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Free Radical Polymerization of Methyl Methacrylate: Modeling and Simulation by Moment Generating Function

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ABSTRACT

The batch bulk isothermal polymerization of methyl methacrylate (MMA), in which the initiation is achieved by the decay of an initiator and termination by disproportionation is considered for modeling. According to the kinetic diagram one can make a deduction of the mathematical model in terms of the moment generating function and in terms of moments which give the distribution of the molecular weights. In order to quantify the gel and glass effects, the relations proposed by Chiu et al. are used [1]. The results given by the two solving techniques, generating function and moments, are compared and discussed. The comparison of the simulation and the experimental data represents the model validation and thus a guarantee for its use in various studies of polymer engineering.

Key Words: free radical polymerization, methyl methacrylate, moment generating function, moment of molecular weight distribution

INTRODUCTION

The main conditions which must be fulfilled by a mathematical model in order to be appreciated as a good model are:

–To describe adequately the experimental data on a range of conditions as large as possible.

–To be easily manipulated so to be useful in complex engineering studies.

The development of the kinetic model of a polymerization process has to pass over a series of difficulties among which the most important are the large number of molecular species, and consequently a large number of non-linear equations, and structural changes of the system due to the increase of viscosity or the volume modifications.

To obtain a model with a finite number of equations which can be solved relatively easy, one has to use moment generating functions or moments of molecular weight distribution.

The reaction kinetic is significantly affected by the increase of the viscosity, especially in homogeneous polymerization systems (mass and solution). The most sensitive to the increase of viscosity is the termination rate constant, strongly dependent on the diffusion of the macroradicals. Considering that the

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termination rate constant diminishes on the whole domain of conversion, one can observe an auto-acceleration of the reaction, accompanied by an increase of the polymerization degree, even in isothermal conditions (known as gel effect). At relatively high conversion, the propagation rate constant lowers and the polymerization tends to stop before the monomer is wholly consumed (glass effect).

The models proposed for these phenomena are represented by empirical correlations of rate constants with different parameters of the system [2, 3], or are based on molecular theories of the diffusion [1, 4, 5]. Even the latter approaches contain empirical parameters, which make the model flexible and applicable to the experimental data. On the other hand, some models introduce diffusional restrictions upon the rate constants, on different intervals, so that there appears interrupting points in the model [6–8]. Others are continuous models [1], which are recommended for engineering studies such as simulation, optimization, control or sensitivity analysis.

The model proposed by Chiu [1] is one of the most used models based on phenomenological aspects. The diffusional limitations have been considered as component part of the termination process. Although it contains adjustable parameters, the model is often used because it does not have discontinuity points and its results make the experimental data to fit reasonably in different reaction conditions.

Achilias and Kiparissides [9] extended the Chiu's model with several parameters estimated directly from experiments. They used the diffusion theory of Vrentas and Duda [10].

Recently, Ray et al. have proposed a model for the MMA polymerization, useful in batch or semi-batch operating conditions [11]. The equations expressing the change of diffusion coefficients are written upon the Vrentas and Duda's theory of free volume [10], being then simplified according to Chiu's method.

The modeling and simulation of the MMA polymerization have been often approached. Thus the literature offers kinetical models written in various forms resulting from approximations [6, 8, 12], different relations for the gel and glass effects, different values for kinetic constants and, of course, very diverse experimental data.

The present study realizes a satisfactory integration of these aspects.

Kinetic Model

The mathematical model of radical batch bulk isothermal polymerization of MMA is based on the following kinetic diagram:

Initiation:

$$I \xrightarrow{k_d} 2R^{\bullet} \tag{1}$$

$$R^{\bullet} + M \xrightarrow{k_i} P_1^{\bullet} \tag{2}$$

Propagation:

$$P_n^{\bullet} + M \xrightarrow{k_p} P_{n+1}^{\bullet} \tag{3}$$

Termination by disproportionation:

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_t} D_n + D_m \tag{4}$$

where I is the initiator, $R^{\bullet}$ the initiating radical, M the monomer, $P_1^{\bullet}$ polymer radical which consists of a structural unit, $P_n^{\bullet}$ the growing macroradical with n monomer units and D_n is a dead polymer with n monomer units.

The decomposition of the initiator follows the relationship:

$$\frac{dI}{dt} = -k_d t \tag{5}$$

or

$$I = I_0 e^{-k_d t} \tag{6}$$

where I_0 is the initial concentration of the initiator.

From eqns (2) and (3), the material balance equation for the monomer concentration results:

$$\frac{dM}{dt} = -k_i M R^{\bullet} - k_p M \sum_{n=1}^{\infty} P_n^{\bullet} \tag{7}$$

The conversion equations of the radical concentrations are:

$$\frac{dR^*}{dt} = 2fk_dI - k_iR^*M \qquad (8)$$

$$\frac{dP_1^*}{dt} = k_iMR^* - k_pMP_1^* - k_tP_1^*\sum_{n=1}^{\infty}P_n^* \qquad (9)$$

$$\frac{dP_n^*}{d_t} = k_pMP_{n-1}^* - k_pMP_n^* - k_tP_n^*\sum_{n=1}^{\infty}P_n^* \qquad (10)$$

If one assumes the quasi-steady-state approximation for the initial radicals, it results:

$$\frac{dR^*}{dt} = 0 \qquad v_{in} = k_iR^*M = 2fk_dI \qquad (11)$$

where v_{in} is the initiation rate.

Let us define the generating function, H(s, t), of the polymer active species:

$$H(s,t) = \sum_{n=1}^{\infty}s^nP_n^* \qquad (12)$$

s being a formal parameter.
For s = 1:

$$H(1,t) = \sum_{n=1}^{\infty}P_n^* \qquad (13)$$

which it would then represent the total concentration of radicals.

The eqn (10), in which n=1 to ∞, multiplied by s^n are mathematically processed to obtain the derivative with respect to time of the moment generating function:

$$\frac{\partial H(s,t)}{\partial t} = 2fk_dIs - k_pM(1-s)H(s,t) - k_tH(s,t)H(1,t) \qquad (14)$$

The total concentration of radicals, H(1, t) can be obtained from eqn (14) being:

$$\frac{dH(1,t)}{dt} = 2fk_dI - k_tH^2(1,t) \qquad (15)$$

The monomer concentration is obtained from:

$$\frac{dM}{dt} = -2fk_dI - k_pMH(1,t) \qquad (16)$$

The model neglects the decrease of initiator efficiency, (f), and variation of the volume during the process, but it considers the variation of the termination and propagation rate constants resulting from the gel and glass effects [1]:

$$k_t = k_{t^0}\frac{C}{C+\theta_tk_{t^0}H(1,t)} \qquad (17)$$

$$k_p = k_{p^0}\frac{C}{C+\theta_pk_{p^0}H(1,t)} \qquad (18)$$

where the parameter C is correlated with the conversion of the monomer, x, by:

$$\log C = \frac{1-x}{A+B(1-x)} \qquad (19)$$

The characteristic migration times for termination, θ_t, and propagation, θ_p, are given by the relations:

$$\theta_t = \frac{\theta_t^0}{I_0}\exp[E_{\theta t}/(RT)] \qquad (20)$$

$$\theta_p = \theta_p^0\exp[E_{\theta p}/(RT)] \qquad (21)$$

$$A = C_1 - C_2(T - T_{gp})^2 \qquad (22)$$

$$DP_n^{inst} = \frac{1}{1-q} \qquad (23)$$

A, B, C, C_1, C_2, are terms in diffusion equations and T_{gp} is the glass transition temperature of the polymer.

The instantaneous numeric and gravimetric degrees of polymerization are calculated as follows:

$$DP_w^{inst} = \frac{1+q}{1-q} \qquad (24)$$

where q represents the probability of propagation calculated as:

$$q = \frac{k_p M}{k_p M + k_t H(1,t)} \tag{25}$$

The cumulative degrees of polymerization can be computed by solving the following integrals:

$$DP_n^{cum} = \frac{x}{\int_0^x \frac{dx}{DP_n^{inst}}} \tag{26}$$

$$DP_w^{cum} = \frac{1}{x}\int_0^x DP_w^{inst}\,dx \tag{27}$$

The moments for the molecular weight distribution of the macroradicals are defined:

$$\lambda_k = \left[\left(s\frac{\partial}{\partial s}\right)^k H(s,t)\right]_{s=1} = \sum_{n=1}^{\infty} n^k P_n^{\bullet} \tag{28}$$

Similarly, we can have a generating function of the dead chains:

$$G(s,t) = \sum_{n=1}^{\infty} s^n D_n \tag{29}$$

and the moments μ_k (k=0, 1, 2) for the molecular weight distribution of the polymer:

$$\mu_k = \left[\left(s\frac{\partial}{\partial s}\right)^k G(s,t)\right]_{s=1} = \sum_{n=1}^{\infty} n^k D_n \tag{30}$$

From eqns (5) and (16) and by the derivation of the eqns (28) and (30) in relation with time the following model in terms of moments is obtained:

$$\frac{dI}{dt} = -k_d I \tag{31}$$

$$\frac{dM}{dt} = -2fk_d I - k_p M \lambda_0 \tag{32}$$

$$\frac{d\lambda_0}{dt} = 2fk_d I - k_t \lambda_0^2 \tag{33}$$

$$\frac{d\lambda_1}{dt} = 2fk_d I + k_p M_0 (1-x)\lambda_0 - k_t \lambda_0 \lambda_1 \tag{34}$$

$$\frac{d\lambda_2}{dt} = 2fk_d I + k_p M_0 (1-x)(2\lambda_1 + \lambda_0) - k_t \lambda_0 \lambda_2 \tag{35}$$

$$\frac{d\mu_0}{dt} = k_t \lambda_0^2 \tag{36}$$

$$\frac{d\mu_1}{dt} = k_t \lambda_0 \lambda_1 \tag{37}$$

$$\frac{d\mu_2}{dt} = k_t \lambda_0 \lambda_2 \tag{38}$$

H(1, t) was replaced with λ_0, from eqns (13) and (28).

RESULTS AND DISCUSSION

In order to calculate I, H(1, t) and M, we did solve numerically the system of differential eqns (5), (15) and (16) using a program for Stiff equation written in Fortran and a Pentium Computer at 120 MHz. The integration was made with a variable step calculated within the numerical algorithm. Then the instantaneous degrees of polymerization were obtained from eqns (23) and (24), as well as the cumulative values of the polymerization degrees using the eqns (26) and (27).

The rate constants, the parameters describing the gel and glass effects, and the properties of the reaction mass are given in Table 1.

The first simulation was made at T=70 °C, I_0=25.8 mol/m^3 and the results are presented in Figures 1–3.

Figure 1 shows the dependence of monomer conversion on time. One can note that the reaction is almost complete in 50 min. The sudden increase in monomer conversion at a transformation degree of

Table 1. Parameters used for MMA polymerization [1, 12, 16].

Parameter	Constant value
K_d^0	1.053×10^{15} s^{-1} (for initiation with AIBN)
k_{p0}^0	4.917×10^{2} $m^3/(mol\ s)$
k_{t0}^0	9.8×10^{4} $m^3/(mol\ s)$
E_d	1.2845×10^{5} J/mol
E_p	1.822×10^{4} J/mol
E_t	2.937×10^{3} J/mol
f	0.58 (AIBN)
B	0.03
C_1	0.15998
C_2	7.812×10^{-6} K^{-2}
T_{gp}	387 K
θ_p^0	3.99822×10^{-12} s
$E_{\theta p}$	1.02451×10^{5} J/mol
θ_t^0	2.8883×10^{-18} $(mol\ s)/m^3$
$E_{\theta t}$	1.48924×10^{5} J/mol
k_d	$k_d^0 \exp(-E_d/(RT))$
k_{t0}	$k_{t0}^0 \exp(-E_t/(RT))$
k_{p0}	$k_{p0}^0 \exp(-E_p/(RT))$

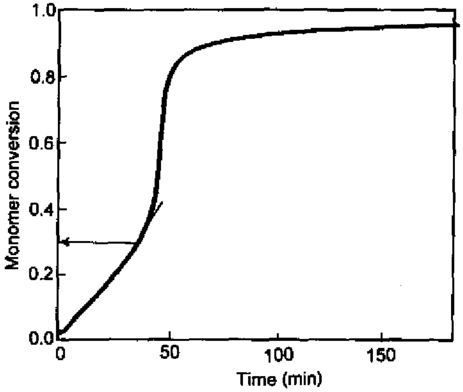

Figure 1. Conversion-time curve for MMA at 70 °C and I_0=25.8 mol/m^3.

about 30%, is attributed to the fact that the diffusion controls the reaction beyond this value. The decrease in the termination rate constant results in a steep growth of the reaction rate due to the increasing number of free radicals in the system. The maximum conversion attained in these conditions (T=70 °C, I_0=25.8 mol/m^3) is 98% and the onset of gel effect corresponds to a conversion of 30% (critical conversion in Figure 1) [13].

Figure 2 shows the variation of the instantaneous numeric and gravimetric molecular weights with the monomer conversion. For a conversion over 30%, the molecular weight shows an increase with an order of magnitude by virtue of the decrease of termination rate constant (gel effect). Moreover, this decrease results in more steps in the propagation phase. The subsequent decrease of the molecular weight, with about two orders of magnitude, appears since the propagation rate constant lowers when the glass temperature is reached (glass effect). One should note also that the two instantaneous molecular weights ($\bar{M}_n$ and $\bar{M}_w$) are parallel over the entire range of conversion, meaning that the instantaneous chains have a constant polydispersity, (Q≅2), as a consequence of the disproportionation mechanism.

The cumulative molecular weights show a similar tendency, but the $\bar{M}_w^{cum}$, increases more quickly than $\bar{M}_n^{cum}$ (Figure 3).

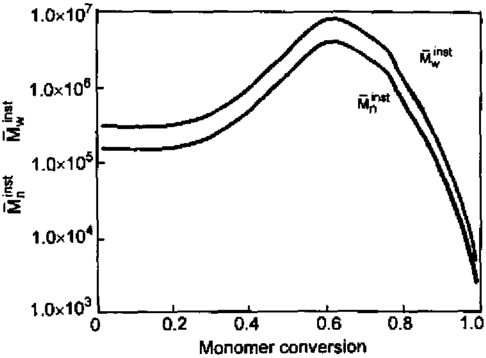

Figure 2. Dependence of $\bar{M}_n^{inst}$ and $\bar{M}_w^{inst}$ on MMA conversion at 70 °C and I_0=25.8 mol/m^3.

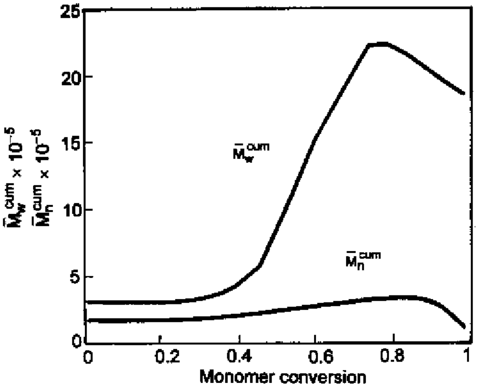

Figure 3. Dependence of $\overline{M}_n^{cum}$ and $\overline{M}_w^{cum}$ on MMA conversion at T=70 °C and I_0=25.8 mol/m^3.

As one expects, the significant increase in the cumulative molecular weight takes place in the first 50 min due to the monomer conversion leaped to about 80%, in this period (Figures 1 and 3).

Another possibility for obtaining the monomer conversion and the molecular weights consists in solving the model written in terms of moments (eqns (31–38) and eqns (17, 18) which are considered for the variation of the k_t and k_p values). In the eqns (17) and (18), $H(1, t)=\lambda_0$. The moments λ_k and μ_k are used to determine the numeric and gravimetric polymerization degrees, as it follows:

$$DP_n^{cum} = \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \qquad (39)$$

$$DP_w^{cum} = \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1} \qquad (40)$$

In Figures 4 and 5 the results obtained by the two methods are compared (integration by generating functions and by moments). The monomer conversion obtained by these two solving techniques are identical, so it is not presented.

Figures 4 and 5 show a better consensus of the obtained data concerning the numeric average molecular weight and the polydispersity index. The important growth in $\overline{M}_w$, depicted in Figure 3 generates an increase of the polydispersity. More conspicuous differences reveal the values for the gravimetric average molecular weight. These discrepancies can be attributed to the numerical algorithm that approximates the computation.

For a monomer conversion beyond 90%, the polydispersity shows a sharp increase because of short chains formation, as the concentration of the free radicals is lower (Figure 5).

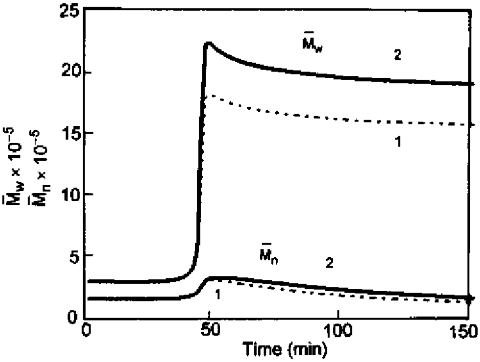

Figure 4. Average molecular weights-time curves obtained by the method of moments (1) and the method of the generating functions (2) at T=70 °C and I_0=25.8 mol/m^3.

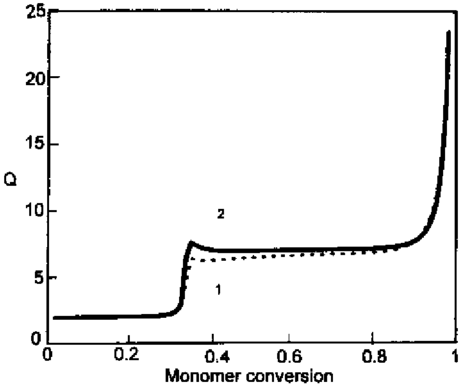

Figure 5. Polydispersity-monomer conversion curves obtained by the method of moments (1) and the method of generating functions (2) at T=70 °C and I_0=25.8 mol/m^3.

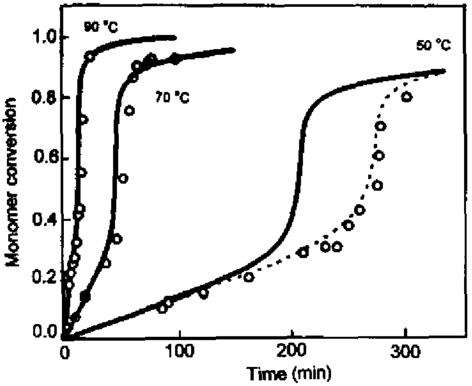

Figure 6. Comparison between simulated (solid line) and experimental data (o) [14] at different temperatures and I_0=25.8 mol/m^3.

Any model must be validated by comparing with the experimental data corresponding to the simulated conditions.

Balke and Hamielec [14] have given a complete set of experimental data for a large range of reaction conditions, which can be found in many recent studies. Using these experimental data together with those obtained by solving the model one can draw Figures 6 and 7. The results of the model, regardless of what solving method is used, estimate well the conversion data at 70 and 90 °C (Figure 6). The differences which appear for T=50 °C are due to the supposition of constant volume. The dashed curve in Figure 6 is the result of the simulation on a model in which the volume contraction during the polymerization was considered [15]. Figure 7 represents the variation of the numeric and gravimetric average molecular weights for T=70 °C and I_0=27.14 mol/m^3. One should note a good agreement between simulation and experimental data.

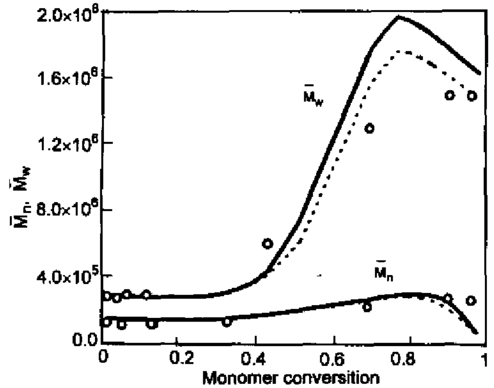

Figure 7. Comparison between average molecular weights obtained by simulation (solid line: generating function; dashed line: moments) and experiments (o) [14] at T=70 °C, I_0=27.14 mol/m^3.

CONCLUSION

A kinetic model for batch bulk free radical polymerization of MMA, in a relatively simple form, was deduced. The model was written in terms of moment generating function and in terms of moments of molecular weight distribution. The model was completed with relations which quantify the gel and glass effects and a series of numeric values in order to obtain a satisfactory approximation of the experimental data.

–Analyzing the results provided by the two types of processing methods (the method of moments and the method of the generating functions) one can say that they are comparable. The choice of the appropriate method of calculation, whose predictions are closer to the available experimental data, depends on the incidental differences that might appear.

–Alternatively, one can choose the more convenient method by taking into account the complexity of the required calculation. In this respect, the method of moments has an eight-equations (31–38) system to be solved. Its predictions are the temporal profiles of the initiator concentration, monomer conversion, and of the numeric and gravimetric average molecular weight. On the other hand, the method of generating functions contains only three differential eqns (6), (15) and (16). It yields the temporal variations of the initiator concentration, monomer conversion, and of the instantaneous molecular weights. In order to obtain the cumulative molecular weights of the polymer one should solve some integrals in the considered monomer conversion range.

The selection of one of these methods should be done taking into account several criteria, such as: the expected results, the agreement with the experimental data and the availability of adequate software and hardware facilities.

–The main purpose of this article is to offer to the chemical engineers a simple and precise model, and with good results useful in different other studies.

SYMBOLS

A, B, C_1, C_2, C	Terms in diffusion equations for propagation and termination rate constants.
D_n	Dead polymer molecule with n units of monomer.
DP_n^{inst}, DP_w^{inst}	Instantaneous numeric and gravimetric average degree of polymerization.
DP_n^{cum}, DP_w^{cum}	Cumulative numeric and gravimetric average degree of polymerization.
$E_d, E_p, E_t,$	Activation energies of initiation, propagation and termination (J/mol).
$E_{\theta p}, E_{\theta t},$	Activation energies for θ_p and θ_t (J/mol).
f	Initiator efficiency.
H(s, t)	The generating function of the polymer species.
I	Initiator concentration (mol/m^3).
k_d	Rate constant for initiation (s^{-1}).
k_i	Propagation rate constant for primary radical (m^3/mol s).
k_p, k_t	Rate constants for propagation and termination in the presence of gel effect (m^3/mol s).
k_{p0}, k_{t0}	Rate constants for propagation and termination in the absence of gel and glass effect (m^3/mol s).
$k_d^0, k_{p0}^0, k_{t0}^0$	Frequency factors for rate constant of initiation, propagation and termination in the absence of gel and glass effects (m^3/mol s).
M	Monomer concentration (mol/m^3).
M_n^{inst}, M_w^{inst}	Instantaneous numeric and gravimetric molecular weight.
$\overline{M}_n^{cum}, \overline{M}_w^{cum}$	Cumulative numeric and gravimetric molecular weight ($\overline{M}_n^{cum}$, $\overline{M}_w^{cum}$ without superscript refers cumulative molecular weight).
$P_n^{\bullet}$	Macroradical with n units of monomer.
$R^{\bullet}$	Primary radical.
R	Universal gas constant (J/mol K).
Q	Polydispersity.
q	Probability of propagation.
T	Temperature (K).
T_{gp}	Glass transition temperature of polymer (K).
t	Time (s).
x	Monomer conversion.

Greek Letters

θ_t, θ_p	Characteristic migration times (s).
θ_t^0, θ_p^0	Pre-exponential factors for θ_t (mol.s/m^3) and θ_p (s).
μ_k	k-th moment of all dead polymer species (mol/m^3).
λ_k	k-th moment of all polymer radicals, (mol/m^3).

Subscripts

0	Inlet value or value in absence of gel and glass effects.

Superscripts

0	Pre-exponential value.

REFERENCES

1. Chiu W.Y., Carrat G.M., Soong *D.S.,Macromolecules,* **16**, 348, 1983.
2. Frus N. and Hamielec A.E., *ACS Symp. Ser.*, **24**, 82, 1976.
3. Ross R.T. and Laurence R.L., *AIChE Symp Ser.* **160**, 74, 1976.

4. Russel G.T., Gilbert R.G., and Napper D.H., *Macromolecules*, **25**, 2459, 1992.
5. Sharma D.K. and Soane D.S., *Macromolecules*, **21**, 700, 1988.
6. Marten F.L. and Hamielec A.E., *ACS Symp. Ser.*, **43**, 104, 1979.
7. Cardenas J. and O'Driscoll K.F., *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2097, 1977.
8. Tulig J.T., Tirrell M., *Macromolecules*, **15**, 459, 1982.
9. Achilias D. S. and Kiparissides C.J., *Macromolecules*, 25, 3739, 1992.
10. Vrentas J.S. and Duda J.L., *A.I.Ch.J.*, **25**,1,1979.
11. Ray B.A., Saraf N.D. and Gupta K.S., *Polym. Eng. Sci.*, **35**, 16, 1290, 1995.
12. Vaid R.N. and Gupta S.K., *Polym. Eng. Sci.*, **31**, 2, 1991.
13. Curteanu S. and Bulacovschi V., *Hung J. Ind. Chem.*, in press (submitted in May 1997).
14. Balke S.T. and Hamielec A.E., *J. Appl. Polym. Sci.*, **17**, 905, 1975.
15. Petrovan S. and Curteanu S., *Hung J. Ind. Chem.*, in press, (submitted in May 1997).
16. Kumar R.V. and Gupta S.K., *Polymer*, **32**, 17, 3233, 1991.