Polymerization Reactor: The Influence of "Gel Effect" in Batch and Continuous Solution Polymerization of Methyl Methacrylate

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Synopsis

This article describes the influence of gel effect in the free radical polymerization of methyl methacrylate. A mathematical model has been developed which tries to predict the performance of batch and continuous polymerization reactors under dynamic and steady-state conditions. The influence of diffusion phenomena on the process kinetics (gel effect) is very important. The autoacceleration in the polymerization rate of the batch reactor and the multiple steady state for the continuous stirred tank reactor (CSTR) are connected with the attainment of critical conditions in the system. Such a model is useful for the design of the reactor and the choice of the control system.

INTRODUCTION

The knowledge of diffusion phenomena and gel effect (Trommsdorff effect) in free radical polymerization is crucial in the description of the polymerization process at high conversion.

Termination reactions and the propagation rate at high conversion are controlled by diffusion phenomena with consequent autoacceleration on the polymerization rate.

In this connection, the onset of a "gel effect" is important, since it affects not only the rate of conversion but, more importantly, the molecular weight distribution of the polymeric products.

Several authors have proposed semiempirical relationships between the rate constants and the reaction conditions.[1-6]

The free volume of solution is a particularly important parameter in relating the influence of chain polymer mobility to the termination constant.

A few years ago, Ross and Laurence[3] developed an interesting relationship for bulk polymerization of methyl methacrylate (MMA) that has been recently extended by Schmidt and Ray[7] to solution polymerization. Meanwhile, Soh and Sundberg[6] have carried out a fundamental study of diffusion-controlled polymerization.

This article attempts to survey the influence of the gel effect in solution free radical polymerization of MMA. For this purpose, we have developed a

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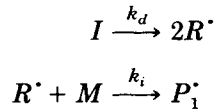
mathematical model to predict the performances of batch and continuous polymerization reactors under dynamic and steady-state conditions.

The model makes it possible to predict conversion-time curves, heat flux, and polymer properties as the average molecular weight and polydispersity, under different operative conditions.
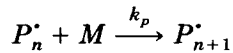
DEVELOPMENT OF THE REACTOR MODEL

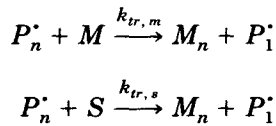The kinetic mechanism used for our study is the following, which is typical for free radical polymerization.
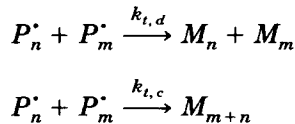
Initiation:

$$I \xrightarrow{k_d} 2R^{\cdot}$$

$$R^{\cdot} + M \xrightarrow{k_i} P_1^{\cdot}$$

Propagation:

$$P_n^{\cdot} + M \xrightarrow{k_p} P_{n+1}^{\cdot}$$

Chain transfer:

$$P_n^{\cdot} + M \xrightarrow{k_{tr,m}} M_n + P_1^{\cdot}$$

$$P_n^{\cdot} + S \xrightarrow{k_{tr,s}} M_n + P_1^{\cdot}$$

Termination:

$$P_n^{\cdot} + P_m^{\cdot} \xrightarrow{k_{t,d}} M_n + M_m$$

$$P_n^{\cdot} + P_m^{\cdot} \xrightarrow{k_{t,c}} M_{m+n}$$

where I is the initiator, $R^{\cdot}$ is the (primary) free radical species, M is the monomer, S is the solvent, $P_n^{\cdot}$ is the growing polymer chain, M_n is the dead polymer chain and k_d, k_i, k_p, $k_{tr,m}$, $k_{tr,s}$, $k_{t,d}$, and $k_{t,c}$ are the kinetic constants relevant to each single corresponding step.

In order to predict the average molecular weight of the polymer and its distribution, the moments of the molecular weight distribution can be used. These moments can be defined by

$$\lambda_j = \sum_{n=1}^{\infty} n^j |P_n|$$

$$\mu_j = \sum_{n=1}^{\infty} n^j |M_n|$$

$$\epsilon_j = \sum_{n=1}^{\infty} n^j |P_n| + \sum_{n=2}^{\infty} n^j |M_n|$$

where λ_j, μ_j, and the ϵ_j are the j-th order moment of the growing, dead and global polymer chains, respectively.

The physical significance of the leading moments is very useful in forming the modeling equations.

For example, λ_o is the concentration of growing chains, μ_o is the concentration of dead polymer chains, ϵ_1 is the number of monomer units n the polymer chains. The technique of the generating function[8] is indeed a useful approach in determining the values of the distribution moments.

The generating functions for this system are defined as:

$$G(s, t) = \sum_{n=1}^{\infty} s^n P_n(t) \text{ for growing polymer chains}$$

$$F(s, t) = \sum_{n=1}^{\infty} s^n M_n(t) \text{ for dead polymer chains}$$

$$H(s, t) = \sum_{n=1}^{\infty} s^n (P_n(t) + M_n(t)) \text{ for growing and dead polymer chains}$$

Use of these functions provides the moments of the molecular weight distribution of the j-th order

$$\lambda_j = \left(\frac{\partial^j G(s, t)}{\partial s^i} \right)_{s=1} ; \qquad \mu_j = \left(\frac{\partial^j F(s, t)}{\partial s^j} \right)_{s=1}$$

$$\epsilon_j = \left(\frac{\partial^j H(s, t)}{\partial s^j} \right)_{s=1}$$

The parameters characterizing polymer quality, as averages of molecular weight and polydispersity, are obtained from the calculation of the j-th order moment using the following relations:

$$\overline{M}_n = \frac{\epsilon_1 - M}{\epsilon_o - M} W; \qquad M_w = \frac{\epsilon_2 - \epsilon_1 - M}{\epsilon_o - M} W$$

$$PD = \frac{(\epsilon_o - M)(\epsilon_2 + \epsilon_1 - M)}{(\epsilon_{1'} - M)^2}$$

(W = molecular weight of monomer)

According to this procedure, the mass and heat balance equations for species and moments relevant to CSTR reactor under dynamic conditions are the following:

mass balance $q_o X_{io} - qX_i - Vr_{xi} = d(VX_i)/dt$

heat balance $c_p(q_o \rho_o T_o - q\rho T) - V\Delta H_p r_m - Q_s = \rho c_p d(VT)/dt$

where X_i is the concentration of a generic species and r_{xi} is the relevant reaction rate, Q_s is the heat removed by the heat exchange devices.

The reaction rate for the single species of the reacting system are:

$$r_i = k_d I$$

$$r_m = -2k_d fI - \left(k_p + k_{tr,m}\right)M\lambda_o + k_{td}P_1\lambda_o + k_{tr,m}MP_1 + k_{tr,s}SP_1$$

$$r_{P1} = 2k_d fI + (k_{tr,m}M + k_{tr,s}S)\lambda_o - k_{tr,m}MP_1 - k_pMP_1$$

$$- (k_{td} + k_{tc})P_1\lambda_o - k_{tr,s}SP_1$$

$$r_{\lambda o} = 2k_d fI - (k_{tc} + k_{td})\lambda_o^2$$

$$r_{\lambda 1} = 2k_d fI - k_{tr,m}M(\lambda_1 - \lambda_o) + k_pM\lambda_o - (k_{tc} + k_{td})\lambda_o\lambda_1$$

$$- k_{tr,s}S(\lambda_1 - \lambda_o)$$

$$r_{\epsilon o} = -0.5k_{tc}\lambda_o^2 - k_pM\lambda_o + k_{tr,s}S\lambda_o$$

$$r_{\epsilon 1} = k_{tr,s}S\lambda_o$$

$$r_{\epsilon 2} = 2k_pM\lambda_1 + k_{tc}\lambda_1^2$$

In converting from monomer to polymer, the density of the reaction system is increased, so this change must be taken into consideration in the reactor model.

Let us define the volume contraction factor as follows

$$\epsilon = \frac{\rho_m}{\rho_p} - 1$$

where ρ_m is the density of the monomer and ρ_p is the density of the polymer.

This change in density gives rise to a contraction of volume during the reaction; if it is assumed that the additivity of the volumes is valid, the expression of volume change during the reaction is the following:

$$V = V_o(1 + \epsilon\phi_mC)$$

where V_o is the initial volume of solution, ϕ_m is the initial volume fraction of the monomer, and C is the conversion.

In comparison with this assumption, the model equation for a batch reactor is given in Table I.

In the case of a CSTR reactor, assuming that the volume of the reactor is constant, the change in density influences the value of the outlet flowrate q; this varies according to the following expression:

$$q = q_o(1 + \epsilon\phi_mC)$$

TABLE I
Balance Equations for the Isothermal Batch Reactor

$$\frac{dV}{dt} = -\frac{V_o \epsilon \phi_m}{M_o} \frac{dM}{dt}$$

$$\frac{dI}{dt} = \xi \frac{dM}{dt} I + r_i$$

$$\frac{dM}{dt} = \frac{r_m}{(1 - \xi M)}$$

$$\frac{dS}{dt} = \xi \frac{dM}{dt} S$$

$$\frac{d\epsilon_o}{dt} = \xi \frac{dM}{dt} \epsilon_o + r_{\epsilon_o}$$

$$\frac{d\epsilon_1}{dt} = \xi \frac{dM}{dt} \epsilon_1 + r_{\epsilon_1}$$

$$\frac{d\epsilon_o}{dt} = \xi \frac{dM}{dt} \epsilon_o + r_{\epsilon_o}$$

$$\frac{d\epsilon_1}{dt} = \xi \frac{dM}{dt} \epsilon_1 + r_{\epsilon_1}$$

$$\frac{d\epsilon_2}{dt} = \xi \frac{dM}{dt} \epsilon_2 + r_{\epsilon_2}$$

where:

$$V = V_o(1 + \epsilon \phi_m C)$$

$$\xi = \frac{\epsilon \phi_m}{(1 + \epsilon \phi_m C)M_o}$$

The model equations for a CSTR reactor under dynamic conditions are given in Table II.

The analysis of the dynamic behavior of the CSTR and the batch reactor was carried out by solving numerically the relevant set of ordinary differential equations by means of the Runge-Kutta variable-step method. The steady-state conditions of the CSTR are calculated by solving the system of algebraic equations using the Newton-Raphson method.

The specific reaction system analyzed in this article is the polymerization of methyl methacrylate (MMA) in ethyl acetate solution initiated by azo-bisisobutyrronitrile (AIBN) in a temperature interval of 20 K between 328 and 348 K. The values of the kinetic constants utilized (Table III), were obtained from data in the literature,[9] whereas the value of the constant of transfer to the solvent was obtained from experimental data.[10]

The relation of Ross and Laurence,[3] slightly modified to match solution polymerization conditions, was used to explain the influence of chain–polymer mobility on the termination kinetic constant.[11]

The free volume of solution V_f is the parameter used for correlating the diffusion phenomena with the values of the kinetic constants. This parameter

TABLE II
Balance Equations for the CSTR Reactor

$$\frac{dI}{dt} = \frac{I_o - I}{\tau} + r_i$$

$$\frac{dM}{dt} = \frac{M_o - M}{\tau} + r_m$$

$$\frac{dS}{dt} = \frac{S_o - S}{\tau}$$

$$\frac{d\lambda_o}{dt} = -\alpha \frac{\lambda_o}{\tau} + r_{\lambda_o}$$

$$\frac{d\lambda_1}{dt} = -\alpha \frac{\lambda_1}{\tau} + r_{\lambda_1}$$

$$\frac{d\epsilon_o}{dt} = \frac{M_o - \alpha\epsilon_o}{\tau} + r_{\epsilon_o}$$

$$\frac{d\epsilon_1}{dt} = \frac{M_o - \alpha\epsilon_1}{\tau} + r_{\epsilon_1}$$

$$\frac{d\epsilon_2}{dt} = -\alpha \frac{\epsilon_2}{\tau} + r_{\epsilon_2}$$

where:

$$q = q_o(1 + \epsilon\phi_m C)$$

$$\alpha = 1 + \epsilon\phi_m C$$

TABLE III
Values of Kinetic Parameters for Free Radical
Polymerization of MMA Initiated by AIBN

$k_d = 1.33 \times 10^{15} \exp(-30700/RT)$

$k_p = 4.41 \times 10^5 \exp(-4350/RT)$

$k_{tr, m} = 4.67 \times 10^{-2} \exp(-888/RT)$

$k_{tr, s} = 6.55 \times 10^{14} \exp(-24000/RT)$

$k_{to} = 6.5 \times 10^7 \exp(-700/RT)$

$k_{t, d} = 0.108 k_t$

$k_{t, c} = 0.892 k_t$

$f = 0.4$

$v_{f, m} = 0.025 + 0.001(T - 167)$

$v_{f, m} = 0.025 + 0.001(T - 181)$

$v_{f, p} = 0.025 + 0.00048(T - 387)$

$v_{f, cr} = 0.1856 - 2.965 \times 10^4(T - 273.16)$

$v'_{t, cr} = 0.055$

$g_t = 0.10575 \exp(17.15 v_f - 0.01715(T - 273.16)$ for $v_f > v_{f, cr}$

$g_t = 2.3 \times 10^{-6} \exp(75 v_f)$ for $v_f \leq v_{f, cr}$

$g_p = 1$ for $v_f > v'_{f, cr}$

$g_p = 7.1 \times 10^{-5} \exp(171.53 v_f)$ for $v_f \leq v'_{t, cr}$

$\Delta H_p = -14{,}000$ cal/mol

can be calculated from the specific contribution of the individual species:

$$v_f = v_{f,m}\phi_m + v_{f,s}\phi_s + v_{f,p}\phi_p$$

where ϕ_m, ϕ_s, and ϕ_p are the volume fraction with $v_{f,m}$, $v_{f,s'}$ and $v_{f,p}$ are the specific free volume of monomer, solvent, and polymer, respectively.

The critical free volume of solution is an important parameter in that the mobility of a chain is greatly reduced in the case of smaller free volume values. The relation can be represented by the following analytical expressions[6,7]:

$$v_{f,m} = 0.025 + 0.001(T - 167)$$

$$v_{f,s} = 0.025 + 0.001(T - 181)$$

$$v_{f,p} = 0.025 + 0.00048(T - 387)$$

$$v_{f,cr} = 0.01856 - 2.965E\text{-}04(T - 273.16)$$

$$v'_{f,cr} = 0.055$$

$$k_t = k_{t,o}\big|0.010575\exp(17.15v_f - 0.01715(T - 273.16)\big| \qquad \text{if } v_f > v_{f,cr}$$

$$k_t = k_{t,o}\big[2.3 \times 10^{-6}\exp(75v_f)\big] \qquad \text{if } v_f \le v_{f,cr}$$

The behavior of the $k_t/k_{t,o}$ versus conversion at different values of ϕ_m is reported in Figure 1.
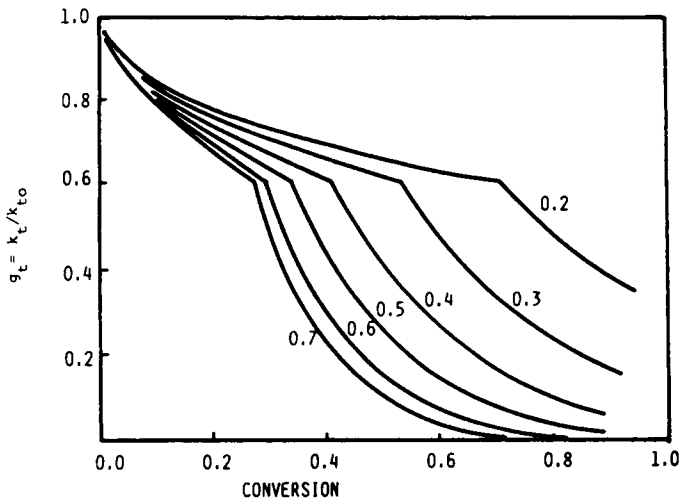

Fig. 1. Influence of monomer concentration on the termination rate constant for solution polymerization of MMA at 65°C.
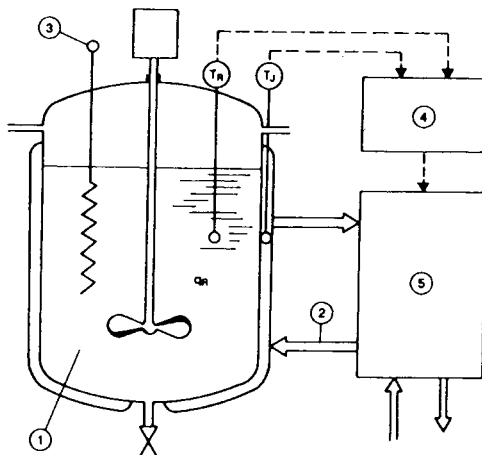
Fig. 2. Schematic representation of the reactor used in this work. (1) Reactor; (2) heat transfer medium; (3) heater; (4) Control instrument; (5) thermostatic unit.

At still higher conversion, the mobility of monomer is also reduced and the values of the propagation rate decrease rapidly.

$$k_p = k_{po} \qquad \text{if } v_f > v'_{f,cr}$$

$$k_p = k_{po} \left| 7.1 \times 10^{-5} \exp\left(171.53 v_f\right)\right| \qquad \text{if } v_f \leq v'_{f,cr}$$

EXPERIMENTAL APPARATUS

An outline of the apparatus used in the experimental runs is shown in Figure 2. It is designed in such a way that isothermal experiments may be carried out under different conditions.

The jacketed glass reactor can contain two liters and is equipped with a stirrer for mixing the reactant system. The reactor temperature is monitored continuously using two thermocouples, one of which is used for data acquisition by a recorder, whereas the other is used for temperature control.

A thermostat is used to maintain a selected temperature inside the reactor by comparing it with the temperature of the jacket.

The head of the reactor has five connections used for nitrogen, monomer solution, initiator inlets, thermocouples, and stirrer fittings.

The stabilized commercial monomer (MMA) supplied by Inalco was washed with NaOH (5% solution) to remove the inhibitor. The monomer and the solvent were dried with anhydrous calcium chloride and distilled.

The radical initiator (AIBN) was dissolved in chloroform and recrystallized in ethanol.

Prior to any run, the monomer solution and the reactor were purged with nitrogen in order to ensure an inert atmosphere.

Measured quantities of monomer and solvent were introduced into the reactor and heated to the operating temperature; a measured quantity of AIBN solution was then added to the reactor.
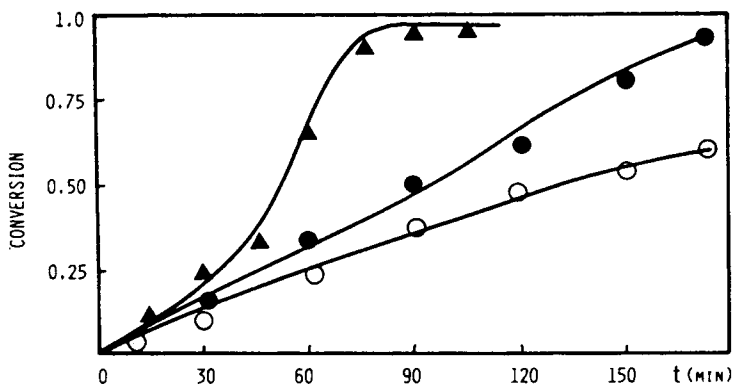
Fig. 3. Comparison between conversion-time curves predicted by model and experimental data. $T = 65°C$. Our experiment: (○) $\phi_m = 0.3$, $I_o = 1.1\%$; (●) $\phi_m = 0.5$, $I_o = 1.1\%$. Ref. 6: (▲) $\phi_m = 1.0$, $I_o = 0.5\%$.

During polymerization, samples were taken by a sampling system placed at the bottom of the reactor. These were analyzed gravimetrically to determine conversion; the average molecular weights were determined by viscosimetry.

Using these measurements it was possible to determine the density and the volume contraction during polymerization.

RESULTS

To verify the model's ability to predict the results of the experiments, several polymerization runs of MMA were carried out in the presence of AIBN in a batch reactor under different operating conditions.[10] To extend this analysis to a large range of operating conditions, the experimental data reported by Balke and Hamielec[2] and by Ito[12] were also used.

The results of the model's prediction are compared with the experimental conversion time data at different values of ϕ_m (Figs. 3 and 4); analogously, the
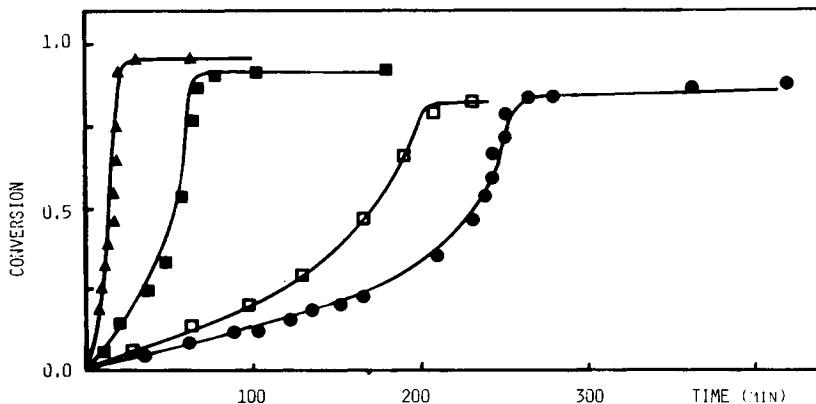

Fig. 4. Comparison between conversion-time curves predicted by the model and experimental data. Bulk polymerization of MMA: ▲: $T = 90°C$, $I_o = 0.5\%$, Ref. 6; ■: $T = 70°C$, $I_o = 0.5\%$, Ref. 6; □: $T = 50°C$, $I_o = 0.5\%$, Ref. 6; ●: $T = 45°C$, $I_o = 1.15\%$, Ref. 12.

TABLE IV

Comparison Between Experimental and Theoretical Average Molecular Weight and Polydispersity Values Obtained in Runs at Different Values of ϕ_m

| ϕ_m	Conversion	M_w Experimental	M_w Theoretical	PD Experimental	PD Theoretical
		Operating condition: $T = 65°C$; $[I]_o = 1.1\%$			
0.3	0.30	61,000	59,300		2.10
0.3	0.60	58,200	56,000		2.15
0.5	0.30	98,500	102,000		2.09
0.5	0.45	91,000	94,000		2.17
0.5	0.60	86,600	88,000		2.20
		Operating condition: $T = 70°C$; $[I]_o = 0.5\%$			
1	0.14	272,000	263,000	2.39	2.05
1	0.33	391,000	387,000	3.20	2.70
1	0.59	898,000	865,000	5.02	4.86
1	0.76	1,175,000	1,193,000	5.20	5.31
1	0.90	1,380,000	1,350,000	5.39	5.46
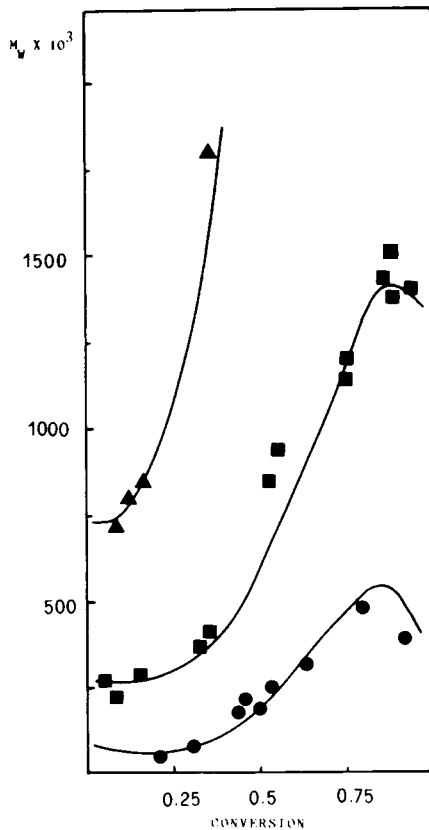
Fig. 5.   Comparison between the values of M_w versus conversion predicted by the model and experimental data. Bulk polymerization of MMA. ●: $T = 90°C$, $I_o = 0.5\%$, Ref. 6; ■: $T = 70°C$, $I_o = 0.5\%$, Ref. 6; ▲: $T = 50°C$, $I_o = 0.5\%$, Ref. 6.
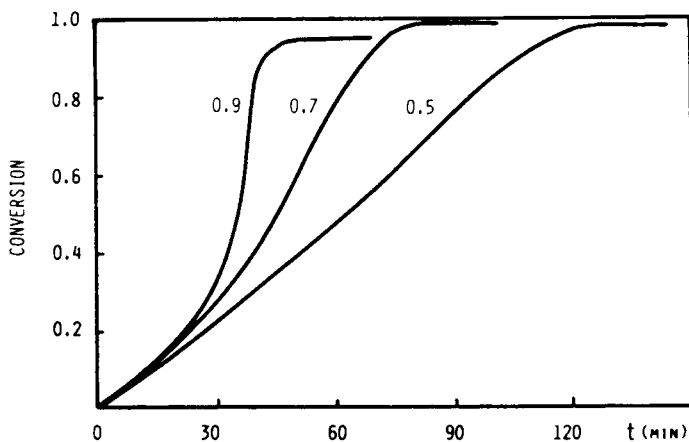

Fig. 6.   Predicted conversion-time curves for MMA solution polymerization in batch reactor at different values of ϕ_m. $T = 70°C$, $I_o = 1.1\%$.
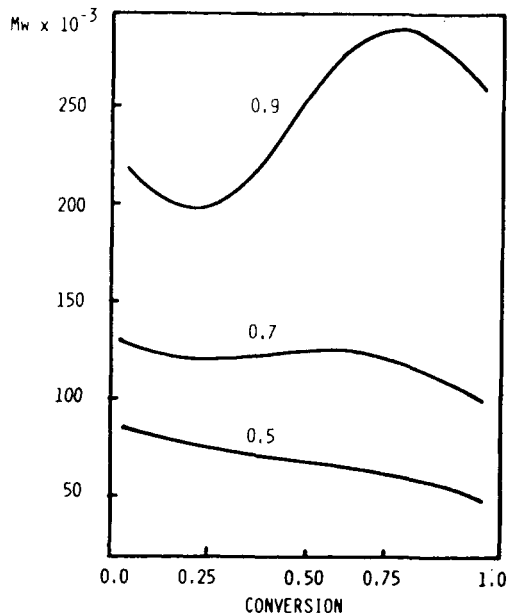
Fig. 7. Predicted values weight-average molecular weight versus conversion for MMA solution polymerization in batch reactor at different values of ϕ_m. $T = 70°C$, $I_o = 1.1\%$.

experimental average molecular weights and polydispersities are compared with the values predicted by the model (Table IV, Fig 5).

All the experimental data can explained remarkably well by the model for polymerization in a very large range of initial concentrations of the monomer.

Using the predictions supplied by the model, it is possible to analyze the influence of gel effect on the performance of continuous and discontinuous polymerization reactors.

By the analysis of theoretical and experimental conversion curves for conversions ϕ_m larger than 0.5, a sharp acceleration can be observed in the
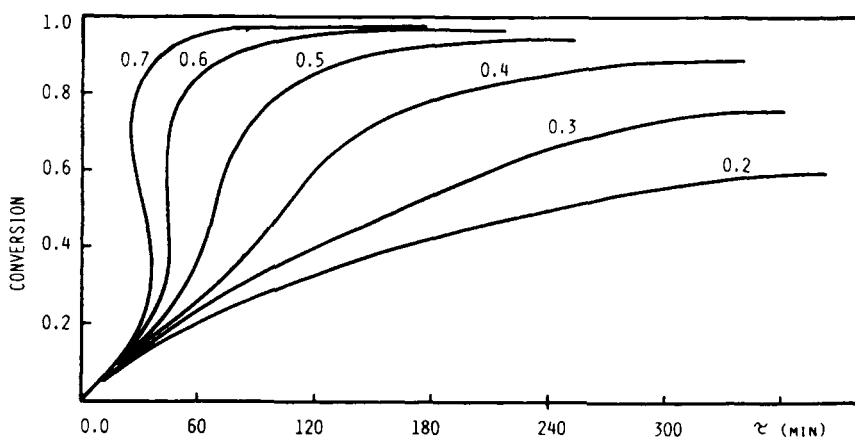

Fig. 8. Steady states for MMA solution polymerization in CSTR reactor at different values of ϕ_m. $T = 65°C$.

batch polymerization runs, corresponding to the point at which the critical value of free volume in the reaction solution is reached (Figs. 3 and 6).

This acceleration is also connected with a certain increase in the average molecular weight, this increase obviously reaches its highest value when the bulk polymerization conditions are attained.

The average molecular weight versus conversion curves are given in Figure 7. Using the predictions supplied by the model, a theoretical analysis of continuous polymerization reactor (CSTR) behavior was carried out for steady-state and dynamic conditions in order to evaluate the influence of the different operating conditions upon the yields and the properties of the products.

The steady-state model predictions, under given conditions, are contained in Figure 8 while Figure 9 shows in particular, the conversion versus the residence time (τ) at different temperatures.

On the basis of the models prediction, the possibility of obtaining a multiple steady state exists for an inlet monomer volume fraction ϕ_m higher than 0.5; this phenomenon, already predicted by other authors, is connected with the interaction between kinetic and diffusional phenomena. Indeed, in a concentrated solution system, for values of free volume near the critical value, a slight increment in the conversion can produce a very sharp reduction in polymer chain mobility, and, consequently, in the value of the termination constant. Under these conditions, a slight increment in the reactor residence time can give rise to a large increase in the conversion, because of the possibility of obtaining a multiple steady state.

In the same way, the average molecular weights are greatly influenced by the reduction in chain mobility; the large increase in the value of $\overline{M}_w$ is connected with the attainment of the critical volume of solution.

The influence of different operating conditions on the average molecular weight is summarized in Figure 10. For values of ϕ_m larger than 0.5, the value of $\overline{M}_w$ versus conversion reaches a maximum and decreases rapidly at higher values of conversion.
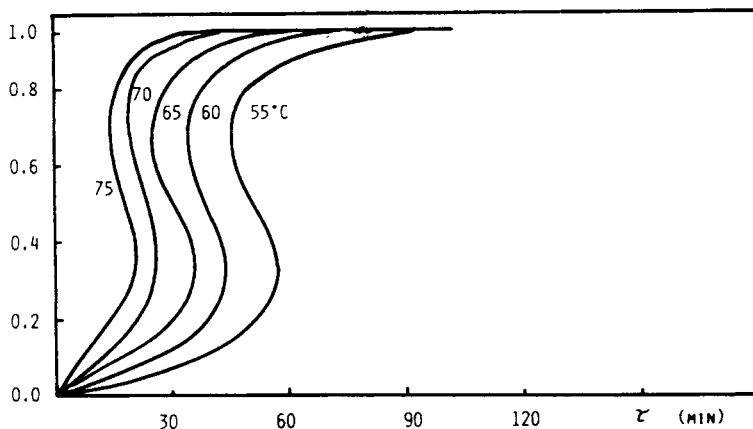

Fig. 9. Steady states for MMA solution polymerization in CSTR reactor at different temperatures. $\phi_m = 0.7$.

CONCLUSIONS

The model for solution polymerization of NMA proposed here is indeed a very efficient tool for the investigation of the behavior of different polymerization reactors. Our model does not yet have fitted parameters, but it can predict very well the performance of the solution polymerization reactor both in batch and continuous operation.

Especially interesting are the ability of the model to predict the average values of the molecular weights and the attainment of critical free volume conditions.

The influence of solvent fraction on the performance of the reactor is very important because the mobility of polymer chains depends greatly upon the presence of solvent in the reactor.

The autoacceleration in the conversion-time curves of the batch reactor and the multiple steady state for the CSTR reactor is connected with the attainment of the critical value in the free volume of the reactant solution.
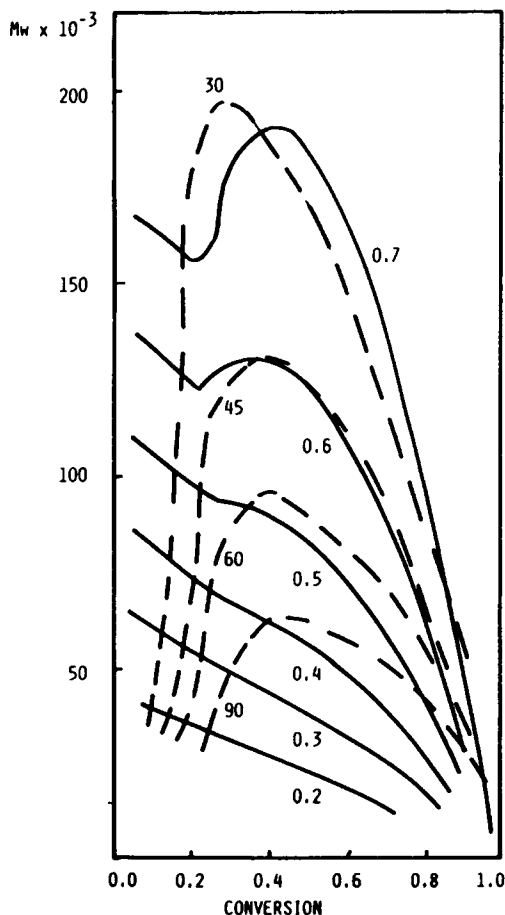

Fig. 10.   Weight-average molecular weight versus conversion at steady state for MMA solution polymerization in CSTR reactor at different values of ϕ_m (——) and τ (- - -). $T = 65°C$, $I_o = 1.1\%$.

This phenomenon has been observed to greatly influence average molecular weight values.

Because the kinetic scheme for MMA polymerization is similar to the general kinetic scheme which applies to the free-radical polymerization of vinyl monomers, the patterns of behavior discussed above may then be anticipated when these other monomers are polymerized. At present, we are extending this model to describe reactor behavior in nonisothermal conditions.

The development of such a model is useful for the design of the reactor and for the choice of the control system; in this way reactor operation can be optimized and the desired quality of products obtained.

NOMENCLATURE

c_p	specific heat
f	initiator efficiency
$F(s, t)$	generating function for the dead polymer chains
$G(s, t)$	generating function for the growing polymer chains
$H(s, t)$	generating function for the total polymer chains
g_t	ratio: k_t/k_{to}
I	initiator
k_d	initiator decomposition rate constant
k_i	initiation rate constant
k_p	propagation rate constant
k_t	termination rate constant
$k_{tr, m}$	chain transfer rate constant for monomer
$k_{tr, s}$	chain transfer rate constant for solvent
M	monomer
M_n	dead polymer chains
$\overline{M}_n$	number average molecular weight
$\overline{M}_w$	weight-average molecular weight
P_n	growing polymer chains
q	volumetric flow rate
$R^{\bullet}$	free radical
r_i	reaction rate for generic species
S	solvent
t	time
T	temperature
V	reactor volume
v_f	free volume
X_i	concentration of generic species
W	molecular weight of monomer
PD	polydispersity
λ_j	moment of jth order for growing chains
ϵ_j	moment of jth order for total polymer chains
ρ	density
τ	residence time
ϕ	volume fraction

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Subscripts

m	monomer
p	polymer
s	solvent
i	generic species
o	at the initial condition
cr	at the critical condition

References

1. R. S. Knorr and K. F. O'Driscoll, *J. Appl. Polym. Sci.*, **14**, 2683 (1970).
2. S. T. Blake and A. E. Hamielec, *J. Appl. Polym. Sci.*, **17**, 905 (1973).
3. R. T. Ross and R. L. Laurence, *A.I.Ch.E. Symp. Ser.*, **72**, 74 (1976).
4. R. Jaisinghami and W. H. Ray, *Chem. Eng. Sci.*, **32**, 811 (1977).
5. F. L. Marten and A. E. Hamielec, *Am. Chem. Soc. Symp. Ser.*, **104**, 43 (1979).
6. S. K. Soh and D. C. Sundberg, *J. Polym. Sci. Chem. Ed.*, **20**, 1299 (1982).
7. A. D. Schmidt and W. H. Ray, *Chem. Eng. Sci.*, **36**, 1401, (1981).
8. W. H. Ray, *J. Macromol. Sci. Revs.*, **C8**, 1, (1972).
9. J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., Interscience, New York, 1975.
10. C. Moutier, thesis, University of Pisa, 1983.
11. G. Maschio and C. Moutier, G.R.I.C.U. Symp. Milan, 21–23 June 1983.
12. K. Ito, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 401, (1975).