POLYMERIZATION OF VINYL CHLORIDE

by

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POLYMERIZATION OF VINYL CHLORIDE

TO MY PARENTS

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ABSTRACT

Herein is reported an experimental evaluation of a model after Abdel-Alim and Hamielec, for bulk and suspension polymerization of vinyl chloride for the conditions of nonisothermal polymerization and polymerization with multiple initiator systems.

The model predictions for these rather extreme conditions are reasonable. It appears that with minor modifications the model could be used to design initiator systems and to develop new molecular weight recipes for commercial initiators.

ACKNOWLEDGEMENTS

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INTRODUCTION

There is urgent need in the PVC industry for a mathematical model for mass and suspension polymerization which can accurately pre- dict conversion-time histories and molecular weight development using multiple initiator systems under isothermal and nonisothermal condi- tions. Such a model would be used to design multiple initiator systems to minimize batch times and to develop new molecular weight recipes.

Many models have been proposed and published and they will be discussed later. However, only one model gives accurate predictions even at high conversions and complete molecular weight calculations. This model was developed by Abdel-Alim and Hamielec. Unfortunately this model up to the present time has been tested under the following rather restricted conditions: Isothermal polymerization using only one initiator (AIBN) at three temperature levels of 30°, 50° and 70°C. It was therefore decided to test the applicability of this model using nonisothermal polymerization and multiple initiator systems. In addi- tion, Lucidol Division of Pennwalt Corporation, a U.S. peroxide pro- ducer has recently published rather extensive rate data for isothermal suspension polymerization of vinyl chloride using one and two initiator systems. These rate data were also used to test the applicability of the model.

Parts I and II also include a rather extensive review of PVC technology and the various models that have been published for mass and suspension polymerization of vinyl chloride.

PART I.   GENERAL

I.1 GENERAL

The term Polyvinyl Chloride, or PVC, indicates homopolymers of vinyl chloride and incorrectly copolymers containing amounts of vinylidene chloride, vinyl acetage, ethylene, propylene or acrylates.

Being a very well known member of the family of vinyl polymers, PVC ranks as the second most important polymer after ethylene. Its annual production rate in the U.S.A. has increased at an average annual growth rate of the order of twelve percent.

Until about forty years ago, PVC was considered a laboratory curiosity. In 1974, the production volume was 9.2 million metric tons world-wide, including 2.2 million metric tons in the U.S.A. (Figure 1). Assuming a minimum predicted annual growth rate of the order of eight percent, these figures will be increased to 14.6 and 3.5 million tons by 1980. The event of vinyl chloride being established as a probable carcinogenic seems to have had only a short term negative impact. On the long term, by substantially reducing monomer and polymer waste, using much larger polymerization reactors and eliminating residual monomer from the PVC resin industry seems to be able to overcome the toxicity problem. At the present time the 1-5 ppm monomer limit has already been achieved by some manufacturers. Another positive factor is that only 43% of PVC is made from material based on petroleum. Additionally, a cubic centimeter of PVC contains only 0.60 g hydrocarbon, while polymers such

FIGURE 1
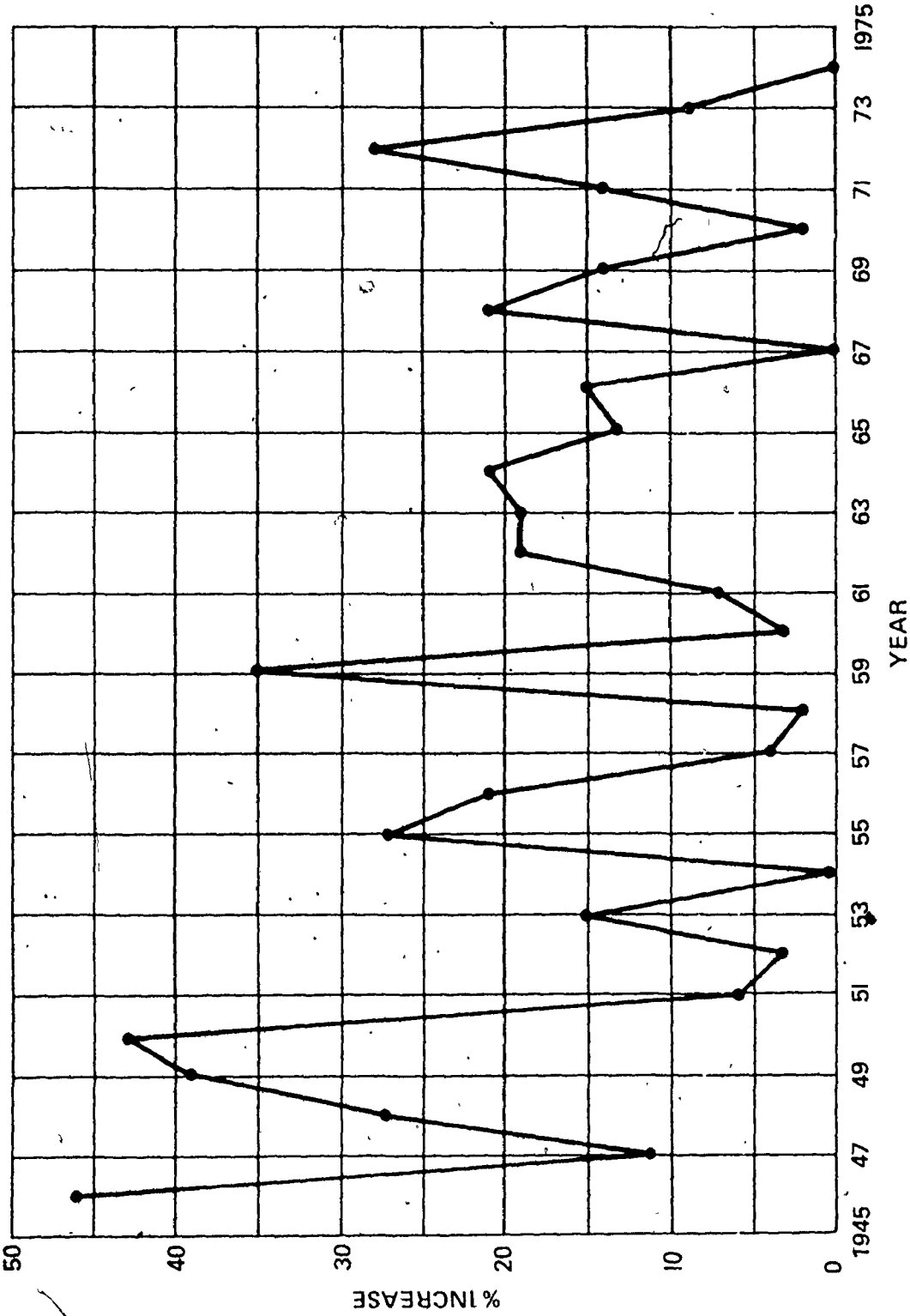
POLYVINYL CHLORIDE GROWTH RATE IN THE US (8)

as polyethylene, polypropylene, ABS and polystyrene contain at least
0.90 g hydrocarbon. This is expected to influence the growth rate
positively.

Polyvinyl chloride is a very versatile polymer and finds extensive use in a great variety of products. In the construction industry
it is used for flooring, wire insulation, waste and water pipes, window
frames, external siding, etc. Phonograph records, balls, cans, toys and
garden hoses are some other applications. A large number of fabricating
methods allows the formulation of the final product. Film coating, blow
molding, injection molding, extrusion and calendering are the most
common.

The resin is commercially produced via bulk, suspension, emulsion and solution processes. Each one of these processes has its own
advantages and disadvantages. Suspension is the most important method,
accounting for about 80% of the total PVC production. All the above
processes are heterogeneous, the polymer being insoluble in its own
monomer and in water.

The molecular properties and the polymer microstructure seem to
depend almost exclusively on the reaction temperature. But macroproperties such as particle size, particle size distribution, bulk density and
porosity, seem to vary substantially with the type of process. In the
following chapters we will briefly discuss most of the above mentioned
characteristics of PVC. The low price, the good compounding ability,
physical, chemical and weathering properties, as well as excellent

processability contribute to the rapid growth of PVC production world-wide.

PVC is one of the most extensively investigated and studied polymers. Such studies deal with polymerization kinetics, polymer characterization, degradation, rheology, processing and more recently toxicity. There are still, despite the huge commercial production of PVC, many problems that have not been solved. For example, the mechanism of polymer particle formation is not yet completely understood and there is no mathematical model describing the particle size and the size distribution. We believe that with the recent advent of improved analytical instruments and techniques, it will be possible to further explore and better understand these mechanisms in the near future.

I.2 THE MONOMER

Vinyl chloride is a toxic,colourless gas with a pleasant sweet odour. It is normally used as compressed liquified gas. The atmospheric boiling point is -13.8°C and the vapour pressure at room temperature is about 50 psi. It is extremely volatile and flammable.

I.2.1 Preparation

Current commercial processes for production of vinyl chloride monomer (VCM) are the following:

(a) Acetylene and HCl react directly over mercury chloride to produce vinyl chloride

$$CH \equiv CH + HCl \rightarrow CH_2 = CHCl + Heat$$
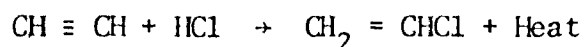
Acetylene is obtained from the petrochemical industry or from calcium carbide.

The catalyst may be either mercury chloride[4,5] or even other halogenated heavy metal[6].

Arsine, phosphine and other compounds act as poisons to the reaction, so the gas streams have to be dry and clean.

(b)   Ethylene and chlorine react to produce ethylene dichloride. followed by cracking to produce vinyl chloride and HCl.

$$CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl - CH_2Cl$$

$$CH_2Cl - CH_2Cl \xrightarrow{500°C} CH_2 = CHCl + HCl \uparrow$$
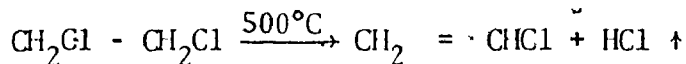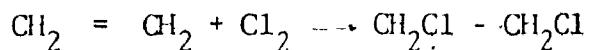
(c)   The balanced process: This combines the previous two methods. Here the hydrogen chloride produced in (b) reacts according to the first method to produce VCM.   This method has been used commercially in Japan and a flowsheet of the process is given by Buckley[7].

(d)   The oxychlorination technique;   This may be carried out in one or two steps.

Two step process:

Oxychlorination followed by pyrolysis

$$2HCl + \tfrac{1}{2}O_2 + Cl_2 + 2C_2H_4 \longrightarrow 2C_2H_4Cl_2 + H_2O$$

$$C_2H_4Cl_2 \longrightarrow CH_2CHCl + HCl$$
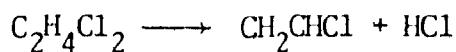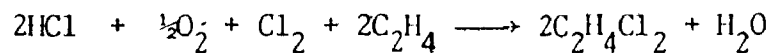
One step process:

Combines oxychlorination with pyrolysis

$$\tfrac{1}{2}O_2 + Cl_2 + 2C_2H_4 \longrightarrow 2CH_2ClCl + H_2O$$
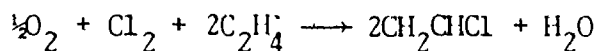
Almost all VCM produced today is based on ethylene and on oxychlori-
nation processes commercialized since 1960. The change from acetylene
to ethylene based processes reduced the price of VCM by a factor of about
two and this is one main reason for the increased production and use of
polyvinyl-chloride.

I.2.2 Monomer Quality and Impurities

The quality of VCM is always a very important factor in polymeri-
zation because impurities may affect the reaction kinetics and the quality
of the final product. Today most of the quality problems have been eli-
minated and the vinyl chloride produced is of a high purity. Typical
analysis of the monomer used for PVC production is shown in Table 1.

Impurities may affect the kinetics via the initiation and chain
transfer steps. As an example we have found that iron oxides contribute
to a faster initiator decomposition. Using stainless steel ampoules we
found that the reaction rates are higher compared to the rates we measured
using glass ampoules. These higher reaction rates may be due to the
presence of iron oxides on the inner surface of the stainless steel am-
poules.

I.2.3 Physical Properties

Selected physical properties of VCM are summarized in Table 3.
A list of empirical equations relating selected physical properties of
VCM to temperature is given in Table 2.

TABLE 1

TYPICAL QUALITY CONTROL ANALYSIS OF VINYL CHLORIDE[8]

PROPERTY	TYPICAL ANALYSIS
APPEARANCE	CLEAR, FREE OF SUSPENDED MATTER
COLOR	COLORLESS, WATER-WHITE
ACIDITY, AS HCl	< 1 PPM
IRON, AS Fe	0.2 PPM
NON-VOLATILE RESIDUE	10 PPM
WATER	45 PPM
SULFUR, AS SO_2	< 1 PPM
PEROXIDES	< 0.06 PPM
ACETALDEHYDE	< 1 PPM
ACETYLENE	< 1 PPM
OXYGEN	500 PPM
METHYL CHLORIDE	100 PPM
BUTADIENE	10 PPM

TABLE 2

EMPIRICAL CORRELATION OF VINYL CHLORIDE PHYSICAL PROPERTIES[8]

VAPOR PRESSURE mm Hg	$LOG_{10}P = 7.356 - 1170t$ °C
DENSITY gm/cc	$\rho = 047.9 - 1.89t$°C
LIQUID VISCOSITY CENTIPOISES	$LOG_{10}\mu = -3.957 \times 10^{-3}t$°C$-0.626$
HEAT CAPACITY, LIQUID cal/gm/°C	$C_p = 0.0758t$°C $+ 18.67$
LATENT HEAT OF VAPORIZATION K cal	$\Delta Hv = 5014 - 17.04t$°C
SURFACE TENSION dynes/cm	$\sigma = 1953 - 0.1413t$ (°C)
HEAT CAPACITY VAPOR cal/gm/°C	$C_p = 12.13 + 0.0275t$(°C)

TABLE 3

SELECTED PHYSICAL PROPERTIES OF VINYL CHLORIDE

PROPERTY	TEMP°C	VALUE
Molecular Weight	-	62.501
Boiling Point at 760 mm Hg, °C	-	-13.80
Melting Point, °C	-	-153.69
Colour	-	Colorless
Density, Liquid, gm/ml	25	0.9013
Viscosity, Liquid Cps	25	0.185
Viscosity, Vapor Cps	25	0.0108
Surface Tension, Dynes/cm	25	16.0
Refractive Index D Line	25	1.3642
Vapor Pressure, mm Hg	25	2943
Heat Capacity Cp, Cal/mol/°C -Liquid	25	20.56
-Vapor	25	12.82
Latent Heat of vaporization, H_v, cal/mol	25	4710
Latent Heat of Fusion, H_m, cal/mol	-	1,172
Heat of Formation, H_f, K Cal/mol	25	8480
Free Energy of Formation, G_F, K Cal/mol	-	12.386
Heat of Polymerization, H_p, K Cal/mol	-	-25.3 ± 0.5
Flash Point, Cleveland Open Cup, °C	-	-78
Explosive Limit, Vol % in air	-	3.6 - 26.4
Critical Temperature, t_c, °C	-	147
Critical Pressure, P_c, Atmospheres	-	56
Critical Volume, V_c, cc/mol	-	179
Critical Compressibility, (PV/RT), Z	-	0.29
Dielectric Constant at 10^5 Herz	-21	7.05
Dissipation Factor at 10^5 Herz	-21	0.0011
Solubility of Water in Vinyl Chloride, wt%	25	0.11
Autogeneous Ignition Temperature, °C	-	472.22
Solubility of Vinyl Chloride in Water, wt%	30	0.1

I.2.4 <u>Safety - Toxicity</u>

The flammability of VCM has been the cause of several serious fires and explosions due to accumulation of vinyl chloride. It is easily ignited by a spark in the explosive composition range of 3.6% - 26% in air.

Two additional hazards, acroosteolysis and angiosarcoma are attributed to VCM. In acroosteolysis, the bone in the fingers slowly dissolves. If contact with VCM is eliminated in the early stages, the bone may regenerate completely in one or two years.

Even though VCM was considered to be very low in toxicity, researchers found that it causes angiosarcoma, a form of liver cancer, even at concentrations as low as 50 ppm. Because of the carcinogenic properties of the monomer, worker exposure is not allowed to exceed 1 ppm in an 8 hour day. For higher concentrations, masks and other protective equipment, combined with continuous monitoring systems (chromatographs) have to be used.

One additional precaution was to reduce the amount of monomer contained in the polyvinyl chloride resin. This amount was about 0.2% VCM before January 1975. This is equal to 37 million lbs of vinyl chloride during 1974. Recently companies offer very pure PVC resin containing only 1 ppm.

I.3 POLYMERIZATION TECHNIQUES.

Polyvinyl chloride is commercially produced by bulk, suspension emulsion and solution polymerization. The suspension process is the major manufacturing technique. 80% of the total PVC is produced by suspension polymerization, 12% by emulsion, 7.5% by bulk and 0.5% by solution polymerization[8]. The suspension process is favoured because it has the advantage of good process control and low cost of separation and drying the resin. The literature contains few details of commercial processes. A brief review of the main processes is given below.

I.3.1 Bulk Process[9]

In this process the monomer is polymerized without diluents. The important advantage of this method is the production of polymer free of impurities. A major problem is heat removal, and the control of the reaction rate presents serious difficulties. The bulk process was of no commercial interest until the middle 60s, when Pechiney-St.Gobain developed a new process.

In the original one step process[10] a 3000 gallon ball mill was used as the reactor. The balls are used to convert the precipitated fluffy PVC into a fine powder suitable for extrusion and calendering. Further development led to the Rhône-Poulenc bulk process, schematically shown in Figure 2. This is a two stage process[11]. During the first step, polymerization up to 10% conversion occurs in a standard vertical high shear agitated reactor, the so-called prepolymerizer. Half of the monomer is fed into the reactor. The agitation speed and the temperature

FIGURE 2
PRODUCTION OF POLYVINYL CHLORIDE
BY THE RHONE-PROLIG BULK PROCESS
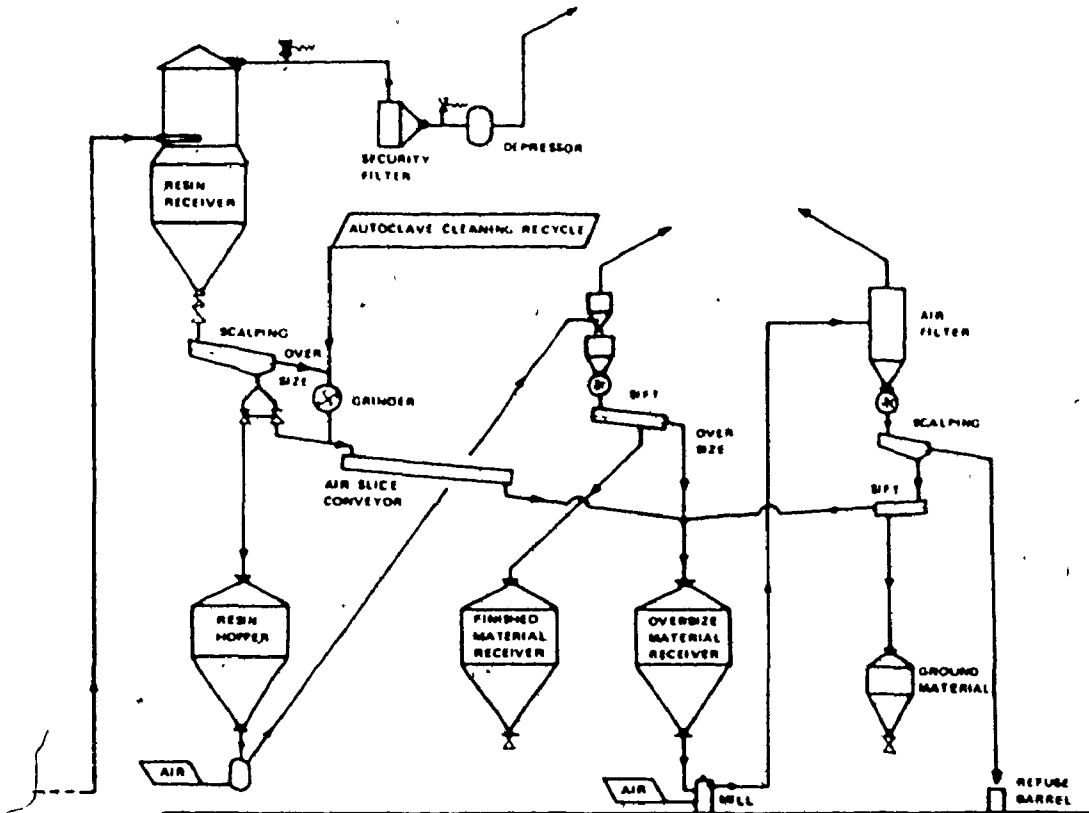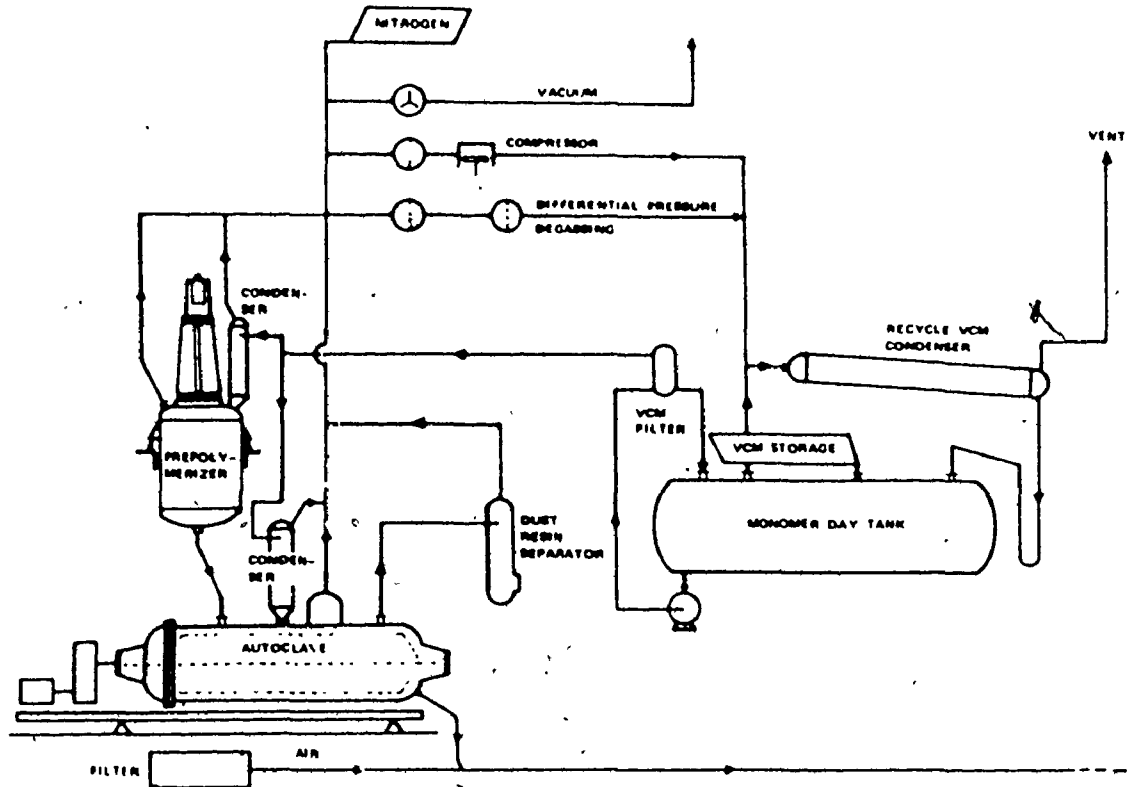
determine the size of the polymer particles which act as seeds for the second stage[12].

During the second step the reaction mixture is transferred from the polymerizer to the main reactor. The second half of the monomer is fed, together with the mixture from the first stage, into the specially designed, well agitated horizontal reactor where the reaction goes up to 75-80% conversion. The horizontal autoclave reactor is called the post-polymerizer and is loaded with scraper blade type agitation to be able to handle the PVC powder during the last stages of the reaction. The reaction is completed in 5-9 hours and stops simply by evaporating the unreacted monomer which is condensed and recycled. The system of the two reactors is shown in Figure 3.
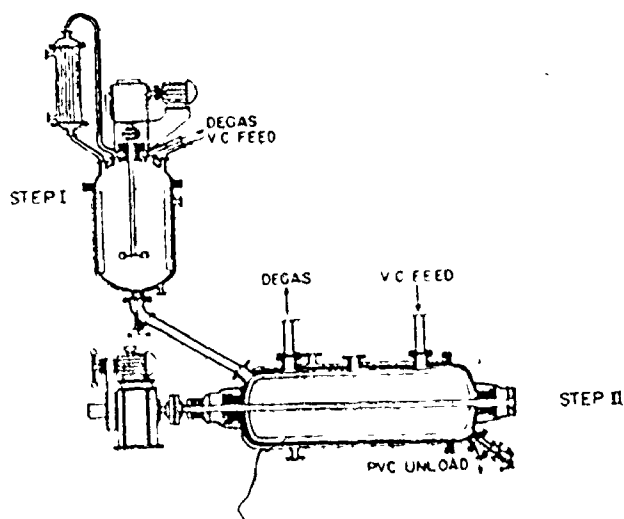
Figure:3

Thus, one line consists of one big prepolymerizer equipped with a reflux condenser and cooling jacket, four main reactor autoclaves connected in

parallel, a VCM compressor, storage tanks, filters and auxiliary equipment. One line has an average capacity of 30-45 million pounds of dry-blend resin per year. Pechiney has also patented a vertical reactor with two agitators, and a reflux condenser. This reactor has a capacity of 10,000 gal and may replace the horizontal post-polymerizers in the future.

1.3.2 Suspension Process

Currently this is the most important method for PVC production. About 80% of the total PVC made today is produced by the suspension process. In this technique, the continuous phase is water, with vinyl chloride monomer droplets dispersed in the water phase by means of suspension agents. The particle size range obtained is 50-150 microns. The cost of manufacturing is significantly lower than for emulsion and solution processes. Impurities also, such as emulsifiers, suspension agents and protective colloids, are at a substantially lower level than emulsion resins. The types and amounts of suspension agents commercially used are the subjects of numerous patents and affect particle size, size distribution, porosity and the shape of the particles.

It should also be mentioned that, since water is the continuous phase, we do not have very significant heat transfer problems and the process control is good. A schematic of a suspension polymerization plant is shown in Figure 4.

1.3.3 Emulsion Process

By using an emulsifying agent we can produce a fine particle size dispersion in water. The polymer emulsion may be coagulated and
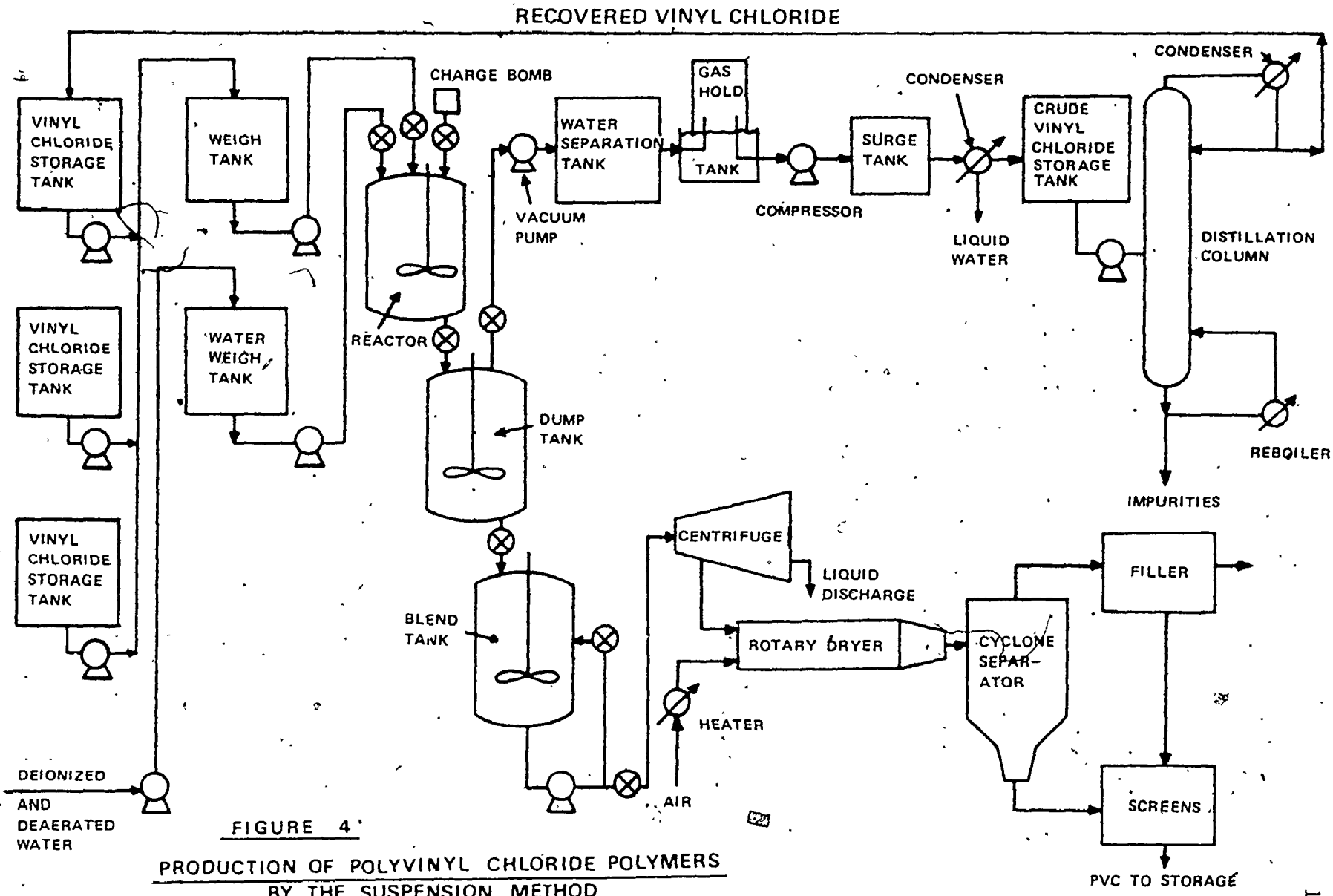
FIGURE 4

PRODUCTION OF POLYVINYL CHLORIDE POLYMERS
BY THE SUSPENSION METHOD

dried for processing applications, or it may be spray dried to produce plastisol resins. For latex applications the particle sizes produced are extremely fine. The polymerization equipment is similar to the suspension process and the water, as in suspension, permits the effective heat removal. Disadvantages of the method are the high cost of manufacture and the high levels of emulsifiers and protective colloids in the final product. A schematic plan of the emulsion process is shown in Figure 5.

1.3.4   Solution Process

The Union Carbide solution process, described by a number of patents, was developed for vinyl chloride-vinyl acetate copolymers. The products are highly uniform and the applications are mainly solution coating and fiber resins where the high quality and uniformity justify the higher production cost. The polymerization is carried out in solvents usually organic hydrocarbons. The process uses standard reactors continuously fed with the co-monomers, hydrocarbon solvent and initiators. The slurry produced is continuously fed into solid-liquid separators. The solvent and the residual co-monomers are recovered and recycled continuously. The disadvantage of the method is the high cost due to the need for efficient solvent recovery.
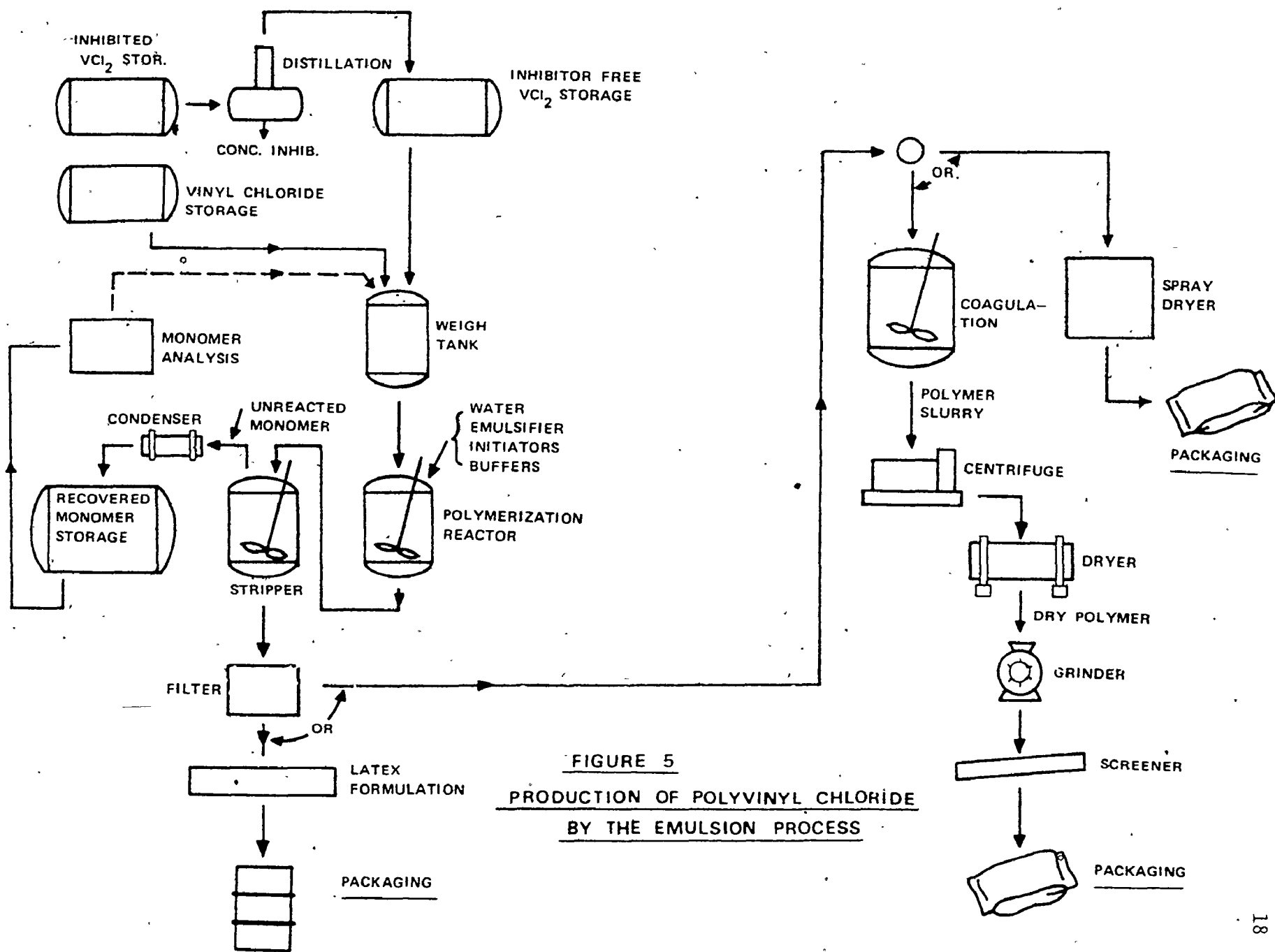
FIGURE 5

PRODUCTION OF POLYVINYL CHLORIDE
BY THE EMULSION PROCESS

I.4   PVC PROPERTIES

I.4.1   Microproperties

(a)   Chain configuration

The carbon atom in the vinyl chloride molecule is mainly responsible for the three different modes of addition of a new monomer unit on the polymer chain during propagation. The three different modes are known as head-to-tail, head-to-head and tail-to-tail structure, (as shown in Figure 6). Marvel and coworkers[13] have shown the head-to-tail structure to be predominant (greater than 99%) in PVC homopolymer. The carbon atom is also responsible for the variable chain stereoregularity.

Since the terminal carbon atom on each radical is free to rotate, there are two different arrangements for the chlorine atom contained in the CHCl group. When all the chlorine atoms are found in the same position (relative to the plane containing the backbone carbon-carbon bonds), an isotactic chain results; (See Figure 6). In this figure the dotted line bonds lie below the plane of the paper, the thin triangular bonds lie above this plane. When the chlorine atoms are in an alternating configuration, the result is a syndiotactic chain; (see Figure 6).

An extensive investigation of the stereoregularity of PVC homopolymers as a function of polymerization temperature (in the range -50°C to 70°C) was obtained by high resolution NMR (220 MHz) [14,15].

FIGURE 6
PVC CHAIN CONFIGURATION

HEAD-TO-TAIL   HEAD-TO-HEAD   TAIL-TO-TAIL
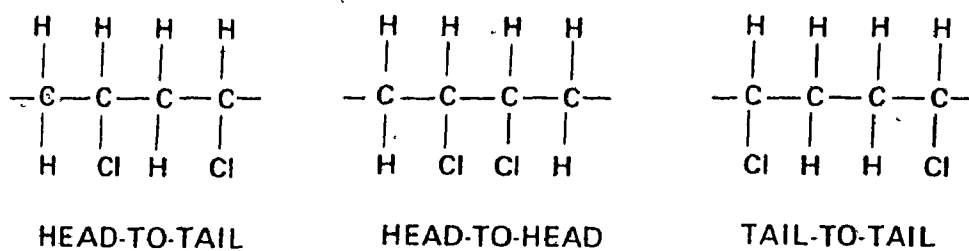
(A)
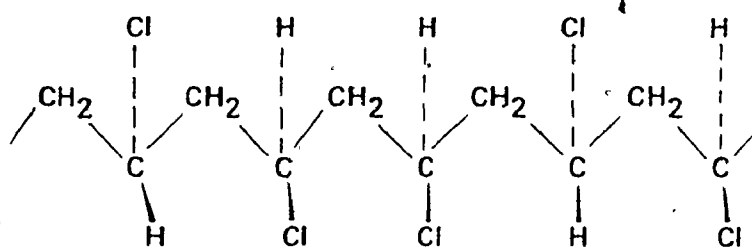
(ATACTIC)

(B)
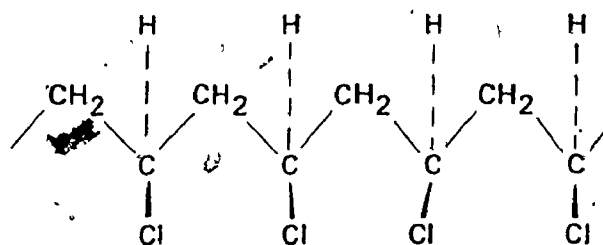
(ISOTACTIC)

(C)
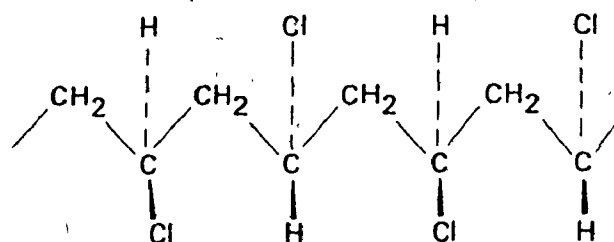
(SYNDIOTACTIC)

(D)

The Arrhenius equation obtained is given as

$$\ln \frac{1-s}{s} = 0.8455 - \frac{349.3}{T}$$

where s is the instantaneous fraction of syndiotactic diads. (See Figure 7).

(b) Branching

Transfer reactions to polymer usually give rise to branching effects. The degree of branching is determined by infrared analysis on polyethylene obtained through reduction of PVC. The lower the polymerization temperature, the lower the degree of branching. Generally branching is not highly prevalent in PVC polymerized below room temperature. Many workers have shown that the degree of branching drops with temperature and is zero for polymer prepared at 75°C.[16] Lyngaae Jorgensen[15] reported that the degree of branching in commercial PVC is 0.4 to 0.5 CH_3/100 CH_2; 10% are long branches and 90% are short branches.

FIGURE 7
RELATION OF SYNDIOTACTICITY AND AGGREGATION

Plot of $\mathrm{Ln}\,\dfrac{1-A}{A}$ (vertical axis, from 2.0 to above 4.0) versus $\mathrm{Ln}\,\dfrac{1-S}{S}$ (horizontal axis, from -0.30 to -0.26)
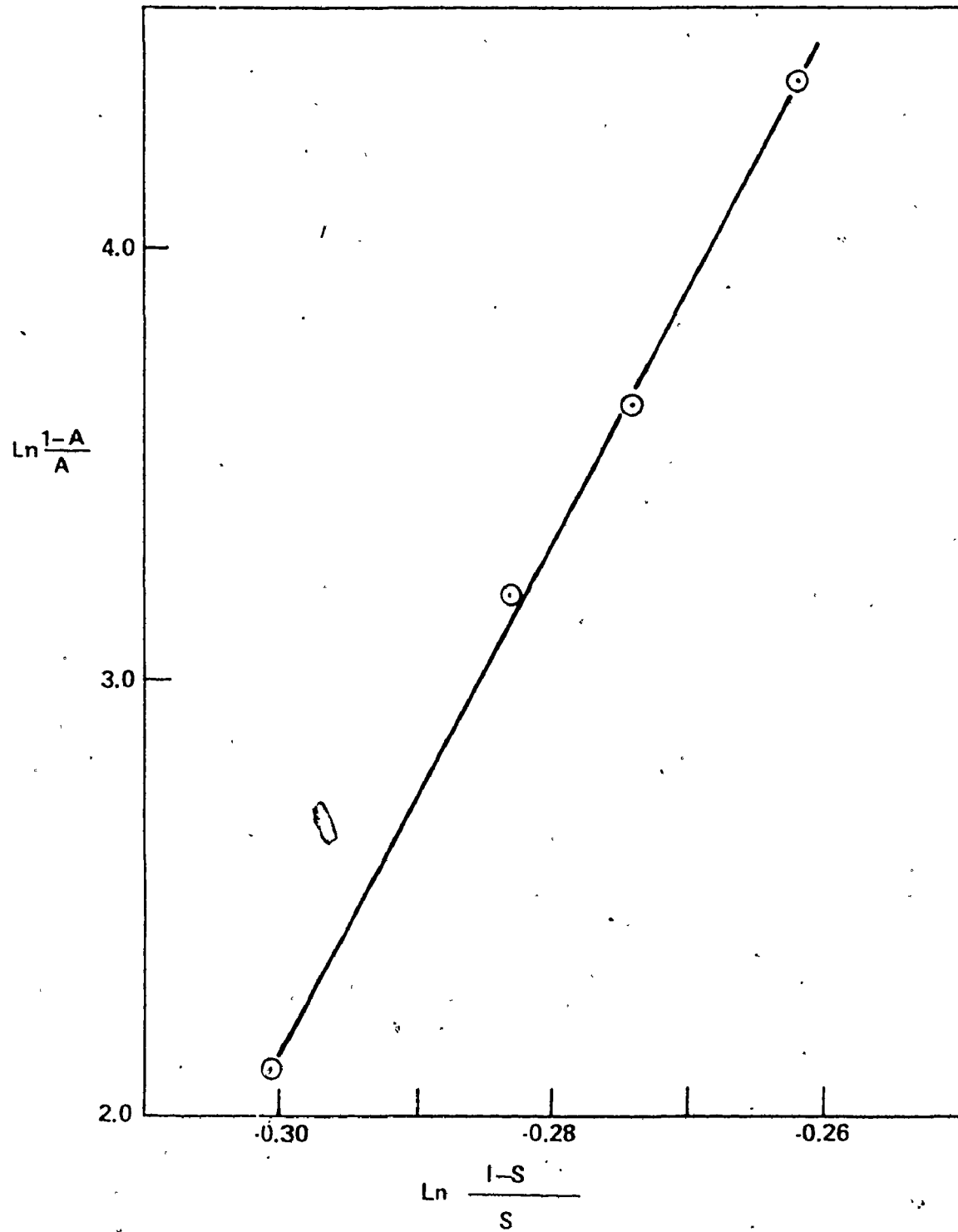
(c) Molecular Weight Distribution (MWD)

It has been established experimentally that the amount of branching is negligible in PVC. Simple kinetic analysis in such a case shows that when transfer to monomer is the dominant step in the molecular weight development then the molecular weight distribution, produced in both monomer and polymer phases, is the most probable distribution.

$$W(r) = \frac{r}{(r_n)^2} \exp(-\frac{r}{r_n})$$

where r is the chain length, $W(r)$ the weight fraction of chain length r and $\bar{r}_n$ is the number average chain length. Then the ratio of the weight average molecular weight $\bar{M}_w$ to the number average molecular weight $\bar{M}_N$ theoretically will be 2.0.

Many workers compared theoretical MWD with experimentally measured ones and found them in excellent agreement[17,18]. They also found that MWD does not vary with conversion during the course of the reaction, provided that conditions are isothermal.

I.4.2 Macroproperties of PVC

(a) Glass Transition Temperature (Tg).

Tg is defined as the temperature below which polymers are glassy, hard and brittle. Above Tg polymers are softer, more flexible and have better impact strength. Some of the important physical properties of the polymers change significantly near the Glass Transition Temperature. Specific volume and shear modules are examples of properties that change at Tg. Table 4 shows some typical values for Tg.

TABLE 4

Tg For Some Common Polymers

	$Tg(°C)$
Polyethylene	-110
Polyisoprene	- 70
Polypropylene	- 18
Polyvinyl chloride	82
Polyvinyl acetate	30
Polystyrene	100
Polymethyl methacrylate	105

Reding et al.[19] showed that there is a negative linear dependence of Tg on polymerization temperature; the dependence of Tg on temperature is shown in Figure 8.

Plasticization or copolymerization of vinyl chloride usually tends to reduce Tg significantly, increasing the softness and the flexibility of the final product.

(b) Crystalline Melting Temperature (Tm)

Tm is defined as the melting temperature of the crystalline domain of the polymer. Tm is higher than Tg. The melting point of PVC depends on polymerization temperature and more specifically on stereo-regularity and crystallinity. The Tm for commercial PVC (prepared at about 50-60°C) is found to be about 200°C.

(c) Crystallinity - Molecular aggregation

Polyvinyl chloride is not generally classified as a crystal-line polymer. Crystallinity and molecular aggregation are relatively low

GLASS TRANSITION TEMPERATURE AS A FUNCTION OF POLYMERIZATION TEMP.
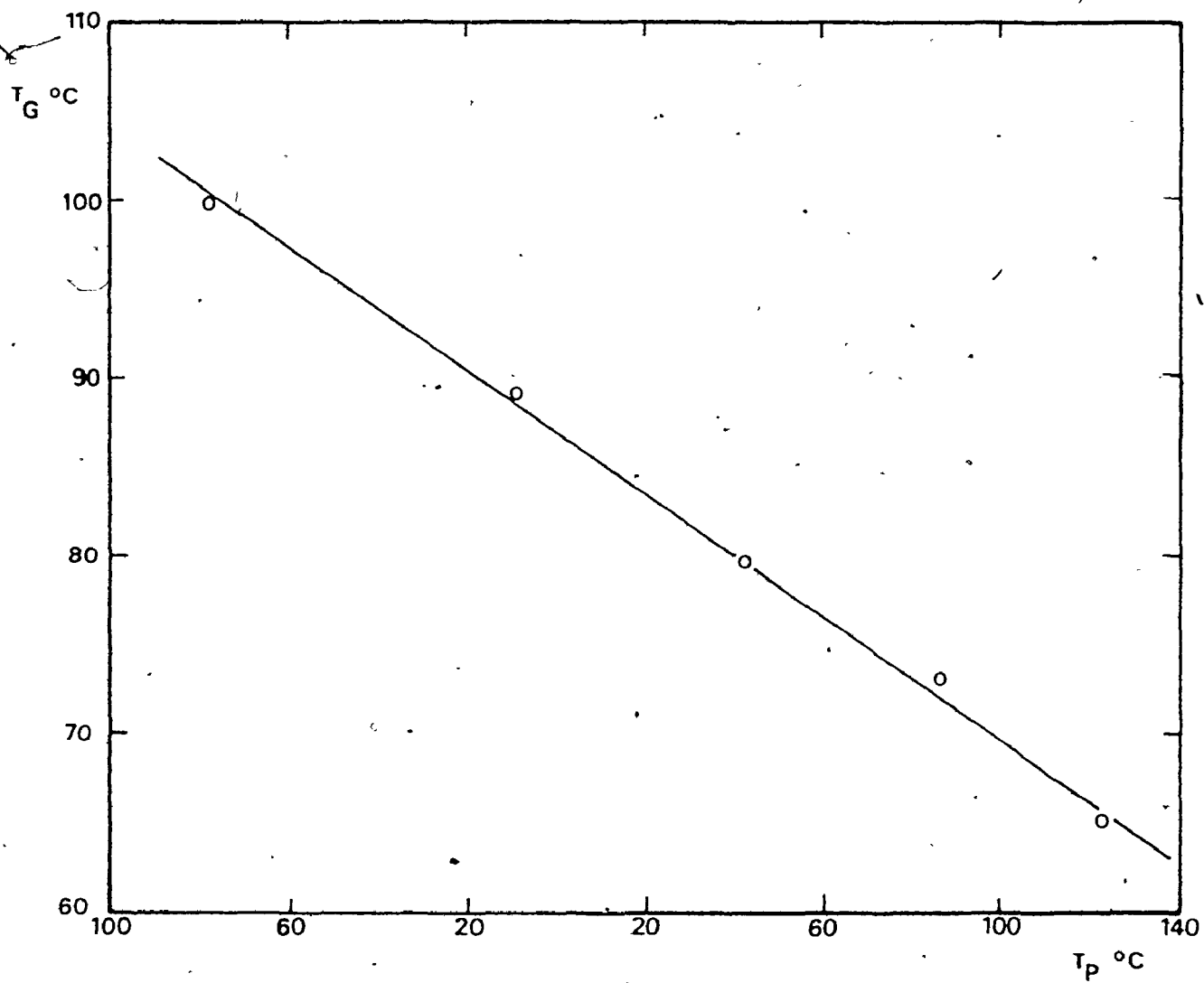
FIGURE 8

in commercial PVC polymers, but they both seem to influence the melt rheology and processing characteristics of the polymer, as well as the stability of the particles. They are both associated with the syndiotactic sequences, their length and the molecular weight. Crystal structure is typical of syndiotactic polymers with a repeat distance corresponding to four chain carbon atoms.

Commercial polymers produced at temperatures between 30 and 70°C have low degrees of crystallinity and aggregation. Crystallinity is between 5-15% and only weak molecular aggregates exist and range from 0% above 50°C to 10% at 30°C. Both crystallinity and aggregation increase rapidly below room temperature as shown in Table 5. If the reaction temperature is as low as -10°C, then 80% of the PVC produced is in the form of molecular aggregates and crystallinity increases to about 60%. Heating is the usual way to disintegrate the aggregates. Several studies show that aggregates persist in the rigid and plasticized melts affecting melt viscosity and extrusion characteristics.

(d) Polymer particle size

The shape, the size and particle substructure influence very significantly the utility of a polymer. Plasticizer absorption, bulk density, particle flow and melt rheology are some of the properties affected.

The particle size of the resin produced depends on the process type and conditions. The type and the amount of additives, as well as the degree and type of agitation, may modify the particle size produced.

TABLE 5

POLYMERIZATION TEMP. °C	SYNDIOTACTIC DIADS (FRACTION)	DEGREE OF BRANCHING ($CH_3/100$ CH_2)	WEAK AGGREGATES %	STRONG AGGREGATES %	CRYSTALLINITY % (X_c)
90	-	0.27	0	0	11.3
70	.17	-	0	0	-
60	.21	0.20	0	0	11.3
50	.24	0.20	0	0	13.2
45	-	-	1.2	0	-
40	.28	-	2.5	0	-
35	-	-.	3.9	0	-
30	.32	-	10.9	0	-
20	.36	0.15	-	0	15.0
-10	.50	-	64.3	14.2	-
-15	-	0.05	-	-	57.3
-30	.61	-	0	82.8	-
-50	.76	-	0	87.1	-
-75	-	0.0	-	-	84.2

PARTICLE SIZE DISTRIBUTION OF SUSPENSION AND BULK PVC
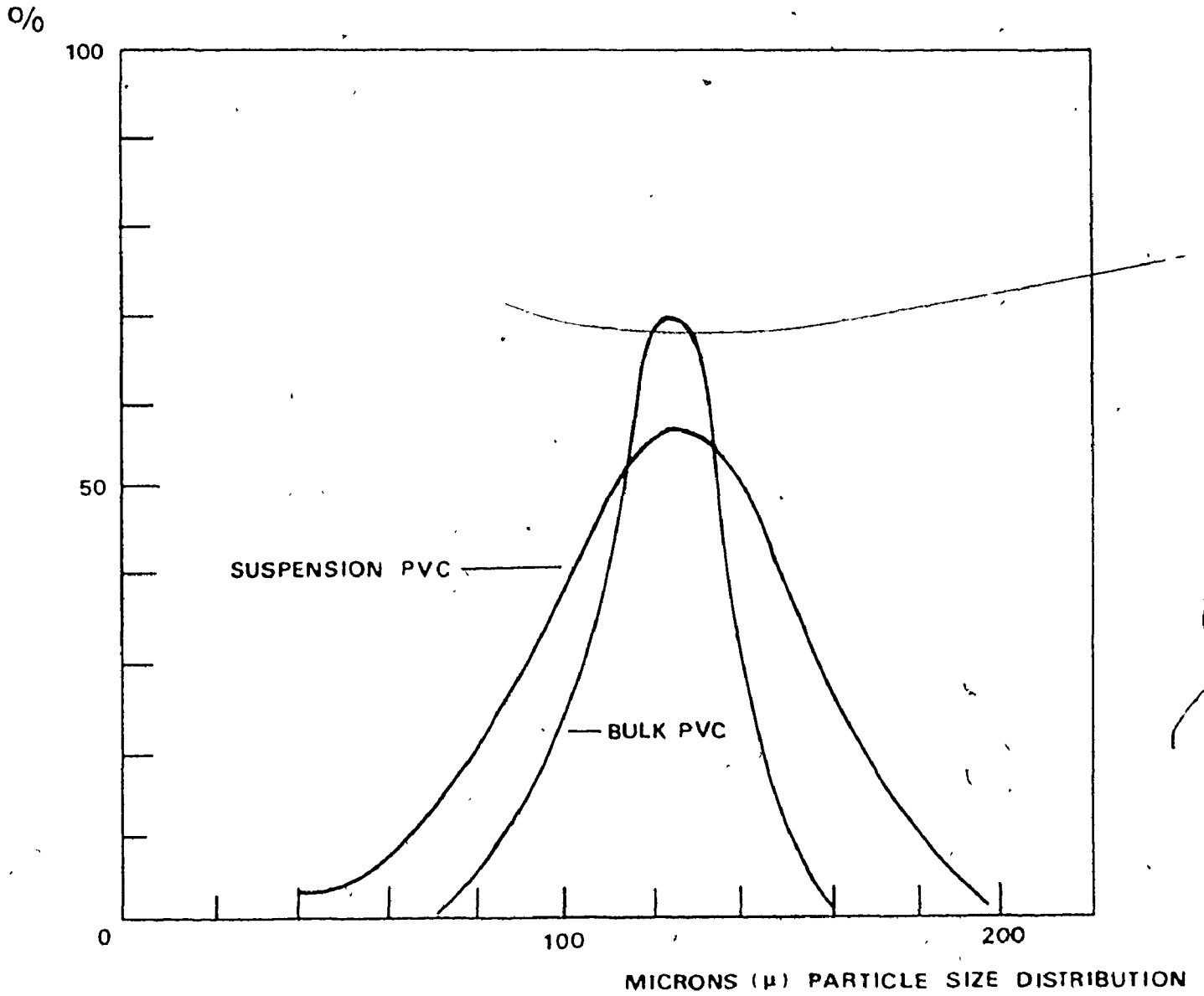
FIGURE 9

The particles produced from suspension PVC are usually 20 to 250 micron. They are characterized by highly spherical substructure particles 0.1 to 1.0 micron, and a pericellular skin apparently caused by the suspension agents.

The bulk PVC particles are similar in size to suspension PVC but are less spherical and have an open surface structure. Another characteristic is the narrower particle size distribution, as shown in Figure 9.

The emulsion particles range from 0.01 to 1.0 micron and they are usually quite dense compared to the suspension or bulk produced particles.

(e) Particle porosity

Another important factor in PVC polymer processing is the particle porosity. For plastisols we want the surface porosity to be low to reduce plasticizer absorption, but we want the internal porosity to be high so that it can rapidly absorb large amounts of plasticizer at the fusion temperature. Low porosity is also desirable for extrusions or injection molding. It facilitates extruder feeding and resin melting.

Generally the resins produced by the Rhône-Poulenc process have the highest porosity, suspension resins have somewhat lower porosities and emulsion resins have even lower.

For the determination of particle porosity two methods are used: mercury porosimetry (for the determination of total pore volume, and pore size) and gas absorption (B.E.T. method with nitrogen or argon) to deter-

mine the total surface area of the porous particles.

(f) Solubility and Theta solvents

We define a theta solvent as a solvent in which the dimensions of the molecular coils remain unperturbed by solvent effects. Benzyl alcohol at 155.4°C is the only reported theta solvent for PVC.

The solubility of PVC depends on molecular weight, molecular aggregation and crystallinity. In general, PVC is swollen by aromatic hydrocarbons but remains almost unaffected by alcohols or aliphatic hydrocarbons. Similar to other polymers, low molecular weight polymer is more soluble in the same solvent than high molecular weight polymers.

The most widely used complete solvents for PVC are tetrahydrofurane (THF) and cyclohexanone. Dimethylformamide is also an excellent solvent but affects polymer stability.

I.5 P.V.C. TECHNOLOGY

Since PVC is not a very stable polymer, to improve its quality and make it more useful for different applications, we have to add certain ingredients. There are several categories of additives, each one of them offering one or more useful properties to the final product. Plasticizers added to the hard brittle polymer convert it to soft, flexible material. Stabilizers offer extended life and good properties during and after thermal fabrication and outdoor exposure. Other additives for·special uses, e.g. fillers, colorants, together with the plasticizers and stabilizers, give to the final PVC product a very wide

range of properties and applications. The volume of literature
covering this subject is very large$^{(3, 20-33)}$.

I.5.1   Plasticizers

The most commonly used plasticizers are low molecular weight
solids or heavy non-volatile liquids which are able to solvate and
soften the polymer. They are divided into two classes based on their
compatibility with PVC. Primary plasticizers have good compatibility
and solvate PVC. Secondary plasticizers have limited solubility and
compatibility. There is no sharp dividing line between the two cate-
gories.

Another method of classification of plasticizers is by mole-
cular weight. Monomeric plasticizers have molecular weights usually
below 500; polymeric ones have molecular weights between 500 and 2,000.
Among the properties considered before selecting a particular plasti-
cizer are the cost, performance, volatility, flammability, compounding
ability and finally light and heat stability.

I.5.2   Stabilizers

It is well known that PVC degrades when exposed to various forms
of energy. The degradation is usually evidenced by the evolution of
hydrogen chloride. Chemical compounds which are capable of reacting
with and neutralizing this hydrogen chloride split off by the polymer
are called Stabilizers. They are usually classified according to their
chemical structure. A pattern of usage of PVC polymers in different
applications is given in Tables 6 and 7.

TABLE 6

U.S. CONSUMPTION OF PVC RESIN IN 1974[8]

A) MAJOR END-USE CATEGORIES

	METRIC TONS
CONSTRUCTION	1,040,000
HOUSEHOLD USES	290,000
PACKAGING	145,000
ELECTRICAL USES	186,000
CONSUMER GOODS	236,000
TRANSPORTATION	118,000
MISCELLANEOUS	91,000
EXPORT	68,000

TABLE 7

U.S. CONSUMPTION OF PVC RESIN IN 1974[8]

B) BY FABRICATION PROCESS AND PRODUCT LINE

		METRIC TONS
1)	EXTRUSION -	
	RIGID PIPE AND TUBING	505,000
	WIRE AND CABLE	164,000
	FILM AND SHOOTING	101,000
	OTHER	185,000
	TOTAL	955,000
2)	CALENDERING	
	FILM AND SHOOTING	248,000
	FLOORING	88,000
	TEXTILE	39,000
	TOTAL	375,000
3)	DISPERSION	
	PLASTISOL FORMULATING AND MOLDING	71,000
	TEXTILE AND PAPER COATING	86,000
	FLOORING	67,000
	TOTAL	224,000
4)	MOLDING	
	COMPRESSION (PHONOGRAPH RECORDS)	68,000
	INJECTION	105,000
	BLOW	35,000
	TOTAL	208,000
5)	SOLUTIONS	68,000
6)	ALL OTHER	131,000

I.6 COPOLYMERS OF PVC

The PVC homopolymer has limited properties. These properties may be modified and improved by copolymerization. Vinyl chloride co-polymerizes readily with a number of commercial monomers. The final copolymers have better processibility, adhesion (especially to metal), impact strength, stability, etc.

The reactivity ratios of common comonomers are given in Table 8.

TABLE 8

REACTIVITY RATIOS FOR COMMON VCM-COMONOMERS[8] .

Monomer	r_1	r_2	T°C	Composition WT.%
VA_c	7.8	0:6	40	0.30
VCl_2	0.3	3.2	60	0.15
Propylene	2.27	0.3	60	0.50
Acrylonitrile	0.074	3.7	50	
Maleic Anh.	0.296	0..008	75	
Ethylene	7.85	0:2	70	
Ethylene	3.6	0.24	90	

The most important comonomer is vinyl acetate. These copolymers usually contain 2 - 20% vinyl acetate. This increases the softness

giving better processibility and also better adhesion, solubility and impact strength. A disadvantage is the lower stability. To impart increased adhesion to metals, sometimes maleic anhydride is incorporated.

For vinyl acetate copolymers the composition spread is not great, except for high conversions. So the polymer can safely be produced by normal batch operation with conversions below 80%. Applications are mainly plastic sheets and phonograph records.

Vinylidene chloride is the second most common comonomer. In the 5-20% concentration range, it allows better processing at lower temperatures. Here, due to the wide composition spread, a semibatch operation is required in order to maintain the composition within a reasonable narrow margin.

Propylene copolymers have the advantage of increased stability, especially at the lower fabrication temperatures where they can be used. The scrap can be recycled more easily than the homopolymer, so it is recommended for blown bottles and similar applications.

PART II.   REACTION KINETICS

II.1 THEORY OF HOMOGENEOUS BULK POLYMERIZATION[24]

Before we study the heterogeneous free radical polymerization of VCM we find useful a brief discussion of the chemistry of the homogeneous reaction. We will place particular emphasis on reaction steps which influence the rate of reaction and molecular weight distribution. One basic assumption that we make here is that kinetic rate constants associated with live or dead polymer chains, are independent of chain length.

Reaction steps

II.1.1 Initiation

The only interesting form of initiation for PVC is chemical initiation. The other two major types of free radical initiation, thermal and radiation, are of no interest for the PVC, therefore they will not be discussed

Chemical initiation in its simplest form involves the decomposition of an unstable species into two free radicals which can immediately react with monomer to begin the propagation of a polymer chain. A simplified scheme of the reactions taking place is given below:

$$I \xrightarrow{\;k_d\;} 2R_C^{\bullet} \qquad\qquad \text{(II-1)}$$

$$R_C^{\bullet} + M \xrightarrow{\;k_{pc}\;} R_1^{\bullet} \qquad\qquad \text{(II-2)}$$

$$R_1^{\bullet} + M \xrightarrow{\;k_p\;} R_2^{\bullet} \qquad\qquad \text{(II-3)}$$
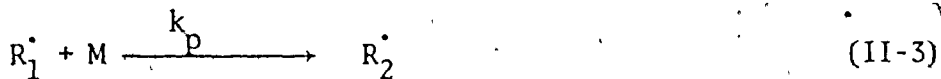
where I represents the initiator, R_C the primary radical, M the monomer, R_1, R_2 propagating radicals containing 1 and 2 monomer units respectively. k_p is the propagation rate constant and k_{pc} is the rate constant for the indicated reaction.

For the initiator I we assume a first order decomposition, so we have:

$$I = I_o e^{-k_d t} \qquad (II-4)$$

where I_o is the initial initiator concentration and k_d is the decomposition rate constant.

Initiators are usually compounds with bond dissociation energies in the range 25-40 kcal/gmol , and it is only a small number of categories of organic compounds (those with O-O, S-S, N-O bonds), that satisfy this requirement. Mainly organic peroxides and azo-compounds are used for commercial applications.

The choice of a specific initiator depends upon its reactivity at the polymerization temperature. Since, as we will see later, the molecular weight development and hence the quality of the polymer depend almost exclusively on the reaction temperature, we usually select an initiator which is most effective at the desired reaction temperature. The reactivity of the initiator is also expressed in terms of the initiator half life, $t_{\frac{1}{2}}$, defined as

$$t_{\frac{1}{2}} = \frac{\ln 2}{k_d} \qquad (II-5)$$

Half lives are very dependent on temperature and for commercial poly-merizations are usually in the range up to 10 hours. We should keep in mind that the decomposition rate of an initiator can vary considerably from solvent to solvent and this, as we will see, leads to errors in the calculations of conversions and reaction rates.

Referring again to the initiation reactions, we now define the rate of initiation, R_I, as the rate of generation of propagation radicals including only one monomer unit, $R_1^{\cdot}$. So, from equation (II-2) we have:

$$R_I = k_{pc} R_C^{\cdot} M \qquad (II-6)$$

At the same time a balance over the primary radicals gives:

$$\frac{1}{V} \frac{dN_C^{\cdot}}{dt} = 2k_d I - k_{pc} R_G^{\cdot} M \qquad (II-7)$$

where   V - total volume of reaction mixture

$N_C^{\cdot}$ - total moles of primary radicals.

Now by applying the Stationary State Hypothesis (SSH), i.e. by assuming that there is an equilibrium state between the generation and consumption rate of the primary radicals, we see that $N_C^{\cdot}$ should remain constant, so $dN_C^{\cdot}/dt = 0$, and equation (II-7) becomes:

$$\frac{1}{V} \frac{dN_C^{\cdot}}{dt} = 2k_d I - k_{pc} R_C^{\cdot} M = 0$$

$$\therefore \quad k_{pc} R_C^{\cdot} M = 2k_d I \qquad (II-8)$$

and substituting (II-8) back into (II-6) we obtain

$$R_I = 2k_d I \qquad (II-9)$$

To account for the initiator efficiency, we now introduce f, the initiator efficiency factor. So equation (II-9) becomes

$$R_I = 2fk_dI \qquad (II-10)$$

And substituting for I from equation (ii-4) we have:

$$R_I = 2fk_dI_oe^{(-k_dt)} \qquad (II-11)$$

The efficiency factor f represents an empirical coefficient between 0 and 1. We usually observe f to fall with increasing reaction temperatures, and conversions from monomer to polymer.

Often, for commercial applications, we use multiple initiator systems. For example, a "fast" initiator to accelerate the heat up of a batch of monomer and a slow one to complete the reaction up to high conversions. Another feature of the multiple-initiator systems is that they may be used to reduce the batch time. This subject will be investigated more completely later in this study. Assuming additivity of the initiation rates, the total rate is given by:

$$R_I = 2\sum_{i=1}^{N} f_i k_{di} I_i \qquad (II-12)$$

where N is the number of initiators.

II.1.2 Propagation

When a propagating free radical reacts with a monomer unit, this leads to the growth of a live polymer chain:

$$R_r^{\bullet} + M \xrightarrow{\quad k_p \quad} R_{r+1}^{\bullet} \qquad (II\text{-}13)$$
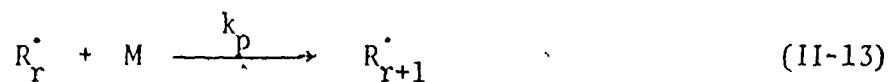
where $R_r^{\bullet}$: is a polymer radical containing r monomer units

M : is a monomer molecule

k_p : is the propagation rate constant

The average life of a polymer radical is of the order of 0.1 to 1 second. The average chain length may be as large as 10^6 monomer units.

Propagation reactions are the ones responsible for the development of the microstructure of the polymer chain. As pointed out before, the existence of a substituted carbon atom gives rise to three different ways of addition (head to tail - head to head - tail to tail) of a new monomer unit during propagation (see also PVC microproperties). The propagation rate constant, k_p, usually has a low activation energy, (of the order of 5-6 kcal/gmol), therefore it shows little variation with temperature.

Among the important features of all chain polymerizations is high exothermic heat of reaction, and the principal reactions responsible for the heat of polymerization are the propagation reactions. For Vinyl Chloride it has been found that the heat of reaction $-\Delta H_p$ is 23.0 kcal/ gmol.

II.1.3 Chain Transfer

During a free radical polymerization reaction, transfer reactions may take place between the growing polymer chains and the monomer, the initiator, the solvent if any, or the polymer. These reactions may be represented as follows:

$$R_r^{\cdot} + M \xrightarrow{k_{f_m}} P_r + M^{\cdot} \qquad \text{(Monomer)}$$

$$R_r^{\cdot} + I \xrightarrow{k_{f_I}} P_r + I^{\cdot} \qquad \text{(initiator)}$$

$$R_r^{\cdot} + S \xrightarrow{k_{f_s}} P_r + S^{\cdot} \qquad \text{(solvent)}$$

$$R_r^{\cdot} + P_s \xrightarrow{k_{f_p}} P_r + R_s^{\cdot} \qquad \text{(polymer)}$$
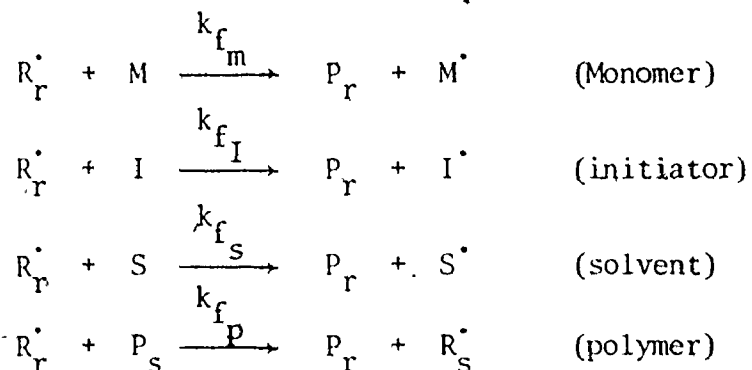
The above transfer functions, except the transfer to polymer, tend to shift the molecular weight distribution (MWD) to lower molecular weights. Transfer to polymer may produce branched polymer. This will not change the total number of polymer molecules and therefore the number average molecular weight will not change. However, since transfer to polymer shifts the MWD to higher molecular weights, we should expect a dramatic increase of the weight average molecular weight, giving rise to a large increase in polydispersity.

More specifically now, in the case of Vinyl Chloride, it has been established that the dominant transfer reaction is the transfer to monomer. [40]

II.1.4 Termination

Termination can occur either by combination:

$$R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{t_c}} P_{r+s}$$
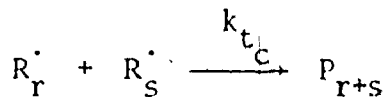
or by disproportionation in which a hydrogen atom is transferred from one polymer chain to the other:

$$- CH_2 - CHX^{\cdot} + {}^{\cdot}CHX - CH_2 - \xrightarrow{k_{t_d}} CH_2 - CH_2X + XHC = CH -$$
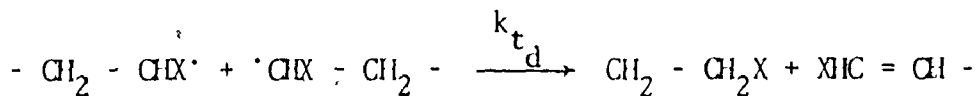
where k_{t_c} and k_{t_d} are termination rate constants. Typical values of k_t's are in the range $10^6 - 10^8$ liter/(gmol)(sec). Even though both termination reactions can occur simultaneously, in the case of Vinyl Chloride termination is exclusively by disproportionation.

It should be emphasized that termination reactions are responsible for the exclusive consumption of radicals. It may be shown that the change in the total radical concentration $[R^{\cdot}]$ is given by:

$$\frac{dR^{\cdot}}{dt} = R_I - k_{t_d}[R^{\cdot}]^2$$

By applying again the Stationary State Hypothesis:

$$R_I - k_{t_d}[R^{\cdot}]^2 = 0$$

$$\therefore \quad R^{\cdot} = (\frac{R_I}{k_{t_d}})^{\frac{1}{2}} \qquad\qquad (II-14)$$

This is an expression for the total radical concentration that we will use to develop the rate equation.

II.1.5 Development of Rate Equation

According to chemical equation (II-13) the polymerization rate R_p is given by:

$$R_p = k_p \, M \, R^\cdot$$

and by substituting for $R^\cdot$ from (II-14) we have:

$$R_p = k_p \, M \left(\frac{R_I}{k_{t_d}} \right)^{\frac{1}{2}} \tag{II-15}$$

Equation (II-15) is the expression for the rate of polymerization of an homogeneous system with chemical initiation and termination by disproportionation. This equation may be solved analytically for some special cases or numerically.

II.2 LITERATURE REVIEW

The first attempts to polymerize vinyl chloride in sealed tubes were made in 1872 by Baumann[25]. Further studies were done in 1912 by Ostromisleysky[26], who initiated the reaction by sunlight, and by Klatte and Rollett[27] in 1917, who obtained a patent to use peroxides rather than sunlight to initiate the reaction. In 1922 Plausen[28] produced PVC directly from dry acetylene and hydrogen chloride under pressure at 150° - 200°C. Since then many other workers have studied experimentally the polymerization of vinyl chloride. Talamini and Peggion[29] give a review of these works.

Some of the most important mathematical models proposed after

1950 are discussed below.

II.2.1 <u>Bengough and Norrish (1950)</u>[30]

These workers observed a period of acceleration (over the first 40% of conversion) and they noticed that the increase in the rate of polymerization is proportional to the polymer concentration to the power two thirds. Accordingly they postulated that the trapping of the free radicals in the polymer particles is primarily due to chain transfer between growing polymer chains and dead polymer molecules which produce free radicals in the surface of the dead polymer, and constitute stabilized centers of polymer growth. They also proposed that the reaction rate had an initiator dependence of $I^{\frac{1}{2}}$.

Assuming equal monomer concentrations [M] in both monomer and polymer phases, they derived the following rate expression:

$$-\frac{d[M]}{dt} = (k_p + k_{f_m})(\frac{fk_d}{k_t})^{\frac{1}{2}} \left[[M] + \frac{k_{f_p}}{k_{f_m}} K'[P]^{2/3} \right] [I]^{\frac{1}{2}}$$

This model fits experimental data only up to small conversions. The main disadvantage of this model is that it assumes significant transfer to polymer. This would automatically lead to significant branching, but the latter has been proven to be not valid for PVC.

II.2.2 <u>Schindler and Breitenbach (1955)</u>[31]

These workers proposed a model in which they postulate that precipitated polymer particles are swollen by the monomer and that the growing radicals arise inside them by both initiation in the polymer

phase as well as by diffusion of radicals from the liquid monomer phase. The rate acceleration is due to a decrease in the termination rate. The rate constant k_t was assumed to decrease with conversion in the following empirical form:

$$k_t = \frac{k_{t_o}}{1 + ax}$$

where k_{t_o} is the value of k_t at zero conversion, x is the conversion and a is an adjustable parameter.

By assuming (i) that the propagation rates in the monomer phase, in the polymer phase and of monomeric radicals are the same, and (ii) that the rate constants for chain transfer to monomer are the same for both phases, they arrived at the following expressions for the conversion x:

$$x = k_p \frac{[M]}{[M]_o} \left(\frac{fk_d\,[I]}{k_t}\right)^{\frac{1}{2}} \left[1 + \frac{a}{4} k_p[M]\left(\frac{fk_d\,[I]}{k_t}\right)^{\frac{1}{2}} t\right] t$$

where $[M]_o$ is the initial monomer concentration and $[I]$ is the initiator concentration.

This clearly shows that the degree of conversion in the initial stages is proportional to the 1/2 power of the initiator concentration, but in the later stages it becomes proportional to $[M]^2$ and to $[I]$. Thus the degree of conversion consists of two terms, one of which is characteristic of homogeneous polymerization and gives rise to 1/2 order in initiator level, and the second depends on the first power of the initiator concentration and may be ascribed to the heterogeneous

polymerization.

Finally they conclude that the overall reaction order is between 0.5 and 1 depending on the relative importance of the two terms.

They show experimentally that at short reaction times the reaction rate depends on the initiator concentration to the 1/2 power but they do not include any molecular weight calculations.

II.2.3 Magat (1955)[32]

Magat tried to apply the usual kinetic scheme (initiation-propagation-mutual termination), by assuming that the quasi-steady state hypothesis cannot be applied because the termination rate constants are very low. He also assumes that there are no transfer reactions to the monomer or polymer. This leads to a very simple mechanism. By integrating the resulting system of the differential equations, he obtained the following expression for the degree of conversion x:

$$ x = \frac{k_p}{k_t} \, \ell n \, \{\cosh[fk_d[I] \cdot t^2]^{\frac{1}{2}}\} $$

This model fits experimental data up to 20-30% conversions. It also ignores transfer reactions to monomer which, as has been shown, are very significant for the molecular weight development.

II.2.4 Mickley, Michaels and Moore (1962)[33]

These workers studied the polymerization of PVC in the presence

of a solvent as well as in bulk. They assume no termination in the polymer particles.

By applying the steady state hypothesis they arrived at an expression for the rate similar to the one given by Schindler and Breitenbach. This expression is as follows:

$$R_p = K M I^{\frac{1}{2}} + f(P) \cdot I^{\frac{1}{2}}$$

They claim that the first term is the contribution of the homogeneous polymerization, with heterogeneous polymerization represented by the second term. They also observe that $f(P)$ is proportional to the polymer concentration P at low conversions and to $P^{\frac{2}{3}}$ at high conversions. (The latter observation is in agreement with the work of Bengough and Norrish).

The main features of the mechanism proposed by these authors include, (a) normal liquid phase kinetics, (b) radical occlusion by coalescence, (c) shallow penetration of radical activity into particles, (d) negligible mutual termination in the particles, (e) escape of trapped radical activity by monomer transfer, and (f) limitation of short chain radical escape by propagation and transfer to monomer.

Such a model, because it contains a large number of parameters, is difficult and complicated to use. It assumes no termination in the polymer particles, it fits data only up to moderate conversions and does not attempt to predict any molecular weights.

II.2.5 Cotman, Gonzalez and Claver (1967)[34]

These workers studied bulk polymerization techniques as well as particle properties. According to them, the nature of precipitated PVC changes with conversion. At the onset of the reaction, particles insoluble in monomer are produced. At very low conversions ($<1\%$) they grow into agglomerate units which grow further in size by deposition of additional particles. Polymerization is characterized by autoaccelerated rates due to progressive reduction in termination rate. The decrease in k_t is due to a decreased mobility of the free radical produced by chain transfer reactions.

. . At very low conversions they observed a decrease in the polymerization rate before the autoacceleration starts. This is explained by rapid particle coalescence which reduces the surface area and increases the termination rate. Also the authors indicate that the assumption of a "quasi steady state" and the use of single valued rate constants is not valid.

II.2.6 Talamini et al (1968)[35]

This model proposed by Talamini et al. is rather interesting because chronologically it was the first to predict successfully conversions up to approximately 70%. It states that the polymerization reaction takes place in two phases practically from the onset of the reaction. With increasing conversion the amount of the dilute phase decreases, while that of the concentrated phase increases. It is

assumed that both phases have constant composition in the whole range of their coexistence. The termination rate is assumed to be lower in the polymer phase due to high viscosity (gel effect). Accordingly the reaction rate is higher.

Assuming that phase separation occurs at zero conversion, we can express the overall reaction rate as the sum of the specific polymerization rate in the dilute (monomer) and concentrated (polymer) phase:

$$- \frac{dM}{dt} = R_M M_M + R_P M_P$$

$$\therefore \quad W_o \frac{dx}{dt} = R_M (W_o - xW_o - AxW_o) + Ax\, W_o R_P$$

$$\therefore \quad \frac{dx}{dt} = R_M (1 - x - Ax) + Ax\, R_P \qquad (II-16)$$

where W_o = weight of initial monomer

R = polymerization rate

x = degree of conversion

A = monomer to polymer ratio in the polymer phase

M,P . refer to the monomer and polymer phase respectively.

By assuming that the ratio R_P/R_M is constant and equal to Q, then:

$$R_P = Q \cdot R_M \quad \text{and}$$

$$\therefore \quad \frac{dx}{dt} = (1 + qx) R_M \qquad (q=1-x-Ax+QAx) \qquad (II-17)$$

Integrating (II-17) with x = 0 at t = 0

$$\therefore \quad x = \frac{1}{q} [\exp (q\, R_M\, t) - 1] \qquad (II-18)$$

where R_M is given from the classical theory of homopolymerization as:

$$R_M = k_p \left(\frac{f k_d}{k_t} \right)^{\frac{1}{2}} \cdot [I]^{\frac{1}{2}} = K[I]^{\frac{1}{2}}$$

where k_p = propagation rate constant

f = efficiency factor of the in tiator

k_d = decomposition rate constant of the initiator

k_t = termination rate constant

$[I]$ = concentration of the initiator

By expanding the exponential term of equation (II-18) in series:

$$x = \frac{1}{q} \sum_{m=1}^{\infty} \frac{(qk)^n}{n!} [I]^{n/2} t^n$$

This equation predicts conversion versus time data up to about 70% conversion, but the model does not include a prediction of molecular weights.

II.2.7 Ugelstad et al. (1971-1973)[36, 37].

The model proposed by these workers is similar to the one proposed by Mickley et al. and the Talamini model.

It also assumes a two phase system, a polymer phase consisting of polymer particles swollen with monomer and a liquid phase consisting of practically pure monomer. This model overemphasizes the transport of radicals to and from the polymer particles. The advantage of this model is mainly that it takes into account that the polymer phase is subdivided in discrete polymer particles growing with time and conversion. This may lead in the future to the derivation of mathematical techniques to

derive, starting with the same fundamental equations, the theoretical expressions for the particle size distributions. The latter has not been done and will be extremely useful for practical applications.

By assuming quasi steady state conditions, then the equations for the number of moles of radicals in the two phases may be expressed as:

$$\rho_L - k_a [R^\cdot]_L + k_{d_c} [R^\cdot]_p - 2k_{t_L} [R^\cdot]_L^2 V_L = 0 \qquad \text{(II-19)}$$

$$\rho_p + k_a [R^\cdot]_L - k_{d_c}[R^\cdot]_p - 2k_{t_p}[R^\cdot]_p^2 V_p = 0 \qquad \text{(II-20)}$$

where ρ = the rate of radical formation

$[R^\cdot]$ = the radical concentrations

V = volumes

k_t = termination constants

k_a = rate constant for the absorption of radicals into the particles

k_{d_c} = rate constant for the desorption of radicals from the particles.

The values of k_a and k_{d_c} are given in (37) as follows:

$$k_a = 4\pi D_L \cdot N \cdot r \qquad \text{and} \qquad k_d = 4\pi D_p \cdot \frac{r}{NV^2}$$

where N is the total number of polymer particles

D_L = the diffusion coefficient of radicals being absorbed

D_p = the effective diffusion coefficient for radical escape from particles.

r = the polymer particle radius

V = the polymer particle volume.

It may be further assumed that if the terms $k_a[R^\cdot]_L$ and $k_{d_c}[R^\cdot]_p$ are dominating, then one may approximately assume an equilibrium distribution of radicals between the two phases.

$$[R^\cdot]_p = \frac{k_a}{k_{d_c}} \cdot [R^\cdot]_L = Q [R^\cdot]_L \quad \text{where } Q = \text{const.} \quad \text{(II-21)}$$

By adding equations (II-19) and (II-20) we obtain

$$\rho - 2k_{t_L} [R^\cdot]_L^2 V_L - 2k_{t_p} [R^\cdot]_L^2 V_p = 0 \qquad \text{(II-22)}$$

where ρ is the total rate of formation of radicals $= 2k_d[I]$

From equations (II-21) and (II-22) solving for $[R^\cdot]_L$ one obtains:

$$[R^\cdot]_L = \left(\frac{k_d[I]}{V_L k_{t_L} + V_p k_{t_p} Q^2}\right)^{\frac{1}{2}} \qquad \text{(II-23)}$$

The rate of reaction is:

$$-\frac{dM}{dt} = k_p \left([R^\cdot]_L M_L + [R^\cdot]_p M_p \right) \qquad \text{(II-24)}$$

where M_L and M_p are the number of monomer moles in the liquid and polymer phase respectively.

Substituting equation (II-23) into (II-24) and expressing the rates in conversion units, one finally gets:

$$\frac{dx}{dt} = \left(\frac{k_d[I]}{V_L k_{t_L} + V_p k_{t_p} Q^2}\right)^{\frac{1}{2}} k_p (1-x-Ax+QAx)$$

where Λ is the monomer to polymer weight ratio in the polymer phase equal to 0.47 at 50°C.

By using values for k_d and k_p given in the literature, they had to estimate three parameters, k_{t_L}, k_{t_p}, Q. The values of these parameters which fitted the experimental results were obtained by a non linear curve fitting procedure. The model fits the experimental data up to 70-75% conversions but there is no information how the model behaves at high conversions. Ugelstad's model also does not deal with molecular weight calculations.

II.2.8 O.F. Olaj (1975) [38]

O.F. Olaj et al. have developed a model according to which the instantaneous rate of change of conversion $\frac{dx}{dt}$ is given by:

$$\frac{dx}{dt} = const. + K \sqrt{x}$$

where K is a kinetic constant depending on the reaction temperature and the initial level of initiator.

The model seems to be oversimplified and has been tested for a narrow temperature range (about 50°C), and for conversions not exceeding 60%. An additional disadvantage of the model is that it does not include any molecular weight calculations. In general we may say that the model is very restricted and useful only for a narrow range of conditions..

II. 3. THE PRESENT MODEL

II. 3. 1. Abdel Alim's Model

The model used in the present study was developed by Abdel Alim and Hamielec[40], is similar to Ugelstad's model and may be considered as a modification of Talamini's model.

Like the previous models, it also assumes that polymerization takes place in two phases, the monomer and the polymer rich phase. Both phases are in equilibrium. In such a system, the polymer produced being insoluble in its own monomer, precipitates out of the continuous monomer phase. As reaction proceeds, the mass of polymer rich phase grows while the monomer rich phase diminishes. Experimental evidence indicates that the existence of the two phase heterogeneous system begins after less than 1% conversion, (practically from the onset of the reaction), and lasts until about 70-80% conversion depending on the temperature.

The main features of the present model are:

1. It predicts accurately conversions over the whole range from zero up to the limiting value.

2. It includes, for the first time, complete molecular weight calculations.

The basic assumptions made are the following:

(i) The monomer phase is assumed to be polymer free and the monomer concentration in the polymer phase is constant. Monomer and polymer phases coexist until the monomer phase disappears.

(ii) The termination rate constant in the polymer phase, because of increased viscosity (gel effect phenomena), is lower, giving rise to a higher reaction rate. It is also assumed that the ratio of the reaction rate in the polymer phase to the rate in the monomer phase is constant.

By calling the conversion at which the monomer phase disappears x_c we can further assume that below x_c the specific polymerization rates R_{P_M} and R_{P_P} (in the monomer and the polymer phases respectively) are independent of conversion provided that the reaction is isothermal. Then we can express the overall polymerization rate R_p as follows:

$$R_P = R_{P_M} V_M + R_{P_P} V_P \qquad\qquad (II\text{-}25)$$

where V_M = volume of monomer rich phase

V_P = volume of polymer rich phase.

It is easy to show that

$$V_M = \frac{1}{\rho_M} (1 - \frac{x}{x_c}) \qquad\qquad (II\text{-}26A)$$

$$V_P = \frac{1}{\rho_M} (\frac{x}{x_c} - x) + \frac{1}{\rho_P} \cdot x \qquad\qquad (II\text{-}26B)$$

and $\qquad V_{TOTAL} = V_T = V_M + V_P = V_{T_o} (1 - Bx)$

with $\qquad B = (1 - \frac{\rho_M}{\rho_P})$

where ρ_M = the density of the monomer

ρ_P = the density of the polymer

V_{T_o} = the volume of the unit mass of monomer $(= \frac{1}{\rho_M})$

A)   For $x < x_c$

If we take into account the variation of the volume of the reaction mixture with conversion, then eq. (I.I-4) becomes

$$I = I_o \frac{\exp(-k_d t)}{(1 - Bx)} \qquad (II-27)$$

Now we can express the specific polymerization rates as follows:

$$R_{P_M} = k_{P_M} M_M \left(\frac{R_{I_M}}{k_{t_M}} \right)^{\frac{1}{2}} \qquad (II-28)$$

$$R_{P_P} = k_{P_P} M_P \left(\frac{R_{I_P}}{k_{t_P}} \right)^{\frac{1}{2}} \qquad (II-29)$$

where subscripts M,P refer to the monomer and polymer phase respectively.

R_I is the initiation rate

M is the concentration of monomer

If M_o is the molecular weight of monomer, it is easy to show that:

$$M_M = \frac{\rho_M}{M_o}$$

$$M_P = \frac{\rho_M}{M_o} \left[(1 - x_c)/(1 - x_c + x_c \frac{\rho_M}{\rho_P}) \right]$$

We will now introduce two parameters of the system

$$\frac{k_{P_P}/k_{t_P}^{\frac{1}{2}}}{k_{P_M}/k_{t_M}^{\frac{1}{2}}} = P \qquad \text{and} \qquad \frac{I_{o_M}}{I_{o_P}} = P_K$$

Since the polymerization in the polymer phase might be diffusion

controlled we would expect the termination rate constant k_{tp} to be significantly smaller than k_{tM}. The result is a net increase of the reaction rate in the polymer phase. The difference between R_{P_M} and R_{P_P} is expressed by introducing the parameter P. We expect P to be a constant greater than unity.

The second parameter, P_K, is the partition coefficient of the initiator and is expressing the distribution of the initiator between the monomer and the polymer phase. So equation (II-29) becomes:

$$R_{P_P} = k_{P_M} M_M \left(\frac{R_{I_M}}{k_{tM}}\right)^{\frac{1}{2}} \cdot \frac{P}{P_K^{\frac{1}{2}}} \cdot \frac{(1 - x_c)}{(1 - x_c + x_c \frac{\rho_M}{\rho_P})}$$

$$= R_{P_M} \frac{P}{P_K^{\frac{1}{2}}} \frac{(1 - x_c)}{(1 - x_c + x_c \frac{\rho_M}{\rho_P})} \qquad (II\text{-}30)$$

Substituting (II-30), (II-28), (II-26A) and (II-26B) back into (II-25) we finally obtain the rate expression in terms of % conversion per unit time:

$$\frac{dx}{dt} = R_M \left[(1 - \frac{x}{x_c}) + \frac{P}{P_K^{\frac{1}{2}}} \frac{(1 - x_c)}{x_c} \cdot x \right]$$

$$\therefore \quad \frac{dx}{dt} = R_M (1 + Qx) \qquad (II\text{-}31)$$

with $$Q = \frac{\frac{P}{P_K^{\frac{1}{2}}}(1 - x_c) - 1}{x_c} \qquad (II\text{-}32)$$

and $\quad R_M = k_{P_M} \left(\dfrac{2f_{k_d} I_o}{k_{t_M}} \right)^{\frac{1}{2}} (1 - Bx)^{-\frac{1}{2}} \cdot \exp\left(-\dfrac{k_d t}{2} \right)$ $\qquad$ (II-33)

as given from the theory of the homogeneous free radical polymerization.

B) $\qquad$ For $x > x_c$

For conversions above x_c the monomer phase disappears and the polymer phase consists of polymer particles swollen with monomer. In such a case diffusion control in the polymer rich phase leads to much lower k_t values as the polymer concentration increases.

Abdel Alim and Hamielec[40] use an empirical expression to account for the gel effect by assuming that the constant

$$.k = k_{P_p} \left(\frac{2f_{k_d}}{k_{t_p}} \right)^{\frac{1}{2}} \propto (1 - x)$$

or more specifically:

$$k = \frac{P}{P_K^{\frac{1}{2}}} \cdot k_{P_M} \left(\frac{2f_{k_d}}{k_{t_m}} \right)^{\frac{1}{2}} \frac{(1 - x)}{(1 - x_c)}$$

and the final rate expression is:

$$\frac{dx}{dt} = R_M \cdot \frac{P(1 - x)^2}{P_K^{\frac{1}{2}} (1 - x_c)} \qquad (II\text{-}34)$$

where R_M is again given from (II-33).

Mixed Initiators

We have seen in the previous section that for nonisothermal polymerizations the rate equation may be expressed as follows:

$$\frac{dx}{dt} = k_P \left(\frac{R_I}{k_t} \right)^{\frac{1}{2}} (1 + Qx)(1 - Bx)^{-\frac{1}{2}} \tag{II-34}$$

In the case of mixed initiators, assuming additivity of the initiation rates we obtain the following expression:

$$R_I = 2 \sum_{i=1}^{N} f_i \, k_{d_i} \, I_{o_i} \, \exp(-k_{d_i} t) \tag{II-35}$$

where N is the number of initiators used. The above is valid only for isothermal conditions where K_{d_i} is constant.

Substituting (II-35) back into (II-34) we have:

$$\frac{dx}{dt} = \frac{k_p (1 + Qx)}{(k_t (1-Bx))^{\frac{1}{2}}} \cdot \left\{ 2 \sum_{i=1}^{N} f_i \, k_{d_i} \, I_{o_i} \, \exp(-k_{d_i} t) \right\}^{\frac{1}{2}}$$

or more generally:

$$\frac{dx}{dt} = G(x, T) \cdot F([I]_{o_i}, t, T) \tag{II-36}$$

where F is a function of time t, temperature T and initial concentration of each initiator, and G is a function of temperature T and conversion x.

For most practical applications it is desirable to obtain uniform heat generation rate. This leads to a better process control. On the other hand, the cooling system of the reactor may be designed to work

most of the time in its maximum capacity, in other words, more efficiently. The optimal policy is to remove heat at the maximum possible rate at all times. To obtain uniform heat generation rate, $\frac{dx}{dt}$ should be kept as constant as possible throughout the conversion range of interest (usually between 0-70%), i.e.

$$\frac{dx}{dt} = k \qquad (II-37)$$

The rate k is usually determined by the heat removal capacity of the cooling system and would typically lie in the range of 0.07 - 0.20 h^{-1}. From eq. (II-36) and (II-37) we obtain:

$$F(I_{o_i}, t, T) = \frac{k}{G(x,T)} \qquad (II-38)$$

Thus by specifying k and using a model for the polymerization which gives G(x,T) it is possible from eq. (II-38) to calculate values of F as a function of time. Subsequently, from the calculated F values, we can calculate the initial concentrations of the initiators that would give a constant rate of reaction.

As an example, let us consider the suspension polymerization of vinyl chloride. A model for the reaction has already been discussed and eq. (II-31) gives its final form. It is easy to see then in our case:

$$G(x,T) = \frac{k_p (1 + Qx)}{[k_t (1 - Bx)]^{\frac{1}{2}}} \qquad (II-39)$$

and for i initiators:

$$F(I_{o_i}, t, T) = [2f_1 k_{d_1} I_{o_1} \exp(-k_{d_1} t) + 2F_2 k_{d_2} I_{o_2} \exp(-k_{d_2} t)$$

$$+ \ldots + 2f_i k_{d_i} I_{o_i} \exp(-k_{d_i} t) \ldots]^{\frac{1}{2}} \qquad \text{(II-40)}$$

Finally, combining equations (II-38, II-39 and II-40) we obtain:

$$F^2(I_{o_i}, t, T) = 2 \sum f_i k_{d_i} I_{o_i} \exp(-k_{d_i} t) = \left(\frac{k}{G(x,T)}\right)^2$$

Figure 10 shows plots of $\left(\frac{1}{G(x,T)}\right)^2$ for a series of temperatures between 45 and 70°C.

· By specifying the value of k, it is possible by means of these plots to calculate the initial concentration of initiators which will give a constant reaction rate. The decomposition rate constants and the efficiency factors of the individual initiators must be known of course. Unfortunately, this is not always the case. For further illustration, consider the two initiators[42]: Acetylcyclohexylsulfonyl peroxide (ACSP) and Diisopropylperoxydicarbonate (IPP).

The parameter values for f and k_d were taken from the literature and, as we will see, may not be very accurate for a number of reasons. Suppose now that we want to carry out a polymerization at 50°C using these two initiators, such that the rate is constant and equal to:

$$\frac{dx}{dt} = k' = 11\%/h = 3.10^{-5} \text{ sec}^{-1}$$

with this rate it takes:

3,333 sec to obtain 10% conversion, and

16,667 sec to obtain 50% conversion.

Using Figure 10, we find the values of $\left(\frac{1}{G(x,T)}\right)^2$ for $x = 10\%$ and $x = 50\%$ at 50°C to obtain the following two equations:

$$2 \times 3.49 \cdot 10^{-5} I_{O_i} \exp(-3.49 \cdot 10^{-5} \times 3.333) + 2 \times 0.7 \times 4.2 \times 10^{-4} \cdot I_{O_2}$$

$$\exp(-4.2 \cdot 10^{-4} \cdot 3,333) = (3 \times 10^{-5})^2 \cdot 153 = 1.377 \times 10^{-7}$$

$$2 \times 3.49 \cdot 10^{-5} I_{O_1} \exp(-3.49 \cdot 10^{-5} \cdot 16,667) + 2 \times 0.7 \cdot 4.2 \cdot 10^{-4} I_{O_2}$$

$$\exp(-4.2 \cdot 10^{-4} \cdot 16,667) = (3 \times 10^{-5})^2 \times 22.03 = 1.987 \times 10^{-8}$$

Solving the system we obtain

$$I_{O_1} = 4.99 \times 10^{-4} \text{ gmol/1t}$$

$$I_{O_2} = 7.36 \times 10^{-4} \text{ gmol/1t}$$

A test run with these two initiator concentrations gave a poly-merization rate somewhat above the desired 11% per hour, indicating that the true parameter values were slightly different. However, the poly-merization rate was almost constant. By adjusting the initial concentrations to the following levels:

$$I_{O_1} = 3.35 \times 10^{-4} \text{ gmol/1t}$$

$$I_{O_2} = 7.83 \times 10^{-4} \text{ gmol/1t}$$

$(\frac{1}{G(x)})^2$ VERSUS CONVERSION CURVES
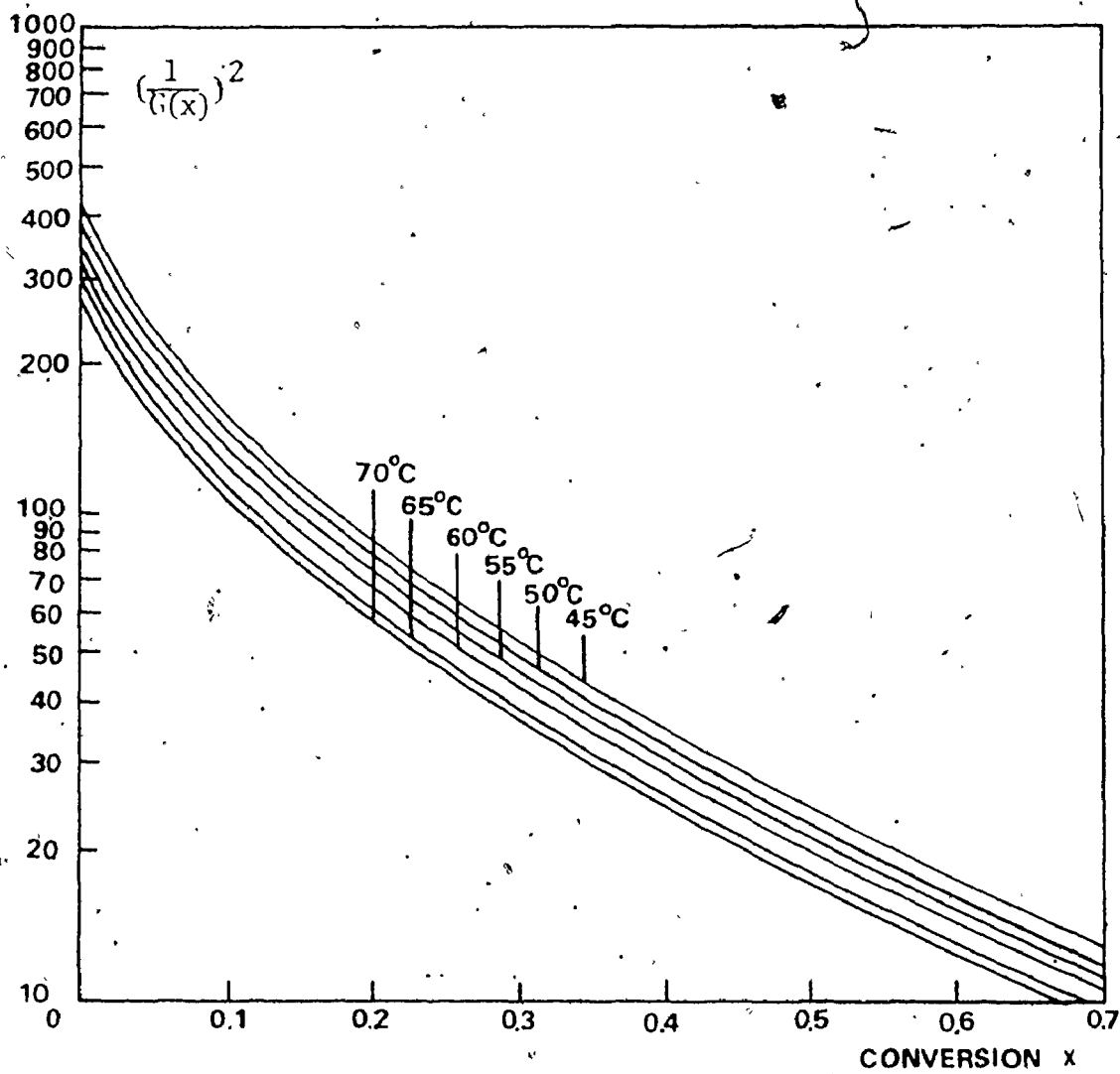
FIGURE 10

it was finally possible to obtain a polymerization with the desired rate. Figure 11 shows the experimental conversion history obtained using the corrected initiator concentrations.

CONVERSION VS. TIME DATA @ 50°C
(Multiple Initiator System)

Curve	Initiator	Concentration g/100 g VCl	Moles x 10	Time to 90% Conversion (Hrs.)
A	Acetyl Cyclo-hexylsulfonyl Peroxide	.0204	9.18	8.5
	Diisopropyl peroxydicarbonate	.0031	3.93	
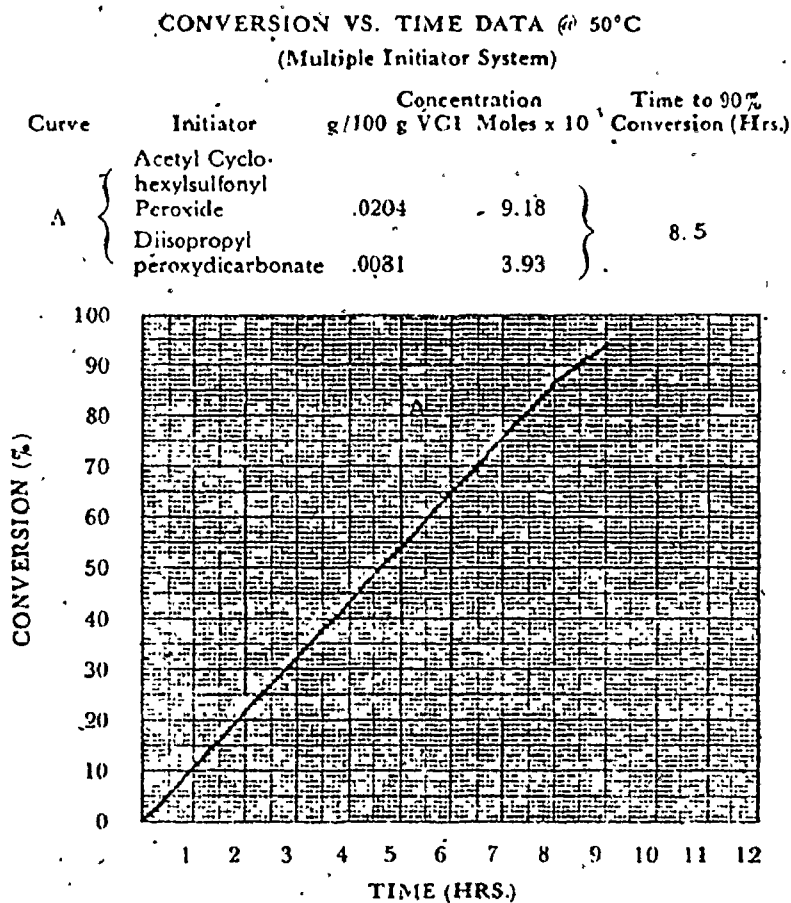
Figure: 11

It is seen that the correct initiator concentrations are not very different from the calculated values. Therefore we find this technique useful even if the parameter values for f and k_d are not known accurately.

Molecular Weight Development

In the bulk polymerization of vinyl chloride, it has been well established from previous studies that the dominant reaction in controlling the molecular weight is transfer to monomer. When we use initiators with high decomposition rate constants and when the initiation rates are high, then termination by disproportionation is not negligible. Since it may affect the molecular weight development it has to be taken into account.

To calculate the molecular weight distributions and the number and weight molecular weight averages $\bar{M}_W$ and $\bar{M}_N$, we use the following equations, as derived in reference (43):

$$\tau_p = C_M + \frac{k_{t_p} R_{p_p}}{k_p^2 M_p^2} \qquad \tau_M = C_M + \frac{k_{t_M} R_{p_M}}{k_p^2 M_M^2} \qquad (II\text{-}41)$$

where p refers to the polymer phase,

M refers to the monomer phase

k_t is the termination rate constant

k_p is the propagation rate constant

C_M is the ratio of k_{f_m}/k_p

k_{f_m} is the rate constant for the transfer to monomer reaction

Since for vinyl chloride we have no termination by combination, we may assume that the rate constant for termination by combination $k_{t_C} = 0$ and therefore parameter $\beta^{(43)}$ is equal to zero. The parameter β is defined as

follows:

$$\beta = \frac{k_{t_c} R_p^{\cdot}}{k_p^{2}[M]^2}$$

So, if $\beta = 0$, we obtain the following expression for the number and weight average chain lengths $\bar{r}_N$ and $\bar{r}_p$:

$$2 \bar{r}_{N_p} = \bar{r}_{W_p} = \frac{2}{\tau_p} \qquad 2 \bar{r}_{N_M} = \bar{r}_{W_M} = \frac{2}{\tau_M}$$

From the above expressions we would expect the polydispersity

$$PD = \frac{\bar{r}_{W_p}}{\bar{r}_{N_p}} = \frac{\bar{r}_{W_M}}{\bar{r}_{N_M}} = 2.0 \qquad (II-42)$$

Experimental evidence shows[40] that the actual values of PD are close to 2.0.

Now that we know the average chain lengths, we are able to find the instantaneous distributions, in this case equal to the most probable distributions:

$$W(r)_p = r \tau_p^{2} \exp (-\tau_p r)$$

and

$$W(r)_M = r \tau_M^{2} \cdot \exp (-\tau_M r)$$

By integrating the instantaneous distributions we obtain expressions for the cumulative molecular weight distributions. They are as follows:

$$\mathrm{cum}(\bar{r}_N) = x \cdot \left\{ \int_0^x \left[\left(\frac{R_{p_p} V_p}{R_{p_M} V_M + R_{p_p} V_p} \right) \frac{1}{\bar{r}_{N_p}} + \left(\frac{R_{p_M} V_M}{R_{p_M} V_p + R_{p_p} V_p} \right) \frac{1}{r_{N_M}} \right] dx \right\}^{-1} \quad \text{(II-43)}$$

$$\mathrm{cum}(\bar{r}_W) = \frac{1}{x} \int_0^x \left[\left(\frac{R_{p_p} V_p}{R_{p_M} V_M + R_{p_p} V_p} \right) \bar{r}_{W_p} + \left(\frac{R_{p_M} V_M}{R_{p_M} V_M + R_{p_p} V_p} \right) \bar{r}_{W_M} \right] dx \quad \text{(II-44)}$$

PART III.   EXPERIMENTAL RESULTS AND DISCUSSION

III.1 EXPERIMENTAL

III.1.1 Scope of Experiments

The scope of the experiments performed herein was to provide data which, together with Lucidol's data, would permit the characterization of five commercial initiators. They would also evaluate the applicability of Abdel Alim's model for isothermal polymerizations using multiple initiator systems and for nonisothermal polymerizations. This was to be done using ampoule reactors in batch mode.

III.1.2 Reagents

The Vinyl Chloride Monomer (VCM) used for our experiments was of commercial grade and was provided by Hooker Chemicals, Grand Island, N.Y. Table 1 gives a typical analysis of VCM similar to the grade we used. Chemical initiators were also provided by Hooker and made by Lucidol Division of Pennwalt Corporation. No further purification of monomer was done in this study.

III.1.3 Preliminary experiments.

The vinyl chloride monomer, (VCM), at room temperature is a toxic colourless gas. To keep it liquified, one has to use sealed ampoules under pressure. The pressures developed at the usual reaction temperatures (between 30 and 70°C) may go up to 180 psi, which is the vapour pressure of VCM at 70°C. Therefore, for reasons of safety we

decided to use 316 stainless steel ampoules, 1/4" diameter and approximately 4" long.

After several experiments and after the analysis of approximately 50 samples, it was concluded that the conversion-time histories obtained using the steel ampoules were not accurate. One of the reasons, observed in industry as well, is that the metallic surface of the ampoule acts as a catalyst for the decomposition of the initiator (usually organic peroxides). This gives rise to an unpredictable change in the initiator decomposition rate and hence the initiation rate. Since the polymerization rate R_p is proportional to the square root of the initiation rate, this means that a higher initiation rate would lead to a higher R_p, and finally higher than expected or predicted by the model conversions as a function of time.

Another problem is related to fouling on steel. As PVC is formed, it tends to deposit on the inner surface of the reactor. This tends to reduce the heat transfer coefficient of the system, thus giving rise to higher reaction temperatures and reaction rates. This is a well known problem in industry. To avoid deposits on the inner surface of the big commercial stirred tank reactors, the metallic surface is specially treated with chemicals.

Because of the above problems we decided to use glass ampoules. Glass is inert and PVC does not have the tendency to deposit on glass as it does on steel. Of course, even with glass ampoules, the diameter of

the ampoule is critical. Due to the poor thermal conductivity of PVC and due to the relatively high heat of polymerization (23.0 kcal/gmol), there is a temperature profile in the ampoule which is a function of its cylindrical radius R. Section III.1.4 deals with this problem.

III.1.4 The Heat Transfer Problem

Since the reaction mixture is homogeneous, we may assume, in a crude calculation, that we have no axial heat transfer. We also assume that the resistance of the glass wall is negligible. So under these two assumptions a heat balance may be expressed (in cylindrical coordinates):
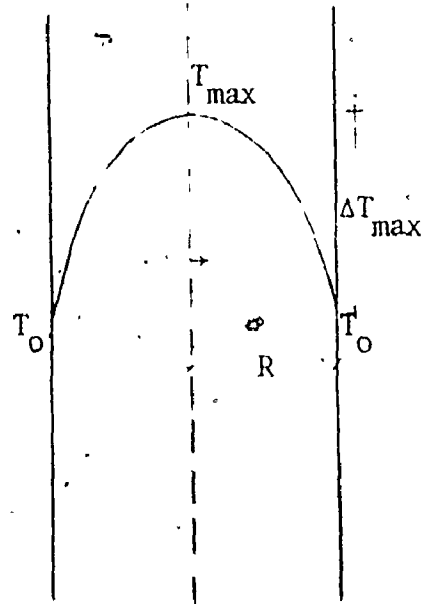
$$K \cdot \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r}\right) + \dot{Q} = 0 \qquad (III-1)$$

where $\dot{Q}$ is the heat generation rate per unit volume and unit time. So:

$$\dot{Q} = (\Delta H) \cdot \frac{dC}{dt} = (\Delta H) \cdot C_0 \frac{dx}{dt} \qquad (III-2)$$

To find now the maximum $\dot{Q}$, it is sufficient in our crude calculation to substitute $\frac{dx}{dt}$ with $\left(\frac{dx}{dt}\right)_{max}$ which in our case, as well as in industrial processes does not exceed 30% per hour (or $0.30 \ hr^{-1}$). So:

$$\dot{Q}_m = (\Delta H) \cdot C_0 \cdot \left(\frac{dx}{dt}\right)_{max} \qquad (III-3)$$

Now, to solve the differential equation, we integrate twice with boundary conditions:

$$r = 0 \quad \frac{dT}{dr} = 0 \qquad (BC.1)$$

$$r = R \quad T = T_0 \qquad (BC.2)$$

And the solution is:

$$T - T_0 = \frac{\dot{Q}_m}{4K} (R^2 - r^2)$$

This indicated a parabolic temperature profile. It is easy to show that the maximum temperature is at $r = 0$. So:

$$\Delta T_{max} = T_{max} - T_0 = \frac{\dot{Q}_m}{4K} R^2 \qquad (III-4)$$

If, for example, the maximum $(\frac{dx}{dt})$ is 20%/h = 0.2 h^{-1}, by substituting (III-3) into (III-4) we obtain:

$$\Delta T_{max} = 20 \ R^2 \ °C, \text{ where R is the ampoule radius in cm.}$$

If we allow ΔT_{max} to be not more than 1°C, we can see, from Figure 12, that we have to use ampoules with $R \leq 2.2$ mm.

For our experiments we decided to use glass ampoules with R = 1.5 mm because even at high reaction rates the $(\Delta T)_{max}$ does not exceed the limit of 1°C. The ampoules were 12" long and the wall thickness was approximately 0.3 mm.

ΔT ACROSS THE AMPOULE AS A FUNCTION OF RADIUS R
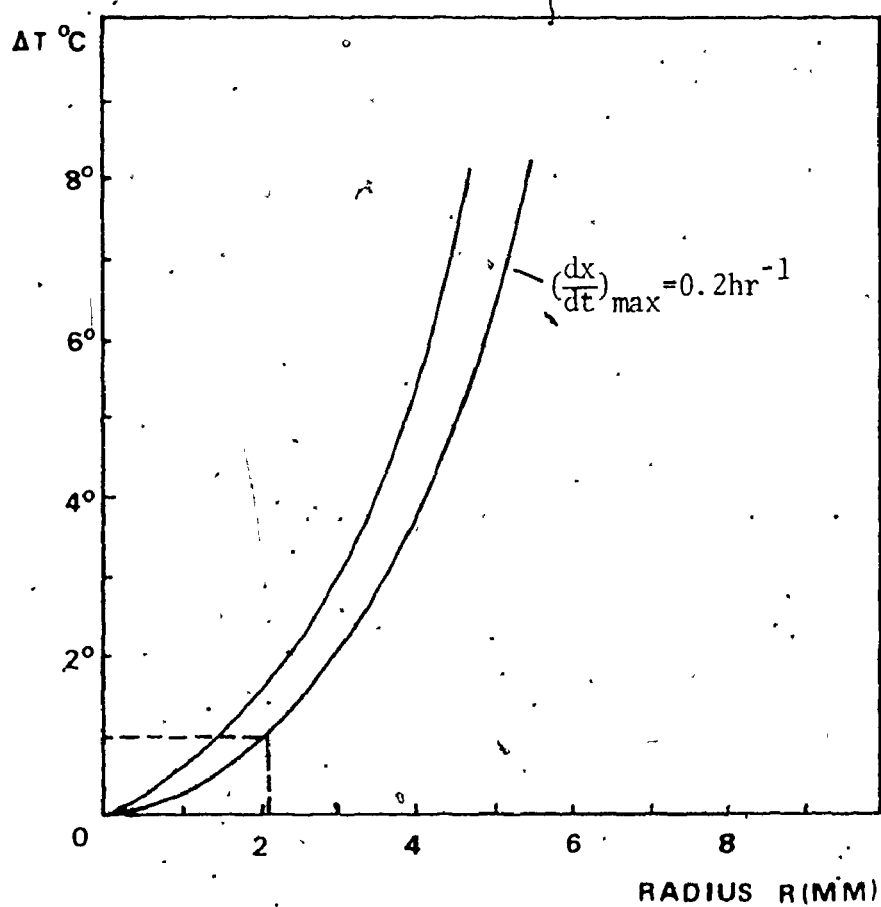

FIGURE 12

III.1.5 Experimental Procedure

Using 12" long glass ampoules we performed isothermal and non-isothermal experiments at different temperature levels.

The ampoules are first cleaned with methyl alcohol and carefully dried. They are then loaded with 10-15 mg of initiator and attached to the main vacuum line and carefully degassed. (Oxygen is known to be a strong inhibitor of the polymerization reaction). High vacuum, of the order of 10^{-6} mm Hg is obtained by using a vacuum and a diffusion pump connected in series (See Figure 13). Then the line is filled with nitrogen and evacuated again to ensure the absence of any traces of oxygen. Vinyl chloride gas is then allowed to enter the line and predetermined amounts of monomer are condensed in the ampoules cooled by liquid nitrogen. After they are filled, the ampoules are carefully sealed and kept in liquid nitrogen. They are then placed in a constant temperature bath controlled to $\pm 0.1°C$ where the reaction occurs. When the reaction time expires, the ampoule is taken out of the bath and quenched in liquid nitrogen to stop the reaction. The top of the ampoule is cut to let the unreacted monomer vent off. The remaining polymer is weighed and from the initial mass of monomer placed in the ampoule, the degree of conversion is calculated gravimetrically.

III.1.6 Experimental conditions

In the experiments described herein, the following extensively used commercial initiators at the following temperature levels were used:

EXPERIMENTAL DEVICE
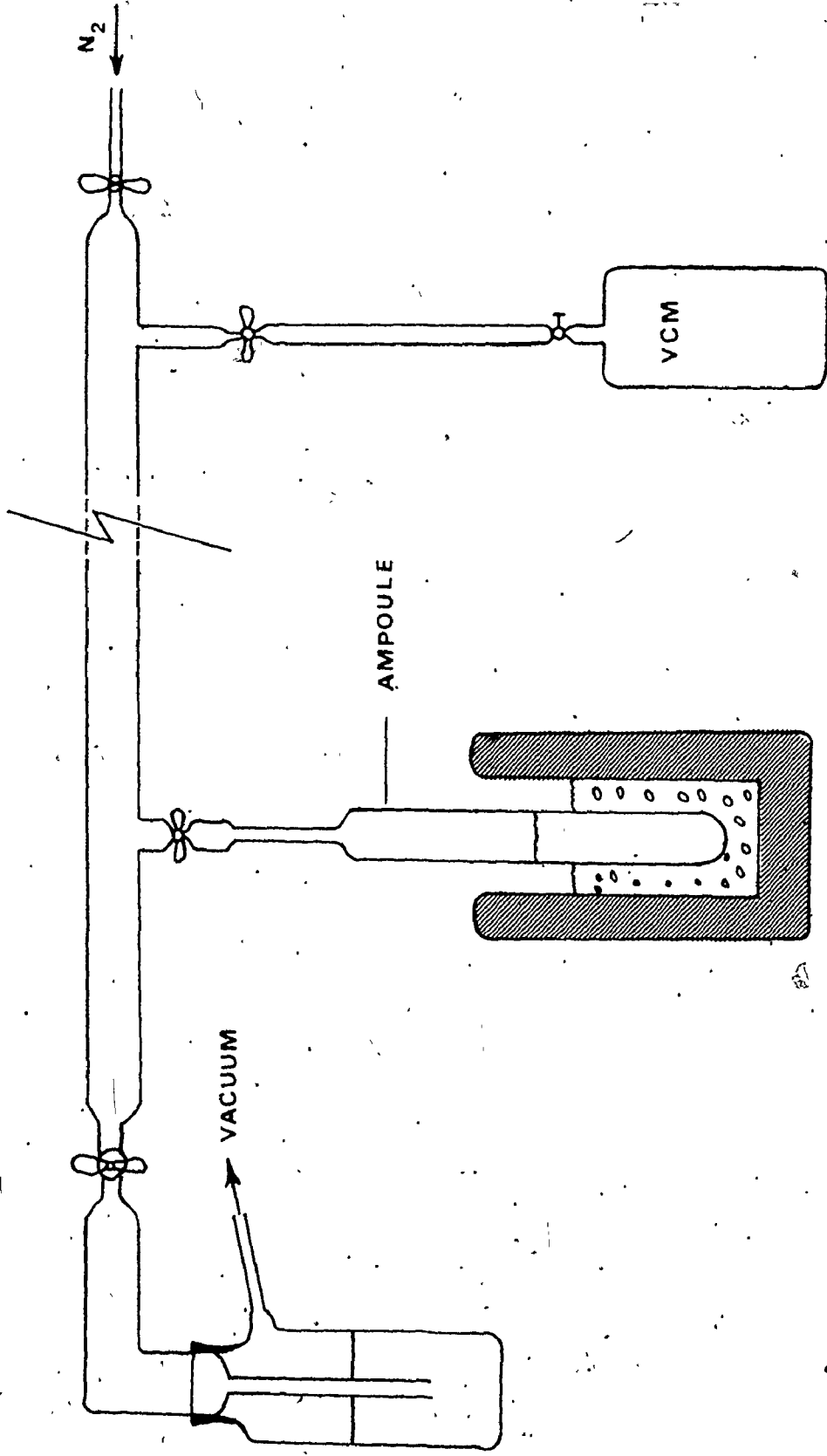
FIGURE 13

Chemical Name	Trade Name	Temp. °C
Lauryl Peroxide	L.P.	50°, 55°
Dicyclohexylperoxydicarbonate	L-229	35°, 40°

The experimental data obtained are shown in Figures 14 and 15. These data supplement rate data supplied by Lucidol.

ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE
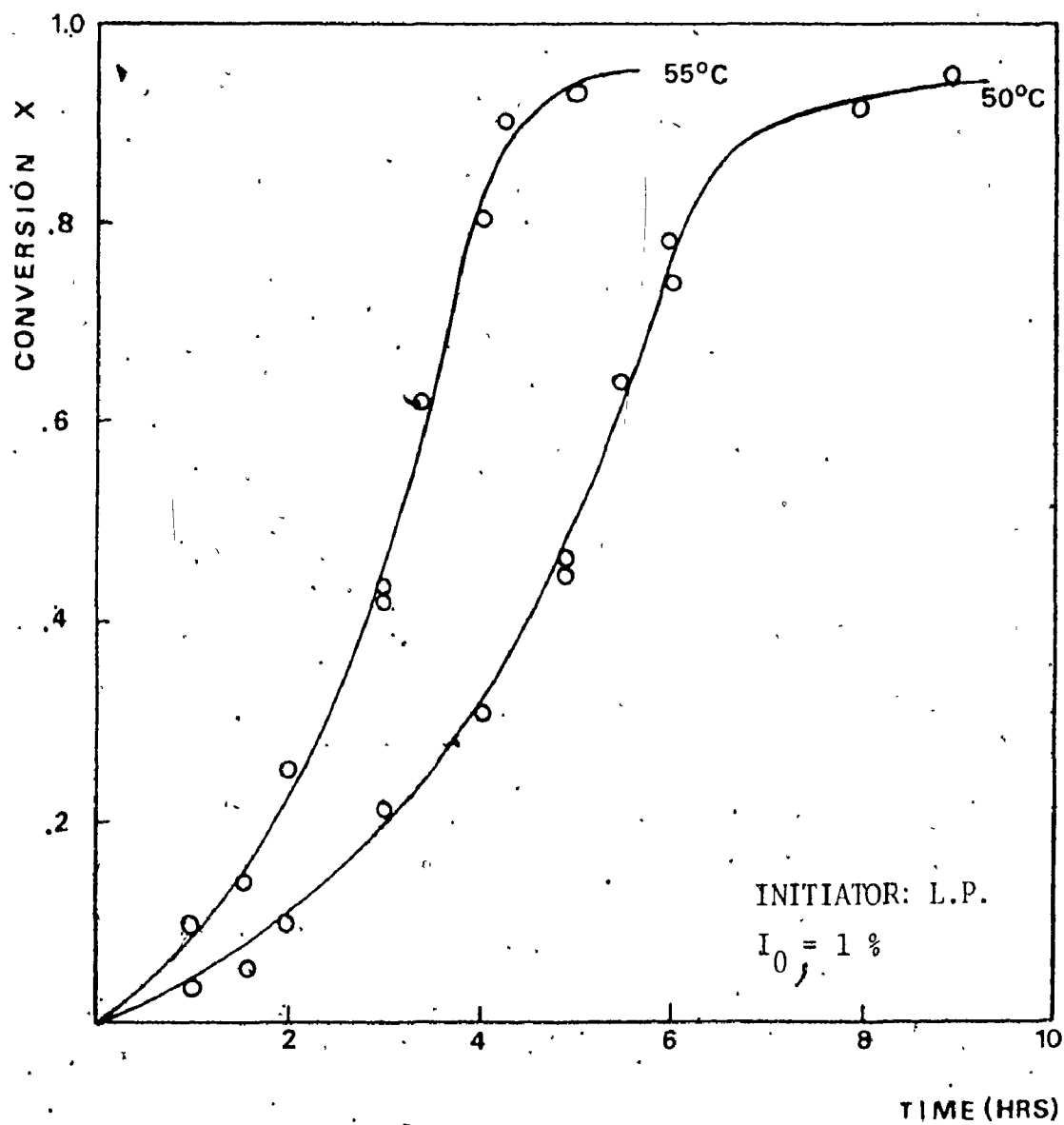
FIGURE 14

ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE
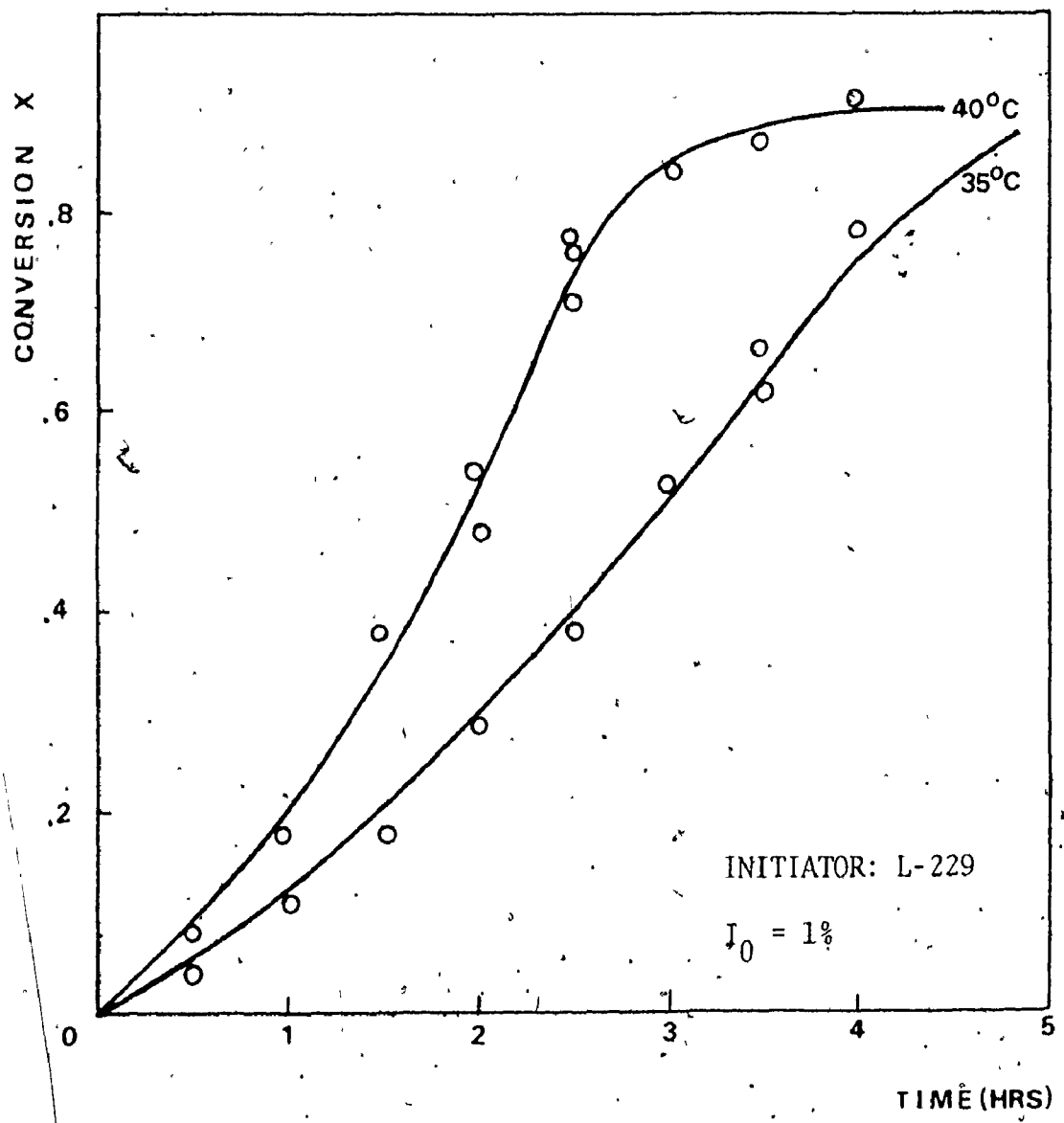
FIGURE 15

III.1.7 Lucidol's Experiments

) Lucidol's experiments were carried out using an autoclave reactor. Two hundred g of VCM were polymerized during each experiment using the suspension technique. The stainless steel autoclave was immersed in a calorimeter and measurements were obtained in the form of calorimetric data. The reaction is highly exothermic (23.0 Kcal/gmol) and by measuring the rate of heat transfer from the reactor to the calorimeter, one can calculate the reaction rate.

From the theory of heterogeneous polymerization, it is well known that at $x = x_c$ the monomer phase disappears. As a result of this, the pressure in the reactor starts to fall. So, at the point where the pressure in the autoclave drops, this is an indication that the conversion is at $x = x_c$.

Calculation of rate of polymerization

Based on a total charge of 200 gr VCM and assuming that the heat of polymerization is 23.0 Kcal/gmol, the total heat liberated at 100% conversion is $\frac{200}{62.5} \times 23,000 = 73,600$ cal; and the rate of polymerization in % hr^{-1} is:

$$\frac{Y \text{ cal}}{\text{min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{100\%}{73,600 \text{ cal}} = Y \cdot 8.15 \times 10^{-2}\% \text{ hr}^{-1}$$

So, from the calorimetric data given in cal/min, using the above coefficient we may readily obtain rate data in hr^{-1}. In order to convert the

rate data into conversion data, we simply integrate the rate data using any standard numerical integration routine. In Appendix II we tabulate Lucidol's suspension calorimetric data.

The following Table contains information concerning the chemical names of the initiators used by Lucidol as well as the temperature levels at which the experiments were carried out.

CHEMICAL NAME	COMMERCIAL NAME	TEMP °C
Di-(secbutyl)-peroxydicarbonate	L-225	50, 55
Di-(2-ethyl-hexyl)-peroxydicarbonate	L-223M75	50, 55
Acetyl-cyclo-hexylsulfonyl peroxide	L-228P	45, 50, 55

All the conversion-time curves obtained after the numerical integration are given in Figures 16, 17 and 18. The levels of the initiator concentrations are expressed on a pure basis, i.e. parts of pure initiator per 100 parts of monomer (phm).

III.2 PARAMETER ESTIMATION

The model developed by Abdel-Alim and Hamielec[40] requires the estimation of a number of parameters. As presented in equations (II-31), (II-32), (II-33) and (II-40), there are seven groups of parameters that have to be estimated: P, f, k_d, p_K, x_c, C_M and the ratio $k_{p_M}/k_{t_M}^{\frac{1}{2}}$ as defined in Section II.

To establish some of these parameters, Abdel-Alim and Hamielec used the single initiator AIBN, whose characteristics are well known, (k_d is the same for many different solvents), and performed isothermal experiments at 30°, 50° and 70°C. Analyzing their data[40] they obtained estimates for the four parameters P, x_c, C_M and $k_{p_M}/k_{t_M}^{1/2}$. The expressions for these parameters are given in the following Table.

Parameter	Temperature Dependence T in °C.		
	30°	50°	70°
P	23.0	22.7	16.7
x_c	$0.86 - 2.0 \times 10^{-3} \cdot T$		
$k_{p_M}/k_{t_M}^{1/2}$	$0.0725 \cdot \exp\left[\frac{-1718}{R}\left(\frac{1}{273.16+T} - \frac{1}{323.16}\right)\right]$ in $\frac{g\ mol \cdot s}{\ell t}$		
C_M	$1.098 \times 10^{-3} \exp\left[\frac{-5444}{R}\left(\frac{1}{273.16+T} - \frac{1}{323.16}\right)\right]$		

From the above four parameters, x_c, C_M and $k_{p_M}/k_{t_M}^{1/2}$ are independent of

the type of initiator used and of the degree of conversion. Thus the above expressions can be used for any initiator. The remaining parameter, P, together with f, k_d and p_K, depend on the type of initiator used and therefore they have to be estimated separately for each type of initiator.

To obtain the parameter estimates that would give the best statistical fit of the model to the experimental data, we used UWHAUS, a nonlinear least squares routine. The method used is briefly described in Appendix I. The parameter estimates computed by the least squares routine are tabulated in Tables 9, 10 and 11. Table 9 includes the estimates obtained using the rate data provided by Lucidol. Table 10 shows the estimates obtained using the conversion data calculated from the rates.

A careful examination of both Tables shows that:

(a) Comparing the estimates one by one, we see that estimated parameters from both rate and conversion data are comparable.

(b) The fourth parameter, the partition coefficient p_K, is always less than one, notably between 0.2 and 0.5 in most of the cases. This indicates that the initiator concentration in the polymer phase is higher than its concentration in the monomer phase.

As we can see from the Tables of Correlations of Appendix I, some of the parameters are highly correlated between them, therefore the estimates in some cases have broad confidence limits. In an effort to reduce the correlations between the parameters we decided to minimize the number of parameters that have to be estimated. So, even though

TABLE 9

PARAMETER ESTIMATION [*]

Initiator	%	Temp. °C	P	f	k_d [**]	P_K
L.P.	.1	50	-	-	-	-
	1	55	-	-	-	-
L-229	1	35	-	-	-	-
	1	40	-	-	-	-
L-225	.075	50	33.10	.56	4.706	0.318
	.05	55	27.48	.62	11.981	0.516
L-223M75	.065	50	34.79	.57	4.085	.640
	.075	55	27.40	.56	7.513	.723
L-228P	.1	45	12.65	.56	11.561	.472
	.045	50	18.75	.81	20.230	.435
	.075	55	12.65	.58	29.560	.659

[*] Estimates based on and calculated from rate data.

[**] $k_d \cdot 10^5 \ \text{sec}^{-1}$

TABLE 10

PARAMETER ESTIMATION [*]

Initiator	%	Temp. °C	P	f	k_d [**]	P_K
L.P.	1	50	28.90	.60	.301	.296
	1	55	23.50	.62	.658	.453
L-229	1	35	29.31	.59	.790	.356
	1	40	19.52	.60	1.392	.127
L-225	.075	50	40.91	.49	5.374	.176
	.05	55	26.91	.49	11.941	.377
L-223M75	.065	50	34.01	.45	2.615	.101
	.075	55	32.66	.47	5.395	.164
L-228P	.1	45	13.24	.51	10.88	.453
	.045	50	17.35	.84	19.58	.335
	.075	55	15.76	.54	32.27	.220

[*] Estimates based on and calculated from conversion data

[**] $k_d \cdot 10^5 \ sec^{-1}$

TABLE 11

PARAMETER ESTIMATION [*]

Initiator	%	Temp °C	P	f	k_d [**]
L.P	1.0	50	31.56	.59	.285
	1.0	55	20.57	.63	.611
L-229	1.0	35	21.23	.59	.620
	1.0	40	24.54	.60	1.321
L-225	.075	50	31.90	.45	5.602
	.05	55	32.10	.46	10.650
L-223M75	.065	50	33.81	.47	3.636
	.075	55	29.67	.46	6.888
L-228P	.10	45	13.14	.59	8.01
	.045	50	13.84	.37	15.92
	.075	55	14.38	.33	33.57

[*] Estimates calculated from conversion data. Eliminated one
of the parameters by setting $P_K = 1.0$.

[**] $k_d \cdot 10^5$ sec^{-1}

there is a definite preference of the initiator for the polymer phase, we decided to keep p_K constant. By setting $p_K = 1.0$ we assume even distribution of the initiator between the two phases and at the same time we have to estimate only 3 parameters now, namely P, f and k_d. Table 11 shows these estimates which are very similar to the estimates of Tables 9 and 10. The correlations between the parameters are somehow lower now, but still remain relatively high. The high correlation between P and f is reduced significantly in the case of L.P.O. but at the same time the correlation between f and k_d remains high, something expected because of the way f and k_d are linked in the model.

Figures 14 and 15 show the experimental results obtained at McMaster University. Figures 16, 17 and 18 show the conversion-time histories obtained after the numerical integration of Lucidol's calorimetric data. The solid lines represent the model simulation curves. As can be seen, there is a good agreement between experimental points and model prediction up to high conversions.

In the following pages we tabulate the parameters that were estimated by using UWHAUS for each individual initiator. In the same tables we give the exact experimental conditions as well as the confidence limits for each estimated parameter. From the estimated k_d values for at least two different temperature levels we are able to calculate the activation energies E and the frequency factors, and include them in the tables. Figure 18A contains the Arrhenius curves.

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ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE
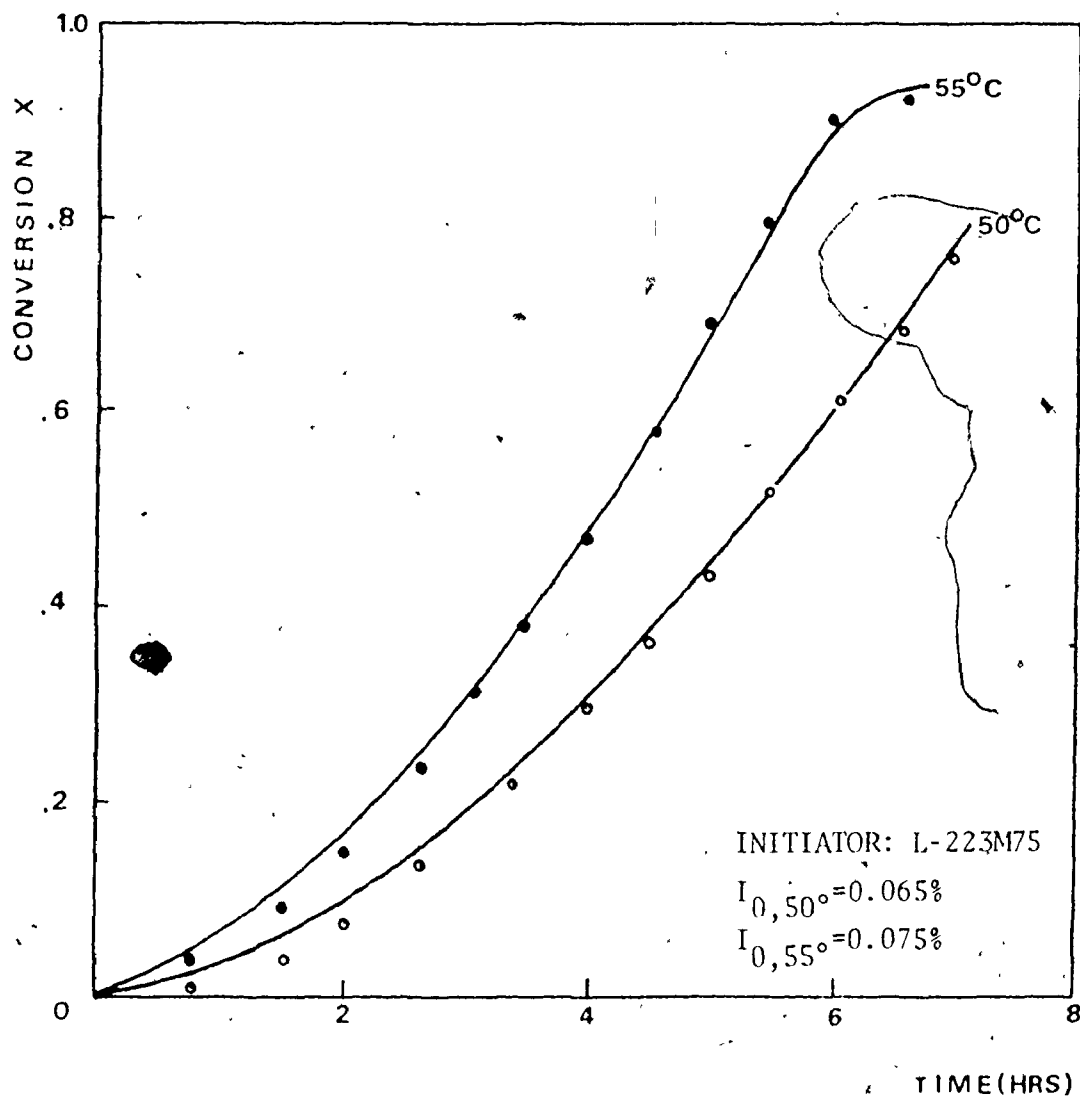
FIGURE 16

ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE
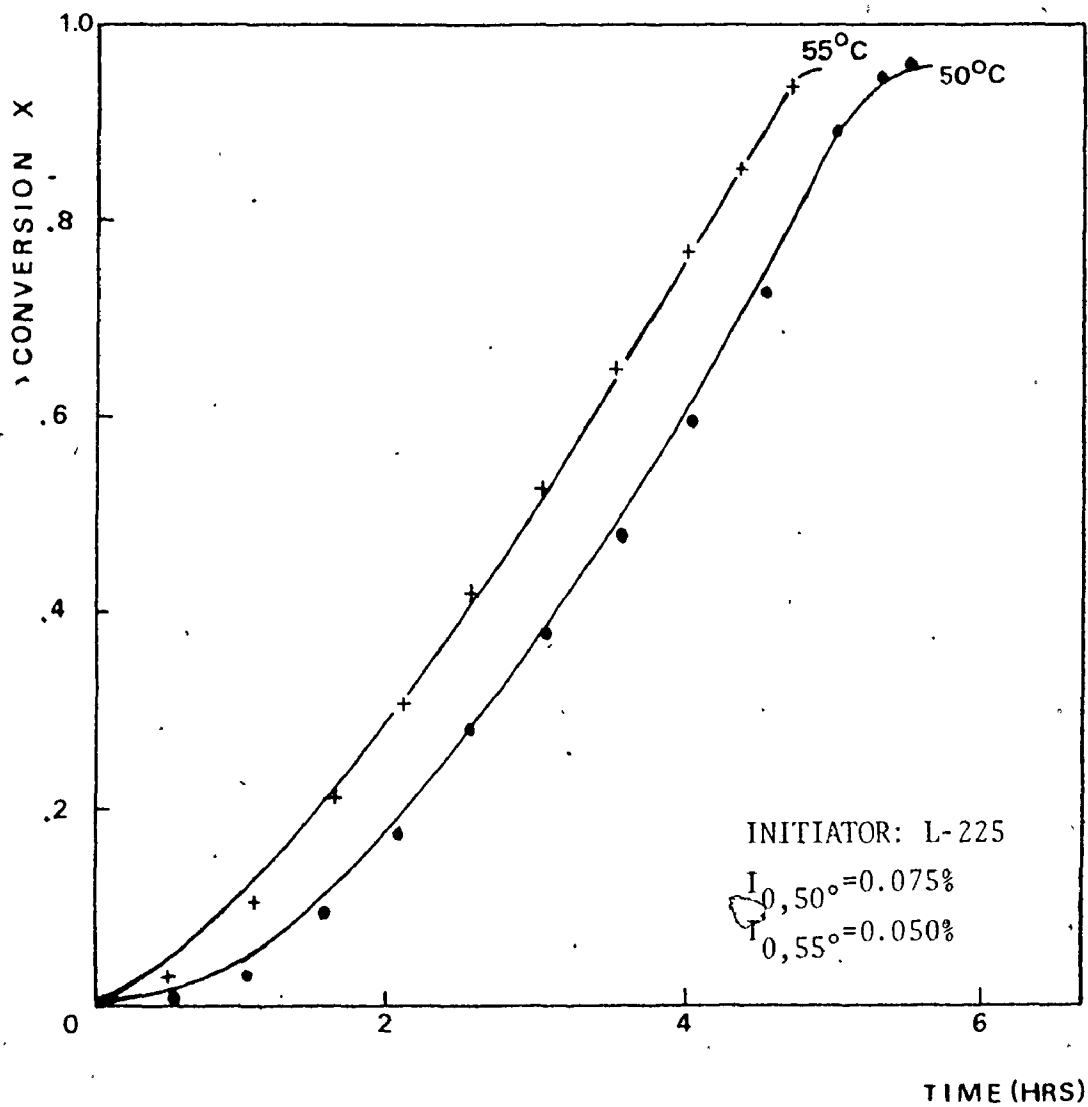
FIGURE 17

ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE
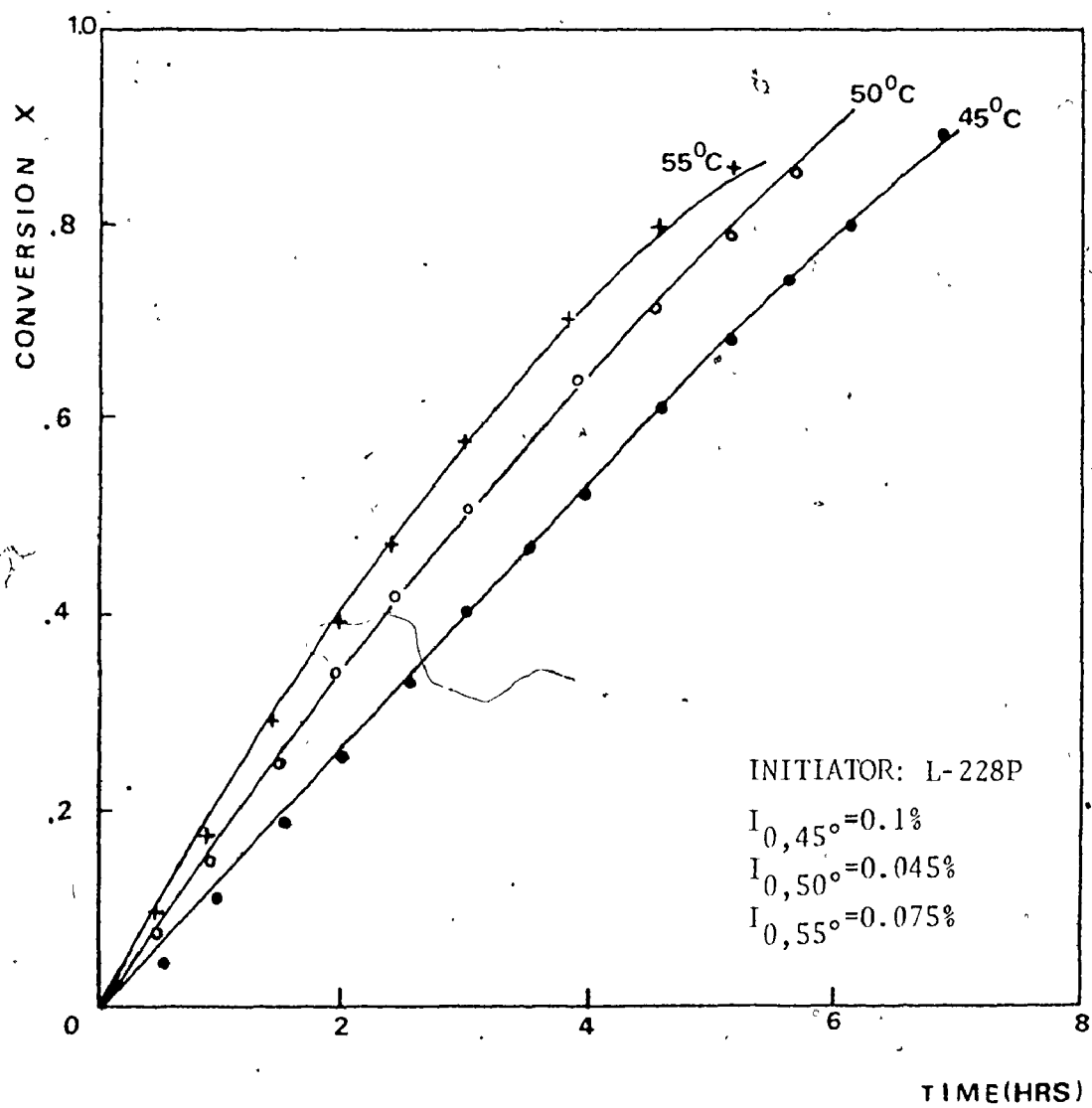
FIGURE 18

TABLE 12

Experimental Conditions and Parameter Estimates
for Lauryl Peroxide

T °C	CI_o gmol/ℓt	P	f	$k_d \times 10^5$ sec^{-1}
50	$2.51 \propto 10^{-2}$	31.56 ± 4.3	0.63 ± 0.07	$.285 \pm 0.023$
55	$2.51 \propto 10^{-2}$	20.57 ± 2.7	0.59 ± 0.08	$.611 \pm 0.037$
65	-	-	-	2.83 *
75	-	-	-	12.03 *
E = 33.350 kcal/gmol		A = 1.02×10^{17} sec^{-1}		

TABLE 13

Experimental Conditions and Parameter Estimates
for L-229

T °C	CI_o gmol/ t	P	f	$k_d \cdot 10^5$ sec^{-1}
35	3.49×10^{-2}	24.5 ± 8.2	$.60 \pm 0.16$	$1.461 + 0.396$
40	3.49×10^{-2}	11.2 ± 3.4	$.59 \pm 0.08$	1.571 ± 0.187

* Data provided by N. Fisher, Rhone Poulenc Industries, Aubervillers, France.

TABLE 14

Experimental Conditions and Parameter
Estimates for   L-223M75

T °C	CI_o gmol/ℓt	P	f	$k_d \times 10^5$ sec^{-1}
50	1.88×10^{-3}	33.81 ± 3.1	0.47 ± 0.06	3.636 ± 0.213
55	2.17×10^{3}	29.67 ± 2.3	0.46 ± 0.06	6.888 ± 0.398
E = 26.9 kcal/gmol A = 2.124×10^{17} h^{-1}				

TABLE 15

Experimental Conditions and Parameter
Estimates for   L-225

T °C	CI_o gmol/ℓt	P	f	$k_d \times 10^5$ sec^{-1}
50	3.201×10^{-3}	32.10 ± 4.10	0.45 ± 0.06	5.602 ± 0.345
55	2.130×10^{-3}	31.90 ± 2.70	0.46 ± 0.05	10.650 ± 0.568
E = 27.1 kcal/gmol A = 4.105×10^{17} h^{-1}				

TABLE 16

Experimental Conditions and Parameter·Estimates
for L-228P

T °C	CI_o gmol/ℓt	P	f	$k_d \times 10^5$ sec^{-1}
45	4.5×10^{-3}	13.14 ± 1.8	$.59 \pm 0.08$	8.01
50	2.02×10^{-3}	13.84 ± 2.1	$.37 \pm 0.06$	15.92
55	3.37×10^{-3}	14.38 ± 2.1	$.33 \pm 0.03$	33.57
43	-	-	-	4.583 *
50	-	-	-	14.722 *
52	-	-	-	19.638 *
	$E = 32.133$ kcal/gmol		$A = 8.28 \times 10^{17}$ sec^{-1}	

* Data provided by N. Fisher, Rhone Poulenc Industries, Aubervilliers, France.

ARRHENIUS DIAGRAM
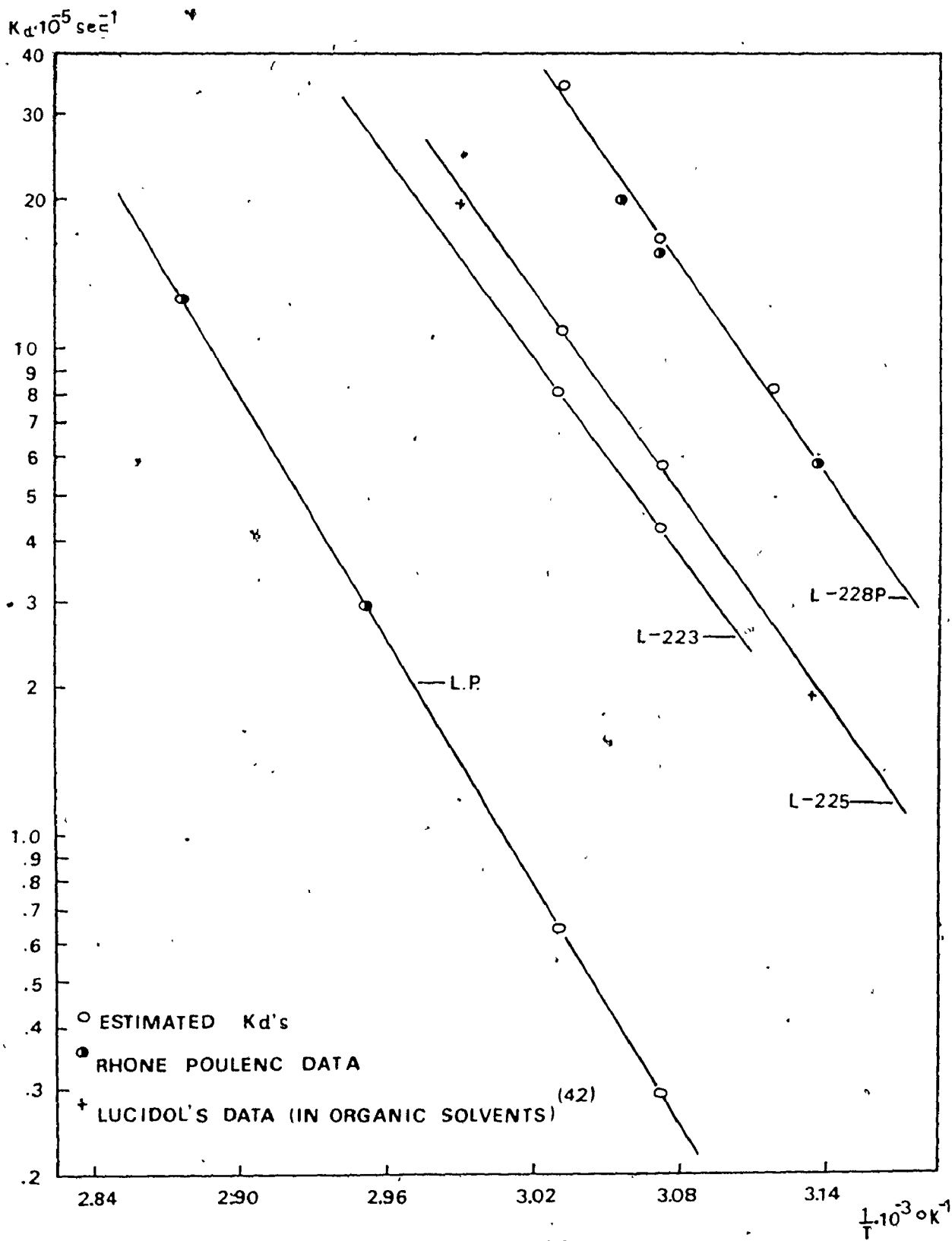
FIGURE 18A

III.3. NONISOTHERMAL CONDITIONS

After we have obtained the parameter estimates and have established the Arrhenius equations for each individual initiator, we are now in a position to test how the model performs under nonisothermal conditions.

In order to test the model, we follow the same experimental procedure. After the ampoules are loaded with initiator and VCM and sealed, they are placed in a constant temperature bath where the temperature is kept at 60°C ± 0.1°C for 90 minutes. They are then transferred to another constant temperature bath kept at 50°C, until high conversions are obtained. The experimental data obtained are shown in Figure 17. They are in good agreement with the model predictions represented by the solid lines. The initiator used was Lauryl Peroxide.

The model predictions were obtained by using the following expressions for the parameters:

$$CI_o = 2.51 \times 10^{-2} \ gmol/\ell t$$

$$k_d = 1.02 \times 10^{17} \ exp \ (\frac{-33.350}{RT}) \qquad (T \ in \ °K)$$

$$f = 0.60$$

p_K was held constant and equal to 1.0

NONISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE

INITIATOR: L.P.

$I_0 = 1\%$
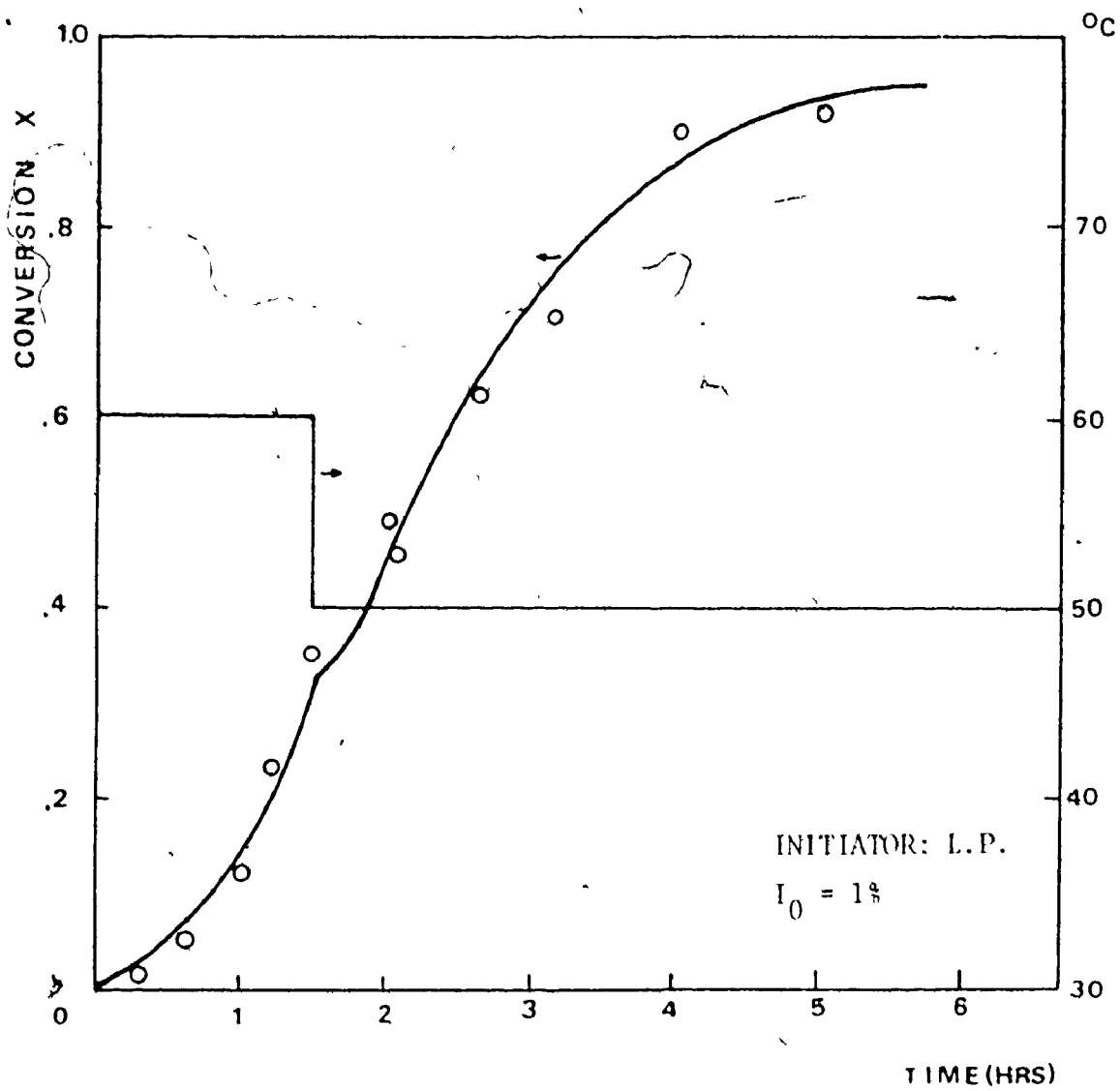
FIGURE 19

III.4 MULTIPLE INITIATOR SYSTEMS.

As outlined in Part II, it is possible by combining two or more initiators to obtain linear conversion curves.

Using the correct amounts of initiators, Lucidol were able to conduct two experiments at 50°C and 55°C that yielded linear conversion-time histories. The two initiators used were L-223M75 and L-228P. By using the parameters estimated previously, the experimental data were simulated by using Abdel-Alim's model.

In figure 20, two linear conversion curves are shown. The solid lines represent the simulation curves as calculated by the model. The model parameters used are the same as tabulated in Tables 14 and ·16 for 50° and 55°C.

III.5 DISCUSSION

After analyzing a wide variety of experimental results, we are now in a position to evaluate the significance of the data reported herein for Abdel-Alim's model.

(a)   The new data obtained for Lauryl Peroxide are very reasonable and Abdel-Alim's model fits the experimental data very well. The k_d values estimated by UWHAUS are in excellent agreement with data obtained from Rhône-Poulenc, France. As shown in the Arrhenius diagram (Figure 18A) all four k_d's are practically on the same straight line. This enables us to calculate the activation energy E, and the frequency factor A, (by linear regression),

ISOTHERMAL POLYMERIZATION OF VINYL CHLORIDE

MULTIPLE INITIATOR SYSTEMS

0.035% L-223 + 0.030% L-228P at 50°C
0.035% L-223 + 0.035% L-228P at 55°C
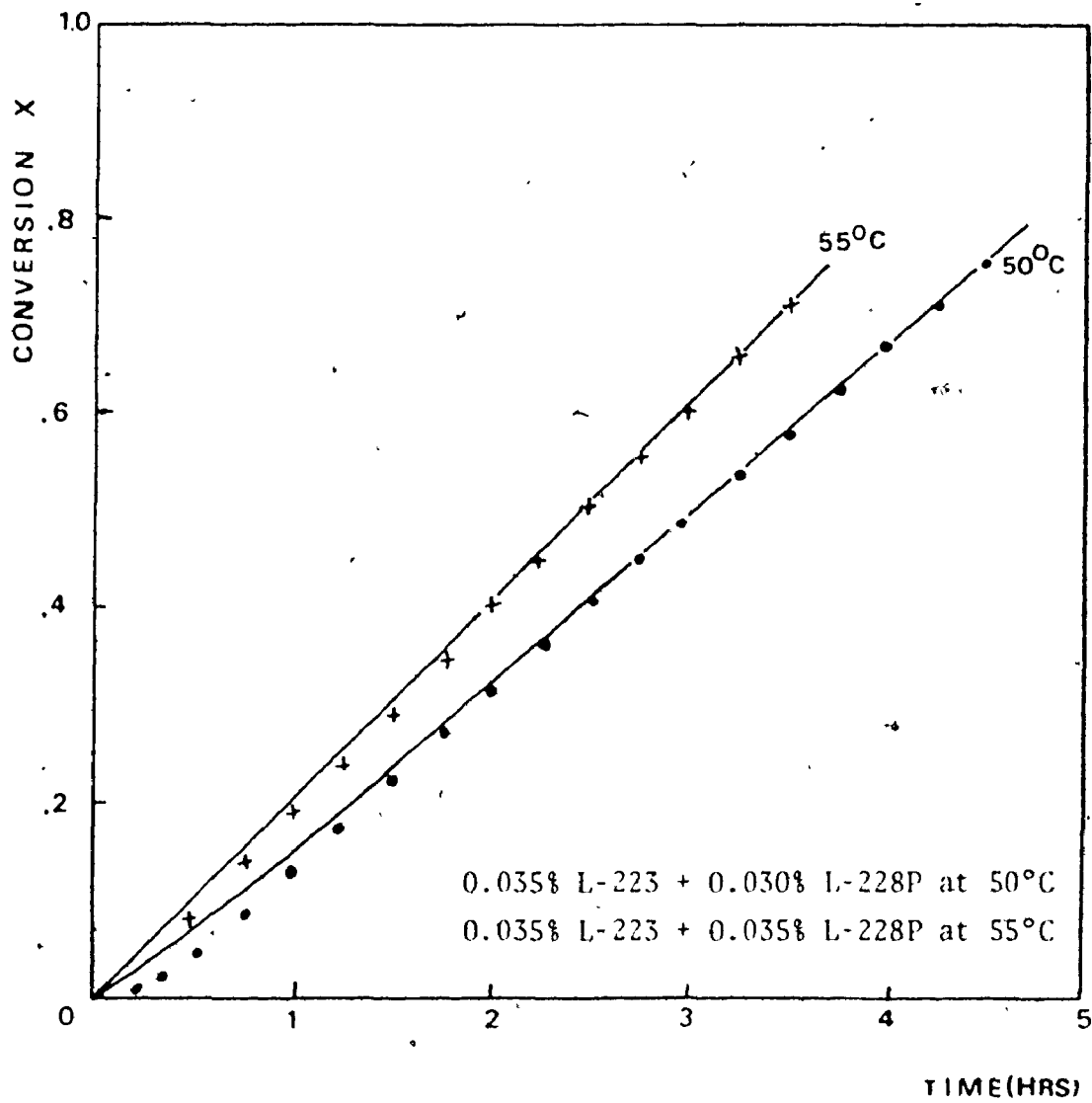
FIGURE   20

and present them in the form of an Arrhenius equation:

$$k_d = 1.02 \times 10^{17} \exp(\frac{-33,350}{RT}) \qquad \text{(T in °K)}$$

(b)   For the commercial initiators L-223 and L-225, Lucidol's data were analyzed and from the estimated k_d values the activation energy and frequency factor for each initiator were calculated.

The calculated activation energies are comparable to the values reported by Lucidol. Lucidol has obtained the decomposition rate constants (k_d) from decomposition data in organic solvents. The Table below compares activation energies.

INITIATOR	ACTIVATION ENERGY E	
	Present work	Lucidol's[42]
Di-(sec-butyl)-peroxydicarbonate (L-225)	27.1	27.0 in O.M.S.
Di-(2-ethyl-hexyl)-peroxydicarbonate (L-223M75)	26.9	30.0 in O.M.S.

(c)   The experimental data for ACSP (L-228P) are again reasonable and the k_d values estimated by UWHAUS are very comparable to the Rhône-Poulenc data as shown in Table 16. Again by linear regression we obtained the activation energy E and frequency factor A as shown in the following Arrhenius equation:

$$k_d = 8.28 \quad 10^{17} \exp(\frac{-32,133}{RT}) \qquad \text{(T in °K)}$$

(d)   In the case of L-229, which is a much more "active" initiator, compared to Lauryl peroxide, we encountered some experimental

problems. Because of the high decomposition rate constant of L-229, small amounts were required (5-10 mg) and even at low reaction temperatures, high reaction rates and low reproducibility of the experimental results was a problem. Additionally, high correlations of the estimated parameters lead to broad confidence limits, and lower accuracy. Therefore we do not intend to propose an Arrhenius equation for L-229.

e) In the case of PVC, it has been established [40] that transfer to monomer is the dominant transfer reaction, therefore, nonisothermal conditions is the only simple way to modify molecular weights and obtain wider molecural weight distributions. The method is extensively applied in industry and the ability of the model to predict conversions, given any type of reaction temperature profile, is considered to be a positive feature.

f) Multiple initiator systems help further improve the efficiency of the batch process. In the case of two initiators, a fast initiator is used to accelerate the first stages of the reaction and when the fast initiator is consumed, the second one, usually a slower initiator, continues the reaction until high conversions. The ability of the simulation program to handle practically any number of initiators, at any temperature level is considered as an additional advantage.

We finally believe that by proposing new Arrhenius equations for commercial initiators and establishing a good performance of the model under nonisothermal conditions and by using multiple initiator systems we have contributed to the recognition of the validity and applicability of the model in a wide range of conditions.

III. 6 Summary and conclusions.

After a number of preliminary experiments,isothermal experiments were performed using glass ampoules.Two commercial initiators were used and the data obtained,together with Lu-. cidol's data were analyzed.

By fitting the model response to the experimental points using a special nonlinear regression routine,parameter values were estimated and found to be in good agreement with values published in the literature.Subsequently,nonisothermal experiments were performed and the nonisothermal data together with Lucidol's isothermal data for multiple initiator systems were simulated using the model.

Both cases are of industrial interest.Nonisothermal conditions are necessary in order to develop new molecular weight recipes. Multiple initiator systems,properly designed,help reduce batch times,improve process control and maximize heat removal.In Part II we give a simple method to calculate the initiator concentrations necessary to obtain constant reaction rates.

In both cases ,the model predictions were in good agreement with experimental results,thus indicating that the model has a wide range of applicability that may be extended to nonisothermal conditions and multiple initiator systems.

Parameter estimation enabled us to propose new Arrhenius equations for two widely used commercial initiators. We believe that the accuracy of the model is sufficient for industrial applications.

Additional molecular weight measurements are necessary in order to establish the validity of the model molecular weight predictions by comparing them with experimental results.

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APPENDIX I

APPENDIX I

Statistical Analysis

To develop a model that describes the true mechanism of the re-
action would be very complicated and difficult; therefore we believe
that a good practical model is one that is capable of predicting satis-
factorily conversion and molecular weights. Such a model would include
parameters that are to be estimated from experimental data. The present
section deals with the mathematical technique of model fitting.

From the previously described model we see that we have to
estimate the following parameters: P, P_K, f and k_d, which vary from
initiator to initiator. Since the model is nonlinear the parameter
estimates are obtained using a nonlinear least squares regression rou-
tine.

We assume that the present model may be written as:

$$y = \underline{n}\ (x,\beta) + \underline{\xi}$$

where $\underline{y}$ is the vector of observations, $\underline{x}$ is the matrix of the indepen-
dent variables, $\underline{\beta}$ is the vector of parameters and $\underline{\xi}$ the vector of un-
observable errors; n is the expected value of y (as calculated by
using the model in this case). If m is the number of observations, then
for the uth observation we have:

$$y_u = \eta(x_{1_u}', x_{2_u}, \ldots, x_{K_u}, \beta_1, \beta_2, \ldots, \beta_p) + \xi_u$$

$$u = 1, \ldots, m$$

We now make the following assumptions (which in our case are usually true):

1) The model is correct, i.e. $\eta = E(y)$.

2) The settings of the independent variables are fixed known values.

3) The errors ξ are independent random variables, normally distributed and with expected value equal to zero.

As we see, the model contains k independent variables and p parameters to be estimated.

If we call the quantity

$$\sum_{u=1}^{n} [y_u - \eta(x_u, \beta)]^2$$

the sum of squares of the residuals, (SSR), the least squares estimates of the p parameters, is the choice of β values that minimize this sum. It is mathematically possible to obtain explicit expressions for the parameter values if the model is linear. In the case of a nonlinear model, we have to use a search routine.

The method followed here is the one known as the "Marquardt's Method"[49]. This is a combination or "compromise" between the method of steepest descent and the linearization method and makes use of the advantages of both previous methods[48].

Expanding the model in Taylor series about some initial guessed values $\underline{\beta}^0$ for the parameters we get:

$$\eta(x_u, \beta) = \eta(x_u, \underline{\beta}^0) + \sum_{i=1}^{p}\left[\frac{\partial \eta(x_u, \beta)}{\partial \beta_i}\right]_{\beta_i^0}(\beta_i - \beta_i^0) + K$$

where K includes all the nonlinear terms.

Assuming that the nonlinear terms K may be neglected as a first approximation and by defining $\left[\frac{\partial \eta}{\partial \beta_i}\right]_{\beta_i^0} = X_{iu}^0$ and $\delta_i^0 = \beta_i - \beta_i^0$ we have:

$$\eta_u = \eta_u^0 + \sum_{i=1}^{p} X_{iu}^0 \, \delta_i^0$$

or

$$y_u = \eta_u^0 + \sum_{i=1}^{p} X_{iu}^0 \, \delta_i^0 + \xi_u$$

and finally for the Residuals R_u^0 :

$$R_u^0 = y_u - \eta_u^0 = \sum_{i=1}^{p} X_{iu}^0 \, \delta_i^0 + \xi_u \qquad u = 1,..,n \text{ and } i = 1,...,p$$

or in matrix form

$$\underline{R}^0 = \underline{X}^0 \, \underline{\delta}^0 + \underline{\xi}$$

which is the linearized form of our model. For this linear model, from the theory of linear models we readily have an expression for $\underline{\delta}^0$ as given in [48]:

$$\hat{\underline{\delta}}^0 = (\underline{X}^{0'}\underline{X} + \lambda I)\,\underline{X}^{0'}\,\underline{R}^0$$

where λ is a positive constant and $\underline{I}$ is the identity matrix

In the above expression the term $\lambda I \; \underline{X}^{0'} \; \underline{R}^{0}$ represents the steepest descent part of the method.

So, for $\lambda \rightarrow \infty$ the method reduces to steepest descent only

    for $\lambda \rightarrow 0$ "   "   "   " linearization only.

After we obtain the $\underline{\hat{\delta}}^{0}$: $\beta^{1} = \beta^{0} + \underline{\hat{\delta}}^{0}$ is the improved guess for the parameter vector. The iteration continues until β converges within specified limits, or the SSR remains unchanged.

The routine that performs the above calculations is called UWHAUS. We usually start the calculations with a relatively large value of λ that is divided by a constant number, i.e. decreased after each iteration. This means that in the first few iterations the steepest descent method dominates. This is desirable because from theory we know that the steepest descent method always moves towards the right solution, regardless of how bad the initial guesses are. As the number of iterations increases, the contribution of the linearization method becomes higher, because this method converges faster at the end.

The UWHAUS routine also calculates variances and confidence limits. So the estimated variance-covariance matrix of the parameters is given by:

$$\text{Estimated} \quad \text{var}(\hat{\beta}) = (X' \; X)^{-1} \; S^{2} = C_{ij} \; S^{2}$$

where S^{2} is an estimate of σ^{2} (is the variance of the observations).

The approximate individual confidence limits for the parameters (on linear hypothesis) are:

$$\pm\, t_{(n-p),a/2} \cdot \sqrt{C_{i_i} \cdot S^2}$$

where $t_{(n-p),a/2}$ is the value of the student distribution for $(n-p)$ degrees of freedom at the a level of significance (obtained from tables).

The approximate correlation matrix for the estimated parameters (again on linear hypothesis) is given by:

$$r_{ij} = \frac{C_{ij}}{\sqrt{C_{i_i} C_{jj}}}$$

We see if r_{ij} is close to one, this means that the parameters β_i and β_j are highly correlated.

The following are tables of the correlations and the SSR for each initiator at two or three different temperature levels.

TABLE OF CORRELATIONS 1

(BASED ON RATE DATA)

Initiator	Temp.°C		P	f	K_d	P_K
L-223	50	P	1.000			
		f	-.9899	1.000		
		K_d	.9578	-.9889	1.000	
		P_K	.5955	-.5479	.4869	1.000
L-223	55	P	1.000			
		f	-.9982	1.000		
		K_d	.1706	-.2208	1.000	
		P_K	.8338	-.8109	-.1183	1.000
L-225	50	P	1.000			
		f	-.9989	1.000		
		K_d	.8883	-.8869	1.000	
		P_K	.8522	-.8477	.6894	1.000

TABLE OF CORRELATIONS 2

(BASED ON RATE DATA)

Initiator	Temp. °C		P	f	K_d	P_K
L-225	55	P	1.000			
		f	-.9995	1.000		
		K_d	-.0619	.0559	1.000	
		P_K	.8737	-.8656	.0132	1.000
L-228P	45	P	1.000			
		f	-.9996	1.000		
		K_d	.8883	-.8869	1.000	
		P_K	.8522	-.8477	.6894	1.000
L-228P	50	P	1.000			
		f	-.9994	1.000		
		K_d	.8935	-.8943	1.000	
		P_K	-.9012	.9020	-.9994	1.000
L-228P	55	P	1.000			
		f	-.9994	1.000		
		K_d	.8263	-.8207	1.000	
		P_K	.9163	-.9108	.8588	1.000

TABLE OF CORRELATIONS 3

(BASED ON CONVERSION DATA.)

Initiator	Temp.°C		P	f	K_d	P_K
L-223	50	P	1.000			
		f	-.9327	1.000		
		K_d	.8832	-.9923	1.000	
		P_K	.8709	-.9617	.9731	1.000
L-223	55	P	1.000			
		f	-.9679	1.000		
		K_d	.8076	-.9459	1.000	
		P_K	-.5830	.7194	-.6330	1.000
L-225	50	P	1.000			
		f	-.8339	1.000		
		K_d	.2438	-.7257	1.000	
		P_K	-.0927	.3429	-.3081	1.000
L-225	55	P	1.000			
		f	-.9967	1.000		
		K_d	.0205	-.9502	1.000	
		P_K	-.8541	.8711	-.7730	1.000

TABLE OF CORRELATIONS   4

(BASED ON CONVERSION DATA.)

Initiator	Temp.°C		P	f	K_d	P_K
L-228P	45	P	1.000			
		f	-.9970	1.000		
		K_d	.9823	-.9872	1.000	
		P_K	-.0238	.0963	-.0848	1.000
L-228P	50	P	1.000			
		f	-.9843	1.000		
		K_d	.9352	-.9505	1.000	
		P_K	-.4368	.5860	.5877	1.000
L-228P	55	P	1.000			
		f	-.9558	1.000		
		K_d	.9228	-.9404	1.000	
		P_K	-.5455	.7580	-.7369	1.000

TABLE OF CORRELATIONS 5

BASED ON 3 ESTIMATED PARAMETERS

Initiator	Temp. °C	P	f	k_d
L.P	50	P 1.000 f -.1916 1.000 k_d -.0929 -.9191 1.000		
L.P	55	P 1.000 f -.3410 1.000 k_d .2270 -.0320 1.000		
L-229	35	P 1.000 f -.9793 1.000 k_d .8934 .9894 1.000		
L-229	40	P 1.000 f -.0108 1.000 k_d -.2198 -.9726 1.000		

TABLE OF CORRELATIONS 6

BASED ON 3 ESTIMATED PARAMETERS

Initiator	Temp. °C	P	f	k_d
L-223	50	P 1.000 f -.9 88 1.000 k_d .9606 -.9712 1.000		
L-223	55	P 1.000 f -.9527 1.000 k_d .8011 -.9158 1.000		
L-225	50	P 1.000 f -.8412 1.000 k_d .1510 -.6575 1.000		
L-225	55	P 1.000 f .8796 1.000 k_d .8126 -.8038 1.000		

TABLE OF CORRELATIONS 7

BASED ON 3 ESTIMATED PARAMETERS

Initiator	Temp. °C	P	f	k_d
L-228P	45	P 1.000		
		f -.9189	1.000	
		k_d .9548	-.9632	1.000
L-228P	50	P 1.000		
		f -.9375	1.000	
		k_d .9188	-.8924	1.000
L-228P	55	P 1.000·		
		f -.9252	1.000	
		k_d .7713	-.7144	1.000

APPENDIX   II

VINYL CHLORIDE SUSPENSION POLYMERIZATION
AND AUTOCLAVE REACTOR RESULTS.

Calculation of Rate of Polymerization

Based on a total charge of 200 g vinyl chloride in the autoclave reactor and assuming that the heat of polymerization ΔH_p = 23 kcal/mol, the total heat liberated at 100% conversion is 73,600 cals.

Rate of polymerization = Y cals/min.

$$Y \text{ cals/min} = \frac{Y \text{ cals}}{\text{min}} \times \frac{60 \text{ mins}}{1h} \times \frac{100\%}{73,600 \text{ cals}}$$

$$= Y \times 8.15 \times 10^{-2} \, \%/h$$

Note:

All initiator concentrations are expressed on a pure basis.

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.065 PHM LUPERSOL 223 AT 50°C

Time (mins)	Rate (Cals/Min)		Time (mins)	Rate (Cals/Min)
45	18		190	158
50	39		200	158
55	40		210	163
60	56		220	140
65	52	* 230	129
70	59		240	143
75	69		250	144
80	75		260	154
85	72		270	158
90	87		280	157
95	93		290	167
100	95		300	175
105	100		310	174
110	102		320	178
115	101		330	195
120	113		340	194
125	114		350	201
130	127		360	206
135	132		370	212
140	126		380	223
145	133.		390	225
150	135		400	230
155	131		410	233
160	139		420	235
170	145		430	216
180	142		440	226

* Approximately 80% conversion

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.075 PHM LUPERSOL 223 AT 55°C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
10	74	190	196
20	12	200	202
30	30	210	206
40	58	* 220	216
50	84	230	220
60	110	250	228
70	132	260	236
80	154	270	238
90	158	280	248
100	164	290	256
110	174	300	260
120	186	310	272
130	160	320	276
140	168	330	282
150	170	340	276
160	174	350	278
170	186	360	222
180	190	370	132

* Pressure drop begins.

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.075 PHM LUPERSOL 225 AT 50°C

Time (mins)	Rate (Cals/Min)		Time (mins)	Rate (Cals/Min)
30	34		170	242
40	72		180	248
50	98		190	260
60	124		200	264
70	142		210	276
80	148		220	282
90	190		230	284
100	198		240	300
110	208		250	318
120	238		260	334
130	244		270	358
140	232		* 280	428
150	236		290	452
160	236		300	312

* Pressure drop begins.

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.05 PHM LUPERSOL 225 AT 55°C

Time (mins)	Rate (Cals/Min)		Time (mins)	Rate (Cals/Min)
10	106		150	274
20	104		160	274
30	138		170	282
40	180		180	282
50	200		190	288
60	224		200	292
70	234		210	294
80	250		220	304
90	250		230	310
100	268	*	240	322
110	242		250	334
120	252		260	358
130	260		270	382
			280	324

* Pressure drop begins.

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.1 PHM LUPERSOL 228P AT 45°C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
5	94	160	178
10	98	170	172
15	124	180	169
20	130	190	167
25	140	200	170
30	142	210	163
35	168	220	160
40	162	230	161
45	170	240	162
50	168	250	158
55	170	260	154
60	172	270	148
65	176	280	154
70	168	290	150
75	174	300	152
80	186	310	154
85	188	320	155 *
90	182	330	155
95	182	340	166
100	186	350	178
105	186	360	182
110	176	370	188
115	180	380	182
120	182	390	142
130	177	400	106
140	178	410	92
150	179	420	79

* Pressure drop

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.045 PHM LUPERSOL 228P AT 50°C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
15	230	140	196
20	231	150	192
25	204	160	190
30	215	170	193
35	218	180	190
40	232	190	188
45	235	200	178
50	241	210	179
55	231	220	174
60	240	230	172
65	233	240	173
70	242	250	169
75	240	260	168
80	238	270	166
85	244	280	165
90	242	290	157
95	238	* 300	150
100	230	310	155
105	229	320	159
110	231	330	169
115	222	340	160
120	197	350	150
130	19	360	117

* pressure drop begins.

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.075 PHM LUPERSOL 228P AT 55°C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
5	202	135	228
10	242	140	230
15	206	145	230
20	222	150	220
25	244	160	217
30	238	170	202
35	244	180	207
40	282	190	203
45	250	200	192
50	258	210	184
55	258	220	180
60	256	225	170 *
65	260	230	148
70	258	235	150
75	260	240	148
80	256	250	148
85	256	260	142
90	252	270	146
95	252	280	132
100	250	290	134
105	248	300	124
110	248	310	126
115	242	320	120
120	246	330	114
125	238	340	110
130	232		

* Pressure drop

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.03 PHM LUPERSOL 228P + 0.035 PHM LUPERSOL 223 AT 50° C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
10	290	165	214
15	132	170	228
20	164	175	216
25	174	180	220
30	192	185	222
35	194	190	216
40	204	195	214
45	202	200	224
50	212	205	214
55	216	210	216
60	220	215	224
65	224	220	210
70	218	225	216
75	216	230	214
80	218	235	·208
85	220	240	232
90	224	245	222
95	226	250	236
100	208	255	226
105	212	260	228
110	246	265	246
115	230	270	240
120	244	275	234*
125	244	280	240
130	240	285	228
135	228	290	232
140	216	295	232
145	214	300	222
150	206	305	212
155	228	310	208
160	218		

*Pressure drop begins

VINYL CHLORIDE SUSPENSION POLYMERIZATION

0.035 PHM LUPERSOL 228P + 0.035 PHM LUPERSOL 223 AT 55°C

Time (mins)	Rate (Cals/Min)	Time (mins)	Rate (Cals/Min)
5	30	110	264
10	368	120	262
15	246	130	277
20	272	140	283
25	266	150	257
30	284	160	268
35	296	170	286
40	296	180	295
45	284	190	294
50	294	200	303
55	290	210	306 *
60	304	220	291
65	306	230	284
70	304	240	281
80	307	250	268
90	277	260	196
100	260	270	184

* Pressure drop begins.