

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Diffusion-Controlled Free Radical Polymerization. Effect on Polymerization Rate and Molecular Properties of Polyvinyl Chloride

A. E. Hamielec^a; R. Gomez-vaillard^{ab}; F. L. Marten^{ac}

^a Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada ^b

Universidad Autonoma Metropolitana, Iztapalapa, Mexico ^c Air Products and Chemicals, Inc.,

Allentown, Pennsylvania

To cite this Article Hamielec, A. E. , Gomez-vaillard, R. and Marten, F. L.(1982) 'Diffusion-Controlled Free Radical Polymerization. Effect on Polymerization Rate and Molecular Properties of Polyvinyl Chloride', Journal of Macromolecular Science, Part A, 17: 6, 1005 – 1020

To link to this Article: DOI: 10.1080/00222338208056498

URL: <http://dx.doi.org/10.1080/00222338208056498>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Diffusion-Controlled Free Radical Polymerization. Effect on Polymerization Rate and Molecular Properties of Polyvinyl Chloride

A. E. HAMIELEC, R. GOMEZ-VAILLARD,* and F. L. MARTEN[†]

Department of Chemical Engineering
McMaster University
Hamilton, Ontario, Canada

ABSTRACT

At high conversions of monomer (or high polymer concentrations), chain entanglements and a glassy-state transition (significant reduction in free volume) can have a profound effect on the relative rates of free-radical reactions which control the molecular structure of polymer chains. In particular, it will be shown that a diffusion-controlled propagation leads to the production of very low molecular weight chains with one terminal double bond per polymer molecule and to chains with a higher frequency of long-chain branching than might normally be expected at high polymer concentrations. On the basis of these results for diffusion-controlled polymerizations, polymer reactor operating procedures which should give higher productivity and a more thermally stable PVC are suggested. It is also suggested that the short chains and highly branch polymer molecules which are produced under monomer-starved conditions may in large part be due to diffusion-controlled propagation.

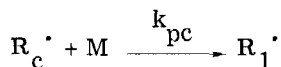
*Present address: Universidad Autonoma Metropolitana, Iztapalapa, Mexico 13 D.F.

[†]Present address: Air Products and Chemicals, Inc., Allentown, Pennsylvania 18105.

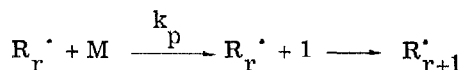
INTRODUCTION

The concepts of diffusion-controlled reactions on a microscopic scale will now be introduced by referring to a set of elementary reactions which might be operative in the synthesis of PVC. The bimolecular reactions will then be classified according to the size of the reactants and their intrinsic reactivity. The set of elementary reactions follows:

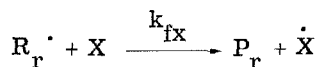
Initiation



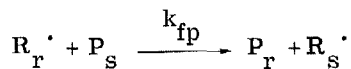
Propagation



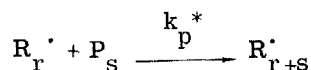
Transfer



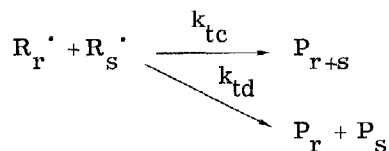
where X is monomer, initiator, or chain transfer agent



Terminal-Double Bond Reactions



Termination



CLASSIFICATION OF BIMOLECULAR REACTIONS

1. Two small molecules $k_{pc} \sim 10^3 \text{ L}/(\text{g}\cdot\text{mol})(\text{s})$
2. Macromolecule and a small molecule

$$k_{fx} \text{ and } k_{fp} \cong 1.0 \text{ L}/(\text{g}\cdot\text{mol})(\text{s})$$

Transfer to polymer is considered equivalent to transfer to a small molecule as an atom is abstracted from a monomer unit along the chain rather than from the chain end. In a concentrated solution, this is, of course, a much easier task.

$$k_p \sim 10^3 \text{ L}/(\text{g}\cdot\text{mol})(\text{s})$$

3. Two macromolecules

$$k_p^* \sim 10^3 \text{ L}/(\text{g}\cdot\text{mol})(\text{s})$$

$$k_{tc}, k_{td} \sim 10^8 \text{ L}/(\text{g}\cdot\text{mol})(\text{s})$$

We will make the hypothesis that reactions which involve large molecules and are intrinsically rapid under chemical control will be reduced in rate sooner or at lower polymer concentrations due to diffusion limitations than those reactions which are less rapid and involve small molecules. It is an accepted fact that termination reactions become diffusion controlled very early in a polymerization, leading to an increase in the radical population and an acceleration in the rate of polymerization. It is also well known that for polymerization temperatures below the glass transition temperature of the polymer being synthesized, a glassy-state transition occurs with the propagation reaction rate falling to effectively zero [4-8]. The propagation rate clearly becomes limited by diffusion of monomer to the radical center. Figure 1 shows limiting conversion data for PVC. At limiting conversion the polymer-monomer solution is a glass and the polymerization temperature equals the glass transition temperature (T_g) of the solution. T_g data measured using other analytical techniques are also shown [9, 10]. The effects of chain entanglements and glassy-state transition are clearly shown in Fig. 2. Hayden and Melville [11] investigated the bulk polymerization of methyl methacrylate at 22.5°C, a temperature much lower than the T_g of PMMA which is about 110°C. They followed the decrease of both termination and propagation constants and the polymerization rate during the course of reaction. From the data in Fig. 2 it is clear that the T_g of

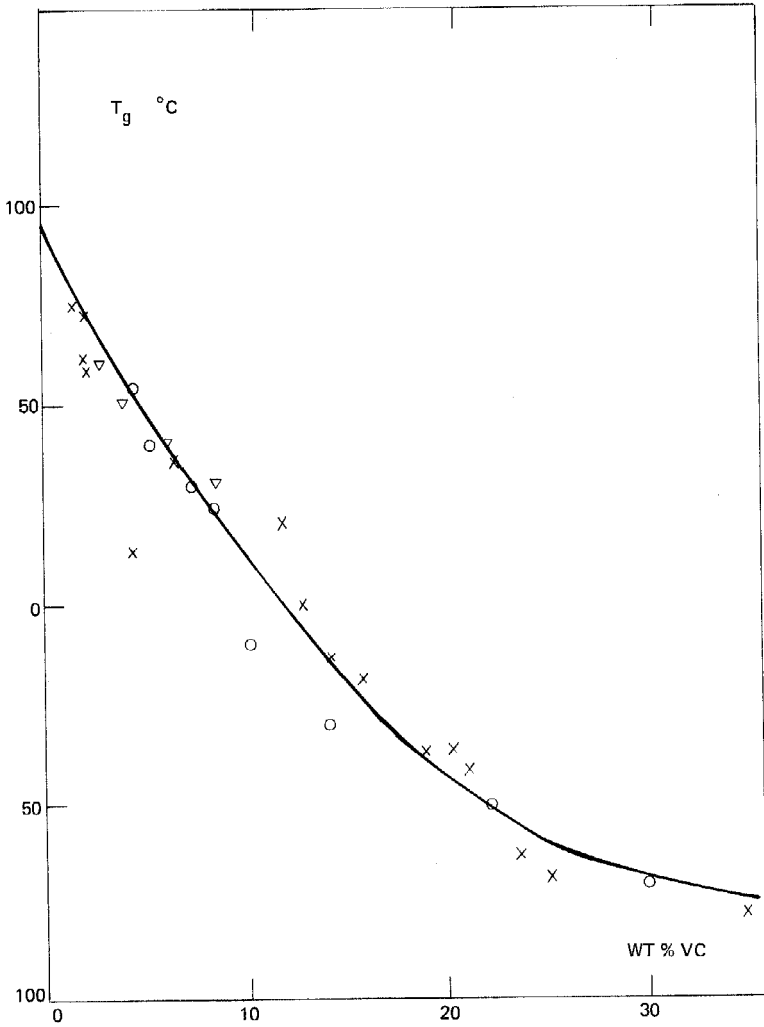


FIG. 1. T_g of PVC/VCM solutions. (∇) Data measured by means of deviation from Flory-Huggins isotherm after Berens [9]. (\times) Data measured thermomechanically after Ibragimou [10]. (\circ) Limiting conversion data [8].

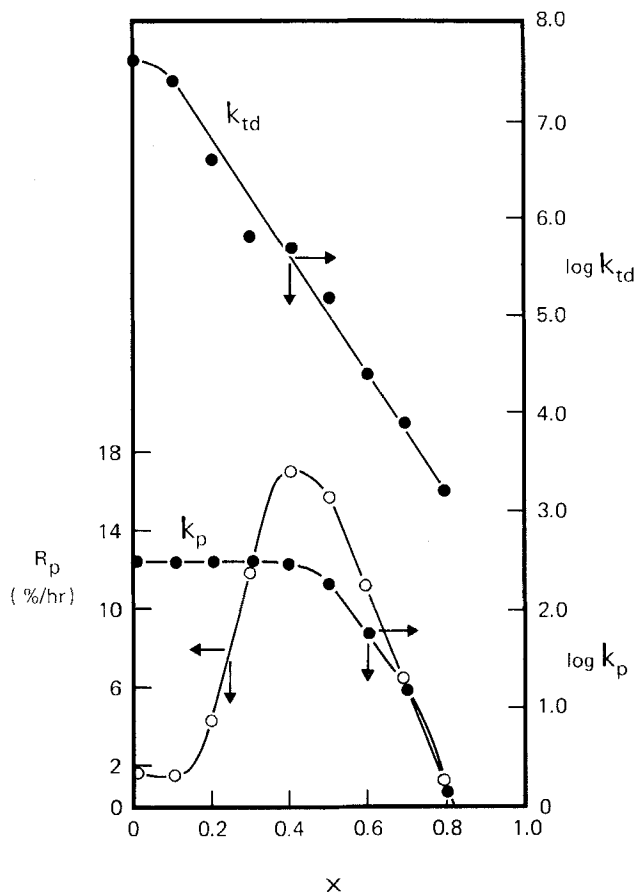


FIG. 2. Bulk polymerization of methyl methacrylate at 22.5°C with AIBN. Effect of conversion on propagation and termination rate constants after Hayden and Melville [11].

a solution containing about 80 wt% PMMA and 20 wt% MMA is 22.5°C. As expected, the termination constant (k_t) begins to fall at low conversions. It is of particular interest to note that the propagation constant (k_p) begins to fall at about 45% conversion, much before the glass transition point. In other words, we might expect a significant effect of diffusion-controlled propagation on polymer structure synthesized at higher conversions. On the basis of our original hypothesis, we would expect that the following rate constant ratios, k_{ft}/k_p , k_{ft}/k_p , k_{fm}/k_p , and k_{fp}/k_p , would increase appreciably with conversion

when the propagation reaction becomes diffusion controlled. The structure of the polymer chains depends on these rate constant ratios and one would therefore expect the molecular weight and the frequency of long-chain branching to increase dramatically. The transfer to monomer reaction deserves special consideration because of its importance in PVC synthesis. One would expect the ratio k_{fm}/k_p to remain constant even under diffusion control because the propagation and transfer-to-monomer reactions both involve the same reactants, a macroradical and monomer. The actual situation may be more subtle, however. One could imagine that the dynamics of the chain end depend somewhat on the Brownian motion of monomer molecules in its vicinity. Under a monomer-starved condition near the glass transition point, one could reasonably expect k_p and k_{fm} to fall in value. Our hypothesis is that k_p , which is associated with a reaction of much greater intrinsic reactivity, will fall much more than k_{fm} with the result that the ratio k_{fm}/k_p increases and the molecular weight decreases. Of course, there is a considerable degree of speculation involved and refinements must wait until there is adequate experimental data. The calculations on molecular weight development presented herein may have to be modified as more information on elementary reactions in PVC synthesis becomes available [12-15].

KINETIC MODELING OF DIFFUSION-CONTROLLED POLYMERIZATIONS

To estimate the dependence of the termination constant (k_t) on polymer concentration, molecular weight, and temperature, the following is assumed: The termination reaction becomes diffusion controlled and k_t falls with an increase in polymer concentration when the diffusion coefficient of a macroradical D_p becomes equal to or less than a critical diffusion coefficient ($D_p \leq D_{pcr}$). It is further assumed that the termination rate constant beyond this polymer concentration can be taken as proportional to the diffusion coefficient D_p of a polymer molecule in an entangled polymer matrix ($k_t \propto D_p$). Using arguments proposed by Bueche [8, 16] to derive an expression for the diffusion coefficient of a polymer molecule in an entangled polymer matrix, one can express k_t as

$$k_t \propto \bar{M}_w^n \exp(-A/V_f) \quad (1)$$

A consideration of the diffusion of a monomer molecule in an entangled polymer matrix leads to

$$k_p \propto \exp(-B/V_f) \quad (2)$$

Similar expressions for other small molecules such as initiator, chain transfer agent, and solvent can be used. Assuming volume additivity, V_f may be approximated by

$$V_f = (0.025 + \alpha_p(T_p - T_{gp}))\phi_p + (0.025 + \alpha_m(T_p - T_{gm}))\phi_m + (0.025 + \alpha_s(T_p - T_{gs}))\phi_s \quad (3)$$

where T_p is the polymerization temperature and T_{gp} , T_{gm} , T_{gs} are glass transition temperatures of polymer, monomer, and solvent, respectively. ϕ_p , ϕ_m , and ϕ_s are volume fractions of polymer, monomer and solvent, respectively. α_p , α_m , and α_s are the differences between the coefficient of volumetric expansion above and below the glass transition temperature for polymer, monomer, and solvent, respectively. The limiting conversion X_ℓ can be estimated using Eqs. (4) and (5):

$$T_p = T_g = \frac{\alpha_p T_{gp} \phi_p + \alpha_m T_{gm} (1 - \phi_p)}{\alpha_p \phi_p + \alpha_m (1 - \phi_p)} \quad (4)$$

$$X = \frac{(\rho_p/\rho_m)\phi_p}{1 - (1 - \rho_p/\rho_m)\phi_p} \quad (5)$$

for a monomer-polymer solution. Here T_g is the glass transition temperature of the polymer-monomer solution, X_ℓ is the limiting conversion, and ρ_p and ρ_m are polymer and monomer densities, respectively. At the point where the reacting mixture becomes a glass, $T_p = T_g$, and it is assumed that $V_f = 0.025$. These values are substituted into Eq. (3) to obtain Eq. (4). Equation (4) permits one to solve for ϕ_p which is then substituted in Eq. (5) to give X_ℓ . Again, additivity of volumes is assumed.

A general rate expression for homogeneous solution, bulk, and suspension polymerization has previously been derived [8] and follows:

$$\frac{dx}{dt} = \frac{[k_{p0} \exp(-B(\frac{1}{V_f} - \frac{1}{V_{f_{cr2}}}))](1-X)R_I^{1/2}}{\bar{M}_w \alpha} \frac{[k_{t0}(\frac{cr1}{\bar{M}_w}) \exp(-A(\frac{1}{V_f} - \frac{1}{V_{f_{cr1}}}))]^{1/2}}{\alpha} \quad (6)$$

$$R_I = \sum_{i=1}^N 2f_i k_{di} [I]_i \quad (7a)$$

$$[I]_i = \frac{N_{I_i}}{V_0(1-\epsilon X)} \quad (7b)$$

$$\frac{dN_{I_i}}{dt} = -k_{di} N_{I_i} \quad (7c)$$

$$\bar{M}_{w_{inst}} = \frac{2M_m(\tau + \beta/2)}{(\tau + \beta)^2} \quad (8a)$$

$$\bar{M}_w = \frac{1}{X} \int_0^X \bar{M}_{w_{inst}} dx \quad (8b)$$

$$\tau = \frac{k_{td}^{1/2} R_I^{1/2}}{k_p[M]} + \frac{k_{fm}}{k_p} + \frac{k_{fx}[X]}{k_p[M]} \quad (8c)$$

$$\beta = \frac{k_{tc}^{1/2} R_I^{1/2}}{k_p[M]} \longrightarrow \frac{k_{tc}^{1/2} R_I^{1/2}}{k_p[M]} \quad (8d)$$

Conversion Interval	1: $\alpha = 0,$	$A = 0$	$B = 0$
	2: $\alpha = 1.75,$	$A = A,$	$B = 0$
	3: $\alpha = 1.75,$	$A = A,$	$B = B$

In Conversion Interval 1, there is no diffusion limitation. In Interval 2, termination is diffusion controlled. In Interval 3, both termination and propagation are diffusion controlled. We will now apply these general rate expressions to the subsaturation polymerization of vinyl chloride and focus on molecular weight development.

SUBSATURATION POLYMERIZATION OF VCM

($X > X_c$, where X_c is the conversion when free monomer does not exist and reactor pressure begins to fall.)

Molecular Weight Development

When molecular weight development is controlled largely by transfer reactions and the amount of polymer produced by termination is small, molecular weight and branching development can be calculated using the set of equations after Graessley [17] which follow:

$$dQ_0/dX = C_M \quad (9)$$

$$dQ_1/dx = 1 \quad (10)$$

$$\frac{dQ_2}{dx} = 2 \left(\frac{1 + C_p Q_2}{C_M + \frac{C_p X}{1 - X}} \right) \quad (11)$$

$$\frac{d(Q_0 \bar{B}_N)}{dx} = C_p \left(\frac{X}{1 - X} \right) \quad (12)$$

where

$$C_M = k_{fm}/k_p, \quad C_p = k_{fp}/k_p$$

$$\bar{M}_N = M_m Q_1/Q_0 = 62.5X/Q_0 \quad (13a)$$

$$\bar{M}_w = M_m Q_2/Q_1 = 62.5Q_2/X \quad (13b)$$

The initial conditions are:

$$X = X_c, \quad Q_0 = X_c C_{M_0}, \quad Q_1 = X_c, \quad Q_2 = 2X_c / C_{M_0},$$

$$\bar{B}_N = 0$$

The parameters C_M and C_p may be expressed as

$$C_M = C_{M_0} \exp \left(B_M \left(\frac{1}{V_F} - \frac{1}{V_{F_{crM}}} \right) \right) \quad (14)$$

$$C_p = C_{p_0} \exp \left(B_p \left(\frac{1}{V_F} - \frac{1}{V_{F_{crp}}} \right) \right) \quad (15)$$

B_M , $V_{F_{crM}}$ and B_p , $V_{F_{crp}}$ are parameters which can be found by

fitting rate and molecular weight data. Over the conversion range where transfer to monomer and polymer are not diffusion controlled, we may set $B_M = B_p = B$ and $V_{F_{crM}} = V_{F_{crp}} = V_{F_{cr2}}$. B and $V_{F_{cr2}}$

may be found fitting only rate data.

The whole polymer \bar{M}_N , \bar{M}_W , and \bar{B}_N , the number-average number of branch points per polymer molecule, may be found by integrating Eqs. (9)-(15). One can also calculate $\bar{\lambda}_N$, the number of long branches per 1000 monomer repeat units, using

$$\bar{\lambda}_N = 1000 M_R (\bar{B}_N / \bar{M}_N)$$

where M_R is the molecular weight of the repeat unit. It is of interest to examine the variation of molecular weight and long-chain branching frequency for polymer produced in the conversion interval, $X > X_c$.

We will now calculate $\bar{M}_{N_{inst}}$, \bar{M}_N , \bar{M}_W , and $\bar{\lambda}_N$ for VCM polymerization using two pairs of B and $V_{F_{cr2}}$. These calculated quantities

are tabulated in Table 1. The effect of these parameters on molecular weight and branching development is clearly seen. To choose the correct pair of parameters, one can use limiting data and rate data for $X > X_c$. The pairs ($B = 0.25$, $V_{F_{cr2}} = 0.059$) and ($B = 0.20$,

$V_{F_{cr2}} = 0.085$) both gave a limiting conversion of 0.96. A consideration

TABLE 1. The Influence of Diffusion-Controlled Propagation on Molecular Weight and Branching Development-Batch Polymerization of VCM at 50°C and $X > X_C$, ($C_{M_0} = 1.22 \times 10^{-3}$ and $C_{P_0} = 1.0 \times 10^{-4}$)

V_F	X	$\bar{M}_{N_{inst}}$	\bar{M}_N	\bar{M}_W	$\bar{\lambda}_N$
$B = 0.25 V_{F_{cr2}} = 0.059$					
0.059	0.884	51,000	51,000	102,000	0
0.050	0.906	24,000	42,000	109,000	2.1
0.045	0.917	13,600	36,000	120,000	5.5
$B = 0.20 V_{F_{cr2}} = 0.085$					
0.085	0.820	51,000	51,000	102,000	0
0.075	0.845	37,000	49,000	105,000	0.2
0.065	0.870	25,000	47,000	120,000	0.6
0.055	0.894	14,100	42,000	165,000	2.5
0.045	0.917	6,300	34,000	260,000	10.9
0.040	0.928	3,600	30,000	663,000	32

of rate data for $X > X_C$ at 50°C after Abdel-Alim and Hamielec [19] revealed that $B = 0.20$ and $V_{F_{cr2}} = 0.085$ were the better pair and

should be used for molecular weight and branching calculations.

Let us again discuss the effect of diffusion-controlled propagation on molecular weight and long-chain branching development. When the radical center is in a monomer-starved condition, the dynamics of the macroradical chain may be significantly altered and as a consequence $k_{p0}[M]_C$ (where k_{p0} is the propagation constant under normal chemical control of propagation and $[M]_C$ is the monomer concentration at the radical center) may not equal the rate of monomer consumption per radical. The effective k_p may be considerably smaller than k_{p0} . A similar argument can be used for the transfer to monomer reaction with the change in macroradical dynamics reducing k_{fm} by a smaller extent than k_p . This is effectively a restatement of the original hypothesis. The rationale for the increased branching frequency is clear. Consider a finite conversion interval ΔX where propagation is diffusion controlled. A reduced propagation rate increases the polymerization time for ΔX and thus increases the number of

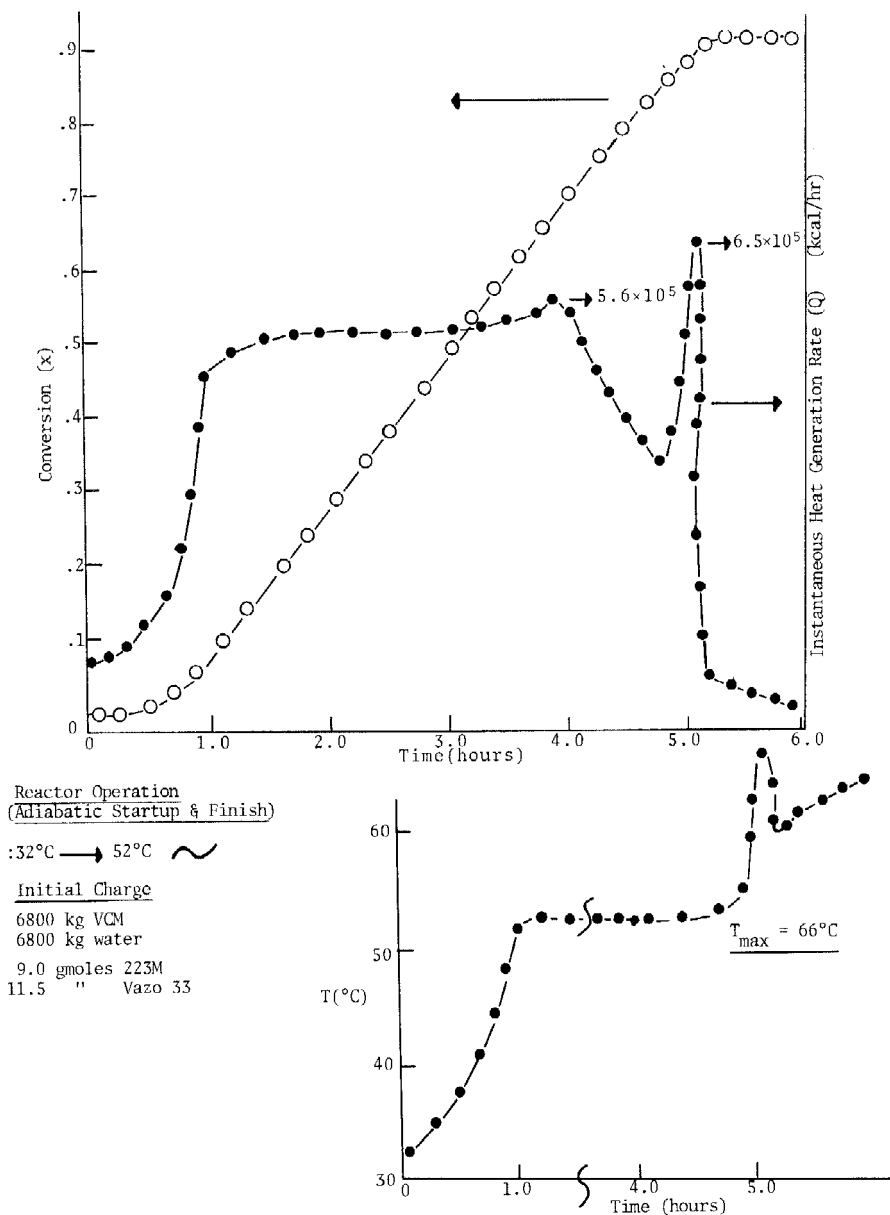
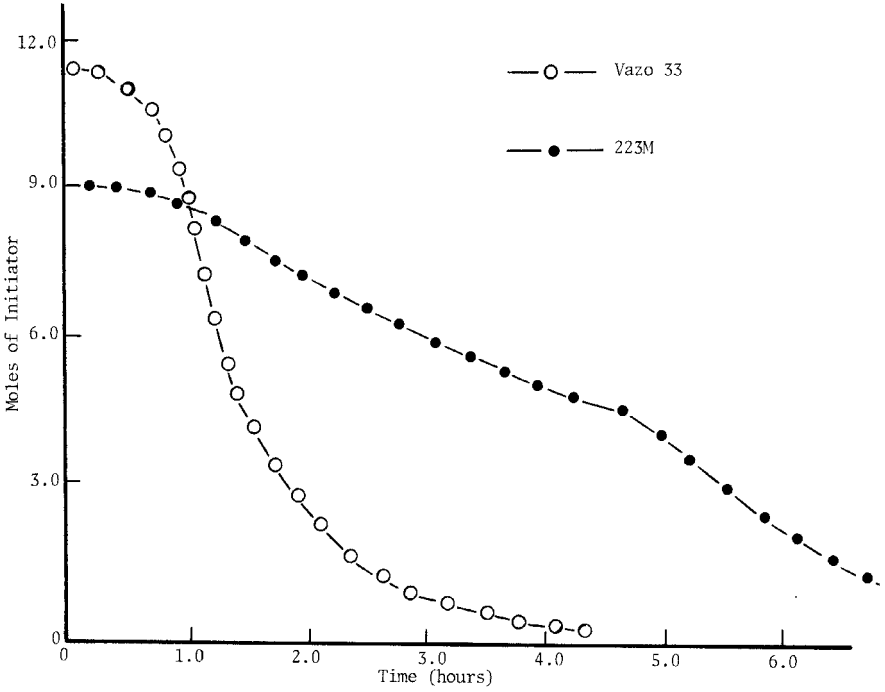


FIG. 3A. Suggested operation of a suspension reactor to maximize production rate and improve thermal stability of PVC resin. Temperature programming involving adiabatic heatup and finishing with a dual initiator system.



Reactor Operation
 (Adiabatic Startup & Finish)
 :32°C → 52°C ~~~~~
 Initial Charge
 6800 kg VCM
 6800 kg water
 9.0 gmoles 223M
 11.5 gmoles Vazo 33

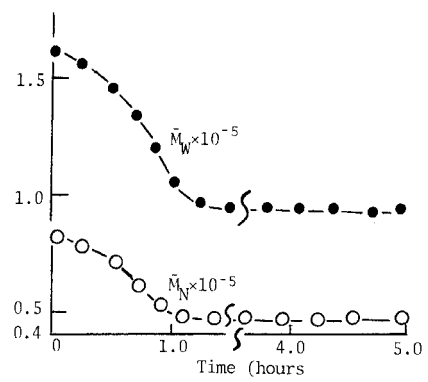


FIG. 3B. Suggested operation of a suspension reactor to maximize production rate and improve thermal stability of PVC resin. Removal of active residual initiator and molecular weight development.

Downloaded At: 07:37 25 January 2011

long-chain branches via chain transfer to polymer which occurs. We are, of course, assuming that the transfer to polymer reaction is either not diffusion controlled or that its reduction is less than that of k_p .

We have neglected the generation of long branches via terminal double bond reaction. It is probable that this reaction, which is not important at $X < X_C$, is less important at $X > X_C$. There is evidence that this reaction becomes diffusion controlled at relatively low conversions even when the polymerization temperature is above the glass transition temperature of the polymer being synthesized [20]. Measurements on the molecular structure of PVC synthesized at subsaturation conditions [1-3, 12-15] have revealed that very short chains containing terminal double bonds are produced. In addition, the number of long branches per 1000 monomer units is considerably larger than one might expect on the basis of chain transfer to polymer at high conversions. These observations are in qualitative agreement with our hypothesis that these abnormal effects are due to diffusion-controlled propagation. A great deal of research is required to establish the validity of this hypothesis unambiguously.

SUGGESTED OPERATING PROCEDURE OF A SUSPENSION REACTOR TO MAXIMIZE PRODUCTION AND OBTAIN PVC RESIN WITH IMPROVED THERMAL STABILITY

Thermal stability of PVC resin can be adversely affected when a suspension reactor is operated at high conversions in an attempt to increase production per batch. High levels of active residual initiator in the resin product can also be deleterious. A reactor-operating procedure which can overcome some of these limitations is shown graphically in Figs. 3A and 3B. The suggested procedure is to permit the reaction temperature to rise at the end of the batch where the heat generation rate has begun to fall due to limitations imposed by a glassy-state transition and diffusion-controlled propagation. The increase in temperature increases the free volume and decreases the influence of diffusion control on molecular weight and branching development. Intuitively, one would expect the increase in temperature to lower \bar{M}_N and raise $\bar{\lambda}_N$. Under diffusion-controlled propagation the opposite is true as the dependence on the free volume is much greater than the dependence of \bar{M}_N and $\bar{\lambda}_N$ on temperature. At a conversion of 91% the $\bar{\lambda}_N$ calculated for the simulations shown in Figs. 3A and 3B was 1.48 long branches per 1000 monomer units. The same simulation but with the temperature kept constant at 52°C to the end of the batch at a conversion of 91% gave a $\bar{\lambda}_N = 11.6$. The recommended procedure of raising the temperature at the end of the batch

should give a PVC resin with higher thermal stability. Additional benefits include a shorter polymerization time and a lower level of active initiator in the PVC resin product. This should lead to a PVC resin with a higher thermal stability.

REFERENCES

- [1] E. M. Sorvik, J. Polym. Sci., Polym. Lett. Ed., **14**, 735 (1976).
- [2] E. M. Sorvik and T. Hjertberg, J. Macromol. Sci.-Chem., **A11(7)**, 1349 (1977).
- [3] T. Hjertberg and E. M. Sorvik, J. Polym. Sci., Polym. Chem. Ed., **16**, 645 (1978).
- [4] S. T. Balke and A. E. Hamielec, J. Appl. Polym. Sci., **17**, 905 (1973).
- [5] R. T. Ross and R. L. Laurence, AIChE Symp. Ser., **160**, 72, 74 (1976).
- [6] N. Friis and A. E. Hamielec, in Emulsion Polymerization (Am. Chem. Soc. Symp. Ser. 24), American Chemical Society, Washington, D.C., 1976, p. 82.
- [7] D. C. Sundberg and D. R. James, J. Polym. Sci., Polym. Chem. Ed., **16**, 523 (1978).
- [8] L. Marten and A. E. Hamielec, in Polymerization Reactors and Processes (Am. Chem. Soc. Symp. Ser. 104), American Chemical Society, Washington, D.C., 1978, p. 43.
- [9] A. R. Berens, The Sorption of Gases and Vapors in PVC Powders (Am. Chem. Soc. Symp. Ser. 39), American Chemical Society, Washington, D.C., 1978, p. 236.
- [10] I. Y. Ibragimov, D. N. Bort, and V. N. Efremova, Vysokomol. Soedin., Ser. B, **16(5)**, 376 (1974).
- [11] P. Hayden and Sir Harry Melville, J. Polym. Sci., **43**, 201 (1960).
- [12] W. H. Starnes, Jr., F. C. Schilling, L. M. Plitz, R. E. Cais, D. J. Freed, and F. A. Bovey, "Recent Studies on PVC Using Carbon-13 NMR. Direct Structural Evidence for the Presence of Tertiary Chloride and for the Involvement of Free Chlorine Atoms in the Mechanism for Chain Transfer to Monomer During Vinyl Chloride Polymerization," Abstracts-Third International Symposium on PVC, Case Western Reserve University, Cleveland, Ohio, August 10-15, 1980.
- [13] T. Hjertberg and E. M. Sorvik, "Anomalous Structures Influencing the Thermal Stability of PVC," Abstracts-Third International Symposium on PVC, Case Western Reserve University, Cleveland, Ohio, August 10-15, 1980.
- [14] T. Hjertberg and E. M. Sorvik, "Polymerization of VCM at Subsaturation Pressure," Abstracts-Third International Symposium on PVC, Case Western Reserve University, Cleveland, Ohio, August 10-15, 1980.

- [15] D. Braun and G. Holzer, "Polymerization of Vinyl Chloride at Atmospheric Pressure—Structure and Thermal Stability of the Polymers," Abstracts—Third International Symposium on PVC, Case Western Reserve University, Cleveland, Ohio, August 10-15, 1980.
- [16] F. Beuche, Physical Properties of Polymers, Wiley-Interscience, New York, 1962.
- [17] W. W. Graessley, W. C. Uy, and A. Gandhi, Ind. Eng. Chem., Fundam., 8, 696 (1969).
- [18] N. Friis and A. E. Hamielec, J. Appl. Polym. Sci., 19, 97 (1975).
- [19] A. H. Abdel-Alim and A. E. Hamielec, Ibid., 16, 783 (1972).
- [20] N. Friis, D. Goosney, J. D. Wright, and A. E. Hamielec, Ibid., 18, 1247 (1974).

Note Added in Proof. Diffusion-controlled propagation applied to the recently published mechanism after Starnes [12] leads to similar conclusions. At high conversions the chlorine atom radical concentration and the number of tertiary chlorines on the PVC chains increase dramatically.