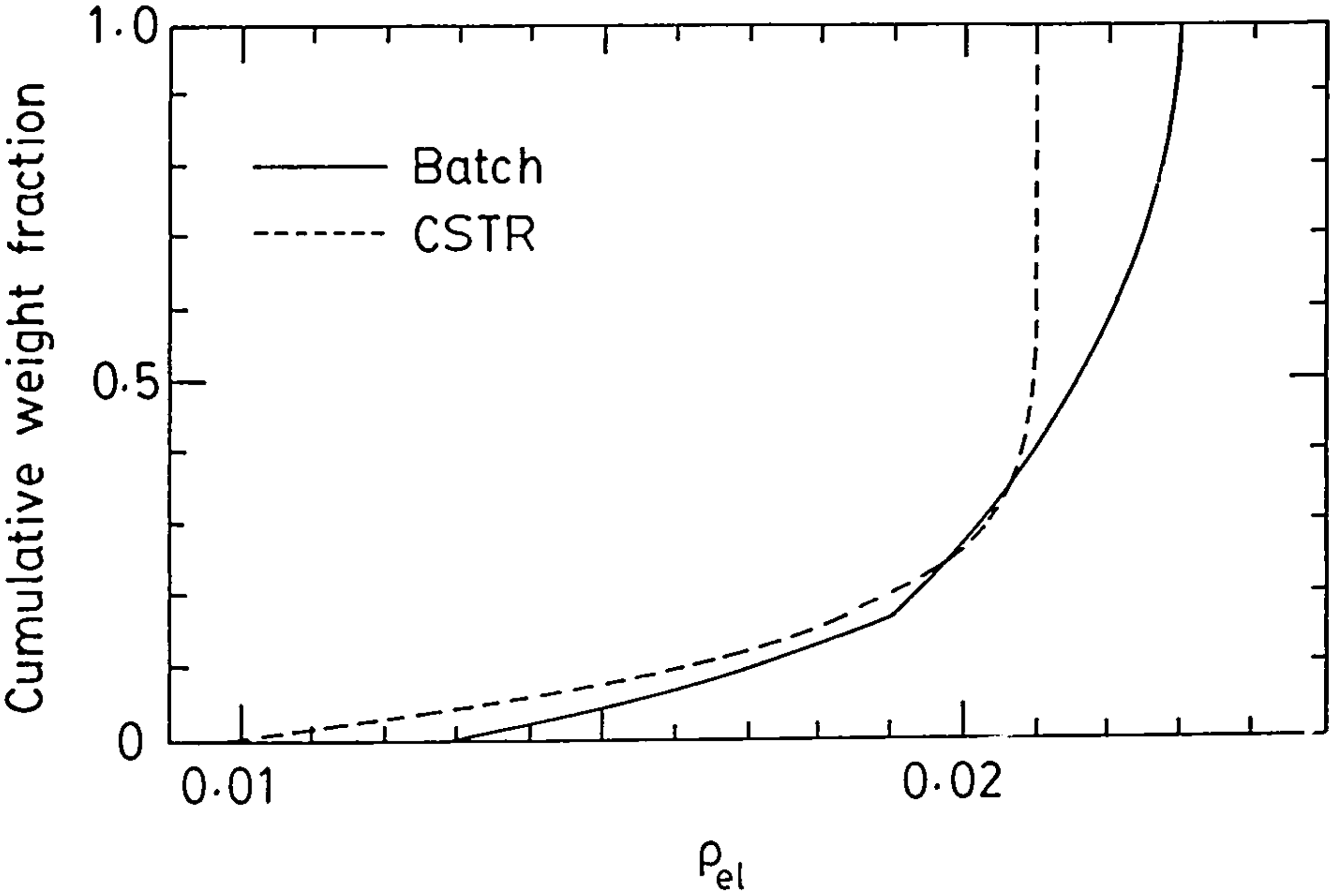


Figure 3.3.10 Cumulative weight fraction of the primary polymer molecules whose elastic crosslinking density is smaller than ρ_{el}. $k_p^{*0}/k_p = 2.0$, $r_1 = 0.5$, $r_2 = 2.0$, $f_{20} = 0.01$, $x = 0.8$, $k_{cp} = 0$.

4. DISCUSSION AND RECOMMENDATIONS FOR FUTURE RESEARCH

The present kinetic theory accounts for the history of the generated network structure, and therefore, is realistic for networks formed via free radical polymerization. In particular, the concept of crosslinking density distribution changes one of the limitations of mean-field theories. This theory gives satisfactory predictions for copolymerization of methyl methacrylate and ethylene glycol dimethacrylate when simple models for cyclization and bimolecular termination reactions are used. However, there are many problems to be solved in order to build more realistic models.

Strong cyclization is characteristic of free radical copolymerization of vinyl and divinyl monomer [Dusek (1982)], since only active centers on chain ends whose concentration is fairly low can add another double bond in free radical polymerization, and therefore, the probability of finding a pendant double bonds located on another polymer molecule may be small. In order to build a realistic model for cyclization reactions, it will be necessary to consider the local concentration of each type of double bond and its mobility around a radical center located on a polymer molecule. However, it seems a formidable task to build such a model in the context of a mean-field theory. It may be convenient to divide cyclization reactions into primary and secondary cyclization at this stage in the development of kinetic models for cyclization reactions, since their behavior may be somewhat different. Primary cyclization may be the main cause of the delay of the gel point for a dilute monomer solution with low mole fraction of divinyl monomer, while secondary cyclization may have a significant effect for a system with high monomer concentration and/or high mole fraction of divinyl monomer. Larger primary polymer chain length increases the effect of secondary cyclization strongly, while it has relatively minor effect on primary cyclization. To make more realistic calculations with the present kinetic theory, it will be necessary to build more sophisticated models both for primary and secondary cyclization. Furthermore, when the effect of cyclization is significant, one needs to pay close attention when calculating copolymer compositions.

The reactivity of pendant double bonds appears to decrease even for the symmetric divinyl monomers whose chemical double bond reactivity should be the same as mono-vinyl monomer, such as with methyl methacrylate (MMA) / ethylene glycol dimethacrylate (EGDMA) copolymerization. However, what is the origin of this decrease? From a chemical point of view, it seems reasonable to consider that the reactivity of both double bonds in EGDMA are the same. We think it is caused by steric hindrance, which is sometimes called "shielding effect" [Minnema, Staverman (1958)]. Usually even the termination reaction rate is not reduced until the point of gelation, so that it may be difficult to believe that steric hindrance or diffusion control of the crosslinking reaction is significant. However, it seems possible to have significant steric hindrance for a crosslinking reaction between huge molecules. This steric hindrance in the pre-gelation period may be schematically shown in Figure 4.0.1. The reaction between huge molecules (**A** and **B**) may be sterically hindered, since there are many inaccessible pendant double bonds and radical centers. Since a much larger number of smaller molecules (**C**). which can not be sterically hindered, exist in the reaction system, the contribution of the reaction between huge molecules may be negligible to the overall crosslinking reaction rate, however, this reaction has a fairly significant effect on the formation rate of a gel molecule. For example, let us examine Figure 2.4.4 again. The model predicts average chain length up to $\bar{P}_w$= 2000 very well, however, the calculated gel point $x_{c,cal.}$= 0.344 deviates much from the observed gel point $x_{c,obs.}$= 0.423. This may be an indirect evidence that the reaction rate between huge molecules is decreased.

In the post-gelation period, there should be many radical centers and pendant double bonds on the gel molecule. Since the mobility of these radical centers and double bonds are fairly restricted, the apparent reactivity of pendant double bonds should decrease. Especially at high conversions, the mobility of sol molecules or even that of monomer may decrease sufficiently to affect reaction rates.

From the above consideration it may be better to regard the

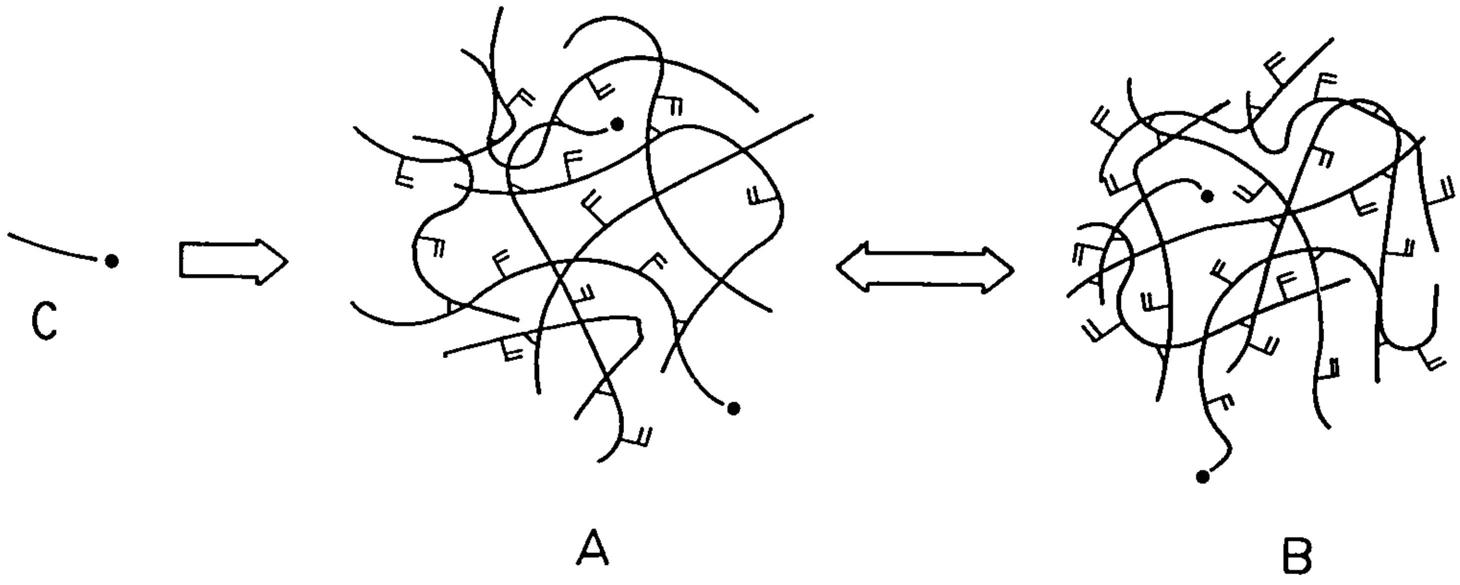


Figure 4.0.1 Physical effect on the reactivity of pendant double bonds (pre-gelation period). The reaction between huge molecules A and B may be slower than the overall reaction rate, since there are inaccessible pendant double bonds and radical centers. However, the reaction between A and C may not be hindered sterically.

apparent reactivity of pendant double bonds as structure dependent as well as chain length dependent. This is a very important feature of network formation in free radical copolymerization. Therefore, if a constant value is assumed for the reactivity of pendant double bonds, for example, the best value for the prediction of gel point may not be the same for the prediction of average chain length of sol fractions or crosslinking density. If the reaction rate between huge molecules is reduced, the structure of huge molecules becomes tighter than smaller ones, since only smaller molecules can diffuse into huge molecules. Tight structure increases the probability of secondary cyclization, and it becomes even tighter. Tighter structure further decreases reaction rate between huge molecules. Therefore, it is natural that decreased reactivity of pendant double bonds and secondary cyclization occur simultaneously. From these considerations, it seems reasonable that micro-gels are formed in the pre-gelation period [Spevacek, Dusek (1980)], and as a result, spatially inhomogeneous network structures are formed. The existence of a crosslinking density distribution with a significant variance shows that polymer networks synthesized by free radical polymerization are inherently inhomogeneous on a microscopic scale, and the molecular size dependent crosslinking reaction enhances this character and results in the formation of inhomogeneous networks on a macroscopic scale.

The relative effects of cyclization and decreased reactivity of pendant double bonds change with polymerization conditions.

Qualitatively, up to moderately high mole fractions of divinyl monomer, a general description of these effects may be as follows. At low monomer concentration (low $[M]_0$), the effect of primary cyclization is important, and as the mole fraction of divinyl monomer (f_{20}) increases, the effect of secondary cyclization and deceased reactivity of pendant double bonds becomes significant. At high $[M]_0$, the effect of primary cyclization is small, since the probability of finding vinyl groups other than those on its own chain is large. The effect of the secondary cyclization and decreased reactivity of pendant double bonds becomes significant as f_{20} increases. (See Table 4.0.1.)

Kinetics of bimolecular termination reactions may be another key factor if a more realistic model is to be developed. We applied an empirical correlation shown in Equation (3.1.2-a,b,c). Obviously this correlation is not exact. Since we estimated four parameters from time-conversion curve, this average termination rate constant should be the number-average termination rate constant. This termination rate constant can be applied to make a calculation of the number-average chain length of the primary polymer molecules, while it may appreciably underestimate the weight-average chain length [Zhu et al. (1989a)], which is very important for the calculations of various mass properties. Furthermore, it is quite natural to consider that the kinetic behavior of radical centers located on gel and sol are different.

Although until relatively high conversions only specific reactions (crosslinking and termination reactions) may be diffusion controlled,

Table 4.0.1 A general description of non-ideal effects.

	low f_{20} ⇨	moderately high f_{20}
low $[M]_0$	PRIMARY	PRIMARY STERIC
⇩		
high $[M]_0$		STERIC

PRIMARY : primary cyclization.

STERIC : decreased reactivity of pendant double bonds.
&
secondary cyclization.

all reactions may be diffusion controlled at very high conversions due to the glass transition effect. In order to control the network structure of final products, studies in these regions will be important.

Reaction kinetics are even more complicated for high mole fractions of divinyl monomer. The increase in radical concentration is so fast that even the stationary-state hypothesis for radicals is not valid [Zhu et al. (1989b)]. For homopolymerization of divinyl monomer, it is reported that even the rate of shrinkage of the system can not keep up with conversion during the polymerization process [Kloosterboer et al. (1988a,b)]. For high mole fractions of divinyl monomer polymer radicals which are bound to the polymer network are fairly stable even if the temperature is increased above the glass transition temperature [Zhu et al. (1989b,d)]. Furthermore, a considerable number of pendant double bonds are trapped in a polymer network and remain unreacted. The heterogeneity of a system increases as the mole fraction of divinyl monomer increases, and this may have a significant effect on the kinetics of network formation. From ESR analysis, it was found that two types of radicals exist at high conversions, namely, liquid state and solid state [Zhu et al. (1989b,d)]. It is quite natural to guess that the kinetic behavior of these two types of radicals is considerably different. The inability to properly model the kinetics of cyclization and the effect of heterogeneity of the system are the main disadvantages of a mean-field theory. However, the percolation theory which is considered to be equivalent to a non-mean-field theory is still too immature to describe the whole course of network formation. A problem with the percolation theory is that the mobility of molecules is too restricted, while when using a mean-field theory the molecules are too mobile.

There are still many problems to be solved before a more realistic model for network formation in free radical polymerization is found, and more reliable measurements will be necessary to clarify the complicated phenomena involved. We do, however, believe that the present kinetic theory will provide greater insight into the important phenomena in non-linear free radical copolymerization.

5. CONCLUSIONS

A new kinetic theory for free radical copolymerization with long chain branching and crosslinking has been proposed. This kinetic theory accounts for the history of the generated structure as well as all of the important elementary reactions involved in free radical polymerization, and can be used to make calculations of various important properties during network formation such as onset of gelation, weight fraction of sol and gel, number- and weight-average chain length of sol fraction, crosslinking density as a function of the birth time of a primary polymer molecule, etc. This theory reduces to Flory's theory of network formation under special limiting conditions.

The substance and derivation of the pseudo-kinetic rate constant method was made clear. The concept has proven to be quite useful for treating a free radical polymerization system which consists of two or more components not only for linear polymers but also branched polymers.

A rigorous method of treating the kinetics of crosslinking reactions has been proposed. It was found that each primary polymer molecule experiences a different history of crosslinking in free radical copolymerizarion, and therefore, the crosslinking densities of primary polymer molecules whose birth times are different may not be the same. The existence of a crosslinking density distribution with a significant variance is a very important feature of network formation in free radical copolymerization, and shows that polymer networks synthesized by free radical copolymerization are inherently inhomogeneous on a microscopic scale. The concept of crosslinking density distribution has changed one of the limitations of network models based on a mean-field theory, and it clarifies the difference from an equilibrium system.

Cyclization reactions are very important in free radical copolymerization of vinyl/divinyl monomers. In free radical polymerization a pendant double bond is consumed only through a polymer radical whose concentration is very low and whose life time is very short, and therefore, the local environment in the vicinity of a radical center has a significant effect, and it is highly probable for a radical center located on a polymer chain to find a pendant double bond on its own chain rather than that on another polymer molecule. From the point of view of kinetics it is convenient to divide cyclization reactions into two groups, namely, primary and secondary cyclization. Very simple models for both types of cyclization have been developed.

In the pre-gelation period, an infinite set of equations describing the chemical kinetics has been solved by the method of moments assuming each polymer radical possesses only one radical center. In the case of chain transfer to polymer, it was proven that this reaction plus termination by disproportionation can never cause gelation, however, if the bimolecular termination reaction includes combination, gelation is predicted to occur under certain conditions.

Although the fundamental concept of this method is different from Flory's theory, they give practically equal predictions.

In the post-gelation period, Flory's theory for network formation has been generalized by application of the crosslinking density distribution. This generalized theory gave satisfactory predictions for the bulk copolymerization of methyl methacrylate and ethylene glycol dimethacrylate.

Kinetics of network formation in free radical copolymerization of acrylamide and N,N'-methylene-bis-acrylamide in aqueous solution (56.6 g-comonomer/L) at 25°C have been studied. It was found that as high as 80% of the pendant double bonds are consumed immediately on polymerization and are wasted in primary cyclization. Primary cyclization is responsible for the delay in the onset of gelation at low mole fractions of divinyl monomer with low comonomer concentrations. The decreased reaction rate between huge molecules due to steric hindrance in the pre-gelation period contributes to micro-gel formation, and consequently, to formation of spatially inhomogeneous networks.

This theory should assist one to design superior quality network polymer systems and can be used to control various polymerization processes. Although it is generally believed that the crosslinking density is higher for the polymers synthesized by continuous stirred tank reactors (CSTR) than those by batch reactors, this has been shown not to be true for vinyl/divinyl copolymerizations. In a CSTR, polymers with significantly different crosslinking densities are produced due to the broad residence time distribution. This is a clear difference from batch reactors in which it is caused by the difference in the mole fraction of pendant double bonds among primary polymer molecules with different birth time. In batch reactors, the variance of the crosslinking density distribution is zero under Flory's simplifying assumptions, however, it becomes significant as the actual conditions cause deviations from Flory's assumptions.

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GLOSSARY OF PRINCIPAL SYMBOLS

b	the accumulated number of moles of comonomers bound in polymer chains when the given primary polymer molecule is born (Section 3.3).
f	initiator efficiency
f	functionality of a structure unit (Section 1.1).
f_1, f_2	mole fraction of M_1 and M_2 in the monomer mixture. For vinyl/divinyl copolymerization, the subscript 1 is used to designate mono-vinyl monomer, 2 is used for divinyl monomer.
f_{20}	initial mole fraction of divinyl monomer in the monomer mixture.
F_1, $\overline{F}_1$	instantaneous and accumulated mole fraction of M_1 bound in the polymer chain. For vinyl/divinyl copolymerization, the subscript 1 is used to designate mono-vinyl monomer.
F_2, $\overline{F}_2$	instantaneous and accumulated mole fraction of M_2 bound in the polymer chain. For vinyl/divinyl copolymerization, the subscript 2 is used to designate divinyl monomer.
g	an empirical constant to account for the effect of physical chain entanglement in the swelling equation (Equation 3.3.1).
k_{cp}, k_{cs}	kinetic rate constant for primary and secondary cyclization.
k_d	rate constant for the initiator decomposition.

k_{11}, k_{12}, etc.	copolymerization propagation constants for a radical of the type indicated by the first subscript with a monomer indicated by the second.
k_{fm}, k_{fT}, k_{fp}	pseudo-kinetic rate constant for chain transfer to monomer, small molecule (T), and polymer.
k_p	pseudo-kinetic rate constant for propagation reaction.
k_p^*	pseudo-kinetic rate constant for crosslinking reaction.
k_p^{*0}	a part of pseudo-kinetic rate constant for crosslinking reaction which shows an average reactivity of pendant double bonds.
$k_{p,e}^{*0}$	pseudo-kinetic rate constant for crosslinking plus secondary cyclization. (See Equation (3.2.1).)
k_{p13}^*, k_{p23}^*, k_{p33}^*	kinetic rate constant of crosslinking reaction for a radical of the type indicated by the first number with pendant double bonds.
k_{tc}, k_{td}	pseudo-kinetic rate constant for termination by combination, and that by disproportionation.
n	accumulated number of moles of comonomers bound in the chain (Section 3.3).
n_0	initial total number of moles of comonomers (= $[M]_0 V_0$) (Section 3.3).
N_θ	number of monomer units which are bound in polymer chains at $x = \Theta$.
m, m_2	accumulated number of moles of comonomers fed in the semi-batch period (Section 3.3), and that for divinyl monomer.

$[M]$, $[M]_0$ total monomer concentration of comonomers (= $[M_1]+[M_2]$), and initial total monomer concentration (= $[M_1]_0+[M_2]_0$).

M_1, M_2, $[M_1]$, $[M_2]$ monomers 1 and 2 in copolymerization and their concentrations. For vinyl/divinyl copolymerization, the subscript 1 is used to designate mono-vinyl monomer, and 2 is used for divinyl monomer.

p, p_c extent of reaction of double bonds and that at the gel point.

P_r, $[P_r]$ polymer molecules with chain length r and its concentration.

P_n, $\bar{P}_n$ instantaneous and accumulated number-average chain length.

P_{np}, $\bar{P}_{np}$ instantaneous and accumulated number-average chain length of primary polymer molecules.

P_w, $\bar{P}_w$ instantaneous and accumulated weight-average chain length.

P_{wp}, $\bar{P}_{wp}$ instantaneous weight-average chain length of primary polymer molecules.

q_i normalized i-th moment of polymer distribution (see Equation (2.4.9)).

Q_i i-th moment of polymer molecule distribution (see Equation (2.4.8a)).

r chain length.

r_1, r_2 reactivity ratios.

$r^v{}_1$, $r^v{}_2$ reactivity ratios defined with respect to vinyl groups.

$[R^\bullet]$	total polymer radical concentration.
$R_r^\bullet$, $[R_r^\bullet]$	polymer radical with chain length r and its concentration.
$R_1^\bullet$, $R_2^\bullet$, $[R_1^\bullet]$, $[R_2^\bullet]$	polymer radicals whose active center is located on M_1 and M_2, and their concentrations.
t	time.
$\bar{t}$	mean residence time in CSTR (Section 3.3).
V, V_0	reaction volume, and its initial value.
w_r	weight chain length distribution of primary polymer molecules.
W_g, W_s	weight fraction of gel and sol.
x, x_c	total monomer conversion (= $([M]_0V_0-[M]V)/([M]_0V_0)$), and that at the gel point.
x_{pd}, x_{pd}^0	pendant double bond conversion, and its value at zero monomer conversion.
x_w	total monomer conversion by weight (Section 3.2).
y_i	normalized i-th moment of polymer radical distribution (see Equation (2.4.10)).
Y_i	i-th moment of polymer radical distribution (see Equation (2.4.8b)).
Z	normalized total number of moles of monomer unit bound in polymer chains (= n/n_0) (Section 3.3).
β	= (termination rate by combination)/(propagation rate)
η	average number of secondary cycles formed per crosslink.
θ	birth conversion of the given primary polymer molecule.

ρ, $\bar{\rho}$ crosslinking density, and its accumulated value.

ρ_a, ρ_i, $\bar{\rho}_a$, $\bar{\rho}_i$ additional and instantaneous crosslinking density. Overscript bars are used to designate accumulated (overall) values.

ρ_c, ρ_{cp}, ρ_{cs} cyclization density (= ρ_{cp}+ ρ_{cs}), primary and secondary cyclization density.

$\rho_{cs,a}$, $\rho_{cs,i}$ secondary cyclization density of additional and instantaneous type.

ρ_{el}, $\rho_{el,a}$, $\rho_{el,i}$ elastic crosslinking density (see Equation (2.3.12)), and its additional and instantaneous type.

τ [(rate of chain transfer to monomer and other small molecules)+ (rate of termination by disproportionation)]/(propagation rate)

$\Phi_1^{\bullet}$, $\Phi_2^{\bullet}$, $\Phi_3^{\bullet}$ mole fraction of radical of type indicated by subscripts. Subscript 1 is used to designate mono-vinyl monomer, 2 is used for divinyl monomer, and 3 is used for pendant double bonds.

ψ present conversion.

Overscript bar is used to designate the accumulated value up to a given conversion.

APPENDIX

A. The Pseudo-Kinetic Rate Constant Method

A-1. Derivation of Pseudo-Kinetic Rate Constants.

As a simplest example, let us consider a binary copolymerization whose elementary reactions are shown in Table 2.1.1. The balance equation for polymer radicals with chain length r, $R^\bullet_{r,*}$, is given by

$$\begin{aligned}\frac{1}{V}\frac{d(V[R^\bullet_{r,*}])}{dt} = {} & \Big((k_{11}[M_1]+k_{12}[M_2])[R^\bullet_{r-1,1}]+(k_{21}[M_1]+k_{22}[M_2])[R^\bullet_{r-1,2}]\Big) \\ & -\Big((k_{11}[M_1]+k_{12}[M_2])[R^\bullet_{r,1}]+(k_{21}[M_1]+k_{22}[M_2])[R^\bullet_{r,2}]\Big) \\ & -\Big((k_{f11}[M_1]+k_{f12}[M_2])[R^\bullet_{r,1}]+(k_{f21}[M_1]+k_{f22}[M_2])[R^\bullet_{r,2}]\Big) \\ & -(k_{fT1}[R^\bullet_{r,1}]+k_{fT2}[R^\bullet_{r,2}])[T] \\ & -\Big((k_{td11}+k_{tc11})[R^\bullet_1][R^\bullet_{r,1}]+(k_{td22}+k_{tc22})[R^\bullet_2][R^\bullet_{r,2}] \\ & \quad +(k_{td12}+k_{tc12})([R^\bullet_1][R^\bullet_{r,2}]+[R^\bullet_2][R^\bullet_{r,1}])\Big) \\ & \qquad\qquad (\text{for } r \geqslant 2) \qquad (\text{A1})\end{aligned}$$

where $[R^\bullet_{r,1}]$ is the concentration of polymer radical with chain length r whose active center located on monomer 1, and

$$[R^\bullet_{r,*}]=[R^\bullet_{r,1}]+[R^\bullet_{r,2}] \qquad (\text{A2})$$

$$[R^{\bullet}_{1}]=\sum_{r=1}^{\infty}[R^{\bullet}_{r,1}] \qquad \text{(A3)}$$

$$[R^{\bullet}_{2}]=\sum_{r=1}^{\infty}[R^{\bullet}_{r,2}] \qquad \text{(A4)}$$

Applying the following mole fractions to Equation (A1),

$$\Phi^{\bullet}_{r,1} = [R^{\bullet}_{r,1}]/[R^{\bullet}_{r,*}] \qquad \text{(A5)}$$

$$\Phi^{\bullet}_{r,2} = [R^{\bullet}_{r,2}]/[R^{\bullet}_{r,*}] \qquad \text{(A6)}$$

$$\Phi^{\bullet}_{1} = [R^{\bullet}_{1}]/([R^{\bullet}_{1}]+[R^{\bullet}_{2}]) = [R^{\bullet}_{1}]/[R^{\bullet}] \qquad \text{(A7)}$$

$$\Phi^{\bullet}_{2} = [R^{\bullet}_{2}]/[R^{\bullet}] \qquad \text{(A8)}$$

$$f_1 = [M_1]/([M_1]+[M_2]) = [M_1]/[M] \qquad \text{(A9)}$$

$$f_2 = [M_2]/[M] \qquad \text{(A10)}$$

, one obtains

$$\begin{aligned}\frac{1}{V}\frac{d(V[R^{\bullet}_{r,*}])}{dt} = {} & \Big[(k_{11}f_1+ k_{12}f_2)\,\Phi^{\bullet}_{r-1,1}+ (k_{21}f_1+ k_{22}f_2)\,\Phi^{\bullet}_{r-1,2}\Big][M][R^{\bullet}_{r-1,*}] \\ & -\Big[(k_{11}f_1+ k_{12}f_2)\,\Phi^{\bullet}_{r,1}+ (k_{21}f_1+ k_{22}f_2)\,\Phi^{\bullet}_{r,2}\Big][M][R^{\bullet}_{r,*}] \\ & -\Big[(k_{f11}f_1+ k_{f12}f_2)\,\Phi^{\bullet}_{r,1}+ (k_{f21}f_1+ k_{f22}f_2)\,\Phi^{\bullet}_{r,2}\Big][M][R^{\bullet}_{r,*}] \\ & -(k_{fT1}\,\Phi^{\bullet}_{r,1}+ k_{fT2}\,\Phi^{\bullet}_{r,2})[T][R^{\bullet}_{r,*}] \\ & -\Big[k_{td11}\,\Phi^{\bullet}_{1}\,\Phi^{\bullet}_{r,1}+ k_{td12}(\Phi^{\bullet}_{1}\,\Phi^{\bullet}_{r,2}+ \Phi^{\bullet}_{2}\,\Phi^{\bullet}_{r,1})+ k_{td22}\,\Phi^{\bullet}_{2}\,\Phi^{\bullet}_{r,2} \\ & \quad + k_{tc11}\,\Phi^{\bullet}_{1}\,\Phi^{\bullet}_{r,1}+ k_{tc12}(\Phi^{\bullet}_{1}\,\Phi^{\bullet}_{r,2}+ \Phi^{\bullet}_{2}\,\Phi^{\bullet}_{r,1})+ k_{tc22}\,\Phi^{\bullet}_{2}\,\Phi^{\bullet}_{r,2}\Big] \\ & [R^{\bullet}][R^{\bullet}_{r,*}] \qquad \text{(A11)}\end{aligned}$$

If the mole fraction of radical type is independent of chain length, namely,

$$\Phi^{\bullet}_{1} = \Phi^{\bullet}_{1,1} = \Phi^{\bullet}_{2,1} = \Phi^{\bullet}_{3,1} = \cdots\cdot = \Phi^{\bullet}_{r,1} = \cdots\cdots \qquad \text{(A12)}$$

$$\Phi^{\bullet}_{2} = \Phi^{\bullet}_{1,2} = \Phi^{\bullet}_{2,2} = \Phi^{\bullet}_{3,2} = \cdots\cdot = \Phi^{\bullet}_{r,2} = \cdots\cdots \qquad \text{(A13)}$$

, Equation (A11) reduces to

$$\frac{1}{V}\frac{d(V[R^{\bullet}_{r,*}])}{dt} = k_p[M][R^{\bullet}_{r-1,*}] - k_p[M][R^{\bullet}_{r,*}] - k_{fm}[M][R^{\bullet}_{r,*}] - k_{fT}[T][R^{\bullet}_{r,*}] - (k_{td} + k_{tc})[R^{\bullet}][R^{\bullet}_{r,*}] \qquad (\text{for } r \geqslant 2) \quad \text{(A14)}$$

where the definitions for k_p, k_{fm}, k_{fT}, k_{td}, and k_{tc} are given by Equations (2.1.3)-(2.1.7) in the text.

Applying the same procedure, the following equations can be derived.

$$\frac{1}{V}\frac{d(V[R^{\bullet}_{1,*}])}{dt} = R_I + k_{fm}[M][R^{\bullet}] + k_{fT}[T][R^{\bullet}] - k_p[M][R^{\bullet}_{1,*}] - k_{fm}[M][R^{\bullet}_{1,*}] - k_{fT}[T][R^{\bullet}_{1,*}] - (k_{td} + k_{tc})[R^{\bullet}][R^{\bullet}_{1,*}] \qquad \text{(A15)}$$

$$\frac{1}{V}\frac{d(V[P_r])}{dt} = k_{fm}[M][R^{\bullet}_{r,*}] + k_{fT}[T][R^{\bullet}_{r,*}] + k_{td}[R^{\bullet}][R^{\bullet}_{r,*}] + (1/2)k_{tc}\sum_{s=1}^{r-1}[R^{\bullet}_{s,*}][R^{\bullet}_{r-s,*}] \qquad \text{(A16)}$$

The balance equations (A14)-(A16) are exactly the same as those for homopolymerization, and therefore, the equation for chain length distribution as well as overall rate expression are the same as those for homopolymerization. Therefore, the necessary condition for the applicability of the pseudo-kinetic rate constants is that the mole fraction of radical type does not change with chain length (Equations (A12) and (A13)). We identify when the above condition is applicable with negligible error in the next section.

If the pseudo-kinetic rate constant method is applicable, it is straight forward to derive the instantaneous weight-chain length distribution, $W(r)$ (= $r(d[P_r]/dt)/(-d[M]/dt)$). By application of the stationary-state hypothesis for polymer radicals, $W(r)$ is given by [Balke, Hamielec (1973)]

$$W(r) = (\tau+\beta)[\tau + (\beta/2)(\tau+\beta)(r-1)]\, r \exp[-(\tau+\beta)] \qquad \text{(A17)}$$

where $\tau = (k_{td}[R^\bullet] + k_{fm}[M] + k_{fT}[T])/(k_p[M])$

$\beta = k_{tc}[R^\bullet]/(k_p[M])$.

When the bimolecular termination rate constants are diffusion controlled and are chain length dependent, $W(r)$ is given by

$$\begin{aligned} W(r) = {} & r(\bar{\tau}+\bar{\beta})\, \tau(r)\Big(\prod_{m=1}^{r} \Phi(m)\Big) \\ & + (r/2)(\bar{\tau}+\bar{\beta})^2 \sum_{s=1}^{r-1} \beta(s,r-s)\Big(\prod_{m=1}^{s} \Phi(m)\Big)\Big(\prod_{m=1}^{r-s} \Phi(m)\Big) \end{aligned} \qquad \text{(A18)}$$

where $\tau(r) = (k_{td}(r)[R^{\bullet}] + k_{fm}[M] + k_{fT}[T])/(k_p[M])$

$\beta(r) = k_{tc}(r)/(k_p[M])$

$\Phi(r) = 1/(1 + \tau(r) + \beta(r))$

$k_{td}(r)$ and $k_{tc}(r)$ are the average kinetic rate constants for termination by disproportionation and by combination respectively for polymer radicals with chain length r. $\overline{\tau}$ and $\overline{\beta}$ are the average values over all chain lengths.

A-2. Necessary Conditions for the Applicability of the Pseudo-Kinetic Rate Constant Method

In this section we identify when Equations (A12) and (A13) are applicable with negligible error. It is obvious that if $\Phi^{\bullet}_{1,1} \neq \Phi^{\bullet}_{1}$, Equations (A12) and (A13) are mathematically incorrect. However, if $\Phi^{\bullet}_{r,1}$ converges rapidly to its overall value, $\Phi^{\bullet}_{1}$, Equations (A12) and (A13) may be practically satisfied.

Limiting and Overall Radical Fractions of Type 1: If $\Phi^{\bullet}_{r,1}$ converges, the limiting value, $\Phi^{\bullet}_{\infty,1}$, must coincide with the overall value, $\Phi^{\bullet}_{1}$, in order to satisfy Equations (A12) and (A13). First, let us derive the limiting radical fraction, $\Phi^{\bullet}_{\infty,1}$.

The balance equation for polymer radical of type 1 with chain length r is given by

$$d[R^{\bullet}_{r,1}]/dt = k_{11}[R^{\bullet}_{r-1,1}][M_1] + k_{21}[R^{\bullet}_{r-1,2}][M_1] - k_{11}[R^{\bullet}_{r,1}][M_1] - k_{12}[R^{\bullet}_{r,1}][M_2] - t_1[R^{\bullet}_{r,1}] \qquad (A19)$$

where $t_1[R^{\bullet}_{r,1}]$ is the production rate of dead polymers from $R^{\bullet}_{r,1}$, and t_1 is given by

$$t_1 = (k_{td11} + k_{tc11})[R^{\bullet}_1] + (k_{td12} + k_{tc12})[R^{\bullet}_2] + k_{f11}[M_1] + k_{f12}[M_2] + k_{fT1}[T] \tag{A20}$$

By application of the stationary-state hypothesis to Equation (A19), one obtains

$$[R^{\bullet}_{r,1}] = \frac{k_{11}[R^{\bullet}_{r-1,1}] + k_{21}[R^{\bullet}_{r-1,2}]}{k_{11}[M_1] + k_{12}[M_2] + t_1}[M_1] \tag{A21}$$

Similarly,

$$[R^{\bullet}_{r,2}] = \frac{k_{22}[R^{\bullet}_{r-1,2}] + k_{12}[R^{\bullet}_{r-1,1}]}{k_{22}[M_2] + k_{21}[M_1] + t_2}[M_2] \tag{A22}$$

Therefore, $[R^{\bullet}_{r,1}]/[R^{\bullet}_{r,2}]$ (= A_r) is given by

$$A_r = \frac{[M_1]}{[M_2]} \bullet \frac{U_1(k_{22}[M_2] + k_{21}[M_1])}{U_2(k_{11}[M_1] + k_{12}[M_2])} \bullet \frac{k_{11}A_{r-1} + k_{21}}{k_{22} + k_{12}A_{r-1}} \tag{A23}$$

where U_1 and U_2 are the probability of growth for polymer radical of type 1 and 2 respectively, namely, U_1 and U_2 are given by

$$U_1 = \frac{k_{11}[M_1] + k_{12}[M_2]}{k_{11}[M_1] + k_{12}[M_2] + t_1} \tag{A24}$$

$$U_2 = \frac{k_{22}[M_2] + k_{21}[M_1]}{k_{22}[M_2] + k_{21}[M_1] + t_2} \qquad \text{(A25)}$$

If A_r converges to A, A must satisfy the following quadratic equation.

$$A^2 + (k_{21}/k_{12})(r_2 - \mu r_1)A - (k_{21}/k_{12})^2 \mu = 0 \qquad \text{(A26)}$$

where r_1 and r_2 are reactivity ratios, and

$\mu = f_1(r_2 f_2 + f_1)U_1/[f_2(r_1 f_1 + f_2)U_2]$.

When U_1/U_2=1, Equation (A26) reduces to

$$\left(A - \frac{k_{21} f_1}{k_{12} f_2}\right)\left(A + \frac{k_{21}}{k_{12}} \cdot \frac{r_2 f_2 + f_1}{r_1 f_1 + f_2}\right) = 0 \qquad \text{(A27)}$$

, and therefore,

$$\Phi^{\bullet}_{\infty,1} = \frac{k_{21} f_1}{k_{21} f_1 + k_{12} f_2} \qquad (U_1/U_2 = 1) \qquad \text{(A28)}$$

However, in general, $\Phi^{\bullet}_{\infty,1}$ changes with U_1/U_2.

Next, let us consider the overall radical fraction, $\Phi^{\bullet}_1$. The balance equation for $R^{\bullet}_1$ and $R^{\bullet}$ are given by

$$d[R^{\bullet}_1]/dt = i_1[M_1] + k_{21}[R^{\bullet}_2][M_1] - k_{12}[R^{\bullet}_1][M_2] - t_1[R^{\bullet}_1] \qquad \text{(A29)}$$

$$d[R^{\bullet}]/dt = i_1[M_1] + i_2[M_2] - t_1[R^{\bullet}_1] - t_2[R^{\bullet}_2] \qquad \text{(A30)}$$

where $i_1[M_1]$ and $i_2[M_2]$ are the formation rate of $R^{\bullet}_{1,0,1}$ and $R^{\bullet}_{0,1,2}$ respectively. For example, i_1 is given by

$$i_1 = k_1[R^{\bullet}_{in}] + k_{f11}[R^{\bullet}_1] + k_{f21}[R^{\bullet}_2] + k'_{p1}[T^{\bullet}] \qquad \text{(A31)}$$

where k'_{p1} is the reinitiation rate constant by $T^{\bullet}$.
By application of the stationary-state hypothesis for Equations (A29) and (A30),

$$\frac{[R^{\bullet}_1]}{[R^{\bullet}_2]} = \frac{I_1 t_2 + k_{21}[M_1]}{I_2 t_1 + k_{12}[M_2]} \qquad \text{(A32)}$$

where $I_1 = i_1[M_1]/(i_1[M_1] + i_2[M_2])$, and $I_2 = 1 - I_1$.

In terms of U_1 and U_2, Equation (A32) can be written as follows.

$$\frac{[R^{\bullet}_1]}{[R^{\bullet}_2]} = \frac{\dfrac{k_{21}}{k_{12}}\left(I_1 \dfrac{1-U_2}{U_2}(r_2 f_2 + f_1) + f_1\right)}{I_2 \dfrac{1-U_1}{U_1}(r_1 f_1 + f_2) + f_2} \qquad \text{(A33)}$$

Therefore, $\Phi^{\bullet}_1$ is dependent on the absolute value of U_1 and U_2. When $1 > U_1$, $U_2 > 0.99$, Equation (A33) can be approximated by

$$\Phi^{\bullet}_1 = \frac{k_{21} f_1}{k_{21} f_1 + k_{12} f_2} \qquad \text{(A34)}$$

As is shown in Equation (A28), if $1 > U_1, U_2 > 0.99$, $\Phi^{\bullet}_{\infty,1} = \Phi^{\bullet}_{1}$. Furthermore, it is worth noting here that the usual copolymer composition equation known as the Mayo-Lewis equation [Mayo, Lewis (1944)] assumes that Equation (A34) is valid, so that the condition, $1 > U_1, U_2 > 0.99$, is also necessary to apply the Mayo-Lewis equation. Since the instantaneous number-average chain length, P_n, is approximately equal to the inverse of the probability of producing dead polymer from polymer radicals, i.e., $P_n \approx 1/(1 - U)$, P_n needs to be larger than a few hundred in order to satisfy the Mayo-Lewis equation and $\Phi^{\bullet}_{\infty,1} = \Phi^{\bullet}_{1}$.

Calculation of $\Phi^{\bullet}_{r,1}$: Now, let us investigate how $\Phi^{\bullet}_{r,1}$ changes with chain length. First, we derive the bivariate distribution of chain length and composition for polymer radicals.

By application of the stationary-state hypothesis for $R^{\bullet}_{m,n,1}$, $[R^{\bullet}_{m,n,1}]$ is given by the following difference equation.

$$[R^{\bullet}_{m,n,1}] = U_1 P_{11}([R^{\bullet}_{m-1,n,1}] + (k_{21}/k_{11})[R^{\bullet}_{m-1,n,2}]) \qquad \text{(A35)}$$

where P_{11} is the probability that a growing chain with M_1 end adds another M_1 monomer unit, which is given by $P_{11} = k_{11}[M_1]/(k_{11}[M_1]+k_{12}[M_2])$. Similarly, $[R^{\bullet}_{m,n,2}]$ is given by

$$[R^{\bullet}_{m,n,2}] = U_2 P_{22}([R^{\bullet}_{m,n-1,2}] + (k_{12}/k_{22})[R^{\bullet}_{m,n-1,1}]) \qquad \text{(A36)}$$

where P_{22} is the probability that a growing chain with M_2 end adds another M_2 monomer unit.

$[R^{\bullet}_{1,0,1}]$ and $[R^{\bullet}_{0,1,2}]$ are given by

$$[R^{\bullet}_{1,0,1}] = U_1 P_{11} i_1 / k_{11} \qquad \text{(A37)}$$

$$[R^{\bullet}_{0,1,2}] = U_2 P_{22} i_2 / k_{22} \qquad \text{(A38)}$$

From difference equations (A35) and (A36) with initial conditions (A37) and (A38), one can readily formulate the following equations for $[R^{\bullet}_{m,n,1}]$ and $[R^{\bullet}_{m,n,2}]$.

$$[R^{\bullet}_{m,n,1}] = U_1^m U_2^n P_{11}^m P_{22}^n \left[\frac{i_1}{k_{11}} \sum_{j=1} \binom{m-1}{j}\binom{n-1}{j-1} X^j + \frac{i_2}{k_{12}} \sum_{j=1} \binom{m-1}{j-1}\binom{n-1}{j-1} X^j \right] \qquad (m, n \geqslant 1) \qquad \text{(A39)}$$

$$[R^{\bullet}_{m,n,2}] = U_1^m U_2^n P_{11}^m P_{22}^n \left[\frac{i_1}{k_{21}} \sum_{j=1} \binom{m-1}{j-1}\binom{n-1}{j-1} X^j + \frac{i_2}{k_{22}} \sum_{j=1} \binom{m-1}{j-1}\binom{n-1}{j} X^j \right] \qquad (m, n \geqslant 1) \qquad \text{(A40)}$$

where $X = P_{12}P_{21}/(P_{11}P_{22}) = 1/(r_1 r_2)$, P_{12} is the probability that a growing chain with M_1 end adds M_2 monomer unit, and similar definition for P_{21}.

Therefore, the concentration of polymer radical of type 1 with chain length r, $[R^{\bullet}_{r,1}]$, is given by

$$[R^{\bullet}_{r,1}] = \sum_{m=1}^{r-1} [U_1^m U_2^{r-m} P_{11}^m P_{22}^{r-m} (\frac{i_1}{k_{11}} \sum_{j=1} \binom{m-1}{j}\binom{r-m-1}{j-1} X^j + \frac{i_2}{k_{12}} \sum_{j=1} \binom{m-1}{j-1}\binom{r-m-1}{j-1} X^j)] + U_1^r P_{11}^r \frac{i_1}{k_{11}} X^r \tag{A41}$$

Similarly, $[R^{\bullet}_{r,2}]$ is given by

$$[R^{\bullet}_{r,2}] = \sum_{n=1}^{r-1} [U_1^{r-n} U_2^n P_{11}^{r-n} P_{22}^n (\frac{i_1}{k_{21}} \sum_{j=1} \binom{r-n-1}{j-1}\binom{n-1}{j-1} X^j + \frac{i_2}{k_{22}} \sum_{j=1} \binom{r-n-1}{j-1}\binom{n-1}{j} X^j)] + U_2^r P_{22}^r \frac{i_2}{k_{22}} X^r \tag{A42}$$

By application of the above equations, one can calculate the mole fraction of radical type 1 as a function of chain length, r. ($\Phi^{\bullet}_{r,1} = [R^{\bullet}_{r,1}]/([R^{\bullet}_{r,1}]+[R^{\bullet}_{r,2}])$.)

Table A1 shows some of the calculation conditions and their results. If the number-average chain length, P_n, is larger than a few hundred, $1 > U_1$, $U_2 > 0.99$, so that U_1/U_2 is practically unity. Case I and II show $\Phi^{\bullet}_{r,1}$ for $U_1/U_2=1$, and Case III and IV are for $U_1/U_2 \neq 1$. In all cases $\Phi^{\bullet}_{r,1}$ reaches its limiting value, $\Phi^{\bullet}_{\infty,1}$, within ten steps.

In Case IV, the pseudo-kinetic rate constants are not valid since $\Phi^{\bullet}_{\infty,1} \neq \Phi^{\bullet}_1$. In case IV, U_1 must be smaller than 0.9, so that oligomeric polymers would be produced if f_1 is not much smaller than unity ($P_n \sim 10$). For this case, even the Mayo-Lewis equation is not valid.

When the number-average chain length is larger than a few hundred, the contribution of polymer radicals with chain length smaller than ten to the kinetics of copolymerization are likely negligible, and therefore, the pseudo-kinetic rate constant method would be applicable.

Table A1 Calculated mole fraction of polymer radical of type 1 ($\Phi^{\bullet}_{r,1}$)

Calculation conditions

$r_1 = 0.4$, $r_2 = 0.6$, $f_1 = 0.25$, $k_{21}/k_{12} = 2$

	U_1/U_2	i_1/i_2
I	1	1
II	1	2
III	0.99	1
IV	0.9	1

	$\Phi^{\bullet}_{r,1}$			
r	I	II	III	IV
1	0.35443	0.52336	0.35213	0.33071
2	0.41063	0.36819	0.40872	0.39061
3	0.39744	0.40748	0.39549	0.37719
4	0.40061	0.39820	0.39866	0.38027
5	0.39985	0.40043	0.39791	0.37956
6	0.40004	0.39990	0.39809	0.37973
7	0.39999	0.40002	0.39805	0.37969
8	0.40000	0.39999	0.39806	0.37970
9	0.40000	0.40000	0.39805	0.37970
10	0.40000	0.40000	0.39805	0.37970

∞	0.4	0.4	0.39805	0.37970
$\Phi^{\bullet}_1$	0.4*	0.4*	0.39795*	0.37855*

* $\Phi^{\bullet}_1$ changes with the absolute values of U_1 and U_2. Shown values are based on $U_2 = 1$.

B. Instantaneous Bivariate distribution of Chain Length and Composition for Linear Copolymers

In statistical copolymerization, the chain length of a copolymer is finite, and therefore, the compositions as well as the chain lengths of the individual polymer molecules can not be identical. Therefore, for copolymer chains produced instantaneously there is a bivariate distribution of composition and chain length.

It was Simha and Branson [Simha, Branson (1944)] who proposed a very extensive and rather complete treatment of the statistics of copolymerization applying the terminal model, however, their results were in fairly complex formulations and therefore difficult to apply directly. Stockmayer [Stockmayer (1945)] proposed a simple expression for the bivariate distribution of chain length and composition by replacing summations with integrals and factorials with expressions based on Stirling's approximation. Strictly, Stockmayer's bivariate distribution is valid only for long chains. In order to treat oligomeric molecules, application of discrete mathematics such as the Markov chain theory is necessary [Price (1962),(1979)]. Applying the Markov chain theory, the mathematics for higher order models such as the penultimate model [Merz et al. (1946)] and pen-penultimate model [Ham (1958)] as well as that for monomer components larger than two are straight forward.

However, the Stockmayer bivariate distribution is a very simple equation, and is useful for the estimation of the chemical heterogeneity of copolymers. It is, therefore, important to know its substance and when it is applicable. In this Appendix, we investigate the Stockmayer bivariate distribution in connection with the pseudo-kinetic rate constant method.

B-1. Equivalence of the Stockmayer Bivariate Distribution and the Pseudo-Kinetic Rate Constant Method.

Let us denote the Stockmayer bivariate distribution by $W^*(r,y)$. Here, r is the chain length and y is the deviation from the mean composition of instantaneously formed copolymer molecules, i.e., $y = F_1 - F_{1,mean}$ (or $y = F_{2,mean} - F_2$). If the terminal model for copolymerization is valid and the molecular weight of monomer 1, M_{w1}, and that of monomer 2, M_{w2}, are equal, the Stockmayer bivariate distribution states that the weight fraction of copolymer whose chain length is r to r+dr and composition deviation y to y+dy is given by the following equation.

$$W^*(r,y)\, drdy = W(r)dr\ \mathrm{Comp}(y|r)dy \qquad \text{(B1)}$$

Namely, the Stockmayer bivariate distribution, $W^*(r,y)$, consists of the product of weight-chain length distribution, $W(r)$, and composition distribution, $\mathrm{Comp}(y|r)$, which is given by the conditional probability distribution given the chain length r. (Although equal monomer molecular weights are assumed in Equation (B1), we shall develop an equation which accounts for comonomers with different molecular weights in Appendix B-4.)

The fundamental equations for the derivation of the bivariate distribution are Equations (A39) and (A40). Stockmayer's approximations are

1) Fractorials are approximated by Stirling's formula.
2) Summations are approximated by integrals.
3) Instantaneous weight-chain length distribution of copolymers are approximated by an imaginary distribution in which all copolymers possess the same composition, $F_{1,mean}$.

These approximations are, essentially, equivalent to the assumptions required for the pseudo-kinetic rate constant method to be valid. Therefore, it should be possible to derive pseudo-kinetic rate constants from the Stockmayer bivariate distribution.

Let us assume that the Mayo-Lewis equation, the Stockmayer bivariate distribution, and the pseudo-kinetic rate constant method are valid, namely, the average chain length is large enough. By following Stockmayer's procedure, polymer radical concentration whose chain length is r, $[R^{\bullet}_{r,*}]$, is given by the following equation. (Please refer to equation (A20) in [Stockmayer (1945)].)

$$[R^{\bullet}_{r,*}] = \frac{(k_{21}[M_1] + k_{12}[M_2])(i_1[M_1] + i_2[M_2])}{k_{12}k_{21}\,(r_1[M_1]^2 + 2\,[M_1][M_2] + r_2[M_2]^2)}\,\xi^r \qquad \text{(B2)}$$

where $\xi = U_1^{(F_{1,mean})}\ U_2^{(F_{2,mean})}$.

Therefore,

$$\begin{aligned}
\ln \xi &= -\ (F_{1,mean})\ \ln(1/U_1)\ -\ (F_{2,mean})\ \ln(1/U_2) \\
&\simeq -\ (F_{1,mean})\ t_1/(k_{11}[M_1]+k_{12}[M_2]) \\
&\qquad -\ (F_{2,mean})\ t_2/(k_{22}[M_2]+k_{21}[M_1])
\end{aligned} \tag{B3}$$

(Please note that $t_1 \ll k_{11}[M_1]+k_{12}[M_2]$ and $t_2 \ll k_{22}[M_2]+k_{21}[M_1]$.)

$$\xi^r = \exp[-r\ \frac{k_{21}\,[M_1]\,t_1\ +\ k_{12}\,[M_2]\,t_2}{k_{12}\,k_{21}\ (r_1[M_1] + 2\,[M_1][M_2] + r_2[M_2]^2)}] \tag{B4}$$

Equation (B4) can be simplified as follows.

$$\begin{aligned}
&k_{12}k_{21}(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2) \\
&\quad = k_{21}[M_1](k_{11}[M_1]+k_{12}[M_2])\ +\ k_{12}[M_2](k_{21}[M_1]+k_{22}[M_2]) \\
&\quad = (k_{21}[M_1]+k_{12}[M_2])[M]((k_{11}f_1+k_{12}f_2)\Phi_1^{\bullet}\ +\ (k_{21}f_1+k_{22}f_2)\Phi_2^{\bullet}) \\
&\quad = (k_{21}[M_1]\ +\ k_{12}[M_2])[M]k_p
\end{aligned} \tag{B5}$$

where k_p is the pseudo-kinetic rate constant for the propagation reactions which is given by Equation (2.1.2) in the text, and $\Phi_1^{\bullet}$ is given by Equation (A34).

$$\begin{aligned}
&k_{21}t_1[M_1]+k_{12}t_2[M_2]\\
&\quad = k_{21}[M_1][R_2^\bullet](k_{t11}\Phi_1^\bullet/\Phi_2^\bullet + k_{t12}) + k_{12}[M_2][R_1^\bullet](k_{t22}\Phi_2^\bullet/\Phi_1^\bullet + k_{t21})\\
&\qquad + k_{21}[M_1](k_{f11}[M_1]+k_{f12}[M_2]+k_{fT1}[T])\\
&\qquad + k_{12}[M_2](k_{f22}[M_2]+k_{f21}[M_1]+k_{fT2}[T])\\
&\quad = (k_{12}[R_1][M_2]/(\Phi_1^\bullet\Phi_2^\bullet))(k_{t11}{\Phi_1^\bullet}^2+2k_{t12}\Phi_1^\bullet\Phi_2^\bullet+k_{t22}{\Phi_2^\bullet}^2)\\
&\qquad + (k_{21}[M_1]+k_{12}[M_2])[M][((k_{f11}f_1+k_{f12}f_2)\Phi_1^\bullet+(k_{f21}f_1+k_{f22}f_2)\Phi_2^\bullet)\\
&\qquad\qquad\qquad + (k_{fT1}\Phi_1^\bullet + k_{fT2}\Phi_2^\bullet)[T]/[M]]\\
&\quad = (k_{21}[M_1] + k_{12}[M_2])(k_t[R^\bullet] + k_{fm}[M] + k_{fT}[T]) \qquad \text{(B6)}
\end{aligned}$$

where $k_{t11} = k_{tc11} + k_{td11}$ with similar definition for k_{t12} and k_{t22}, and k_t $(= k_{tc}+k_{td})$, k_{fm}, and k_{fT} are the pseudo-kinetic rate constants which are given by Equations (2.1.4)-(2.1.7) in the text. The relationship $k_{21}[R_2^\bullet][M_1]=k_{12}[R_1^\bullet][M_2]$, was used in the above calculation.

By application of the stationary-sate hypothesis for total radical concentration, $[R^\bullet]$,

$$\begin{aligned}
i_1[M_1] + i_2[M_2] &= t_1[R_1^\bullet] + t_2[R_2^\bullet]\\
&= k_t[R^\bullet]^2 + k_{fm}[M][R^\bullet] + k_{fT}[T][R^\bullet] \qquad \text{(B7)}
\end{aligned}$$

From Equations (B4)-(B7), Equation (B2) reduces to

$$[R_{r,*}^\bullet] = [R^\bullet](\tau+\beta)\exp[-(\tau+\beta)r] \qquad \text{(B8)}$$

Therefore, the instantaneous weight-chain length distribution, $W(r)$, is given by

$$W(r) = \frac{r(d[P_r]/dt)}{(-d[M]/dt)}$$

$$= \frac{k_{fm}[M][R^{\bullet}_{r,\star}] + k_{fT}[T][R^{\bullet}_{r,\star}] + k_{td}[R^{\bullet}][R^{\bullet}_{r,\star}] + \frac{1}{2}\sum_{s=1}^{r-1} k_{tc}[R^{\bullet}_{s,\star}][R^{\bullet}_{r-s,\star}]}{k_p[M][R^{\bullet}]}$$

$$\simeq \quad (\tau+\beta)(\tau+(\beta/2)(\tau+\beta)(r-1))\, r\exp[-(\tau+\beta)] \qquad \text{(B9)}$$

, which coincides with Equation (A17).

Therefore, from the point of view of chain length distribution the pseudo-kinetic rate constant method and the Stockmayer bivariate distribution are equivalent.

B-2. Instantaneous Copolymer Composition Distribution

An essential part of Stockmayer's approximation for the derivation of the bivariate distribution reside in the copolymer composition distribution, $Comp(y|r)$. Stockmayer's instantaneous copolymer composition distribution is given by

$$Comp(y|r) = \frac{1}{\sqrt{2\pi}\,\sigma}\exp\left(-\frac{y^2}{2\sigma^2}\right) \qquad \text{(B10)}$$

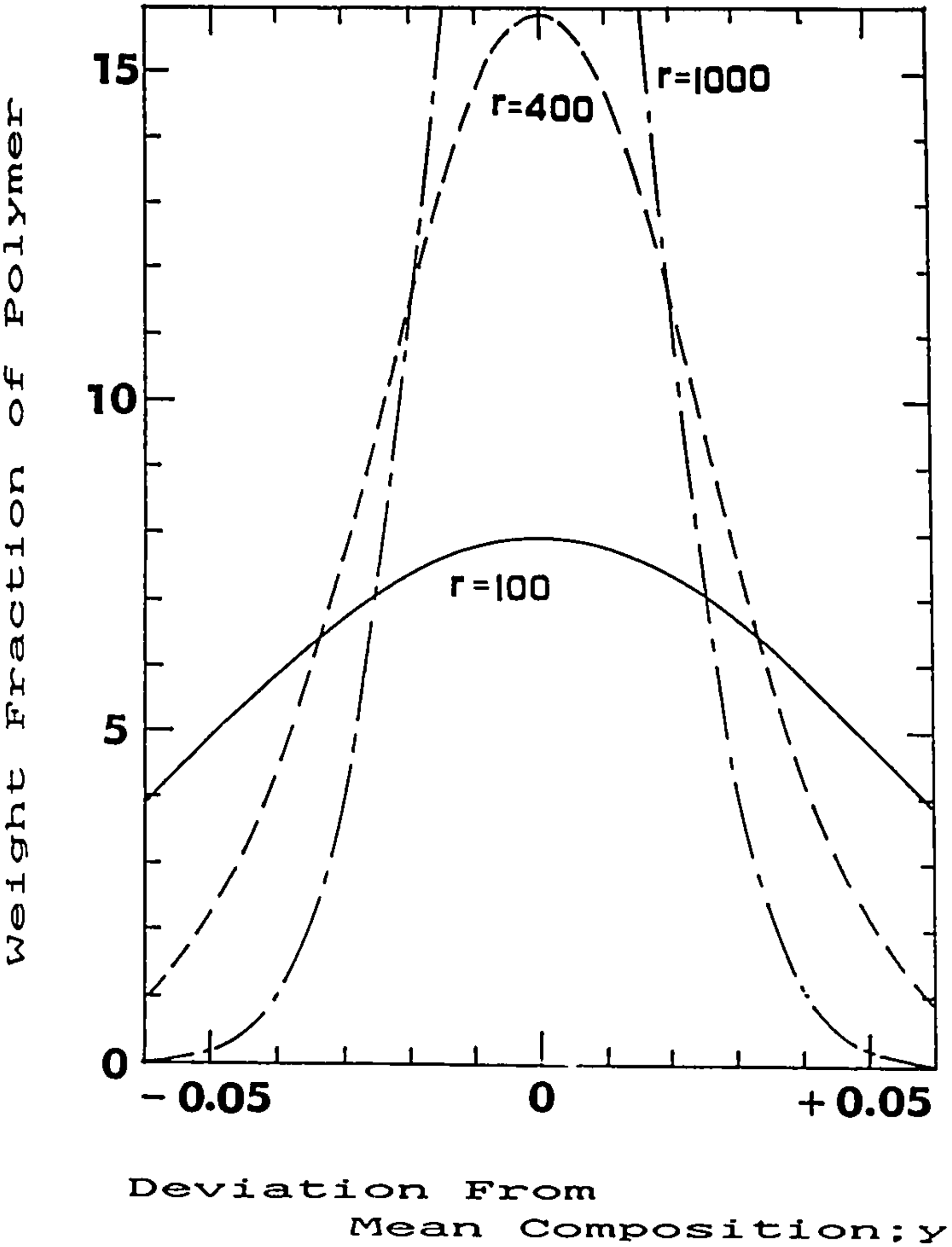


Figure B1 Effect of chain length on composition distribution.

($r_1 r_2 = 1.0$; instantaneous overall composition, $F_{1,mean} = 0.5$.)

where the variance, σ^2, is given by

$$\sigma^2 = F_{1,mean} F_{2,mean} K / r$$
$$K = [1 + 4 F_{1,mean} F_{2,mean} (r_1 r_2 - 1)]^{0.5}$$

Namely, the composition distribution is given by a normal distribution whose variance is inversely proportional to chain length, and therefore, as the chain length increases, the variance of the copolymer composition distribution becomes smaller as is shown in Figure B1. Roughly speaking, if the chain length is smaller than 300, less than 50wt% of the copolymer molecules have a composition within the range, $F_{1,mean}-0.02$ to $F_{1,mean}+0.02$, so that the effect of composition distribution may be significant.

Recently, low molecular weight copolymers have become very important in the coatings industry, and therefore the kinetics of oligomeric copolymer synthesis has become an attractive research area [Hill et al. (1982); Galbraith et al. (1987); O'Driscoll and Davis (1989)]. Stockmayer's bivariate distribution should be useful to calculate the chemical heterogeneity of short copolymer chains, however, it is important to know its limitations. Let us check the approximate lower limit of chain length for the application of Stockmayer's copolymer composition distribution.

The instantaneous copolymer composition distribution for polymer radicals with chain length r,

$$\frac{[R^{\bullet}_{m,r-m,*}]}{\sum_{m=0}^{r} [R^{\bullet}_{m,r-m,*}]}$$

, can be calculated exactly from Equations (A39), (A41), and (A42). On the other hand, Stockmayer's composition distribution gives

$$\frac{[R^{\bullet}_{m,r-m,*}]}{\sum_{m=0}^{r} [R^{\bullet}_{m,r-m,*}]} = \frac{1}{r} \frac{1}{\sqrt{2\pi}\ \sigma} \exp(- \frac{y^2}{2\sigma^2}) \tag{B11}$$

Figure B2 shows some of calculation results when $U_1=U_2=1$. Although the degree of agreement changes when different values for r_1, r_2, k_{21}/k_{12}, f_1, and i_1/i_2 are used, roughly speaking Stockmayer's composition distribution should be applicable for chain lengths larger than 50 if the average chain length is large enough ($U_1 \simeq 1$ and $U_2 \simeq 1$).

B-3. Bivariate Distribution for Binary Copolymerization with Chain Length Dependent Bimolecular Termination

It is of great interest to know whether the Stockmayer bivariate distribution and the pseudo-kinetic rate constant method are applicable when chain length dependent bimolecular termination of polymer radicals is significant. As shown in Equation (B1), Stockmayer's bivariate distribution shows that the chain length distribution and the composition distribution are independent. Let us clarify when Equation

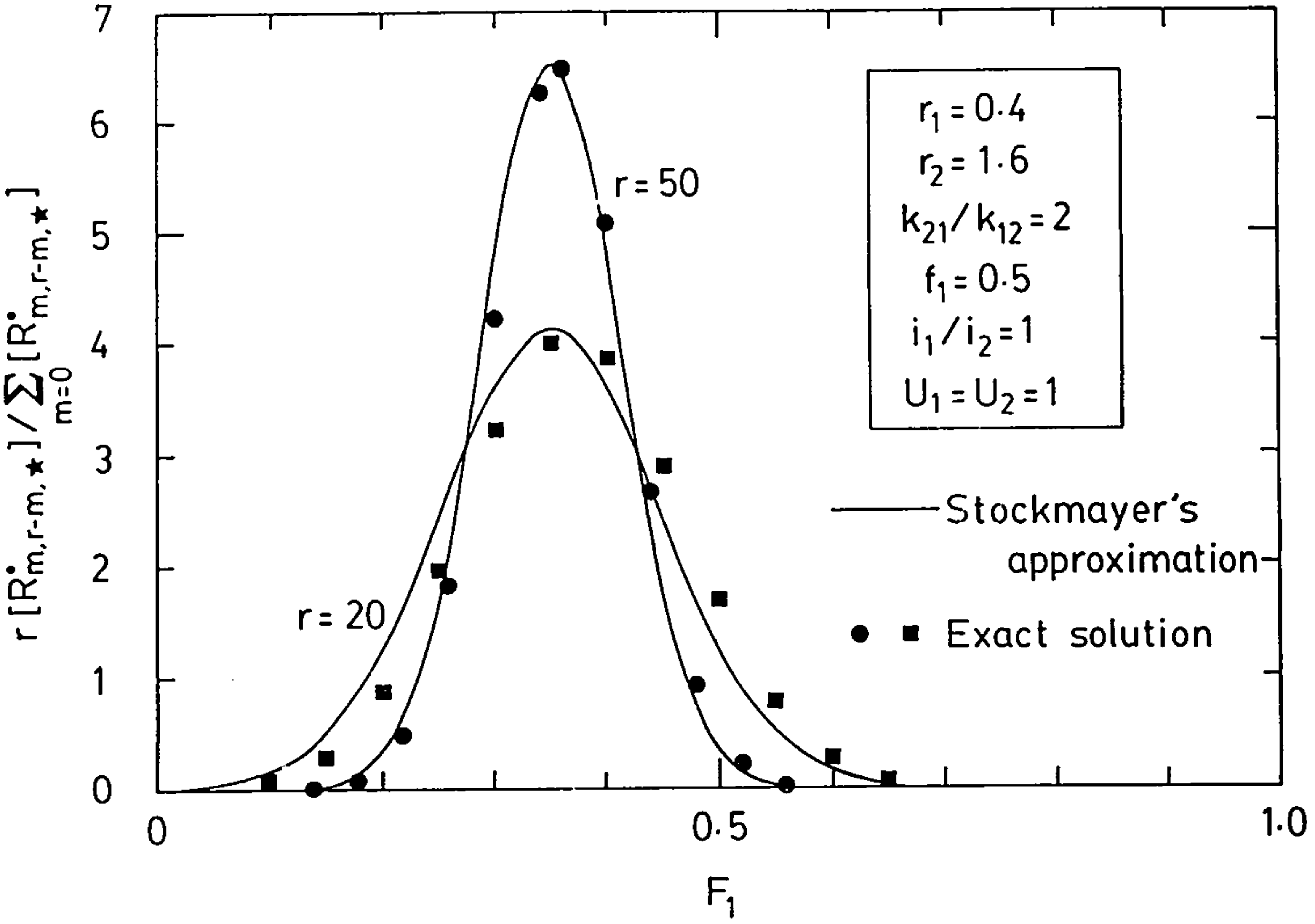


Figure B2 Calculated copolymer composition distribution.

(B1) is valid.

Now, let us consider the derivation of the bivariate distribution from the beginning accounting for the chain length dependences of t_1 and t_2. The balance equation for $R^{\bullet}_{m,n,1}$ is given by

$$d[R^{\bullet}_{m,n,1}]/dt = (\text{Formation rate of } R^{\bullet}_{m,n,1}) - (\text{Consumption rate of } R^{\bullet}_{m,n,1}) \qquad \text{(B12)}$$

The consumption rate of $R^{\bullet}_{m,n,1}$ is given by

$$(k_{11}[M_1] + k_{12}[M_2] + t_1(r))[R^{\bullet}_{m,n,1}] \qquad \text{(B13)}$$

where $r = m+r$.

Let us consider the formation rate of $R^{\bullet}_{m,n,1}$. When m=3 and n=1 ,

$$\begin{aligned}
&(\text{Formation rate of } R^{\bullet}_{3,1,1}) \\
&\quad = (\text{Formation rate of polymer radical whose sequence is } 1 \rightarrow 2 \rightarrow 1 \rightarrow 1) \\
&\qquad + (1 \rightarrow 1 \rightarrow 2 \rightarrow 1) + (2 \rightarrow 1 \rightarrow 1 \rightarrow 1) \\
&\quad = i_1 [M_1] (U_1(1)\, U_2(2)\, U_1(3)\, P_{12} P_{21} P_{11} \\
&\qquad\qquad + U_1(1)\, U_1(2)\, U_2(3)\, P_{11} P_{12} P_{21}) \\
&\qquad + i_2 [M_2]\, U_2(1)\, U_1(2)\, U_1(3)\, P_{21} P_{11}^2 \qquad \text{(B14)}
\end{aligned}$$

where

$$U_1(r) = \frac{k_{11}[M_1] + k_{12}[M_2]}{k_{11}[M_1] + k_{12}[M_2] + t_1(r)}$$

$$U_2(r) = \frac{k_{22}[M_2] + k_{21}[M_1]}{k_{22}[M_2] + k_{21}[M_1] + t_2(r)} \quad .$$

Now, let us assume that the ratio,

$$U_2(r)/U_1(r) = B \qquad \text{(B15)}$$

, is constant independent of chain length. In this case, Equation (B14) reduces to

$$\begin{aligned}
&(\text{Formation rate of } R^{\bullet}_{3,1,1})\\
&= i_1[M_1]\,(B\prod_{r=1}^{3}U_1(r))\,\binom{2}{1}\binom{0}{0}\,P_{11}P_{12}P_{21}\\
&\qquad + i_2[M_2]\,(B\prod_{r=1}^{3}U_1(r))\,\binom{2}{0}\binom{0}{0}\,P_{21}P_{11}^{2}\\
&= R_I^{'}\,(B\prod_{r=1}^{3}U_1(r))\,P_{11}^{3}\,P_{22}\,(\frac{I_1}{P_{11}}\binom{2}{1}\binom{0}{0}X + \frac{I_2}{P_{12}}\binom{2}{0}\binom{0}{0}X)
\end{aligned} \qquad \text{(B16)}$$

where $R_I^{'} = i_1[M_1] + i_2[M_2]$, $I_1 = i_1[M_1]/(i_1[M_1]+i_2[M_2])$, and $I_2 = 1-I_1$. In general, the formation rate of $R^{\bullet}_{m,n,1}$ is given by

$$\begin{aligned}
&(\text{Formation rate of } R^{\bullet}_{m,n,1})\\
&= R_I^{'}\,B^{n}\prod_{s=1}^{m+n-1}U_1(s)\,[P_{11}^{m}P_{22}^{n}\,(\frac{I_1}{P_{11}}\sum_{j=1}\binom{m-1}{j}\binom{n-1}{j-1}X^{j}\\
&\qquad + \frac{I_2}{P_{12}}\sum_{j=1}\binom{m-1}{j-1}\binom{n-1}{j-1}X^{j})]\\
&\qquad (m, n \geqslant 1)
\end{aligned} \qquad \text{(B17)}$$

The quantity in the brackets is the probability that a polymer radical with chain length r (r=m+n) consists of m units of M_1 and n units of M_2 and M_1 as the end unit. Let us denote this probability $P_1(m,n|r)$. By substituting Equations (B13) and (B17) into Equation (B12), and by applying the stationary-state hypothesis, one obtains

$$[R^{\bullet}_{m,n,1}] = \frac{R_I'}{k_{11}[M_1] + k_{12}[M_2]} \left(\prod_{s=1}^{r} U_1(s)\right) B^n P_1(m,n|r) \qquad (r = m+n) \qquad \text{(B18)}$$

If fractorials are approximated by Stirling's formula and summations are replaced by integrals as was used by Stockmayer, $P_1(m,n|r)$ is given by

$$P_1(m,n|r) = \frac{[M_1]\,(r_1\,[M_1] + [M_2])}{r_1[M_1]^2 + 2\,[M_1][M_2] + r_2\,[M_2]^2} \, \frac{1}{r} \, \frac{1}{\sqrt{2\pi}\,\sigma} \exp(-\frac{y^2}{2\sigma^2}) \qquad \text{(B19)}$$

As shown in Appendix B-2, this approximation may be acceptable for chains larger than 50. Therefore, $[R^{\bullet}_{m,n,1}]$ is given by

$$[R^{\bullet}_{m,n,1}] = \frac{[M_1]\,/\,k_{12}}{r_1[M_1]^2 + 2\,[M_1][M_2] + r_2\,[M_2]^2} \, R_I' \left(\prod_{s=1}^{r} U_1(s)\right) B^n \, \frac{1}{r} \, \frac{1}{\sqrt{2\pi}\,\sigma} \exp(-\frac{y^2}{2\sigma^2}) \qquad \text{(B20)}$$

Since $[R^{\bullet}_{m,n,2}]$ can be similarly derived, $[R^{\bullet}_{m,n,*}]$ ($= [R^{\bullet}_{m,n,1}]+[R^{\bullet}_{m,n,2}]$) is given by

$$[R^{\bullet}_{m,n,*}] = \frac{k_{21}[M_1] + k_{12}[M_2]}{k_{12}k_{21}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)} R_I'\left(\prod_{s=1}^{r} U_1(s)\right) B^n \left[\frac{1}{r}\frac{1}{\sqrt{2\pi}\,\sigma}\exp\left(-\frac{y^2}{2\sigma^2}\right)\right] \qquad \text{(B21)}$$

Now, if the number-average chain length which is calculated from the chemically controlled termination rate constants, $P_n{}^0$, is larger than a few hundred, namely, $1 > U_1(0),\ U_2(0) > 0.99$, $|B - 1|$ must be much smaller than unity. In this case, the composition dependence of B^n may be much smaller than the final term in the brackets, and it may be reasonable to substitute $B^{(rF_{2,mean})}$ for of B^n.

Let us check this assumption by numerical calculations. If the following ratio, $R(r,B)$, is very close to unity, it would be reasonable to use the above approximation.

$$R(r,B) = \frac{\sum_{n=0}^{r} B^n \exp\left[-\frac{y^2}{2\sigma^2}\right]}{\left(\sum_{n=0}^{r}\exp\left[-\frac{y^2}{2\sigma^2}\right]\right)\cdot B^{(r F_{2,mean})}} \qquad \text{(B22)}$$

In order to calculate the "worst" case, we consider the condition where the variance of the compositional distribution is maximum. For most free radical copolymerization systems, $0 < r_1 r_2 < 1$, so that the maximum variance, $1/(4r)$, would be obtained when $r_1 r_2 = 1$ and $F_{1,mean} = 0.5$. Figure B3 shows one of the calculation results at chain length, $r=100$. From Figure B3, $R(100,B)$ may be considered unity for practical purposes when $|B - 1| < 0.01$. If $P_n{}^0$ is larger than a few hundred, $1 > U_1(r),\ U_2(r) > 0.99$, so that the condition $|B - 1| < 0.01$ must be satisfied.

In summary, if the ratio, $U_2(r)/U_1(r)$, is independent of chain length, and if $P_n{}^0$ is larger than a few hundred, $[R^{\bullet}_{m,n,*}]$ can be approximated by

$$[R^{\bullet}_{m,n,*}] = \frac{k_{21}[M_1] + k_{12}[M_2]}{k_{12}k_{21}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)} R_I' B^{(rF_{2,mean})}$$

$$\left(\prod_{s=1}^{r} U_1(s)\right) \left[\frac{1}{r} \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{y^2}{2\sigma^2}\right)\right]$$

$$= [R^{\bullet}_{r,*}]\, \mathrm{Comp}(y|r) \qquad \text{(B23)}$$

The above equation shows that Equation (B1) is valid.

Next, let us derive the weight-chain length distribution of dead polymers from Equation (B23). Please note that if Equation (B23) is valid, it is straight forward to show that $\Phi^{\bullet}_{r,1}$ is independent of chain length, which means that the pseudo-kinetic rate constant method

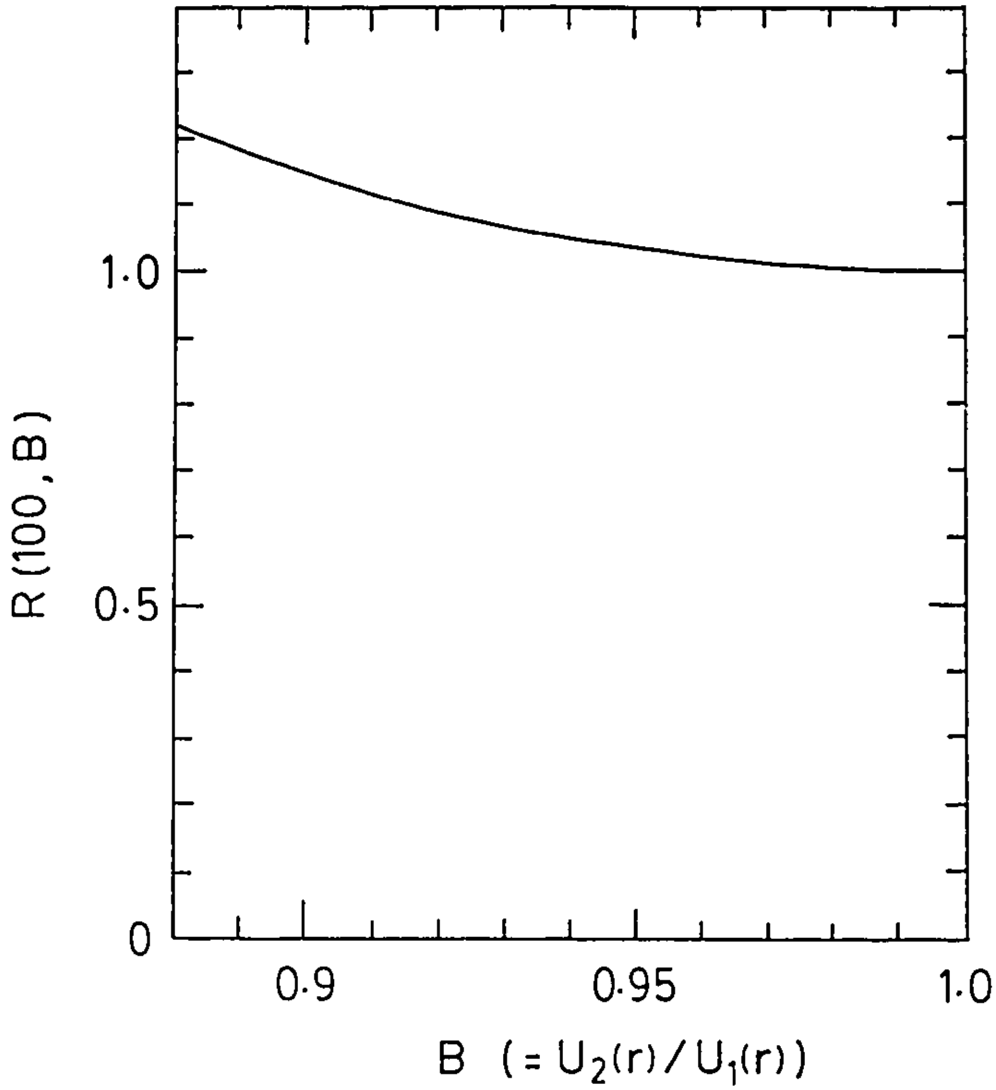


Figure B3 Effect of $U_2(r)/U_1(r)$ on chain length distribution. $F_{2,mean} = 0.5$ and $r_1 r_2 =$ [illegible]. Practically, when $|B - 1| < 0.01$, chain length distribution and [illegible] ition distribution may be considered independent. (R(100,0 [illegible] 1.00511 ; R(100,0.99) = 1.00126) is valid. Now, we prove this by checking whether Equation (A18) can be derived from Equation (B23).

$$
\begin{aligned}
[R^{\bullet}_{r,*}] &= \sum_{m=0}^{r} [R^{\bullet}_{m,r-m,*}] \simeq \int_{0}^{r} [R^{\bullet}_{m,r-m,*}]\,dm \\
&= r\int_{-\infty}^{+\infty} [R^{\bullet}_{m,r-m,*}]\,dy \\
&= \frac{k_{21}[M_1] + k_{12}[M_1]}{k_{12}k_{21}\,(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2)}\, R'_I\, B^{(r F_{2,mean})} \left(\prod_{s=1}^{r} U_1(s)\right)
\end{aligned}
\tag{B24}
$$

$$
\begin{aligned}
[R^{\bullet}_{r,*}]/[R^{\bullet}_{r-1,*}] &= B^{(F_{2,mean})}\, U_1(r) \\
&= U_1(r)^{(F_{1,mean})}\, U_2(r)^{(F_{2,mean})}
\end{aligned}
\tag{B25}
$$

$$
\begin{aligned}
\ln([R^{\bullet}_{r,*}]/[R^{\bullet}_{r-1,*}]) &= -\,(F_{1,mean})\ \ln[1 + t_1(r)/(k_{11}[M_1]+k_{12}[M_2])] \\
&\quad -\,(F_{2,mean})\ \ln[1 + t_2(r)/(k_{22}[M_2]+k_{21}[M_1])] \\
&\simeq -\,(F_{1,mean})\ t_1(r)/(k_{11}[M_1]+k_{12}[M_2]) \\
&\quad -\,(F_{2,mean})\ t_2(r)/(k_{22}[M_2]+k_{21}[M_1]) \\
&= -\,\frac{k_{21}[M_1]t_1(r) + k_{12}[M_2]t_2(r)}{(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2)k_{12}k_{21}}
\end{aligned}
\tag{B26}
$$

From Equations (B5) and (B6), Equation (B26) reduces to

$$\begin{aligned} [R^\bullet_{r,*}]/[R^\bullet_{r-1,*}] &= \exp[-(\tau(r) + \beta(r))] \\ &\simeq 1 - (\tau(r) + \beta(r)) \\ &\simeq 1/[1 + \tau(r) + \beta(r)] \equiv \Phi(r) \\ &\qquad (\tau(r) + \beta(r) \ll 1) \qquad \text{(B27)} \end{aligned}$$

The initial term, $[R^\bullet_{1,*}]$, is given by

$$[R^\bullet_{1,*}] = (\overline{\tau} + \overline{\beta})[R^\bullet]/(1 + \tau(1) + \beta(1)) \qquad \text{(B28)}$$

Therefore, $[R^\bullet_{r,*}]$ is given by

$$[R^\bullet_{r,*}] = (\overline{\tau} + \overline{\beta})\left(\prod_{s=1}^{r} \Phi(s)\right)[R^\bullet] \qquad \text{(B29)}$$

The formation rate of dead polymer with chain length r is given by

$$\begin{aligned} \frac{d[P_r]}{dt} &= k_{fm}[M][R^\bullet_{r,*}] + k_{fT}[T][R^\bullet_{r,*}] + k_{td}(r)[R^\bullet][R^\bullet_{r,*}] \\ &\quad + \tfrac{1}{2}\sum_{s=1}^{r-1} k_{tc}(s,r-s)[R^\bullet_{s,*}][R^\bullet_{r-s,*}] \\ &= k_p[M][R^\bullet](\overline{\tau} + \overline{\beta})\,\tau(r)\left(\prod_{m=1}^{r}\Phi(m)\right) \\ &\quad + \tfrac{1}{2}k_p[M][R^\bullet](\overline{\tau} + \overline{\beta})^2\left[\sum_{s=1}^{r-1}\beta(s,r-s)\left(\prod_{m=1}^{s}\Phi(m)\right)\left(\prod_{m=1}^{r-s}\Phi(m)\right)\right] \end{aligned}$$

(B30)

The weight-chain length distribution, $W(r)$, is given by

$$
\begin{aligned}
W(r) &= \frac{r(d[P_r])}{(-d[M]/dt)} \\
&= r(\bar{\tau}+\bar{\beta})\ \tau(r)\ \left(\prod_{m=1}^{r}\Phi(m)\right) \\
&\quad + (r/2)(\bar{\tau}+\bar{\beta})^2 [\sum_{s=1}^{r-1}\beta(s,r-s)\left(\prod_{m=1}^{s}\Phi(m)\right)\left(\prod_{m=1}^{r-s}\Phi(m)\right)
\end{aligned}
\qquad (B31)
$$

Equation (B31) coincides with Equation (A18).

The Stockmayer bivariate distribution and the pseudo-kinetic rate constant method are both applicable even when chain length dependent bimolecular termination of polymer radicals is significant if the following conditions are satisfied.

1) The terminal model for copolymerization is valid.
2) The number-average chain length which is calculated from chemically controlled kinetic rate constants, P_n^0, is larger than a few hundred.
3) The following ratio,

$$\frac{U_1(r)}{U_2(r)} = \frac{(\text{probability of growth for } R^\bullet_{r,1})}{(\text{probability of growth for } R^\bullet_{r,2})}$$

, is independent of chain length.

For high polymers these conditions are likely to be satisfied. (Please note $U_1 \simeq 1$ and $U_2 \simeq 1$ for high polymers.)

The bivariate distribution, $W^*(r,y)$, is given by

$$W^*(r,y)\,dr\,dy = [r(\bar{\tau}+\bar{\beta})\,\tau(r)\,(\prod_{m=1}^{r}\Phi(m)) + (r/2)(\bar{\tau}+\bar{\beta})^2[\sum_{s=1}^{r-1}\beta(s,r-s)\,(\prod_{m=1}^{s}\Phi(m))(\prod_{m=1}^{r-s}\Phi(m))]\,dr \cdot [\frac{1}{\sqrt{2\pi}\,\sigma}\exp(-\frac{y^2}{2\sigma^2})]\,dy \qquad (B32)$$

B-4. Effect of Comonomers with Different Molecular Weights

Recently, a modified Stockmayer equation which accounts for comonomers with different molecular weights was proposed by Tacx et al. [Tacx et al. (1988)]. In their paper, a correction factor was derived and they investigated conditions where this correction factor has significant effect on the bivariate distribution. Unfortunately, the physical meaning of this correction factor as derived by Tacx et al. is obscure. In this section, we derive a correction factor whose physical interpretation is clear.

As shown in the previous section, the original Stockmayer bivariate distribution $W^*(r,y)$ is given by

$$W^*(r,y)\,drdy = [W(r)\,dr][N(0,\sigma^2)\,dy] \qquad (B33)$$

where $W(r)$ is the weight chain length distribution, and $N(0,\sigma^2)$ is a normal distribution with mean 0 and variance σ^2. In short, the bivariate distribution is the product of both distributions, and the composition distribution is given by a normal distribution.

When $M_{w1} \neq M_{w2}$, the bivariate distribution which accounts for the different molecular weights of the comonomers ($W(r,y)$) is given by

$$W(r,y)\,dr\,dy = \frac{(M_{w1} F_1 + M_{w2} F_2)\ [W^*(r)\,dr][N(0,\sigma^2)\,dy]}{\int_r \int_y \ (M_{w1} F_1 + M_{w2} F_2)\, W^*(r)\, N(0,\sigma^2)\,dy\,dr} \qquad \text{(B34)}$$

(denominator of Equation (B34))

$$\begin{aligned}
&= \int_r W^*(r) \quad \int_y \ (M_{w1} F_1 + M_{w2} F_2)\, N(0,\sigma^2)\,dy\,dr \\
&= (M_{w1} F_{1,mean} + M_{w2} F_{2,mean}) \ \int_r W^*(r) \ \int_y N(0,\sigma^2)\,dy\,dr \\
&\qquad + (M_{w1} - M_{w2}) \ \int_r W^*(r) \ \int_y y\, N(0,\sigma^2)\,dy\,dr \\
&= M_{w1} F_{1,mean} + M_{w2} F_{2,mean} \qquad \text{(B35)}
\end{aligned}$$

$$W(r,y)\,dr\,dy = \frac{M_{w1} F_1 + M_{w2} F_2}{M_{w1} F_{1,mean} + M_{w2} F_{2,mean}} \ [W^*(r)\,dr]\,[N(0,\sigma^2)\,dy] \qquad \text{(B36)}$$

The final equation form is quite simple, and all one needs is the correction factor

$$(\text{correction factor}) = \frac{M_{w1} F_1 + M_{w2} F_2}{M_{w1} F_{1,\text{mean}} + M_{w2} F_{2,\text{mean}}} \qquad \text{(B37)}$$

The physical meaning of the correction factor is obvious, that is,

$$(\text{correction factor}) = \frac{\begin{bmatrix}\text{average molecular weight of a monomer unit} \\ \text{for individual chain.}\end{bmatrix}}{\begin{bmatrix}\text{average molecular weight of a monomer unit} \\ \text{for all chains.}\end{bmatrix}} \qquad \text{(B38)}$$

In a recent paper [Tacx et al. (1988)], the following correction factor was proposed.

$$(\text{correction factor}) = 1 + \frac{y\,(1-k)}{k + F_{1,\text{mean}}(1-k)} \qquad \text{(B39)}$$

where $k = M_{w2}/M_{w1}$. It is straight forward to show that Equation (B39) and (B37) are equivalent. However, Equation (B37) provides a clearer physical meaning for the correction factor, so that it is self-evident when the correction factor has a significant effect on the bivariate distribution.

The Stockmayer bivariate distribution is now being tested experimentally by cross-fractionation techniques [Stejskal et al. (1981); Tacx et al. (1989)].

C. Copolymer Composition Equation for Very Low Mole Fractions of Divinyl Monomer

As is discussed in the text, usual copolymer equation known as the Mayo-Lewis equation can not be applied for vinyl/divinyl copolymerization since monomer consumption by radical centers on just reacted pendant double bonds is not accounted for. However, if the mole fraction of divinyl monomer is small, the Mayo-Lewis equation may be a good approximation. Furthermore, if the initial mole fraction of the divinyl monomer, f_{20}, is far smaller than unity, say less than 5×10^{-3}, it may be reasonable to neglect the monomer consumption by propagation of $R_2^\bullet$ chain ends as a first approximation. In this special but quite often used cases in gelation experiments, the copolymer equation may be given by

$$d[M_1]/d[M_2] = r_1 \ ([M_1]/[M_2]) \qquad \text{(C1)}$$

Necessary conditions for the application of the above equation was made clear by Jaacks (1972). Integrating Equation (C1), one obtains

$$(1 - x\,\bar{F}_1/f_{10}) = (1 - x\,\bar{F}_2/f_{20})^{r_1} \qquad \text{(C2)}$$

As a further approximation it may be possible to apply the following equation.

$$\bar{F}_2 = (f_{20} / x)\ [1- (1-x)^{1/r_1}\ ] \qquad \text{(C3)}$$

D. Crosslinking Density Distribution under Flory's Simplifying Assumptions

Let us examine the crosslinking density distribution under Flory's simplifying conditions which are listed in Section 1.1.-[B] (p.15). In these limiting conditions, the pseudo-kinetic rate constants for crosslinking, k_p^*, and that for propagation, k_p, reduce to

$$k_p^* = k_{11}[F_2(\Theta) - \rho_a(\Theta,\psi)] \qquad \text{(D1)}$$

$$k_p = k_{11}[1 + f_2(\psi)] \qquad \text{(D2)}$$

Only for this simplified condition does the Mayo-Lewis equation apply for the calculations of the copolymer composition with reactivity ratios $r_1 = 0.5$, $r_2 = 2.0$, since instantaneous copolymer composition is determined solely by the mole fractions of comonomers existing at the moment, i.e., the process is the Bernoulli trials. From the Meyer-Lowry equation,

$$1 - \psi = [(1-f_{20})/(1-f_2)]^2\ (f_2/f_{20}) \qquad \text{(D3)}$$

, and therefore,

$$d\psi/df_2 = -[(1-f_{20})^2\ (1+f_2)]/[f_{20}\ (1-f_2)^3] \qquad \text{(D4)}$$

From equations (D1), (D2), and (2.2.6) in the text, one obtains

$$F_2(\Theta)/[F_2(\Theta)- \rho_a(\Theta,\psi)] = [f_2(\Theta)\ (1- f_2(\psi))]/[(1- f_2(\Theta))\ f_2(\psi)] \tag{D5}$$

Since $F_2 = 2f_2/(1+f_2)$, $\rho_a(\Theta,\psi)$ is given by

$$\rho_a(\Theta,\psi) = \frac{2\,f_2(\Theta)}{1+f_2(\Theta)} - 2\,\frac{1-f_2(\Theta)}{1+f_2(\Theta)} \bullet \frac{f_2(\psi)}{1-f_2(\psi)} \tag{D6}$$

The instantaneous crosslinking density, $\rho_i(x)$, is given by

$$\rho_i(x) = \int_0^x \frac{\partial \rho_a(\Theta,x)}{\partial x}\, d\Theta$$

$$= \frac{2\,f_{20}\,x}{1-f_{20}}\ \frac{(1-f_2(x))^2\,(f_{20}-f_2(x))}{(f_2(x)+1)\,[f_{20}\,(1-f_2(x))^2 - f_2(x)\,(1-f_{20})^2\,]} \tag{D7}$$

Therefore, $\rho(\Theta,\psi)$ is given by

$$\rho(\Theta,\psi) = \rho_i(\Theta) + \rho_a(\Theta,\psi)$$

$$= \frac{2\,(1-f_2(\Theta))}{1+f_2(\Theta)} \bullet \frac{f_{20}\,(1-f_2(\psi)) - (1-f_{20})\,f_2(\psi)}{(1-f_{20})\,(1-f_2(\psi))} \tag{D8}$$

In terms of the number of units,

$$\rho^{f}(\Theta,\psi) = \frac{\rho(\Theta,\psi)}{1+\rho_{i}(\Theta)}$$

$$= \frac{2\,[\,f_{20}\,(1-f_{2}(\psi)\,)-(1-f_{20}\,)\,f_{2}(\psi)\,]}{(1+f_{20}\,)\,(1-f_{2}(\psi)\,)} \qquad \text{(D9)}$$

Equation (D9) indicates that the crosslinking density with respect to the number of units is solely a function of the present conversion ψ. A sample calculation is shown in Figure D1. Therefore, for Flory's simplifying condition the variance of crosslinking density distribution is zero.

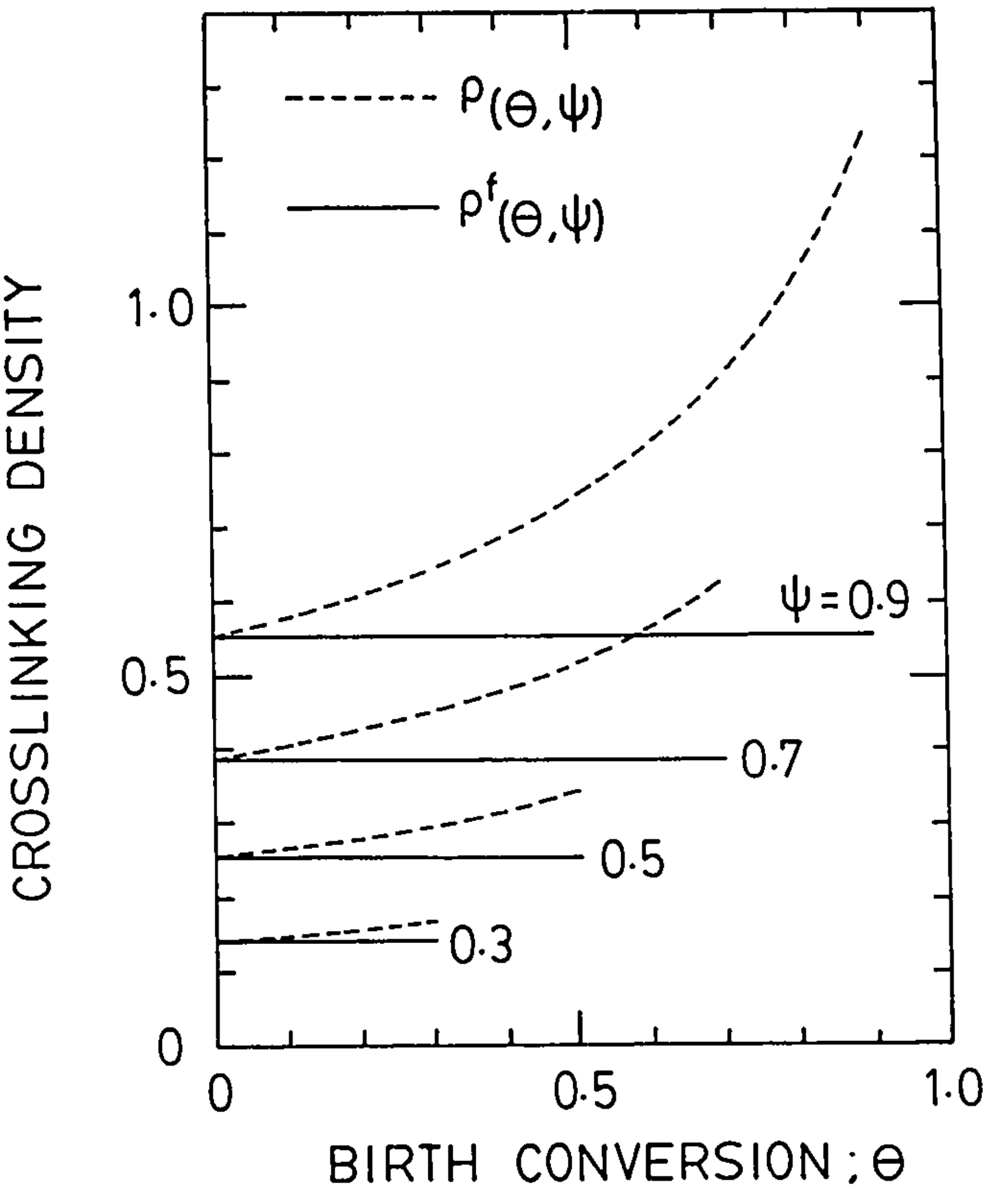


Figure D1 Crosslinking density distribution under Flory's simplifying assumptions. $f_{20} = 0.5$.

E. Applicability of Simplified Pseudo-Kinetic Rate Constant for Crosslinking Reactions (Equation (2.4.4))

As is shown in the text (Section 2.4-[A]), the application of the simplified pseudo-kinetic rate constant for crosslinking reaction (Equation (2.4.4)) to calculate second or higher moments is approximate. The errors associated with the use of Equation (2.4.4) could be checked by calculating the following ratio, E.

$$E(r,s) = \frac{\bar{k}_p^{*0}(r,s)\,[\bar{F}_2(s) - \bar{\rho}_a(s) - \bar{\rho}_c(s)]}{k_p^{*0}\,[\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c]}$$

$$\simeq \frac{[\bar{F}_2(s) - \bar{\rho}_a(s) - \bar{\rho}_c(s)]}{[\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c]} \qquad (\Phi_3^{\bullet} \ll 1) \qquad \text{(E1)}$$

Instead of using Equation (E1), it is possible to test the applicability of Equation (2.4.2) by considering Equation (E2).

$$E'(\Theta,\psi) = \frac{[F_2(\Theta) - \rho_a(\Theta,\psi) - \rho_c(\Theta,\psi)]}{[\bar{F}_2(\psi) - \bar{\rho}_a(\psi) - \bar{\rho}_c(\psi)]} \qquad \text{(E2)}$$

Qualitatively, at a given conversion ψ, if the Ratio $E'(\Theta,\psi)$ does not deviate much from unity for any given birth conversion Θ (ϵ . ψ), which means the mole fraction of live pendant double bonds are almost the same for all primary polymer molecules no matter when they were born, Equation (2.4.4) is applicable for the calculation of moments.

For simplicity let us assume there is no cyclization. When the mole fraction of divinyl monomer is far smaller than unity ($f_2 \ll 1$), one can derive an analytical solution to Equation (E2).

$$E'(\Theta,\psi) = \frac{\psi(1-r_1 K)(1-\psi)^K (1-\Theta)^{R-K}}{r_1\left[(1-\psi)^K - (1-\psi)^{(1/r_1)}\right]} \qquad \text{(E3)}$$

where $K = k_p^{*0}/k_p$ and $R = (1-r_1)/r_1$. When $f_2 \ll 1$, r_2 is not important. If f_2 is large and/or the effect of cyclization is important, one can use numerical calculations. For example, if the reactivities of all monomeric double bonds are the same, namely, r_1=0.5 and K=1, the mole fraction of live pendant double bonds is the same for all primary polymer molecules as shown in Figure E1. In this case the crosslinking density is given by

$$\rho(\Theta,\psi) = 2\, f_{20}\, \psi \qquad \text{(E4)}$$

However, if the reactivity of pendant double bonds is one half of the monomeric double bonds, namely, K=0.5, the mole fraction of live pendant double bonds changes with the birth time of the primary polymer molecule as shown in Figure E2. Figure E3 shows the effect of the reactivity of pendant double bonds (k_p^{*0}/k_p), and Figure E4 shows the effect of reactivity ratio (r_1). Though $E'(\Theta,\psi)$ may deviate significantly from unity for high conversions, for low conversions (say less than 20%) the error is likely negligible. Since gelation is quite often observed at fairly low conversions for copolymerizations of vinyl/divinyl monomers, it seems reasonable to apply Equation (2.4.4) at least until the point of gelation.

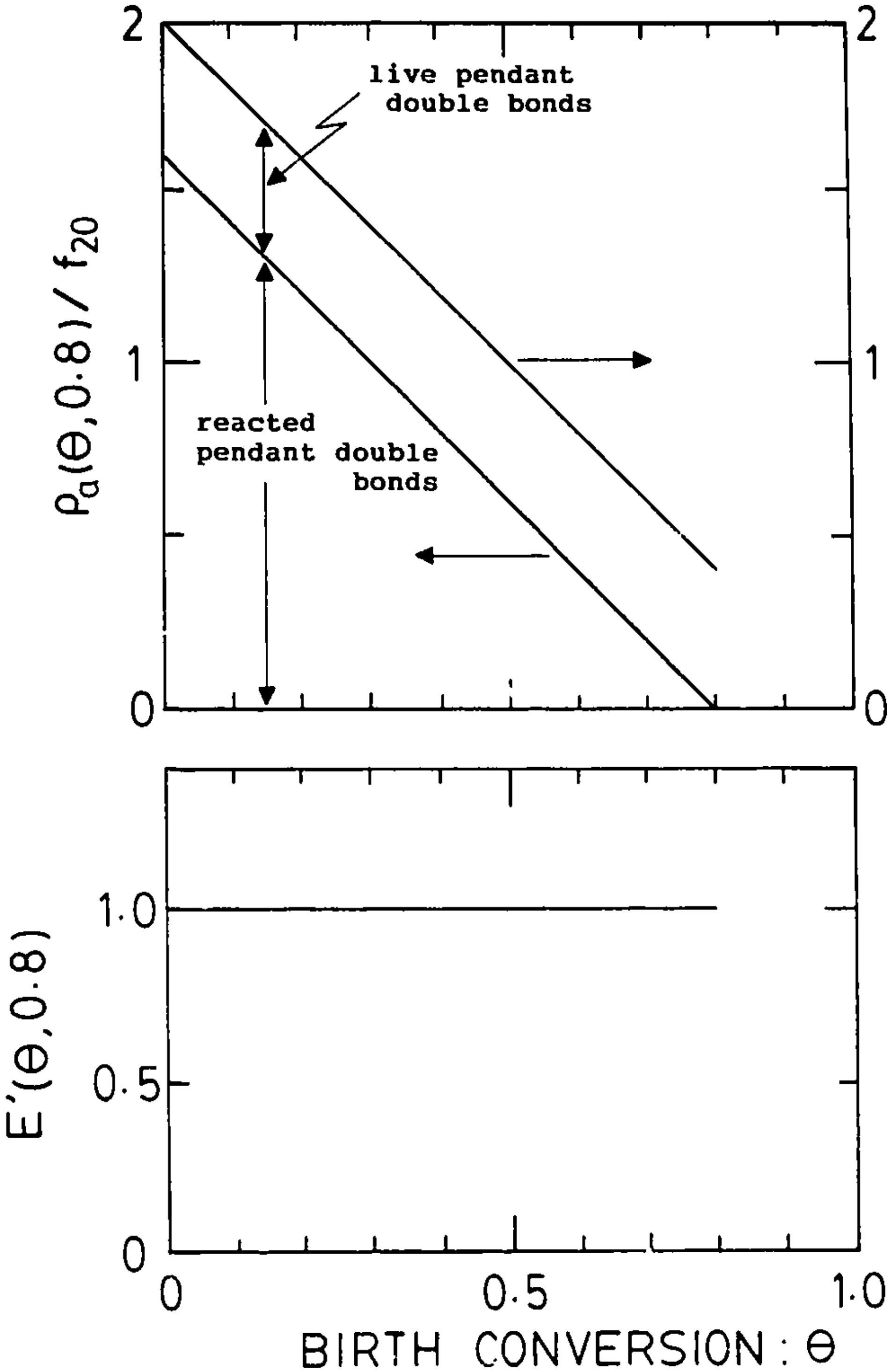


Figure E1 Calculated mole fraction of live pendant double bonds.

$K=1.0$, $r_1=0.5$, $\psi=0.8$, $f_{20}\ll 1$, $\rho_c=0$.

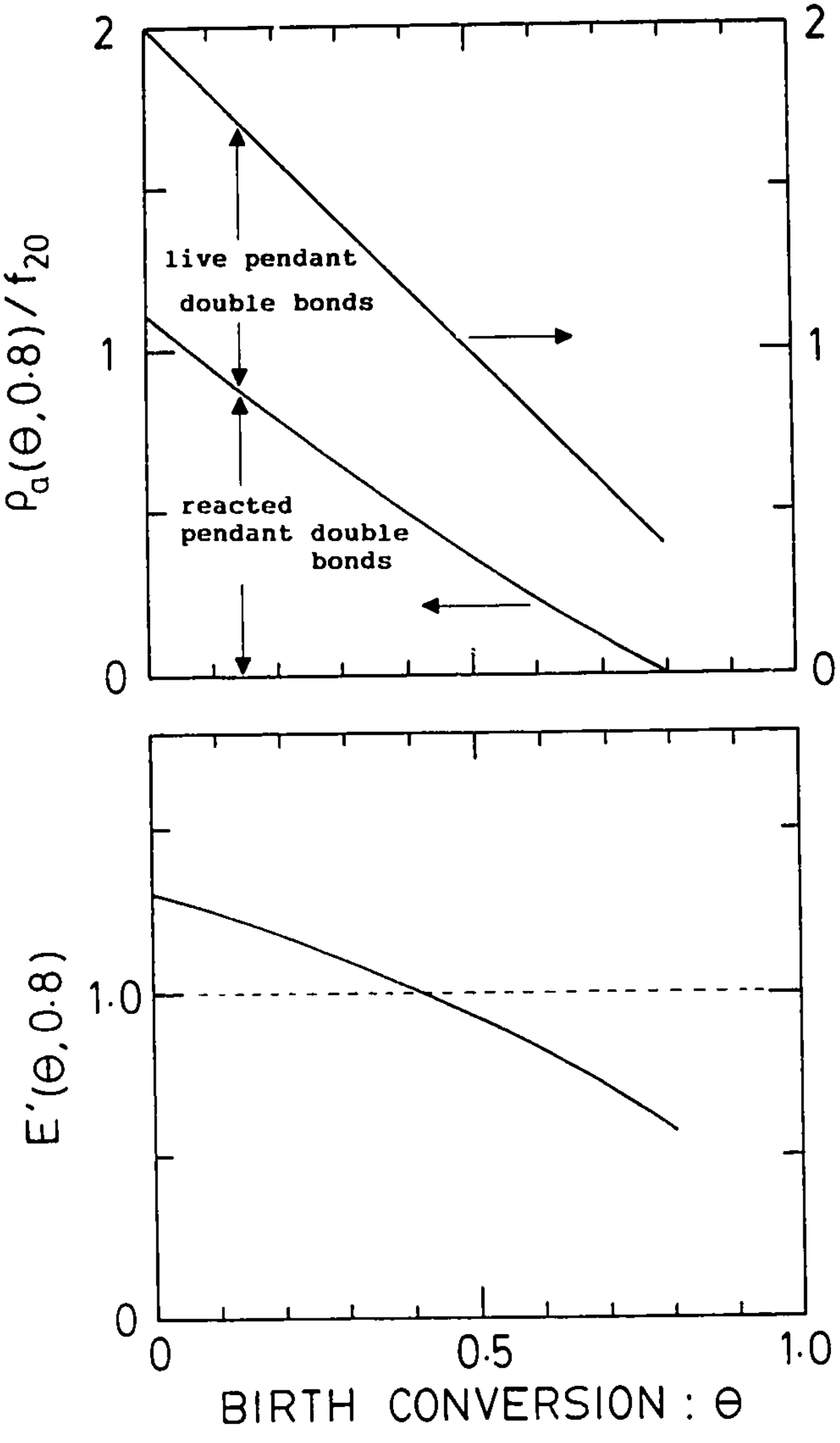


Figure E2 Calculated mole fraction of live pendant double bonds.

$K = 0.5$, $r_1 = 0.5$, $\psi = 0.8$, $f_{20} \ll 1$, $\rho_c = 0$.

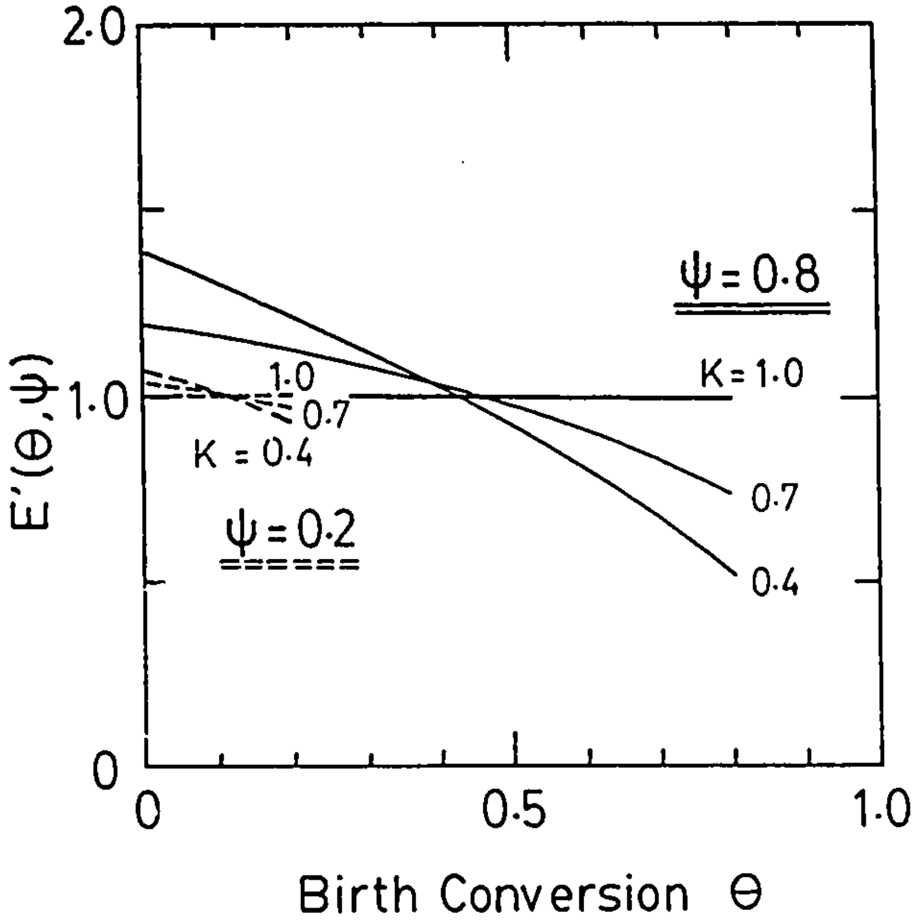


Figure E3 The effect of pendant double bond reactivity on the applicability of Equation (2.4.4). $f_2 \ll 1$, $\rho_c = 0$, $r_1 = 0.5$. When the reactivities of all double bonds are equal ($r_1 = 0.5$, $K = 1.0$) and $\rho_c = 0$, $E'(\Theta,\psi) = 1$, i.e., the mole fraction of live pendant double bonds is the same for all primary polymer molecules. In this case, Equation (2.4.4) is strictly valid.

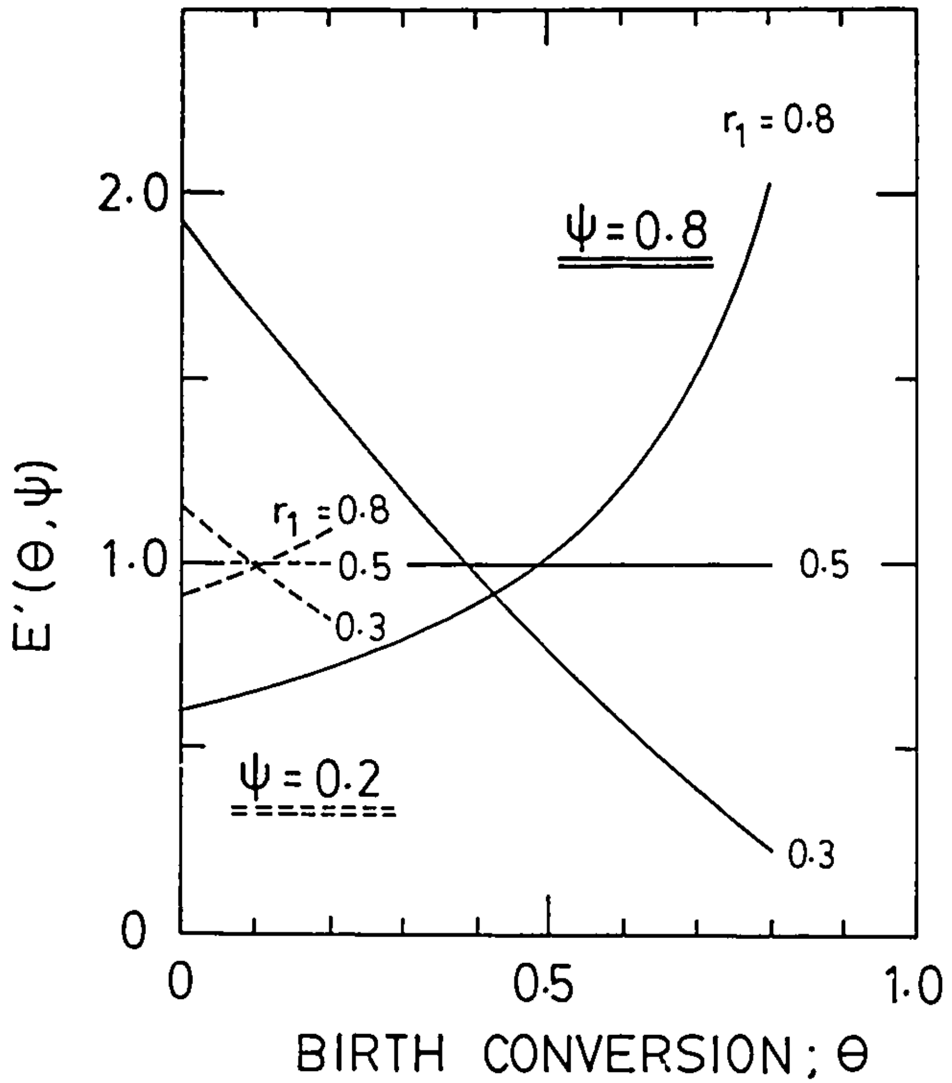


Figure E.1 The effect of reactivity ratio on the applicability of Equation (2.4.4). $f_2 \ll 1$, $\rho_c = 0$, $K = 1.0$.

F. Derivation of Moment Equations

For batch reactor, balance equations of polymer radical with chain length r, $[R_r^\bullet]$, are given by

For r=1,

$$\frac{1}{V}\frac{d(V[R_1^\bullet])}{dt} = R_I + (k_{fm}[M]+k_{fT}[T]+k_{fp}[P_1])[R^\bullet] - (k_p+k_{fm})[M][R^\bullet]$$

$$-k_{fT}[T][R_1^\bullet] - (k_{td}+k_{tc})[R^\bullet][R_1^\bullet] - (k_p^*+k_{fp})Q_1[R_1^\bullet] \qquad (F1)$$

where R_I is the rate of initiation.

For $r \geqslant 2$,

$$\frac{1}{V}\frac{d(V[R_r^\bullet])}{dt} = k_p[M][R_{r-1}^\bullet] + k_{fp}r[P_r][R^\bullet] + k_p^* \sum_{s=1}^{r-1} s[R_{r-s}^\bullet][P_s]$$

$$-(k_p+k_{fm})[M][R_r^\bullet] - k_{fT}[T][R_r^\bullet] - (k_{td}+k_{tc})[R^\bullet][R_r^\bullet]$$

$$-(k_p^*+k_{fp})Q_1[R_r^\bullet] \qquad (F2)$$

From Equations (F1) and (F2), one can readily formulate the following equation.

$$\frac{1}{V}\;\frac{d(VY_i)}{dt} = \frac{1}{V}\sum_{r=1}^{\infty} r^i\,.\,\frac{d(V[R_r^\bullet])}{dt}$$

$$= R_I + (k_{fm}[M] + k_{fT}[T])\,Y_0 + k_{fp}Q_{i+1}\,Y_0$$

$$+ k_p^* \sum_{j=1}^{i} \binom{i}{j} Q_{j+1}\,Y_{i-j} + k_p[M]\sum_{j=0}^{i-1}\binom{i}{j} Y_j$$

$$- [\,k_{fm}[M] + k_{fT}[T] + (k_{td} + k_{tc})\,Y_0 + k_{fp}Q_1\,]\,Y_i \qquad \text{(F3)}$$

Invoking the stationary-state hypothesis,

$$y_i = [\tau+\beta+C_{p(i+1)} + \sum_{j=1}^{i}\binom{i}{j} C^*_{p(j+1)}\;y_{i-j} + \sum_{j=0}^{i-1}\binom{i}{j} y_j\,]\,/\,(\tau+\beta+C_{p1}) \qquad \text{(F4)}$$

In practice, τ and β have the magnitude of 10^{-6} - 10^{-2} in free radical polymerization, and therefore,

$$\tau+\beta \ll 1 \leq y_i \qquad \text{(F5)}$$

Therefore, Equation (F4) reduces to Equation (2.4.12) in the text. Further approximation is possible by considering the fact that $y_i \ll y_{i-1}$ as it is shown in Figure 2.4.2, namely,

$$\sum_{j=0}^{i-1}\binom{i}{j} y_i \simeq i\,y_{i-1} \qquad \text{(F6)}$$

In this case y_i is given by

$$y_i = \frac{i\, y_{i-1} + C_{p(i+1)} + \sum_{j=1}^{i} \binom{i}{j} C^*_{p(j+1)}\, y_{i-j}}{\tau + \beta + C_{p1}} \tag{F7}$$

The balance equation for polymer molecule with chain length r, P_r, is given by

$$\frac{1}{V}\,\frac{d(V[P_r])}{d\,t} = \left(k_{fm}[M] + k_{fT}[T] + k_{td}[R^\bullet] + k_{fp}\sum_{s=1}^{\infty} s\,[P_s]\right)[R_r^\bullet] + \tfrac{1}{2}k_{tc}\sum_{s=1}^{r-1}[R_s^\bullet]\,[R_{r-s}^\bullet] - (k_p^* + k_{fp})\, r\,[P_r]\,[R^\bullet] \tag{F8}$$

Therefore, the i-th moment of polymer molecule distribution, Q_i, is given by

$$\frac{1}{V}\,\frac{d(V Q_i)}{d\,t} = \left[k_{fm}[M] + k_{fT}[T] + (k_{td} + k_{tc})Y_0 + k_{fp}Q_1\right]Y_i + \tfrac{1}{2}k_{tc}\sum_{j=1}^{i-1}\binom{i}{j} Y_j\, Y_{i-j} - (k_p^* + k_{fp})\, Q_{i+1}\, Y_0 \tag{F9}$$

The above equation can be transformed into the conversion domain, x, using Equation (F10).

$$\frac{[M]_0 V_0}{V}\,\frac{d\,x}{d\,t} = k_p[M]\,[R^\bullet] \tag{F10}$$

$$\frac{dq_i}{dx} = (\tau+\beta+C_{p1})y_i + \tfrac{1}{2}\beta \sum_{j=1}^{i-1} \binom{i}{j} y_j \, y_{i-j} - C^*_{p(i+1)} - C_{p(i+1)} \qquad \text{(F11)}$$

Substituting Equation (F4) into Equation (F11), the following equation can be derived.

$$\frac{dq_i}{dx} = \tau+\beta+ \sum_{j=0}^{i-1} \binom{i}{j} y_j + \tfrac{1}{2}\beta \sum_{j=1}^{i-1} \binom{i}{j} y_j \, y_{i-j} + \sum_{j=1}^{i-1} \binom{i}{j} C^*_{p(j+1)} \, y_{i-j} \qquad \text{(F12)}$$

Applying the relationship (F6), one obtains Equation (2.4.15) in the text. Further approximation is possible by application of Equation (F6).

$$\frac{dq_i}{dx} = i\,y_{i-1} + \tfrac{1}{2}\beta \sum_{j=1}^{i-1} \binom{i}{j} y_j \, y_{i-j} + \sum_{j=1}^{i-1} \binom{i}{j} C^*_{p(j+1)} \, y_{i-j} \qquad \text{(F13)}$$

G. Crosslinking and Degradation of Pre-Formed Polymer Chains

G-1. Crosslinking of Polymers

Polymers can be crosslinked by application of valcanization, peroxide, radiation, etc. [Odian (1981)]. In this section, the peroxide crosslinking is considered as an example. Peroxide crosslinking involves the formation of polymer radicals via hydrogen abstraction by the peroxy radicals. Crosslinking occurs by coupling of the polymer radicals. The elementary reactions are shown below.

Peroxide Crosslinking

$$I \longrightarrow 2R^{\bullet}_{in} \qquad (k_d)$$

$$R^{\bullet}_{in} + P_r \longrightarrow R^{\bullet}_r + R_{in}H \qquad (k_x)$$

$$R^{\bullet}_r + R^{\bullet}_s \longrightarrow P_{r+s} \qquad (k_{tc})$$

Since the mobility of $R^{\bullet}_{in}$ is larger than polymer radicals, combination reaction between polymer radicals and initiator radicals may be significant, however, this reaction can be accounted for by the decrease in the initiator efficiency, f. Side reactions such as chain scission, intramolecular reactions, etc. are usually accompanied, although they are not considered here.

Balance equations for polymers and polymer radicals are given by

$$d[P_r]/dt = -k_x[R^{\bullet}_{in}]r[P_r] + (1/2)k_{tc}\sum_{s=1}^{r-1}[R^{\bullet}_s][R^{\bullet}_{r-s}] \qquad (G1)$$

$$d[R_r^\bullet]/dt = k_x[R_{in}^\bullet]r[P_r] - k_{tc}[R_r^\bullet][R^\bullet] = 0 \qquad (G2)$$

Volume change during crosslinking reaction is neglected. By application of the method of moments, one obtains

$$dQ_0/dt = -(1/2)k_x[R_{in}^\bullet]Q_1 \qquad (G3)$$

$$dQ_1/dt = 0 \quad , \text{ i.e., } Q_1 \text{ ; constant.} \qquad (G4)$$

$$dQ_2/dt = k_x[R_{in}^\bullet]Q_2^{\,2}/Q_1 \qquad (G5)$$

Let us use z, which is defined below, as an independent variable.

$$z = \int_0^t k_x[R_{in}^\bullet]\, dt \qquad (G6)$$

z is equivalent to the crosslinking density, ρ.

$$dQ_0/dz = -Q_1/2 \qquad (G7)$$

$$dQ_2/dz = Q_2^{\,2}/Q_1 \qquad (G8)$$

By integrating the above equations, one obtains the number-average chain length of crosslinked polymer, $\overline{P}_n(z)$, and the weight-average chain length of crosslinked polymer, $\overline{P}_w(z)$, as follows.

$$1/\overline{P}_n(z) = 1/\overline{P}_n(0) - z/2 \qquad (G9)$$

$$\overline{P}_w(z) = \overline{P}_w(0)/[1 - z\,\overline{P}_w(0)] \qquad (G10)$$

where $\overline{P}_n(0)$ and $\overline{P}_w(0)$ are the number- and weight-average chain length of the initial polymer distribution. Equations (G9) and (G10) agree with Flory's equation [Flory (1953)]. Equation (G10) shows that if the number average chain length of the initial chain length distribution, $\overline{P}_n(0)$, is the same, gelation would be observed faster as the polydispersity of initial distribution increases.

Chain Length Distribution: The chain length distribution of crosslinked polymers is also possible to calculate. From Equation (G2) and its zeroth moment equation, one obtains

$$[R_r^\bullet] = r[P_r]Y_0/Q_1 \qquad (G11)$$

By substituting into Equation (G1),

$$d[P_r]/dz = -r[P_r] + (1/2Q_1)\sum_{s=1}^{r-1}[s[P_s](r-s)[P_{r-s}]] \qquad (G12)$$

(Please note that $k_{tc} = k_x[R^{\bullet}_{in}]Q_1/(Y_0)^2$ is derived from the total radical concentration balance.)

By multiplying chain length, r,

$$dr[P_r]/dz = -r^2[P_r] + (r/2Q_1)\sum_{s=1}^{r-1}[s[P_s](r-s)[P_{r-s}]]$$

$$\simeq -r^2[P_r] + (r/2Q_1)\int_0^r s[P_s](r-s)[P_{r-s}]\, dr \qquad (G13)$$

Since the weight chain length distribution, W(r), is given by

$$W(r) = r\,[P_r]/\,Q_1 \qquad (G14)$$

, one obtains the following integro-differential equation.

$$dW(r)/dz = -rW(r) + (r/2)\int_0^r W(s)\,W(r-s)\,ds \qquad (G15)$$

The above equation is the same as an equation derived by Saito for radiation crosslinking [Saito (1958),(1972)]. Kimura [Kimura (1962), (1964); Kells, Guillet (1969)] gave the solution for Equation (G15). Let us consider the case where the initial chain length distribution is given by the random distribution. The random distribution is the chain length distribution which would be obtainable if we cut at random a circular polymer molecule of infinite chain length, and it is the same as the instantaneous chain length distribution in free radical polymerization when polymer molecules are produced by termination by disproportionation and/or chain transfer to small molecule.

$$W^0(r) = (r/u^2)\ \exp(-r/u) \qquad \text{(G16)}$$

where $W^0(r)$ is the initial weight-chain length distribution, and u is the number-average chain length.

In this case, the weight-chain length distribution, W(r), for crosslinked polymers are given by [Saito (1972)].

$$W(r) = (r/u^2)\ \exp[-(uz+1)r/u] \sum_{k=0}^{\infty} [(k+1)!\ (2k+1)!]\ (r/u)^{3k}\ (uz)^k \qquad \text{(G17)}$$

(Please note that there is an error in the exponential part of equation (63) in [Saito (1972)].) Saito's definition of the density of crosslinks, x, is related to our crosslinking density, z, as z = 2x. Figure G1 shows the change in chain length distribution during crosslinking by application of the above equation. Since $\bar{P}_w/\bar{P}_n = 2$ for the initial distribution, please note that uz=0.5 corresponds to the condition at the gel point. Figure G2 shows the change in the

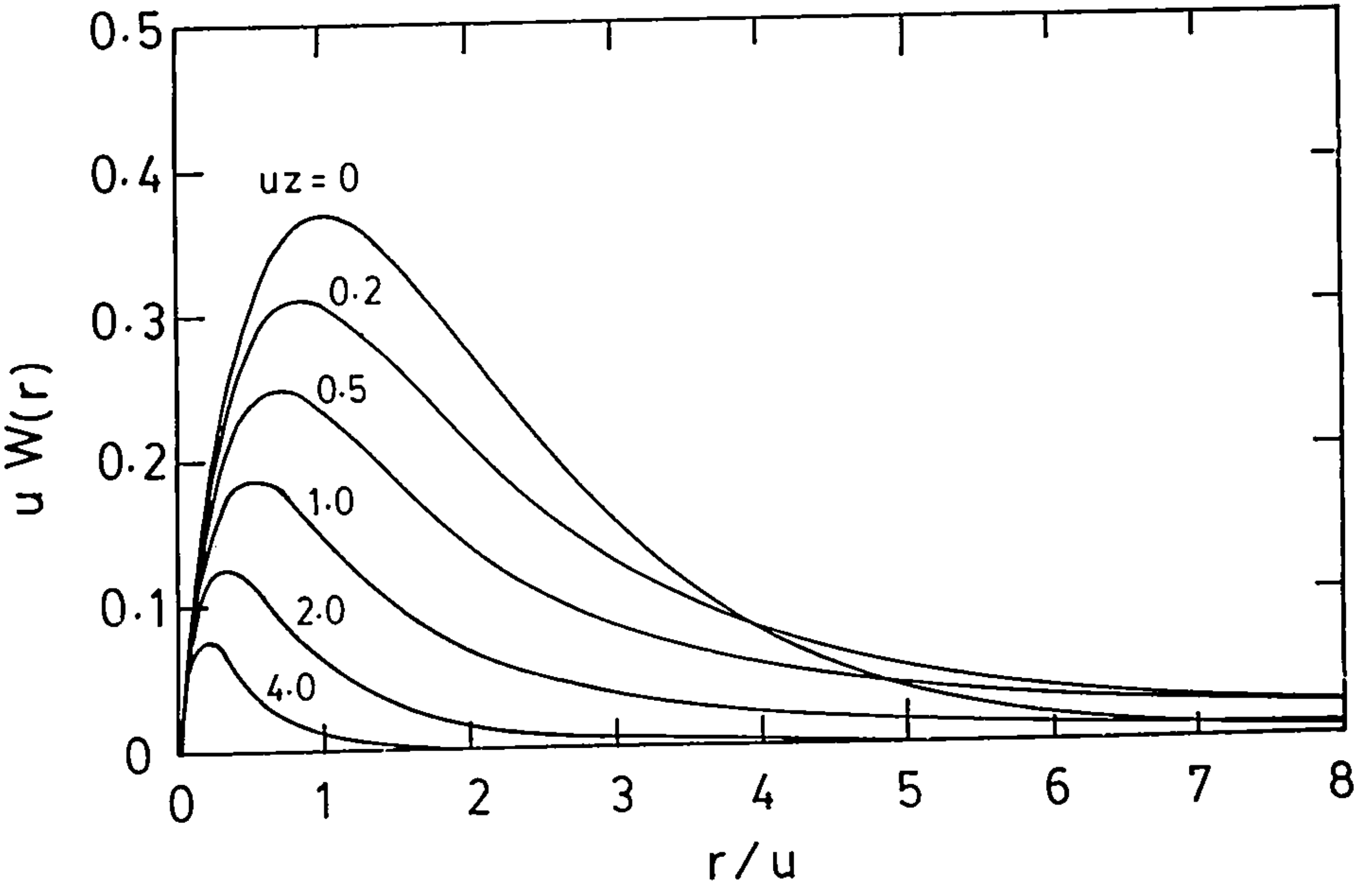


Figure G1 Change in chain length distribution during crosslinking. Initial chain length distribution is random ($\bar{P}_w(0)/\bar{P}_n(0) = 2$). $uz = 0.5$ shows the chain length distribution at the gel point.

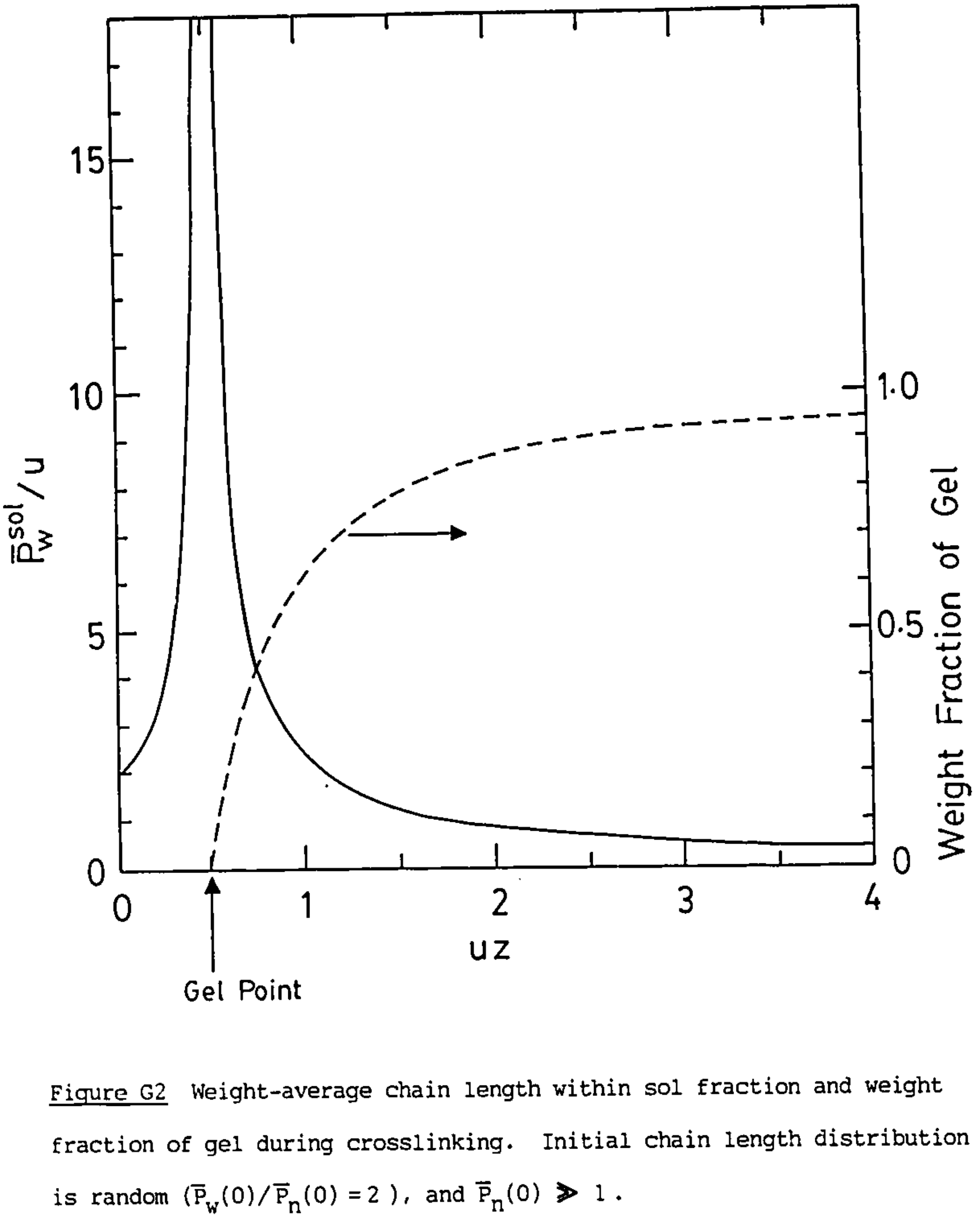


Figure G2 Weight-average chain length within sol fraction and weight fraction of gel during crosslinking. Initial chain length distribution is random ($\overline{P}_w(0)/\overline{P}_n(0) = 2$), and $\overline{P}_n(0) \gg 1$.

weight-average chain length within sol fraction and gel growth during crosslinking reaction.

G-2. Degradation of Polymers

Let us consider the peroxide degradation whose elementary reactions are shown below.

Peroxide Degradation

$$I \longrightarrow 2R^{\bullet}_{in} \qquad (k_d)$$

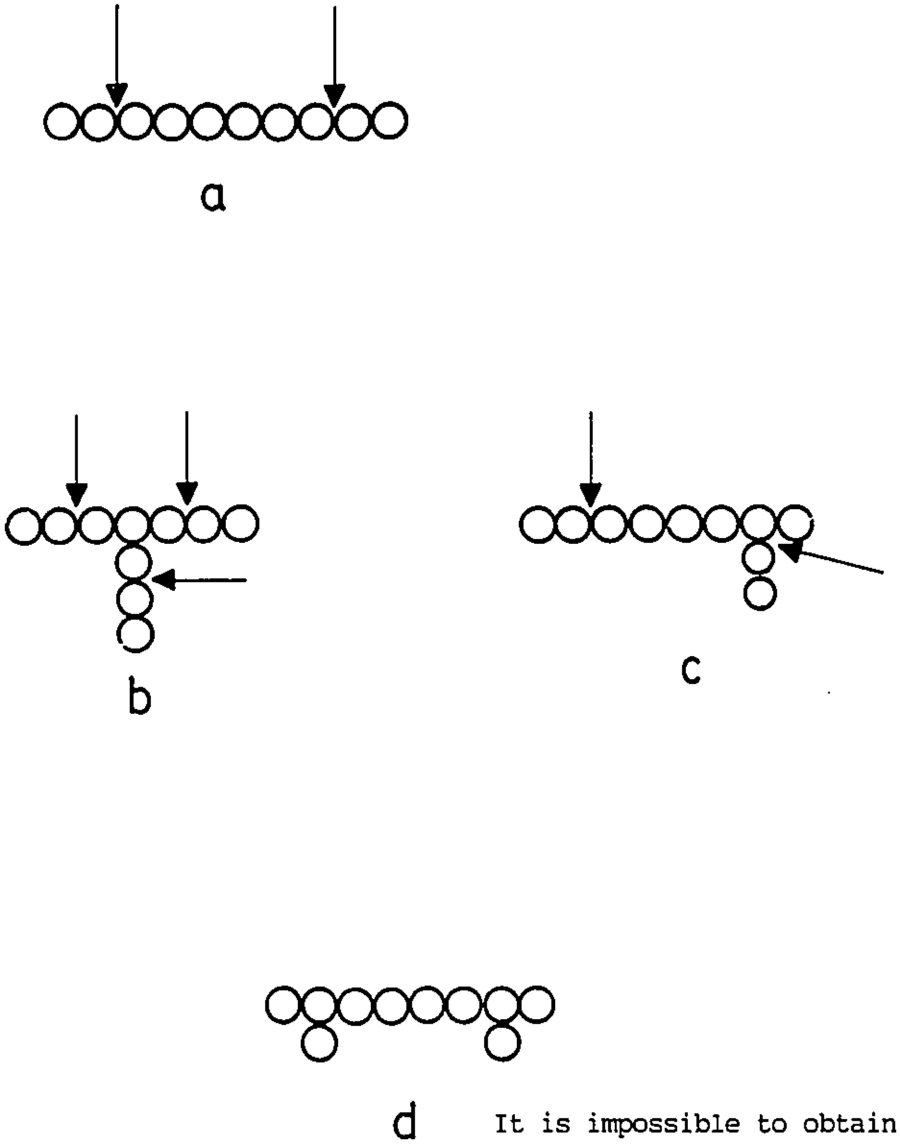
$$R^{\bullet}_{in} + P_r \longrightarrow P_s + R^{\bullet}_{r-s} \qquad (k_s)$$

$$R^{\bullet}_{r} + R^{\bullet}_{in} \longrightarrow P_r \qquad (k_{ti})$$

Since the mobility of an initiator radical is much larger than that of a polymer radical, let us assume that termination with initiator radical is dominant.

Let us consider the scission reaction ($R^{\bullet}_{in} + P_r \longrightarrow P_s + R^{\bullet}_{r-s}$). As a simple example, if r=10 and s=8, how many possible scission points are there in a polymer molecule? If P_r is a linear polymer, the number of possible scission points is always two (see Figure G3-a). However, if P_r is a branched polymer, the number of possible scission points changes with its configuration (see Figure G3-b,c,d). Therefore, in this section let us assume that the initial polymers are linear.

The balance equations are given by



It is impossible to obtain P_8 with one scission.

Figure G3 Molecular configuration and scission points.

$$d[R_r^\bullet]/dt = k_s[R_{in}^\bullet] \sum_{s=r+1}^{\infty} [P_s] - k_{ti}[R_{in}^\bullet][R_r^\bullet] = 0 \qquad \text{(G18)}$$

$$d[P_r]/dt = -k_s[R_{in}^\bullet]r[P_r] + k_s[R_{in}^\bullet] \sum_{s=r+1}^{\infty} [P_s] + k_{ti}[R_r^\bullet][R_{in}^\bullet]$$

$$= -k_s[R_{in}^\bullet]r[P_r] + 2k_s[R_{in}^\bullet] \sum_{s=r+1}^{\infty} [P_s] \qquad \text{(G19)}$$

For chain scission reactions, the method of moments is not applicable without assuming a closure rule, i.e.,

$$Q_i = \text{func.}(Q_0, Q_1, \ldots\ldots, Q_{i-1})$$

, since higher order moments do not cancel out [Tzoganakis et al. (1988)]. We now consider the weight-chain length distribution. Let us use an independent variable, y, which is defined by

$$y = \int_0^t k_s[R_{in}^\bullet]\, dt \qquad \text{(G20)}$$

whose physical meaning is the density of scission points.

By application of the above independent variable, Equation (G19) reduces to

$$d(r[P_r])/dy = -r^2[P_r] + 2r \sum_{s=r+1}^{\infty} [P_s]$$

$$\simeq -r^2[P_r] + 2r \int_r^{\infty} [P_s]\, ds \qquad \text{(G21)}$$

Therfore, we obtain the following integro-differential equation.

$$dW(r)/dy = -rW(r) + 2r \int_r^{\infty} (W(s)/s)ds \qquad \text{(G22)}$$

The solution for the above equation is given by [Saito (1958),(1972)]

$$W(r) = [\ W^0(r) + ry \int_r^{\infty} ((2+ys-yr)W^0(s)/s)\, ds\ ]\ \exp(-ry) \qquad \text{(G23)}$$

where $W^0(r)$ is the initial weight chain length distribution. As y increases, the second term in brackets may become dominant compared with the first term, and therefore, W(r) may approach $(A\, r\, \exp(-ry))$, where A is a constant. The polydispersity, P_D (= $\overline{P}_w/\overline{P}_n$), therefore may approach two independent of the initial chain length distribution.

The weight-average chain length, $\overline{P}_w$, can be calculated from [Saito (1958)]

$$\overline{P}_w(y) = (2/y) - (2/y^2) \int_0^{\infty} ([1- e^{-ry}]W^0(r)/r)\, dr \qquad \text{(G24)}$$

For example, let us consider the Schulz-Zimm distribution [Peebles (1975)].

$$W(r) = \frac{b^b}{u\Gamma(b)} \bullet \left(\frac{r}{u}\right)^b \bullet \exp\left(-\frac{br}{u}\right) \qquad \text{(G25)}$$

where u is the number-average chain length, and $\Gamma(b)$ is the gamma function. When b=1, Equation (G25) reduces to the random distribution (Equation (G16)), and when b increases to infinity, the Schulz-Zimm distribution tends to be a monodisperse system. If the initial weight chain length distribution is given by the Schulz-Zimm distribution, we have

$$\frac{\bar{P}_w(y)}{\bar{P}_w(0)} = \left[uy - 1 + \left(\frac{b}{b+uy}\right)^b\right] \frac{2b}{(1+b)(uy)^2} \qquad \text{(G26)}$$

(Please note that Saito's equation (19) in [Saito (1972)] needs a correction.)

Since the number-average chain length is given by the following equation independent of the initial distribution,

$$1/\bar{P}_n(y) = 1/\bar{P}_n(0) + y \qquad \text{(G27)}$$

, the polydispersity, P_D, is given by

$$P_D(y) = \frac{\bar{P}_w(y)}{\bar{P}_n(y)}$$

$$= \frac{2(1+uy)}{(uy)^2}\left[uy-1+\left(\frac{b}{uy+b}\right)^b\right] \qquad \text{(G28)}$$

Figure G4 shows the change in polydispersity during chain scission. Regardless of the initial polydispersity, the polydispersity of degraded polymer approaches two.

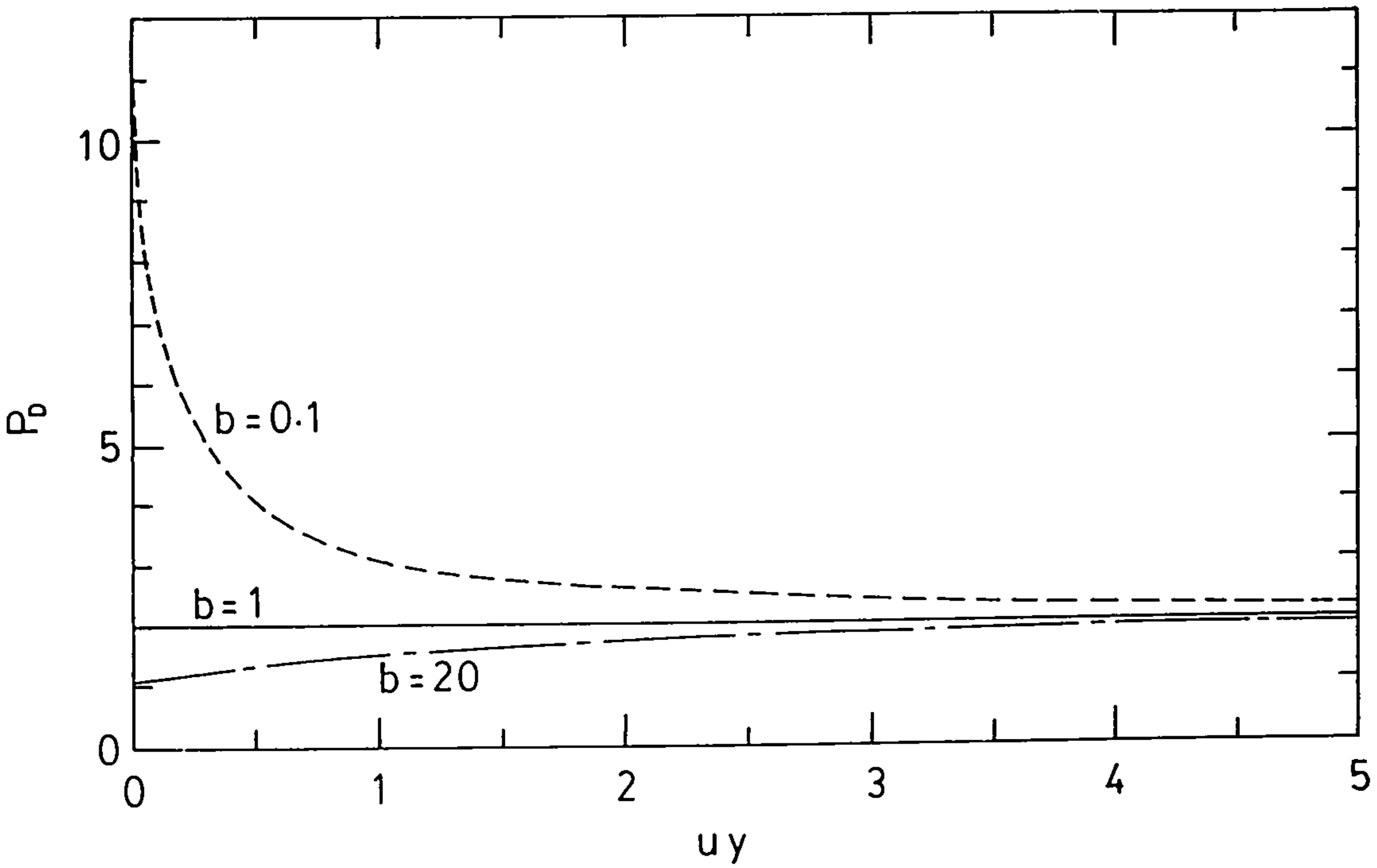
According to Saito [Saito (1958),(1972)], the chain length distribution, W(r), is given by the following equation if the initial chain length distribution is given by the Schulz-Zimm distribution.

$$uW(r) = [\,2DE+(1-D)DE^2+\frac{1}{\Gamma(b)}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}(bD)^{b+k}C_k\,]\,e^{-DE} \qquad \text{(G29)}$$

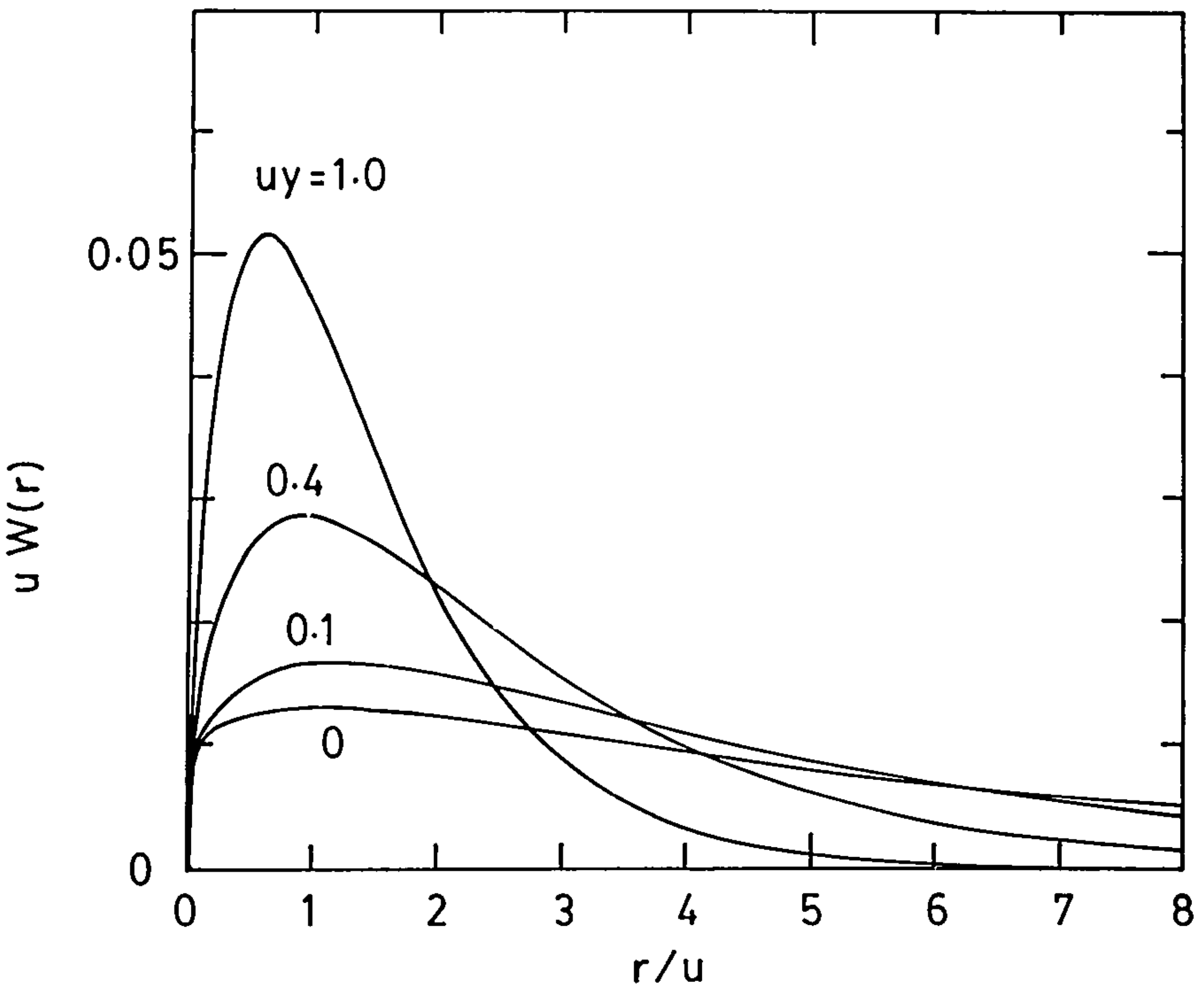
where D = r/u, E = uy, and

$$C_k = \frac{(b+k)(b+k+1)-2(b+k+1)DE+(DE)^2}{(b+k)(b+k+1)} \qquad \text{(G30)}$$

Typical calculation results for the degradation of a broad distribution (P_D= 6) is shown in Figure G5, and those for a narrow distribution (P_D= 1.05) is shown in Figure G6.



<u>Figure G-1</u> Change in polydispersity (P_D) during random degradation. Initial chain length distribution is given by the Schulz-Zimm distribution. Independent of initial polydispersity, the polydispersity of degraded polymers approaches two.



<u>Figure G5</u> Change in chain length distribution during random degradation. Initial chain length distribution is given by the Schulz-Zimm distribution with b = 0.2 ($\bar{P}'_w(0)/\bar{P}_n(0) = 6$).

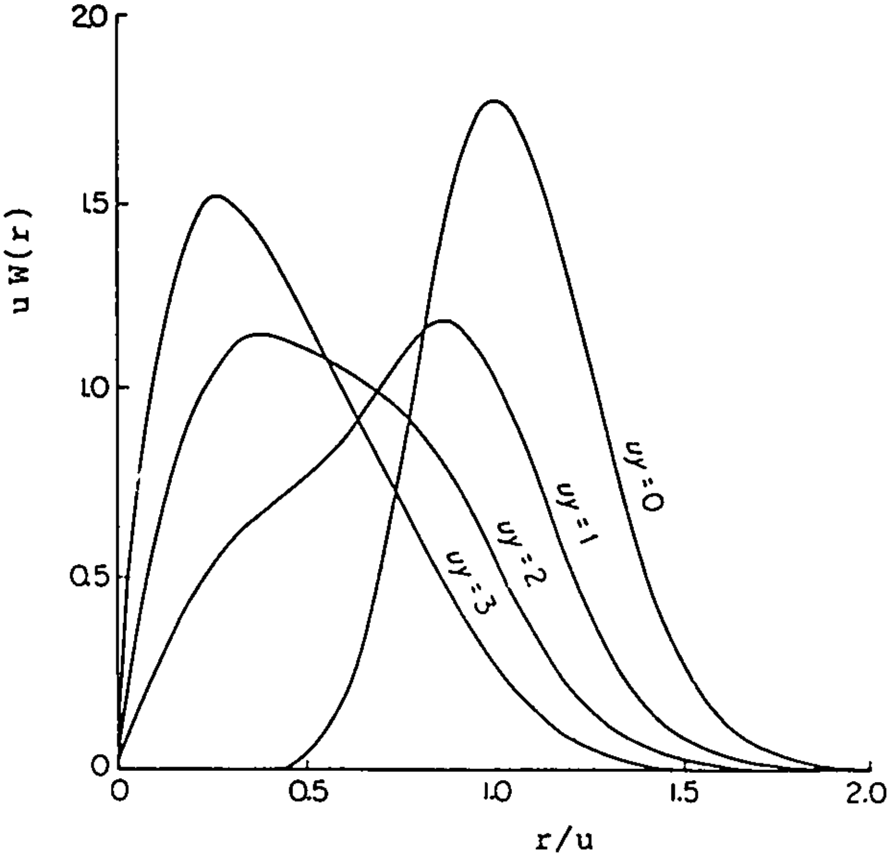


Figure G6 Change in chain length distribution during random degradation. Initial chain length distribution is given by the Schulz-Zimm distribution with b = 20, i.e., $\overline{P}_w(0)/\overline{P}_n(0) = 1.05$. (Taken from [Saito (1972)].)

G-3. Crosslinking with Degradation

Although the polymer radicals produced by degradation and those via hydrogen abstraction in crosslinking reactions may react, as a first approximation, let us assume that crosslinking and degradation occur independently of each other. This assumption may be acceptable when the densities of crosslinking and chain scission are small. In this case we may be able to treat the problem as if degradation occurs first and then crosslinking follows. The weight-average chain length is, therefore, given by

$$\bar{P}_w(y,z) = \frac{\bar{P}_w(y)}{1 - z\bar{P}_w(y)}$$

$$= \frac{\dfrac{2}{y} - \dfrac{2}{y^2}\displaystyle\int_0^\infty \frac{1 - e^{-ry}}{r} \cdot W^0(r)\, dr}{1 - \dfrac{2z}{y} + \dfrac{2z}{y^2}\displaystyle\int_0^\infty \frac{1 - e^{-ry}}{r} \cdot W^0(r)\, dr} \qquad \text{(G31)}$$

As a necessary condition for gelation to occur,

$$2z/y > 1 \quad \text{, i.e.,} \quad z > y/2 \qquad \text{(G32)}$$

As a rough idea, while two chains are being scissored, at least one tri-branching point has to be formed in order for gelation to occur.

This is equivalent to stating that one crosslinking reaction must occur before four chains are scissored. (Please note that crosslinking density is a density of tri-branching points.)

If the initial weight chain length distribution is random, namely, b=1 in the Schulz-Zimm distribution, the weight-average chain length of scissored polymer chains, $\overline{P}_w(y)$, is given by (see Equation (G26))

$$\overline{P}_w(y) = \overline{P}_w{}^0/(1+ uy) \qquad \text{(G33)}$$

where $\overline{P}_w{}^0$ is the weight-average chain length of the initial polymers.

By substituting the above equation into Equation (G10) the following relationship has to be satisfied at the gel point.

$$1- [\overline{P}_w{}^0/(1+ uy_c)]\, z_c = 0 \qquad \text{(G34)}$$

where z_c and y_c are the crosslinking density and the scission density at the gel point. z_c is, therefore, given by

$$z_c = 1/\overline{P}_w{}^0 + y_c/2 \qquad \text{(G35)}$$

$1/\overline{P}_w{}^0$ is the necessary crosslinking density in order for gelation to occur when chain scission does not occur. Equation (G35) shows that additional $y_c/2$ of crosslinking density is necessary to form a gel molecule.

H. A Proof that Chain Transfer to Polymer with Termination by Disproportionation cannot Form an infinitely Large Molecule

In our earlier paper [Tobita, Hamielec (1988)], it was shown that a gel molecule can never be formed by chain transfer to polymer with termination by disproportionation. However, in the proof a constant kinetic rate constant independent of conversion for termination, k_{td}, was assumed. One may question the validity of this proof when diffusion controlled termination occurs, and k_{td} decreases dramatically. The proof for this more general case is given below.

The fundamental equation for the second order moment for this case is given by

$$\frac{dq_2}{dx} = \frac{2[(1-x)+\varepsilon q_2]}{(1-x)\tau + \varepsilon x} \qquad \text{(H1)}$$

$$q_2 = 0 \text{ at } x = 0.$$

(Please note that the terminal double bond polymerization is neglected.) Practically, ε (= k_{fp}/k_p) can be regarded as a constant. Since τ and ε are positive, both numerator and denominator of the right hand side of Equation (H1) are positive for $0 \leqslant x \leqslant 1$. τ may decrease if diffusion controlled termination occurs, and it makes dq_2/dx larger. However, even though the effect of diffusion controlled termination is extremely significant, τ is always larger than $\tau_{min.}$ ($\tau_{min.} > 0$). Practically, if k_t is very small, τ is dominated by chain transfer term, i.e., $\tau \geqslant k_{fm}/k_p$. This is equivalent to stating that an infinitely large molecule can never be formed by linear polymerization. Therefore, the following inequality holds.

$$\frac{dq_2}{dx} = \frac{2[(1-x)+\varepsilon q_2]}{(1-x)\tau + \varepsilon x} < \frac{2[(1-x)+\varepsilon q_2]}{(1-x)\tau_{min.} + \varepsilon x} \qquad (H2)$$

Thus, if q_2' which is defined by Equation (H3) does not go infinity, an infinitely large molecule can be proven not to be formed.

$$\frac{dq_2'}{dx} = \frac{2[(1-x)+\varepsilon q_2']}{(1-x)\tau_{min.} + \varepsilon x} \qquad (H3)$$

$$q_2' = 0 \text{ at } x = 0.$$

Equation (H3) can be solved analytically.

$\varepsilon \neq \tau_{min}$.

$$q_2' = \frac{1}{\varepsilon + \tau_{min.}} \left[(2x-1) + \left(\frac{\tau_{min.} + (\varepsilon - \tau_{min.})x}{\tau_{min.}} \right)^{[2\varepsilon/(\varepsilon - \tau_{min.})]} \right] \qquad (H4)$$

When x=1,

$$q_2' = \frac{1}{\varepsilon + \tau_{min.}} [1 + (\varepsilon/\tau_{min.})^{[2\varepsilon/(\varepsilon - \tau_{min.})]}] \quad ; \text{ finite value.} \qquad (H5)$$

$\underline{\varepsilon = \tau_{min}}$.

$$q_2' = \frac{1}{2\,\varepsilon}\,[\,(\,2x-1\,) + e^{2x}\,] \qquad \text{(H6)}$$

When x=1,

$$q_2' = \frac{1+e^2}{2\,\varepsilon} \qquad \text{; finite value.} \qquad \text{(H7)}$$

Therefore, an infinitely large molecule can never be formed by chain transfer to polymer with termination by disproportionation.

I. Equivalence of the Method of Moments and Flory's Theory in the Pre-Gelation Period

The equivalence of the method of moments and Flory's theory in the pre-gelation period can be proven theoretically in two limiting cases, namely, [CASE I] gelation occurs at very low conversions, and [CASE II] low mole fraction limit of divinyl monomer with Flory's simplifying assumptions.

CASE I: The normalized second order moment, q_2 (see Equations (2.4.9) and (2.4.20) in the text), is given by

$$\frac{dq_2}{dx} = P_{wp}\left[1 + \frac{k_p^* q_2}{k_p (1-x)}\right]^2 \tag{I1}$$

By application of the change of variables shown below,

$$s = 1 - x \tag{I2}$$

$$v = (k_p^* q_2)/(k_p s) \tag{I3}$$

, Equation (I1) can be rewritten as follows.

$$s(dv/ds) = -v - \alpha(1 + v)^2 \tag{I4}$$

where $\alpha = k_p^* P_{wp}/k_p$.

Therefore,

$$\int_0^v \frac{dv}{v + \alpha(1+v)^2} = - \int_1^s \frac{ds}{s} \qquad \text{(I5)}$$

Since the conversion at gel point, x_c, is far smaller than unity, all pseudo-kinetic rate constants as well as monomer and radical concentration can be assumed constant until the gel point. Therefore, $P_{wp}k_p^*/k_p = \alpha$ is nearly constant. The solution for Equation (I5) is given by

$$v = ab[1 - s^{\alpha(a-b)}]/[a - b\, s^{\alpha(a-b)}] \qquad \text{(I6)}$$

where $a = [-(2\alpha+1) + (4\alpha+1)^{0.5}]/(2\alpha)$

$b = [-(2\alpha+1) - (4\alpha+1)^{0.5}]/(2\alpha)$

As will be shown in Equation (I8), the conversion at the gel point, x_c, has the magnitude of $1/\alpha$ when $x_c \ll 1$. That means $\alpha \gg 1$. Therefore, the following approximations may be acceptable.

$$a \simeq -1 + 1/(\alpha)^{0.5} \quad , \quad b \simeq -1 - 1/(\alpha)^{0.5}$$

$$s^{\alpha(a-b)} \simeq (1-x)^{2\sqrt{\alpha}} \simeq 1 - 2(\alpha)^{0.5}x$$

Equation (I6) can be approximated by the following equation.

$$v \simeq (\alpha)^{0.5}(1-1/\alpha)x/[1/(\alpha)^{0.5} - (\alpha)^{0.5}x - x]$$

$$\simeq \alpha x/(1 - \alpha x) \qquad \text{(I7)}$$

Therefore q_2 is given by

$$q_2 \simeq \alpha x/[(k_p^*/k_p)(1-\alpha x)] \qquad \text{(I8)}$$

The validity of Equation (I8) is shown in Figure I1 and I2. When $\alpha > 10$, Equation (I8) seems acceptable. Since $q_1 = x$, the weight-average chain length $\overline{P}_w$ is given by

$$\overline{P}_w = q_2/q_1 = P_{wp}/(1-\alpha x) \qquad \text{(I9)}$$

The crosslinking density, $\overline{\rho}$, is given by Equation (2.2.9). Since k_p^*/k_p is constant,

$$\overline{\rho} = \frac{(k_p^*/k_p)}{x}\left(\ln[\frac{1}{(1-x)}] - x\right) \cong \frac{k_p^* x}{k_p} \qquad (x \ll 1) \qquad \text{(I10)}$$

Substituting Equation (I10) into Equation (I9), one obtains

$$\overline{P}_w = P_{wp}/(1-\ \overline{\rho}\ P_{wp}) \simeq \overline{P}_{wp}/(1-\ \overline{\rho}\ \overline{P}_{wp}) \qquad \text{(I11)}$$

, which corresponds to Flory's equation (Equation (2.4.30)).

<u>CASE II</u>: In the low mole fraction limit of divinyl monomer with Flory's simplifying conditions, the following approximation is acceptable.

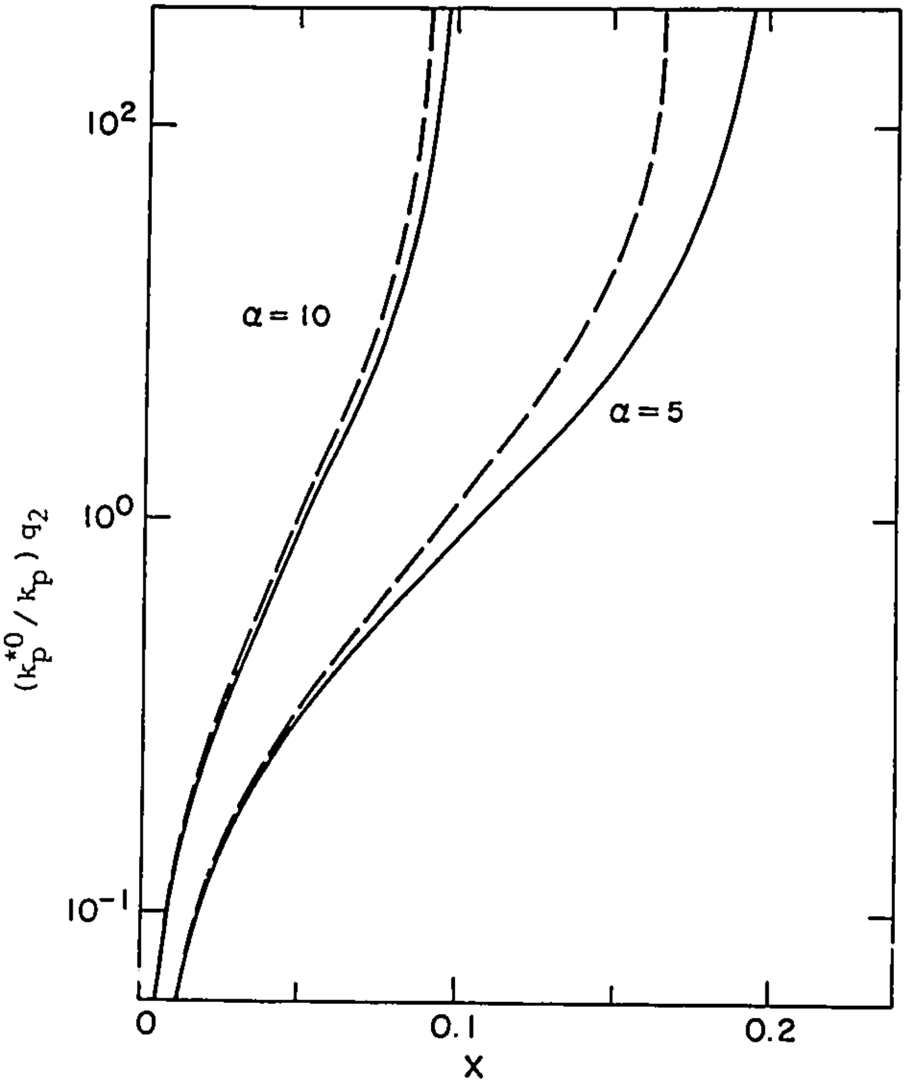
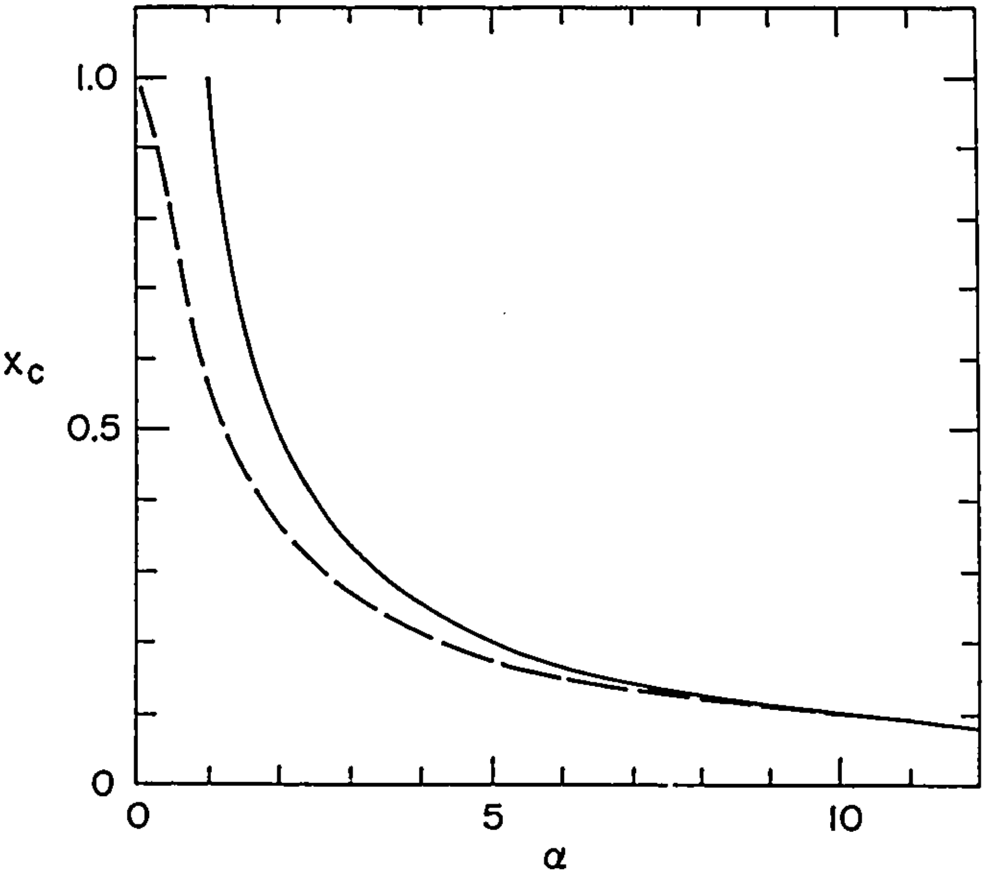


Figure I1 Comparison of solutions for q_2. — — — —; Equation (I6)

————; Equation (I8).



<u>Figure I2</u> Comparison of the calculated gel point.

— — — —; Equation (I6)

————; Equation (I8).

$$k_p^*/k_p \simeq \overline{F}_2 - \overline{\rho}_a \qquad \text{(I12)}$$

$$F_2 \simeq 2f_2 \simeq 2f_{20}(1-x) \qquad \text{(I13)}$$

$$\overline{F}_2 \simeq f_{20}(2-x) \qquad \text{(I14)}$$

The overall additional crosslinking density $\overline{\rho}_a$ can be calculated by

$$\frac{d[x\,\overline{\rho}_a(x)]}{dx} = \frac{k_p^*\,x}{k_p(1-x)} \cong \frac{(\overline{F}_2 - \overline{\rho}_a)\,x}{(1-x)} \qquad \text{(I15)}$$

with initial condition $\overline{\rho}_a=0$ at $x=0$. Equation (I15) can be solved analytically, and the following equations can be derived.

$$k_p^*/k_p = \overline{F}_2 - \overline{\rho}_a = 2f_{20}(1-x) \qquad \text{(I16)}$$

$$\overline{\rho} = 2\overline{\rho}_a = 2f_{20}\,x \qquad \text{(I17)}$$

Substituting Equation (I16) into Equation (I1), one obtains an analytical solution.

$$x\,\overline{P}_{wp} = [1/(2f_{20})][1-(1/(1+2f_{20}q_2))] \qquad \text{(I18)}$$

Substituting the relationship $q_2 = q_1\overline{P}_w = x\,\overline{P}_w$, one obtains

$$\overline{P}_{wp} = \frac{1}{2f_{20}x} \left[1 - \frac{1}{1+2f_{20}\; x\; \overline{P}_w} \right] \qquad (I19)$$

Since the overall crosslinking density, $\overline{\rho}$, is given by Equation (I17), the weight-average chain length $\overline{P}_w$ is given by

$$\overline{P}_w(x) = \frac{\overline{P}_{wp}(x)}{[1-\overline{\rho}(x)\; \overline{P}_{wp}(x)]} \qquad (I20)$$

, which corresponds to Flory's equation Equation (2.4.30).

J. A Kinetic Method to Calculate Sol/Gel Ratio

The gel once formed acts like a great sponge rapidly consuming sol polymer molecules and radicals reducing their concentrations. Radical centers located on gel have longer lives due to their greatly decreased mobility. The greatly reduced termination rate of these radicals on gel molecule results in a large increase in radical concentration and in an autoacceleration in polymerization, which is often called the "gel effect".

The following reactions are considered to be responsible for growth in the weight of gel molecule.

a) The addition of monomer to gel radical centers with rate $k_p[M][R_g^\bullet]$ where $[R_g^\bullet]$ is the concentration of gel radical centers in moles per liter.

b) The addition of radical centers located on sol polymer molecules to double bonds bound in gel with rate $k_p^* \; Y_{1,s}Y_{1,g}$ where $Y_{1,s}$ is the total moles of monomer units bound in sol polymer radicals per liter and $Y_{1,g}$ is the same quantity for the gel molecule.

c) The addition of gel radical centers to double bonds bound in sol polymer molecules with rate $k_p^* \; [R_g^\bullet]Q_{2,s}$ where $Q_{2,s}$ is the second order moment of the chain length distribution of sol polymer molecules. The i-th moment of sol polymer molecules is given by

$$Q_{i,s} = \sum_{r=1}^{\infty} r^i [P_{r,s}] \qquad (J1)$$

where $[P_{r,s}]$ is the concentration of sol polymer of chain length r.

d) The termination by combination of sol polymer radicals with gel radicals with rate $k_{tc,sg}[R_g^\bullet]Y_{1,s}$ where $k_{tc,sg}$ is the termination rate constant for combination of sol and gel radicals.

To develop an equation which describes gel growth beyond the point of gelation, let us assume that the entire reaction volume is occupied by gel molecules uniformly. The equation which describes gel growth follows

$$\frac{1}{V}\frac{d(VY_{1,g})}{dt} = k_p[M][R_g^\bullet] + k_p^{*}Y_{1,s}Y_{1,g} + k_p^{*}[R_g^\bullet]Q_{2,s} + k_{tc,sg}[R_g^\bullet]Y_{1,s} \qquad (J2)$$

The weight fraction of gel and sol can be defined as follows.

$$W_g = V\,Y_{1,g}/(V_0\,[M]_0\,x) \qquad (J3)$$

$$W_s = V\,Q_{1,s}/(V_0\,[M]_0\,x) \simeq 1 - W_g \qquad (J4)$$

By application of the above weight fractions, Equation (J2) can be written in the conversion domain as follows.

$$\frac{dW_g}{dx} = \frac{\Phi_g^\bullet - W_g}{x} + \frac{k_p^*/k_p}{1-x}\left[\overline{P}_{n,s'}\ \Phi_s^\bullet W_g + \overline{P}_{w,s}\Phi_g^\bullet W_s\right] + \frac{\beta_{sg}}{x}\ \overline{P}_{n,s'}\,\Phi_s^\bullet\,\Phi_g^\bullet \qquad (J5)$$

where $\overline{P}_{n,s'}$ and $\overline{P}_{w,s}$ are number-average chain length of sol polymer radicals and weight-average chain length of sol polymer molecules respectively. $\Phi_s^\bullet$ and $\Phi_g^\bullet$ are mole fraction of radical centers located on sol and gel, and $\beta_{sg} = k_{tc,sg}[R^\bullet]/k_p[M]$.

However, there are several problems concerning the solution of the above equation. One of the problems is that the pseudo-kinetic rate constant for crosslinking reaction, Equation (2.4.4), may not be acceptable for high conversion region as is shown in Appendix E. Another problem with the use of Equation (J5) is that one does not know the initial condition for Equation (J5), namely, at present there is no theory available to give the conditions right at the gel point. If the change in weight-average chain length for sol molecules ($\overline{P}_{w,s}$) is known, it may be possible to obtain a solution by assuming the initial weight fraction of gel, $W_g(x_c)$, arbitrary because the calculation is not too sensitive to the initial condition. Nevertheless, there is no theoretical basis for that condition.

One method of circumventing this is to combine the present analysis with an equation for the critical change of weight-average chain length of sol polymers. Let us use the Flory/Stockmayer theory

[Flory (1947a); Stockmayer (1943),(1944)] as an example, although the percolation theory gives another exponent for the critical change [Stauffer et al. (1982)]. Based on the Flory/Stockmayer theory,

$$\bar{P}_{w,s} = \bar{P}_{wp,s}/(1 - \rho^{sol}\,\bar{P}_{wp,s}) \qquad \text{(J6)}$$

where $\bar{P}_{wp,s}$ is the weight-average chain length of the primary polymer molecules which belong to sol fraction, and ρ^{sol} is the crosslinking density of sol polymers and is given by

$$\rho^{sol} \doteq \rho\,(1 - W_g) \qquad \text{(J7)}$$

Applying Equations (J6) and (J7) and assuming k_t is independent of the size of the molecule at the gel point, one can calculate the initial slope of gel growth as follows.

$$\lim_{x \to x_c} \frac{d\,W_g}{d\,x} = \frac{(k_p^*/k_p)^2\, x_c\, \bar{P}_{wp}(x_c)\; P_{wp}(x_c)}{(1 - x_c)^2} \qquad \text{(J8)}$$

$$\simeq \frac{k_p^*}{k_p}\, P_{wp}(x_c) \qquad (x_c \ll 1) \qquad \text{(J9)}$$

Equation (J8) or (J9), and $W_g(x_c) = 0$ give the initial condition for Equation (J5).

One of the calculated results is shown in Figure J1. The calculated results agree with the statistical theories [Flory (1947a); Miller, Macosko (1976)]. In the calculations, the effect of chain length drift in primary polymer molecules mainly due to the strong effect of diffusion controlled termination (and propagation at very high conversions) in the post gelation period was neglected. Therefore, these calculations should be understood as valid when chain transfer to small molecules is significant, so that chain length drift in primary polymer molecule is negligible.

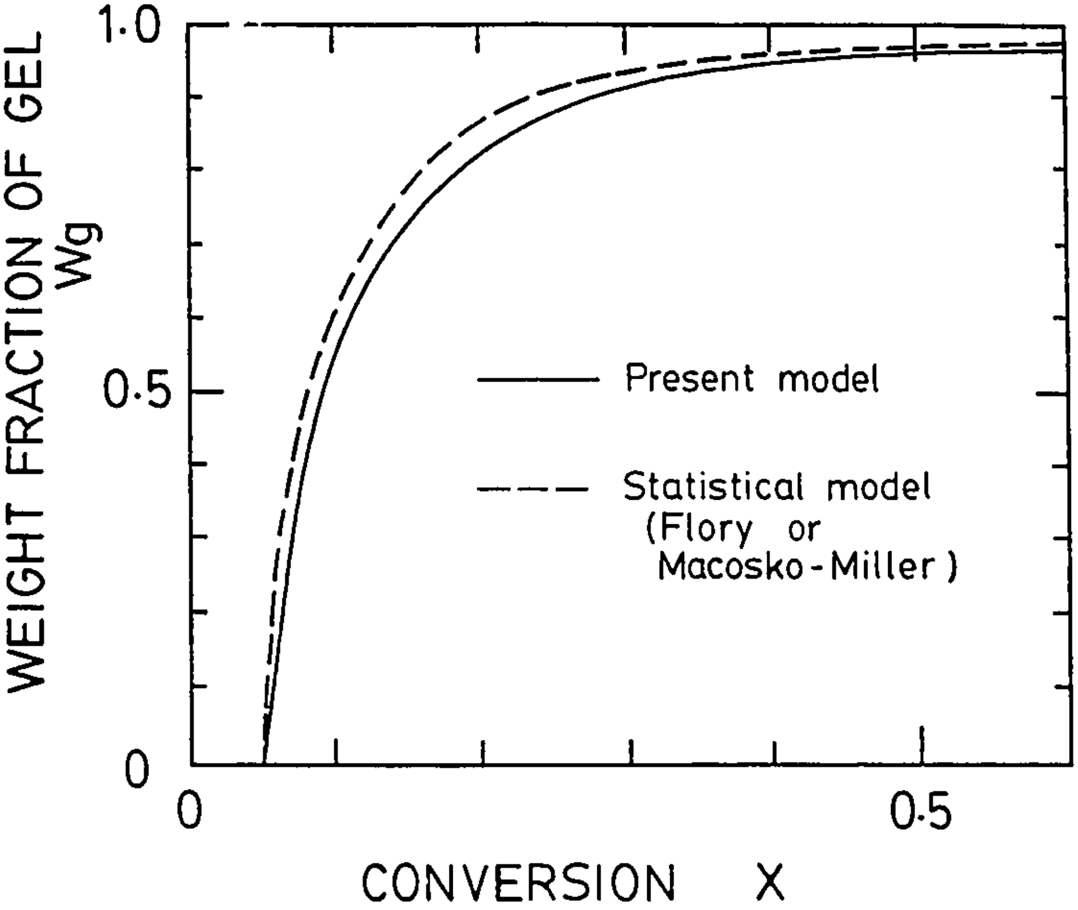


Figure J1 Comparison between Equation (J5) and the statistical model. $f_{20} = 1 \times 10^{-3}$, $\tau = 2 \times 10^{-4}$, $\beta = 0$, reactivities of all double bonds are equal.

K. Experimental Data for Copolymerization of MMA/EGDMA

Abbreviations		
	MMA	methyl methacrylate
	EGDMA	ethylene glycol dimethacrylate
	AIBN	azobisisobutyronitrile
	CTA	carbon tetrabromide, which was used as a chain transfer agent.

Reaction temperature : 70°C
Initiator concentration : 0.30 wt% of AIBN.

C001

Monoмer solution : MMA 99.90 wt%
EGDMA 0.10 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0322	0.0000	0.0322
10.0	0.0411	0.0000	0.0411
20.0	0.0847	0.0000	0.0847
30.0	0.1400	0.0000	0.1400
40.0	0.1903	0.0000	0.1903
50.0	0.2925	0.0393	0.2531
55.0	0.3431	0.0299	0.3202
55.0	0.3480		
60.0	0.3925	0.0294	0.3632
65.0	0.4961	0.2236	0.2724
70.0	0.6811	0.6023	0.0788
75.0	0.8922	0.8725	0.0197
80.0	0.9240	0.9160	0.0080
90.0	0.9225	0.9159	0.0067
110.0	0.9148	0.9077	0.0071
130.0	0.9160	0.9103	0.0057
150.0	0.9231	0.9144	0.0086

C003

Monomer solution : MMA 99.70 wt%
EGDMA 0.30 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0487	0.0000	0.0487
30.0	0.1613	0.0000	0.1613
30.0	0.1482	0.0000	0.1482
40.0	0.2303	0.0044	0.2259
50.0	0.2670	0.1232	0.1438
50.0	0.2651	0.1306	0.1345
55.0	0.3391	0.2404	0.0987
60.0	0.4328	0.3756	0.0572
65.0	0.7245	0.7127	0.0118
70.0	0.9202	0.9163	0.0039
80.0	0.9284	0.9284	0.0000

90.0	0.9539	0.9539	0.0000
120.0	0.9549	0.9549	0.0000
150.0	0.9521	0.9521	0.0000

C005

Monomer solution : MMA 99.50 wt%
EGDMA 0.50 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
5.0	0.0298	0.0078	0.0220
10.0	0.0416	0.0074	0.0342
13.0	0.0628	0.0088	0.0540
17.0	0.0835	0.0166	0.0669
20.0	0.0916	0.0070	0.0846
22.0	0.1139	0.0164	0.0975
25.0	0.1203	0.0104	0.1099
28.0	0.1233	0.0090	0.1143
30.0	0.1387	0.0157	0.1230
35.0	0.1694	0.0150	0.1543
40.0	0.2124	0.1087	0.1038
50.0	0.2842		
50.0	0.3043	0.2539	0.0504
60.0	0.4786	0.4632	0.0129
65.0	0.8519	0.8494	0.0025
70.0	0.8986	0.8976	0.0010
75.0	0.9011	0.8988	0.0023
80.0	0.9172	0.9172	0.0000
100.0	0.9323	0.9323	0.0000
150.0	0.9437	0.9437	0.0000
200.0	0.9474	0.9474	0.0000

C010

Monomer solution : MMA 99.00 wt%
EGDMA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
5.0	0.0215	0.0000	0.0215
10.0	0.0498	0.0015	0.0484
20.0	0.0952	0.0020	0.0933
30.0	0.1589	0.1150	0.0439
40.0	0.2468	0.2249	0.0219
45.0	0.3135	0.2984	0.0151
50.0	0.4785	0.4701	0.0084
55.0	0.8939	0.8939	0.0000
60.0	0.9307	0.9307	0.0000
65.0	0.9308	0.9308	0.0000
70.0	0.9350	0.9350	0.0000
90.0	0.9361	0.9361	0.0000
120.0	0.9336	0.9336	0.0000

C050

Monomer solution : MMA 95.00 wt%
EGDMA 5.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
3.0	0.0030	0.0000	0.0030
5.0	0.0218	0.0000	0.0218
5.0	0.0179	0.0000	0.0179
10.0	0.0669	0.0543	0.0126
10.0	0.0624	0.0427	0.0197
13.0	0.0928	0.0781	0.0147
15.0	0.0954	0.0944	0.0010
20.0	0.1736	0.1726	0.0010
22.0	0.2271	0.2257	0.0015
25.0	0.2833	0.2824	0.0010
28.0	0.5776	0.5776	0.0000
30.0	0.7706	0.7706	0.0000
35.0	0.9467	0.9467	0.0000
40.0	0.9689	0.9689	0.0000
45.0	0.9701	0.9701	0.0000
50.0	0.9890	0.9890	0.0000
60.0	0.9860	0.9860	0.0000
80.0	0.9890	0.9890	0.0000
90.0	0.9756	0.9756	0.0000
120.0	0.9506	0.9506	0.0000
150.0	0.9596	0.9596	0.0000

C150

Monomer solution : MMA 85.00 wt%
EGDMA 15.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
2.0	0.0029	0.0000	0.0029
4.0	0.0058	0.0000	0.0058
6.0	0.0416	0.0319	0.0097
8.0	0.0430	0.0366	0.0063
10.0	0.0770	0.0750	0.0019
12.0	0.1016	0.1010	0.0006
15.0	0.2089	0.2069	0.0020
18.0	0.8415	0.8386	0.0030
20.0	0.9224	0.9209	0.0014
22.0	0.9197	0.9183	0.0014
25.0	0.9244	0.9244	0.0000
30.0	0.9320	0.9320	0.0000
60.0	0.9333	0.9333	0.0000
100.0	0.9374	0.9374	0.0000
150.0	0.9259	0.9259	0.0000

C250

Monomer solution : MMA 75.00 wt%
EGDMA 25.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
2.0	0.0034	0.0000	0.0034
3.0	0.0127	0.0029	0.0108
5.0	0.0417	0.0383	0.0034
7.0	0.0531	0.0527	0.0005
8.0	0.0722	0.0712	0.0010
10.0	0.0879	0.0879	0.0000
12.0	0.2703	0.2703	0.0000
14.0	0.8108	0.8108	0.0000
16.0	0.9027	0.9027	0.0000
18.0	0.8974	0.8974	0.0000
20.0	0.9142	0.9142	0.0000
25.0	0.9246	0.9246	0.0000
30.0	0.9302	0.9302	0.0000
60.0	0.9357	0.9357	0.0000

CC0005

Monomer solution : MMA 99.95 wt%
EGDMA 0.05 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0433	0.0000	0.0433
10.0	0.0476	0.0000	0.0476
20.0	0.0873	0.0000	0.0873
20.0	0.0908	0.0000	0.0908
30.0	0.1337	0.0000	0.1337
40.0	0.1779	0.0000	0.1779
40.0	0.1858	0.0000	0.1858
50.0	0.2364	0.0000	0.2364
60.0	0.2855	0.0000	0.2855
70.0	0.3306	0.0000	0.3306
80.0	0.3949	0.0000	0.3949
90.0	0.4860	0.0000	0.4860
95.0	0.5538	0.0000	0.5538
100.0	0.6173	0.0000	0.6173
105.0	0.7634	0.0000	0.7634
107.0	0.8376	0.0000	0.8376
110.0	0.8651	0.0000	0.8651
110.0	0.8558	0.0000	0.8558
120.0	0.8849	0.0000	0.8849
130.0	0.9048	0.0000	0.9048
140.0	0.9032	0.0000	0.9032
150.0	0.9025	0.0000	0.9025
170.0	0.8926	0.0000	0.8926
200.0	0.8965	0.0000	0.8965

CC001

Monomer solution : MMA 99.90 wt%
EGDMA 0.10 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0403	0.0000	0.0403
20.0	0.0874	0.0000	0.0874
30.0	0.1283	0.0000	0.1283
40.0	0.1912	0.0000	0.1912
50.0	0.2462	0.0000	0.2462
60.0	0.3039	0.0000	0.3039
61.0	0.3070	0.0000	0.3070
70.0	0.3733	0.0000	0.3733
80.0	0.4264	0.0000	0.4264
90.0	0.5119	0.0000	0.5119
95.0	0.5855	0.0000	0.5855
95.0	0.5873	0.0000	0.5873
95.0	0.6050	0.0000	0.6050
100.0	0.7277	0.0000	0.7277
103.0	0.8469	0.0000	0.8469
106.0	0.8581	0.0000	0.8581
106.0	0.8652	0.0000	0.8652
110.0	0.8848	0.0000	0.8848
120.0	0.8849	0.0000	0.8849
140.0	0.8978	0.0000	0.8978
170.0	0.9005	0.0000	0.9005
200.0	0.9005	0.0000	0.9005

CC003

Monomer solution : MMA 99.70 wt%
EGDMA 0.30 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
20.0	0.0854	0.0000	0.0854
20.0	0.0875	0.0000	0.0875
31.0	0.1349	0.0000	0.1349
40.0	0.1879	0.0000	0.1879
50.0	0.2396	0.0000	0.2396
60.0	0.3051	0.0000	0.3051
70.0	0.3630	0.0000	0.3630
70.0	0.3632	0.0000	0.3632
75.0	0.4065	0.0156	0.3098
80.0	0.4496	0.0103	0.4393
85.0	0.4975	0.0598	0.4377
90.0	0.5760	0.2158	0.3602
95.0	0.6591	0.3762	0.2829
100.0	0.8050	0.5352	0.2698
103.0	0.8624	0.5947	0.2677

105.0	0.8668	0.5966	0.2703
110.0	0.8937	0.6246	0.2691
110.0	0.8956	0.6267	0.2689
120.0	0.9144	0.6352	0.2792
130.0	0.9156	0.6406	0.2750
140.0	0.9152	0.6293	0.2845
140.0	0.9143	0.6436	0.2707
170.0	0.9218	0.6473	0.2745
170.0	0.9173	0.6685	0.2488
200.0	0.9204	0.6531	0.2674

CC005

Monomer solution : MMA 99.50 wt%
EGDMA 0.50 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0447	0.0000	0.0447
20.0	0.0938	0.0000	0.0938
30.0	0.1453	0.0000	0.1453
40.0	0.1906	0.0000	0.1906
50.0	0.2526	0.0049	0.2476
60.0	0.3225	0.0103	0.3122
65.0	0.3497	0.0143	0.3354
70.0	0.3627	0.0951	0.2676
75.0	0.4232	0.1998	0.2235
80.0	0.4563	0.2628	0.1936
85.0	0.5174	0.3619	0.1555
90.0	0.5828	0.4654	0.1174
95.0	0.7181	0.6207	0.0974
100.0	0.7956	0.6938	0.1018
105.0	0.8336	0.7397	0.0939
110.0	0.8570	0.7639	0.0931
120.0	0.8860	0.7958	0.0902
140.0	0.8760	0.7760	0.0999
170.0	0.8663	0.7758	0.0904
200.0	0.8887	0.7759	0.1128

CC010

Monomer solution : MMA 99.00 wt%
EGDMA 1.00 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
20.0	0.0820	0.0000	0.0820
40.0	0.2002	0.0131	0.1871
40.0	0.2025	0.0182	0.1843
50.0	0.2537	0.1415	0.1122
60.0	0.3220	0.2372	0.0849

70.0	0.3987	0.3331	0.0656
70.0	0.3912	0.3303	0.0604
80.0	0.4898	0.4510	0.0391
85.0	0.5753	0.5441	0.0312
90.0	0.6648	0.6371	0.0277
95.0	0.8033	0.7831	0.0202
100.0	0.8599	0.8385	0.0213
105.0	0.8679	0.8472	0.0207
110.0	0.8874	0.8674	0.0200
110.0	0.8817	0.8792	0.0025
120.0	0.8986	0.8803	0.0183
140.0	0.9015	0.8736	0.0250
170.0	0.8973	0.8821	0.0152
200.0	0.9038	0.8773	0.0265

CC020

Monomer solution : MMA 98.00 wt%
EGDMA 2.00 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
10.0	0.0452	0.0000	0.0452
20.0	0.0953	0.0000	0.0953
30.0	0.1734	0.0846	0.0888
40.0	0.2094	0.1570	0.0523
50.0	0.2871	0.2431	0.0440
60.0	0.3534	0.3209	0.0324
65.0	0.4130	0.3913	0.0217
70.0	0.4743	0.4587	0.0156
75.0	0.5511	0.5427	0.0084
80.0	0.6749	0.6674	0.0075
85.0	0.8462	0.8420	0.0042
90.0	0.8927	0.8864	0.0063
95.0	0.8928	0.8883	0.0046
100.0	0.8891	0.8891	0.0000
110.0	0.8967	0.8967	0.0000
120.0	0.9150	0.9150	0.0000
140.0	0.9065	0.9065	0.0000
170.0	0.9027	0.9027	0.0000
200.0	0.9228	0.9228	0.0000

C2C01

Monomer solution : MMA 99.00 wt%
EGDMA 1.00 wt%
CTA 2.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
20.0	0.0813	0.0000	0.0813
30.0	0.1289	0.0000	0.1289

40.0	0.1820	0.0000	0.1820
50.0	0.2251	0.0000	0.2251
55.0	0.2582	0.0000	0.2582
60.0	0.2980	0.0211	0.2769
70.0	0.3395	0.1491	0.1904
75.0	0.3710	0.2185	0.1528
80.0	0.4211	0.2809	0.1402
80.0	0.4308	0.2828	0.1480
85.0	0.4420	0.3091	0.1330
90.0	0.5234	0.4101	0.1133
95.0	0.6279	0.5490	0.0789
100.0	0.6496	0.5551	0.0738
105.0	0.7873	0.7170	0.0703
110.0	0.8444	0.7711	0.0733
115.0	0.8600	0.7815	0.0785
125.0	0.8631	0.7824	0.0807
140.0	0.8720	0.7920	0.0799
170.0	0.8786	0.7881	0.0805
200.0	0.8740	0.7966	0.0774

C4C01

Monomer solution : MMA 99.00 wt%
EGDMA 1.00 wt%
CTA 4.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
20.0	0.0671	0.0000	0.0671
40.0	0.1560	0.0000	0.1560
60.0	0.2710	0.0203	0.2507
70.0	0.3113	0.0207	0.2906
80.0	0.3637	0.0259	0.3378
90.0	0.4033	0.0167	0.3866
90.0	0.3991		
95.0	0.4218	0.0172	0.4046
95.0	0.4307		
100.0	0.4677	0.0912	0.3765
105.0	0.4885	0.1927	0.2958
110.0	0.5171	0.2159	0.3012
120.0	0.5930	0.3636	0.2294
130.0	0.7040	0.5007	0.2033
140.0	0.7880	0.5997	0.1884
170.0	0.8262	0.6518	0.1744
200.0	0.8240	0.6492	0.1747

Homopolymerization of MMA

CMMA

Monomer solution : MMA 100.00 wt%
CTA 0.00 wt%

TIME [min.]	CONVERSION
10.0	0.0498
20.0	0.0996
30.0	0.1532
40.0	0.2146
50.0	0.2627
55.0	0.3029
60.0	0.3452
65.0	0.4513
70.0	0.6570
70.0	0.6591
70.0	0.6443
75.0	0.8837
85.0	0.9000
90.0	0.9059
100.0	0.9059
120.0	0.9069

CCMMA

Monomer solution : MMA 100.00 wt%
CTA 1.00 wt%

TIME [min.]	CONVERSION
20.0	0.0928
40.0	0.1705
60.0	0.2794
70.0	0.3281
80.0	0.4098
90.0	0.4857
100.0	0.5974
105.0	0.7146
110.0	0.8285
115.0	0.9184
120.0	0.9411
150.0	0.9558
200.0	0.9639

Homopolymerization of EGDMA

CEGDMA

Monomer solution : EGDMA 100.00 wt%
CTA 0.00 wt%

TIME [min.]	CONVERSION	GEL CONV.	SOL CONV.
1.0	0.0157	0.0148	0.0009
2.0	0.0180	0.0157	0.0023
3.0	0.0515	0.0455	0.0060
4.0	0.0603	0.0472	0.0131
5.0	0.1231	0.1058	0.0174
6.0	0.1432	0.1266	0.0166
7.0	0.2414	0.2217	0.0196
8.0	0.2508	0.2327	0.0180
9.0	0.3373	0.3207	0.0166
10.0	0.3751	0.3628	0.0123
15.0	0.6482	0.6282	0.0000
20.0	0.7244	0.7244	0.0000
25.0	0.7603	0.7603	0.0000
30.0	0.7754	0.7754	0.0000
40.0	0.7870	0.7870	0.0000
50.0	0.7945	0.7945	0.0000
70.0	0.8003	0.8003	0.0000
90.0	0.8310	0.8310	0.0000
120.0	0.8438	0.8438	0.0000

L. Publications Based on the Present Research

As of December 1, 1989, the following papers have been published or accepted for publication.

Tobita, H.; Hamielec, A.E., "A Kinetic Model for Network Formation in Free Radical Polymerization", Makromol. Chem., Macromol. Symp., **20/21**, 501 (1988).

Tobita, H.; Hamielec, A.E., "Modeling of Network Formation in Free Radical Polymerization", Macromolecules, **22**, 3098 (1989).

Tobita, H.; Hamielec, A.E., "Network Formation in Free Radical Copolymerization: Pseudo-Kinetic Rate Constant Method for Copolymers with Long Branches", in Computer Application in Applied Polymer Science II (ACS Symposium Series **404**); Provder, T., Ed.; American Chemical Society: Washington, D.C.; p.242 (1989).

Tobita, H.; Hamielec, A.E., "Network Formation in Free Radical Polymerization", in Integration of Fundamental Polymer Science and Technology - Volume IV; Lemstra, P.J.; Nelissen, L., Eds.; Elsevier Applied Science Publishers: Barking, UK (1990).

Tobita, H.; Hamielec, A.E., "Modeling Emulsion Copolymerization: Crosslinking Kinetics", Makromol. Chem., Macromol. Symp., (accepted for publication).

Tobita, H.; Hamielec, A.E., "Crosslinking Kinetics in Free Radical Copolymerization", in Polymer Reaction Engineering; Reichert, K.-H. ; Geiseler, W., Eds.; VCH Verlagsgesellschaft: New York; p.43 (1989).

Tobita, H.; Hamielec, A.E., "Crosslinking Kinetics in Polyacrylamide Networks", Polymer (accepted for publication).