FREE-RADICAL COPOLYMERIZATION KINETICS OF STYRENE/DIVINYLBENZENE

FREE-RADICAL COPOLYMERIZATION KINETICS OF STYRENE/DIVINYLBENZENE

BY

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To my mother, **Lupita Lima**, for her immense love and sacrifice. For being the best model and example of love to life and courage to fight against everything and everyone (including oneself) in order to accomplish our ideals.

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ABSTRACT

An effective model for the bulk, solution and suspension copolymerization of styrene/divinylbenzene (DVB) has been developed. Its effectiveness is understood as a compromise between sound theoretical basis and simple mathematical structure, which makes possible the solution of its governing equations using conventional computational tools.

To build the model a comprehensive analysis of the elementary reactions and restrictions caused by the physical environment imposed by the growing polymer was made. The main issues considered in the model are: diffusion-controlled initiation, propagation and bimolecular termination reactions; different reactivities of double bonds; effect of solvent, chain transfer agent, inhibitor, type of crosslinker (m-DVB, p-DVB or mixtures of both), type of initiator; as well as crosslinking and primary-secondary cyclization reactions.

In building the model, it was necessary to review and improve the conventional theory of diffusion-controlled free radical polymerization kinetics. Important contributions in this area came out as a result. Among those contributions, the most important are: the demonstration that using a "parallel" approach for modelling effective kinetic constants which are "diffusion-controlled" (widely used in this field) is incorrect, the proposal of an effective way to calculate molecular weight averages, and the proposal of a model for calculation of non-equilibrium free volume.

By performing a detailed compilation and analysis

of experimental information available in the literature, all our objectives could be satisfactorily accomplished without having to perform additional experiments. Most of the experimental data and model predictions are in excellent agreement for pre and post-gelation periods. However, it is recognised that the real behavior of the polymerizing system is so complex (even the experimental techniques for characterization of network polymers are still in the development stage), that the model developed herein must be considered as a first realistic approximation to the real situation. Some guidelines for the improvement of this model (mostly associated to secondary cyclization) and preliminary qualitative calculations associated to these modifications have been given.

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TABLE OF CONTENTS

NOMENCLATURE

1. GENERAL INTRODUCTION

2. AUTO-ACCELERATION EFFECT IN FREE RADICAL POLYMERIZATION. A COMPARISON OF THE CCS AND MH MODELS

COMPARISON OF THE STRUCTURE OF THE CCS AND MH MODELS

3. BATCH REACTOR MODELLING OF THE FREE RADICAL COPOLYMERIZATION KINETICS OF STYRENE/ DIVINYLBENZENE UP TO HIGH CONVERSIONS

REFERENCES

APPENDICES (for Chapter 3)

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

For Chapter 2

A	Overlap factor in the MH (also referred as A_{MH}) or the PM models to account for the fact that the same free volume is available to several molecules and also for separation once the molecules are together, in translational termination by combination.
A(T)	Free volume parameter in the CCS model. Defined by equation (15).
AIBN	2,2′-azobis(isobutyronitrile) (initiator).
AK	Achilias-Kiparissides model.
a_{seg}	Parameter used in the AK model which accounts for the relative importance of translational and rotational diffusion coefficients of polymer molecules.
B	Overlap factor in diffusion/separation of monomer molecules in a polymeric solution (used in the PM model).
B(T)	Free volume parameter in the CCS model. Defined by equation (16).
B_a	Overlap factor in the "approach" of a monomer molecule to a polymer radical.
B_d	"Free parameter" in the Fujita free volume theory (it may depend on the motional modes of the diffusing unit).
B_f	Overlap factor for free volume dependence in calculation of relaxation time for non-equilibrium free volume estimation.
B_s	Overlap factor in the "separation" of a monomer molecule from a polymer radical.

CCS	Chiu-Carratt-Soong model. CCSA is used in the case where θ_p is negligible and CCSB when this parameter is considered in the model.
C_{rd}	Proportionality factor to account for reaction-diffusion termination kinetic constant in the AK, MH (modified) and PM models, l mol^{-1}.
D	Overlap factor for diffusion/separation of initaitor fragments. Used in the PM model.
D_I, D_{I0}	Diffusion coefficient of initiator fragments in the reacting medium (subscript "0" at x=0), cm^2 s^{-1}.
D_m, D_{m0}	Diffusion coefficient of monomer in the reacting medium (subscript "0" at x=0), cm^2 s^{-1}.
D_p, D_{p0}	Diffusion coefficient of polymer in the reacting medium (subscript "0" at x=0), cm^2 s^{-1}.
D_{pa}	Diffusion coefficient for approach of a polymer radical to another polymer radical, cm^2 s^{-1}.
D_{pe}	Effective diffusion coefficient of the polymer, cm^2 s^{-1}.
D_{ps}	Diffusion coefficient for separation of polymer radicals from each other, cm^2 s^{-1}.
E_m	Energy associated to the monomer to overcome the attractive forces from neighboring molecules, cal/mol.
E_{ma}	Same as E_m, but related to the case when the monomer molecule approaches a polymer radical molecule, cal/mol.
E_{ms}	Same as E_m, but related to the case when the monomer molecule separates from a polymer radical segment next to it, cal/mol.
E_p	Energy associated to a polymer segment to overcome the attractive forces from neighboring molecules, cal/mol.
EVM	"Error in variables method". Used for non-linear multivariate parameter estimation.

f	Initiator efficiency (as a function of conversion).
f°	Initial initiator efficiency.
F_{seg}	Parameter to account for the probability that two radicals react when their active centers come into close proximity.
I	Initiator (it may also be used as initiator concentration).
I'	Species formed from recombination of initiator fragments (it may also refer to its concentration).
I_0	Initial initiator concentration, mol/l
$[I]$	Initiator concentration, mol/l.
IPM	Instantaneous Property Method.
j_{c0}, j_{c0}	Entanglement spacing. (Subscript "0" for j_c at $x=0$).
K_{11}	Parameter used in the Vrentas-Duda free volume theory, $cm^3\ g^{-1}\ K^{-1}$.
K_{13}	Parameter used in the Vrentas-Duda free volume theory, $cm^3\ g^{-1}\ K^{-1}$.
K_{21}	Parameter used in the Vrentas-Duda free volume theory, °K.
K_{22}	Parameter used in the Vrentas-Duda free volume theory, °K.
K_{33}	Parameter used in the Vrentas-Duda free volume theory, °K.
$K_3(T)$	Temperature dependent constant used in the MH model to "onset" the gel effect.
k_B	Boltzmann's constant (1.3806×10^{-23} J/K).
k_c	Intrinsic chemical kinetic constant.
k_c'	Intrinsic chemical kinetic constant for a side reaction.

k_{chem}	Intrinsic chemical kinetic constant.
k_d	Initiator decomposition kinetic constant, s^{-1}.
k_D	Diffusion kinetic constant for approach of one molecule towards another one.
k_{-D}	Diffusion kinetic constant for separation of one molecule from another one very close to it.
k_{diff}	Diffusion kinetic constant.
k_{eff}	Effective kinetic constant.
k_{fm}	Kinetic constant for chain transfer to monomer, $l\ mol^{-1}\ s^{-1}$.
k_{fp}	Kinetic constant for chain transfer to polymer, $l\ mol^{-1}\ s^{-1}$.
k_{fT}	Kinetic constant for chain transfer to a small molecule (solvent or added chain transfer agent), $l\ mol^{-1}\ s^{-1}$. (It may also be shown as k_{fs} for the solvent).
k_i	Kinetic constant for formation of a "polymer" of length "i".
k_p, k_p^0	Kinetic constant for propagation reaction (subscrit "0" for k_p at x=0 or intrinsic chemical value), $l\ mol^{-1}\ s^{-1}$.
$k_t(i,j)$	Bimolecular termination kinetic constant between polymer radicals of sizes "i" and "j" (chain length dependet k_t), $l\ mol^{-1}\ s^{-1}$.
$\bar{k}_{tn}$	(or k_t). Overall number average termination kinetic constant ($\bar{k}_{tcn}$ $+\bar{k}_{tdn}$ $+k_{trd}$), $l\ mol^{-1}\ s^{-1}$.
$\bar{k}_{tcn}$	Effective number average termination by combination kinetic constant, $l\ mol^{-1}\ s^{-1}$.
$\bar{k}_{tcw}$	Effective weight average termination by combination kinetic constant, $l\ mol^{-1}\ s^{-1}$.
$\bar{k}_{tdn}$	Number average termination by disproportionation kinetic constant, $l\ mol^{-1}\ s^{-1}$.

$\bar{k}_{tdw}$	Weight average termination by disproportionation kinetic constant, l mol^{-1} s^{-1}.
k_{trd}	Reaction diffusion termination kinetic constant (or residual termination kinetic constant), l mol^{-1} s^{-1}. (Also shown as $k_{t,res}$).
$\bar{k}_{tw}$	Overall weight average termination kinetic constant ($\bar{k}_{tcw}$ +$\bar{k}_{tdw}$+k_{trd}), l mol^{-1} s^{-1}.
M	Monomer (also referred as monomer concentration).
[M]	Monomer concentration, mol/l.
$[M]_0$	Initial total monomer concentration, mol/l.
MH	Marten-Hamielec model.
M_{jI}	Molecular weight of the jumping initiator fragment.
M_{jm}	Molecular weight of the jumping monomer molecule.
M_{jp}	Molecular weight of the jumping polymer segment.
M_{js}	Molecular weight of the jumping solvent molecule.
MM	Method of Moments.
MMA	Methyl methacrylate monomer.
N_A	Avogadro number (6.023×10^{23}).
P_m	Polymer molecule (dead polymer) of size "m".
PM	Present model (model developed in this paper).
P_n	Instantaneous number average chain length.
$\bar{P}_n$	Accumulated number average chain length.
P_w	Instantaneous weight average chain length.

$\overline{P}_w$	Accumulated weight average chain length.
$\overline{P}_{w,cr2}$	Critical value of the accumulated weight average chain length, at which termination becomes diffusion controlled (MH model).
r	Chain length.
R	Universal constant of gases, equal to 1.987 cal mol^{-1} K^{-1}.
r_1	Radius of the "initiator reaction sphere" (used by Achilias and Kiparissides, 1992, in their derivation of "f"), cm.
r_2	Radius of the "diffusion sphere" (used by Achilias and Kiparissides, 1992, in their derivation of "f"), cm.
R^2	Correlation coefficient in least squares linear regression.
r_B	"Radius" of the polymer molecule (used in the AK model), cm.
r_e	"Segment length" (used in the AK model), cm.
R_{fv}	Rate of "generation" of free volume, 1/s.
R_H	"Hydraulic radius" of the polymer, cm.
R_i	Effective separation ratius for molecule "i" (used in the PM derivation).
$R^{\cdot}_{in}$	Primary radical from initiator decomposition (or its concentration, mol/l).
r_m	Monomer radius, cm.
$R^{\cdot}_m$	Concentration of polymer radical of size m, mole/l.
t	Time, seconds or termination if used as subscript.

T	Small molecule (solvent, chain transfer agent, etc) or temperature, °C (°K in Arrhenius expressions).
[T]	Concentration of small molecule, mole/l.
$T^{\cdot}$	Radical formed from chain transfer to a small molecule (solvent or chain transfer).
T_{gi}	Glass transition temperature for species i, °C.
V	Volume in liters, unless otherwise defined.
V_f	Fractional free volume.
$\hat{V}_f$	Specific free volume of the mixture, cm^3/g.
V_f^*	Critical fractional free volume (from the Bueche free volume theory).
$V_{f,cr1}$	Critical fractional free volume for onset of the auto-acceleration effect.
$V_{f,cr2}$	Critical fractional free volume for glassy effect.
V_{feq}	Fractional free volume at equilibrium conditions.
V_{fi}	Fractional free volume of species "i".
V_{fo}	Initial fractional free volume (at zero conversion).
V_i	Volume of species i, liters.
$\hat{V}_i^0$	Specific volume for species "i", cm^3/g.
$\hat{V}_i^*$	Specific "critical" free volume for species "i" (used in the Vrentas-Duda free volume theory), cm^3/g.
V_o	Initial volume, liters.
V_t	Total volume, liters.
x	Molar monomer conversion.
X_{c0}	Critical degree of polymerization for entanglements of the pure polymer.

Y_o	Zeroth moment of the polymeric radical distribution. (Total polymer radical concentration), mol/l.

Greek Letters

α_i	Expansion coefficient for species i, 1/°C.
β^*	Parameter used in Bueche's free volume theory and defined by equation (57).
β_n	Ratio of "number average" termination by combination rate to propagation rate.
β_w	Ratio of "weight average" termination by combination rate to propagation rate.
γ	Overlap factor (AK model).
γ_I	Overlap factor for the initiator (AK model).
δ	Excess free volume coefficient in the MH model, adim., or average root mean square end-to-end distance per square root of the number of monomer units in a chain (used in the AK model), cm.
ϵ_i	$=k_{i0}/k_{p0}$
η_s	solvent viscosity (used in the AK model), Pa*s.
$\bar{\rho}$	Accumulated crosslinking density.
ρ_i	Density of species "i", g/cm^3.

θ_p, θ_t	"Migration times" for propagation and termination, respectively (used in the CCS model), s.
ξ_{13}	Ratio of the critical molar volume of the jumping unit to the critical molar volume of the polymer (used in the AK model).
σ	Lennard-Jones radius, cm.
τ_0	Reference relaxation time, seconds.
τ_n	Ratio of transfer and "number average" termination by disproportionation rates to propagation rate.
τ_w	Ratio of transfer and "weight average" termination by disproportionation rates to propagation rate.
ϕ_i	Volume fraction of species "i".
ω_i	weight fraction of species "i".

For Chapter 3

A	Effectiveness factor to account for overlap of free volume and separation of reactive radicals.
AIBN	2,2'-azobis(isobutyronitrile) (initiator).
B_t	Adjustable parameter for free volume dependence of relaxation time.
BPO	Benzoyl peroxide (initiator).
C_1	Empirical parameter to account for initiator efficiency decrease during the post-gelation period (found to be negligible).

C_2	Empirical parameter to account for propagation kinetic constant decrease during the post-gelation period (found to be negligible).
C_3	Empirical parameter to account for termination kinetic constant decrease during the post-gelation period (found to be equal to one).
Cp_i	Ratio of k_{fp} and k_p.
Cp^*_i	Ratio of kp^* and k_p.
C°_{rd}	Proportionality factor for reaction-diffusion termination constant during the pre-gelation period.
C_{rd}^{gp}	Upper value of C°_{rd} at the gel point.
D	Effectiveness factor to account for overlap of free volume and separation of fragment-radical molecules.
DPPH	Hydrated, 1,1-diphenyl-2-picrylhydrazyl (inhibitor).
DVB	Divinyl benzene (monomer "2" or crosslinker).
EVM	"Error in variables method". Used for non-linear multivariate parameter estimation.
f	Initiator efficiency (as a function of conversion).
f°	Initial initiator efficiency.
f_1	Relative vinyl monomer (styrene) concentration.
f_2	Relative divinyl monomer (DVB) concentration.
f_{20}	Initial divinyl monomer concentration (molar fraction).
F_1	Instantaneous relative composition of monomer 1 in polymer.
F_2	Instantaneous relative composition of monomer 2 in polymer.
$\overline{F}_2$	Accumulated copolymer composition (molar

	relative content of DVB in copolymer).
I	Initiator.
[I]	Initiator concentration, mole/l.
k_1	Propagation kinetic constant between a primary radical formed by initiator decomposition and a unit of monomer 1 (styrene).
k_2	Propagation kinetic constant between a primary radical formed by initiator decomposition and a unit of monomer 2 (DVB).
k_{ij}	Propagation kinetic constant of radical type i (i=1, 2, or 3) adding monomer j (j= 1, 2), l mole^{-1} s^{-1}. (Also shown as kp_{ij}).
k_{cp}	Proportionality constant between primary cyclization density and mole fraction of divinyl monomer bound in the polymer chains.
k_{cs}	Proportionality constant between the average number of secondary cycles per crosslink and the fraction of "free" pendant double bonds in the primary polymer molecule.
k_d	Initiator decomposition kinetic constant, s^{-1}.
k_{fij}	Kinetic constant for chain transfer of radical type i to monomer j, l mole^{-1} s^{-1}. Also shown as k_{fmij}.
k_{fm}	Pseudo kinetic constant for chain transfer to monomer, l mole^{-1} s^{-1}.
k_{fp}	Pseudo kinetic constant for chain transfer to polymer, l mole^{-1} s^{-1}.
k_{fT}	Pseudo kinetic constant for chain transfer to a small molecule (solvent or added chain transfer agent), l mole^{-1} s^{-1}.
k_{fTi}	Kinetic constant for chain transfer of radical i (i=1, 2 or 3) to a small molecule T, l mole^{-1} s^{-1}.
k_p	Pseudo kinetic constant for propagation (also shown as kp_{pse}), l mole^{-1} s^{-1}.

k_p^*	Pseudo kinetic constant for crosslinking reaction (propagation through pendant double bonds or addition of "macromonomer"), l mole^{-1} s^{-1}.
kp_{ij}	Effective (diffusion controlled) propagation kinetic constant for addition of monomer type j into a radical with end unit of monomer i, l mole^{-1} s^{-1}.
kp^{*0}_{i3}	Intrinsic chemical kinetic constant for addition of a pendant double bond (macromonomer) into a radical with end unit of monomer i, l mole^{-1} s^{-1}.
kp^{*}_{i3}	Effective (diffusion controlled) propagation kinetic constant for addition of a pendant double bond (macromonomer) into a radical with end unit of monomer i, l mole^{-1} s^{-1}.
kp^{0}_{ij}	Intrinsic chemical propagation kinetic constant for addition of monomer type j into a radical with end unit of monomer i, l mole^{-1} s^{-1}.
$\bar{k}^0_{tc_{ij}}$	Intrinsic chemical kinetic constant for termination by combination between radical types i and j, l mole^{-1} s^{-1}.
$\bar{k}_{tcn}$	Pseudo kinetic number average termination by combination kinetic constant, l mole^{-1} s^{-1}.
$\bar{k}_{tcn_{ij}}$	Effective (diffusion controlled) number average termination by combination kinetic constant between radical types i and j, l mol^{-1} s^{-1}.
$\bar{k}_{tcw}$	Pseudo kinetic weight average termination by combination kinetic constant, l mol^{-1} s^{-1}.
$\bar{k}_{tcw_{ij}}$	Effective (diffusion controlled) weight average termination by combination kinetic constant, l mole^{-1} s^{-1}.
k_{tcrd}	Reaction diffusion termination kinetic constant (or residual termination kinetic constant), l mole^{-1} s^{-1}.

$\bar{k}_{td}$	Pseudo kinetic termination by disproportionation kinetic constant, l mole^{-1} s^{-1}.
$\bar{k}_{td_{ij}}$	Termination by disproportionation kinetic constant between radical types i and j, l mol^{-1} s^{-1}.
k_z	Pseudo kinetic inhibition kinetic constant, l mol^{-1} s^{-1}.
k_{zi}	Kinetic constant for reaction between inhibitor and a radical of type i (i= 1, 2 or 3), l mol^{-1} s^{-1}.
m-	Accounts for "meta" isomer type.
M	Total monomer (M_1 + M_2)
[M]	Total monomer concentration, mole/l.
$[M]_0$	Initial total monomer concentration, mole/l.
M_1	Monomer 1 (styrene)
$[M_1]$	Concentration of monomer 1, mole/l.
M_2	Monomer 2 (DVB)
$[M_2]$	Concentration of monomer 2, mole/l.
p-	Accounts for "para" isomer type.
$P_{m,n}$	Polymer molecule with m-units of monomer 1 and n-units of monomer 2.
$P^*_{m,n}$	Polymer molecule with m-units of monomer 1 and n-units of monomer 2, with a reactive pendant double bond (also refered as "macromonomer").
P_n	Instantaneous number average chain length.
$\bar{P}_n$	Accumulated number average chain length.

$\bar{P}_{np}^{sol}$	Accumulated number average chain length for the primary polymer molecule in the sol phase.
$[P_r]$	Concentration of (dead) polymer with chain length r, mole/l.
P_w	Instantaneous weight average chain length.
$\bar{P}_w$	Accumulated weight average chain length.
$\bar{P}_{wp}^{sol}$	Accumulated weigth average chain length for the primary polymer molecule in the sol phase.
q_0	Normalized zeroth moment of the polymer distribution.
Q_0	Zeroth moment of the polymer distribution.
q_1	Normalized first moment of the polymer distribution.
Q_1	First moment of the polymer distribution.
q_2	Normalized second moment of the polymer distribution.
Q_2	Second moment of the polymer distribution.
q_3	Normalized third moment of the polymer distribution.
Q_3	Third moment of the polymer distribution.
R	Universal constant of gases, equal to 1.987 cal mol^{-1} K^{-1}.
r_1	Reactivity ratio ($= k_{11}/k_{12}$).
r_2	Reactivity ratio ($= k_{22}/k_{21}$).
$[R^{\cdot}]$	Total polymer radical concentration, mole/l.
R_{fm}	Reaction rate for chain transfer to monomer, mole l^{-1} s^{-1}.

R_{fp}	Reaction rate for chain transfer to polymer, mole l^{-1} s^{-1}.
R_{fs}	Reaction rate for chain transfer to solvent, mole l^{-1} s^{-1}.
R_{fT}	Reaction rate for chain transfer to a small molecule (chain transfer agent), mole l^{-1} s^{-1}.
$[R^{\cdot}_{i}]$	Concentration of polymer radical of size i, mole/l.
$R^{\cdot}_{in}$	Primary radical from initiator decomposition.
$R^{\cdot}_{m,n,i}$	Polymer radical with m-units of monomer 1 and n-units of monomer 2 bound in the polymer chain and with active center located on monomer unit i (i= 1, 2 or 3).
R_p	Reaction rate for propagation, mole l^{-1} s^{-1}.
R_{tc}	Reaction rate for termination by combination, mole l^{-1} s^{-1}.
R_{td}	Reaction rate for termination by disproportionation, mole l^{-1} s^{-1}.
R_z	Reaction rate for inhibition, mole l^{-1} s^{-1}.
S	Solvent, unless otherwise defined.
t	Time, seconds or termination if used as subscript.
T	Small molecule (solvent, chain transfer agent, etc) or temperature, °C (°K in Arrhenius expressions).
[T]	Concentration of small molecule, mole/l.
T_{gi}	Glass transition temperature for species i, °C.
V	Volume in liters, unless otherwise defined.
V_f	Fractional free volume.
V_{fcr2}	Critical fractional free volume for glassy effect.

V_{feq}	Fractional free volume at equilibrium conditions.
V_{fo}	Initial fractional free volume (at zero conversion).
V_i	Volume of species i, liters.
V_o	Initial volume, liters.
V_t	Total volume, liters.
w_g	Instantaneous gel fraction.
$\overline{w}_g$	Accumulated gel fraction.
w_s	Instantaneous sol fraction.
$\overline{w}_s$	Accumulated sol fraction.
x	Total molar monomer conversion.
y_o	Normalized zeroth moment of the polymeric radical distribution
Y_o	Zeroth moment of the polymeric radical distribution, mol/l.
y_1	Normalized first moment of the polymeric radical distribution.
Y_1	First moment of the polymeric radical distribution, mol/l.
y_2	Normalized second moment of the polymeric radical distribution.
Y_2	Second moment of the polymeric radical distribution, mol/l.
Z	Inhibitor.
[Z]	Inhibitor concentration, mol/l.
$[Z]_o$	Initial inhibitor concentration, mol/l.

Greek Letters

α_i	Expansion coefficient for species i, 1/°C.
β	Ratio of termination by combination rate to propagation rate.
δ	Excess free volume coefficient in the single parameter model.
δ'	Proportionality constant for free volume generation term in the three parameter model.
ϵ	Volume contraction factor.
$\overline{\rho}$	Accumulated crosslinking density.
$\overline{\rho}_a$	Additional crosslinking density.
$\overline{\rho}_c$	Cyclization density (primary + secondary).
$\overline{\rho}_{cp}$	Primary cyclization density.
$\overline{\rho}_{cs,a}$	Additional secondary cyclization density.
$\overline{\rho}_i$	Instantaneous crosslinking density.
ρ_m	Monomer density, g/cm^3.
ρ_p	Polymer density, g/cm^3.

τ	Ratio of chain transfer and inhibition rates to propagation rate, or relaxation time (in seconds) in the three parameter model for free volume.
τ_0	Reference relaxation time, seconds.
$\phi^{\bullet}_{i}$	Mol fraction of radical type i (i= 1, 2 or 3).

CHAPTER 1

GENERAL INTRODUCTION

BACKGROUND AND OVERVIEW

Polymers have been known and used for several hundred years. The first sources of polymers known by men were natural resins obtained from certain trees. As time elapsed, these polymers had to be modified in order to diversify their use. Semi-synthetic polymers had been born. The first semi-synthetic material, vulcanized rubber, was discovered by Charles Goodyear in 1838. In 1900, Dr. L.H. Baekelan discovered bakelite, the first synthetic material, which was produced when phenol and formaldehyde were combined. During the twentieth century the polymer industry has grown tremendously. Traditional materials such as glass, wood and many metals have been displaced by polymers in many applications [1].

Despite the criticism from environmentalists, the worldwide production of synthetic polymers continues to grow. Polymer waste has become an urgent topic for industry, providing new and challenging areas for research and development on recycling, reuse and degradation. The technical principles of polymer reaction engineering will no doubt play a significant role in the solution of some of these problems [2].

Every professional in the polymer industry, and more generally in the chemical industry, has a high degree of complicity and moral responsibility for the proper (or improper) and rational (or irrational) way in which natural resources are transformed and the effects these transformation processes have on nature (human and non-human lives, as well as the environment). Therefore, no matter what our activities are (synthesis, design, operation, optimization, control, etc.) or where they are being developed (industry, government or academia), there is a great responsibilty that must be faced and undertaken carefully.

Since 1980, modelling of polymerization reactors has become more comprehensive. Interest has focused on the prediction of polymer properties (chemical composition and molecular mass distribution, long-chain branching, cross-link density, polymer particle size distribution and particle morphology). To develop a predictive model, account must be taken of the chemistry and physics of all of the relevant microscopic processes which occur in the polymerization process. Detailed physical property and thermodynamic data on the partitioning of species among phases is required to quantitatively calculate the concentrations of reactants at the loci of polymerization [2].

The free radical copolymerization of vinyl and divinyl monomers, and in general any kind of (co)polymerization leading to a polymer network, is important in technology, medicine, biotechnology, and agriculture (as construction materials, polymer glasses with high mechanical strength and high thermal stability, rubbers, ion-exchange resins and sorbents, immobilizing media for the stabilization of natural and synthetic catalysts, insoluble polymer reagents which are used, for instance, in peptide synthesis, therapeutic preparations based on modified enzymes, hydrogels with a high degree of swelling, etc.). On the other hand, crosslinked polymer systems serve to develop new promising trends in the investigation of chemical, physical, physicochemical, and mechanical properties of polymers [3].

The use of the terms vinyl and divinyl here is not according to their strict definitions. Here, a vinyl monomer is defined as a monomer with a single reactive double bond (a double bond which will readily add to a radical center) and a divinyl monomer is a monomer which has two such double bonds [2].

The main features of the topological structure of crosslinked polymers are related to the number of crosslinking bridges (or crosslinkages) , their structure, arrangement (between the units of one polymer chain or between different chains), the size of rings which they close, and the distribution of fragments of different types in the polymer system. Hence, it is of particular interest to study the molecular mechanisms for the formation of crosslinking bridges, to investigate the factors affecting the formation of the topological structure of crosslinked polymers when different methods of preparation are used, and to develop new paths and procedures for their synthesis that make it possible to control the structure of the polymer system [3].

Two main groups of methods are used for the preparation of polymer systems with covalent bridge bonds: a) the synthesis of crosslinked polymers from low molecular weight compounds (on the basis of copolymerization or copolycondensation with the participation of polyfunctional compounds), and b) crosslinking of linear polymer chains [3]. In this thesis only free radical copolymerization of mono- and divinyl compounds will be considered.

The experimental investigation of the formation and structure of insoluble crosslinked polymers is a very complex problem. Once the system has reached the insoluble state, the application of many analytical methods becomes impossible. The use of some experimental methods applied to the study of polymers in the solid state is complicated, and the interpretation of data obtained with their aid is difficult. The analysis of some parameters of the topological structure of insoluble crosslinked polymers based on the relationships between certain physical properties and structural characteristics of these systems (e.g., on the basis of the dependence of the degree of swelling on the density of junctions of ideal systems proposed by Flory) is of an approximate, tentative character. Certain information about the structure of the crosslinked polymer may be obtained if the polymer system is investigated in that stage of formation when not all of the polymer has passed into the insoluble state. In fact, the quantity of the soluble polymer part (sol fraction) in a certain reaction stage and its structure (which may be studied by various analytical methods for polymer solution properties) are related to the peculiarities of a given process of the formation of a crosslinked polymer. However, the quantitative isolation of the sol fraction with the retention of a fixed degree of transformation of functional groups is a relatively complex problem. Any conclusion about the structure of the insoluble part of the polymer system (gel fraction) on the basis of an analysis of the sol fraction is usually not sufficiently rigorous. The investigation of the reactions of bridge bond formation on the level of completely soluble polymer systems (usually used to study these complex systems) also involves some experimental difficulties. One of the main difficulties is that the formation of the insoluble fraction in a polymer system is probably already proceeding when the content of interchain crosslinking bridges is still very low and comparable to that of linear components in the polymer being formed. Hence, in order to obtain direct quantitative information about the formation process of soluble polymer structures with bridge bonds and the relationships to the formation of crosslinking bonds, it is necessary to develop and apply special samples and highly sensitive methods of investigation [3].

The copolymerization of mono- and divinyl (or polyvinyl) monomers is a traditional method for the preparation of crosslinked polymers. The formation of each crosslinking bridge results from two succesive reactions, as show in Figure A [3]:

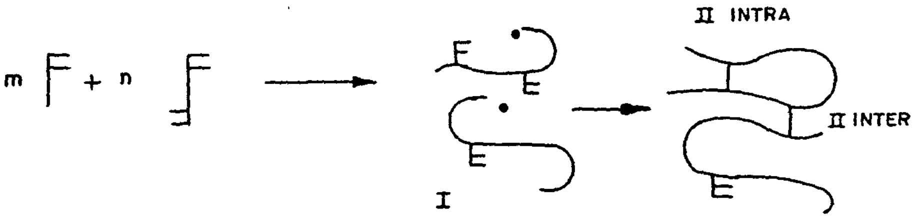

Figure A. Schematic representation of intra- and interchain reactions.

First, the interaction of the growing macroradical with one of the vinyl groups of the divinyl monomer gives a growing chain with a "pendant" vinyl group (structure I in Figure A). Then the reaction of I with the active end of "its own" or "foreign" growing chain leads to the formation of a bridge bond (intrachain bond of the type II_{intra} or interchain bond of the type II_{inter}, respectively). The features of this process indicate that the character of crosslinking bond distribution in the resulting polymer system is determined to a considerable extent by the first of the two successive reactions, i.e., it depends on the distribution of structures of type I. The degree of competition of the second reaction determines the quantitative ratio of structures I to II in the polymer, and its direction determines the fractions of intra- and interchain crosslinks (cyclization and crosslinking densities, respectively) in the total number of crosslinking bridges ($II_{intra} + II_{inter}$). Since under the usual conditions of free radical polymerization it is almost never possible to involve all double bonds (I) linked to polymer chains into the reaction, the structure of the polymer formed in the copolymerization may be represented by the structure shown in Figure A.

Hence, the molecular-topological structure of the crosslinked (co)polymer depends on the number of crosslinking bridges (II) and "pendant" double bonds (I), the ratio of intra- and interchain crosslinks (II_{intra} and II_{inter}) and their distribution in the polymer, as well as on the molecular weight characteristics of linear chains bonded by bridges into a single polymer system. The determination of the parameters that characterize the molecular-topological structure of crosslinked polymers is a very important problem because many properties of crosslinked polymers depend on them. The peculiarities of the molecular-topological structure of crosslinked polymers are related to the chemical structure of initial monomers, their ratio, and the copolymerization conditions (monomer conversion, the concentration and thermodynamic quality of the solvent, and initiator concentration) [3].

The parameters of the molecular-topological structure of the crosslinked polymer (number and distribution of interchain crosslinking bridges and molecular weight characteristics of linear components) also determine other important properties of crosslinked copolymers, such as solubility. According to this property, the formation of the insoluble crosslinked polymer may be divided into two stages. In the first stage, a soluble polymer is formed. It contains pendant vinyl groups and a certain number of crosslinking bridges (of the II_{intra} and II_{inter} types). Then, with an increasing number of II_{inter} in the reaction system, an insoluble polymer network is formed. The moment of the appearance of the insoluble fraction (gel fraction) is usually characterized by the corresponding conversion (gel formation point) or the reaction time during which this conversion is attained (gelation time).

Determination of all the parameters that characterize the molecular-topological structure of an insoluble crosslinked polymer is a very complex experimental problem that has not yet been solved. By using direct methods it was possible to determine only some characteristics, such as the molecular weight of the linear components of the crosslinked polymer and the content of pendant double bonds. Hence, investigation of the formation process and the main features of the topological structure of the crosslinked polymer in the pre-gel stage, in which the polymer system is still completely soluble, is of particular interest. However, in the copolymerization of mono- and divinyl monomers, the insoluble fraction is already formed when the content of crosslinking bridges is very small. In the most common case, the gelation moment shifts toward higher conversions (or is not observed at all) both when the number of effective interchain crosslinks decreases and when the molecular weight of the linear components decreases. Hence, in order to study the formation of a soluble polymer with bridge bonds, methodological approaches (or their combinations) are used that make it possible to decrease the content of interchain bridges and/or to decrease the molecular weight of linear components [3].

A direct result of the diffusion-controlled reactions (termination, propagation and even initiation) in crosslinking systems is the enhanced auto-acceleration in polymerization rate. The "gel" effect (Trommsdorff effect) due to physical entanglement of polymer chains is coupled with the gelation effect due to chemical crosslinking (and cyclization). With a high level of divinyl monomer, auto-acceleration can start at the very beginning of polymerization in almost pure monomer. When a three dimensional network is formed, those reacting species chemically bound to network structures such as pendant double bonds and free radical centres have extremely small diffusion coefficients. The so-called "shielding" effect can significantly suppress their reactivities to such an extent that they may be considered actually trapped. The trapping phenomenon strongly affects polymerization kinetics, and the latter is mainly responsible for the build-up of polymer chain structures affecting, in turn, the polymer properties [4].

It has been widely accepted that the diffusional limitations in most of the kinetic rate constants for elementary reactions in free radical polymerizations with crosslinking are not really constant (i.e., only temperature dependent) and may change by several orders of magnitude during the course of polymerization. These rate constants are the basis for the prediction of reaction behavior and polymer chain properties [4].

As a result of the comprehensive study on the mechanisms and kinetics of free radical polymerization with crosslinking launched by the "McMaster Institute for Polymer Production Technology" (MIPPT), aimed at providing a better understanding of the molecular processes involved in polymer network formation for better control of network structures, two detailed and excellent treatments were developed [4,5]. With these theoretical and experimental kinetic modelling studies, adequate prediction of trends and main features taking place in vinyl/divinyl copolymerization systems were possible to obtain. However, although theoretically meaningful, those models were not useful to perform practical calculations with adequate predictive power. A natural next step was missing. The present research was designed to fulfil and complement that previous work.

OBJECTIVES OF THE RESEARCH

The main goal of this Master of Engineering Thesis is to develop and test an effective model for free radical copolymerization kinetics of vinyl/divinyl monomers. "Effectiveness" is understood as a compromise between simplicity and sound theoretical background. The measure of this effectiveness will be the adequacy of the model to predict the behavior of actual systems under a wide variation of conditions, inside and outside the range of variation of conditions used in the parameter estimation stage.

To accomplish our goal, several secondary objectives were established:

1) Perform a comprehensive and critical review of existent theoretical models.

2) Select, modify or propose specific models for the main phenomena associated to this kind of copolymerization (diffusion-controlled initiation, propagation and termination, as well as primary and secondary cyclization reactions).

3) Develop a computer program for solution of the model equations.

4) Estimate all parameters needed in the model, using statistically acceptable techniques and proper experimental information.

5) Test the performance and effectiveness of the model, using experimental conditions inside and outside the experimental range used in the parameter estimation stage.

For each one of the previous objectives a series of specific activities were established. An overall Project Timing Chart was defined and the planned activities and times for their execution were followed as close to as possible (changes of activities, scope of the thesis and delays were detected early, so that adequate measures were taken, when needed, without affecting the overall goal of the thesis).

OUTLINE OF THE THESIS

This thesis is integrated by two general research projects which were written to be published in a journal ("Polymer Reaction Engineering"). Therefore, each project has its own structure, objectives and conclusions. However, they are interlinked (one is the detailed derivation of important models used in the second). This is further clarified below.

Chapter 1 offers the definition and physical-theoretical context of the system being studied (free radical copolymerization of styrene/divinylbenzene). It therefore gives a physical picture of the system and emphasizes the challenges and present situation of the experimental and theoretical analysis of such system. The main goal of the Thesis and particular objectives aimed at accomplishing that goal are defined. The structure of the thesis is also given in this chapter.

Chapter 2 is devoted to the derivation of effective models for calculation of diffusion-controlled elementary reactions (termination, propagation and initiation). To build these models a comprehensive and objective analysis of the two most popular models available in the literature is undertaken. Important theoretical results are obtained from this comparison and a new model, more powerful and simpler than those analysed, is proposed and extensively tested using bulk and solution styrene homopolymerization data. This chapter is presented as it was submitted to "Polymer Reaction Engineering". In the preparation of this paper the specific contributions of each author are detailed below (in partial fulfilment of the School of Graduate Studies requirements for this kind of Thesis format, namely compilation of technical papers written as result of the M.Eng. research project):

2.a) **Mr. E. Vivaldo-Lima** selected the models to be analysed, performed their theoretical and performance comparison and proposed that the "parallel" approach, widely used in modelling effective kinetic constants in this context, is inadequate. He also developed and tested the new model. The computer programs for simulation and non-linear regression were designed, coded and tested by him.

2.b) **Dr. A.E. Hamielec** suggested doing the theoretical comparison of the models, once the performance behavior had shown that one of the selected models was wrong. In building the new model, some of the most important concepts that the model should consider were suggested by him (such as considering initiation as diffusion-controlled, using different termination kinetic constant averages for calculation of different molecular weight averages and including in the model the concept of non-equilibrium free volume). Important experimental conditions which should be used to test the model were also suggested by him.

2.c) **Dr. P.E. Wood** provided important information on further application of the model (concerning calculation of the particle size distribution of monomer/polymer droplets in suspension polymerization), gave important comments and suggestions about the numerical aspects of the problem and provided the computer facilities which were used to speed up the calculations.

In **Chapter 3**, the diffusion-controlled models for termination, propagation and initiation are extended to the copolymerization case by using the "pseudo-kinetic rate constant method". Detailed general reaction scheme and model equations for the copolymerization case are given in this chapter. The important issues considered in this general model (initiation, inhibition, propagation, termination, chain transfer to monomer, chain transfer to polymer, chain transfer to a small molecule (either solvent or a chain transfer agent), crosslinking, primary and secondary cyclization reactions), as well as its features and limitations are explained. Extensive testing of the model performance is undertaken using experimental data from different sources available in the literature. This chapter constitutes a second paper also submitted to "Polymer Reaction Engineering". The specific contributions of each author are:

3.a) **Mr. E. Vivaldo-Lima** selected the models to be used, either from previous research studies or models derived in this work, compiled and selected the experimental information to be used (to take advantage of several sources of experimental information, the model had to be enriched), designed, coded and tested a program for simulation and non-linear regression estimation purposes (in fact, this program is the same as the one used in Chapter 2; the only difference is the data given as input).

3.b) **Dr. A.E. Hamielec** gave very important recommendations during the developing stage of the model, such as calculating the temperature rise during and after gelation (non-isothermal behavior), eliminating the steady state hypothesis (SSH) for calculation of the moment equations. The appendices presented in this paper were written on recommendation from him, in order to indicate the way in which the present model can be improved.

3.c) **Dr. P.E. Wood** gave recommendations on the numerical problems faced during the non-transient calculations and provided the computer facilities to speed up the calculations. In this case (non-transient calculations), these facilities were of paramount importance.

Figure B shows the sequence followed to accomplish the main goal of this thesis.

Chapter 4 contains a summary of contributions and concepts derived from or used in this thesis. Guidelines on the way our kinetic models can be improved or further tested are offered in this chapter.

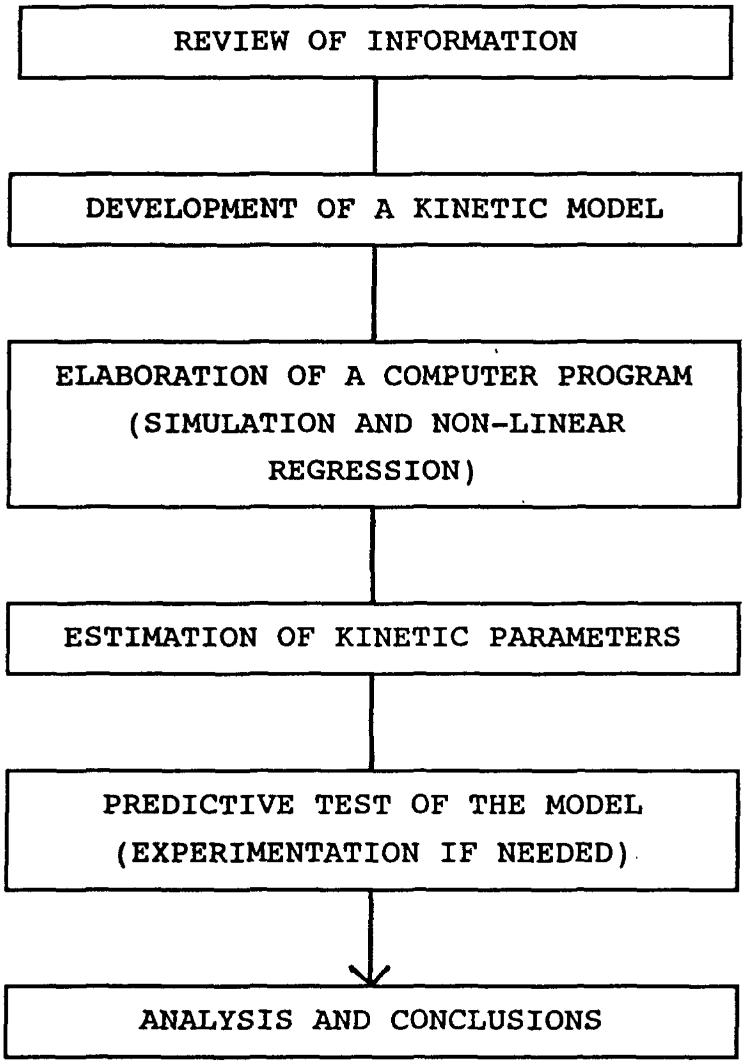

Figure B. Sequence followed to accomplish the objectives of this thesis.

CHAPTER 2

AUTO-ACCELERATION EFFECT IN FREE RADICAL POLYMERIZATION. A COMPARISON OF THE CCS AND MH MODELS.*

ABSTRACT

A comparison of the structure and performance behavior of two popular models for modelling diffusion-controlled kinetics in free radical polymerization (the so called Chiu-Carratt-Soong, CCS, and Marten-Hamielec, MH, models) is presented. It is demonstrated that if some minor modifications are made to each of them, they can be considered equivalent. Taking the best of both models and incorporating into them some of the most recent findings in this area, a new model is developed. This new model has at most the same degree of complexity as the preceding models, but is capable of producing more accurate and reliable predictions, even for weight average molecular weight at high conversions. Bulk and solution styrene polymerization data are used to make the comparison analysis and test the predictive power of the new model, which is remarkable.

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* This paper is dedicated to the late Mr. **Fernando Estrada-González**, a brilliant student, professor and professional of the chemical field. Not only an excellent friend is missing, but a very promising and talented Mexican scientist. "Descanse en Paz". -EVL.

INTRODUCTION

Accurate and theoretically correct modelling of diffusion-controlled free radical polymerization and copolymerization kinetics has been the ultimate goal of many research groups for several decades. A good and complete review on this research effort was published by Mita and Horie (1987). More recent publications have also included short reviews, classification, analysis of existent or proposal of new models (Sharma and Soane, 1988; Russell et. al., 1988; Achilias and Kiparissides, 1988, 1992a; Zhu and Hamielec, 1989; Zhu, 1991; Russell et. al., 1992). Other approaches not mentioned in the previous reviews include calculation of the (number) average translational termination kinetic constant as a semiempirical function depending on the system viscosity (Veeravalli and Rosen, 1990; Budde and Wulkow, 1991; Mahabadi, 1991), calculation of such an average kinetic constant based on the concepts of lumped polymer chain groups (Chaimberg and Cohen, 1990) and "group termination coefficient" (Bamford, 1989, 1990). The importance of this topic and the growing contradiction or uncertainty on reported results of kinetic parameters, among other factors, motivated a group of prominent researchers in this field to meet together and establish firm and agreed values and methods for fundamental rate parameters in free radical polymerizations and critically examine important mechanisms. Some guidelines and recommendations came out as a result (Buback et. al., 1988; Buback et. al., 1992; Gilbert, 1992).

Despite this great and continuous effort, which has led to deeper and increased understanding of the complex physical phenomena taking place in such polymerizations, no further practical improvement has been obtained over the predictive power, reliability of predictions and robustness of parameter estimates of the pioneer empirical or semiempirical models.

The core task of modelling the kinetics of free-radical polymerization with strong auto-acceleration is to quantitatively describe the molecular processes in the bimolecular termination of polymer radicals. Many approaches have been attempted over the past four decades. The efforts concentrated mainly on modelling the segmental diffusion of radical centers, the onset of chain entanglement, the chain length dependent translational diffusion and the diffusion of radical centers by propagation (Zhu, 1991). Most models have focused on describing the translational diffusion, which is considered to be responsible for the auto-acceleration. Several of these models have also considered the diffusion controlled propagation at very high conversions. Recently, some researchers have also modelled the diffusion controlled initiation reaction (Batch and Macosko, 1992; Achilias and Kiparissides, 1992a).

Most kinetic models for diffusion controlled polymerization can be considered to fall into either of the following three categories, regardless of their theoretical background: i) models based on the so called "free-volume theory", ii) models based on scaling laws ("Reptation Theory") and iii) fully empirical models. Among the models based on free volume theory, two of them have been quite popular due to their simplicity and predictive performance when used to model typical polymerization or copolymerization systems. These models are the so called "Marten-Hamielec", MH, (Marten and Hamielec, 1979, 1982) and the "Chiu-Carratt-Soong", CCS

(Chiu et. al., 1983). A recent enhancement of the CCS model has been performed by Achilias and Kiparissides (1988, 1992a). The MH model has been quite successful over the years due to its good performance in the simulation of a diversity of polymerization systems, such as MMA bulk and solution polymerizations (Marten and Hamielec, 1979; Stickler et. al., 1984), MMA polymerization in the presence of prepolymer (Panke, 1986); styrene bulk and solution homopolymerizations (Marten and Hamielec, 1982), vinyl chloride polymerization (Hamielec et. al., 1982; Xie et. al., 1991), MMA/P-methyl styrene copolymerization (Jones et. al., 1986; Bhattacharya and Hamielec, 1986), styrene/acrylonitrile copolymerization (García-Rubio et. al., 1985), P-methyl styrene/acrylonitrile copolymerization (Yaraskavitch et. al., 1987), styrene homopolymerization using bifunctional initiators (Villalobos et. al., 1991) and production of high Tg copolymers of styrene using bifunctional initiators (Villalobos et. al., 1993). On the other hand, the CCS model has been used to model MMA bulk homopolymerization (Chiu et. al., 1983), MMA solution homopolymerization (Louie et. al., 1985), styrene/MMA bulk copolymerization (Sharma and Soane, 1988), styrene bulk homopolymerization (Vivaldo-Lima, 1989a; Vivaldo-Lima and Saldivar-Guerra, 1993), styrene bulk homopolymerization using a "cocktail" (mixture) of initiators (Vivaldo-Lima, 1989b). In its improved version (which will be referred as the AK model), the CCS model has been used to model MMA and styrene bulk homopolymerizations (Achilias and Kiparissides, 1988, 1992a). Nevertheless, both models underpredict the weight average molecular weight at high conversions. The CCS model does not provide very good predictions of solution homopolymerization (see the predicted profiles of MMA solution homopolymerization in Louie et. al., 1985) and its reliability for interpolation and extrapolation calculations is not satisfactory when a mixture of initiators and different isothermal periods are used in a styrene homopolymerization system (Vivaldo-Lima, 1989b).

The ultimate goal of this paper is to develop accurate and simple models for diffusion-controlled phenomena in free-radical polymerization, which can be extended to model copolymerization with crosslinking. The development of such models and their test for modelling homopolymerizations is the scope of the present paper. Their extension to model vinyl-monomer/divinyl-monomer copolymerizations (styrene/divinylbenzene copolymerization) is the scope of another publication (Vivaldo-Lima et. al., 1993). The main features these models were expected to posses included a simple structure, reliable and robust parameters, as well as a sound theoretical background. To achieve this goal a evaluation of the structure and performance of two of the most popular models available in the literature was performed. This analysis led us to the conclusion that the "parallel approach" for calculation of effective diffusion-controlled kinetic constants, although mathematically attractive, may not be physically correct. This "parallel approach" was used by Chiu and coworkers (1983) and has also been used by other authors (Sharma and Soane, 1988; Achilias and Kiparissides, 1988, 1992a; Buback, 1990; Zhu and Hamielec, 1989; Simon and Gillham, 1992; Hutchinson, 1993) and it is even accepted by the International Union of Pure and Applied Chemistry (IUPAC) (Gilbert, 1992). Based on the MH model, a new model was developed. This new model avoids the use of "artificial" onset points, thus having the same attractiveness the CCS model has been famous for; it considers diffusion controlled phenomena in the termination, propagation and initiation reactions; it makes a clear and quantitative difference between number and weight average termination constants (Zhu and Hamielec, 1989) and the concept of non-equilibrium free volume is also incorporated into it, although no attempt was made to estimate the parameters associated with the non-equilibrium free volume model.

To test the performance and reliability of the present model, experimental data for bulk and solution styrene homopolymerization available in the literature from different sources were used. Further testing of the model with more experimental evidence on styrene/divinylbenzene copolymerization data was also undertaken (Vivaldo-Lima et. al., 1993).

COMPARISON OF THE STRUCTURE OF THE CCS AND MH MODELS

Reaction Scheme

In the paper on kinetic modelling of styrene /divinylbenzene free-radical copolymerization (Vivaldo-Lima et. al., 1993), a detailed reaction scheme and associated mathematical equations are given. In that treatment, initiation, inhibition, propagation, crosslinking, transfer to a small molecule (either solvent or transfer agent) and bimolecular termination reactions are considered. The mathematical treatment given there makes use of the "pseudo-kinetic" rate constant method, developed by Hamielec and MacGregor (1983). Using the adequate initial conditions, those equations and the computer program developed to solve them can be used to model the homopolymerization case. For the purposes of this paper, our attention will be focused on initiation, propagation, transfer to solvent, transfer to a monomer and termination reactions. These chemical reactions are given below in the form of equations (1) through (5). The mathematical equations for reaction rate of the different species and the moment equations for polymer radicals and dead polymer molecules can be taken from Vivaldo-Lima et. al. (1993). Indeed, the expressions that result for the homopolymerization case have been described extensively in the literature (for instance, see Marten and Hamielec, 1979, 1982; Chiu et. al., 1983; Vivaldo-Lima and Saldivar, 1993). It should be emphasized, however, that those equations make use of the "Method of Moments" (Ray, 1971) for calculation of the chain length averages. Most of our calculations were obtained using this method. Nevertheless, in modelling homopolymerizations it is possible to obtain the full molecular weight (chain length) distribution by using the "Instantaneous Property Method" (Flory, 1953; Bamford et. al., 1958). In the cases where the full chain length distribution is presented, the instantaneous property method was used to obtain them. This method can be represented by equations (6) through (12). A good review of the comparison and analysis of the different methods to model molecular weight and compositional changes in free-radical copolymerization reactions was recently presented by Achilias and Kiparissides (1992b).

Initiation (k_d):

$$\begin{aligned} &I \rightarrow 2R^{\bullet}_{in} \\ &R^{\bullet}_{in} + M \rightarrow R^{\bullet}_{1} \end{aligned} \tag{1}$$

Propagation (k_p):

$$R^{\bullet}_{m} + M \rightarrow R^{\bullet}_{m+1} \tag{2}$$

Transfer to monomer (k_{fm}):

$$R^{\bullet}_{m} + M \rightarrow P_m + R^{\bullet}_{1} \tag{3}$$

Transfer to a small molecule (solvent) (k_{fT}):

$$R^{\bullet}_{m} + T \rightarrow P_m + T^{\bullet} \tag{4}$$

Termination by combination and disproportionation (k_{tc}, k_{td}):

$$\begin{aligned} &R^{\bullet}_{m} + R^{\bullet}_{n} \rightarrow P_{m+n} \\ &R^{\bullet}_{m} + R^{\bullet}_{n} \rightarrow P_m + P_n \end{aligned} \tag{5}$$

Chain Length calculations with the "Instantaneous Property Method" (IPM):

$$\frac{d[x\overline{w}(r,x)]}{dt} = w(r,x)\,\frac{dx}{dt} \tag{6}$$

$$\frac{d(x\overline{P}_n)}{dt} = (\overline{P}_n - \frac{\overline{P}^2_n}{P_n})\,\frac{dx}{dt} \tag{7}$$

$$\frac{d(x\overline{P}_w)}{dt} = P_w\frac{dx}{dt} \tag{8}$$

where

$$P_n = \frac{1}{\tau_n + \frac{1}{2}\beta_n} \tag{9}$$

$$P_w = \frac{2(\tau_w + 3\beta_w)}{(\tau_w + \beta_w)^2} \tag{10}$$

$$\overline{P}_n = \frac{X}{\int_0^x \frac{dx}{P_n}} \tag{11}$$

$$\overline{P}_w = \frac{1}{X}\int_0^x P_w dx \tag{12}$$

τ_i and β_i are defined by equations (73) and (74), respectively and the remaining symbols are defined in the nomenclature.

The CCS Models

The original Chiu-Carratt-Soong model (Chiu et. al., 1983) allowed the calculation of (number average) propagation and termination kinetic constants for diffusion controlled bulk free-radical homopolymerization. Both propagation and termination were considered to be diffusion controlled from the start of the polymerization and were modelled as a "parallel phenomenon", that is, the effective kinetic constant (either propagation or termination) was proposed to be calculated as the inverse of the sum of inverse-diffusional and inverse-chemical kinetic constants.

Equations (13) and (14) show the expressions they obtained to calculate k_p and k_t, respectively.

$$\frac{1}{k_p(T)} = \frac{1}{k_p^o(T)} + \theta_p(T) \frac{Y_0}{e^{\left[\frac{2.3\phi_m}{A(T)+B(T)\phi_m}\right]}} \qquad (13)$$

$$\frac{1}{k_t(T)} = \frac{1}{k_t^o(T)} + \theta_t(T, I_0) \frac{Y_0}{e^{\left[\frac{2.3\phi_m}{A(T)+B(T)\phi_m}\right]}} \qquad (14)$$

where ϕ_m is the monomer volume fraction. The other symbols are explained in the nomenclature.

To model solution polymerization, ϕ_m in equations (13) and (14) must be replaced by $(1-\phi_p)$, where ϕ_p is the polymer volume fraction (Louie et. al., 1985).

Using the generalized free volume theory of Vrentas and Duda (1977a, 1977b) and the theory of excess chain end mobility, Achilias and Kiparissides (1988) enhanced the original CCS model. In this way, parameters A(T), B(T), θ_p and θ_t in the CCS model were given theoretical meaning, which is described by equations (15) through (18).

$$A(T) = \frac{\xi \hat{V}_m^o \hat{V}_p^{\,*} V_{fp}^2}{\gamma \hat{V}_m^{\,*} \hat{V}_p^o (V_{fm}\xi - V_{fp})} \qquad (15)$$

$$B(T)=\frac{V_{fp}\xi\left(\hat{V}_m^{*}V_{fm}-\hat{V}_p^{*}V_{fp}\frac{\hat{V}_m^{o}}{\hat{V}_p^{o}}\right)}{\gamma\hat{V}_m^{*}\left(\xi V_{fm}-V_{fp}\right)} \tag{16}$$

$$\theta_p(T)=\frac{(r_m'^{2})\,e^{\frac{E_m}{RT}}}{3D_{mo}} \tag{17}$$

$$\theta_t(T,I_o)=\frac{(r_m^{2})\,(\overline{P}_n^{\,2})\,e^{\frac{E_p}{RT}}}{3D_{po}} \tag{18}$$

Some years later these same authors (Achilias and Kiparissides, 1992a) included the effect of diffusion controlled initiation by considering that the efficiency of the initiator falls as polymerization proceeds with a free volume dependence. They also included the "residual termination" or "reaction diffusion" termination in their model. The final model equations they obtained are summarised below.

Initiation

$$\frac{1}{f}=\frac{1}{f_0}+\frac{\tau_{DI}}{f_0\tau_{RI}} \tag{19}$$

where

$$\tau_{DI}=\frac{r_2^3}{3r_1D_I} \tag{20}$$

$$\tau_{RI}=\frac{1}{k_{i0}[M]} \tag{21}$$

$$D_I=D_{I0}e^{-\frac{\gamma\hat{V}_I^{*}M_{jI}}{\hat{V}_f}\left[\frac{\omega_m}{M_{jm}}+\frac{\omega_p}{M_{jp}}\right]} \tag{22}$$

$$\hat{V}_f=\omega_m\hat{V}_m^{*}V_{fm}+\omega_p\hat{V}_p^{*}V_{fp} \tag{23}$$

$$r_1=\sqrt[3]{\frac{6V_m}{\pi N_A}} \tag{24}$$

$$r_2=2(R_H)_0 \tag{25}$$

Termination

$$\frac{1}{k_t}=\frac{1}{k_{t0}}+\tau_{Dt}Y_0 \tag{26}$$

where

$$\tau_{Dt}=\frac{r_t^2}{D_{pe}} \tag{27}$$

$$r_t=\frac{\sqrt{\ln\left(\frac{1000\tau^3}{N_A Y_0\pi^{3/2}}\right)}}{\tau} \tag{28}$$

$$\tau=\sqrt{\frac{3}{2j_c\delta^2}} \tag{29}$$

$$\frac{1}{j_c}=\frac{1}{j_{c0}}+\frac{2\varphi_p}{X_{c0}} \qquad (30)$$

$$D_{pe}=F_{seg}D_p \qquad (31)$$

$$D_p=D_p'\left(\frac{P_w'^2}{P_w^2}\right)e^{-\left(\frac{\gamma}{\xi_{13}}\frac{\omega_m\vartheta_m^*+\omega_p\vartheta_p^*\xi_{13}}{\vartheta_f}+\frac{1}{V_{fm}}\right)} \qquad (32)$$

$$D_p'=\frac{k_B T}{6\pi\eta_s R_H} \qquad (33)$$

$$F_{seg}=\frac{r_e^3[\pi r_e+6\sqrt{2}\,a_{seg}r_B]}{16\pi r_B^4} \qquad (34)$$

$$k_{t,res}=C_{rd}k_p[M] \qquad (35)$$

$$C_{rd}=\frac{\pi N_A}{1500}(\sigma\delta^2+2\delta^3\sqrt{j_c}) \qquad (36)$$

$$\bar{k}_{tn}=k_t+k_{t,res} \qquad (37)$$

Propagation

$$\frac{1}{k_p}=\frac{1}{k_p^0}+\tau_{Dp}Y_0 \qquad (38)$$

$$\tau_{Dp}=\frac{r_m^2}{3D_m} \tag{39}$$

$$r_m \approx r_t \tag{40}$$

$$D_m=D_{m0}e^{-\frac{\gamma\hat{V}_m^*M_{jm}}{\hat{V}_f}\left(\frac{\omega_m}{M_{jm}}+\frac{\omega_p}{M_{jp}}\right)} \tag{41}$$

$$\xi_{13}=\frac{\hat{V}_m^*M_{jm}}{\hat{V}_p^*M_{jp}} \tag{42}$$

Some key points about the CCS and the AK models which should be kept in mind in order to understand the comparison to be made in the following section, are the following:

(a) In both models (CCS and AK) the effective kinetic constants for either propagation, termination or initiation **reactions** are calculated as the contribution of a **purely chemical** kinetic constant and a **purely diffusional** one. All their kinetic constants are modelled as indicated by equation (43).

$$\frac{1}{k_{eff\,i}}=\frac{1}{k_{chem\,i}}+\frac{1}{k_{diff\,i}} \tag{43}$$

where subscript "i" accounts for propagation, termination or initiation.

(b) Both models (CCS and AK) are in fact calculating the number average kinetic constant, in the case of termination.

(c) In the original CCS model, based on the Fujita-Doolittle free volume theory, the free volume parameters are estimated with the polymerization rate information. The AK model is based on the Vrentas-Duda free volume theory and it is claimed by its authors that their parameters can all be estimated from physical and transport properties of the monomer-polymer-initiator mixture.

The Marten-Hamielec (MH) Model.

Based on the Bueche free volume theory (Bueche, 1962), Marten and Hamielec (1979, 1982) developed a model for diffusion-controlled propagation and termination kinetic constants in free radical polymerizations. The (number average) termination kinetic constant was calculated as indicated by equation (44).

$$\bar{k}_{tn}=k_t^0\left(\frac{\bar{P}_{w,cr1}}{\bar{P}_w}\right)^n e^{-A_{MH}\left(\frac{1}{V_f}-\frac{1}{V_{f,cr1}}\right)} \tag{44}$$

where subscript "cr1" accounts for critical values for chain entanglement. At the "onset" of the auto-acceleration ("gel") effect, equation (45) must be satisfied.

$$K_3(T)=\bar{P}^m_{w,cr1}e^{\left(\frac{A_{MH}}{V_{f,cr1}}\right)} \tag{45}$$

When the polymerizing mixture approaches the glassy state, the propagation rate constant is described by equation (46).

$$k_p=k_p^0e^{-\left(\frac{1}{V_f}-\frac{1}{V_{f,cr2}}\right)} \tag{46}$$

where subscript "cr2" accounts for the critical value at which propagation becomes diffusion-controlled ("onset" of diffusion controlled propagation). A_{MH}, $V_{f,cr1}$, $V_{f,cr2}$, m and n are empirical parameters. m and n have been given values of 0.5 and 1.75, respectevely, for either styrene of MMA polymerizations (Marten and Hamielec, 1979, 1982). However, Panke (1986) found out that setting m= n= 0.5 gives equally good results, thus reducing the number of adjustable parameters.

As in the previous case, some key points about the MH model are given below in order to make clearer the subsequent comparison and analysis.

(i) The effective kinetic constants for either propagation or termination are caculated as composed functions, made up of the product of two functions. One function accounts for a chemical phenomenon and the other for a diffusional phenomenon. Equation (47) illustrates this structure.

$$\bar{k}_{tn} = g(chem.behavior) * h(phys.environment) \tag{47}$$

ii) It is the number average kinetic constant which is being calculated when equation (44) is used.

iii) The model is based on the Bueche free volume theory (Bueche, 1962). The model parameters have been usually obtained by performing non-linear regression methods with conversion/time data.

iv) Both k_p and k_{tn} are calculated using non-continuous functions. Therefore, "artificial onset" values are used to model such constants.

Structure of the models

In this section an objective comparison of the theoretical background , which serves as basis for each model, is presented. Although this paper was structured in such a way that the theoretical background is given prior to the performance analysis, the actual sequence followed in the research was somewhat different. Some of the ideas proposed in this paper came out as a result of having analysed preliminary predictions obtained with the CCS and the MH models. The AK model was tested at the end of the project in order to give support to or reject some of the conclusions that were obtained (actually, the last version of the AK model was published when this research was already under way).

The first thing one can observe when the CCS-AK and the MH models are compared, is the way in which chemical (reaction) and physical (diffusion) phenomena are coupled together. As stated in key-point (a) of the "CCS-family model" subsection, both the CCS and the AK models follow a "parallel" circuit-like approach, which is given by equation (43). On the other hand, the MH model has a structure given by equation (47), that is to say, the product of two independent functions. The use of equation (43) in the context of diffusion controlled free radical polymerization has been widely used and implicitly accepted by several researchers over the years. However, it may not be correct. To illustrate our point, think of a parallel pipeline circuit, as shown in Figure 2.1. For a liquid to flow from point A to point B, any path (either a or b) could be chosen. By opening or closing the valves, the flow could be divided or a single path could be chosen. Now, using the same figure, think of "A" as a reagent and "B" as a reaction product. Path "a" accounts for "diffusion" migration of the reagent and "b" accounts for the reaction event itself. There is no way a new radical (propagation reaction) or a "dead" polymer molecule (termination reaction) can be produced by just following path "a" (namely by a pure physical phenomenon). The only way a reaction can take place is if a chemical phenomenon occurs (valve for path "b" can not be "closed" in Figure 2.1). Of course, the physical environment will affect the kinetics (how long it takes for the reaction to occur). Thus, a "diffusion-controlled" reaction should be understood as a "retardation" in the reaction rate. It must be clear that by no means is it implied here that any effective kinetic constant obtained as the inverse of the sum of several reactions is not correct. If several reactions which consume the same species are taking place simultaneously, the parallel approach would be the natural and immediate approach to follow.

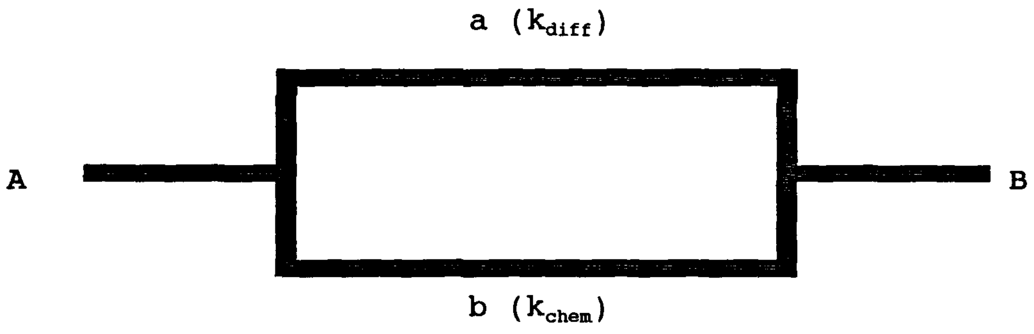

Figure 2.1. Schematic representation of a "parallel" situation.

As stated in Zhu and Hamielec (1989), the use of a single k_t in modelling free radical polymerizations would be valid if termination were chain length independent. Using such a single value in a real polymerization situation (where termination may be quite likely chain length dependent) will result in adequate predictions of reaction rate and number average chain length; however, weight average chain length and higher order averages will be underestimated. In this regard both models, the CCS-AK and the MH (as well as as all models based on the use of a single k_t function), are effectively using the **number average termination kinetic constant,** $\bar{k}_{tn}$. Therefore, if one desires to use a single k_t-function type of model for vinyl/divinyl copolymerizations, it will be anticipated that simultaneous adequate predictions of reaction rate and weight average chain length may not be possible to obtain.

Roughly speaking, the diffusion term of the models studied in this paper can be expressed as the product of two functions, one depending on average chain length and the other on free volume. This relationship is illustrated in equation (48).

$$k_{diff}=a(chain\text{-}length)\cdot b(free\text{-}volume) \tag{48}$$

In the original CCS model the chain length dependence function, a(chain-length), may not be obvious. Propagation is implicitly assumed to be chain length independent and termination is indirectly linked to average chain length through the use of constant θ_t, which depends on $[I]_0$. Changing the initiator initial concentration will somehow set the value of the number average chain length (for constant temperature) to a certain value. This dependence is clearer if equation (18), obtained by Achilias and Kiparissides (1988), is carefully studied. Then, for the CCS model,

$$a(chain\text{-}length) \propto \bar{P}_n^2 \tag{49}$$

In the AK model, initiation and propagation are modelled as chain length independent. Termination, on the other hand, is considered to depend on the instantaneous weight average chain length. From equations (31) to (34), this relationship can be expressed as indicated in equation (50).

$$a(chain\text{-}length) \propto \frac{(P_w^0)^{3.68}}{P_w^{2.56}} \tag{50}$$

In the case of the MH model, propagation is modelled as independent of average chain length and, according to equation (44), termination is considered to depend on the accumulated weight average chain length, as shown in equation (51).

$$a(chain\text{-}length) \propto \left(\frac{\bar{P}_{w,cr1}}{\bar{P}_w}\right)^{1.75} \tag{51}$$

The exponent "1.75" is the one originally proposed by Marten and Hamielec (1979, 1982). However, using "0.5" was found to be equally good (Panke, 1986).

As it was previously stated, the three models studied in this paper so far, are based on the concept of free volume. The three of them calculate "b(free-volume)" as a decaying exponential function. However this function is somehow different in each of them, depending on which free volume theory is being used.

The original CCS model is based on the "Fujita-Doolittle" free volume theory. Accordingly (Fujita, 1961), b(free-volume) is given by equation (52).

$$b(free\text{-}volume) \propto D_{0i} e^{-\frac{B_d}{V_f}} \tag{52}$$

where

$$V_{fi}(T) = V_{fi}(T_{ref}) + \alpha_{fi} \cdot (T - T_{ref}) \tag{53}$$

and B_d is a "free parameter" which may depend on the motional modes of segment "i" (where "i" can be polymer, monomer or solvent). However, Chiu and co-workers (1983) did not include explicit calculation of the fractional free volume in their model. Instead, they lumped all the free volume parameters (free volume at T_{ref}, T_{ref} itself, volumetric expansion coefficient, etc.) into constants A(T) and B(T). This is a serious limitation on the predictive power of the CCS model because any method of estimation of parameters, either statistical or empirical, would quite likely produce non reliable estimates of the parameters (highly correlated).

Achilias and Kiparissides (1988, 1992a) based their model on the Vrentas-Duda free volume theory. In their first version (1988), b(free-volume) was given by equation (54).

$$b(free\text{-}volume) \propto D_{i0} e^{\left(-\frac{E_i}{RT}\right)} e^{-\frac{\gamma}{\hat{V}_f}\left(\omega_m \hat{V}_m^{*} + \omega_p \hat{V}_p^{*} \xi\right)} \tag{54}$$

where

$$\hat{V}_f = \omega_m [K_{11}(K_{21} + T - T_{gm})] + \omega_p [K_{12}(K_{22} + T - T_{gp})] \tag{55}$$

In the last version of their model, Achilias and Kiparissides (1992a) used an expression similar to equation (54), but the energy term was not included (i.e. $E_i=0.0$, i=initiator, monomer, polymer). In equation (54), the term γ is an overlap factor which is introduced because the same free volume is available to more than one molecule.

The MH model is based on Bueche's free volume theory (Bueche, 1962). According to this theory, b(free-volume) is obtained as indicated in equation (56).

$$b(free\text{-}volume) \propto D_{10} e^{-\left(\frac{\beta^* V_f^*}{V_f}\right)} \tag{56}$$

where

$$\beta^* = \ln\left(\frac{V_f^*}{V_f}\right) - 1 \tag{57}$$

and V_f^* is the "critical amount of free volume" which must be associated to a molecule or segment in order for it to jump to a new position. Since this quantity is not well known, Bueche states that for many purposes β^* may be considered as unity (for "reasonable" values of the ratio V_f^*/V_f).

Even though the theoretical background may be different, it can be seen that the previous three free volume theories lead to very similar results (if not identical). Recently, there has been some controversy as to which theory is more general. For instance, Vrentas and Duda (1977a) have claimed that the Fujita theory is a particular case of theirs, a conclusion that was questioned by Fujita (1991) and defended by Vrentas et. al. (1993) and Vrentas and Vrentas (1993). In this study no attempt to find out which theory is more general will be made. For practical purposes the same results are obtained in a polymerization context (except, perhaps, in the CCS model where the Fujita theory was not fully incorporated into the model). The main difference among the theories in a polymerization context seems to be the physical meaning that different authors have given to the exponential parameter, which has been called an "overlap factor", "free parameter" to account for "motional mode" of segments or a parameter related to the "critical amount of free volume", the way this parameter is estimated (either arbitrary reasonable values, non-linear regression estimation or indirect calculation from initial or simplified conditions) and the way the other free volume parameters for each species (monomer, polymer and solvent) are estimated (usually through non-linear regression using diffusivity data).

A very important issue that none of the previous models takes into account, is the concept of excess in free volume, which leads to different limiting conversions depending on the initial amount of initiator (Stickler, 1983). The first kinetic model to include this effect, which becomes more important when crosslinking reactions take place, was developed by Bowman and Peppas (1991).

DEVELOPMENT OF A NEW MODEL

Based on the previous analysis, it may be concluded that none of the previous models possess all the desired characteristics mentioned in the introduction (accuracy, robustness of predictions in reference to the model parameters, simplicity and a sound theoretical background). The MH model provides robust predictions, but predictions of weight average chain length at high conversions are not accurate enough. Besides, it has been criticized for the "artificial" way in which it treats the autoacceleration effect. Neither the CCS nor the AK models can provide good predictions of weight average chain length at intermediate conversions. Moreover, the CCS model has been found to be inadequate to interpolate and extrapolate over the conditions used in the parameter estimation stage (Vivaldo-Lima, 1989a, 1989b) and the predictions of polymerization of MMA carried out in benzene solution are quite bad (Louie et. al., 1985). The AK model, although theoretically more sound than the CCS and the MH models, does not provide predictions accurate enough for bulk homopolymerization of styrene and its behavior to model solution homopolymerization has not been reported (as far as we know). Therefore, it seems necessary to either modify these models or propose a new one in order to accomplish our objectives. This section is devoted to obtaining such a new model (certainly building on the previous ones).

Let us consider two molecules, A and B, that diffuse through a polymeric solution until they are in close contact. Once they are close enough, they may react to form a new molecule, C, or they may diffuse apart. A and B could be a monomer molecule, an initiator fragment or a polymer radical. C could be a new radical of longer size or a dead polymer molecule. This situation can be represented by equation (58) (after Mita and Horie, 1987).

$$A+B \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} AB \rightarrow C \tag{58}$$

where k_D is the diffusion kinetic constant for the approach of the molecules, k_{-D} is the diffusion kinetic constant for separation of the molecules and the chemical kinetic constant for reaction between A and B to produce C is given by k_C. The reaction rate for the production of C will be given by equation (59).

$$\frac{dC}{dt} = k_C[AB] \tag{59}$$

Assuming equilibrium between attraction and separation of molecules A and B, equation (60) can be used.

$$k_D[A]\,[B] = k_{-D}[AB] \tag{60}$$

Combining equations (59) and (60) equation (61) is obtained.

$$\frac{dC}{dt} = k_C\frac{k_D}{k_{-D}}\,[A]\,[B] \tag{61}$$

Therefore, an effective kinetic constant which accounts for diffusion and chemical phenomena can be expressed as it is indicated in equation (62).

$$k_{eff} = k_C\frac{k_D}{k_{-D}} \tag{62}$$

which is of the form of equation (47). This indicates that simultaneous modelling of diffusion and reaction kinetic constants should be done in "series" and not in "parallel".

To calculate k_D the Smoluchowski equation can be used (Mita and Horie, 1987).

$$k_D = 4\pi R_B N_A D_B \tag{63}$$

Due to the fact that separation of the molecules is a diffusive phenomenon, it is reasonable to approximate k_{-D} using the Smoluchowski equation, as well.

$$k_{-D} = 4\pi R_B N_A D_{-B} \tag{64}$$

Substitution of equations (63) and (64) into equation (62) leads to equation (65).

$$k_{eff} = k_C \frac{D_B}{D_{-B}} \tag{65}$$

Now, let us analyse one by one the important diffusion-controlled reactions in free-radical polymerization, namely propagation, termination and initiation.

Propagation

According to the free-volume theory (Fujita, 1961; Bueche, 1962; Vrentas and Duda, 1977a, 1977b) the diffusion coefficient of a small molecule in a polymeric system depends on the free volume of the system, but not on the average chain length of the polymer. To simplify our derivation, let us make use of Bueche's free volume theory (Bueche, 1962), with a slight modification from the Vrentas-Duda (1977a, 1977b) theory to account for the activation energy required to overcome the attractive forces which hold the molecule to its neighbors (Vrentas and Duda, 1977a, 1977b). Then, the diffusion coefficient for approach of a monomer molecule to a polymer radical will be given by equation (66).

$$(D_m)_a=D_{m0}\left(e^{-\frac{E_{ma}}{RT}}\right)\left(e^{-\frac{B_a}{V_{fa}}}\right) \tag{66}$$

where the subscript "a" accounts for "approach" of the monomer molecule to the polymer radical. Similarly, the diffusion coefficient for separation of the monomer molecule from the polymer radical, provided that reaction has not occured, will be given by equation (67).

$$(D_m)_s=D_{m0}\left(e^{-\frac{E_{ms}}{RT}}\right)\left(e^{-\frac{B_s}{V_{fs}}}\right) \tag{67}$$

where subscript "s" accounts for "separation" of the monomer molecule. From equations (65), (66) and (67), the effective propagation kinetic constant will be given by equation (68).

$$k_p=k_p^0 e^{-\frac{(E_{ma}-E_{ms})}{RT}} e^{-\left(\frac{B_a}{V_{fa}}-\frac{B_s}{V_{fs}}\right)} \tag{68}$$

If it is assumed that the activation energy to overcome the attractive forces is the same for approach and separation of the molecules, namely $E_{ma}= E_{ms}$, then the energy term will cancel out in equation (68). An intuitively similar analysis would lead one to the conclusion that the free volume for approach should be the same as the free volume for separation. However, the "overlap" factors may not be the same. Therefore, equation (68) can be simplified to the following equation:

$$k_p=k_p^0 e^{-\frac{B}{V_f}} \tag{69}$$

where $B = B_a - B_s$, and accounts for the fact that the same free volume is available to different molecules and also for the fact that there are some molecules that will separate even when they are close enough to react.

In the following subsections it will be demonstrated that similar equations are obtained for termination and initiation. When non-linear regression methods are used to estimate the unknown parameters, some degree of correlation should be expected, resulting from the fact that they come from equations with similar structure that account for physical phenomena taking place simultaneously. Therefore, it was decided to modify equation (69) somewhat in order to get better estimates of the "overlap" factors for the other reactions. The proposed modification consisted in assuming that "B" in equation (69) can be set equal to one (Bueche, 1962) and a compensation was introduced using a "critical free volume for propagation". In other words, the original model for k_p proposed by Marten and Hamielec (1979, 1982), equation (46), was used in order to improve the reliability of the parameter estimates.

Termination

In the case of bimolecular termination, the diffusion coefficient of a polymer radical molecule has been proposed to depend on the average chain length of the polymer. Nevertheless, if an analysis similar to the one performed for propagation is performed for this case, it will be determined that the average chain length term will cancel out when the ratio D_{pa}/D_{ps} is evaluated, where subscript "pa" accounts for the approach of a polymer radical to another polymer radical and subscript "ps" accounts for separation of such radicals. Therefore, the effective **number average** termination kinetic constant will be given by equation (70).

$$\overline{k}_{ti_n} = k^0_{ti} e^{-(\frac{A}{v_f})} \tag{70}$$

where "i" accounts for either "combination" or "disproportionation" and "A" has a similar meaning as parameter "B" in the propagation case. Up to this point it may be surprising how this proposed equation could equal (not to say improve) the predictive power of the MH or the CCS-AK models if no chain length dependence is explicitly obtained in equation (70). If this equation were to be used to model reaction rate, number and weight average chain lengths, underprediction of weight average chain length would be surely expected. In the following, this apparent contradiction will be overcome by using $k_t(i,j)$ averages, as proposed by Zhu and Hamielec (1989).

In their analysis of chain-length dependent termination for free radical polymerization, Zhu and Hamielec (1989) proposed the use of $k_t(i,j)$ averages to calculate the rate of polymerization and the molecular weight averages, although they made clear that the full molecular weight distribution could not be obtained in all cases. They proposed to calculate a "y-average" chain length in terms of a "y-average" termination kinetic constant, where y= n, w, z, ... For example, for instantaneous number and weight average chain lengths, equations (71) and (72) should be used.

$$P_n = \frac{1}{\tau_n + \frac{1}{2}\beta_n} \tag{71}$$

$$P_w = \frac{2\tau_w + 3\beta_w}{(\tau_w + \beta_w)^2} \tag{72}$$

where

$$\tau_y = \frac{k_{fm}}{k_p} + \frac{k_{fT}[T]}{k_p[M]} + \ldots + \frac{\bar{k}_{tdy}[Y_0]}{k_p[M]} \tag{73}$$

$$\beta_y = \frac{\bar{k}_{tcy}[Y_0]}{k_p[M]} \tag{74}$$

y= n, w, z, ...

In their paper Zhu and Hamielec (1989) proposed a procedure to calculate the number (n), weight (w) and z-average termination kinetic constants from conversion, number and weight average molecular weight data. Although effective, the procedure is quite empirical and rather tedious. Moreover, the averages thus obtained are case-system specific and no statistical information on the reliability of the estimates is obtained. In this paper a simpler and more effective way to do so is proposed. If equation (71) is divided by equation (72) and for simplicity it is assumed that the molecular weight development is controlled by termination by combination (i.e. $\tau_y \approx 0$), then equation (75) is obtained.

$$\frac{k_{tcw}}{k_{tcn}} = \frac{3}{2}\,\frac{P_n}{P_w} \tag{75}$$

This equation clearly indicates that the ratio of weight average to number average termination constants is inversely proportional to the polymer polydispersity. However, it should be noted that equation (75) is expressed in terms of "instantaneous" averages. If accumulated values are desired, some sort of integration should be performed. Integrating equations (71) and (72) over the conversion range and taking their ratio, leads to equation (76).

$$\frac{\bar{P}_n}{\bar{P}_w}=\frac{\frac{2}{3}x^2}{\int_0^x \beta_n dx \int_0^x \frac{dx}{\beta_w}} \tag{76}$$

If it is assumed that k_p and Y_0 do not change during the polymerization (at least at low or intermediate conversions) and the "mean value theorem" of calculus is used, equation (77) can be obtained.

$$\frac{\bar{k}_{tcw}}{\bar{k}_{tcn}}=\frac{\frac{2}{3}x}{(1-\frac{1}{2}x)\ln(\frac{1}{1-x})}\frac{\bar{P}_n}{\bar{P}_w} \tag{77}$$

However, it is our objective to obtain an expression which can be used over the whole conversion range. Therefore, the assumption of k_p and Y_0 remaining constant can not be accepted and equation (77) will not be useful. Nevertheless, it provides important insight. This equation shows that the ratio of number average to weight average termination kinetic constants is proportional to the polymer polydispersity and an additional conversion dependent function. Obtaining a valid expression derived from first principles may not be an easy task (it should be kept in mind that our models are intended to be simple, yet accurate). Therefore, a phenomenological (semi-empirical) approach will be attempted.

The first idea which might come to mind would be to use equation (75) directly, to estimate the accumulated average kinetic constants. Actually, this approach was tested with rather bad results (very high overprediction of weight average chain lengths was obtained at low and intermediate conversions). This behavior indicated that the "conversion-dependent" function was missing. Getting back to the original MH and the AK models, it is observed that the two of them use a ratio of a reference to a present value of weight average chain lenghts, raised to a given power (equations 51 and 50, respectively). Therefore, it could be that the function needed to complete our model for k_{tcw} should have a similar structure, namely that the ratio of a "reference" average chain length (accumulated number average chain length) to a "present" average chain length (accumulated weight average chain length), raised to a certain power (which may be a conversion-dependent power). Based on this analogy and after several sensitivity analysis calculations, equation (78) was obtained.

$$\frac{\bar{k}_{tcw}}{\bar{k}_{tcn}} = \sqrt{\left(\frac{\bar{P}_n}{\bar{P}_w}\right)^x} \qquad (78)$$

where x is monomer conversion. This is the equation that was required to complete our kinetic model for termination.

In the derivation of the previous equations it was assumed that the available free volume for "approach" and "separation" of the polymer radical molecules was the same. However, if it is considered that "separation" of the molecules implies somehow an inefficiency of the termination reaction, then some amount of free volume could be regenerated ("separation" means that the creation of a longer chain was avoided, at least momentarily). In the limit, if all "approaches" were followed by "separation" (no reaction takes place), the free volume associated with the separation phenomenon would be the initial free volume. Of course this limiting situation will not be the case in a polymerization case. However, based on the previous idea it can be proposed that the free volume associated with the separation of the molecules is the initial free volume (the error introduced if this is incorrect would be compensated by the value given to the overlap factor), thus obtaining equations (79) and (80), which would be obtained if a derivation similar to the one proposed by Marten and Hamielec (1979) had been undertaken.

$$\bar{k}_{tcn}=k_{tc}^{0}e^{-A(\frac{1}{V_f}-\frac{1}{V_{f0}})} \tag{79}$$

$$\bar{k}_{tcw}=k_{tc}^{0}\sqrt{(\frac{\bar{P}_n}{\bar{P}_w})^{x}}\,e^{-A(\frac{1}{V_f}-\frac{1}{V_{f0}})} \tag{80}$$

It has been proposed that in the late stages of the polymerization (high conversion regime), a polymer radical loses its center-of-mass mobility and propagation-diffusion becomes the dominant mode of termination (Schulz, 1956; Soh and Sundberg, 1982; Rusell et. al., 1988; Buback, 1990; Zhu, 1991). All models assume that the propagation-diffusion termination kinetic constant is proportional to the frequency of monomer addition to the radical chain end (in Achilias and Kiparissides, 1992a), as expressed in equation (81).

$$k_{trd}=C_{rd}k_p[M] \tag{81}$$

where the subscript "rd" accounts for "reaction-diffusion". Parameter C_{rd} has been given theoretical meaning by Soh and Sundberg (1982) and Russell et. al. (1988). In this paper it will be treated as an adjustment parameter with order of magnitude similar to the values obtained by Buback (1990).

The overall termination kinetic constants (number and weight averages) will then be given by the sum of the translational and reaction-diffusion components, as indicated in equations (82) and (83).

$$\bar{k}_{tn}=\bar{k}_{tcn}+k_{trd} \tag{82}$$

$$\bar{k}_{tw}=\bar{k}_{tcw}+k_{trd} \tag{83}$$

Initiation

To analyse the diffusion controlled initiation reaction a similar analysis to the one used for propagation and termination will be used. However, the treatment will not be identical.

To start with, let us consider the following reaction scheme, which shows the way a primary radical fragment "behaves" in a polymerization system.

$$\begin{array}{c} I\rightarrow 2R_{in}^{\bullet}\rightarrow I' \\ +M \\ k_{-D}\uparrow\downarrow k_{D} \\ R^{\bullet}M \\ \downarrow \\ R_1^{\bullet} \end{array} \tag{84}$$

where the chemical kinetic constant for the reaction from I to get $2R^{\cdot}$ is k_d, the one for the side reaction of recombination of radical fragments (formation of I′) is k_c' and the chemical kinetic constant for production of a radical of chain length 1 ($R_1^{\cdot}$) is k_c. From this reaction scheme, the following rate equations can be derived:

$$\frac{dR_{in}^{\bullet}}{dt}=2k_d I-k_c' I'=2fk_d I-k_p'[M][R_{in}^{\bullet}] \tag{85}$$

where f is an efficiency factor introduced to account for the side reaction to produce I′.

$$\frac{dR_1^{\bullet}}{dt}=k_c[R_{in}^{\bullet}M]=k_c\frac{k_D}{k_{-D}}[M][R_{in}^{\bullet}] \tag{86}$$

where k_D and k_{-D} account for diffusion from and into the "cage", respectively. It has been assumed that an equilibrium between these phenomena is established. If it is assumed that at the start of the polymerization there is no diffusion limitation and that the rate of formation of radicals equals its rate of consumption (steady state hypothesis), then at x=0, equation (87) can be writen.

$$2f_0k_d[I]_0=k_c[M]_0[R_{in}^{\bullet}] \tag{87}$$

At any conversion level, other than x=0, a similar expression can be proposed.

$$2fk_d[I]=k_c\frac{k_D}{k_{-D}}[M][R_{in}^{\bullet}] \tag{88}$$

If equation (88) is divided by equation (87) and the result is rearranged in terms of f, then equation (89) is obtained.

$$f=f_0\frac{k_D}{k_{-D}}\frac{[I]_0[M]}{[I][M]_0} \qquad (89)$$

Assuming that the ratio $[I]_0[M]/([I][M]_0)$ remains constant, and using the free volume theory for the diffusion coefficients of the initiator fragments to get out of and into the "cage" (neighboring molecules surrounding the new generated radicals), equation (90) is obtained.

$$f=f_0e^{-\frac{D}{V_f}} \qquad (90)$$

where D accounts, as in propagation and termination, for the fact that the same volume is available for other molecules and even the same molecule (or another) to return to the "cage". In the first stages of this research a semiempirical derivation of equation (90) was done, by assuming that the initiator efficiency at conversion x could be obtained using the free volume theory and a reference value (initial conditions). Therefore, an alternative equation to the previous one, which in fact was used in most of the calculations presented in this paper is the one shown below, namely equation (91).

$$f=f_0e^{-D\left(\frac{1}{V_f}-\frac{1}{V_{f0}}\right)} \qquad (91)$$

Calculation of free volume

To calculate the overall available free volume, the sum of the individual contributions must be taken. Therefore, following Bueche (1962), this quantity is obtained from the following equation:

$$V_f=\sum_{i}^{N}[0.025+\alpha_i(T-T_{gi})\frac{V_i}{V_t}] \qquad (92)$$

where i= monomer, polymer, solvent, ..., N
By using equation (92) it is implicitly assumed that equilibrium in free volume is reached at every moment during the complete course of polymerization. However, this may not be the case in polymerization reactions with strong auto-acceleration effect at very high conversions, such as crosslinking. Because this effect is more important in crosslinking situations, the derivation of an expression to calculate the non-equilibrium free volume, as well as a small review about this topic, is given in other paper (Vivaldo-Lima et. al., 1993). However, the final expressions obtained in that paper will be included here in order to have a complete kinetic model. To calculate the non-equilibrium free volume, equation (93) can be used.

$$\frac{dV_f}{dt}=-\frac{(V_f-V_{feq})}{\tau}+R_{fv} \qquad (93)$$

where

$$\tau=\tau_0 e^{-B_f(\frac{1}{V_f}-\frac{1}{V_{f0}})} \qquad (94)$$

$$R_{fv}=\delta\left[\frac{d(x\bar{\rho})}{dt}+(x-\bar{\rho})\frac{dx}{dt}\right] \tag{95}$$

$\tau, \bar{\rho}$ are relaxation time and crosslinking density, respectively and V_{feq} can be estimated using equation (92). For a homopolymerization situation, δ in equation (95) can be set equal to zero. To avoid having to estimate additional parameters, equation (92) was used for all the calculations presented in this paper. However, in our other paper (Vivaldo-Lima et. al., 1993) some simulations showing the importance of using the non-equilibrium free volume in copolymerization of vinyl/divinyl monomers and homopolymerization of vinyl monomers are included.

COMPARISON OF THE PERFORMANCE OF THE MODELS

Important Remarks

This section will be devoted to show a comparison of the performance of the models considered in this paper. The predictive power of the MH model in bulk and solution styrene homopolymerization has already been presented (Marten and Hamielec, 1982). The procedure followed by these authors to estimate the unknown parameters was statistically satisfactory. The CCS model has been tested with MMA bulk (Chiu et. al., 1983) and solution (Louie et. al., 1985) homopolymerizations. However, no information was given on the statistical reliability of the estimated parameters, nor on the estimation procedure. More recently, Vivaldo-Lima and

Saldivar-Guerra (1993) obtained estimates of the CCS model parameters for bulk styrene homopolymerization. Although they used a valid statistical method (Marquardt technique), the confidence intervals for the parameters were not reported and the profiles showed in their paper were obtained using specific values for each condition (in fact, their simulations were reported to be a "curve-fitting" exercise). A more detailed documentation on the way the previous research was undertaken (Vivaldo-Lima, 1989a), reveals that the confidence intervals were indeed calculated, but they were quite large (for θ_p and θ_t) and in some of the regression trials, zero was included in the confidence interval (θ_p). Moreover, as has been already mentioned, both the MH and the CCS models are inadequate for prediction of weight average molecular weights (chain lengths) at high conversions.

In order to make the comparison as fair as possible and considering the fact that in the early stages of this research the idea of using different average kinetic values for k_t was already in our minds (however, the structure of the model was not chosen by then, i.e. either "parallel" or "series" approach), it was decided to modify somehow both models. The modifications consisted mainly in obtaining adequate expressions for k_{tw} for each of them (in the MH model diffusion-propagation termination was also considered). Therefore, what will be identified as "MH" and "CCS" models in the plots and discussion of this section, are not the original models, but modified versions, which are defined in equations (96) through (101). The AK model was kept in its original version because the purpose of using it was mainly to analyse the structure and theoretical background of the CCS-family models, as well as confirm or reject the conclusions obtained with the analysis of the CCS original and modified models.

Modified CCS model (CCS, CCSA or CCSB in the plots):

$$k_p=(k_p)_{CCS} \tag{96}$$

$$\bar{k}_{tcn}=(k_{tc})_{CCS} \tag{97}$$

$$\bar{k}_{tcw}=(k_{tc})_{CCS}\sqrt{\left(\frac{\bar{P}_n}{\bar{P}_w}\right)^x} \tag{98}$$

where subscript "CCS" accounts for the original CCS model equations defined in equations (13) and (14).

Modified MH model (MH in the plots):

$$k_p=(k_p)_{MH} \tag{99}$$

$$\bar{k}_{tcn}=k_t^0 e^{-A_{MH}\left(\frac{1}{V_{fm}}-\frac{1}{V_{f,cr1}}\right)}+C_{Id}k_pM \tag{100}$$

$$\bar{k}_{tcw}=\bar{k}_{tcn}\sqrt{\left(\frac{\bar{P}_n}{\bar{P}_w}\right)^x}+C_{Id}k_pM \tag{101}$$

All the calculations using the CCS (modified version), MH (modified version) and our present model (which will be identified as "PM" in the plots and discussion), were performed using the "long chain hypothesis" and the "steady state hypothesis" (SSH). Calculations using the AK model were performed using the "long chain hypothesis", but the SSH assumption was removed in order to be as close as possible to the conditions and treatment of equations undertaken by Achilias and Kiparissides (1992a). In our paper on the copolymerization of styrene/divinylbenzene (Vivaldo-Lima et. al., 1993) it is demonstrated that the use of the SSH is valid for homopolymerizations and even for copolymerizations with crosslinking during the pre-gelation period (in the post-gelation period the SSH was found to be inadequate).

The term "present model" (PM) is understood as the use of equations (46), (79), (80) and (91) for modelling k_p, kt and f. Although their theoretical derivation showed that the use of a substraction term accounting for inverse initial free volume in the exponential kernels of the equations may not be correct, these equations were first derived semi-empirically and many calculations had already been done using them. The only implication of this is that the estimated values of "A" and "D" for termination and initiation will have some amount of systematic error (the theoretically derived expression for propagation was avoided intentionally for the reasons given in the model development section).

Parameter estimation strategy

In this subsection a description of the parameter estimation procedure and the obtained values will be given.

Although estimates of the intrinsic chemical kinetic constants for propagation and termination are reported in literature (for instance, Brandrup, 1975), it has been recognized that strong model assumptions support many of them (parameters are model dependent), thus giving a wide range of values which makes possible for conflicting mechanistic assumptions to be supported with "evidence" from literature (Gilbert, 1992). The values are even more uncertain for k_t^0. Based on this situation and the fact that our preliminary sensitivity analysis simulations showed that significant difference in estimated values for the remaining parameters was obtained depending on the chosen values for k_p^0 and k_t^0, it was decided to include them as part of the "unknown" parameters in the estimation procedure. Due to the characteristics of each model, the estimation procedure was somewhat different. Therefore, a brief description will be given for each model (MH, PM and CCS). All data used for the estimation stage and for the interpolation/extrapolation tests are summarized in Tables 2.1 and 2.2.

To estimate the parameters of the MH model (A, $V_{f,cr2}$, $K_3(T)$, C_{rd}, k_p^0 and k_t^0) a multivariable non-linear regression procedure was attempted (using experimental conversion and weight average molecular weight -when available- as responses). The "error in variables method" (EVM) (Sutton and MacGregor, 1977) was used for such purpose (excellent examples on the use of the EVM in free-radical polymerization situations can be found in García-Rubio's PhD thesis (1981) and Lord's M.Eng. thesis (1984)). The first approach was to include all the parameters in such a procedure. However, due to the structure of the model, very high correlations were obtained. After several analysis it was found that K3(T) and C_{rd} were the cause of such behavior. Therefore, C_{rd} was set equal to the best value obtained in the preliminary trials (which had an order of magnitude well inside the range of values estimated by Buback (1990) for polymerizations of ethylene, MMA and butyl acrylate) and a combined single search-EVM strategy was used for the remaining values. This strategy consisted on using the EVM to estimate A, $V_{f,cr2}$, k_p^0 and k_t^0 at fixed different values of K3(T). The criteria was to get the lowest error-sum of squares as well as the lowest correlation coefficients estimated with the EVM. To perform this estimation procedure data sets 1, 2, 3, 5, 7 and 8 were used (see Table 2.1). The estimates of the parameters are given in Table 2.3.

TABLE 2.1 Summary of Experimental Conditions. Bulk Homopolymerization with AIBN.

Data Set	$[I]_0$ (AIBN)	$[M]_0$	Temp. (°C)	Remarks
1	0.01	8.347	60	(in Marten and Hamielec, 1982)
2	0.024	8.347	60	(in Marten and Hamielec, 1982)
3	0.0164	8.347	60	(Arai and Saito, 1976)
4	0.0216	8.347	60	(Tobolski and Rogers, 1960)
5	0.05	8.347	60	(Nishimura, 1966)
6	0.0036	8.347	60	(Nishimura, 1966)
7	0.0214	8.347	70	(Tobolski and Rogers, 1960
8	0.0212	8.347	80	(Tobolski and Rogers, 1960)
9	0.0210	8.347	90	(Tobolski and Rogers, 1960)
10	0.05	8.347	80	(Nishimura, 1966)

TABLE 2.2 Summary of Experimental Conditions. Solution Homopolymerization with AIBN. (Data from Hui, 1967).

Data Set	$[I]_0$ (AIBN)	$[M]_0$	Temp. (°C)	[Toluene]
1T	0.04	6.69	60	1.8
2T	0.08	6.69	60	1.8
3T	0.04	6.59	70	1.8
4T	0.08	6.60	70	1.8
5T	0.04	6.51	80	1.8
6T	0.08	6.62	80	1.8
7T	0.04	5.02	60	3.6
8T	0.08	5.01	60	3.6
9T	0.04	4.92	70	3.6
10T	0.08	4.92	70	3.6
11T	0.04	4.82	80	3.6
12T	0.08	4.83	80	3.6

To estimate the parameters of the PM model (A, D, $V_{f,cr2}$, C_{rd}, k_p^0 and k_t^0), C_{rd}, k_p^0 and k_t^0 were considered to be the same as in the MH model, A and $V_{f,cr2}$ were obtained using the EVM with data sets 1 and 2, and D was estimated from sensitivity analysis studies around the value obtained with the EVM in preliminary trials (the confidence interval for D when using the EVM included zero, which means that either initiation is not diffusion-controlled or the experimental information was not sufficient for that estimation). The simulation tests showed that D should be included in the model to get adequate limiting conversions. Table 2.4 shows the parameters that were obtained.

Table 2.3 Estimated Kinetic Parameters for the MH model.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_p^0	$275.38e^{-[\frac{8479}{R}(\frac{1}{T(K)}-\frac{1}{333.15})]}, \frac{\ell}{mol*s}$ $R^2 = 0.998781$	EVM
k_{tc}^0	$1.223x10^8e^{-[\frac{7127}{R}(\frac{1}{T(K)}-\frac{1}{333.15})]}, \frac{\ell}{mol*s}$ $R^2 = 0.997066$	EVM
A (or A_{MH})	0.4655 +/- 0.032	EVM
K3(T)	$K3(T) = 593.11e^{\frac{7550.6}{R}(\frac{1}{T(K)}-\frac{1}{333.15})}$ $R^2 = 0.99972$	Single search-EVM
$V_{f,cr2}$	0.034 +/- $8.5x10^{-3}$	EVM
C_{rd}	135, l/mol	See text

Table 2.4 Estimated Kinetic Parameters for the PM model.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_p^0, k_{tc}^0	See Table 3.	EVM with MH model
A	0.465 +/- 0.04	EVM
D	10^{-3} (10^{-4}, 10^{-2})	EVM
$V_{f,cr2}$	0.036 +/- 0.01	EVM
C_{rd}	135, l/mol	See text

The estimation of the CCS model parameters was more complicated. Although Vivaldo-Lima and Saldivar-Guerra (1993) had reported estimated parameters obtained using adequate statistical methods and the detailed information was available (from Vivaldo-Lima, 1989a), the modification to the model introduced here (calculation of k_{tcw}) made it necessary to attempt a re-estimation of such parameters. In their original estimation procedure, Vivaldo-Lima (1989a) used only conversion/time data and an ingenious technique to get initial estimates for input to the Marquardt technique. The parameters considered in his estimation procedure were A(T), B(T), θ_p and θ_t . In our case we attempted to use the values of k_p^0 and k_t^0 estimated with the MH model, but the predicted profiles using those values were quite different compared to the corresponding profiles using the values reported in the paper of Sharma and Soane (1988). Attempting to include these parameters in the EVM estimation procedure were unsuccessful. Therefore, it was decided to fix such parameters to the values reported by Sharma and Soane (1988). The estimated values for parameters A(T), θ_p and θ_t presented in this paper were obtained using data sets 1, 2, 3, 5, 7 and 8 (using sets 4, 6, 9 and 10 only increased the uncertainty of the estimates). B(T) was taken from the results of Vivaldo-Lima and Saldivar-Guerra (1993). In all the attempts θ_p was found to be statistically equal to zero (its confidence interval included zero). That is why in some of the plots there are two profiles for the CCS model. "CCSA" profiles were obtained using θ_p =0.0 and "CCSB" were obtained using the regression model reported by Vivaldo-Lima and Saldivar-Guerra (1993) for this parameter.

Table 2.5 Estimated Kinetic Parameters for the CCS model.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_p^0	$2.79x10^9 e^{-[\frac{10620}{RT}]}, \frac{l}{mol*s}$	Sharma and Soane,1988
k_{tc}^0	$4.839x10^{13} e^{-[\frac{8700}{RT}]}, \frac{l}{mol*s}$	Sharma and Soane,1988
A(T)	$0.37388-2.395x10^{-4}(T-T_{gp})^2$ $R^2= -0.9939$ (CCSA) $0.4428-3.0x10^{-4}(T-T_{gp})^2$ $R^2= -0.99963$ (CCSB)	Linear regression from EVM-obtained parameters
B(T)	0.02	Vivaldo and Saldivar,1993
$\theta_p(T)$ (sec)	10^{-12} (CCSA) $\theta_p(T)=105219e^{[92937(\frac{1}{T(K)}-\frac{1}{333.15})]}$ $R^2= 0.99959$ (CCSB)	EVM Vivaldo and Saldivar,1993
$\theta_t(T,I$ (sec)	$\ln(\theta_t)=-177.87-1.2086\ln(I_0)+\frac{61017.83}{T(K)}$ $R^2= 0.96279$ (CCSA) $\ln(\theta_t)=-177.76-1.3493\ln(I_0)+\frac{60747.71}{T(K)}$ $R^2= 0.96117$ (CCSB)	Linear regression from EVM parameters

All other parameters were given values taken from the literature or reasonable values were used when information was not available. Table 2.6 contains values or functions used to estimate other chemical kinetic constants and Table 2.7 shows all other physical parameters, coming from the free volume theory.

TABLE 2.6 Other Chemical Kinetic Parameters.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_d	$1.053x10^{15}e^{-(\frac{30660}{RT})}, s^{-1}$	Sharma and Soane, 1988
k_{fm}	$2.31x10^{6}e^{-(\frac{12671}{RT})}, \frac{\ell}{mol*s}$	Hui, 1967
k_{fp}	0	
k_{fs}	0	
k_{td}^{0}	$2.19x10^{5}e^{-(\frac{27440.5}{RT})}, \frac{\ell}{mol*sec}$	Villalobos et. al., 1991

In the case of the AK model, most of the parameters were taken from their author's paper (Achilias and Kiparissides, 1992a). Besides the assumption of "long chain hypothesis", the only difference between our calculations using the AK model and those obtained by them, is that even though they mentioned that the polymer diffusion coefficient at "zero" conversion, D_p', can be estimated using the Stokes-Einstein equation (equation 33 in this paper), they did not use it and we did. In the case of solution polymerization, some modifications were made in order to account for the presence of solvent. Instead of using equations (23), (32) and (41), equations

(102), (103) and (104), respectively, must be used.

TABLE 2.7 Other Physical Parameters.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
f_0	0.7	Sharma and Soane, 1988
α_m	0.001, $(°C)^{-1}$	Marten and Hamielec, 1982
α_p	0.00048, $(°C)^{-1}$	Marten and Hamielec, 1982
α_{Tol}	0.007, $(°C)^{-1}$	For Toluene, guess
T_{gm}	-88.1, °C	Marten and Hamielec, 1982
T_{gp}	93.5, °C	Brandrup, 1975
T_{gT}	-160.15, °C	

$$\hat{V}_f=\omega_m\hat{V}_m^*V_{fm}+\omega_p\hat{V}_p^*V_{fp}+\omega_s\hat{V}_s^*V_{fs} \tag{102}$$

$$D_p=D_p'\left(\frac{P_w'}{P_w}\right)^2 e^{-\gamma\left[\frac{1}{\xi_{13}}(\omega_m\hat{V}_m^*+\omega_p\hat{V}_p^*\xi_{13})\frac{1}{\hat{V}_f}+\frac{\omega_s\hat{V}_p^*M_{jp}}{M_{js}\hat{V}_f}-\frac{1}{\xi_{13}V_{fm}}\right]} \tag{103}$$

$$D_m=D_{m0}e^{-\left[\frac{\gamma\hat{V}_m^*M_{jm}}{\hat{V}_f}\left(\frac{\omega_m}{M_{jm}}+\frac{\omega_p}{M_{jp}}+\frac{\omega_s}{M_{js}}\right)\right]} \tag{104}$$

where subscript "s" accounts for "solvent", and

$$\omega_i=\frac{\rho_i V_i}{\rho_m V_m+\rho_p V_p+\rho_s V_s},\ i=m,p,s \tag{105}$$

$$V_{fs}=\frac{\hat{V}_{fs}}{\hat{V}_s^*}=\frac{K_{13}(K_{23}+T-T_{gs})}{\hat{V}_s^*} \qquad (106)$$

To test that our implementation of the AK model was correct, two systems for methyl methacrylate homopolymerization were used, namely MMA bulk polymerization at T= 70 °C and $[AIBN]_0=0.0155$ mol/l (Figure 2 in the paper of Achilias and Kiparissides (1992a)) and MMA bulk polymerization at T= 60 °C and $[AIBME]_0=$ 0.01 mol/l (Figures 9 and 11 in the same paper). To get the same conversion/time profiles (indeed slightly better predictions were obtained), it was necessary to change "a_{seg}" from 0.28 (reported by Achilias and Kiparissides, 1992a) to 0.35 in the case where AIBN was used and both, "a_{seg}" and γ had to be changed from 1.024 and 0.763 to 0.9 and 0.85, respectively, in the case where AIBME was used. In this last case our predictions were slightly worse than those presented by Achilias and Kiparissides. These variations on the parameters mentioned might seem to be "small" (from 12 to 25% on a_{seg} and around 12% for γ), however, our simulation tests showed that very small variations on these parameters (lower than 10%) always produced significant changes in the "auto-acceleration zone". The variation in the parameters might be due to the different way to estimate D_p'. With the available information for polystyrene and AIBN, a_{seg} was "fitted" by "trial and error" using data set 1. Sets 2, 1T and 2T were used to test the "predictive" behavior of the AK model. In Tables 2.8, 2.9 and 2.10 all parameters used in the AK model are summarised.

Table 2.8 Kinetic Parameters for the AK model (From Achilias and Kiparissides, 1992a).

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
$k_p{}^0$	$k_p^0=1.09x10^7 e^{-\frac{7051}{RT}}, \frac{\ell}{mol*s}$	
$k_{tc}{}^0$	$k_{tc}^0=1.7033x10^9 e^{-\frac{2268}{RT}}, \frac{\ell}{mol*s}$	
k_{fm}/k_p	$1.0e^{-\frac{3212}{T}}$	
f_0	0.58	
k_d	See Table 6	

Table 2.9 Initiator and Solvent Parameters for the AK model (From Achilias and Kiparissides, 1992a, unless otherwise stated)

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
M_{jI}	68	
$\hat{V}_I{}^*$	0.913, cm^2/g	
$\frac{e_i}{D_{I0}}$	372.38, s/cm^2	
γ_I	1.0	
M_{js}	92.1 (MW_S)	
$\hat{V}_S{}^*$	0.917	Zielinski and Duda, 1992
γV_{fS}	$0.29542+1.5812x10^{-3}T(°C)$	Zielinski and Duda, 1992

Table 2.10. Monomer-Polymer Parameters for the AK model (From Achilias and Kiparissides, 1992a, unless otherwise stated)

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
V_{fm}	$0.112+6.2\text{x}10^{-4}T(°C)$	
V_{fp}	$0.0245+1.4\text{x}10^{-4}(T - 82)$	T < 82°C
$\hat{V}_m^*$	0.846, cm^3/g	
M_{jm}, M_{jp}	104.14, 163	
γ	0.999	
δ , r_e	$7.4\text{x}10^{-8}$, $16.9\text{x}10^{-8}$, cm	
X_{c0}	385	
a_{seg}	1.35	Trial and error
r_B	$(R_H)_0{}^r$	
D_{m0}	$1.97\text{x}10^{-8}$, cm^2/s	
η_s	$\exp[-22.673+\frac{1758}{T(K)}+1.67\ln(T(K))]$, $Pa*s$	
R_H	$1.31\text{x}10^{-9}M_w^{0.56}$, cm	

Predicted profiles of conversion/time, molecular weight/time and molecular weight distribution for bulk and solution styrene homo-polymerization.

This subsection will be devoted to show the predicted profiles obtained with the four models analysed in this paper (MH, CCS, AK and PM). It should be pointed out that most of the profiles were obtained using the average values or regression models for the respective parameters and not with "optimal" parameters for each condition (therefore, this is not a "curve fitting" excercise).

Figure 2.2 shows predicted profiles of conversion versus time and experimental data at conditions of data set 1 (see Table 2.1). In (a) model predictions using the MH, PM, CCSA and CCSB models are illustrated. It can be seen that MH and PM produce virtually the same results, except for the limiting conversion, which is predicted to be higher with the MH model. CCSA accounts for predictions using $\theta_p \sim 0.0$ and CCSB uses θ_p calculated from the correlation showed in Table 2.5. The profiles are almost equal up to the autoacceleration zone. CCSA predicts total conversion right at the "gel point", whereas CCSB shows a decrease in propagation rate at a lower conversion. In both cases predictions using the CCS model are quite poor (the profiles using the "optimal" parameters obtained with the non-linear regression procedure were much better and indeed almost identical to those showed in the paper of Vivaldo-Lima and Saldivar-Guerra (1993)). Predictions of conversion are much lower during the low and intermediate conversion range and then a strong auto-accelaration effect is predicted to occur at around 1400 minutes. In (b) predictions using the PM model again are shown, but this time the profile is compared to that obtained using the AK model. Although the AK model predictions are better than those using the CCS model, it is observed that a very strong auto-acceleration effect is predicted to occur. The MH and the PM models produce better predictions in this case. Figure 2.3 shows predictions of number and weight average chain lengths versus time at the conditions of data set 1. This behavior is similar as in the conversion/time profiles. Predictions of weight average chain length using the MH model are not very good at high conversions; this model predicts higher values of weight average chain length in this conversion regime than those observed experimentally. The PM seems to produce much better results; however, considering the high experimental error associated with measurements of weight average molecular weight at high conversions, the difference between the MH and the PM predictions could be considered to be non significant. Here again the exaggerated "gel effect" predicted to occur with the AK model is clearly shown. In Figure 2.3(b) the CCSA, CCSB and AK model predictions of average chain length are shown. Both CCSA and CCSB predictions are in clear deviation from the experimental behavior.

Figures 2.4 and 2.5 show predicted versus experimental profiles of conversion/time (Figure 2.4) and number- and weighth- average chain length versus time (Figure 2.5) for bulk styrene homopolymerization at the conditions of data set 2 (Table 2.1). The behavior of the models is similar as in the previous case (data set 1), but now the predictions using the MH and PM differ from each other (although the experimental profile lies in between). In this case the MH model seems to produce slightly better results for both, conversion/time and chain length averages/time profiles. Also, the predictions of weight average chain length using the AK model seem to be better than in the previous case, but there is still a stronger auto-acceleration effect than the one observed experimentally.

Figure 2.6 shows predicted versus experimental profiles of conversion/time (a) and average chain lengths/time (b) for bulk homo-polymerization of styrene at conditions of data set 3. In this case predictions with the AK model were not obtained (as indicated before, it was not attempted to make an exhaustive study of the performance behavior of the AK model, but use it as a reference model for analysis of the "parallel"-structure type of models and their theoretical background). Both the MH and the PM model produced good predictions of number and weight average chain lengths in this case, but they overpredict somewhat conversions in the intermediate regime. The PM predictions of limiting conversion are lower than those obtained experimentally. Although the predictions using the CCS model are better than those obtained for the previous cases, the auto-acceleration effect is clearly exaggerated.

Figure 2.7(a) shows predictions of conversion/time profiles at constant temperature and two initiator levels (the polymerization conditions correspond to those of data sets 5 and 6). Due to the scatter of the data, particularly at the "auto-acceleration zone", the three models (MH, PM, CCSB) seem to produce "adequate" profiles. However, at the high level of initiator both the MH and the PM models overpredict the conversion rate at the intermediate conversion range and the PM model prediction of limiting conversion is significantly lower than the experimental one. Predictions using the MH and the PM models at the lower initiator level are much better. The predictions using the CCSB model show a "strong" auto-acceleration effect, although the average deviation seems to be adequate. Figure 2.7(b) shows predictions of conversion/time profiles at constant initial initiator concentration and two levels of temperature (the conditions used to produce the profiles correspond to those of data sets 7 and 8). The MH model predictions are very good at both levels of temperature; although the PM prediction of limiting conversion at the lower level is lower than the experimental, the overall performance for these two cases is very good. In this case the CCS predictions are poor; at the high temperature level no auto-acceleration is predicted to occur and indeed a monotonous reduction in conversion rate is observed. At the low temperature level an extremely fast conversion rate is predicted to occur at the very beginning of the polymerization. This behavior in the CCS model indicates that either the regression models are not good or the structure of this model is incorrect.

Figure 2.8 shows conversion/time predicted and experimental profiles for styrene polymerization in toluene at conditions of data sets 1T and 2T. Figure 2.8(a) shows predictions using the MH, PM and AK models, whereas Figure 2.8(b) shows predictions using CCSB and AK (both plots correspond to the same system conditions; they were split in order to facilitate visual comparison). Figures 2.9 and 2.10 show the corresponding number- and weight-average/time profiles for data sets 1T and 2T. For these two solution polymerization conditions the MH model predictions of conversion are excellent, although weight average chain lengths are underpredicted as polymerization proceeds. The PM model overpredicts to some extent the conversion/time profiles, but the weight average chain length predictions are the closest to the experimental values. In these two cases the CCSB model predictions are very good. Predictions using the AK model are not good at all in these two cases. There is overprediction of conversion and both chain length averages from the beginning of the polymerization, but what seems to be more serious is the very strong auto-acceleration effect that is predicted to occur at some point in the profiles. This behavior is a clear deviation from the experimental evidence and is surprising if it is considered that most of the parameters were estimated from first principles.

Figures 2.11 to 2.22 show predicted versus experimental conversion/time and number-,weight-average chain length/time profiles at conditions of data sets 3T through 12T. In summary, it is observed that the MH predictions of conversion/time are excellent and weight average chain length/time profiles are very good (some degree of underestimation at high conversions). The PM predictions of weight average chain length/time profiles are excellent and conversion/time profile predictions are from very good to excellent (some degree of overprediction in some cases). The behavior of the CCS model could be called "unstable"; in some cases the predictions are very good (Figures 2.13, 2.14, 2.15, 2.16, 2.19 and 2.20), whereas in the others (Figures 2.11, 2.12, 2.17 and 2.18) the predictions are poor, showing a very strong auto-acceleration effect when this is not so (all cases where this behavior is obseved coincide with the case of polymerizations carried out at 70°C).

To further test the behavior of the PM model, calculations using the "Instant Property Method", IPM, as compared to those using the "Method of Moments", MM, (for calculation of different moments of the molecular weight distribution) were performed. Figures 2.21 and 2.22 show number and weight averages versus time calculations for bulk and solution homo-polymerization of styrene, respectively. It is seen that the predictions are practically identical except, perhaps, for a slightly higher prediction of the limiting weight average chain length in bulk polymerization when the MM is used than is the case when the IPM is used. Conversion/time profiles are not shown because they were identical.

By using the IPM it is possible to calculate the full molecular weight (chain length) distribution. In figures 2.23(a), (b) and (c) predictions of the full chain length distribution at conditions of data sets 1, 2 and 3, respectively and times of polymerization indicated in the plots, are shown. Although no experimental evidence was available, it is seen that the predicted trends are in perfect agreement with the expected behavior (broadening of the chain length distribution as polymerization proceeds). Figures 2.24(a) and (b) show equivalent profiles for solution polymerization at conditions of data sets 1T and 2T.

As mentioned previously, all calculations presented in this paper were obtained assuming equilibrium in free volume at all times during the polymerization (equation (92) was used throughout). The underprediction of limiting conversion in some of the bulk polymerization cases analysed before indicate that non-equilibrium free volume should be used because of the significant difference between "relaxation time" and reaction time at high reaction rates. Simulation profiles showing this behavior are presented in our paper about styrene/divinylbenzene copolymerization (Vivaldo-Lima et. al., 1993).

CONCLUDING REMARKS

A detailed analysis and comparison of the structure and performance of the Chiu-Carratt-Soong (CCS) and the Marten-Hamielec (MH) models was undertaken. The analysis of the stuctures shows that modelling diffusion-controlled kinetic constants following a "parallel" approach is incorrect. Instead, a "serial" approach should be used. Based on first principles of Chemical Engineering Kinetics and including the important reactions and physical phenomena known to take place in free-radical homo- and co-polymerizations (diffusion controlled propagation, termination and initiation; non-equilibrium free volume), as well as the use of different $k_t(i,j)$ averages for modelling different chain length averages, proposed by Zhu and Hamielec (1989), a new model was derived.

The performance of the new model was compared with that of modified versions of the CCS and the MH models (the same approach used in the new model for calculation of k_{tn} and k_{tw} averages was introduced into them). In most cases the proposed model produced better results.

The validity of our conclusion concerning the inadequacy of the "parallel" approach in modelling diffusion-controlled kinetic constants was verified with the performance analysis of the CCS-AK models. These models predict that very strong auto-acceleration effect holds when this is not so. This can be clearly observed in the solution polymerization plots. One reason why this behavior is observed may be that using the "parallel" approach causes estimates of the diffusion coefficient of reacting species be confounded with the the intrinsic chemical kinetic rate constant. If the system under consideration shows very strong auto-acceleration (as is the case with MMA polymerization, which is the main system the CCS-AK models have been tested against), this behavior may not be evident. However, if this auto-acceleration is not that strong (as is the case of styrene polymerization and even weaker when such polymerization is carried out in a solvent -solution polymerization-), then the diffusion and chemical kinetic constants may have similar order of magnitude values and such "confounding" of parameters becomes more evident, as was observed in the profiles of solution styrene polymerization using the CCS (modified) and AK models. This inadequate "parallel" approach also explains some observations made by Zhu (1991), concerning predictions obtained with the first version (Achilias and Kiparissides, 1988) of the AK model (Zhu pointed out that the fact that the calculations of Achilias and Kiparissides (1988) predict that the effective diffusion coefficient of polymer is two orders of magnitude higher than that of the monomer at low monomer conversions (Figure 2 in that paper), had to be considered as an inconsistency).

If the AK model were derived following the "serial" approach, instead of the "parallel" one, and different averages for k_t were considered, or if the PM model were derived following the Vrentas and Duda free-volume theory, the same model would be obtained. Although the Vrentas and Duda free volume theory is more elegant and is considered to be more general, it does not provide a way to calculate the non-equilibrium free volume (in a polymerization context) and, therefore, it gives no better results than other free volume theories, unless non-equilibrium free volume is considered. In our model the non-equilibrium free-volume was included, but no attempt was made to get reliable estimates of the associated parameters.

Recently, Penlidis et. al. (1992) presented a study on the scope and difficulties of mathematical modelling for polymerization systems aiming at process control. They discussed, among other things, the advantages and disadvantages of using "empirical" and "mechanistic" modelling for control applications. Having a model which combines two desireable characteristics, namely simplicity and strong theoretical background, makes the PM model a promising one for application in the control area. However, before claiming such generality, the model must be tested and improved, if necessary, in non-isothermal polymerizations with significant temperature changes, polymerizations in the presence of prepolymer with a very different molecular weight than that produced later during the polymerization and polymerizations in a continuous stirred-tank reactor (Zhu and Hamielec, 1989).

A detailed description of the estimation procedure for model parameters was given, in order for other researchers in this field to be conscious of the limitations, precision and model assumptions directly or indirectly used in such estimation procedures.

ACKNOWLEDGEMENTS

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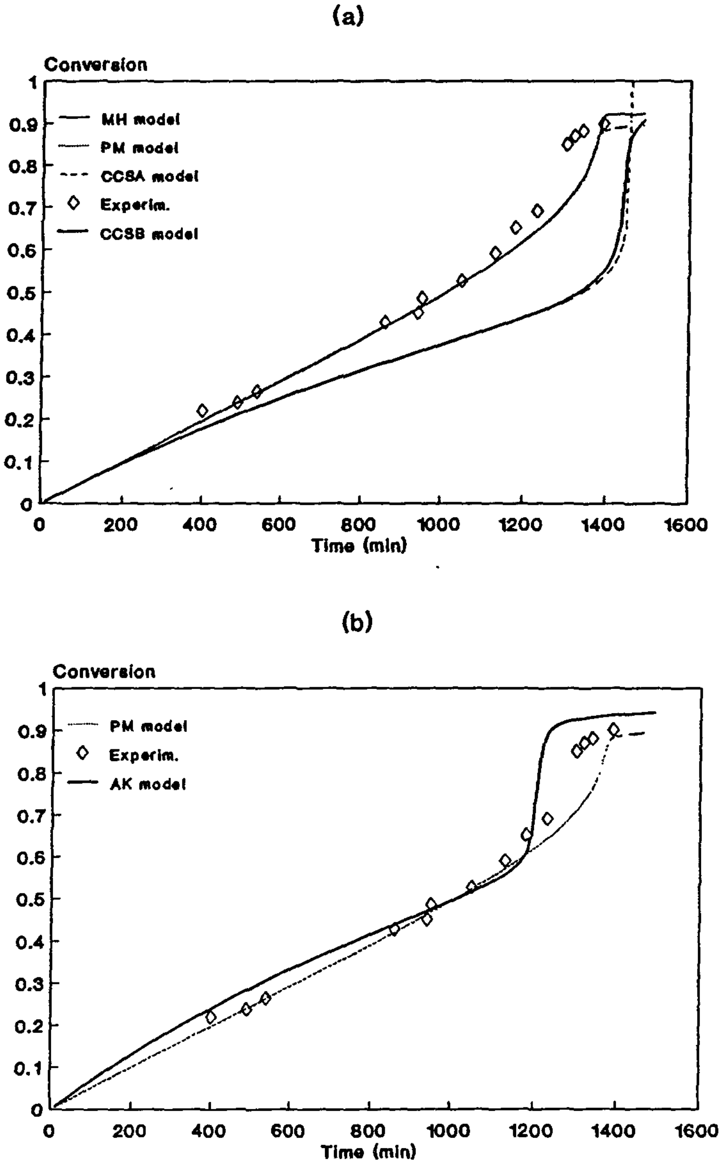

Figure 2.2 Styrene Bulk Homopolymerization. Experimental versus model predictions of conversion/time profiles at conditions of data set 1. (a) Experimental versus MH, PM, CCSA and CCSB model predictions. (b) Experimental versus PM and AK model predictions.

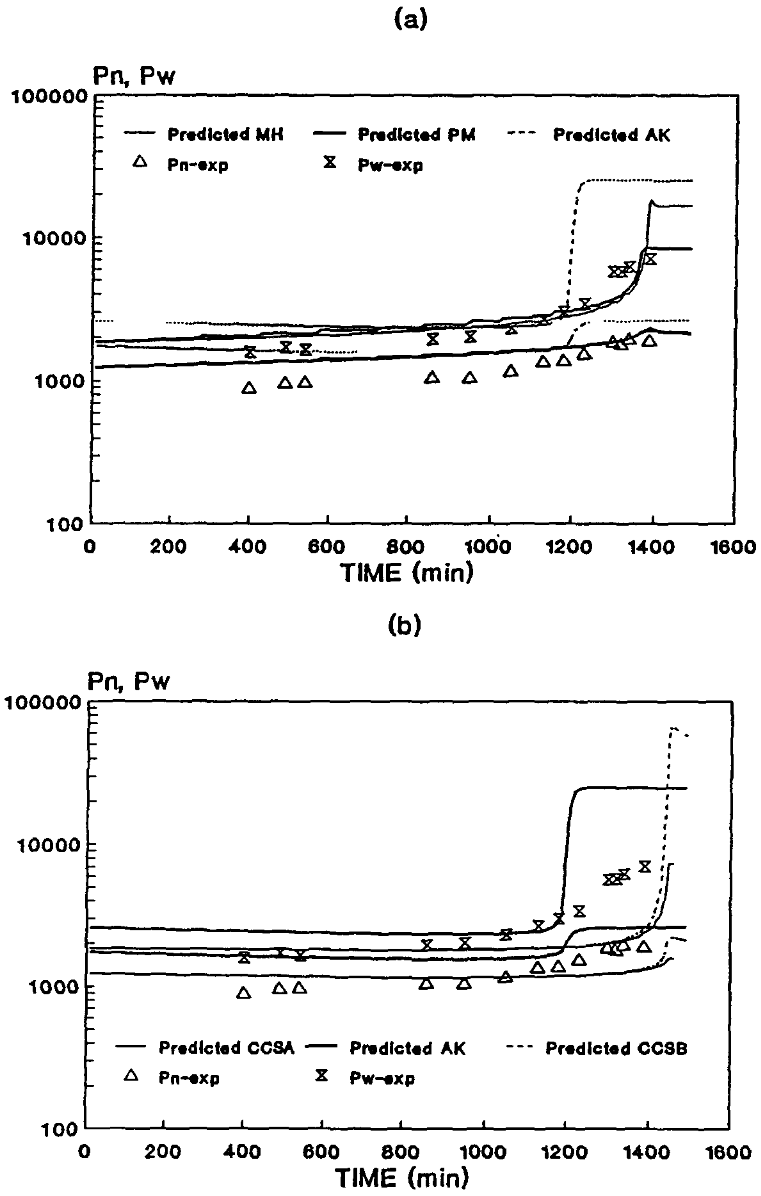

Figure 2.3 Styrene Bulk Homopolymerization. Experimental versus model predictions of number- and weight average chain length/time profiles at conditions of data set 1. (a) Experimental versus MH, PM and AK model predictions. (b) Experimental versus AK, CCSA and CCSB model predictions.

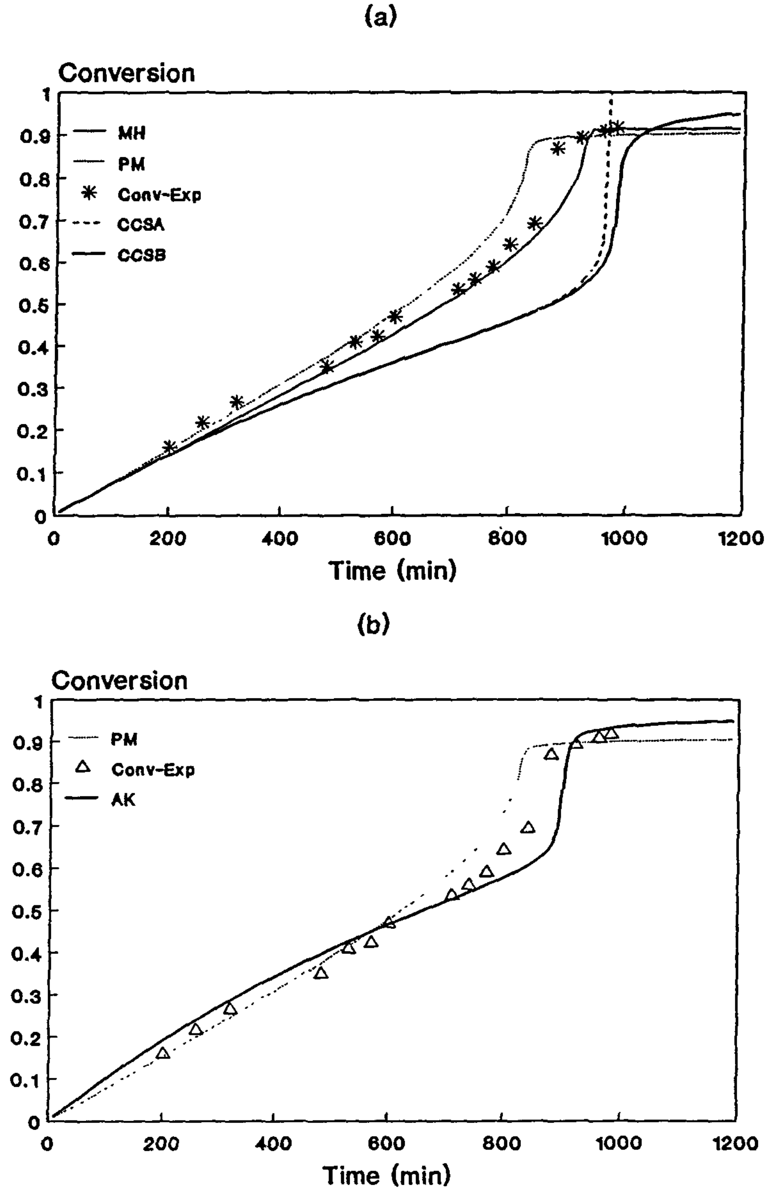

Figure 2.4 Styrene Bulk Homopolymerization. Experimental versus model predictions of conversion/time profiles at conditions of data set 2. (a) Experimental versus MH, PM, CCSA and CCSB model predictions. (b) Experimental versus PM and AK model predictions.

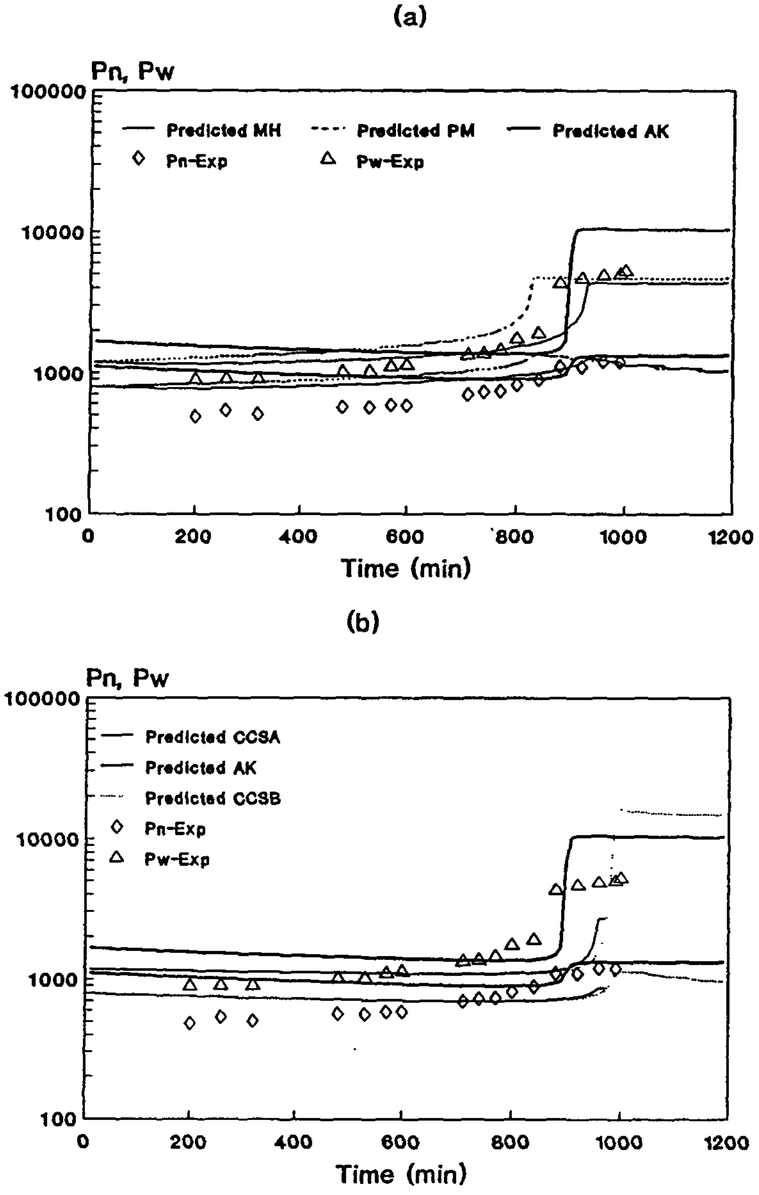

Figure 2.5 Styrene Bulk Homopolymerization. Experimental versus model predictions of number- and weight average chain length/time profiles at conditions of data set 2. (a) Experimental versus MH, PM and AK model predictions. (b) Experimental versus AK, CCSA and CCSB model predictions.

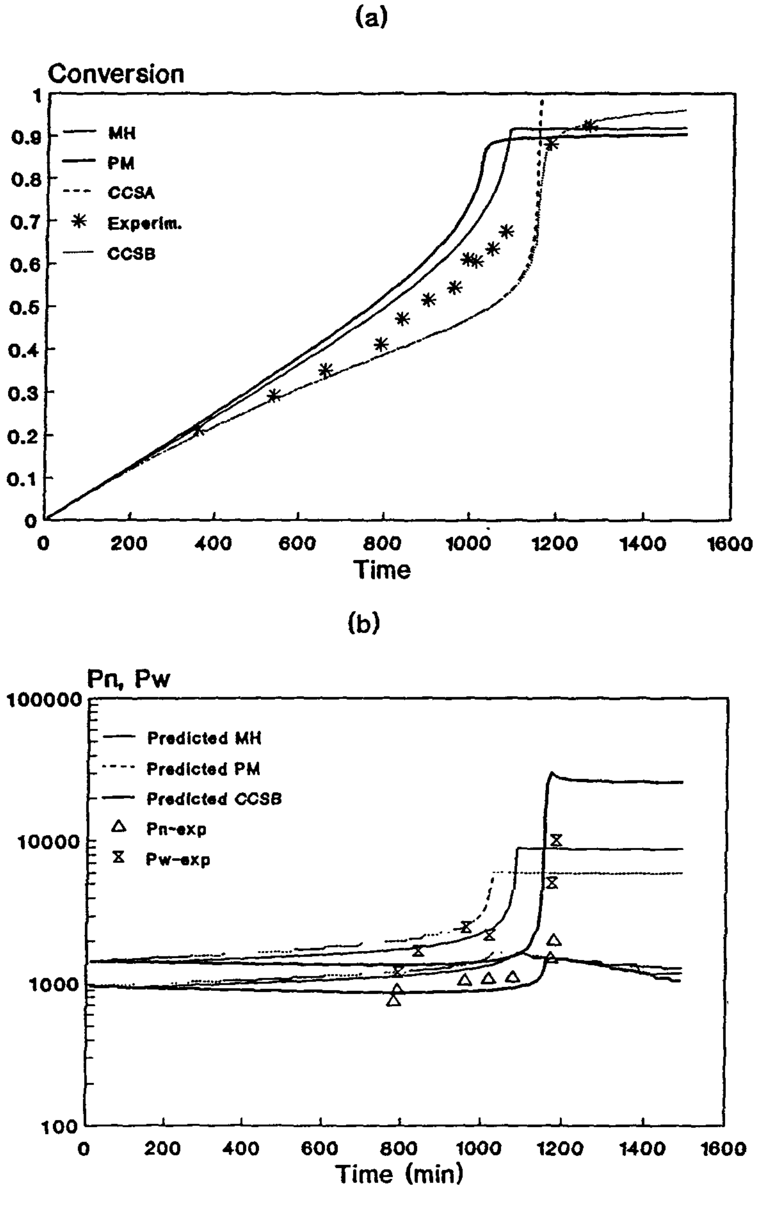

Figure 2.6 Styrene Bulk Homopolymerization. Experimental versus model predictions at conditions of data set 3. (a) Conversion/time profiles showing predictions with the MH, PM, CCSA and CCSB models. (b) Number- and weight average chain length/time profiles for the MH, PM and CCSB models.

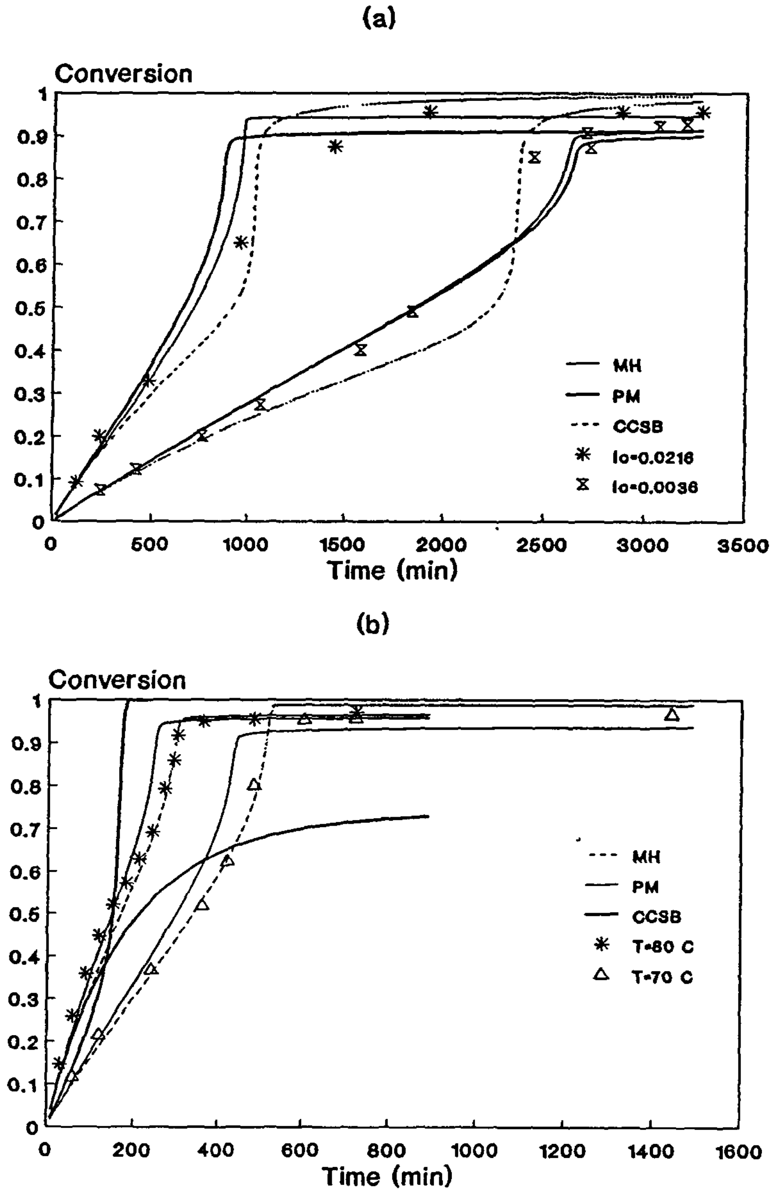

Figure 2.7 Styrene Bulk Homopolymerization. Experimental and predictions using the MH, PM and CCSB models. (a) Conversion/time profiles at constant temperature and two levels of initiator (at conditions of data sets 5 and 6). (b) Conversion/time profiles at constant initiator initial concentration and two levels of temperature (data sets 7 and 8).

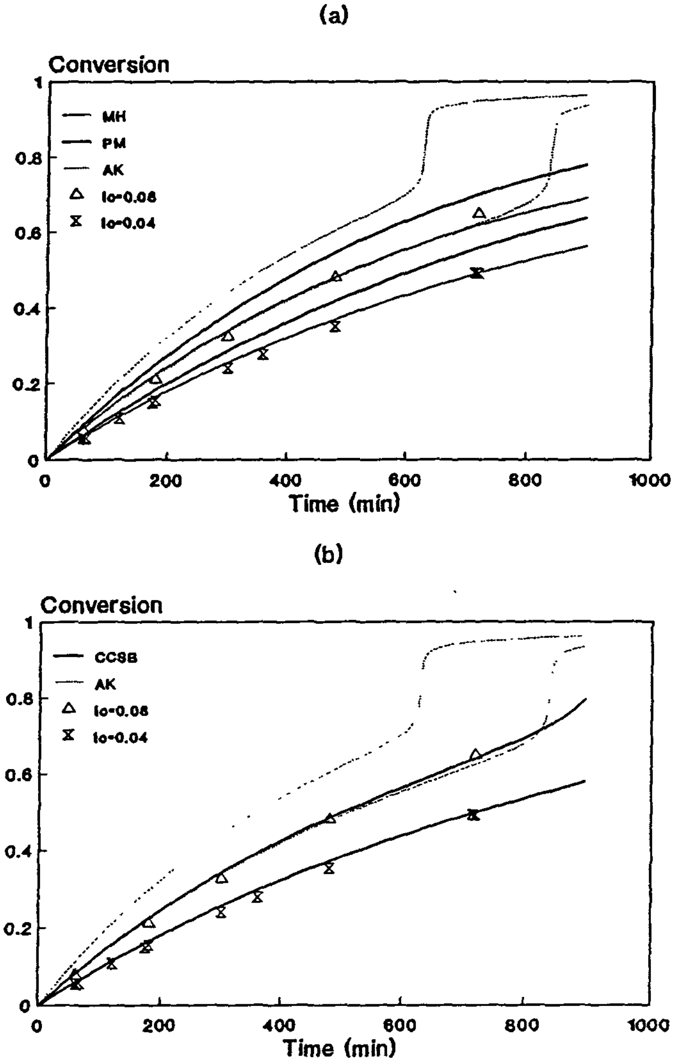

Figure 2.8 Styrene Solution Homopolymerization. Experimental versus predicted conversion/time profiles at conditions of data sets 1T and 2T. (a) Experimental versus predictions using the MH, PM and AK models. (b) Predictions using the AK and CCSB models.

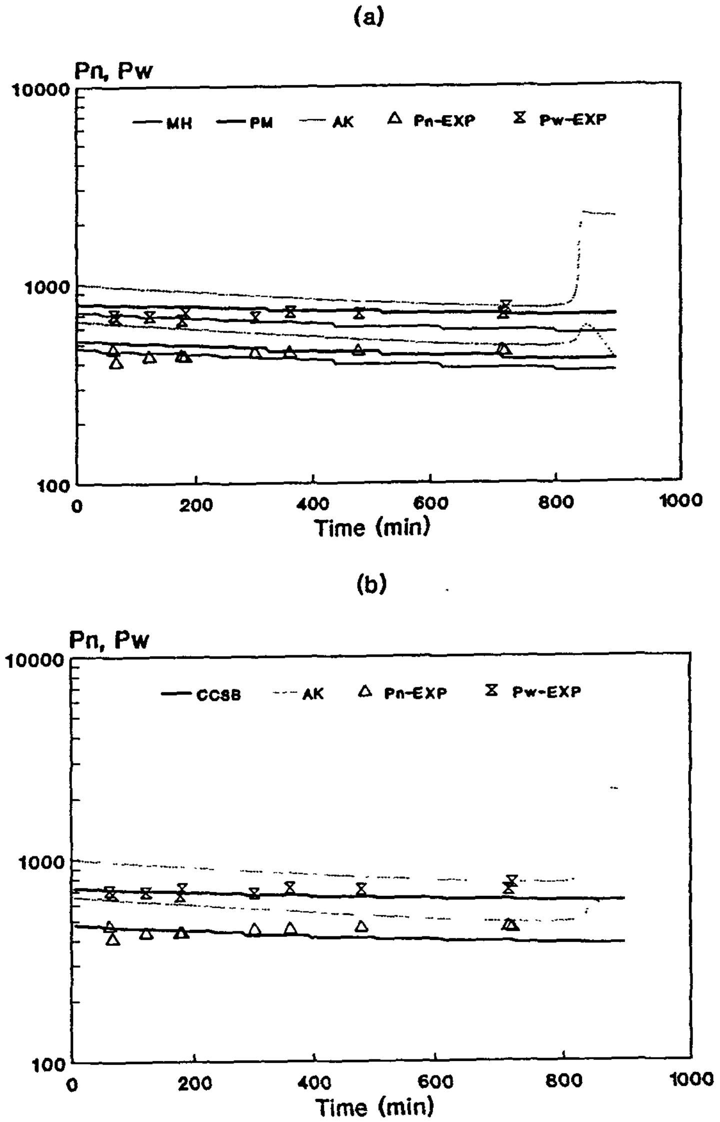

Figure 2.9 Styrene Solution Homopolymerization. Experimental versus predicted n- and w-average chain length/ time profiles at conditions of data set 1T (a) Predictions using the MH, PM and AK models. (b) Predictions using the AK and CCSB models.

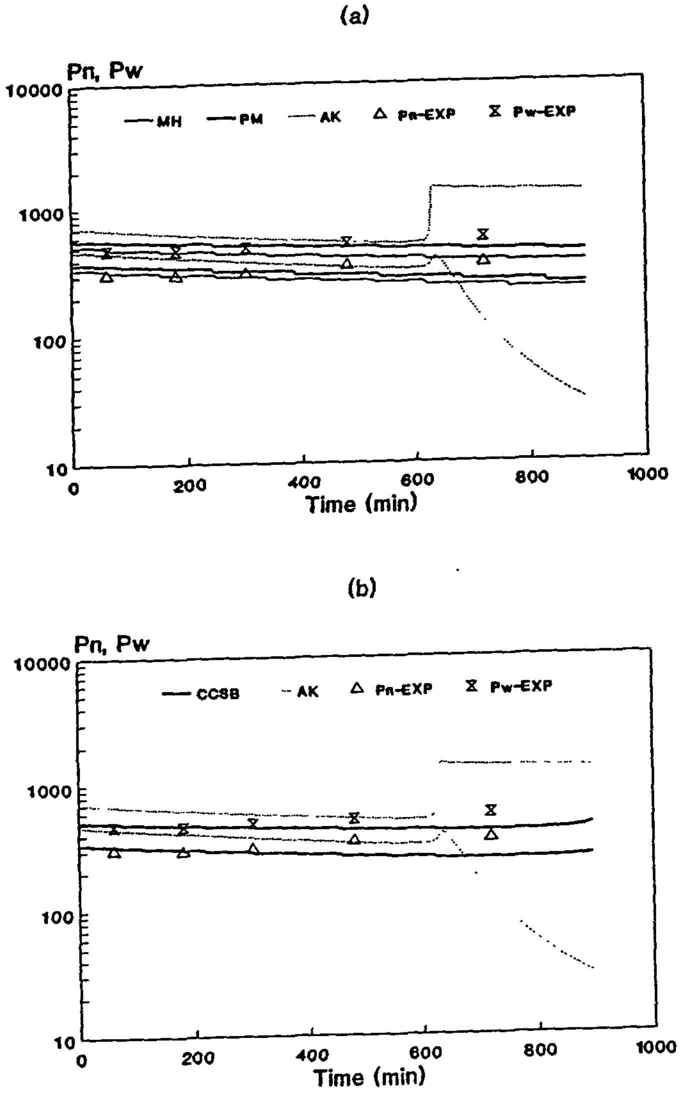

Figure 2.10 Styrene Solution Homopolymerization. Experimental versus predicted n- and w-average chain length/ time profiles at conditions of data set 2T (a) Predictions using the MH, PM and AK models. (b) Predictions using the AK and CCSB models.

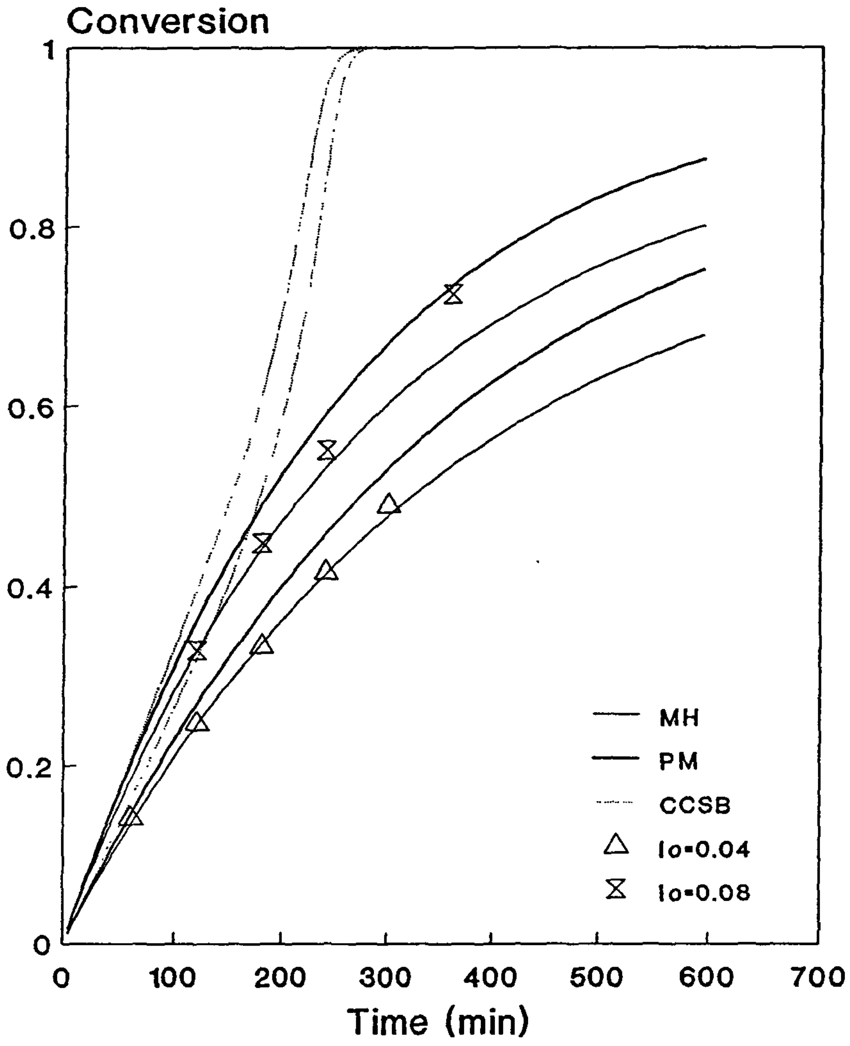

Figure 2.11 Styrene solution homopolymerization. Experimental versus predicted conversion/time profiles at conditions of data sets 3T and 4T. Model predictions with the MH, PM and CCSB models.

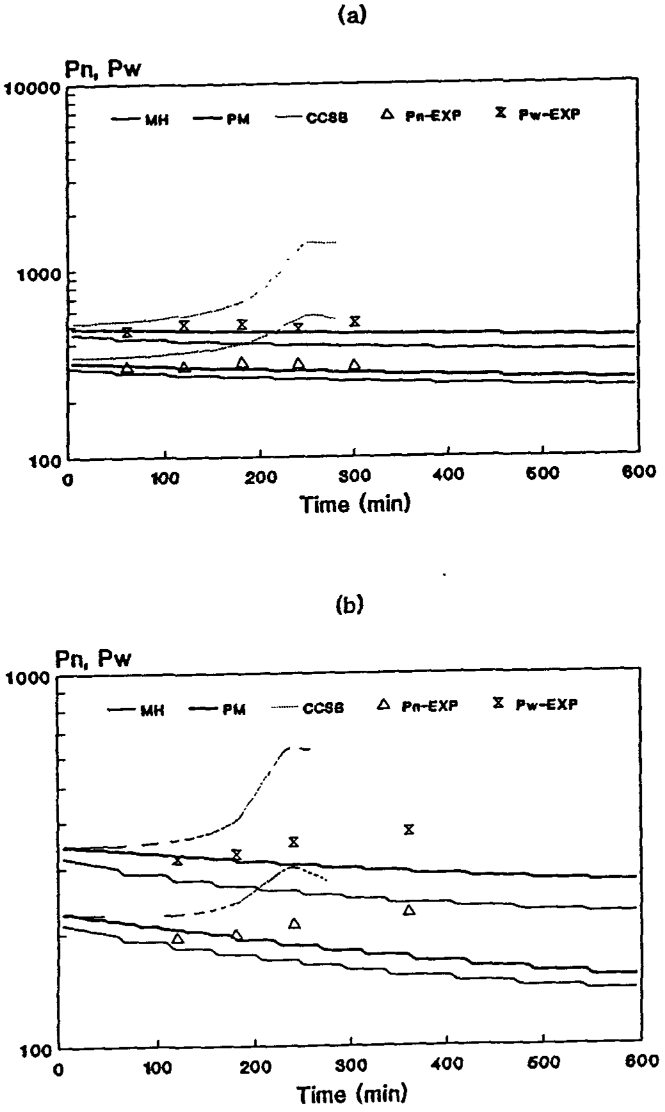

Figure 2.12 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) for n- and w-average chain length/time profiles at conditions of data sets (a) 3T and (b) 4T.

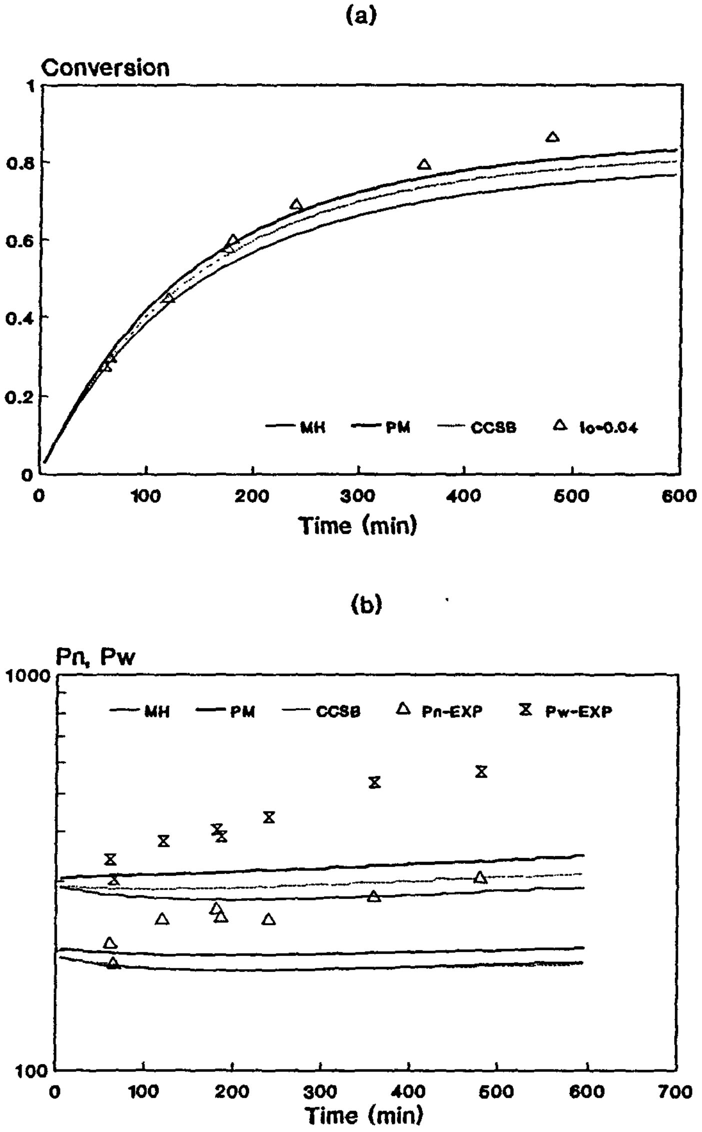

Figure 2.13 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) at conditions of data set 5T. (a) Conversion/time profile. (b) N- and w-average chain length/time profiles.

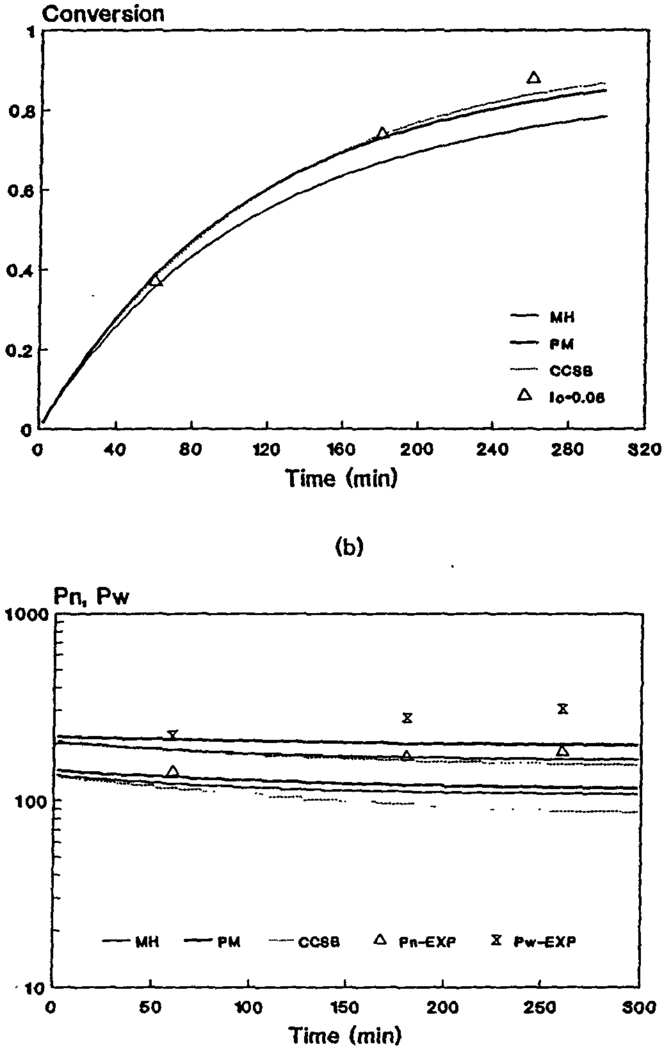

Figure 2.14 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) at conditions of data set 6T. (a) Conversion/time profile. (b) N- and w-average chain length/time profiles.

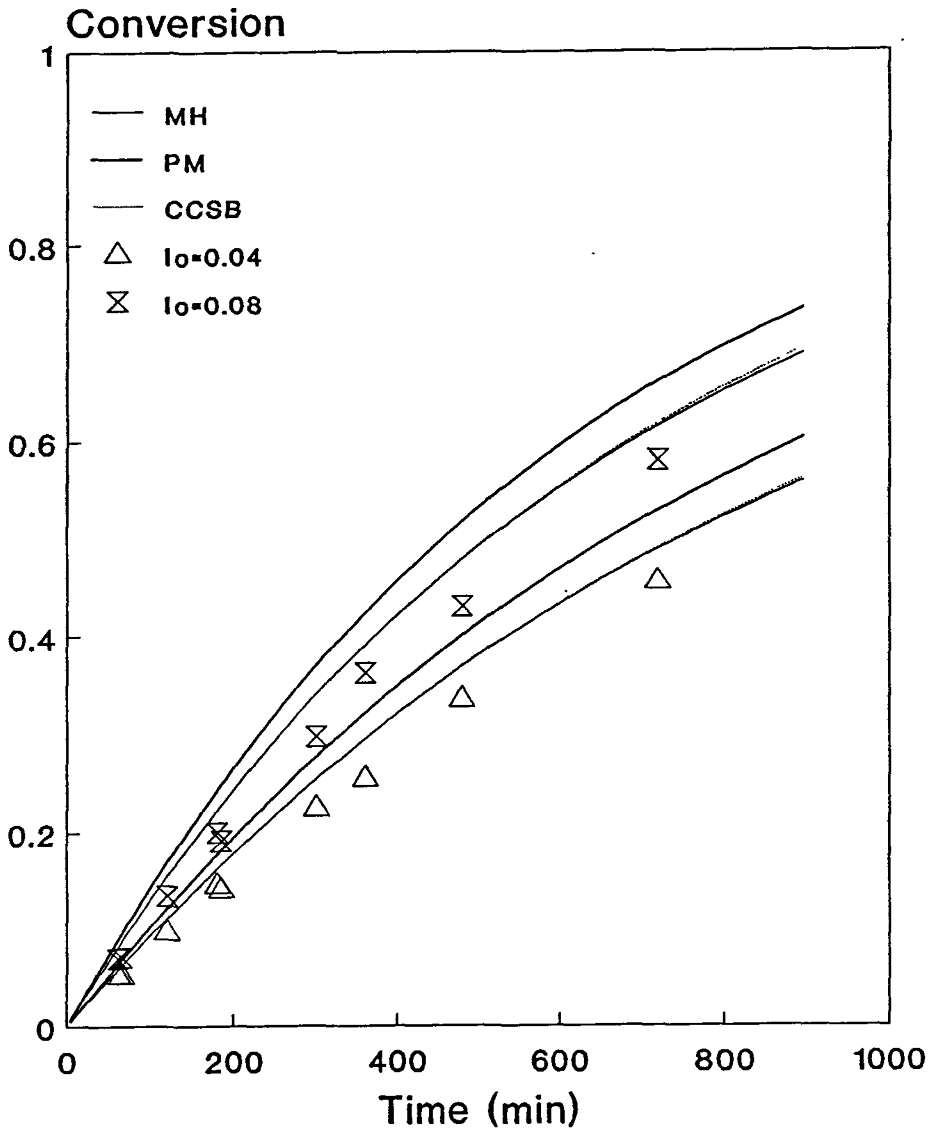

Figure 2.15 Styrene solution homopolymerization. Experimental versus predicted conversion/time profiles at conditions of data sets 7T and 8T. Model predictions with the MH, PM and CCSB models.

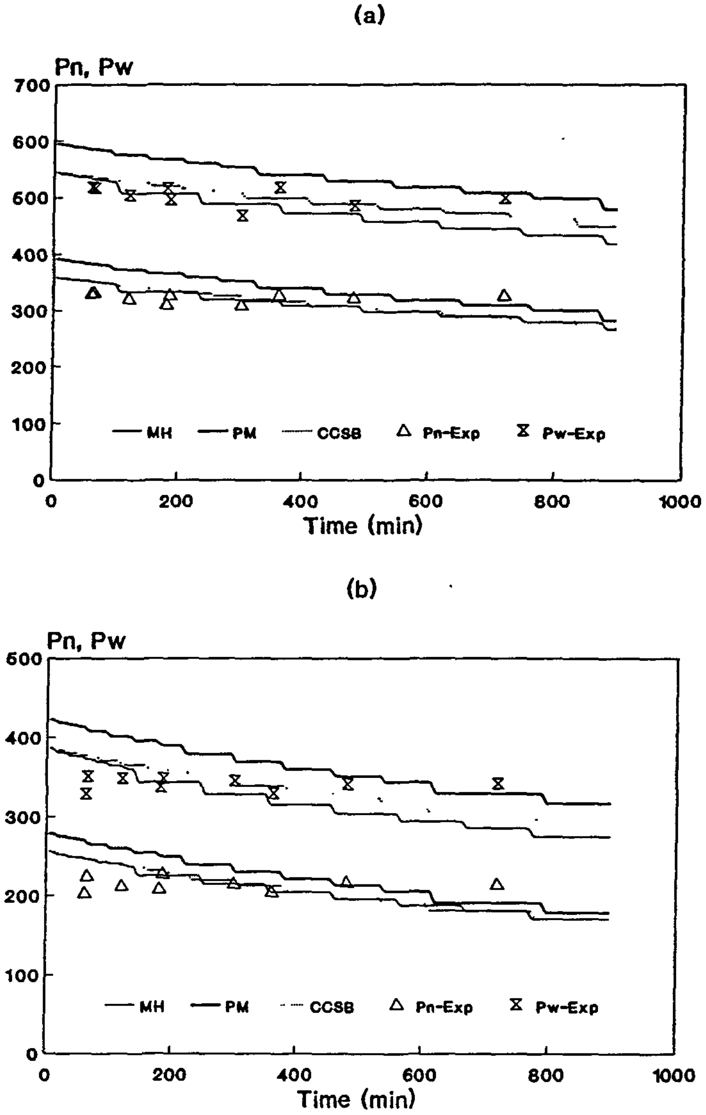

Figure 2.16 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) for n- and w-average chain length/time profiles at conditions of data sets (a) 7T and (b) 8T.

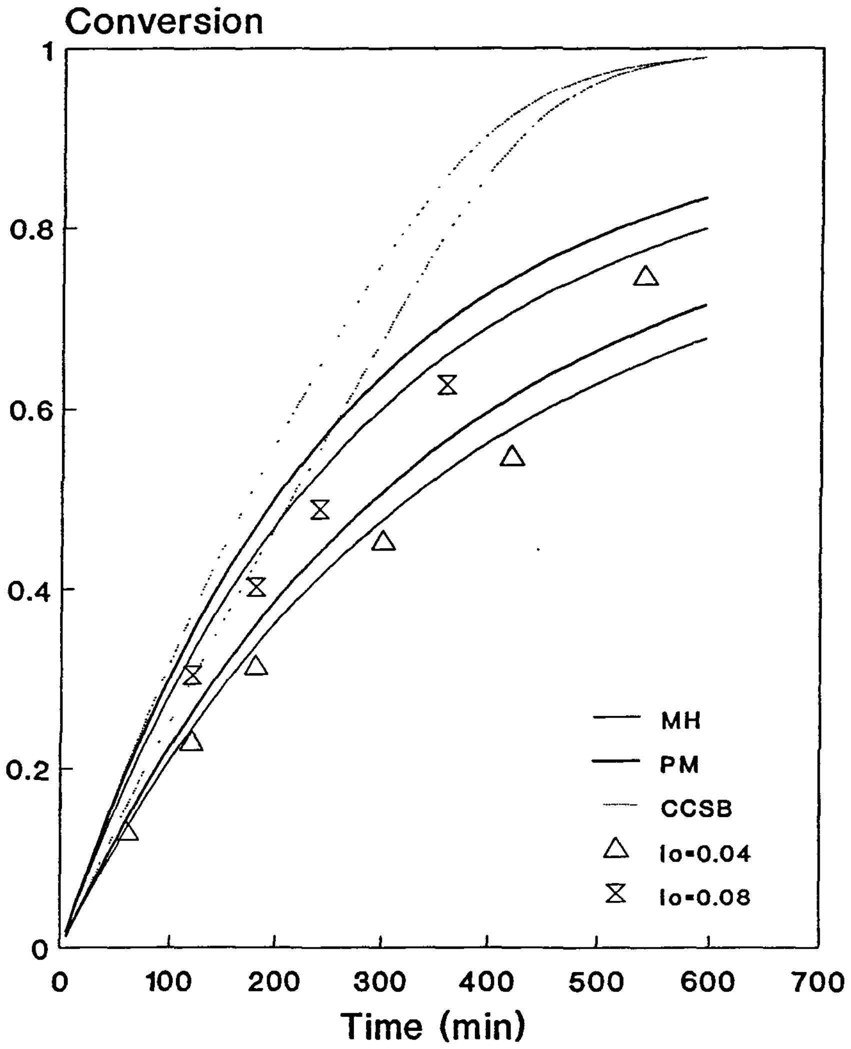

Figure 2.17 Styrene solution homopolymerization. Experimental versus predicted conversion/time profiles at conditions of data sets 9T and 10T. Model predictions with the MH, PM and CCSB models.

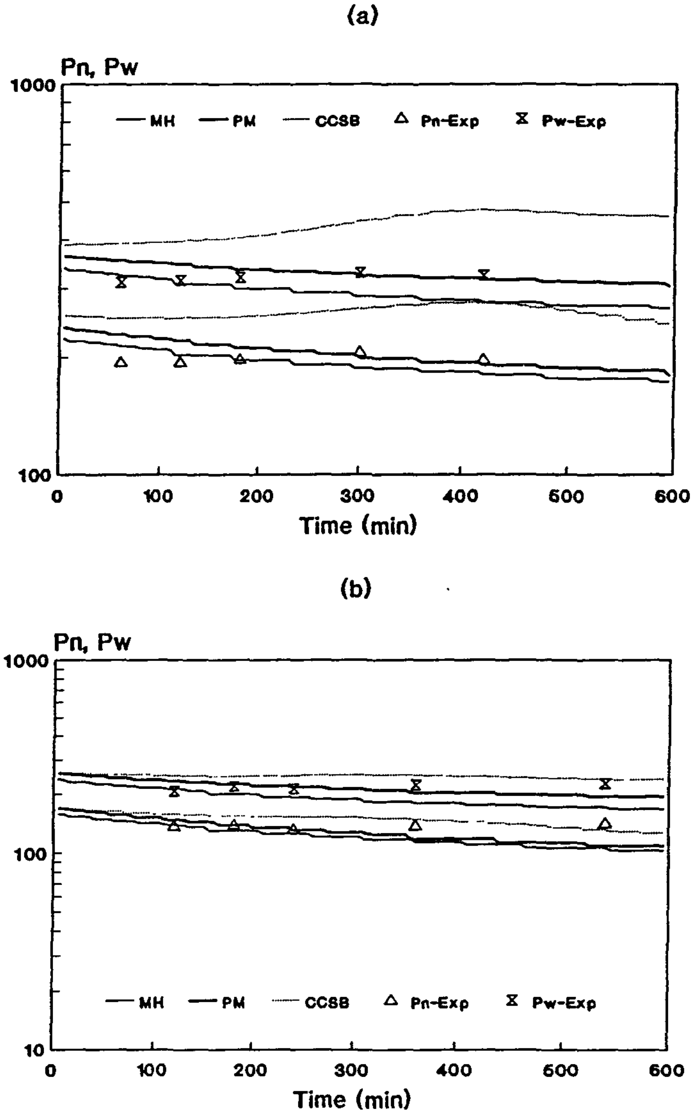

Figure 2.18 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) for n- and w-average chain length/time profiles at conditions of data sets (a) 9T and (b) 10T.

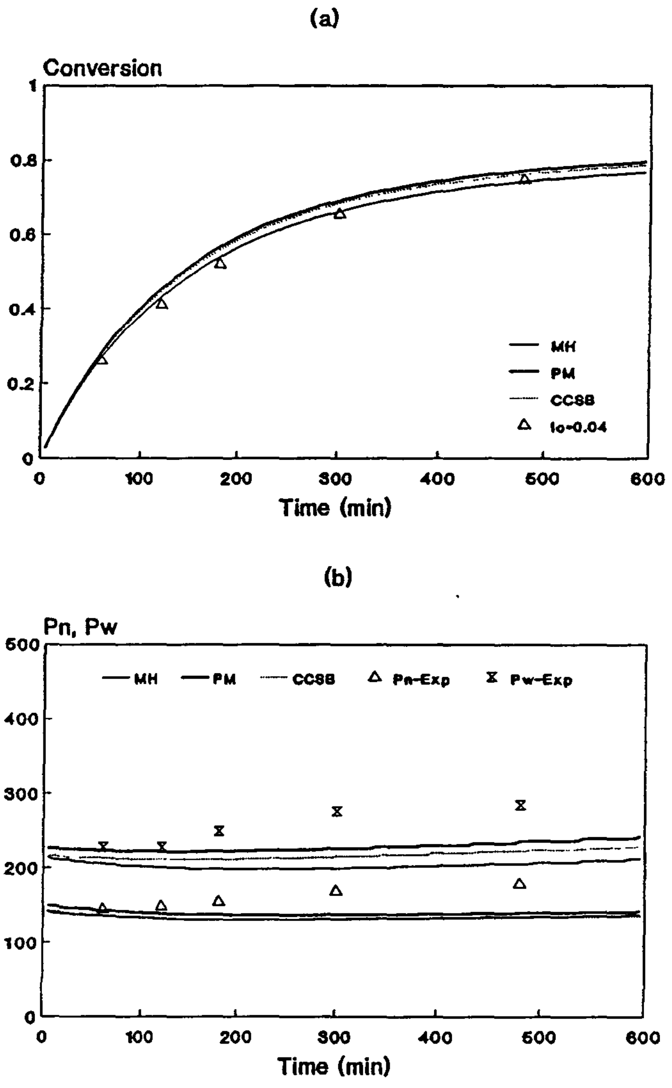

Figure 2.19 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) at conditions of data set 11T. (a) Conversion/time profile. (b) N- and w-average chain length/time profiles.

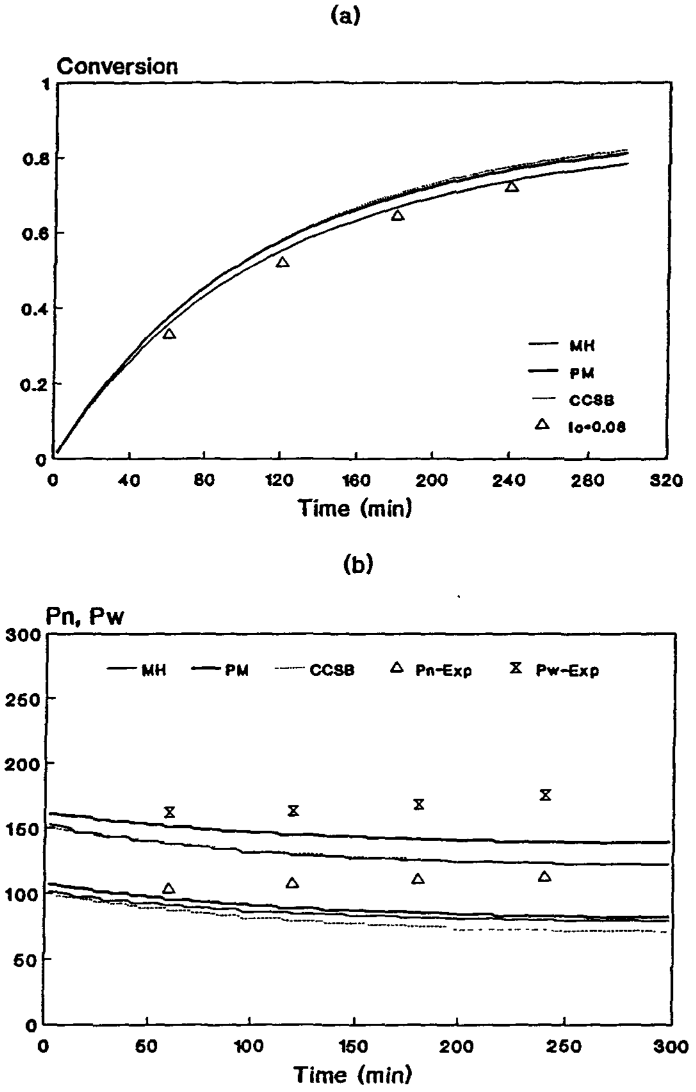

Figure 2.20 Styrene solution homopolymerization. Experimental versus model predictions (MH, PM and CCSB) at conditions of data set 12T. (a) Conversion/time profile. (b) N- and w-average chain length/time profiles.

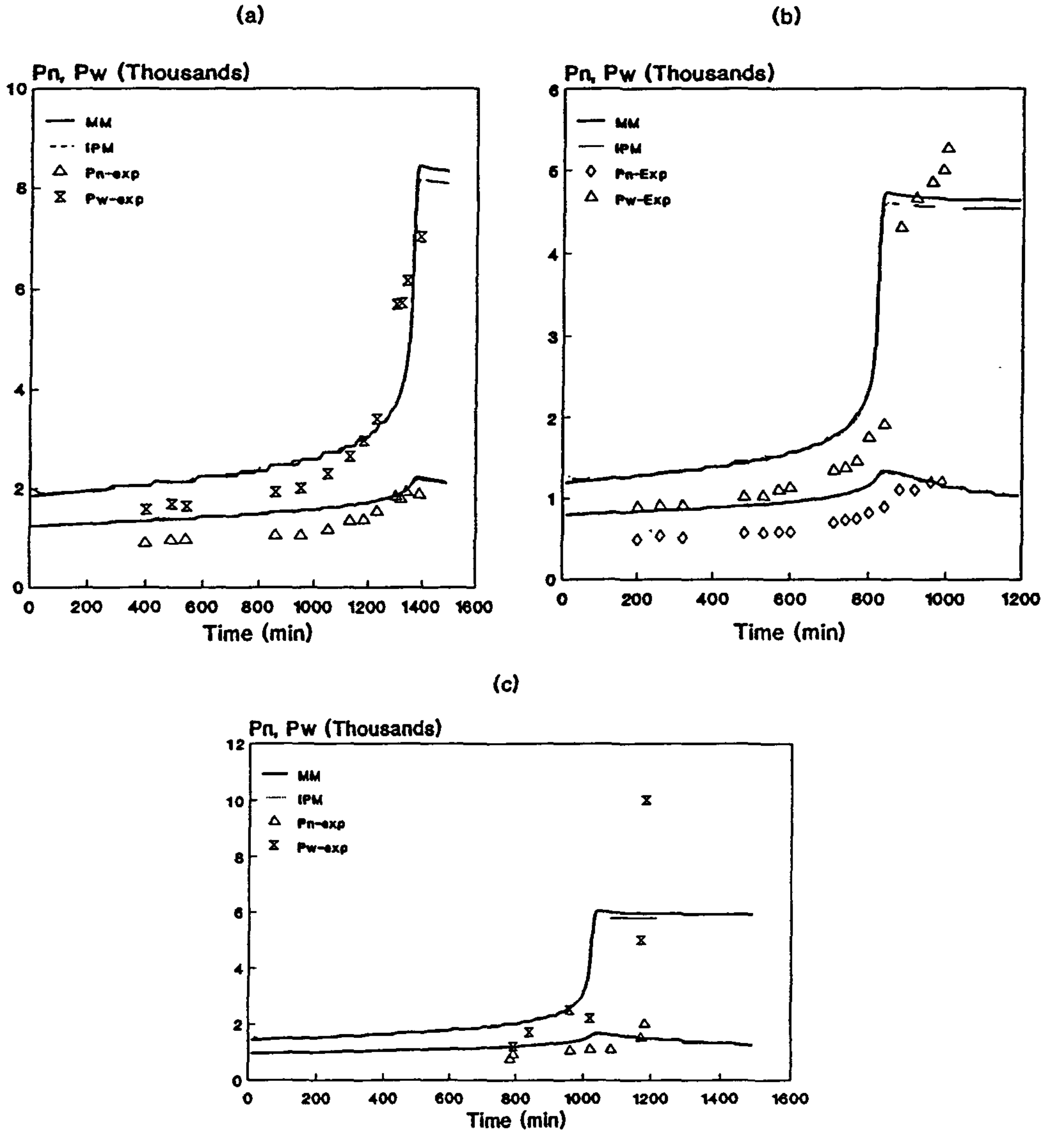

Figure 2.21 Styrene bulk homopolymerization. Comparison of the MM and IPM methods. Predictions of n- and w-average chain length/time profiles at conditions of data sets (a) 1, (b) 2 and (c) 3.

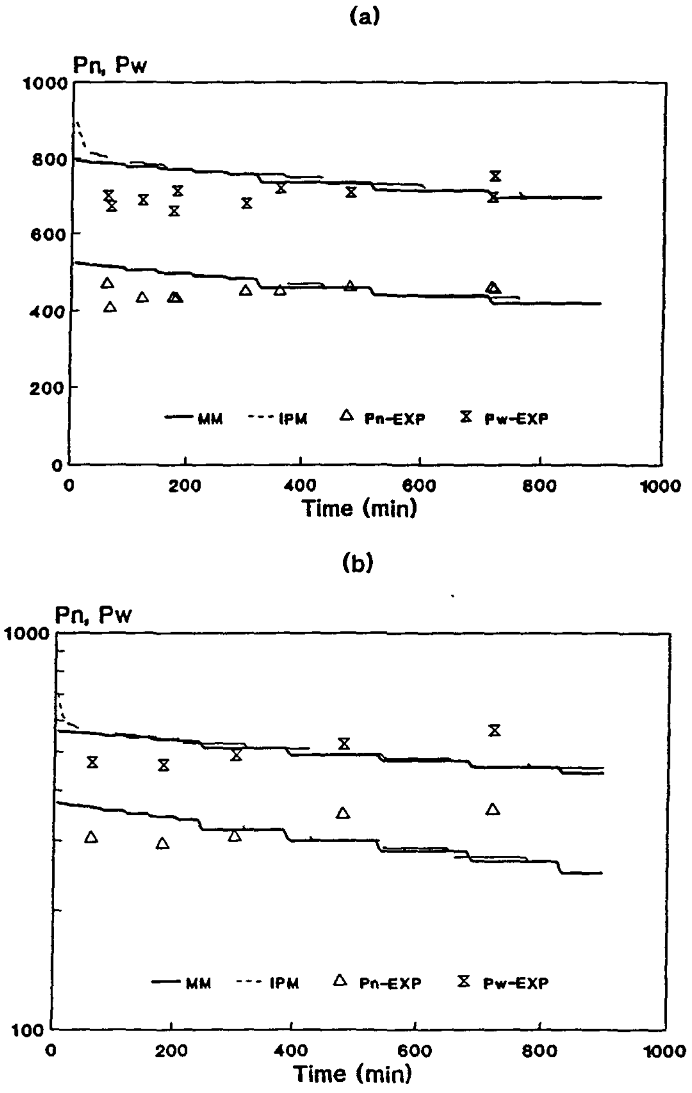

Figure 2.22 Styrene solution homopolymerization. Comparison of the MM and IPM methods. Predictions of n- and w-average chain length/time profiles at conditions of data sets (a) 1T and (b) 2T.

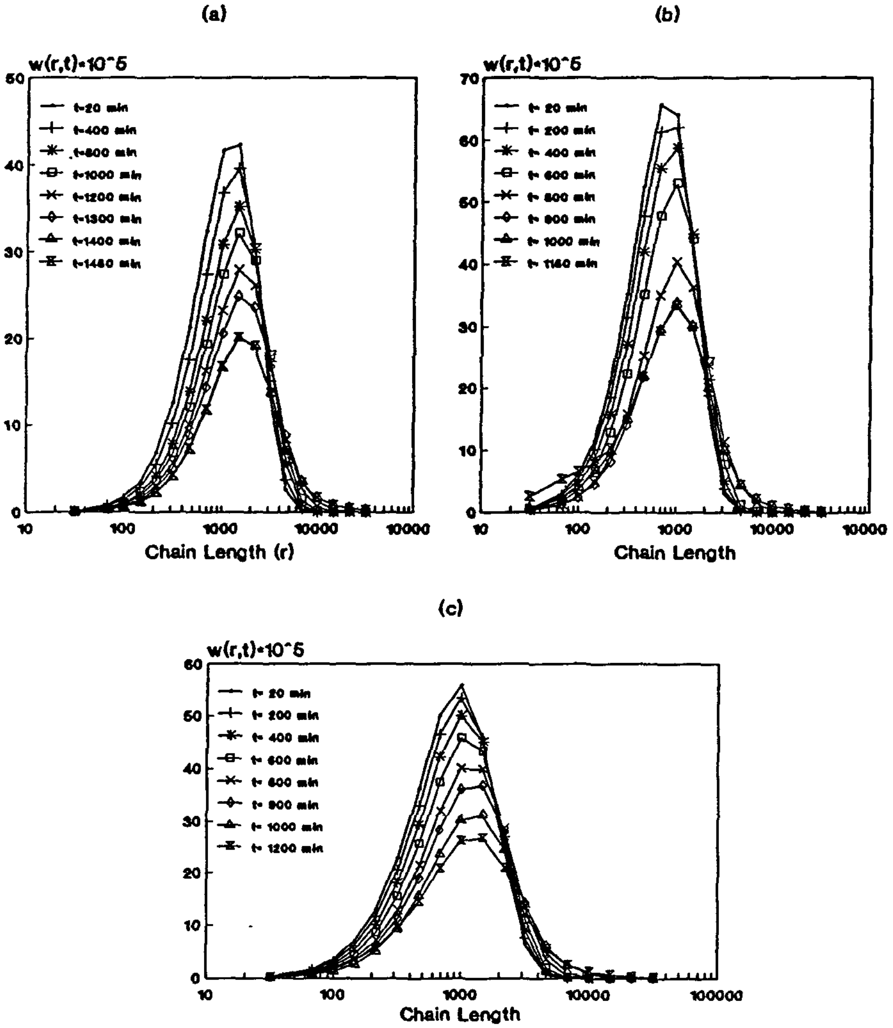

Figure 2.23 Styrene bulk homopolymerization. Calculation of the full chain length distribution (at polymerization times indicated in the plots) at conditions of data sets (a) 1, (b) 2 and (c) 3.

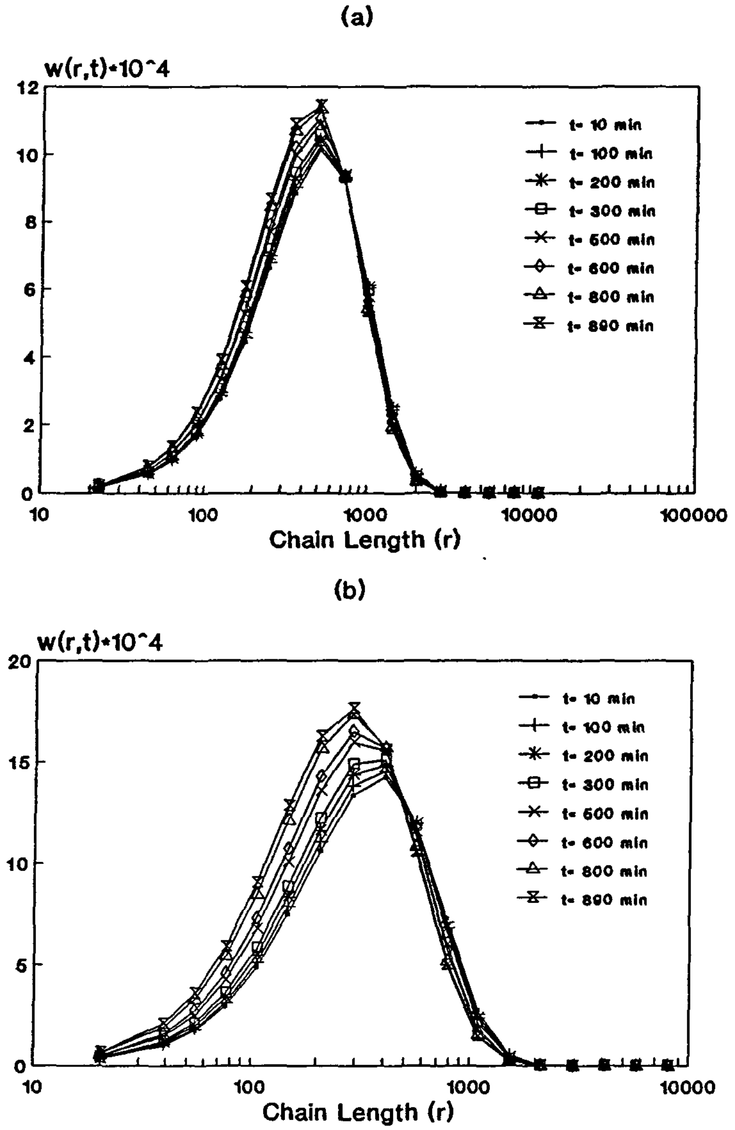

Figure 2.24 Styrene solution homopolymerization. Calculation of the full chain length distribution (at polymerization times indicated in the plots) at conditions of data sets (a) 1T and (b) 2T.

CHAPTER 3

BATCH REACTOR MODELLING OF THE FREE RADICAL COPOLYMERIZATION KINETICS OF STYRENE/DIVINYLBENZENE UP TO HIGH CONVERSIONS.

ABSTRACT

An effective model for the bulk, solution and suspension copolymerization of styrene/divinylbenzene has been developed. Experimental data from different sources and model predictions are in excellent agreement in most cases for pre and post-gelation periods. The effect of solvent, chain transfer agent, inhibitor, type and concentration of crosslinker (m-DVB, p-DVB or a mixture of both), type and concentration of initiator, and temperature are accounted for by the present model.

INTRODUCTION

The ability to predict the synthesis kinetics and properties of polymer networks requires a rather deep understanding of the elementary reactions and their behavior during dramatic physical changes before and after gelation. This is not only important for development of new products, but also to achieve a more effective operation of existing processes. However, the formation and valid characterization of polymer networks are not completely understood, nor adequate for practical calculations are the current kinetic models.

There have been systematic efforts to develop reliable, yet not too complicated models for prediction of the polymerization rate, composition and structure of a polymer gel formed via free-radical mechanisms. Reviews about this topic can be found elsewhere (Dusek and MacKnight, 1988; Tobita, 1990; Zhu, 1991). The present situation is that there are available some theories which can explain to some extent the formation process of a polymer network. Among these theories are the percolation theory (Broadbent and Hammersley, 1957; Hammersley, 1957; Frisch and Hammersley, 1963; Kirkpatrick, 1973; Domb et. al., 1980; Stauffer, 1985) and several mean-field theories, such as the Macosko-Miller statistical model (Macosko and Miller, 1976) or the Tobita-Hamielec kinetics model (Tobita and Hamielec, 1988, 1989a, 1989b, 1989c, 1990a, 1990b, 1992). There have also been published several experimental kinetics studies for the styrene/divinylbenzene (Hild and Okasha, 1985; Hild et. al., 1985; Okasha et. al., 1979; Storey, 1965; Malinski and Klaban, 1971) and for methyl methacrylate/ethylene glycol dimethacrylate (Gordon and Roe, 1956a, 1956b, 1956c, 1956d; Hayden and Melville, 1960; Horie et. al., 1975; Landin and Macosko, 1988; Li et. al., 1989; Loshaek, 1953; Loshaek, 1955; Moran and Martin, 1983; Shultz, 1958; Tian et. al., 1992; Tobita, 1990; Zhu, 1991; Zhu and Hamielec, 1988, 1989, 1991; Zhu et. al., 1990a, 1990b) copolymerizations. Even some semi-empirical attempts to model crosslinking kinetics for use in the polymer composites manufacturing industry are available

(Batch and Macosko, 1992; Tungare and Martin, 1992; Medina-Calderón et. al., 1992).

In order for a model to be effective, it has to account for most of the physical phenomena under consideration, it has to be rather easy to solve with standard computational tools and it should be able to predict reasonably well the experimental behavior of the system being studied both in the interpolation range (range of variation of important variables as used in the parameter estimation stage, if used) and the extrapolation one (conditions out of the range of variables used in the parameter estimation). So far, existent theoretical models, such as the Tobita-Hamielec one, give qualitatively good predictions, but quantitative predictions are obtained using several simplifications and assumptions which are not always of practical use. On the other hand, the empirical models give reasonable good quantitative predictions, but due to their incomplete theoretical background they can not be extended to conditions different from those used in the parameter estimation stage and even their reliability for interpolation purposes is not guaranteed. Moreover, most of the available published, quantitative predictions are limited to the pre-gelation period of the copolymerization.

Using the Tobita-Hamielec model for crosslinking kinetics in the pre-gelation period, an improved version of the Marten-Hamielec model for diffusion controlled kinetics in free radical polymerization (Vivaldo-Lima et. al., 1993), which incorporates Zhu and Hamielec's remarks on the use of different number and weight average termination constants (Zhu and Hamielec, 1989) and a simple phenomenological approach for the termination kinetic constant during the post-gelation period, quantitative predictions of the styrene/divinylbenzene copolymerization at several conditions and covering all the conversion range could be obtained. Predictions are in very good agreement with the experimental information, which includes reaction rate, number and weight average chain lengths, copolymer composition and sol/gel fractions. The effect of solvent, active chain transfer agent, type and amount of initiator (AIBN or BPO), inhibitor concentration, crosslinker type (m-DVB, p-DVB or mixtures of both) and concentration as well as temperature are successfully accounted for in most cases with the present model.

The model equations were solved with and without use of the steady state hypothesis (SSH) assumption for the radical moment equations. The predictions obtained with both models can be considered equivalent for the pre-gelation period. However, the SSH assumption seems to be inadequate in the post-gelation period even when solvent or inhibitor are present.

KINETIC MODEL

Reaction Scheme

The chemical system to be analysed is the free-radical copolymerization of vinyl-divinyl comonomers, namely styrene/divinyl benzene. The relevant chemical reactions which are considered to take place in such a system are the following (Tobita, 1990; Tobita and Hamielec, 1989c):

Initiation

$$I \longrightarrow 2R^{\cdot}_{in} \qquad (k_d)$$

$$R^{\cdot}_{in} + M_1 \longrightarrow R^{\cdot}_{1,0,1} \qquad (k_1)$$

$$R^{\cdot}_{in} + M_2 \longrightarrow R^{\cdot}_{0,1,2} \qquad (k_2)$$

Inhibition

$$R^{\cdot}_{m,n,1} + Z \longrightarrow P_{m,n} \qquad (k_{z1})$$

$$R^{\cdot}_{m,n,2} + Z \longrightarrow P_{m,n} \qquad (k_{z2})$$

$$R^{\cdot}_{m,n,3} + Z \longrightarrow P_{m,n} \qquad (k_{z3})$$

Propagation

$$R^{\cdot}_{m,n,1} + M_1 \longrightarrow R^{\cdot}_{m+1,n,1} \qquad (k_{11})$$

$$R^{\cdot}_{m,n,1} + M_2 \longrightarrow R^{\cdot}_{m,n+1,2} \qquad (k_{12})$$

$$R^{\cdot}_{m,n,2} + M_1 \longrightarrow R^{\cdot}_{m+1,n,1} \qquad (k_{21})$$

$$R^{\cdot}_{m,n,2} + M_2 \longrightarrow R^{\cdot}_{m,n+1,2} \qquad (k_{22})$$

Propagation through pendant double bonds

$$R^{\cdot}_{m,n,1} + P^{*}_{r,s} \longrightarrow R^{\cdot}_{m+r+1,s+n,3} \qquad (kp^{*}_{13})$$

$$R^{\cdot}_{m,n,2} + P^{*}_{r,s} \longrightarrow R^{\cdot}_{m+r,s+n+1,3} \qquad (kp^{*}_{23})$$

$$R^{\cdot}_{m,n,3} + P^{*}_{r,s} \longrightarrow R^{\cdot}_{m+r,s+n,3} \qquad (kp^{*}_{33})$$

Transfer to monomer

$$R^{\cdot}_{m,n,1} + M_1 \longrightarrow P_{m,n} + R^{\cdot}_{1,0,1} \qquad (kf_{11})$$

$$R^{\cdot}_{m,n,1} + M_2 \longrightarrow P_{m,n} + R^{\cdot}_{0,1,2} \qquad (kf_{12})$$

$$R^{\cdot}_{m,n,2} + M_1 \longrightarrow P_{m,n} + R^{\cdot}_{1,0,1} \qquad (kf_{21})$$

$$R^{\cdot}_{m,n,2} + M_2 \longrightarrow P_{m,n} + R^{\cdot}_{0,1,2} \qquad (kf_{22})$$

Transfer to a small molecule (either solvent or transfer agent)

$$R^{\cdot}_{m,n,1} + T \longrightarrow P_{m,n} + T^{\cdot} \qquad (kf_{T1})$$

$$R^{\cdot}_{m,n,2} + T \longrightarrow P_{m,n} + T^{\cdot} \qquad (kf_{T2})$$

Termination

$$\begin{aligned}
R^{\cdot}_{m,n,1}+R^{\cdot}_{r,s,1} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td11}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc11}) \\
R^{\cdot}_{m,n,1}+R^{\cdot}_{r,s,2} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td12}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc12}) \\
R^{\cdot}_{m,n,2}+R^{\cdot}_{r,s,2} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td22}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc22}) \\
R^{\cdot}_{m,n,1}+R^{\cdot}_{r,s,3} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td13}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc13}) \\
R^{\cdot}_{m,n,2}+R^{\cdot}_{r,s,3} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td23}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc23}) \\
R^{\cdot}_{m,n,3}+R^{\cdot}_{r,s,3} &\longrightarrow P_{m,n} + P_{r,s} && (k_{td33}) \\
&\longrightarrow P_{m+r,n+s} && (k_{tc33})
\end{aligned}$$

where $R^{\cdot}_{m,n,i}$ is a polymer radical with m-units of monomer 1 (M_1) and n-units of monomer 2 (M_2) bound in the polymer chain and with the active center located on monomer unit i. $P_{m,n}$ is a polymer molecule with m-units of monomer 1 and n-units of monomer 2. Subscript 3 accounts for pendant double bonds. It is assumed that a polymer radical can have no more than one radical center.

Using the "pseudo-kinetic rate constant method", the previous kinetic scheme can be treated as if it were a homopolymerization (Hamielec and MacGregor, 1983;

Tobita, 1990; Zhu, 1991). To do this the "pseudo-kinetic" rate constants must be defined as follows:

Propagation

$$k_p=\sum_{i}^{2}\sum_{j}^{2}k_{ij}\phi^{\bullet}_{i}f_{j} \tag{1}$$

Propagation through pendant double bonds

$$k_p^{*}=\sum_{i}^{3}k^{*}_{p_{i3}}\phi^{\bullet}_{i}(\overline{F_2}-\overline{\rho_a}-\overline{\rho_c}) \tag{2}$$

Inhibition

$$k_z=\sum_{i}^{3}k_{zi}\phi^{\bullet}_{i} \tag{3}$$

Transfer to monomer

$$k_{fm}=\sum_{i}^{3}\sum_{j}k_{fm_{ij}}\phi^{\bullet}_{i}f_{j} \tag{4}$$

Transfer to a small molecule

$$k_{fT}=\sum_{i}^{3}k_{fT_{i}}\phi^{\bullet}_{i} \tag{5}$$

Termination by disproportionation

$$k_{td}=\sum_{i}^{3}\sum_{j}^{3}k_{td_{ij}}\phi^{\bullet}_{i}\phi^{\bullet}_{j} \tag{6}$$

Termination by combination

$$k_{tc}=\sum_{i}^{3}\sum_{j}^{3}k_{tc_{ij}}\phi^{\bullet}_{i}\phi^{\bullet}_{j} \tag{7}$$

where

$$\phi^{\bullet}_{i}=\frac{[R^{\bullet}_{i}]}{\sum_{j}^{3}[R^{\bullet}_{j}]}=\frac{[R^{\bullet}_{i}]}{[R^{\bullet}]} \tag{8}$$

Mathematical Equations

Pre-Gelation Period

Based on the previous reaction scheme the following differential equations can be derived:

Initiator consumption

$$\frac{d(V[I])}{Vdt}=-k_{d}[I] \tag{9}$$

Inhibitor consumption

$$\frac{d(V[Z])}{Vdt}=-k_{z}[Z]\,[R^{\bullet}] \tag{10}$$

Overall conversion

$$\frac{dx}{dt}=(k_{p}+k_{fm})\,(1-x)\,[R^{\bullet}] \tag{11}$$

where x is defined as

$$x=\frac{V_0[M_1+M_2]_0-V[M_1+M_2]}{V_0[M_1+M_2]_0} \tag{12}$$

Normalized moment equations (Tobita, 1990; Tobita and Hamielec, 1989c) for dead polymer (Steady State Hypothesis assumed):

$$\frac{dq_0}{dt}=(\tau+\frac{\beta}{2}-Cp^*{}_1)\frac{dx}{dt} \tag{13}$$

$$\frac{dq_1}{dt}=\frac{dx}{dt} \tag{14}$$

$$\frac{dq_2}{dt}=\frac{2(1+Cp_2+Cp^*{}_2)(1+Cp^*{}_2)}{\tau+\beta+Cp_1}\frac{dx}{dt}+\beta\frac{(1+Cp_2+Cp^*{}_2)^2}{(\tau+\beta+Cp_1)^2}\frac{dx}{dt} \tag{15}$$

Moment equations (Tobita, 1990; Tobita and Hamielec, 1989c) for polymer radicals (Steady State Hypothesis assumed):

$$Y_0=[R^\bullet]=\frac{\sqrt{k_z{}^2[Z]^2+8fk_dk_t[I]}-k_z[Z]}{2k_t} \tag{16}$$

$$y_0=1 \tag{17}$$

$$y_1=\frac{1+Cp_2+Cp^*{}_2}{\tau+\beta+Cp_1} \tag{18}$$

$$y_2 = \frac{1+Cp_3+Cp^*_3}{\tau+\beta+Cp_1} + \frac{2(1+Cp_2+Cp^*_2)}{(\tau+\beta+Cp_1)^2} \tag{19}$$

where

$$q_i = \frac{VQ_i}{V_0 M_0} \tag{20}$$

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \tag{21}$$

$$y_i = \frac{Y_i}{Y_0} \tag{22}$$

$$Y_i = \sum_{r=1}^{\infty} r^i [R^{\bullet}_r] \tag{23}$$

$$Cp_i^* = \frac{k_p^* q_i}{k_p} \tag{24}$$

$$Cp_i = \frac{k_{fp} q_i}{k_p} \tag{25}$$

$$k_{fp} = \sum_{i}^{3} \sum_{j}^{2} k_{fp_{ij}} \phi^{\bullet}_i \overline{F_j} \tag{26}$$

$$\tau = \frac{R_{td}+R_{fm}+R_{fT}+R_{fS}+R_Z}{R_p} \tag{27}$$

$$\beta = \frac{R_{tc}}{R_p} \tag{28}$$

Polymer Moment Equations (Transient Model)

To remove the steady state hypothesis (SSH), a transient model must be used. Individual calculation of the radical and dead polymer moment equations would result in a closure problem (Tobita, 1990; Zhu, 1991). However, it is the sum of radical and dead polymer concentrations which is needed. If the individual radical and dead polymer equations are summed, it appears as though there is no closure problem. However, it actually remains in equation (33). This equation allows (Y_2+Q_2) to be calculated in terms of Q_2, which is not known explicitly. If Q_2 is expressed as (Q_2+Y_2) - Y_2, it is now Y_2 which is not known. Adding an equation for Y_2 would bring another unknown of higher order (Q_3) and so on. There are three ways to solve this situation:

i) Assume that $Q_2 >> Y_2$ and therefore, Q_2 can be substituted by (Q_2+Y_2) in equations (31) and (33).

ii) Approximate Y_2 with its SSH value.

iii) Propose a relationship between Y_2 and a lower radical moment (say Y_1).

Three approximations were attempted in this work [equations (34) to (36)] in addition to alternative (i), which are discussed later on in this work.

A mass balance analysis for total polymer radical and dead polymer concentrations would lead to the following total polymer moment equations:

$$\frac{d(VY_0)}{Vdt}=2fk_d[I]-k_z[Z]Y_0-(\bar{k}_{tcn}+\bar{k}_{td})Y_0^2 \tag{29}$$

$$\begin{aligned}\frac{d(V[Y_0+Q_0])}{Vdt}&=2fk_d[I]+(k_{fm}[M]+k_{fT}[T])Y_0\\&-k_p^*Y_0([Y_1+Q_1]-Y_1)-\tfrac{1}{2}\bar{k}_{tcn}Y_0^2\end{aligned} \tag{30}$$

$$\begin{aligned}\frac{d(VY_1)}{Vdt}&=2fk_d[I]+(k_{fm}[M]+k_{fT}[T])Y_0+k_{fp}Y_0Q_2\\&+k_p^*Y_0Q_2+k_p[M]Y_0-\{k_{fm}[M]+k_{fT}[T]+(\bar{k}_{tcn}+\bar{k}_{td})Y_0\\&+k_{fp}([Y_1+Q_1]-Y_1)\}Y_1\end{aligned} \tag{31}$$

$$\frac{d(V[Y_1+Q_1])}{Vdt}=2fk_d[I]+(k_{fm}[M]+k_{fT}[T])Y_0+k_p[M]Y_0 \tag{32}$$

$$\begin{aligned}\frac{d(V[Y_2+Q_2])}{Vdt}&=2fk_d[I]+(k_{fm}[M]+k_{fT}[T])Y_0+k_p[M]Y_0\\&+2k_p[M]Y_1+2k_p^*Y_1([Y_2+Q_2]-Y_2)+\bar{k}_{tcw}Y_1^2\end{aligned} \tag{33}$$

$$Y_2=Y_1\frac{P_w}{P_n} \tag{34}$$

$$Y_2=Y_1\sqrt{\frac{P_w}{P_n}} \tag{35}$$

$$Y_2=Y_1\sqrt{\left(\frac{P_w}{P_n}\right)^x} \tag{36}$$

Divinyl monomer consumption

$$\frac{df_2}{dt}=\frac{f_2-F_2}{1-x} \tag{37}$$

where f_2 is the divinyl monomer (DVM) mol fraction and F_2 is the instantaneous DVM mol fraction incorporated into polymer and are calculated as follows:

$$f_1=\frac{M_1}{M_1+M_2} \tag{38}$$

$$f_2=\frac{M_2}{M_1+M_2}=1-f_1 \tag{39}$$

$$F_2=\frac{(k_{12}\phi^\bullet_1+k_{22}\phi^\bullet_2+k_{32}\phi^\bullet_3)\,f_2}{(k_{11}\phi^\bullet_1+k_{21}\phi^\bullet_2+k_{31}\phi^\bullet_3)\,f1+(k_{12}\phi^\bullet_1+k_{22}\phi^\bullet_2+k_{32}\phi^\bullet_3)\,f_2} \tag{40}$$

Accumulated copolymer composition

$$\overline{F_2}=\frac{f_{20}-f_2(1-x)}{x} \tag{41}$$

To calculate the radical fractions, the following set of simultaneous algebraic equations [equations (42) to (44)] should be solved (Tobita, 1990; Tobita and Hamielec, 1989c):

$$k_{12}f'_2\phi^\bullet_1-(k_{21}f'_1+k^*_{23}f'_3)\phi^\bullet_2+k_{32}f'_2\phi^\bullet_3=0 \tag{42}$$

$$(k_{12}f'_2+k^*_{13}f'_3)\phi^{\bullet}_1-k_{21}f'_1\phi^{\bullet}_2-k_{31}f'_1\phi^{\bullet}_3=0 \tag{43}$$

$$\phi^{\bullet}_1+\phi^{\bullet}_2+\phi^{\bullet}_3=1 \tag{44}$$

where

$$f'_1=\frac{f_1(1-x)}{1-x+(\overline{F_2}-\overline{\rho_a}-\overline{\rho_c})x} \tag{45}$$

$$f'_2=\frac{f_2(1-x)}{1-x+(\overline{F_2}-\overline{\rho_a}-\overline{\rho_c})x} \tag{46}$$

$$f'_3=\frac{(\overline{F_2}-\overline{\rho_a}-\overline{\rho_c})x}{1-x+(\overline{F_2}-\overline{\rho_a}-\overline{\rho_c})x} \tag{47}$$

Cross-linking density

From Tobita's work (Tobita, 1990; Tobita and Hamielec, 1989c) the following expressions can be obtained, considering average values for additional and cyclization densities:

$$\overline{\rho}(x)=\overline{\rho_a}(x)+\overline{\rho_i}(x)=2\overline{\rho_a}(x)=2\overline{\rho_i}(x) \tag{48}$$

$$\overline{\rho_{cp}}(x)=k_{cp}\overline{F_2}(x) \tag{49}$$

$$\overline{\rho_{cs,a}}(x)=k_{cs}\overline{\rho_a}(x) \tag{50}$$

Therefore, the rate of average additional cross-linking density will be given by:

$$\frac{d[x\overline{\rho_a}(x)]}{dt}=\frac{k_p^{*0}[\overline{F_2}(x)(1-k_{cp})-\overline{\rho_a}(x)(1+k_{cs})]x}{k_p(1-x)}\frac{dx}{dt} \tag{51}$$

Small molecule (such as solvent or added chain transfer agent)

$$\frac{d(V[T_i])}{Vdt}=-k_{fTi}[T_i][R^{\bullet}],i=solvent,\; transfer\text{-}agent,... \tag{52}$$

To account for volume contraction, the following expression is used:

$$V=V_0[1+(\frac{\rho_m-\rho_p}{\rho_p})x] \tag{53}$$

In equations (15), (19) and (33), β is calculated using $\bar{k}_{tcw}$. In all the remaining cases $\bar{k}_{tcn}$ must be used. Doing so assures that weight average chain lengths are not underpredicted (Zhu and Hamielec, 1989).

Auto-acceleration (Norrish-Trommsdorff) Effect

To account for the autoacceleration effect, an improved version of the Marten-Hamielec (MH) model for calculation of the propagation and termination kinetic constants was used. The initiator efficiency fall off at the end of polymerization was modelled by means of a free-volume approach. The details about the way the MH model was modified are the scope of another publication (Vivaldo-Lima et. al., 1993). Here only the main modifications and final expressions are presented.

The initiator efficiency was considered to decrease as polymerization proceeds due to free-volume reduction. Therefore, the following equation was used:

$$f=f_0 e^{-D\left(\frac{1}{V_f}-\frac{1}{V_{f0}}\right)} \tag{54}$$

The "artificial onset" of the "Norrish-Trommsdorff" effect in the original MH model [use of the parameter K3(T)] (Marten and Hamielec, 1982) was eliminated by taking into account the free-volume restrictions from the beginning of the polymerization and the use of a conversion-dependent termination kinetic constant, as well as the use of different number and weight average values for such parameters. In Vivaldo-Lima et. al. (1993) the following equations were obtained:

$$\overline{k}_{tcn_{ij}}=k^{0}_{tcn_{ij}} e^{-\left[A\left(\frac{1}{V_f}-\frac{1}{V_{f0}}\right)\right]}+k_{tcrd} \tag{55}$$

$$\overline{k}_{tcw_{ij}}=k^{0}_{tcw_{ij}}\left[\frac{P_n}{P_w}\right]^{x/2} e^{-\left[A\left(\frac{1}{V_f}-\frac{1}{V_{f0}}\right)\right]}+k_{tcrd} \tag{56}$$

where k_{tcrd} is the reaction-diffusion termination constant and was calculated as indicated in equation (57).

$$k_{tcrd}=C^{0}_{rd} k_{p_{pse}}(1-x) \tag{57}$$

The "artificial onset" of the glassy effect (propagation kinetic constant dependence on free-volume) was kept in order to get statistically significant estimates of the unknown parameters when using the "error in variables method" (EVM) for non-linear parameter estimation (Vivaldo-Lima et. al., 1993; Sutton and MacGregor, 1977; García-Rubio, 1981). However, this limitation can be removed by considering the free-volume dependence from the beginning of the polymerization, as previously shown for the termination constant.

$$k_{p_{ij}}=k_{p_{ij}}^{0}\,e^{-\left(\frac{1}{V_f}-\frac{1}{V_{f_{cr2}}}\right)} \qquad (58)$$

where

$$V_f=\sum_{i}^{N}\left[0.025+\alpha_i(T-T_{g_i})\frac{V_i}{V_t}\right];\ i=monomer\text{-}1,monomer\text{-}2,polymer\ solvent,transfer\text{-}agent \qquad (59)$$

By using equation (59) it is implicitly assumed that equilibrium in free volume is reached at every moment during the complete course of polymerization. However, this may not be the case in polymerization reactions with strong autoacceleration effect at very high conversions, such as crosslinking. Very recently Anseth et. al. (1993) concluded that the formation of densely crosslinked polymer networks leads to volume relaxation during photopolymerization which may occur over a longer time scale than the reaction kinetics. Therefore, an excess in free volume is present during polymerization and equation (59) would not be correct. One important effect of such excess in free volume would be obtaining higher limiting conversions as the reaction rate is increased (by increasing initiator concentration, for instance), even if the temperature is kept constant. This effect was first reported by Stickler (1983), in the context of MMA polymerization at very high conversions, and it was first modelled by Bowman and Peppas (1991).

The concept of excess in free volume has been known and modelled in the context of physical behavior of polymers. Such is the case in studies of plasticization and antiplasticization of glassy polymers with small molecules (Vrentas et. al., 1988; Vrentas, J.S. and Vrentas, C.M., 1991a, 1991b), diffusion of large molecules in amorphous polymers (Coughlin et. al., 1991), PEEK crystallization (Nakanishi and Jean, 1991), gas adsorption on glassy polymers (Ganesh et. al., 1992), cooling and heating of polymers across the glass transition (Losi and Knauss, 1992), among others. A paper by Tant and Wilkes (1981) contains a review on this subject. The existence and importance of the free volume distribution has been considered (Takeuchi et. al., 1990; Rigby et. al., 1990; Losi and Knauss, 1992). Analysis on the indirect measurement of free volume and its relationships, depending on the definition of free volume, have been made by Gupta and Brahatheeswaran (1991).

From basic thermodynamics, an excess property is defined as the difference between an actual property and the property that would be calculated for the same conditions (temperature, pressure and composition), assuming ideal or equilibrium behavior (Smith and Van Ness, 1975).

The average non-equilibrium free volume in the previous situations has been calculated in two ways. In the first, the excess in free volume is accounted for by adding a non-equilibrium term in the polymer free volume, which is a fraction of its equilibrium value (Vrentas et. al., 1988; Vrentas, J.S. and Vrentas, C.M., 1991a, 1991b; Coughlin et. al., 1991; Ganesh et. al., 1992). In the second case, the rate of free volume change is calculated as the sum of two terms, namely a relaxation term and a production or generation of free volume term (Tant and Wilkes, 1981; Nakanishi and Jean, 1991; Losi and Knauss, 1992). The model proposed by Bowman and Peppas (1991) has this second structure, except for the fact that the generation term is not considered. Based on these ideas two models are proposed to account for non equilibrium free volume in a copolymerization situation.

Our first model considers that the instantaneous free volume is the contribution of two terms: an equilibrium term and an excess one. Therefore, the free volume is calculated as:

$$V_f = V_{f_{eq}} + \delta\,[0.025 + \alpha_p (T - T_{gp})]\,\frac{V_p}{V_t} \qquad (60)$$

where $V_{f_{eq}}$ is given by equation (59).

δ in equation (60) should be proportional to the ratio of relaxation time to a characteristic reaction time. The relaxation time should be proportional to the rate of change of molecular weight and crosslinking density and the characteristic reaction time should be proportional to the conversion rate. It is therefore proposed to calculate δ as indicated in equation (61).

$$\delta = \delta_0 \frac{\frac{d(x\bar{\rho})}{dt} + (x - \bar{\rho})\frac{dx}{dt}}{\frac{dx}{dt}} \qquad (61)$$

In the second model the instantaneous free volume is calculated from equation (62).

$$\frac{dV_f}{dt}=-\frac{(V_f-V_{feq})}{\tau}+R_{fv} \tag{62}$$

where τ is the relaxation time, which is calculated following Tant and Wilkes (1981), as indicated in equation (63), and R_{fv} is the rate of production or generation of free volume. In a crosslinking reaction the formation of polymer network molecules reduces significantly the free volume but, on the other hand, the spaces created between crosslinking units and chain fragments generate some free volume. Therefore, the rate of generation of free volume should be proportional to the rate of change in crosslinking density. This relationship is proposed to be as indicated in equation (64).

$$\tau=\tau_0 e^{B_f(\frac{1}{V_f}-\frac{1}{V_{f0}})} \tag{63}$$

$$R_{fv}=\delta'\left[\frac{d(x\bar{\rho})}{dt}+(x-\bar{\rho})\frac{dx}{dt}\right] \tag{64}$$

The model described by equation (60) will be referred to later as the "single parameter" model and the one described by equation (62) will be referred as the "three parameter" model.

Most of the calculations presented in this paper were obtained using equation (59) (Figures 3.2 to 3.24). In Appendix A, calculations obtained using the non equilibrium models (equation 60 or 62) are presented. The reason for using the equilibrium free volume in most of the calculations was that there were not enough experimental data to get reliable estimates of the required parameters.

Post-Gelation Period

Modelling the post-gelation period in a crosslinking polymerization is a complex problem. Recently, Tobita and Hamielec (1988, 1989a, 1989b, 1989c, 1990a, 1990b, 1992) made a generalization of the Flory-Stockmayer theory. However, they obtained rather complicated expressions which give practically the same results as the original model, when applied to real copolymerization systems. Therefore, it was decided to start from the original Flory-Stockmayer model (Flory, 1947, 1953; Stockmayer, 1943, 1944, 1945) and try to extend the models for diffusion-controlled kinetics, which is crucial to properly explain the kinetic behavior in the post-gelation period. Even though the concept of crosslinking density distribution proposed by Tobita and Hamielec was not used, Flory's Simplifying Assumptions (equal reactivity of all double bonds, independent reactivity of double bonds and absence of intramolecular reactions) were removed by considering cyclization reactions and different reactivities for each species (monomer, divinyl monomer or pendant double bond) over the complete polymerization range, namely during the pre-gelation and the post-gelation periods.

For the post-gelation period, equations (1) to (11) and either equation (16) or (29) (these two last equations depending on the model being used, namely the SSH based model or the transient one) were used.

To calculate the sol fraction, the Flory-

Stockmayer equation (eq. 65) was used.

$$w_s(x) = (\tau+\beta)\int_1^{\infty}(1-\rho w_g)^{r}\left[r\tau+\frac{\beta}{2}(\tau+\beta)r^2\right]e^{-(\tau+\beta)r}dr \tag{65}$$

which has the following analytical solution:

$$w_s(x) = \frac{(\tau+\beta)(1-\rho w_g)e^{-(\tau+\beta)}}{[\ln(1-\rho w_g)-(\tau+\beta)]^3}\Big[\beta(\tau+\beta)[\ln(1-\rho w_g)-(\tau+\beta-1]+[\ln(1-\rho w_g)$$
$$-(\tau+\beta)]\tau-[\ln(1-\rho w_g)-(\tau+\beta)]^2\left[\tau+\frac{\beta}{2}(\tau+\beta)\right]\Big] \tag{66}$$

where $\rho=\rho(x)$ is the crosslinking density and $w_g=w_g(x)=1-w_s(x)$. As can be seen, this equation is implicit in w_s and therefore, it is numerically solved at each integration step of the overall set of differential equations.

To calculate the number and weight average chain lengths for the sol fraction, the following expressions were used (Tobita and Hamielec, 1989c):

$$\bar{P}_n^{sol}(x) = \frac{2\bar{P}_{np}^{sol}(x)}{2-\bar{\rho}^{sol}(x)\bar{P}_{np}^{sol}(x)} \tag{67}$$

$$\bar{P}_w^{sol}(x) = \frac{\bar{P}_{wp}^{sol}(x)}{1-\bar{\rho}^{sol}(x)\bar{P}_{wp}^{sol}(x)} \tag{68}$$

where

$$\bar{P}_{np}^{sol} = \frac{\bar{w}_s(x)}{HG_1\left[\tau+\frac{\beta}{2}HG_1\right]} \tag{69}$$

$$\bar{P}^{sol}_{wp}=\frac{HU}{\bar{w}_s(x)}(LG_2+HVG_1G_3) \tag{70}$$

$$H=L+V \tag{71}$$

$$L=\frac{\tau}{\tau+\beta+\bar{\rho}(x)\bar{w}_g(x)} \tag{72}$$

$$V=\frac{\beta}{\tau+\beta+\bar{\rho}(x)\bar{w}_g(x)} \tag{73}$$

$$U=\frac{G_1}{\tau+\beta+\bar{\rho}(x)\bar{w}_g(x)} \tag{74}$$

$$G_i=i-\bar{\rho}(x)\bar{w}_g(x)\,;i=1,2,3 \tag{75}$$

Kinetic Behavior During the Post-Gelation Period

The kinetic behavior of free-radical (co)-polymerization systems has been the subject of many investigations. It is beyond the scope of this paper to review them. What seems to be clear is that as the polymer grows in size, diffusional limitations gain importance. This situation is particularly true for systems which undergo crosslinking reactions, where the effects of falling termination and propagation, as well as initiator efficiency, occur simultaneously and become important.

From equations (55) and (56) it is clear that the "translational" contribution to the kinetic termination constant falls to a negligible value at the gel point ("infinite" weight average chain length). However, the "reaction diffusion" component is still important. It should be noted that the term C^0_{rd} is not a real constant; it actually depends, among other things, on the polymer "mean diameter" (Buback, 1990). As the average chain length remains moderately constant at low and intermediate conversion levels (at least for polystyrene at low crosslinker concentrations) and considering the fact that the intrinsic termination kinetic constant is much higher than the reaction-diffusion one, most of the behavior during the pre-gelation period is ruled by the evolution of the translational termination constant. As polymerization proceeds, C^0_{rd} actually increases up to a maximum value, which will be referred as C^{gp}_{rd} , reached at the gel point (formation of the gel phase). From there on, it should be constant for the gel phase and it should decrease for the sol phase. This decrease for the sol phase is due to the fact that during the post-gelation period the large molecules from the sol phase become part of the gel until only monomer or oligomers remain in the sol phase.

Once gelation has taken place, two separate phases are present in the system, namely sol and gel. A rigorous treatment for the post-gelation period would require considerion of each phase independently. If it is assumed that a single expression with hybrid characteristics can be used, at least for initiation and propagation and taking into account the ideas mentioned in the previous paragraph, then equations (76) to (80) are obtained.

$$f = (x\bar{w}_{sol})^{C_1 x} f_0 e^{-D\left(\frac{1}{v_f} - \frac{1}{v_{f0}}\right)} \tag{76}$$

$$k_{p_{ij}} = (x\bar{w}_{sol})^{C_2 x} k^0_{p_{ij}} e^{-\left(\frac{1}{V_f} - \frac{1}{V_{f_{cr2}}}\right)} \tag{77}$$

$$\bar{k}_{tcn_{ij}} = \bar{k}_{tcw_{ij}} \approx 0 \tag{78}$$

$$\bar{k}_{tc} \approx k_{tc_{rd}} = \left[C^{gp}_{rd}(x\bar{w}_{sol})^{C_3 x} + C^0_{rd}(x\bar{w}_{gel})^{C_3 x}\right] k_{p_{pse}}(1-x) \tag{79}$$

where

$$C^{gp}_{rd} \approx \frac{\bar{k}_{tw_{pse}}\big|_{x_{gp}}}{k_{p_{pse}}\big|_{x_{gp}}(1-x_{gp})} \tag{80}$$

From the available experimental data for the post-gelation period (Storey, 1965; Batch and Macosko, 1992) it was found that $C_1 = C_2 = 0$ and $C_3 = 1$. Equations (58) and (72) were also used for propagation of macromonomers (macromolecules with pendant double bonds).

As mentioned above, initiation and propagation are considered to occur in a single phase with hybrid behavior. Termination, on the other hand, is being modelled separately for each phase. The results mentioned in the previous paragraph suggest that initiation and propagation should be also modelled independently for each phase. Moreover, the translational component of the termination kinetic constant should increase gradually in the sol phase, due to the reduction of weight average chain length.

RESULTS AND DISCUSSION

Solution of the kinetic model differential equations and parameter estimation strategy

To solve the set of algebraic-differential equations (9) to (11), and (13) to (28) or (29) to (36), two different numerical methods were tested, namely "Adams-Moulton" and "Gear". The first one is a "predictor-corrector" type of method and the second, used for stiff systems of differential equations, requires the evaluation of a Jacobian matrix (matrix of partial derivatives of each response with respect to each independent variable), which is quite time-consuming to evaluate if performed numerically (Conte and De Boor, 1983). This system becomes stiff in the vicinity of the gel point (gel phase formation). If P_w was allowed to increase without any limitation (second and higher order polymer moments tending to infinity), numerical problems would result, regardless of the solution method being used. Therefore, an "infinite value" for Pw was defined (for numerical purposes), which was 10^{10}.

When the Adams-Moulton method is used, consistent results for the pre-gelation period are obtained, regardless of the step size and required accuracy; however, during the post-gelation period the step size is important. When the Gear method was tested, the tolerance (convergence criteria) was very important; the lower the value used the better the results obtained, but the computing time would increase tremendously. The stepsize was important as well, when using Gear's technique. After several tests, it was found that if a rigorous convergence criteria was used (less than 10^{-12}), equivalent results would be obtained with either of the two methods, but computation time was much shorter when using Adams-Moulton. Therefore, the Adams-Moulton technique was used for most of the calculations. The convergence criteria values used were no greater than 10^{-12} and stepsize values around 10 seconds (for the SSH based model) or as low as 0.001 seconds (transient model calculations of a system in presence of an inhibitor). Most of the calculations were obtained with conventional computational tools (IBM compatible PC with 486 microprocessor), except for the transient calculations of comercial DVB with inhibitor, where an IBM RISC System/6000 work station was used to speed up the calculations.

Due to the fact that simulation calculations using the transient model required much more computing time than those using the SSH based model, all the parameter estimation calculations (non-linear regression using the EVM) were performed with the SSH based model. Therefore, unless otherwise stated, all remarks about the parameter estimation stage consider the use of the SSH assumption.

The set of algebraic equations formed with equations (42) to (44) was solved by using a Hybrid-Powell method (Powell, 1970), at each integration step of the differential equation solver. As previously mentioned, equation (66) is implicit in w_g; therefore, a conventional Newton-Raphson technique (Conte and De Boor, 1983) was used to solve it, at each integration step of the solver.

It has been recognized that compilations of literature values of rate parameters often reveal a very wide range of reported values for any particular rate parameter. With such a wide range of values, it is often possible that conflicting mechanistic suppositions can be supported with "evidence" from the literature (Gilbert, 1992). In order to try to comply with some of the Macromolecular Division of the International Union of Pure and Applied Chemistry (IUPAC) recommendations on rate coefficients reporting, a brief description of the parameter estimation procedure that was followed is included in this section. A summary of the procedure is given in Tables 3.1(a) to 3.1(g).

To better accomplish this, our model parameters will be divided into several categories, as indicated below.

Intrinsic chemical kinetic constants for pure monomers.

For styrene, the Arrhenius expressions for calculation of propagation and termination kinetic constants were obtained from a previous study (Vivaldo-Lima et. al., 1993). In this study a multivariate non-linear regression technique using the "error in variables method" (Sutton and MacGregor, 1977) was used, with conversion and weight average chain length as dependent variables (responses).

For divinylbenzene, a combination of a single variable search technique and the EVM was used. If kp_{22} was included as a parameter in the EVM, very high correlations among parameters was obtained. That is why the single variable search was performed. The criterion was to get the best behaved correlation matrix (lowest absolute values) among parameters. It should be pointed out that this estimation procedure was performed only for two different polymerization conditions (one for meta-DVB and other for a mixture of m-DVB/p-DVB). These conditions were the ones where more experimental information was available (a multivariable non-linear regression with conversion, polymer composition and weight average chain length as responses was performed). Once each parameter had been obtained, it was assumed that the ratio kp_{22}/kp_{11} remained constant, independent of temperature, for all the remaining cases. At this stage the best estimates for r_1 and r_2 available in literature (Frick et. al., 1981) were used.

TABLE 3.1(a) Summary of Kinetic Parameters. Intrinsic Chemical Constants for Pure Monomers.

PARAM	VALUE OR FUNCTIONALITY	REMARKS
k°_{11}	$275.38e^{-[\frac{8479}{R}(\frac{1}{T}-\frac{1}{333.15})]}, \frac{\ell}{mol*s}$	EVM estimation. (Vivaldo-Lima et. al., In elaboration)
k°_{22}	$(\frac{k_{22}}{k_{11}})_m=0.95; (\frac{k_{22}}{k_{11}})_p=1.9$	Single search combined with EVM (see text)
k°_{tc}	$1.223x10^8e^{-[\frac{7127}{R}(\frac{1}{T}-\frac{1}{333.15})]}, \frac{\ell}{mol*s}$	EVM (Vivaldo-Lima et al, In elaboration). Individual and cross-terms equal

Copolymer reactivity ratios.

There is ample experimental evidence which shows that the reactivities of DVB isomers are quite different.

It has been observed that the m-DVB monomer propagates much slower than the p-DVB. Even for the p-DVB case, the existent experimental studies reveal that the theoretical values (based on monomer units) $r_1= 0.5$, $r_2=2.0$ do not apply, particularly r_1 (Hild and Okasha, 1985; Hild et. al., 1985; Okasha et. al., 1979; Storey, 1965; Malinski and Klaban, 1971; Frick et. al., 1981). It was attempted in this study to estimate the reactivity ratios together with the propagation constants for pendant double bonds and the cyclization parameters using the EVM, but very high correlations and non-statistically significant values were obtained. Therefore, a statistical analysis compilation reported in the literature (Frick et. al., 1981) was analyzed and even though those values were obtained using the Meyer-Lowry equation, which does not apply for crosslinking copolymerizations at high crosslinker concentrations the errors are small at low conversions for the styrene/DVB system. With values within the r_1-r_2 joint confidence region, a combined "grid-search" and EVM parameter estimation technique was performed, which gave adequate values. It was found that there is disagreement between reported values for copolymer composition for the styrene/p-divinylbenzene system by Hild-Okasha (1985) and Malinski-Klaban (1971). The composition data reported by Malinski and Klaban seemed to be less model dependent. Therefore, the value of $(r_1)_{p\text{-}DVB}$ was estimated using Malinski and Klaban's data.

To estimate $(k^0_{22})_{m\text{-}DVB}$, $(k^0_{22})_{p\text{-}DVB}$, $(r_1)_{m\text{-}DVB}$, $(r_2)_{m\text{-}DVB}$, $(r_2)_{p\text{-}DVB}$ and k_{cp} only data sets 1 and 3 (refer to Table 3.2(a)) were used. For $(r_1)_{p\text{-}DVB}$ sets 5 and 7 (Table 3.2(b)) were also used. In this last case a "trial and error" approach was followed with the remaining parameters being fixed.

For the addition of monomer 1 (styrene) to a pendant double bond (kinetic constant k_{31}) the EVM was used. The ratio k_{32}/k_{31} was assumed to remain constant and equal to r_2. The kinetic constant k^*_{33} was found to be negligibly small.

TABLE 3.1(b) Summary of Kinetic Parameters. Copolymer Reactivity Ratios.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
$(r_1)_m$ $(r_2)_m$	$(k_{11}/k_{12})_m = 0.4$ $(k_{22}/k_{21})_m = 1.0$	Best EVM (set 1) estim. for other param. See text.
$(r_1)_p$ $(r_2)_p$	$(k_{11}/k_{12})_p = 0.13$ $(k_{22}/k_{21})_p = 2.0$	Best estimates from literature to fit sets 5-7.
$(r_1)_{mix}$ $(r_2)_{mix}$	$(r_i)_{mix} = \frac{n^0_{p\text{-}DVB}(r_i)_p + n^0_{m\text{-}DVB}(r_i)_m}{n^0_{p\text{-}DVB} + n^0_{m\text{-}DVB}}$	i = 1, 2
k_{31}	$k_{32}/k_{31} = r_2$	Assumed
	$(k_{31}/k_{11})_m = 0.0067$ $(k_{31}/k_{11})_p = 0.109$	EVM using sets 1 and 3

"Intrinsic" chemical kinetic constants and reactivity ratios for macromonomers (radicals reacting with pendant double bonds).

These parameters were estimated as indicated in the previous situation (refer to Table 3.1(b)), namely with a combined "grid search"-EVM strategy for two different experimental conditions and then used for the remaining conditions. It was found that the intrinsic propagation constants were function of the initial crosslinker concentration. As will be explained later, this dependency can be attributed to the effect of secondary cyclization which was neglected by setting k_{cs}= 0.0.

The parameter which seemed to be more important for the prediction of gel points at high crosslinker concentrations was k^{*0}_{13}. From sensitivity analysis tests and EVM trials, it was found that $k^{*0}_{13} = k^{*0}_{23}$ (which we call k^{*0}_{13}) and $k^{*0}_{33} = 0$. It was also found that $(k^{*}_{13})_{m\text{-}DVB} = 2(k^{*}_{13})_{p\text{-}DVB}$. This means that the "macro-monomer" with a pendant vinyl group originated from p-DVB is less reactive than that generated from m-DVB, which seems contradictory. However, if the environment in the vicinity of the vinyl group (very entangled or even highly cross-linked structure) is considered, it might be possible that degrees of inclination less than 90^0 could promote the reaction, due to steric relief. For a pictorial representation of this situation, see Figure 3.1. Values in brackets for k^{*0}_{13}/k_{11} in Table 3.1(c) indicate the ratio at very high crosslinker initial concentration (pure commercial DVB polymerization), which were obtained using the transient model for the moment equations.

"Free-volume" related parameters (for the modified MH model).

It was assumed that the free-volume parameters for styrene, DVB and cross reactions were equal, due to their similar chemical structures. Therefore, single values for parameters A, D and V_{fcr2} from equations (54) to (58) were used. These values were the ones for styrene homopolymerization, which was studied previously (Vivaldo-Lima et. al., 1993). The estimation procedure was also the multiresponse-EVM (conversion and weight average chain length as responses).

As indicated previously, the parameters for the non equilibrium free volume models were not estimated to fit experimental data. The values reported include the range of variation used in the sensitivity analysis studies. However, these values were used to reproduce conversion rates at conditions with high crosslinker initial concentration, namely commercial DVB polymerization in presence of inhibitor (data set 13 in Table 3.2(c)) and p-DVB bulk copolymerization (data set 5 from Table 3.2(b)).

TABLE 3.1(c) Summary of Kinetic Parameters. Intrinsic Chemical Kinetic Constants for Macromonomers.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k^*_{i3}	$(k^*_{i3}/k_{11})_m = 0.305$ to 0.4 (0.031)	For AIBN. EVM estimation.
	$(k^*_{i3}/k_{11})_p = 0.15$ to 0.18 (0.016)	
	$k^*_{i3}/k_{11} = 0.06255 + 1.245\times10^{-3}/f_{20}$ $r^2 = 0.9896$	For BPO (@ 70 °C) Empirical correlation from this work.
	$k^*_{33} = 0$	Sensitivity Anal.

TABLE 3.1(d) Summary of Kinetic Parameters. Free-volume parameters.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
A	0.465 +/- 0.04	EVM (see text)
V_{fcr2}	0.036 +/- 0.01	EVM (see text)
D	$1.0\text{x}10^{-3}$	EVM for AIBN, fixed for BPO
C°_{rd}	135, l/mol	EVM trials
C_1, C_2	0	Sensitivity analysis
C_3	1	Sensitivity analysis
δ_0	0.1 to 1000	Range of values used in sensitivity analysis for non-equilibrium free volume calculations
δ'	0.1	
τ_0	1 to 200, s	
B_f	0.001 to 1	

Cyclization related parameters.

From the EVM results and some sensitivity analysis, it was found that the consumption of pendant double bonds through secondary cyclization was negligible for styrene/divinylbenzene (however, these analyses were made for cases with relatively low crosslinker concentrations, where secondary cyclization is usually not important and the reference experimental information used for comparison was for the pre-gelation period). Primary cyclization, on the other hand, seemed to be important, particularly at higher solvent levels in the reacting mixture. From the EVM results and also from experimental observation (Tobita, 1990; Tobita and Hamielec, 1989c), k_{cp} was found to be constant for bulk copolymerization and to increase as the solvent concentration is increased, in solution copolymerization.

For sets 1, 3 and 4 (refer to Table 3.2(a)) k_{cp} was estimated using the EVM. For set 2 the same value as in 1 and 4 was used. For set 5 a sensitivity analysis using k_{cp} from sets 1 and 4 as upper limit was made. The best value was used for the remaining cases (sets 6 to 18, Tables 3.2(b) and 3.2(c)).

All the predicted profiles shown in this paper were obtained using $k_{cs}= 0.0$ and decreasing k_{13}^* as f_{20} was increased. However, this decrease can be explained as due to increasing secondary cyclization. The correlations for k_{cs} shown in Table 3.1(e) were obtained from the transient calculations for p-DVB bulk copolymerization with BPO and comercial DVB polymerization with AIBN and inhibitor. In making the calculations using these correlations it was assumed that k^*_{13} decreases when f_{20} is increased because of the increasing importance of secondary cyclization. It was also assumed is that $k^*_{13}= k^*_{23}$ and that the fraction of radicals whose active center is located on pendant double bonds is negligible at the start of polymerization. Based on these assumptions, k_{cs} can be calculated using equation (2) with initial conditions and k^*_{13} for a system with a very low initial crosslinker concentration (in our case sets 1 and 2 were used). From these correlations an empirical model for k_{cs} can be written as:

$$k_{cs}=k_{cs}^0+e_1f_{20}+e_2[I]_0+e_3T \qquad (81)$$

The regression coefficients reported in Table 3.1(e) clearly indicate that secondary cyclization is strongly affected by divinyl monomer concentration, type and concentration of initiator and temperature. Nevertheless, it is not recommended that such empirical correlations be used for predictive purposes, as the statistical significance was not determined and the assumptions of the Least Squares Technique may not be reasonable.

TABLE 3.1(e) Summary of Kinetic Parameters. Cyclization parameters.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_{cp}	0.25	Bulk copolym. Independent of f_{20}
	0.30	Solution copolym. at f_{20} = 0.0196
	0.49	Solution copolym. at f_{20} = 0.05
k_{cs}	0.0	EVM and sensitivity analysis (pre-gel. period)
	k_{cs}= 10251 + 9692(f_{20}) - 202490[BPO] R^2= 0.9721 (@ 70°C) k_{cs}= 939100 - 86900[AIBN]-10266T(°C) R^2= 0.9106 (@ f_{20}= 0.55)	Linear regression with results from transient model. See text.

Intrinsic chemical kinetic constants for species other than monomers (initiator, inhibitor and chain transfer agent).

These values were taken from the literature (see Table 3.1(f)) or guessed in two cases (k_d for BPO and k_{fT3} for solution copolymerization with CCl_4).

Other physical parameters.

The remaining parameters (glass-transition temperatures, initial initiator efficiency, etc. were taken from the literature, as reported in Table 3.1(g)).

Predicted Conversion/Time and Molecular-Weight/Time Profiles

Once a complete set of kinetic parameters had been compiled, all the available experimental conditions were reproduced (data sets 1 to 18), which are shown in Figures 3.2 to 3.24. It should be mentioned that in some cases better profiles would have been obtained if some variation on the parameters was done, but that was avoided in order to develop a model with hopefully real predictive power and not just a curve-fitting exercise.

Figures 3.2 and 3.3 show predicted versus experimental results for the copolymerization of styrene and m-DVB in benzene solution at conditions shown in Table 3.2(a) and the figures themselves. As it was previously mentioned, this system was chosen to estimate most of the parameters for m-DVB because there were sufficient experimental information to do so (reaction rate, copolymer composition, number and weight average

TABLE 3.1(f) Summary of Kinetic Parameters. Intrinsic chemical constants for other species.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
k_d	$1.053x10^{15}e^{-[\frac{30660}{RT}]}, s^{-1}$	For AIBN (Sharma and Soane, 1988)
	$1.2x10^{-5}$, s^{-1} (@ 70 °C)	For BPO, guess
(k_{fI})	0, for AIBN	
	30, $l\ mol^{-1}\ s^{-1}$ (@ 70 °C)	Mean value from Barson's (1989) data. (BPO)
k_{fm}	$2.31x10^{6}e^{-[\frac{12671}{RT}]}, \frac{\ell}{mol*s}$	Hui, 1967
k_{fp}, k_{fs}	0	
k^{0}_{td}	$2.19x10^{5}e^{-[\frac{27440.5}{RT}]}, \frac{\ell}{mol*s}$	Villalobos et. al., 1991
k_z	$1x10^{5}$, $l\ mol^{-1}\ s^{-1}$	Insensitive to temperature.
k_{fT1}	0.05, $l\ mol^{-1}\ s^{-1}$	Barson, 1989
k_{fT2}	0.05, $l\ mol^{-1}\ s^{-1}$	Assumed equal to k_{ft1}
k_{fT3}	490 to 585, $l\ mol^{-1}\ s^{-1}$	Trial and error

TABLE 3.1(g) Summary of Kinetic Parameters. Other parameters.

PARAMETER	VALUE OR FUNCTIONALITY	REMARKS
f°_{AIBN}	0.7	Sharma and Soane, 1988
f°_{BPO}	0.7	Villalobos et. al., 1991
$\alpha_i, \frac{1}{^{\circ}C}$	0.001	Styrene (Marten and Hamielec, 1982)
	0.0008	DVB, guess
	0.00048	Polymer (Marten and Hamielec, 1982)
	0.007	Benzene, guess
	0.007	CCl_4, guess
Tg_i, °C	-88.1	Styrene (Marten and Hamielec, 1982)
	-90.0	DVB, guess
	93.5	Polymer (Brandrup, 1975)
	5.53	Benzene, guess
	-110.0	CCl_4, guess

average molecular weights). Some authors have tried to test their models for crosslinking kinetics using this same experimental information (Tobita, 1990; Tobita and Hamielec, 1989c; Okay, 1992; Xie and Hamielec, 1993). However, their simulations can not simultaneously predict the actual behavior of molecular weight, conversion and composition. When the transient simulations were carried out using the parameters obtained with the SSH-based model, there would be some delay in gelation. Therefore, a refinement of the value of kp^*_{13} was performed in order to obtain the correct gelation time. That is why a range of variation of the ratio kp^*_{13}/k_{11} is given in Table 3.1(c) (the 95% confidence intervals obtained with the EVM were narrower, but are not reported here due to the fact that refinements on the values of kp^*_{13} were made and also the usage of the SSH-based model during the parameter estimation stage).

Figure 3.4 shows predicted total polymeric radical concentrations obtained with the transient model as compared with those obtained using the SSH assumption. It can be observed that the SSH assumption leads to a lower radical consumption rate at the gel point, thus predicting a very high disappearence rate of the sol phase. On the other hand, the calculations show that the SSH assumption is clearly valid for the pre-gelation period.

Figure 3.5 shows predicted and experimental results for copolymerization of styrene and p-DVB in benzene. It can be seen that reaction rate is predicted quite well, but copolymer composition seems to be underpredicted. As mentioned in the previous section, the copolymer composition data reported by Hild and Okasha (1985) were calculated under model assumption considerations. Even if their same results for m-DVB and p-DVB are compared, it is seen that they obtain higher initial DVB content in copolymerization using m-DVB than when using p-DVB, which seems to indicate that their reported values for p-DVB content in the copolymer are suspicious. As in the previous case, the transient and the SSH predictions are compared in Figure 3.6. The same remarks given for styrene/m-DVB apply for styrene/p-DVB on this matter.

TABLE 3.2(a) Summary of Experimental Conditions. Solution Copolymerization with AIBN.

Data Set	$[I]_0$ (Init.)	$[M]_0$	f_{20}	Temp. (°C)	Remarks
1	0.08 (AIBN)	4.08	0.0196 (meta)	60	$[C_6H_6]$=5.562; (Hild and Okasha, 1985) Figures 2, 3 and 4
2	0.08 (AIBN)	4.08	0.0196 (para)	60	$[C_6H_6]$=5.562; (Hild and Okasha, 1985). Figures 5 and 6.
3	0.08 (AIBN)	4.06	0.018 (mix.)	60	$[C_6H_6]$=5.35; (Okasha et. al., 1979). $[CCl_4]$=0.2. See figures 10 to 12
4	0.08 (AIBN)	4.22	0.05 (meta)	60	$[C_6H_6]$=5.22; (Hild et. al., 1985). Figures 7, 8 and 9

TABLE 3.2(b) Summary of Experimental Conditions. Bulk Copolymerization with BPO.

Data Set	$[I]_0$ (Init.)	$[M]_0$	f_{20}	Temp. (°C)	Remarks
5	0.0356 (BPO)	8.25	0.032 (para)	70.1	Storey, 1965 Figures 13 to 15
6	0.0356 (BPO)	8.18	0.082 (para)	70.1	Storey, 1965 Figure 15
7	0.0356 (BPO)	8.06	0.167 (para)	70.1	Storey, 1965 Figures 13 to 15
8	0.011 (BPO)	8.2	0.065 (para)	70	Malinski and Klaban, 1971 Figs. 15 and 16(a)
9	0.011 (BPO)	8.12	0.124 (para)	70	Malinski and Klaban, 1971 Figures 15 and 17(a)
10	0.011 (BPO)	7.94	0.255 (para)	70	Malinski and Klaban, 1971 Figures 15 and 17(b)
11	0.011 (BPO)	7.67	0.444 (para)	70	Malinski and Klaban, 1971 Figures 15 and 17(c)
12	0.011 (BPO)	8.2	0.065 (meta)	70	Malinski and Klaban, 1971 Figures 15 and 16(b)

TABLE 3.2(c) Summary of Experimental Conditions. Bulk Copolymerization with AIBN and inhibitor. Data from Batch and Macosko (1992).

Data Set	$[I]_0$ (Init.)	$[M]_0$	f_{20}	Temp. (°C)	Remarks
13	0.055 (AIBN)	6.84	0.55 (mix.)	72	[DPPH]=0.007 In sets 13 to 18, values of [DPPH] slightly different to those estimated by Batch and Macosko (1992) were used. Figures 18, 19 and 20
14	0.113 (AIBN)	6.75	0.55 (mix.)	72	[DPPH]=0.007 Figures 19, 20 and 23
15	0.172 (AIBN)	6.68	0.55 (mix.)	72	[DPPH]=0.007 Figures 19, 20 and 23
16	0.14 (AIBN)	6.84	0.55 (mix.)	70	[DPPH]=0.01 Figures 21, 22 and 24
17	0.14 (AIBN)	6.84	0.55 (mix.)	75	[DPPH]=0.01 Figures 21, 22 and 24
18	0.14 (AIBN)	6.84	0.55 (mix.)	78	[DPPH]=0.01 Figures 20, 22 and 24

Figures 3.7 and 3.8 show predicted versus experimental results for styrene/m-DVB copolymerization in benzene, but at higher initial concentrations of crosslinker than those of Figures 3.2 and 3.3. Here the predictive power of our model for the post-gelation period can be appreciated, where excellent agreement between experimental and predicted behavior is obtained. In this case the only parameter which was adjusted to predict time of gelation was k_{cp}. As has been observed experimentally, this parameter seems to be non constant for systems with high content of solvent and high initial crosslinker concentrations and even the values obtained by parameter estimation for k_{cp} are in close agreement with those reported in the literature (Tobita and Hamielec, 1989c; Tobita, 1990). Figure 3.9 shows the corresponding profiles for total radical concentration.

Figure 3.10 shows the chain length development in solution copolymerization of styrene and a mixture of meta and para divinylbenzene in presence of a strong chain transfer agent (CCl_4). Our model predictions for this case seem to underpredict weight average chain lengths at intermediate conversion levels. However, if one observes the experimental points it is clear that the GPC values seem to be greater than those obtained with light scattering. Light scattering should provide an upper limit for weight-average chain lengths and therefore the GPC values reported by Okasha et. al. (1979) are suspect. In their investigation, they did not reach the gel point. It is reported that gelation occurred after 10 hours and a figure in their paper appears to indicate that the gel point is reached at about 14 hours. That is why predicted profiles to get gelation at 10 and 14 hours are presented in Figure 3.10(a). If only the experimental results obtained by light scattering (Pw-DDL in the plot) are considered and it is assumed that gelation occurs at a time close to 10 hours, the agreement between experimental results and our predictions is very good (light scattering is an absolute method for branched polymers and gives valid M_w values, whereas values of M_w obtained using GPC are questionable for branched polymers). Figure 3.10(b) shows predicted profiles using both models (transient and non-transient) to get gelation at 10 hrs. The agreement is quite good, however the values of kp^*_{13} used to reproduce the profiles are not the same, as previously explained. Figure 3.11 shows conversion and copolymer composition evolution with time. Conversion is adequately predicted, but composition seems to be underpredicted. The same remarks that were made about Figure 3.5 are applicable for this case (same investigators and same procedure to evaluate copolymer composition as in that case). Figure 3.12 shows profiles of total radical concentration versus time for this case. The SSH is clearly not valid in the post gelation region.

Figure 3.13 shows predictions of conversion versus time for bulk copolymerization of styrene and p-DVB. The experimental results at the higher p-DVB level are substantially higher than those predicted. However, according to the experimental procedure used in obtaining these data (Storey, 1965), temperature rise at the gel point and thereafter must have been considerable. (They used a dilatometer device with a spherical bulb). Zhu and Hamielec (1991) found that temperature rise in ampoule reactors for copolymerization with crosslinking systems is quite high, even when small diameter ampoules are used. Figure 3.14 shows predicted profiles for total radical concentration. It can be observed that for bulk copolymerization without inhibitor, the agreement between the transient and the SSH-based models is almost total, even in the post gelation period. It is our belief that the reason why some discrepancy in the prediction of gelation time between the transient and the non-transient models is observed when there is solvent in the system, whereas total agreement is obtained when there is neither solvent nor inhibitor present, is that in a diluted (or retarded) system, the changes in magnitude of the radical and dead polymer moments during polymerization are more pronounced and their initial individual values lower than those of a system without solvent. This means that dilute and retarded systems are more sensitive to errors in the calculation of moments. It should also be remembered that the moment equations used with the SSH model in this study were those derived by Tobita (1990) and in their derivation, assumptions and simplifications on the relative magnitudes of different moments and relative importance of termination and chain transfer rates, as compared to propagation rate, were made.

Figure 3.15(a) shows the effect of the initial concentration of crosslinker on gelation point at two different levels of BPO. It can be seen that model predictions of conversion at the gel point are in very good agreement with the experimental results. In Figure 3.15(b) the effect on kp^{*0}_{13} is shown. The fact that the intrinsic propagation constant for macromonomers depends on the initial concentration of crosslinker can be attributed to secondary cyclization, which was found to be zero when the EVM parameter estimation procedure was used. However, with this parameter estimation procedure, only experimental data for the pre-gelation period were used (secondary cyclization may not be important during the pre-gelation period, but in the post-gelation period its importance increases). It seems that even though this kinetic constant depends on crosslinker concentration, its dependence on initiator concentration is weak and the two profiles could be considered as one and the same. As explained in the previous section, from this relationship [Figure 3.15(b)] and using equation (2), an estimate of k_{cs} can be obtained (see regression models in Table 3.1(e)).

Figures 3.16 and 3.17 show predicted and experimental copolymer composition (F_2-accumulated) for bulk copolymerization of styrene and p-DVB [also m-DVB in Figure 3.16(b)] at different initial DVB concentrations and using BPO as initiator. It can be observed that the agreement between model predictions and experiments is remarkably good (although some error in the estimates of the reactivity ratios could be present if temperature was not constant in the center of the bulbe used to obtain the experimental data).

In Figures 3.18(a), 3.19 and 3.21 experimental (Batch and Macosko, 1992) and model predictions of the bulk polymerization of commercial DVB (mixture of m-DVB, p-DVB and ethyl-vinyl-benzene, mainly) with AIBN as initiator and hydrated, 1,1-diphenyl-2-picrylhydrazyl (DPPH) as inhibitor, are shown. These model predictions were obtained assuming that the polymerization proceeds isothermally. The agreement is good during the pre-gelation period, up to the gel point. Thereafter the predicted profiles show a smaller decrease of the sol fraction. Considering the extremely high initial concentration of crosslinker (55% mol) in the system and the associated high rates of polymerization and heat generation rate, it is quite likely that the polymerization temperature might increase significantly with time. To estimate the temperature rise and the real behavior of the system, a heat balance was performed, which led to the following differential equation for temperature of the polymerizing mass (T):

$$\left[\frac{dT}{dt}\right]_m = \frac{(-\Delta H)\ {}_rR_p}{n_mCp_m} - \frac{n_wCp_w}{n_mCp_m}\left[\frac{dT}{dt}\right]_w - \frac{UA}{n_mCp_m}(T-T_w) \tag{82}$$

where subscript m stands for monomers/polymer mixture and subscript w for water (assuming that the reacting mixture is being cooled with water). Equation (82) was solved with the other model equations using the same conditions as those indicated in Figure 3.18 for different values of U (overall heat transfer coefficient). It was found that using U=0 (adiabatic limit) produced profiles with identical gelation and sol consumption times as the experimental ones. Finite values for U would produce intermediate profiles between those of Figures 3.19 and 3.20. The predicted profiles considering the temperature rise during the post-gelation period with U=0 are shown in Figures 3.18 and 3.20. In Figures 3.23 and 3.24 temperature evolution profiles are shown for all cases reported by Batch and Macosko (1992). Even though the model predictions of maximum reaction rate are higher than the experimental ones (and therefore the maximum polymerization temperatures should be overpredicted) it seems clear that temperature rose significantly in the post-gelation period in Batch and Macosko's experiments.

It is important to mention that this system (bulk polymerization of commercial quality DVB in the presence of an inhibitor) was the one where the greatest differences between transient and SSH models were observed. When the SSH model was used, the experimental results could be reproduced by correcting for non-isothermal copolymerization, thus secondary cyclization seemed to be negligible. When the transient calculations were attempted using the same parameters as in the non-transient model, gelation would be predicted to occur much earlier and the predicted weight average chain length was much greater. By doing a sensitivity analysis on the effect of changing kp^{*0}_{13}, it was found that the same profiles as in the non-transient model would be obtained by reducing the value of this constant by 25%. However, the profiles predicted with values slightly greater or smaller were very different and oscillations in the predicted dx/dt vs. t curve were observed. This behavior was observed over a large range of kp^{*0}_{13} values (from about 15% up to 80% of the original value used in the SSH calculations). When lower values were used, stability would again be obtained and the agreement in the peak maxima of the experimental and predicted reaction rate versus time profiles would be much better than those obtained with the SSH model. This behavior can be clearly observed in Figures 3.20 and 3.22. With the SSH model, gelation would be predicted to occur at the start of the plateu regions in the reaction rate versus time profiles and the maximum peaks would correspond to disappearance of the sol phase. On the other hand, the transient model predictions would predict gelation to occur at the maximum peaks of the reaction rate versus time profiles, except for set 13, where the previous behavior would also be observed. According to Batch and Macosko (1992), gelation would occur at the peak maximum of such profiles. Therefore, it seems to be clear that secondary cyclization is important during the post-gelation period and that the SSH assumption can lead to incorrect conclusions when applied to inhibited and highly crosslinked systems.

From the previous results (Figures 3.18 to 3.24) it can be observed that the present model is capable of reproducing qualitatively and even quantitatively to a reasonable degree the behavior of the copolymerization during the pre-gelation and post-gelation periods. However it predicts unusually high reaction rates at the very end of polymerization, which also means that the predicted maximum values of w_{gel} (gel fraction) could be higher than the actual ones. In other words, our model predicts complete disappearence of the sol phase when it actually could exist in small amounts.

In reference to the use of equations (34), (35) and (36) for polymer moment concentrations, it was found that there were no significant difference between them. So, the assumption of neglecting the radical second moment term for the sum of polymer and radical second moments was good enough for numerical purposes (that is, assuming that $Q_2 >> Y_2$, which is the simplest case).

A sensitivity analysis study on the effect of non equilibrium free volume is presented in Appendix A of this paper.

In Appendix B of this paper, a model for calculation of the effect of crosslinking density on the polymer glass transition temperature, Tg_p, is presented. Also included in this Appendix is a procedure for decoupling secondary cyclization from crosslinking density in the post-gelation period. Calculations of the degree of "unsaturation" (concentration of pendant double bonds not consumed by crosslinking or cyclization) during the post-gelation period are given, as well.

CONCLUSIONS

An effective model for crosslinking copolymerization kinetics has been developed. Using this model quantitatively reliable predictions of the system behavior can be obtained. This model is based on previous work of Tobita and Hamielec (1988, 1989a, 1989b, 1989c, 1990a, 1990b, 1992) and incorporates several important recommendations made by Zhu and Hamielec (1989, 1991). Based on these recommendations, an improved version of the Marten-Hamielec gel effect model (Vivaldo-Lima et. al., 1993) was extended to copolymerization with crosslinking. It was confirmed that accounting for diffusion-controlled reactions (termination, propagation and initiation) is essential if realistic modelling of free-radical polymerization with crosslinking is to be done.

It was demonstrated that the use of the steady state hypothesis (SSH) for the polymer radical moment equations is usually valid for the pre-gelation period. It could be used to model the post-gelation period, but the kinetic parameters would be model-dependent and therefore, they would not correspond to the actual ones. In some cases, usage of the SSH could lead to wrong mechanistic conclusions of the behavior during the post-gelation period.

Most of the observed phenomena in the copolymerization of styrene and divinylbenzene were adequately predicted. Eventhough the behavior during the post-gelation period was considered, it is recognized that the present model is at best a good first approximation and especially needs improvement in the post-gelation period. Some guidelines in the way this could be done were given.

The important concept of non equilibrium free volume in the context of copolymerization kinetics was considered and modelled. Although no attempt was made to obtain precise parameters for this particular case, it was demonstrated that the predictions are in perfect agreement with the observed trends and reasonable numerical ranges for the non equilibrium free volume parameters were established.

It was demonstrated that secondary cyclization is very important during the post-gelation period. In fact, most of the pendant double bonds are consumed by secondary cyclization during this stage of the copolymerization. Although not quite reliable, our predictions of pendant double bond conversion (and degree of unsaturation) are quite close to the experimental data, even at very high crosslinker concentrations and high conversions.

Some hints and remarks about the parameter estimation procedure and numerical solution of the mathematical equations were given in order to aid in future modelling studies of this kind.

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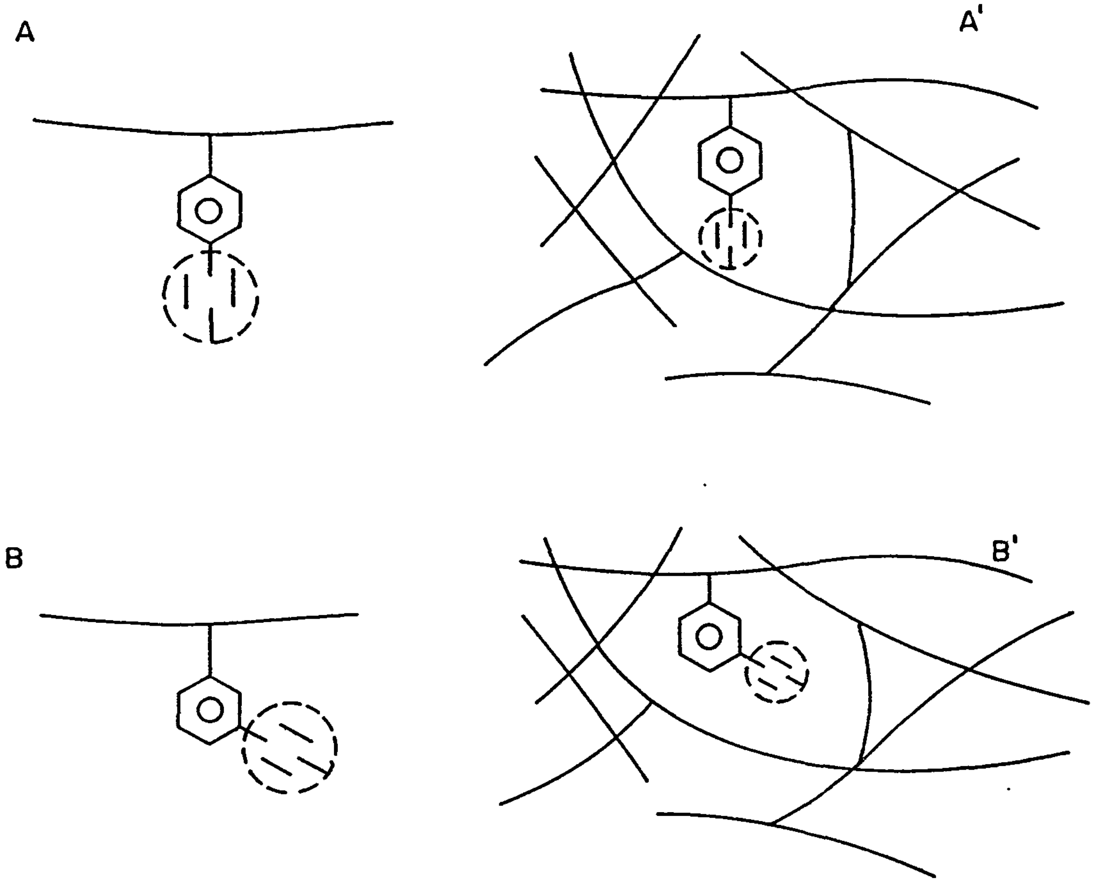


Figure 3.1 Schematic representation of the relative reactivity of pendant vinyl groups. A more reactive than B, but A′ may be less reactive than B′.

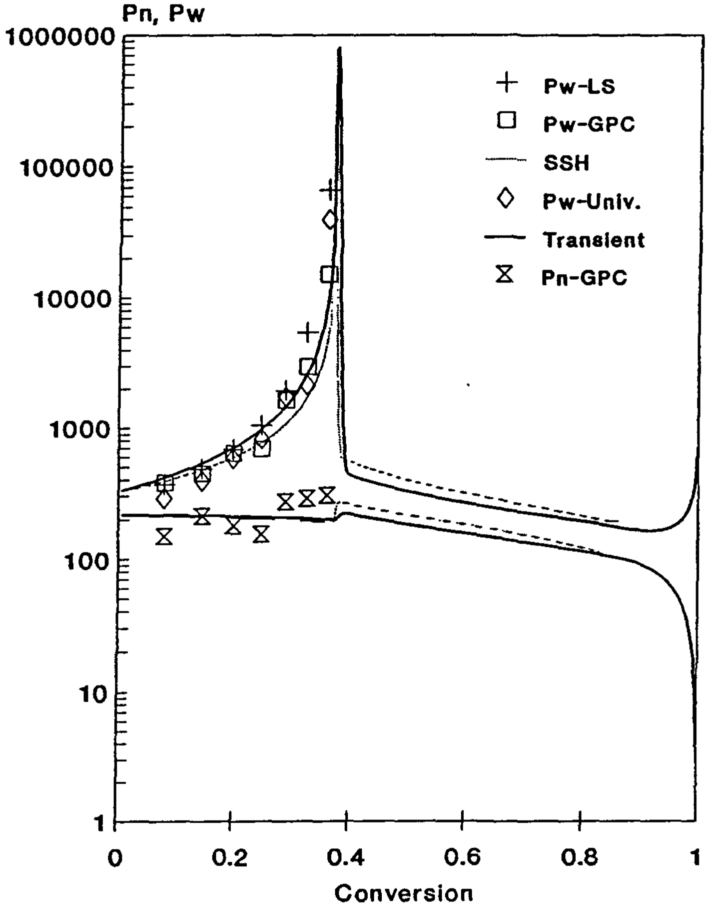


Figure 3.2 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.0196, [C_6H_6]=5.562, T=60°C. Transient (solid lines) and non-transient (dashed lines) predicted versus experimental chain length profiles.

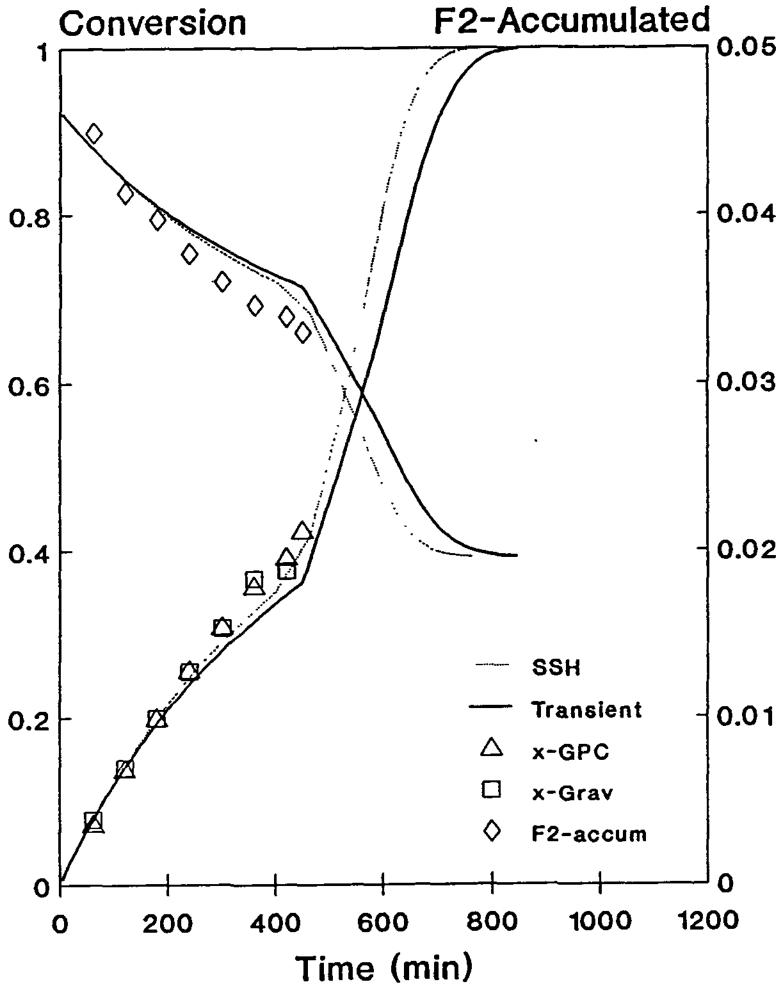


Figure 3.3 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.0196, [C_6H_6]=5.562, T=60°C. Transient (solid lines) and non-transient (dashed lines) versus experimental conversion and copolymer composition profiles.

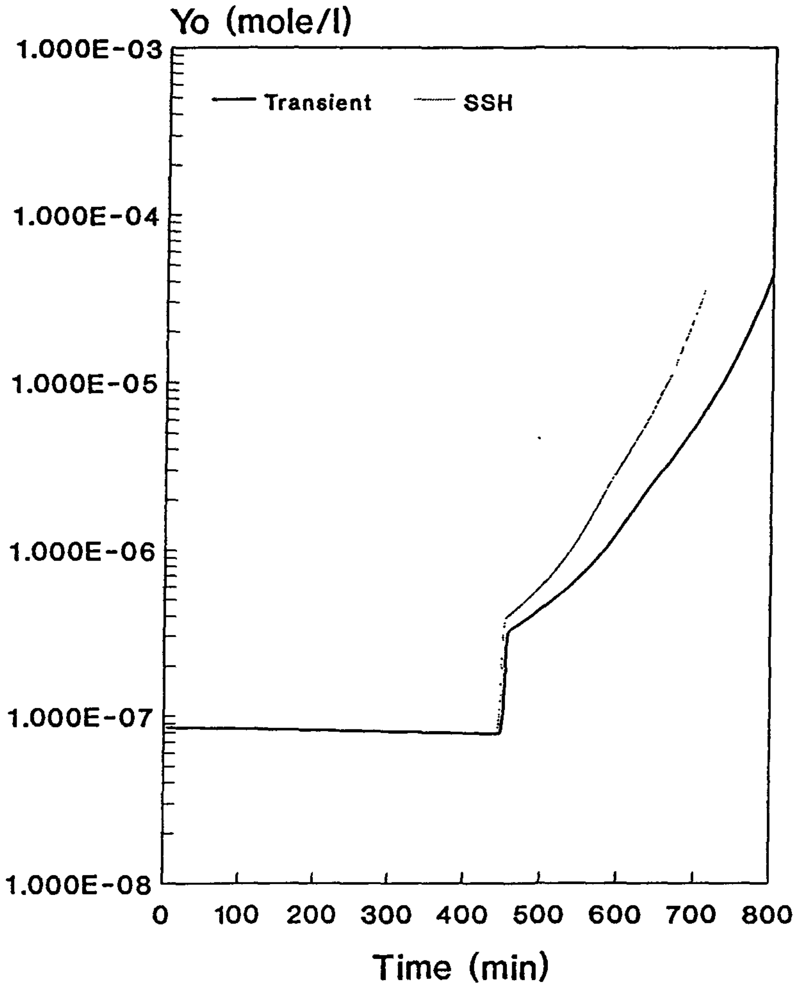


Figure 3.4 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.0196, [C_6H_6]=5.562, T=60°C. Predicted total radical concentration using the SSH assumption (dashed line) as compared to the transient model (solid line).

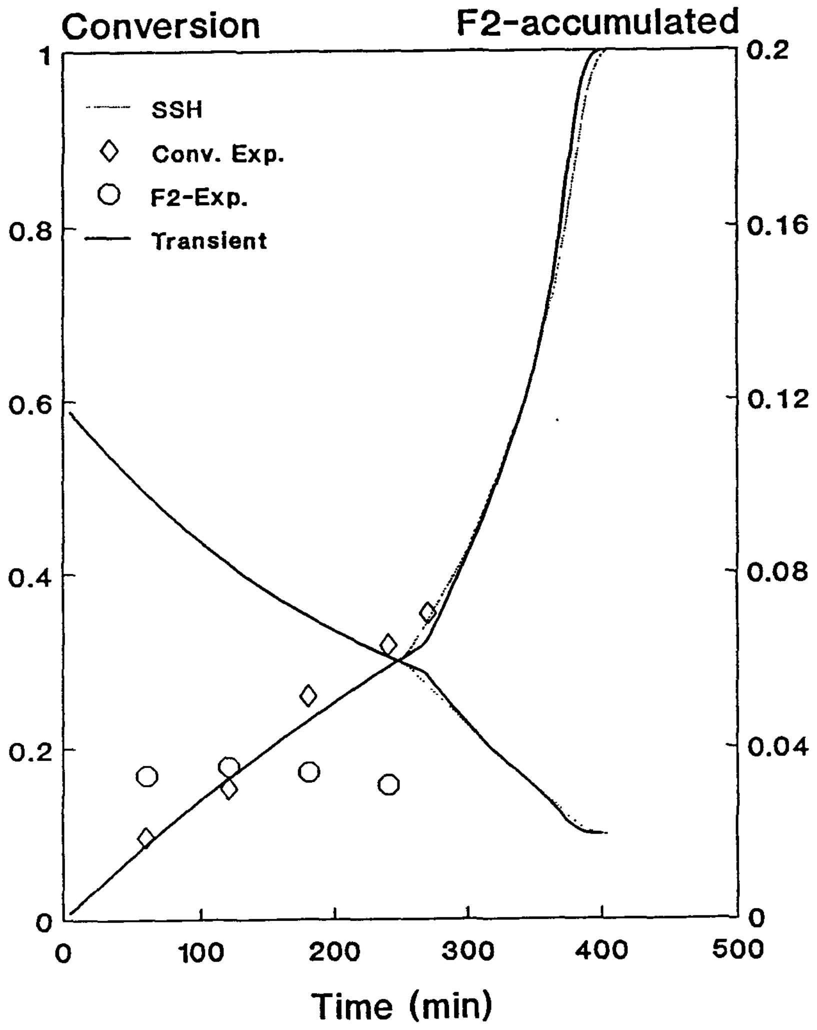


Figure 3.5 Styrene/p-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.0196, [C_6H_6]=5.562, T=60°C. Predicted (solid lines) versus experimental conversion and copolymer composition profiles.

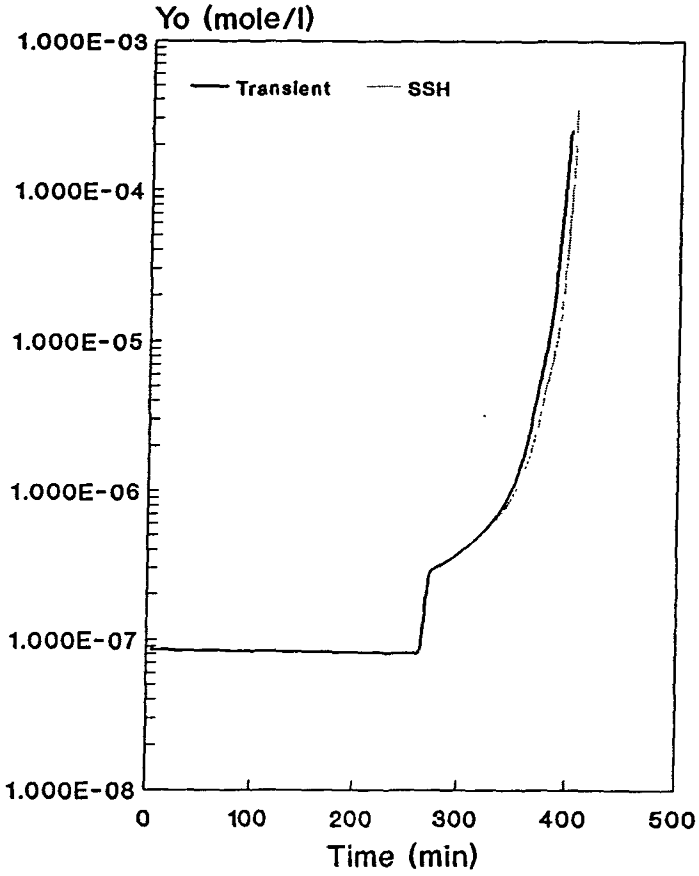


Figure 3.6 Styrene/p-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.0196, [C_6H_6]=5.562, T=60°C. Predicted total radical concentration using the SSH assumption (dashed line) as compared to the transient model (solid line).

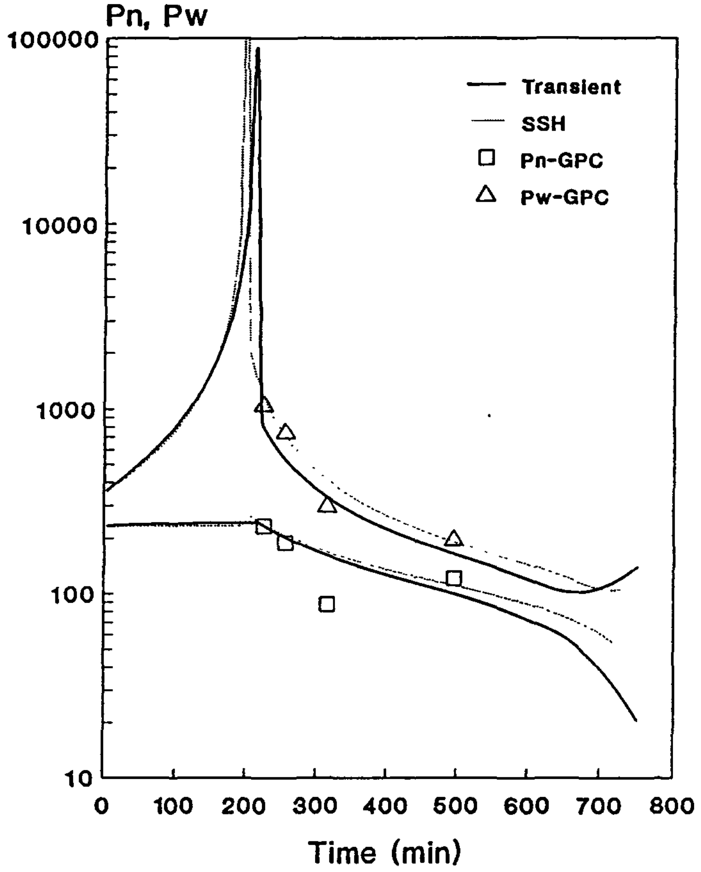


Figure 3.7 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.05, [C_6H_6]=5.22, T=60°C. Predicted (solid lines) versus experimental chain length profiles.

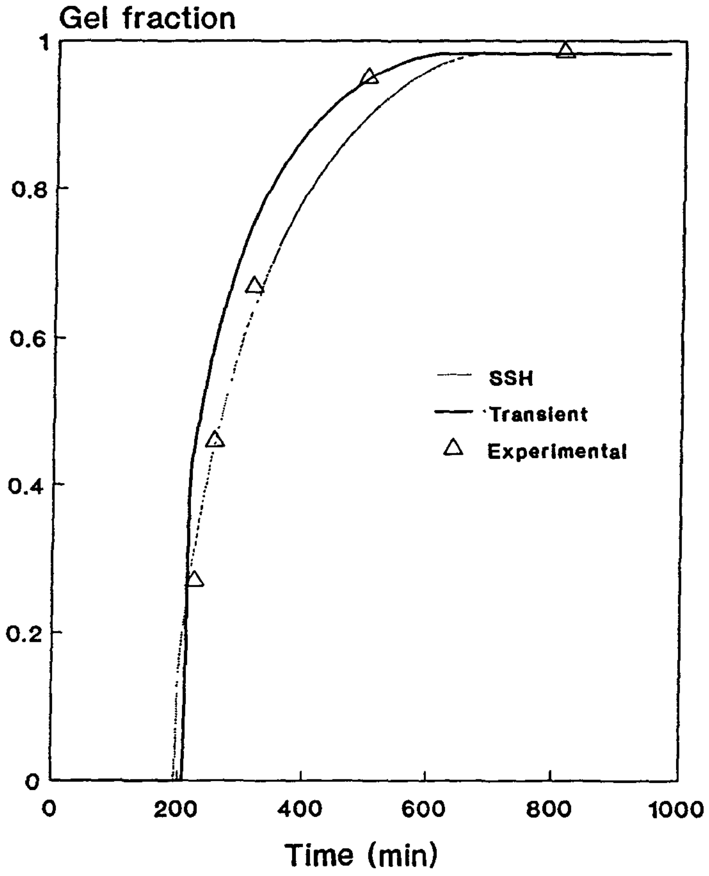


Figure 3.8 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.05, [C_6H_6]=5.22, T=60°C. Predicted (solid line) versus experimental [Δ]gel fraction content.

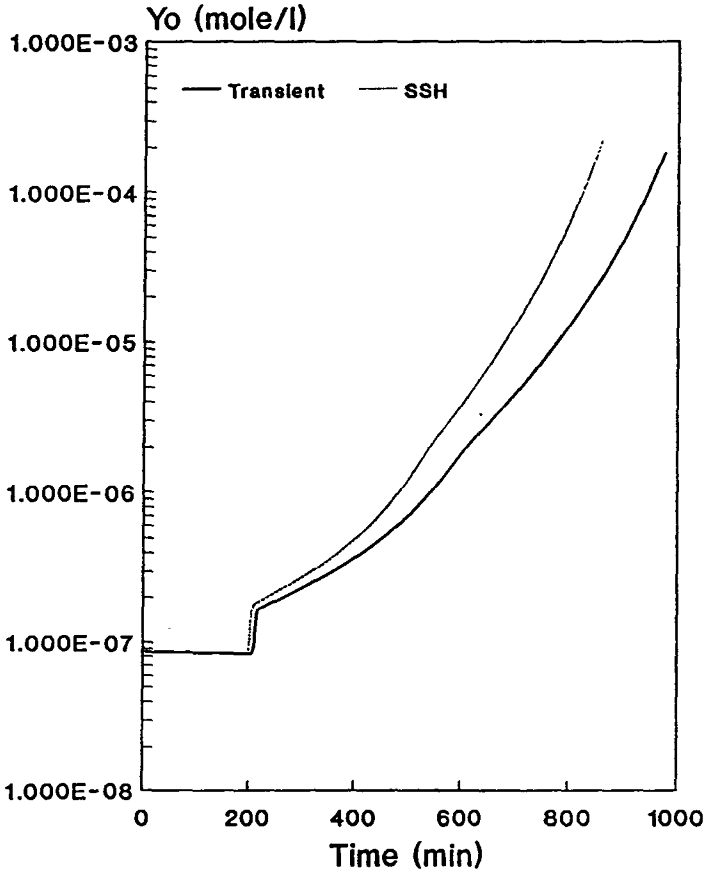


Figure 3.9 Styrene/m-DVB solution copolymerization. [AIBN]=0.08, f_{20}=0.05 , [C_6H_6]=5.22, T=60°C. Predicted total radical concentration using the SSH assumption (dashed line) as compared to the transient model (solid line).

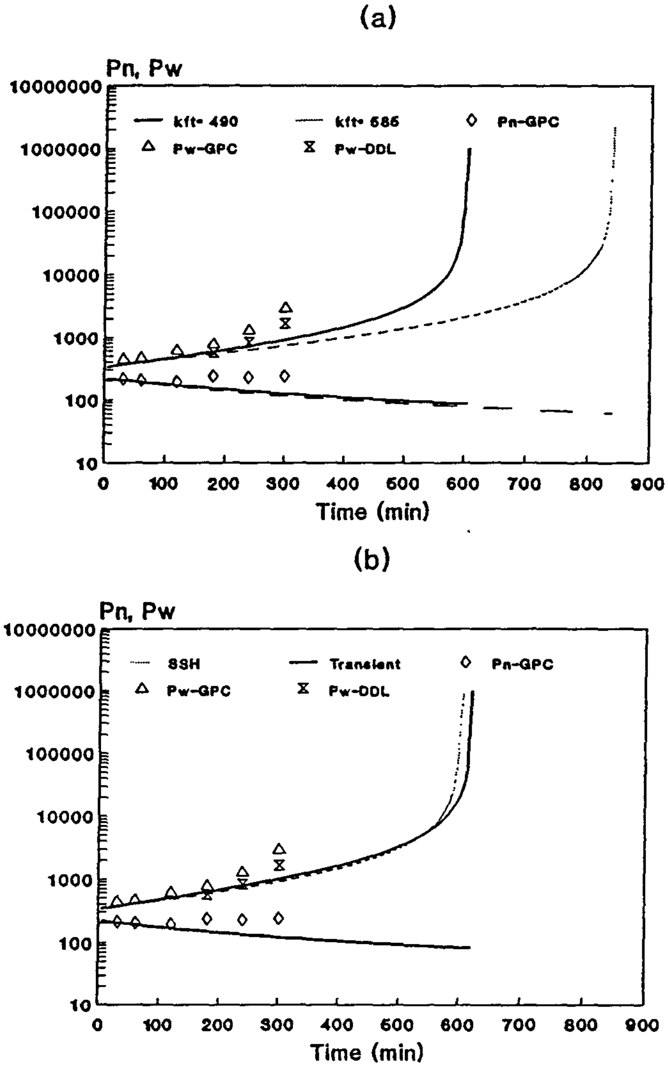


Figure 3.10 Styrene/DVB (mix.) solution copolymerization with added transfer agent. [AIBN]=0.08, f_{20}=0.018, [C_6H_6]=5.35, [CCl_4]=0.2, T=60°C. (a) Non-transient model predictions (SSH) to get gelation at 10 (solid line) and 14 hrs (dashed line) versus experimental chain lengths. (b) Transient (solid line) and non-transient (dashed line) predictions to get gelation at 10 hrs. versus experimental chain lengths.

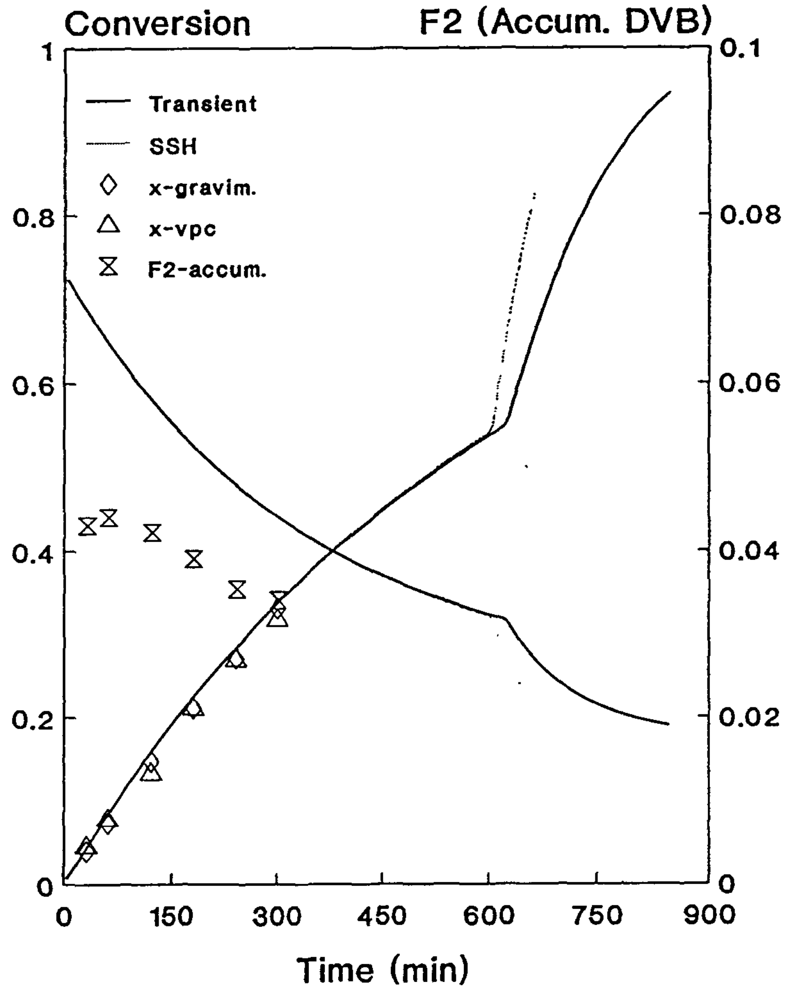


Figure 3.11 Styrene/DVB (mix.) solution copolymerization with added transfer agent. [AIBN]=0.08, f_{20}=0.018, [C_6H_6]=5.35, [CCl_4]=0.2, T=60°C. Transient (solid line), and non-transient (dashed line) conversion and copolymer composition predictions to get gelation at 10 hrs. versus experimental results.

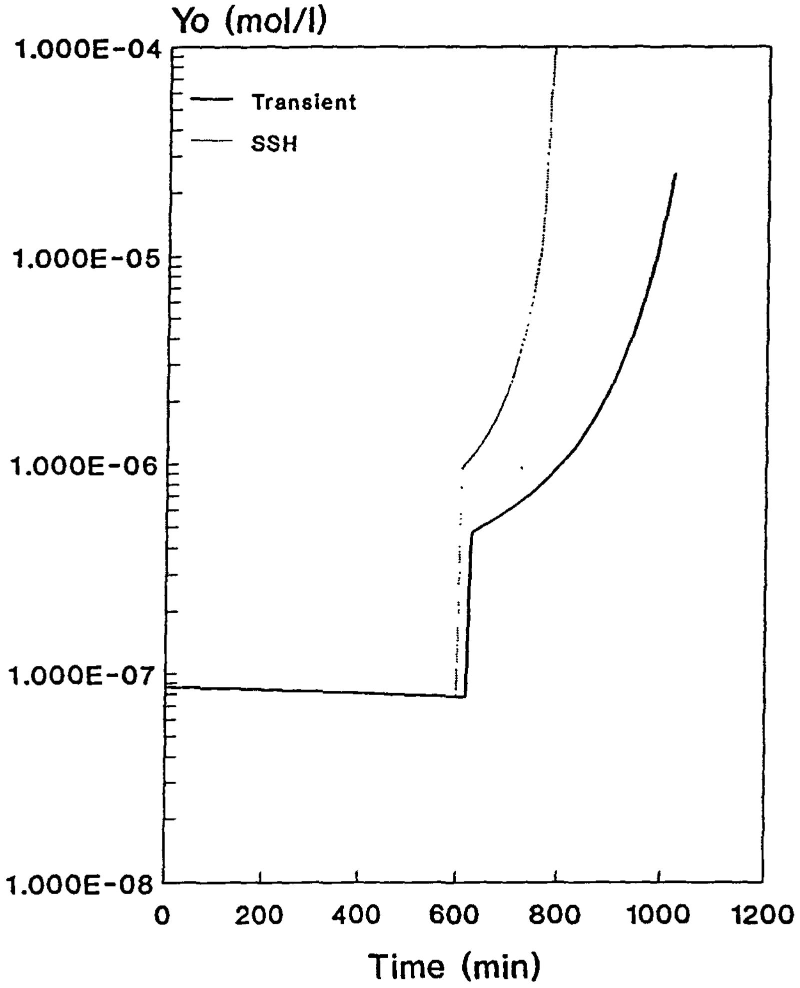


Figure 3.12 Styrene/DVB (mix.) solution copolymerization with added transfer agent. [AIBN]=0.08, f_{20}=0.018, [C_6H_6]=5.35, [CCl_4]=0.2, T=60°C. Predicted total radical concentration using the SSH assumption (dashed line) as compared to the transient model (solid line).

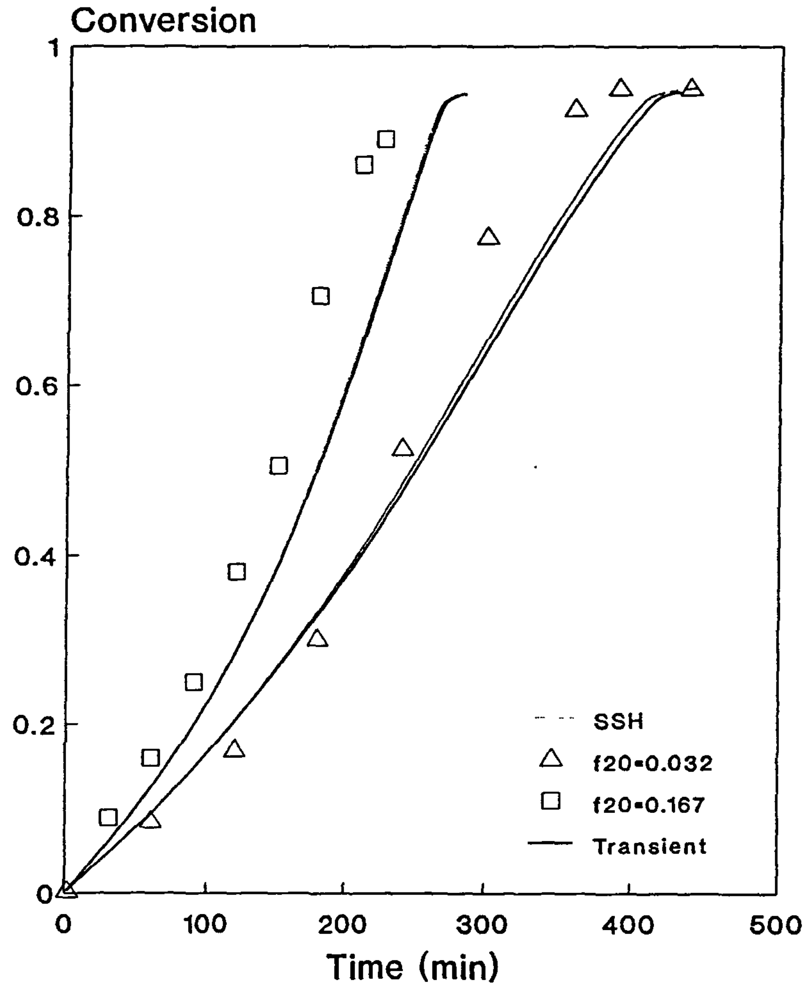


Figure 3.13 Styrene/p-DVB bulk copolymerization. [BPO]= 0.0356, T=70.1 °C. Transient (solid lines) and non-transient (dashed lines) conversion predictions for different crosslinker initial concentrations, as compared to experimental results.

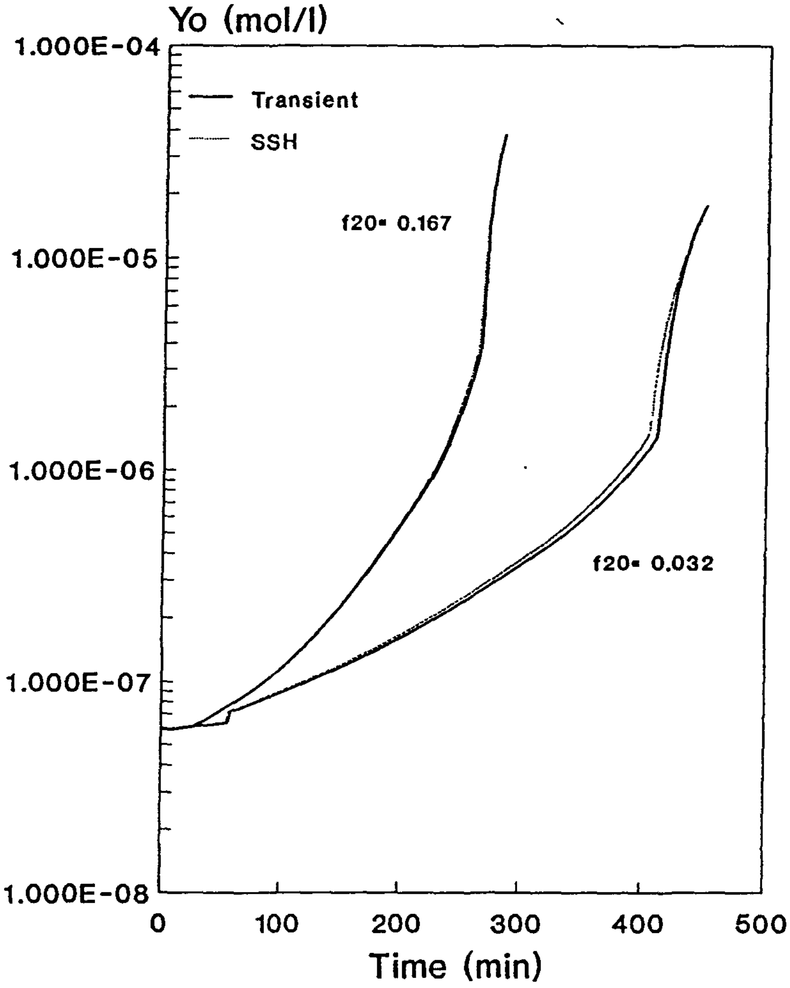
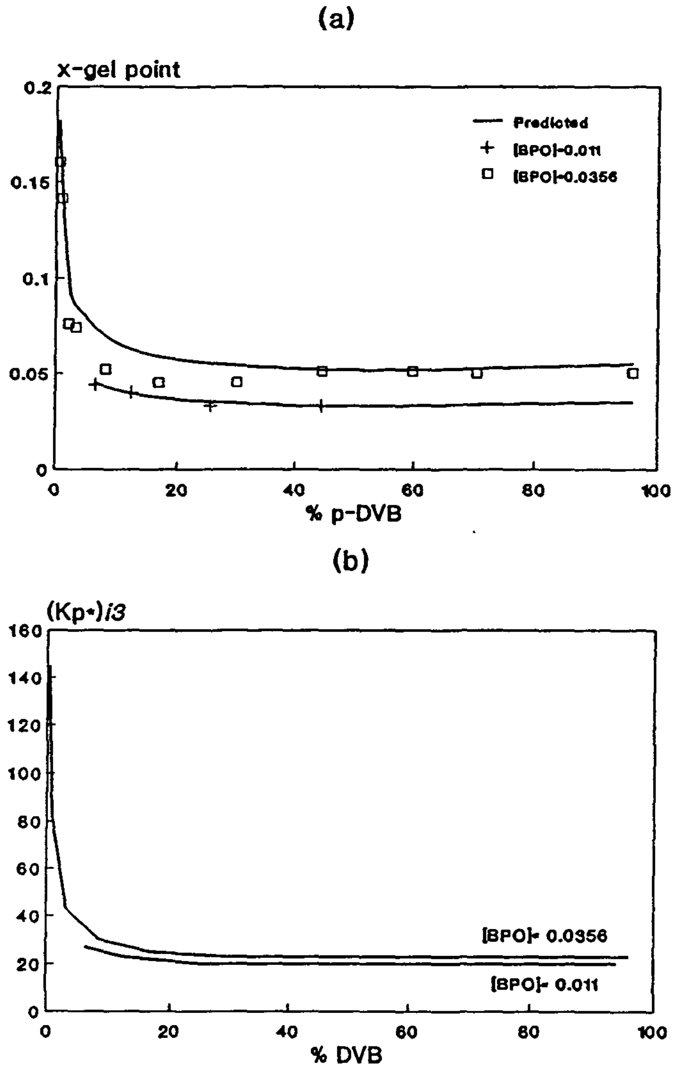


Figure 3.14 Styrene/p-DVB bulk copolymerization. [BPO]= 0.0356, T= 70.1 °C. Predicted total radical concentration using the SSH assumption (dashed lines) as compared to the transient model (solid lines).


(a)

(b)

Figure 3.15 Styrene/p-DVB bulk copolymerization. T=70.1°C. (a) Predicted (solid line) versus experimental gelation points at different crosslinker initial concentrations. (b) Effect of $[BPO]_o$ and f_{20} on kp^*_{13}.

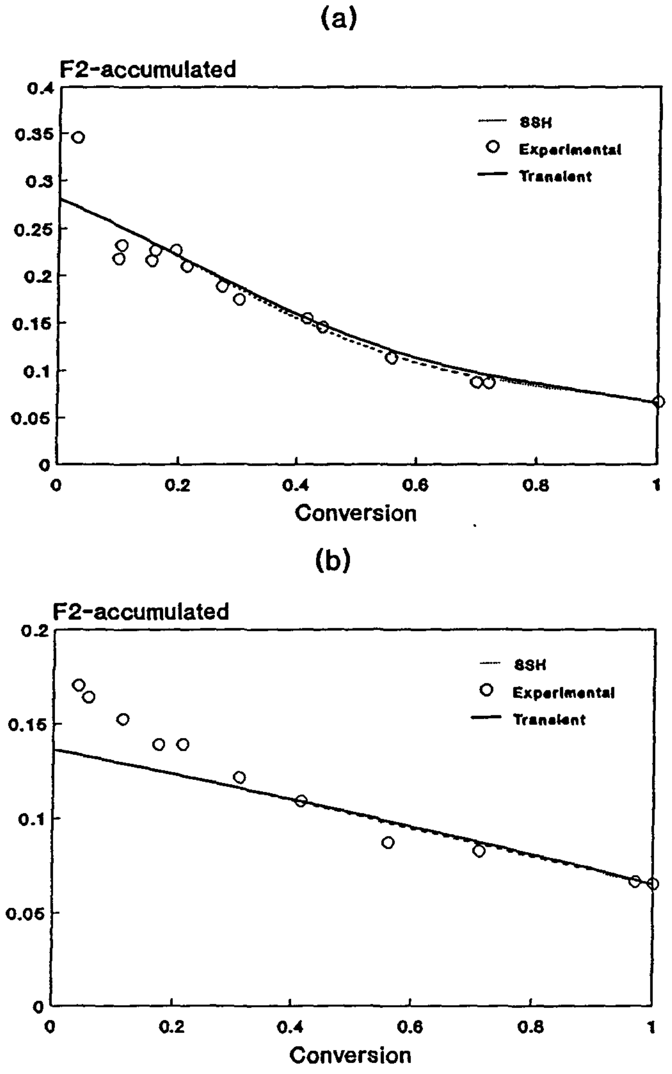


Figure 3.16 Styrene/DVB bulk copolymerization. [BPO]= 0.011, f_{20}= 0.065, T=70 °C. Predicted (solid line) versus experimental [O] copolymer composition for (a) p-DVB and (b) m-DVB.

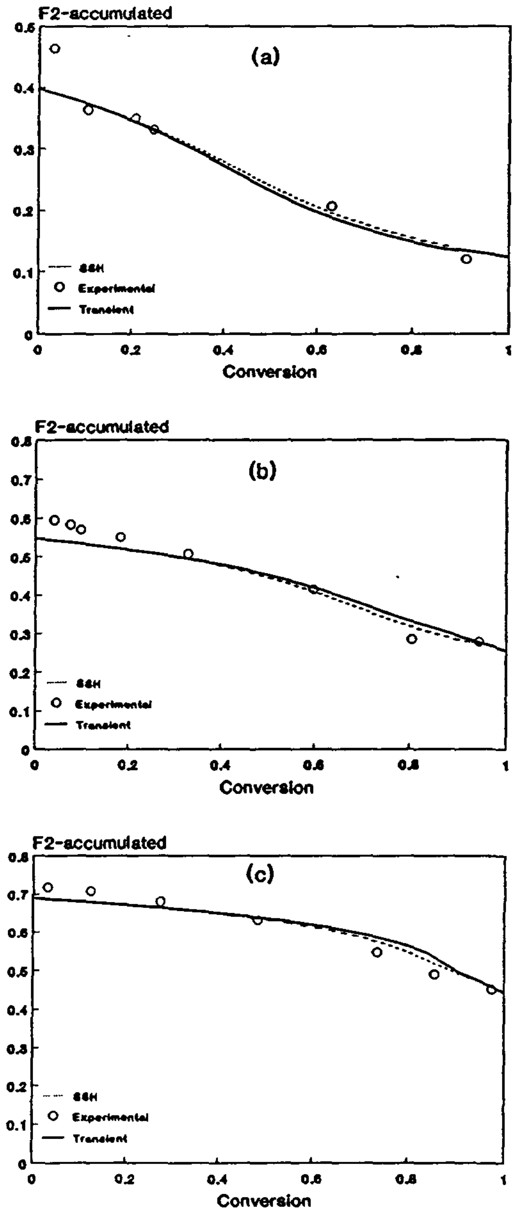


Figure 3.17 Styrene/p-DVB bulk copolymerization. [BPO]= 0.011, T= 70 °C. Predicted (solid lines) versus experimental [O] copolymer composition for (a) f_{20}=0.124, (b) f_{20}= 0.255 and (c) f_{20}= 0.444.

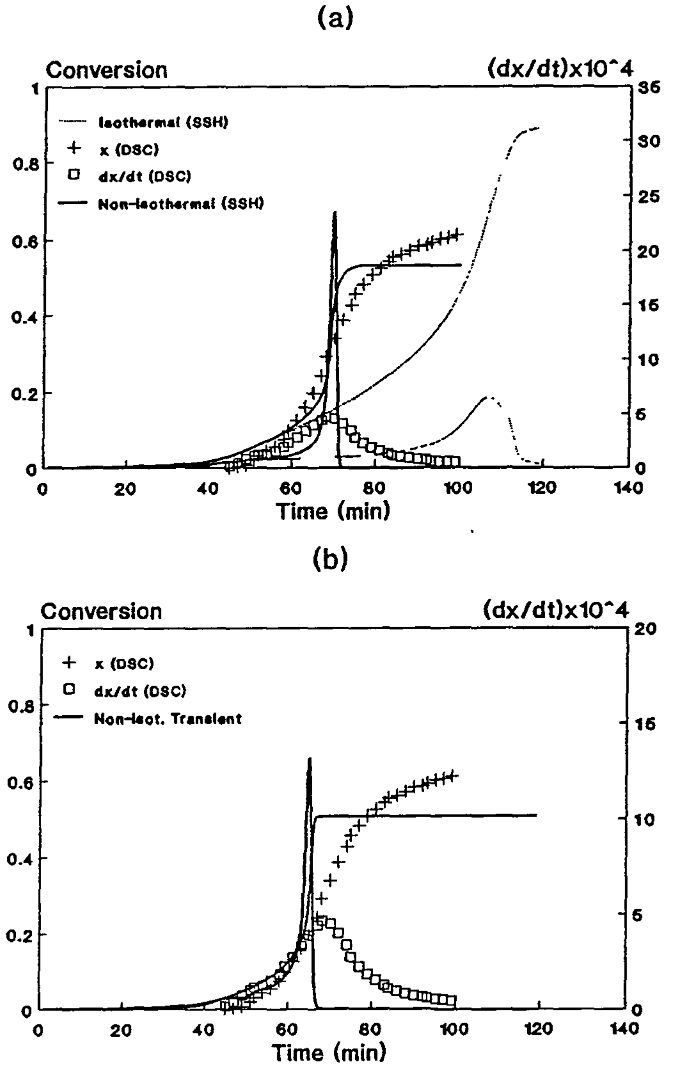


Figure 3.18 Commercial DVB bulk polymerization (ethyl vinyl benzene/p- and m-DVB copolymerization). [AIBN]= 0.055, [DPPH]= 0.007, f_{20}=0.55, T= 72 °C. (a) Non-transient isothermal (dashed lines) and non-transient non-isothermal (solid lines) predictions of conversion and reaction rate versus experimental DSC results. (b) Transient non-isothermal predictions (solid lines) versus experimental results.

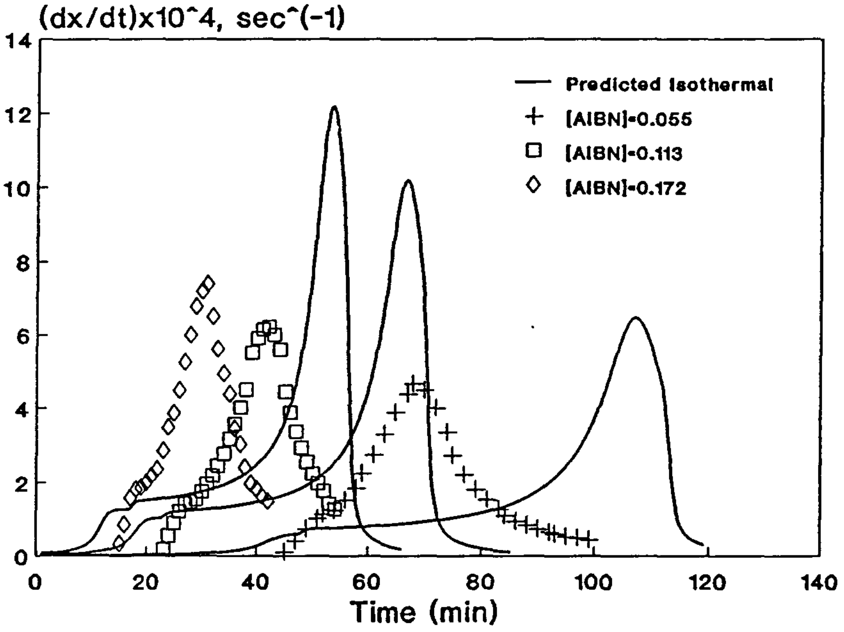


Figure 3.19 Commercial DVB bulk polymerization (ethyl vinyl benzene/p- and m-DVB copolymerization). [DPPH]= 0.007, f_{20}=0.55, T= 72 °C. Predicted non-transient isothermal versus experimental reaction rate.

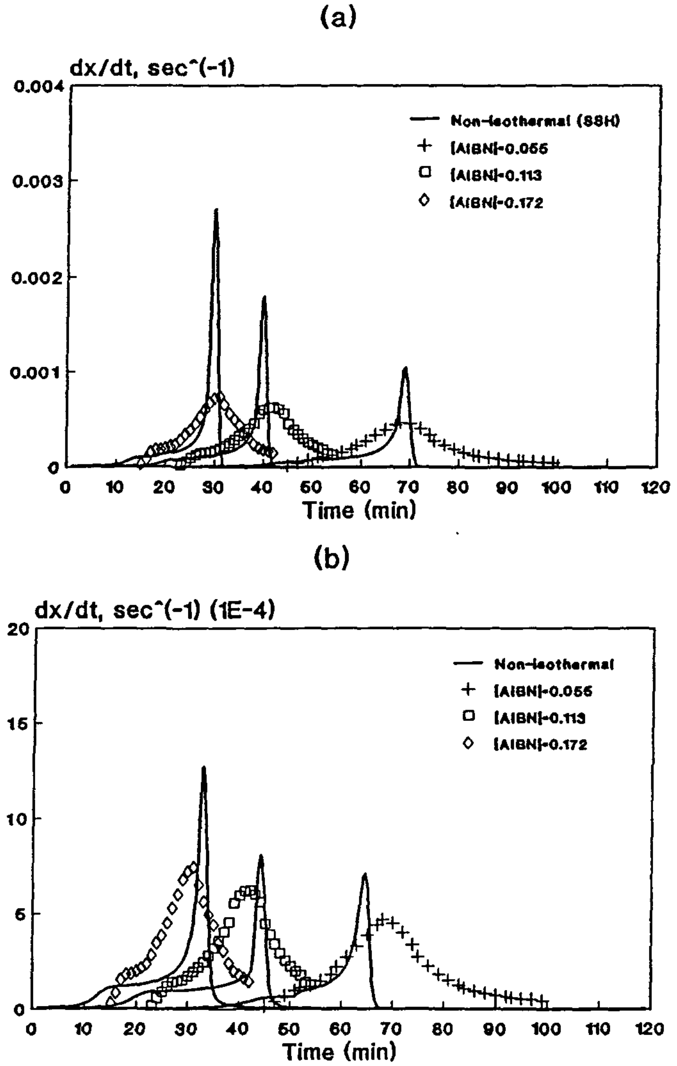


Figure 3.20 Commercial DVB bulk polymerization (ethyl vinyl benzene/p- and m-DVB copolymerization). [DPPH]= 0.007, f_{20}=0.55, T= 72 °C. (a) Predicted non-transient non-isothermal versus experimental reaction rate. (b) Predicted transient non-isothermal versus experimental reaction rate.

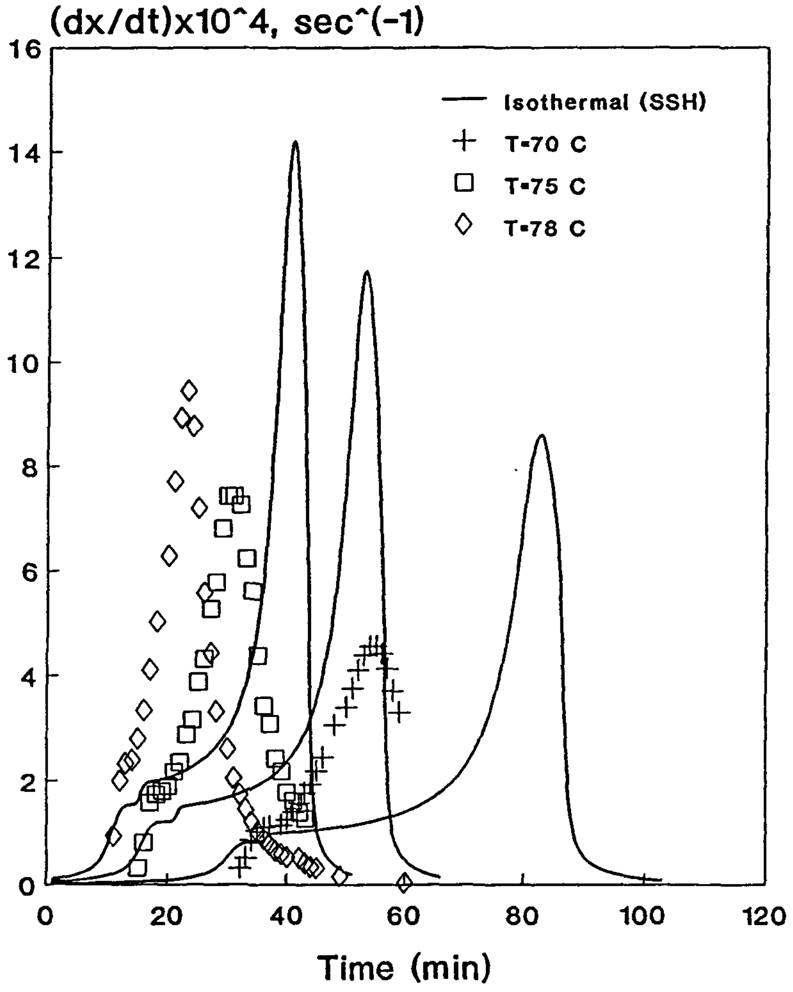


Figure 3.21 Commercial DVB bulk polymerization (ethyl vinyl benzene/p- and m-DVB copolymerization). [AIBN]= 0.14, [DPPH]= 0.007, f_{20}=0.55. Predicted non-transient isothermal versus experimental reaction rate.

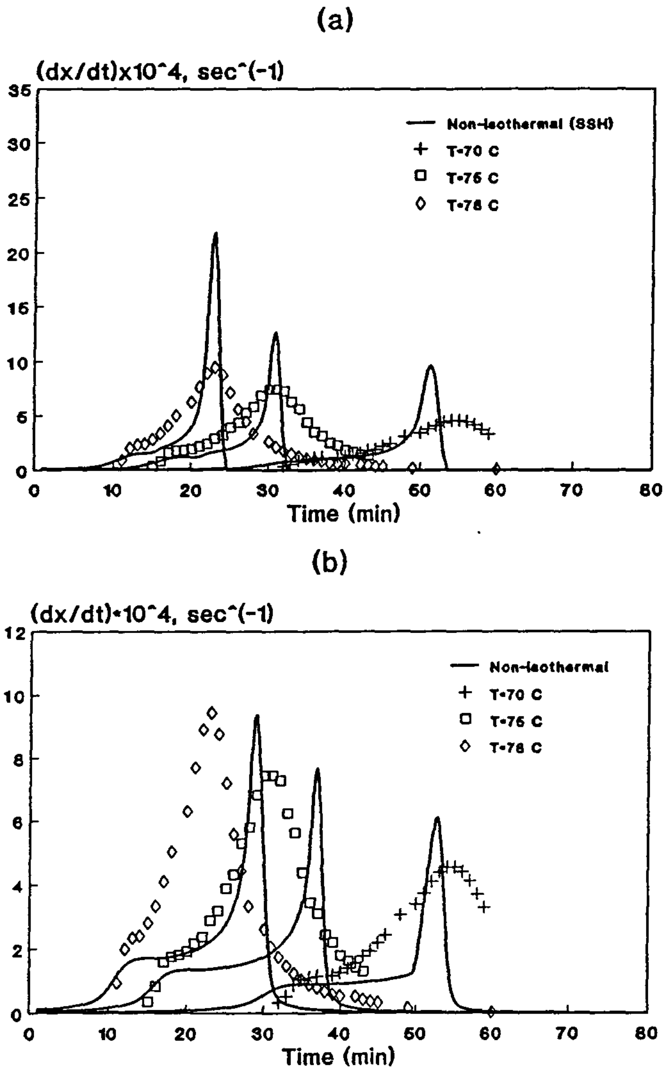


Figure 3.22 Commercial DVB bulk polymerization (ethyl vinyl benzene/p- and m-DVB copolymerization). [AIBN]= 0.14, [DPPH]= 0.007, f_{20}=0.55. (a) Predicted non-transient non-isothermal versus experimental reaction rate. (b) Predicted transient non-isothermal versus experimental reaction rate.

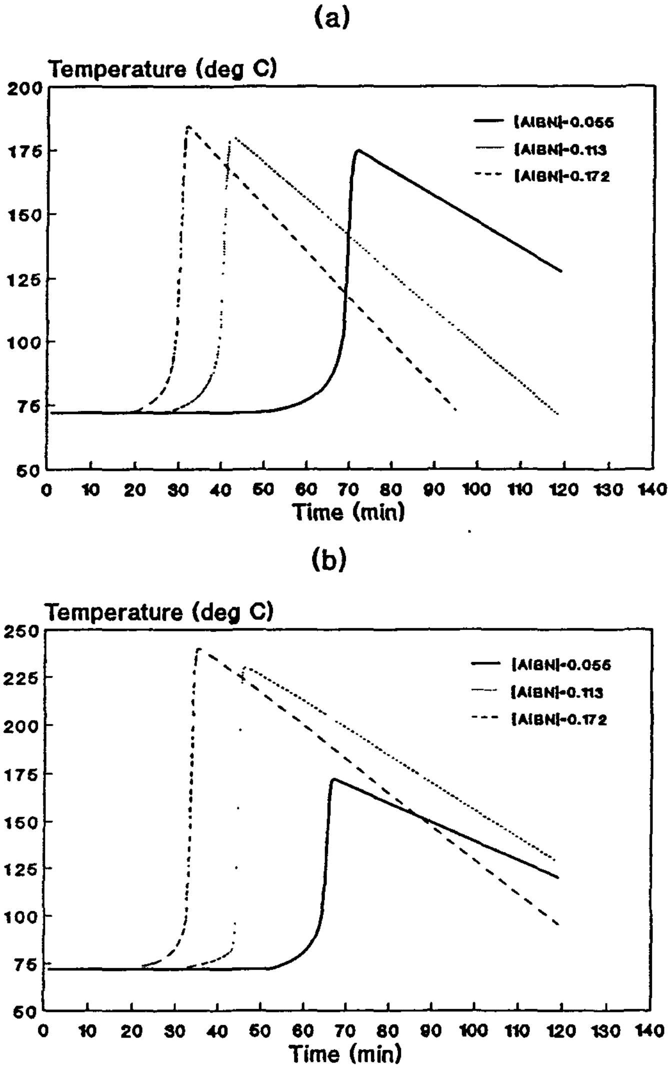


Figure 3.23 Temperature variation in "isothermal" DVB bulk copolymerization. (a) Non-transient model predictions at different initiator initial concentrations. (b) Transient predictions at same conditions as (a).

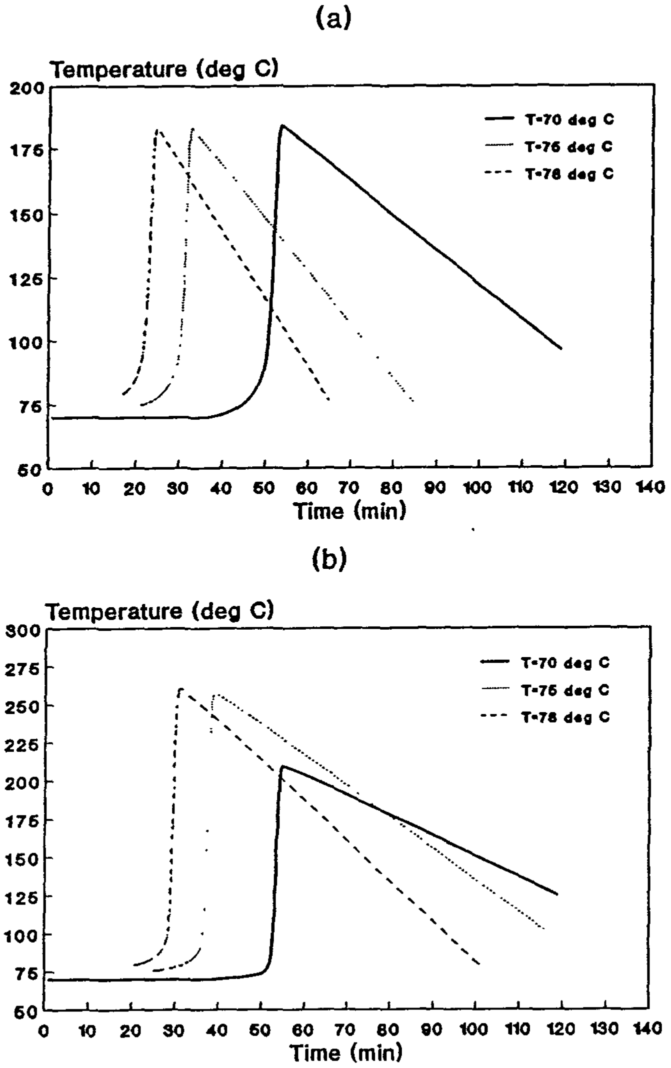


Figure 3.24 Temperature variation in "isothermal" DVB bulk copolymerization. (a) Non-transient model predictions at different initial temperatures. (b) Transient predictions at same conditions as (a).

CHAPTER 4

OVERALL CONCLUSIONS AND RECOMMENDATIONS

An effective model for crosslinking kinetics has been developed and widely tested using experimental data from different sources for styrene/divinylbenzene copolymerizations. Different conditions were considered and successfully predicted: bulk and solution (in toluene) styrene homopolymerization, copolymerization of styrene/m-DVB and styrene/DVB (mixture of m- and p-DVB) using AIBN as initiator carried out in benzene solution with and without added carbon tetrachloride as chain transfer agent, bulk copolymerization of styrene/p-DVB using BPO as initiator and bulk commercial DVB polymerization (copolymerization of ethyl vinyl benzene/m- and p-DVB) using AIBN as initiator and DPPH as inhibitor.

To build the model account was taken of the elementary reactions taking place in the reacting system. The model developed in this thesis centers its attention in diffusion controlled reactions. The excellent agreement between our model predictions and the experimental data show that taking into account diffusion-controlled phenomena in modelling of vinyl/divinyl copolymerizations is esential if realistic predictions are desired.

The model and the computer program to solve the equations are general. By giving the adequate initial conditions, both the model equations and the program can be used for the homopolymerization case.

The specific contributions of this thesis to the field of Polymer Reaction Engineering can be summarized as follows:

4.1) A comprehensive and objective comparison of two of the most popular models for diffusion controlled kinetics in free radical polymerization and copolymerization was undertaken. Their main features and limitations were clearly pointed out. This comparison is important because most of the practical studies in this area use either of the two models.

4.2) A new model for diffusion controlled free radical homopolymerization kinetics was developed. This new model has all the advantages of the CCS-AK and MH models, but their limitations were overcome. Even though this new model has strong theoretical background, its structure is simple and its performance behavior is remarkable. The model was successfuly extended to the copolymerization of vinyl/divinyl monomers by using the "pseudo-kinetic rate constant method".

4.3) It was demonstrated that a "parallel" approach for modelling "diffusion controlled" kinetic constants in free radical polymerization is incorrect. A correct way to model such constants was proposed (following a "serial" approach). This result has very important implications due to the fact that many researchers in this field use the parallel approach. This approach is so widely used that it has even been accepted by the IUPAC.

4.4) An effective way to calculate different k_t averages (k_{tn} and k_{tw}) was proposed and successfuly tested. This idea is very important if accurate predictions of weight average molecular weight are desired.

4.5) A model for calculation of non-equilibrium free volume (very important concept in highly diffusion controlled free radical copolymerization situations) was proposed. Although this is not the first approach to model this phenomenon (the first model was proposed by Bowman and Peppas, 1991), our model seems to include the previous one as a particular case (if there is no free volume "generation" due to crosslinking).

4.6) A general kinetic scheme and associated model equations were used. Although this general kinetic scheme has been used before, some additions are worthy of mention: account was taken of the presence and effect of an inhibitor; the model is not restricted to the use of equal reactivities of double bonds and all the phenomena usually considered in this kind of modelling are present (presence and effect of solvent and active chain transfer agent, as well of chain transfer and cyclization reactions).

4.7) Through the use of a simple approach to model bimolecular termination in the post-gelation period, it was possible to obtain good predictions of the polymer properties during that stage of the polymerization. However, it is recognized that the "effectiveness" of the model for the post-gelation period is not as good as it is for the pre-gelation period.

4.8) The steady state hypothesis (SSH) for the polymeric radical moment equations was removed. Most of the previous kinetic studies had used it, even though there is experimental evidence that such an assumption is invalid for the post-gelation period. Our calculations showed that the SSH is usually valid for the pre-gelation period, but in the post-gelation period its use can produce inadequate results (from unreliable estimates of the kinetic parameters to fundamentally incorrect predictions of the behavior of the system in the post-gelation period).

4.9) Whenever it was possible, statistical information regarding the reliability of the parameter estimates was provided. When that information was not obtained, detailed documentation on the estimation procedures was offered and the limitations on the use of the parameters were pointed out. Although this should not be considered as a "contribution", a trend in this kind of kinetic study seems to be the omission of this information (with the natural consequences that information about kinetic parameters "reported in the literature" are used to "validate" new models without taking into account the reliability of such parameters).

In the following lines some limitations of our kinetic model and/or recommedations on the way it should be further tested or improved are given.

Modelling bimolecular termination in the post-gelation period as a contribution from each phase seems to be adequate. However, translational termination should be incorporated (our model neglects translational termination in the post-gelation period for both, sol and gel) in the sol phase, due to the fact that the reduction in weight average chain length reduces the diffusional limitations in this phase. Initiation, propagation and termination should not be modelled as the same for both phases. A more realistic model for such reactions should be phase specific.

Our models for "diffusion controlled" phenomena in free radical polymerization (initiation, propagation and termination) should be further tested in non-isothermal polymerizations with significant temperature changes, polymerizations in the presence of prepolymer with a very different molecular weight than that produced later during the polymerization and polymerizations in continuous stirred-tank reactors.

Our kinetic model for the copolymerization case should be tested against experimental data for MMA/EGDMA copolymerization, which is a system widely studied and where much experimental information is available. Further improvement of the model should take into account copolymerizations carried out in semi-batch and continuous reactors. Our model could be used as starting point or at least as reference in modelling emulsion copolymerization of vinyl/divinyl monomers, particularly in the final stage of the polymerization (Stage "III" in emulsion polymerization).

Much effort should be concentrated in obtaining better (more realistic) models for secondary cyclization, which was demonstrated to be very important in the post-gelation period (most of the pendant double bonds in the post-gelation period are consumed by secondary cyclization). This should be considered a priority if a real effective model for the post-gelation period is desired.

Once the previous recommendations are taken, a further enhancement of the model could be achieved by including (in a practical quantitative fashion) the concept of crosslinking density distribution, which was not used in this research.

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For Chapter 3

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APPENDICES

A. SIMULATION CALCULATIONS USING NON-EQUILIBRIUM FREE VOLUME

The purpose of this appendix is to present a sensitivity analysis study on the effect of using non equilibrium free volume in the copolymerization kinetics calculations. The non-equilibrium free volume is calculated using either equation (60) (single parameter model) or (62) (three parameter model). These calculations are not included in the body of the paper due to the fact that they are more qualitative than quantitative (no precise parameter estimation for non-equilibrium free volume model parameters was attempted).

Figure A.1 shows predicted profiles of conversion versus time for p-DVB with [BPO]= 0.032 and T = 70.1 °C, using the single parameter model. It can be seen that the excess of free volume produces a slight increase in conversion during the post-gelation period and higher limiting conversions, which would be expected. The same behavior is observed in Figure A.2(a) (same system but using the three parameter model), although the effect is stronger. In this figure the effect of increasing the exponent of the relaxation time function is observed. Figure A.2(b) shows the same system and same model (three parameter model), but this time it is the reference relaxation time which is being changed. Figures A.3(a) and A.3(b) show predicted profiles of fractional free volume as compared to the equilibrium value, for the same system and using the parameters indicated in the figures' captions. It is interesting to observe that when non-equilibrium free volume values are used, the predicted profiles are in better agreement with the experimental information. However, as it was indicated before, the temperature rise in the reactor might have been considerable. It would be difficult to conclude with this information which is the true reason for such deviation.

Equations (60) and (62) were also used to predict the behavior of the comercial DVB polymerization with AIBN and inhibitor. The qualitative results were similar as with p-DVB with BPO, that is a slight increase in conversion was obtained by increasing the rate of production of free volume with either model. However, the changes were minimal even if huge values of the non equilibrium free volume parameters were used. The reason for this is that in this case (data set 13, Table 2.3) the simulations would predict total consumption of initiator, so that no matter how much excess free volume was available, there would not be any more radicals to propagate.

Figure A.4 shows model predictions of styrene/p-DVB bulk copolymerization at 70.1 °C, f_{20}=0.032 and three levels of initiator initial concentration. In (a) calculations were done assuming that the glass transition temperature of the polymer, Tg_p, is not affected by the crosslinking density, whereas calculations shown in (b) take into account the effect of crosslinking density on Tg_p (see Appendix B). Although minimal, there seems to be a difference in the predicted profiles (slightly higher limiting conversion values are obtained when Tg_p is assumed to be constant). However, the effect of reaching different limiting conversions as a result of changing the initiator initial concentration (at constant temperature), first reported by Stickler (1983), is clearly observed. In Figure A.5 the same phenomenon is observed, except that in this case there is no crosslinker in the system (styrene bulk homo-polymerization). These two figures (A.4 and A.5) clearly show that our model for non-equilibrium free volume is adequate.

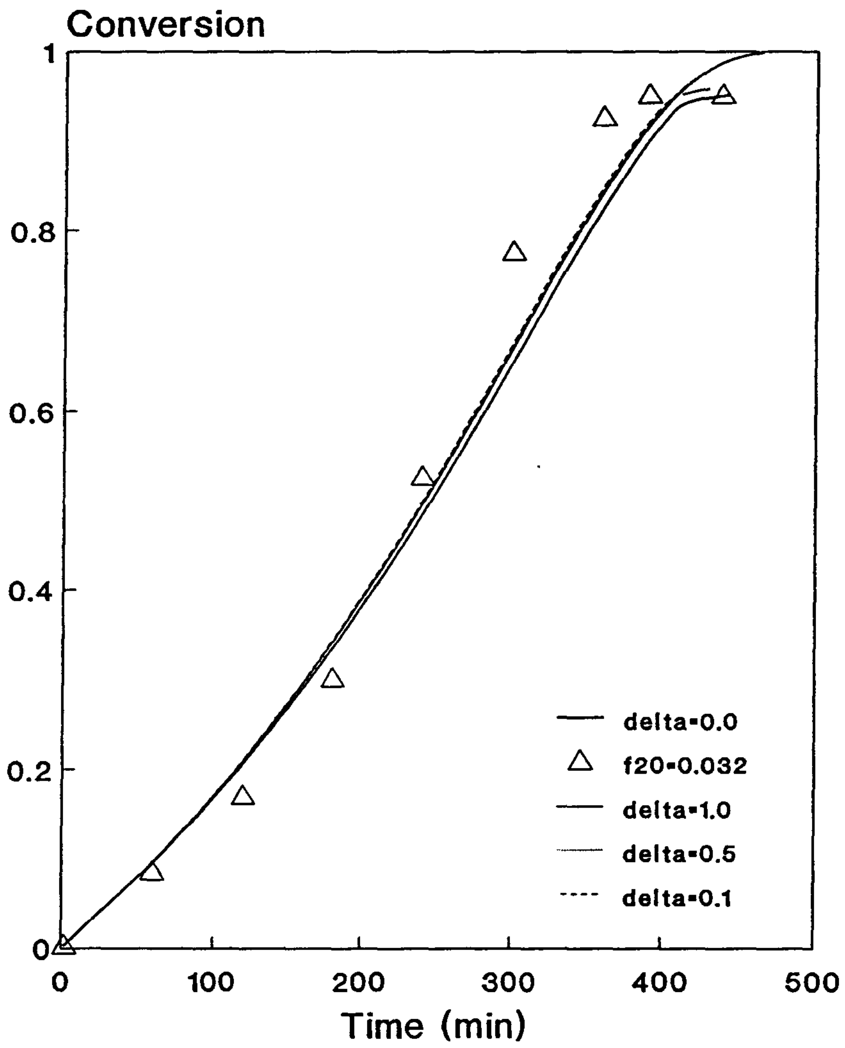

Figure A.1 Conversion rate predictions for p-DVB bulk copolymerization at [BPO]= 0.0356, f_{20}= 0.032 and T= 70.1 °C using the single parameter model for non-equilibrium free volume calculation.

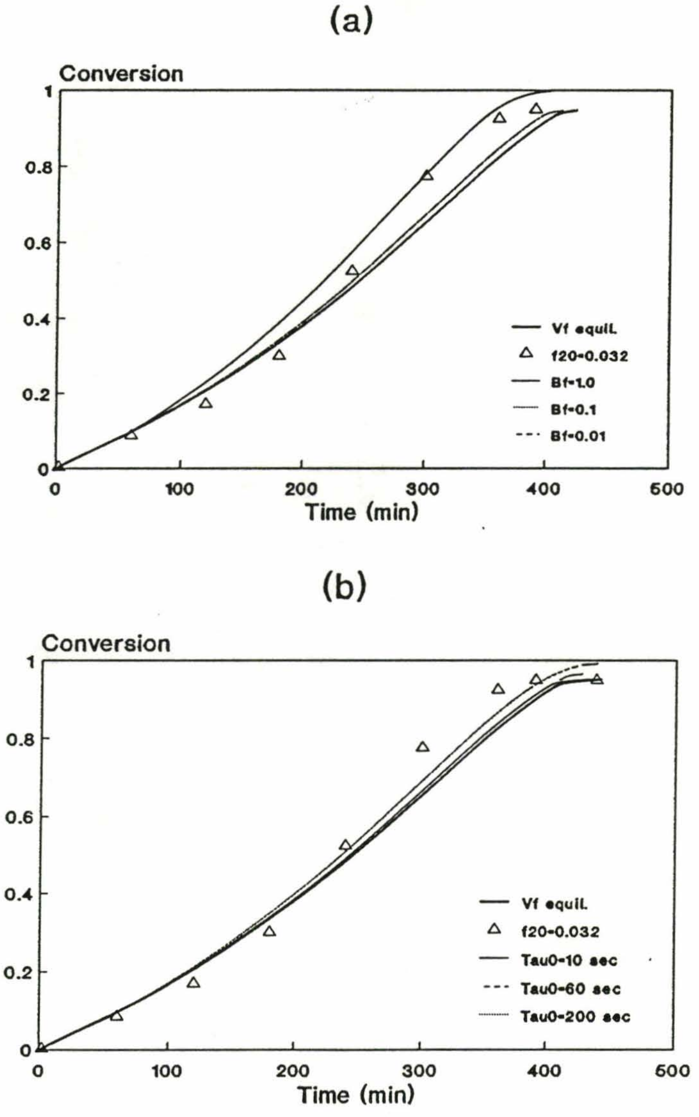

Figure A.2 Conversion rate predictions for p-DVB bulk copolymerization at [BPO]= 0.0356, f_{20}= 0.032 and T= 70.1 °C using the three parameter model for non-equilibrium free volume calculation. (a) δ' =0.1 and τ_0 = 1.0; (b) δ' =0.1 and B_f=0.1

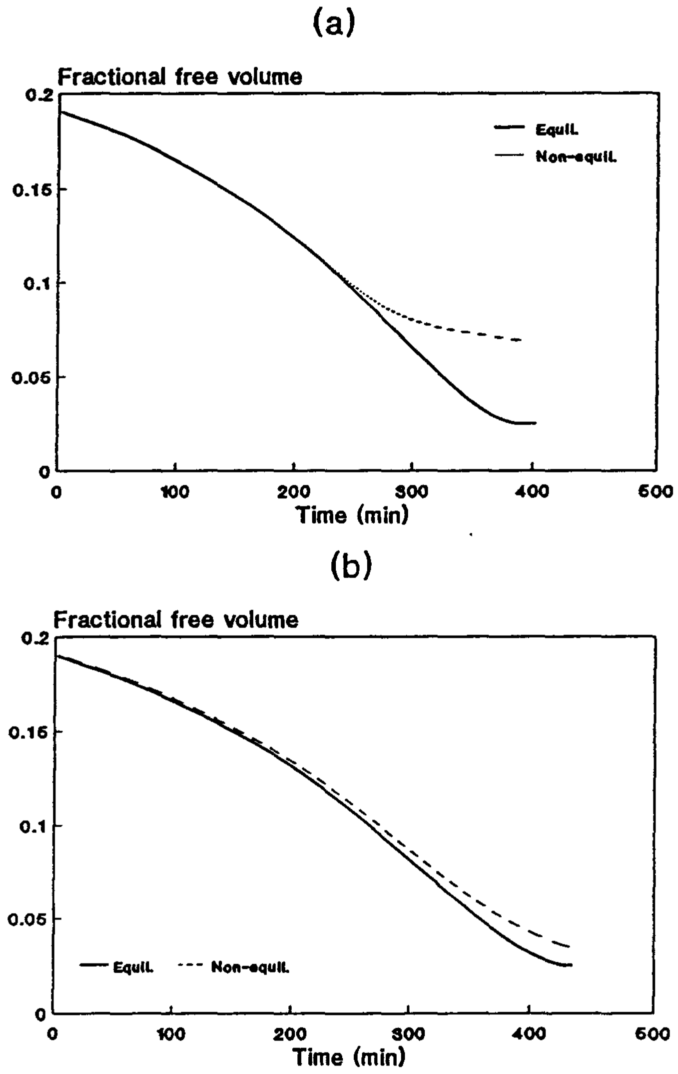

Figure A.3 Free volume predictions for p-DVB bulk copolymerization at [BPO]=0.0356, f_{20}= 0.032 and T= 70.1 °C using the three parameter model for non-equilibrium free volume calculation. (a) δ' =0.1, B_f= 1.0 and τ_0= 1.0; (b) δ' =0.1, B_f= 0.1 and τ_0= 200.0

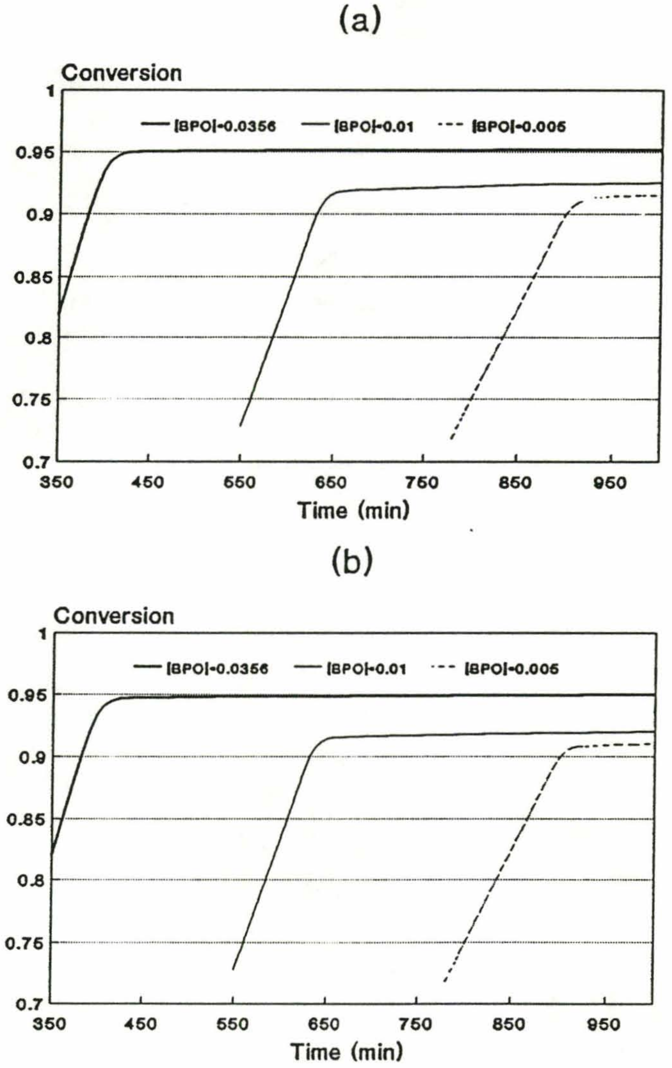

Figure A.4 Free volume predictions for p-DVB bulk copolymerization at f_{20}= 0.032 and T= 70.1 °C, using the three parameter model for non-equilibrium free volume calculation. (a) Tg_p= constant; (b) Tg_p= f(crosslinking density).

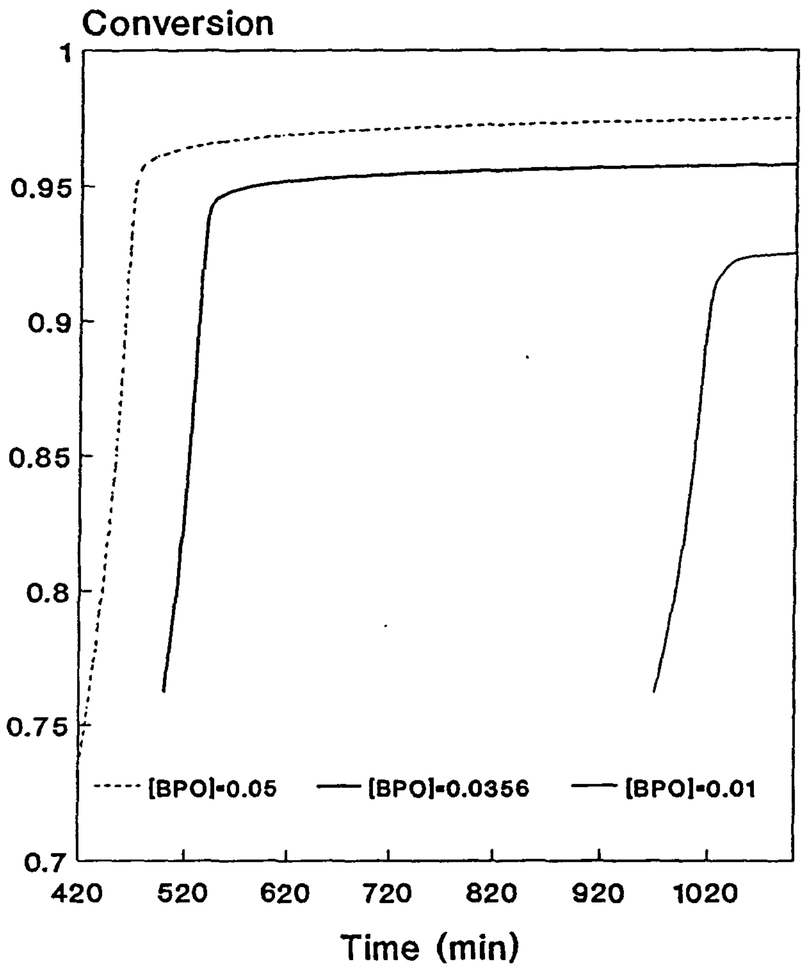

Figure A.5 Free volume predictions for styrene bulk homopolymerization at T= 70.1 °C, using the three parameter model for non-equilibrium free volume calculation.

B. MODELLING T_{gp} DURING THE POST-GELATION PERIOD. CROSSLINKING DENSITY AND UNSATURATION.

This appendix is intended to model the effect that crosslinking density has on the glass transition temperature of the polymer. It is also intended to model and present some calculations on the degree of unsaturation (pendant double bonds not consumed by cyclization or crosslinking reactions) during polymerization and estimate the importance that secondary cyclization has in the post-gelation period.

Effect of crosslinking density on the glass transition temperature of the polymer

It has been recognized for a long period time that the glass transition temperature of a polymer produced via free radical copolymerization of vinyl/divinyl monomers increases with the degree of crosslinking (Fox and Loshaek, 1955) and the "copolymer effect" (crosslinking and molecular weight) (DiBenedetto and Nielsen, 1969). Several models have been proposed to take into account those effects, either by proposing equations to calculate the glass transition temperature of the monomers/solvent/ polymer mixture or explicit models for calculation of the glass transition temperature of the polymer.

DiBenedetto and Nielsen (1969) proposed the following equation to calculate the glass transition temperature of the mixture:

$$\frac{Tg(x)-Tg_0}{Tg_0}=\frac{(\frac{E_x}{E_m}-\frac{F_x}{F_m})x}{1-(1-\frac{F_x}{F_m})x} \tag{B.1}$$

where E_x/E_m is the ratio of lattice energies for crosslinked and hypothetical uncrosslinked polymer, F_x/F_m is the corresponding ratio of segmental mobilities and x is total monomer conversion. This equation has also been used by Pascual and Williams (1990) and Wang and Gillham (1993).

Hale and Macosko (1976) proposed to calculate the glass transition temperature of the mixture as indicated in equation (B.2).

$$Tg(x)=\frac{Tg_u(x)}{1-\frac{K\bar{\rho}}{1-\psi\bar{\rho}^2}} \tag{B.2}$$

where $Tg_u(x)$ is the glass transition temperature of the uncrosslinked system at conversion x (hypothetical after gelation), K is a parameter incorporating the effect of crosslinks on Tg, ψ is a parameter incorporating the effect of non-Gaussian nature of crosslinks at high crosslink density on Tg, and $\bar{\rho}$ is the crosslink density. This equation has been used by Simon and Gillham (1992, 1993) to model the cure kinetics of thermosetting materials.

Mikos et. al. (1986) proposed the following equation for calculation of the glass transition temperature of styrene/DVB copolymers (slight changes in their nomenclature were introduced in order to be consistent with ours):

$$Tg_p=Tg_p'(1+1.2\bar{\rho}) \tag{B.3}$$

where Tg_p' is the glass transition temperature of the uncrosslinked copolymer.

Wisanrakkit and Gillham (1990) proposed to calculate glass transition temperatures for the polymer in each phase (sol and gel). An effective Tg_p would be calculated as indicated in equation (B.4).

$$Tg_p=\omega_{sol}Tg_p^{sol}+\omega_{gel}Tg_p^{gel} \tag{B.4}$$

where

$$\frac{1}{Tg_p^{sol}}=\frac{1}{Tg_p^{\infty}}+\frac{K}{\overline{M}_{n,sol}} \tag{B.5}$$

$$Tg_p^{gel}=Tg_p^{\infty}+K_x\overline{\rho} \tag{B.6}$$

$$K_x=\frac{1}{A_0}\left(Tg_{p,\infty}-Tg_p^{\infty}\right) \tag{B.7}$$

"∞" as superscript in Tg_p accounts for the glass transition temperature of the linear (uncrosslinked) polymer. As subscript, it accounts for the glass transition temperature of the fully cured material. A_0 is the maximum value of the crosslinking density (at x= 1).

In the predictions of pendant double bond conversion, degree of unsaturation and gel fraction, which are to be shown later on in this appendix, equation (B.3) has been used. The reason for doing so is that this equation is specific for styrene/DVB and has the same structure as equation (B.6).

Calculation of pendant double bond conversion and degree of unsaturation

The pendant double bond conversion in a vinyl/

divinyl copolymerization can be calculated using the following equation (after Tobita and Hamielec, 1992):

$$x_{pd}=\frac{\bar{\rho}_{cp}+\bar{\rho}_{cs}+\bar{\rho}}{\bar{F}_2}=k_{cp}+\frac{\bar{\rho}_{cs}+\bar{\rho}}{\bar{F}_2} \qquad \textbf{(B.8)}$$

where x_{pd} is the pendant double bond conversion.

From a mass balance on the concentration of pendant double bonds bound to the polymer, it can be demonstrated that the degree of unsaturation (concentration of unreacted pendant double bonds), expressed as percentage of the total concentration of pendant double bonds, is given by the following equation:

$$\%\text{-}of\text{-}Unsaturation=100(1-k_{cp}-\frac{\bar{\rho}_{cs}}{\bar{F}_2}-\frac{\bar{\rho}}{\bar{F}_2})=100(1-x_{pd}) \qquad \textbf{(B.9)}$$

As mentioned in the parameter estimation section of this paper, all calculations were performed setting k_{cs} =0.0; that is to say, secondary cyclization and crosslinking density are confounded. That means that what was obtained as crosslinking density in our calculations, is in fact the sum of both (crosslinking density and secondary cyclization). One way to separate them without modifying the computer program or the values of the parameters, is to use equation (81) and the predicted values of crosslinking density (crosslinking + secondary cyclization densities). From equations (48), (50) and (81) the following expressions are obtained:

$$\bar{\rho}_{cs}=\frac{k_{cs}\bar{\rho}}{2+k_{cs}} \qquad \textbf{(B.10)}$$

$$\bar{\rho}_{xl}=\frac{\bar{\rho}}{1+\frac{k_{cs}}{2}} \qquad \textbf{(B.11)}$$

where subscript "xl" in equation (B.11) accounts for actual crosslinking density and k_{cs} is calculated using equation (81).

Model predictions of pendant double bond conversion, degree of unsaturation and effect of crosslinking density on Tg_p.

The following figures were obtained using the modifications to our kinetic model mentioned in the previous sections of this appendix. They are intended to further illustrate the capabilities of our kinetic model and some of its weak points, which should be improved in order to make it more useful in actual applications.

Figure B.1(a) shows predicted and experimental profiles of pendant double bond conversion versus total monomer conversion at conditions of data set 8. It can be seen that although not perfect, the agreement between predictions and experimental data is quite good. Figure B.1(b) shows the predicted profile of degree of unsaturation versus conversion and B.1(c) shows predicted gel fraction versus conversion. It is interesting to note that gelation occurs at a conversion level lower that 0.05 and that at a conversion level of 0.3 the amount of sol is very small. These profiles were obtained using Tg_p=constant. The corresponding profiles using equation (B.3) are shown in Figure B.2. The difference in the predicted profiles is almost negligible. This situation seems to indicate that equation (B.3) may not be adequate. A value greater than "1.2" in such equation should be used to get better profiles. The remaining figures were obtained using equation (B.3).

Figure B.3 shows the contributions of primary cyclization, secondary cyclization and crosslinking to the overall pendant double bond conversion. As expected, the conversion level of pendant double bonds due to primary cyclization remains constant thoughout the polymerization, whereas the contributions of secondary cyclization and crosslinking increase as polymerization proceeds. In (a), secondary cyclization and crosslinking are shown as a single profile, but in (b) they are shown independently. It can be clearly seen that secondary cyclization consumes most of the pendant double bonds during the post-gelation period. Although the contribution of crosslinking to pendant double bond conversion may be underpredicted (caution was advised in using the regression models for k_{cs}), it is clear that the number of double bonds required to get a gel is extremely low, so that most of them are consumed by secondary cyclization.

Finally, in Figure B.4 the increase in Tg_p during polymerization and its effect on the degree of unsaturation are shown. Although qualitatively correct, the predictions are clearly inadequate as to be considered quantitatively reliable. As mentioned before, equation (B.3) may not be adequate or it may be also possible that our predictions of crosslinking density were too low (it should be also taken into account that the concentration of crosslinker in this case was quite low).

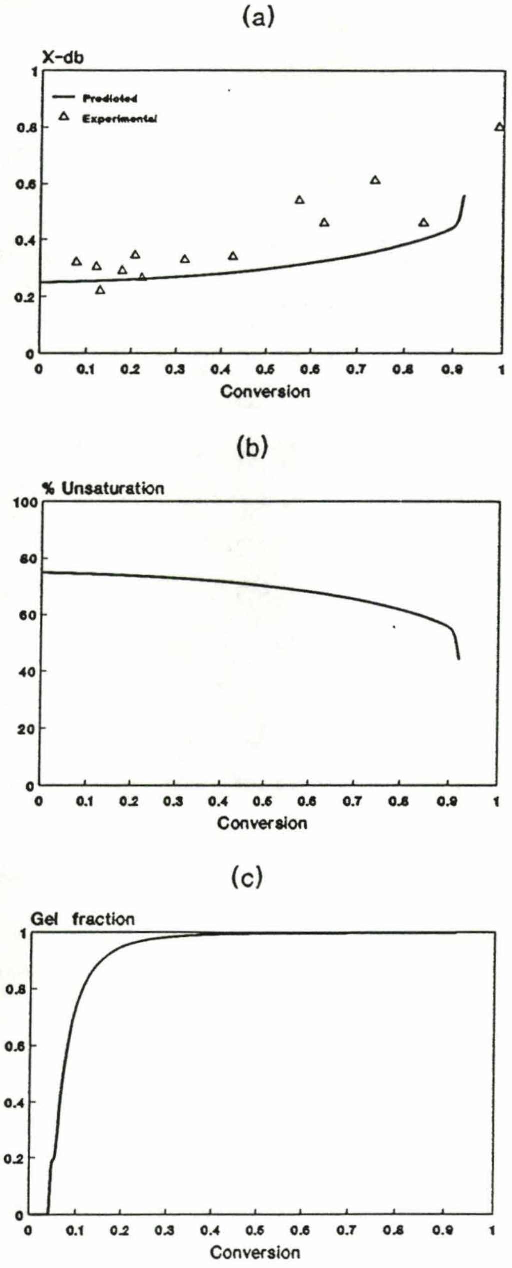

Figure B.1 Styrene/p-DVB bulk copolymerization at T= 70 °C, [BPO]= 0.011 and f_{20} 0.065. Calculations using Tg_p= constant. (a) Pendant double bond conversion versus x; (b) % of unsaturation versus x, and (c) Gel fraction versus x.

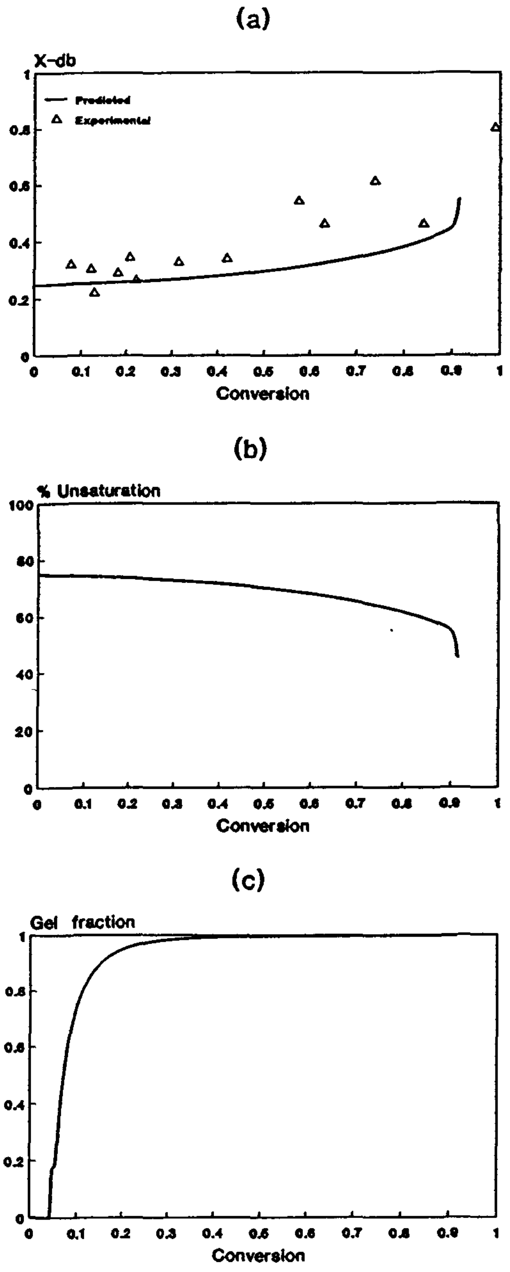

Figure B.2 Styrene/p-DVB bulk copolymerization at T= 70 °C, [BPO]= 0.011 and f_{20} 0.065. Calculations using Tg_p= f(crosslinking density). (a) Pendant double bond conversion versus x; (b) % of unsaturation versus x, and (c) Gel fraction versus x.

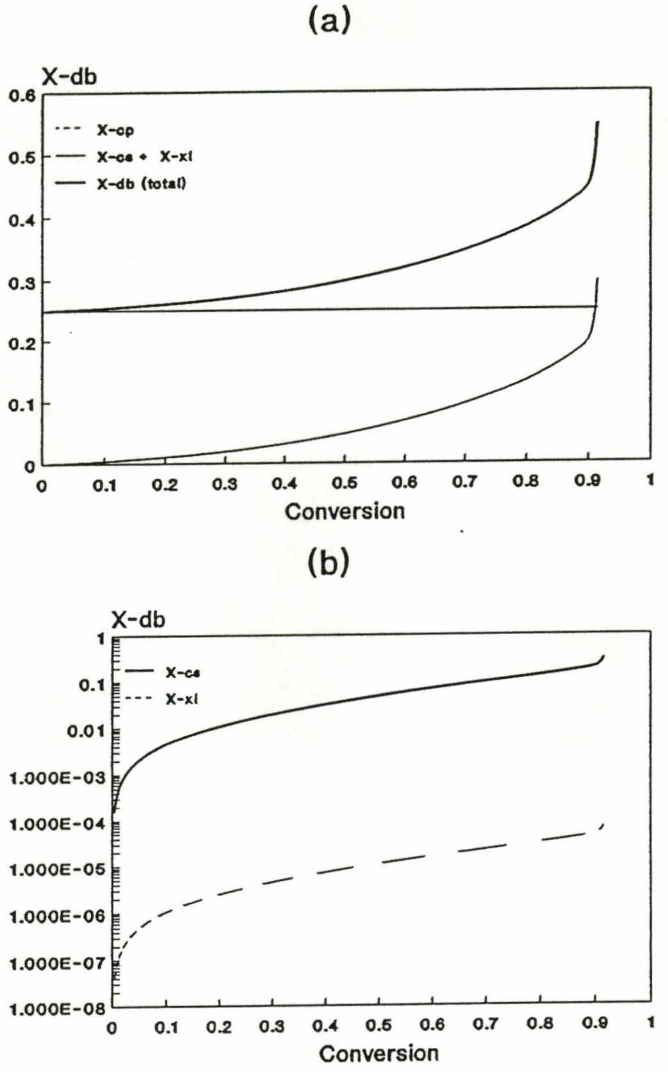

Figure B.3 Styrene/p-DVB bulk copolymerization at T= 70 °C, [BPO]= 0.011 and f_{20} 0.065. Calculations using Tg_p= f(crosslinking density). (a) Contributions of crosslinking, primary and secondary cyclizations to double bond conversion. (b) Decoupling secondary cyclization and crosslinking density.

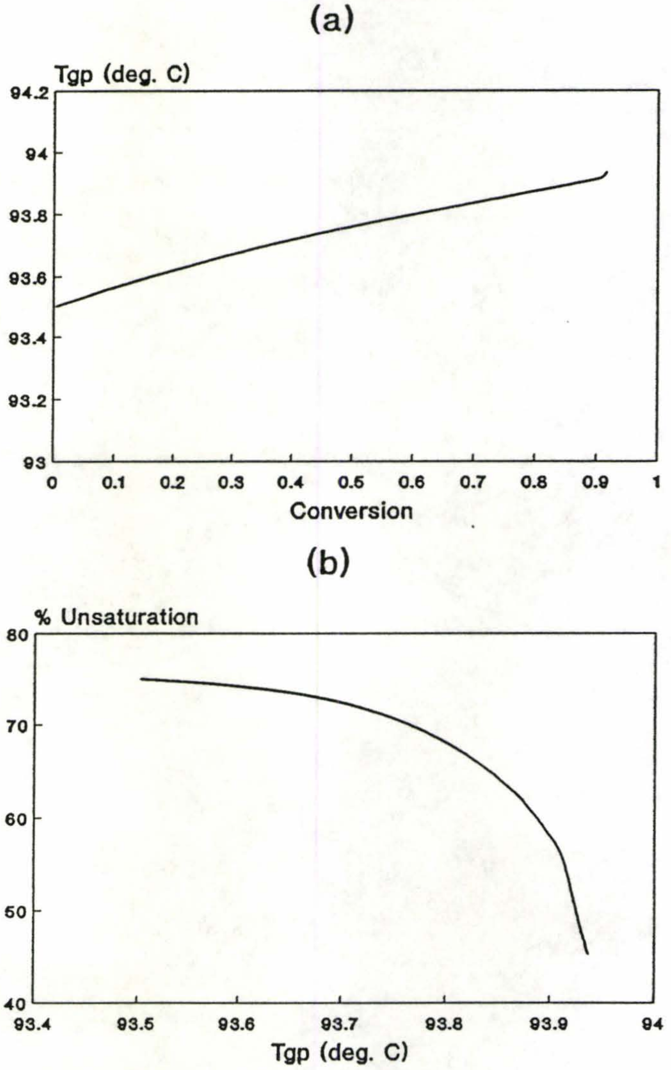

Figure B.4 Styrene/p-DVB bulk copolymerization at T= 70 °C, [BPO]= 0.011 and f_{20} 0.065. Effect of crosslinking density on Tg_p. (a) Tg_p versus x; (b) % of unsaturation versus Tg_p.