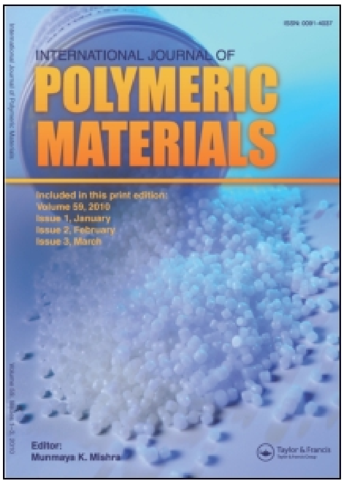

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Influence of the Diffusional Mobility of the Components of Polymerizing Systems on the Rate Constants of Free Radical Polymerization Reactions

V. P. Budtov[a]; G. N. Podosenova[a]
[a] "Plastpolymer" (Okhta Research Company & Production Association), St. Petersburgh, Russia

To cite this Article Budtov, V. P. and Podosenova, G. N.(1995) 'Influence of the Diffusional Mobility of the Components of Polymerizing Systems on the Rate Constants of Free Radical Polymerization Reactions', International Journal of Polymeric Materials, 30: 3, 97 — 122
To link to this Article: DOI: 10.1080/00914039508028589
URL: http://dx.doi.org/10.1080/00914039508028589

Intern. J. Polymeric Mater., 1995, Vol. 30, pp. 97–122
Reprints available directly from the publisher
Photocopying permitted by license only

Influence of the Diffusional Mobility of the Components of Polymerizing Systems on the Rate Constants of Free Radical Polymerization Reactions

V. P. BUDTOV AND G. N. PODOSENOVA

"Plastpolymer" (Okhta Research Company & Production Association), 195108, St. Petersburgh, Russia

(Received May 21, 1993)

Theories that allow us to quantitatively predict the rate constants changes of the main free radical polymerization reactions as function of the diffusional mobility of the polymerization medium are reviewed.

KEY WORDS Rate constants, free radical polymerization, diffusional mobility, theoretical predictions.

INTRODUCTION

The growing interest in the theory of free radical polymerization at high degrees of conversion is due to the following reasons. First, a number of industrial polymerization processes are carried out at high degrees of conversions.[1,2] Secondly, considerable success in understanding the behaviour of concentrated polymer solutions and melts has been achieved.[3-5] Finally, new molecular-weight-distribution measurements,[6-10] and methods of investigation of the kinetics have become available.[11-13]

The rate V and average degree of polymerization P_n of a macromolecule at low degrees of conversions are given by the following equations:

$$V = K_p[M]\left(\frac{V_{in}}{K_t}\right)^{0.5} \tag{1}$$

$$P_n^{-1} = \frac{K_t}{K_p^2[M]^2} V + C_m + C_s \frac{[S]}{[M]} \tag{2}$$

where $[M]$, and $[S]$ are the concentrations of the monomer and chain transfer

S-agent, K_m, and K_s represent the chain transfer constants respectively. $C_m = K_m/K_p$; $C_s = K_s/K_p$, V_{in} is the radical initiation rate; K_p, K_t are the chain propagation and macroradical termination rate constants respectively. $V_{in} = f \times K_d \times [I]$, where f is the initiator efficiency, $[I]$ is the initiator concentration, K_d is the initiator decomposition rate.

Thus, we have to examine the dependences of K_p, K_t, C_m, C_s, K_d, f on polymerization process conditions.

Free radical polymerization of methylmethacrylate (MMA) is influenced by increasing the concentration both in polymerization rate and polymer molecular weight (MW) being increased. This effect contradicts the classical free radical polymerization scheme and is referred to as the gel effect (autoacceleration). This phenomena is associated with a decrease of radical mobility at high polymer concentrations in the polymerization system.[1] The bimolecular termination rate constant K_t depends both on the degree of conversion and on the molecular weights of the radical and "dead" polymer chains. Thus it makes the traditional approach of estimating the radical process, based on the method of molecular-weight distribution moments [MWD] incorrect.[6]

Change in mobility of the polymerization system affects also the rate constants of other chemical reactions, however, these effects are different from that for K_t.

Using the theory of diffusion[4,7,8] for the components of the polymerization system (long-chain radicals, "dead" polymer chain, monomer, initiator, chain transfer) led to quantitative relations for the constants of radical polymerization.

This approach is inadequate to account for radical polymerization and, at the same degree of conversion and media viscosities, gel effects are manifested in some systems (MMA) and are absent in the others (styrene); "evident" and "latent" gel effects.[9]

Some recent papers[10,11] have considered the idea of microinhomogeneity generated during the polymerization process influencing the rate constant of chemical reaction.

The quantitative prediction of the behaviour over a wide conversion range requires knowledge of not only the kinetic model, but also the physical properties of polymerization media. The latter govern the extent of molecular motion and the availability of the reactive sites. Consequently, this influence is propagated on molecular-weight-distribution (MWD) and on the quality of the formed product.

1. BRIEF REVIEW OF PUBLICATIONS

Most theoretical studies of free radical polymerization attempt to produce empirical correlations between the rate constants, molecular weight distribution parameters and degree of conversions. Considerable success has been achieved in prediction of the complicated character of the molecular weight (M) versus conversion (x) dependence, influence of the monomer type, initiator concentration and polymerization temperature. However, some experimental facts remain unexplained: the absence of acceleration in styrene polymerization.

Experimental research has focussed on the determination of the polymerization parameters which govern the change of rate constants with x. These are the viscosity of the media (η), molecular weights of the "dead" polymer (M_m) and radical (M_r), degree of conversion, polymerization temperature, initiator concentration, free volume (V_f).[12-17] Attempts have been made to describe by means of empirical equations these processes. However, the numerous coefficients hold only over fixed ranges of conditions.

Theoretical studies[18-22] have attempted to account for dependence of the rate constants versus conversion and radical length. In recent years,[6] the general solution of the system of differential equations of mass balance for polymerization system has appeared and thus take into account the dependence of the rate constant on the degree of conversion and radical molecular weight. Usually two assumptions are made to account for the K_t versus x and M dependence. Firstly, the identity of the molecular mechanisms of motion for macromolecules and radicals and secondly the correctness of the Smoluchowski equation for the analysis of radical reactions in macromolecules. According to de Gennes,[23] the latter assumption is equivalent to $t_z >> R^2 \cdot D^{-1}$; where R is the mean square radius of gyration and D is the diffusion coefficient of the macromolecule and t_z is the radical lifetime. This inequality holds for radical polymerization, because the radical lifetime is in the range 1–10 s, also as R^2, D^{-1} is of the order of 10^{-2}–10^{-5} s.

Thus the relation for the biradical termination rate constant vs radical length and media properties is

$$K_t = zD_{ij}R_{ij}$$

where D_{ij} is the self-diffusion coefficient and R_{ij} the average mean square radius of i and j macroradicals and z is a numerical coefficient.

The lack of an exact theory of the dependence of the macromolecular self-diffusion coefficient on concentration has limited the use of this approach.[18-20] Functional representations D vs c and M depend on the c and M ranges.[8] In dilute solution, according to Einstein-Stokes diffusion theory D_i/D_1† $\sim i^{-0.5}$ in semidilute solution the Rouse-model gives $D_i/D_1 \sim i^{-1}c^{-0.5}$ $(i < i_e)$ and reptation model leads to $D_i/D_1 \sim i^{-2}c^{-7/4}$ $(i > i_e)$. The i_e parameters depend on the scale of entanglements and characterizes the range of the transition to reptile diffusion mechanisms. Moreover i_e depends also on c and M. As a result, the relations obtained contain empirical parameters, which depend on the c and M values, as well as on experimental conditions and the chosen type of functional representation $D = f(c, M)$ used. Naturally, this uncertainty reduces the practical significance of this approach.

Another defect on this approach arises from the fact, that investigators, discussing the K_t dependence on x and M, do not differentiate between the molecular weights M of the radical itself and the medium ("dead" macromolecules, matrix), in which this radical moves. But M_m of the medium is conditioned by the prehistory of the polymerization process whereas M_r is conditioned by instantaneous values of the reagents concentrations. The results of quantitative calculations carried out without taking into account such discrepancy in M-values, cannot be really precise.

†D_1 is monomer diffusion coefficient, i is the number of monomer units in the chain.

A theory of the diffusional mobility of macromolecules in concentrated solutions was suggested recently.[4,5,7,8] It was shown, that assuming that the D depends on c, M_m, M_r parameters is as following θ conditions

$$D = \frac{D_1(c)}{N^{0.5}}\left[\frac{1}{1.843N^{0.5}} + e^{-1.27\sqrt{c[\eta]}}\right] \tag{3}$$

where N is the number of segments in the diffusing chain (macroradical), $[\eta]$ intrinsic viscosity, which is governed by M_m of the "dead" chains, surrounding the macroradical. This relation holds in the range of moderate concentrations ($c <$ 0.3). However, detailed analysis, as well as the comparison with experimental results confirmed its validity on a more large-scale range.

The diffusion coefficient D_1 of the monomer is equal to (φ = polymer volumetric concentration)

$$D_1(\varphi) = D_1(o)\cdot e^{A\varphi/(1-a\varphi)} = A_1 e^{A_s/(T-T_{gs})-A_p/(T-T_{gp})} \tag{4}$$

where A = 2–4, a = 0.6–1; A_1, A_s, A_p = empirical constants, T_{gs}, and T_{gp} are the glass transition temperatures of monomer and polymer respectively.

A recent review[2] touches upon the problem of solution of the system of differential equations. It is also emphasized in (see Reference 2), the necessity of taking into account K_t vs radical length dependence, makes the computer method of direct numerical or analytical integration of the equations the only one. The accuracy of these results is limited to a certain extent by the correctness of the applied method used for $K_t(M_r)$ calculations.

In spite of the considerable number of experimental and theoretical studies, neither of them gives a theoretical approach to quantitative description of free radical polymerization at relatively high conversions. Moreover, the relations and models suggested, contain numerous parameters, and some of them cannot be found experimentally. The task of describing the chemical kinetics with a termination rate constant, depending on the radical length, still has no adequate solution. The influence of the macroradical length and that of the "dead" macromolecule on the termination rate constant of the radical, has also not yet been carried out.

2. EXPERIMENTAL METHODS AND RESULTS

2.1 Method of "Derivatives" of MWD Moments

The method of "derivatives" of MWD moments of polymerization products, has been used.[24,25] This approach provides the opportunity to study the radical polymerization without any assumptions with regards the dependences of K_t on conversion and radical length. This method is the only one for study of K_t – M_r relationships.

The moment Q_i of molecular-weight-distribution is determined as follows:

$$Q_o = x/P_n; \qquad Q_1 = x; \qquad Q_2 = xP_w; \qquad \text{etc.} \tag{5}$$

where P_w is the weight averaged degree of polymerization. The MWD moments Q_i are connected to the rate constants of chemical reactions. If the Q_i versus x and M relationship is known, one might determine the relation of the corresponding constants versus these parameters. If the dependence of rate constants on x and M is known the dependence Q_i on these values may be calculated.

Using this approach to analyses of the polymerization process we obtain the following set of equations for the moments of radical distribution (Y_n) and "dead" polymer chains (Q_n):

$$\frac{dY_o}{dt} = V_{in} - \int K_{tij} R_i R_j \, d_i \, d_j$$

$$\frac{dY_n}{dt} = K_p[M][(Y + 1)_n - Y_n] - \lambda Y_n - \int K_{tij} R_i R_j i^n \, d_i \, d_j$$

$$\frac{dQ_n}{dt} = \lambda Y_n + \int K_{tij} R_i R_j i^n \, d_i \, d_j \tag{6}$$

where λ characterizes all the processes associated with transfer: $K_m[M] + K_s[S]$; $(Y + 1)_n = Y_n + nY_{n-1} + \cdots + 1$ etc. K_{tij} is the termination rate constant for radicals with length i and j. If K_t is not affected by i and j, the set of equations (6) can be solved and Y_n and G_n may be obtained. If the functional relation $K_t(i, j)$ is shown, the system of equations is solvable.

Further modification of molecular-weight-distribution moments method in account of arbitrary relation $K_t(M)$ has been proposed.[6] A new value $\langle K_t \rangle_n$ = the moment of the biradical termination rate constant for the chemical reactions was introduced:

$$\langle K_t \rangle_n = \frac{\int K_{tij} R_i R_j i^n \, d_i \, d_j}{\int R_i i \, d_i \cdot \int R_j \, d_j} \tag{7}$$

and leads to a simple relation for Q_n if it is assumed that the radicals quasistationary conditions still holds ($dY_n/Dt = 0$). The corresponding moment is associated with the biradical termination rate constant. It is possible to apply the techniques developed for the analysis of polymerization kinetics.

Let us define[21]:

$$C = \frac{\lambda}{K_p[M]}; \quad A_o = \frac{\langle K_t \rangle_o Y_o}{K_p[M]}; \quad Y_o^2 = \frac{V_{in}}{\langle K_t \rangle_o}; \quad \delta_i = \frac{\langle K_t \rangle_i}{\langle K_t \rangle_o} \tag{8}$$

Then system (6) is as follows:

$$\frac{1-x}{M_o}\frac{dQ_o}{dx} = C + A_o; \qquad \frac{1}{2M_o(1-x)}\frac{dQ_2}{dx} = \frac{1}{C + A_o\delta_i};$$

$$\frac{1}{6M_o(1-x)^2}\frac{dQ_3}{dx} = \frac{1}{(C + A_o\delta_i)(C + A_o\delta_2)} \tag{9}$$

It should be emphasized, that the equations obtained (9) differ from the traditional ones only by $\delta_i \neq 1$. Thus, once this parameter is determined, one might use the set (9) to solve any problem of polymerization kinetics, even without knowing the precise relations $K_{tj}(ij)$. Using equations (9) possible errors in the solution of the direct and inverse problems may be predicted.

It should be also pointed, that equation for Q_o does not contain δ_i. As a result, the Q_o value (and consequently M_n) does not depend on taking or not taking into account the correlation $K_t(ij)$ versus i, j. At the same time, Q_2, Q_3, etc. will be considerably more sensitive to the $K_t(i, j)$ versus i, j relation. The same is true for M_w, M_z.

Experimental analysis leads to the universal relation for δ_1 and δ_2:

$$\delta_1 = \delta_2 = 1 - x \tag{10}$$

Theoretical calculations[6,21,22,26] show that δ_1 must decrease from 1 to 0.16, with increasing degrees of conversion. Moreover, calculations[6,26] pointed to equality $\delta_1 = \delta_2$, which fits the experimental results.

Experimental analysis, concerning the molecular-weight-distribution (M_n, M_w, M_z) versus x relation, allows determination of different average moments of K_t. In this case, the zero moment ($\langle K_t \rangle_o$) has a simple physical interpretation and coincides with the standard K_t value, which is traditionally defined from kinetics by the equation:

$$\langle K_t \rangle_o = \frac{V^2}{V_{in}(K_p[M])^2} \tag{11}$$

2.2 Experimental Data

Gel-permeation chromatography (GPC) is the best method for molecular-weight-distribution studies.[27,28]

Polymerization conditions were chosen.[4,7] Assuming the dependence of the diffusion process on concentration and chain length is governed by two parameters: (1) — $c\,[\eta]$ and (2) — the deviation of T of experiment from the glass-transition temperature T_g: $\Delta T = T - T_g(x)$. ΔT value varied with the change of polymerization temperature T (45°–220°C) and T_{gp} (−70°–100°C). To fit these conditions, homologous of alkylmethacrylates were chosen, because the polymerization products of the latter are characterized by permanently decreasing values of T_g when their side-chain length increases. $c[\eta]$ value defines the forces, which distort the velocity field of macromolecular Brownian motion. In the low $c[\eta]$ range, the segmental hydrodynamic interaction of the macromolecule plays the role of this force. As $c[\eta]$ increase intramolecular segmental hydrodynamic interaction weakens due to so-called "screening" effects when the segments of surrounding chains "screen" the segments of the single chosen chain. According to Debye the condition $c[\eta] = 1$ gives the critical value for distinguishing the ranges of polymer coils overlap and homogeneous solutions: average monomer concentration in polymer coils is equal to average monomer concentration in solution. To produce $x[\eta]$ variation the investigations was carried out in different conditions. Processes in the presence of initiator, differing by G-values and termination rate and monomers with various K_p and C_m values in wide conversion range, were studied.

Tables I–III summarize the parameters for samples studied and conditions for their polymerization. All these gave the possibility of varying T and $x[\eta]$ parameters over a wide range.

2.3 Experimental Results on the $K_t/K_p^2(x, M)$ Dependence

Experimental results are shown in Figures 1–5.

The results in the figures are plotted so that only one parameter varies during a series of experiments.

TABLE I

Polymerization condition of investigated polymers

Sample No	Monomer type	T, °C	Initiator	Concentration mol/l	Kp*10^{3} 1/s	Pw*10^{-3}
1	AMA-1	60	PL	10^{-2}	0.5	6
2	AMA-2	60	-"-	10^{-2}	0.5	6
3	AMA-8	60	-"-	10^{-2}	0.5	8.2
4	MMA	50	DAC	$1.5*10^{-2}$	0.25	12
5	-"-	70	-"-	$1.5*10^{-2}$	0.5	6
6	-"-	90	-"-	$1.5*10^{-2}$	33.5	3
7	-"-	70	-"-	$0.5*10^{-2}$	5	6
8	-"-	70	-"-	$1.5*10^{-2}$	5	3
9	-"-	70	PB	$5*10^{-2}$	5	2.3
10	Styrene	45	DAC	$5*10^{-2}$	0.15	8
11	-"-	45	-"-	$2*10^{-1}$	0.1	4
12	-"-	60	PB	$2*10^{-2}$	0.17	1.9
13	-"-	70	DAC	$1.7*10^{-2}$	5	1.1
14	-"-	70	-"-	$5.7*10^{-2}$	5	0.5
15	-"-	70	PB	$0.7*10^{-2}$	0.5	4.5
16	-"-	70	-"-	$1.5*10^{-2}$	0.5	3
17	-"-	90	-"-	$2.6*10^{-3}$	6.4	2.5
18	-"-	90	-"-	$6.4*10^{-3}$	6.4	1.4
19	-"-	90	TBPB	10^{-1}	0.5	1.5
20	-"-	90	-"-	$4*10^{-2}$	0.5	2.2
21	-"-	80	-"-	10^{-1}	0.13	2.2
22	-"-	100	-"-	$3.7*10^{-2}$	1.8	2.25
23	-"-	100	-"-	$1.2*10^{-2}$	1.8	2.85
24	-"- -"-	100	termoini-tiation		$1.8*10^{-4}$	6
25	-"-	120	-"-		$1.2*10^{-3}$	3.7
26	-"-	150	-"-		$1.4*10^{-4}$	3
27	-"-	180	-"-		$1.3*10^{-3}$	2
28	-"-	200	-"-		$4.6*10^{-3}$	1.8

TABLE II

Initiator parameters

Initiator	Half-Termination time range, h	Concentration initiator range, mol/l
PB	0.10–100	$2 \cdot 10^{-[illegible]}$ – $2 \cdot 10^{-3}$
TBPB	10–100	$1 \cdot 10^{-1}$ – $1 \cdot 10^{-[illegible]}$
PL	20	$1 \cdot 10^{-[illegible]}$
DAC	1–15	$5 \cdot 10^{-3}$ – $-5 \cdot 10^{-[illegible]}$

TABLE III

Monomer and polymer main parameters

Main Parameters								
Monomer							Polymer	
	$K_z \cdot 10^4$	a_z	M monomer	Kp, l/mol*s	Ko $10^{-[illegible]}$	Cm 10^4	Tg, °C	range Mw*$10^{-[illegible]}$
Styrene	2.5	0.62	107	175	4.3	1	100	1 – 10
Styrene+ acrylonitrile	2.3	0.67						1 – 10
AMA-1	7.1	0.72	100	460	17	0.1	100	1 – 30
AMA-4	4.6	0.81	140	500	6	0.3	20	1 – 30
AMA-8			200	460	1.7		−25	1.5– 50
AMA-12	4	0.75	250	460	0.75		−70	2 – 50

The degree and rate of polymerization depend on the parameters mentioned above. Decrease of the K_t/K_p value with conversion takes place over the whole temperature range studied. The biradical termination rate constant K_t decreases with x over the whole conversion range. The extent of its decrease depends on the initiator concentration, polymerization temperature and the length of alkyl groups. According to autoacceleration theory all the processes at high values of x increase and become more complicated due to diffusion control of the radical termination reaction.

Let us now consider the effect of temperature and macromolecular weight on the dependence K_t on x. A nonlinear dependence K_t versus x is usually observed and the influence of process conditions depends on extent of conversion. Thus, polymerization temperature does not affect the ratio of the propagation and termination rate constants in low degrees of conversion range, but they differ by hundred and even more times at high degrees of conversion. The same conclusion may be drawn if the length of alkyl radical is varied. At the same time the initiator concentration affects the ratio K_t/K_p^2 only at moderate conversion, whereas at low and high conversions K_t/K_p^2 is practically independent of it. Numerous attempts have been made to describe the functional relation of K_t/K_p^2 vs conversion failed because of its multiformity.

If we compare the processes, that lead to polymer formation with similar M, then the dependence of K_t/K_p^2 value on the degrees of conversions is linear in

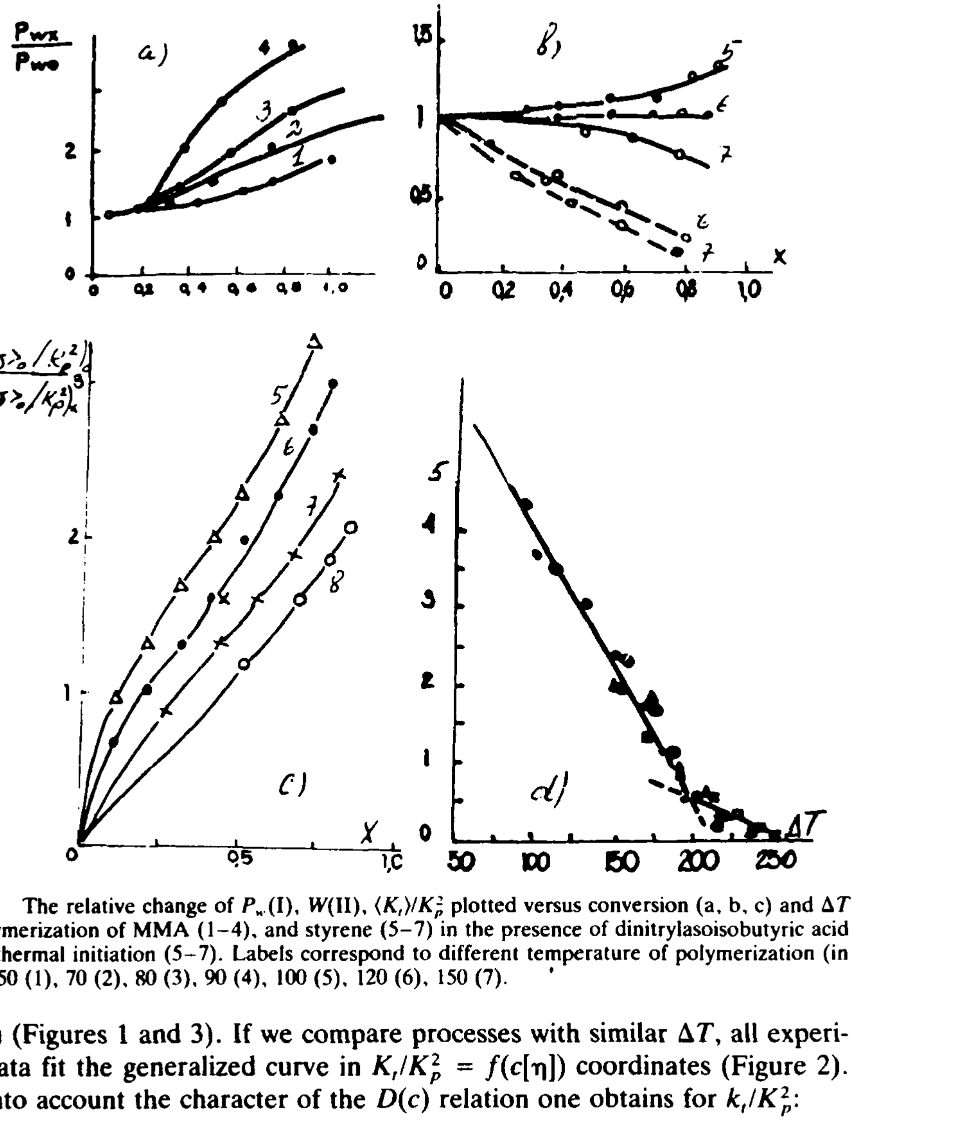

FIGURE 1 The relative change of $P_w(I)$, $W(II)$, $\langle K_t \rangle / K_p^2$ plotted versus conversion (a, b, c) and ΔT (d) for polymerization of MMA (1–4), and styrene (5–7) in the presence of dinitrylasoisobutyric acid (1–4) and thermal initiation (5–7). Labels correspond to different temperature of polymerization (in grades C): 50 (1), 70 (2), 80 (3), 90 (4), 100 (5), 120 (6), 150 (7).

$\lg(K_t/K_p^2)$ (Figures 1 and 3). If we compare processes with similar ΔT, all experimental data fit the generalized curve in $K_t/K_p^2 = f(c[\eta])$ coordinates (Figure 2). Taking into account the character of the $D(c)$ relation one obtains for k_t/K_p^2:

$$\ln \frac{K_t(x)}{K_p^2(x)} \cdot \frac{K_p^2(o)}{K_t(o)} = \frac{220}{T - T_{gs}} + \frac{220}{T - T_{gp}(x)} + 0.38\sqrt{x[\eta]} \qquad (12)$$

This equation has general applicability. It holds over a wide range, including for T_{gp}: $-70°C$ (POMA) ÷ 100°C (PMMA, PS), $[\eta]$: 0 ÷ 10 dl/g and x: 0 ÷ 0.7. The coordinates chosen give information not only on monomer conversion (x), but also on M of the product ($[\eta]$) and on the state of polymerization system (T_g).

2.4 The Influence of Radical Molecular Weight on Rate Constant of Termination

The functional representation $K_t(M)$ is opened to discussion. The results of theoretical studies are contradictory. This is not surprising, since the experimental

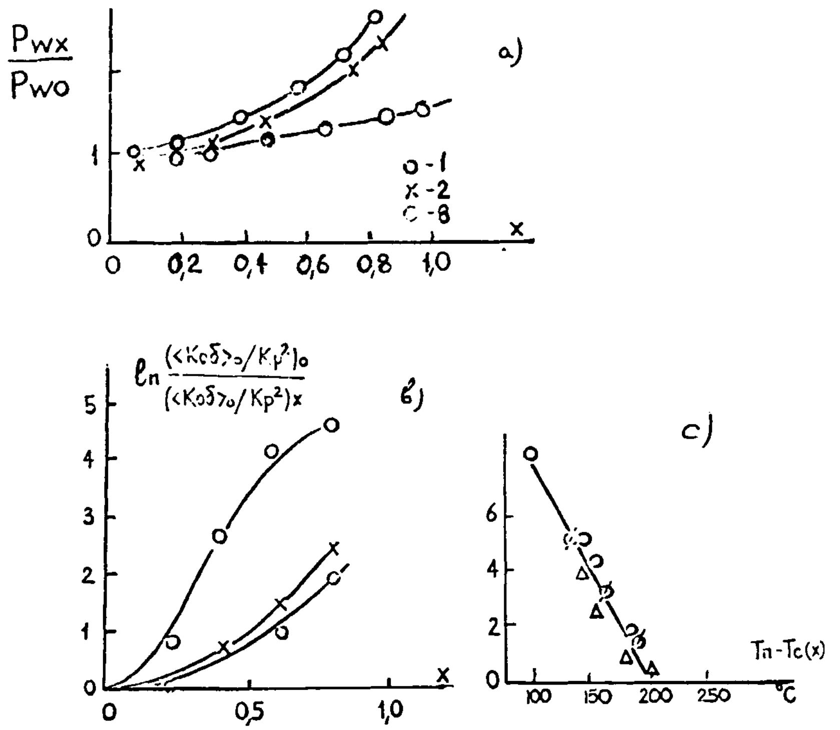

FIGURE 2 The relative change of P_w, $\langle K_t\rangle/K_p^2$ plotted versus conversion and $x[\eta]$ for polymerization of MMA-I (1–3), styrene (4–7) at 45°C (4, 5); 70°C (1–3) and 90°C (6, 7). Figures correspond to different concentration in ((mol/liter)100) of dinitrylasoisobutyric acid 0.5 (1), 1.5 (2), 5 (3, 4), 20 (5), threebutylperbensoate 10 (6), 4 (7).

relations observed can be affected not only by the radical length, but also by the molecular weight of the polymer, surrounding the moving radical. Discussion of the termination rate constant on molecular weight and conversion is carried out without taking into account the difference between the molecular weight of the radical and that of the media in which the radical moves.

The kinetics of polymerization in styrene and methylmethacrylate with independently varied M_m and M_r values were studied.[29,30] This process can be carried out by polymerization of monomer in a solution of its own polymer.[29] In this case variation of c and M detects the influence of polymer concentration and its M_m, while the change of initiator concentration detects the influence of radical length (M_r), since M_r is the reciprocal of the initiation polymerization rate.

Not only was the power law of $K_t(M_r, x)$ established, but also the exponent was obtained (Figure 5).

If the changes in the moments dQ_0/dx, $dQ2/dx$, $dQ3/dx$ are known Equation (9) may be used to solve the reverse problem—i.e., δ_1 and δ_2 determination at any degree of conversions. Estimated values for MMA polymerization process at 60°C in the presence of DAA (0.0056; 0.056; 0.015) m/l are shown in Figure 4. Values of δ_1 and δ_2 fall from 0.8 to 0.1 ÷ 0.2 with increasing x from 0.1 to 0.8. Numerical values of δ_1 and δ_2, as well as the character of their decay with x are similar. Moreover, δ_1, δ_2 are practically unaffected by M_p at constant x. Thus, the change

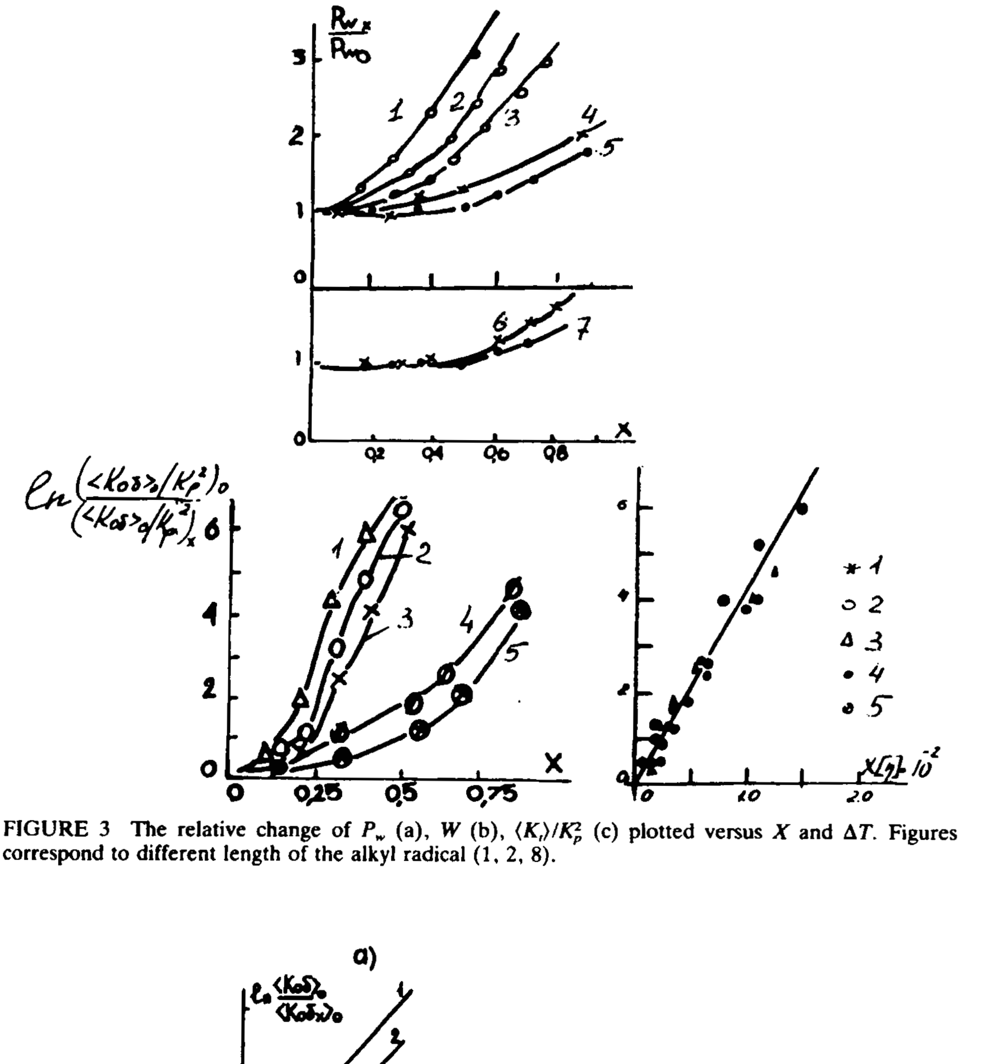

FIGURE 3 The relative change of P_w (a), W (b), $\langle K_t\rangle/K_p^2$ (c) plotted versus X and ΔT. Figures correspond to different length of the alkyl radical (1, 2, 8).

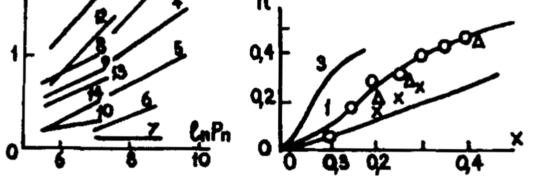

FIGURE 4 The δ_t is plotted versus conversion for polymerization of MMA at 70°C in the presence of dinitrylasoisobutyric acid. Labels correspond to different concentration of initiator in mol/l 100: 0.5 (1), 1.5 (2), 5 (3). Curves represent estimations according to Equation (13).

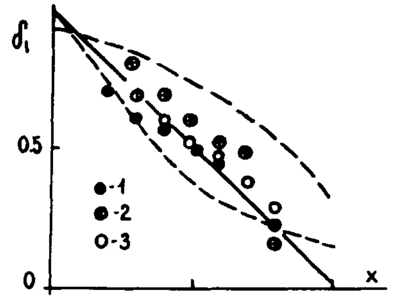

FIGURE 5 The degree of the dependence of $\langle k_t \rangle$ on the radical molecular weight plotted versus conversion for polymerization of styrene (I) and MMA (2, 3) in the presence of PMMA with M 10^5: 2.9 (1, 2) and 2 (3). Curves represent theoretical model estimations according to Equation (15). Labels on the curves correspond to different intrinsic viscosity in *dl/g*.

in δ_1 and δ_2 does not exceed 30%, while M increases three times. The main reason for δ_1, δ_2 changes is due to an increase in polymer concentration. To a first approximation, δ_1, δ_2 versus x is linear

$$\delta_1 = \delta_2 = 1 - ax \tag{13a}$$

where a is an empirical parameter equal to 1 for disproportionation and to 1/2 for recombination.

Experimental the decrease of δ with x fits the theoretical results.[17,26]

3. INFLUENCE OF THE DIFFUSION MOBILITY ON THE RATE CONSTANTS OF CHEMICAL REACTIONS

3.1 Biradical Termination Rate Constant K_t Dependence on Concentration and Molecular Weight

According to the Smoluchowski equation, $K_t(0)$ is defined only by the segment size A_s and D_1 at the θ-conditions in low polymer concentration range:

$$K_t(o) = zA_s \cdot D_1 \tag{13}$$

but is independent of the radical molecular weight and the surrounding medium molecular weight, z is a numerical parameter, A_s the chain segment. When two macromolecules approach each other it is necessary to take into account the sequence of translational movement of macromolecules and reorganization of reacting segments. Then K_t may be obtained from:

$$\frac{1}{K_t} = \frac{1}{ZDR} + \frac{1}{Z'D_1A_s} \tag{14a}$$

and in the low conversion range K_t is given by

$$K_t = \frac{ZZ'}{(Z + Z')} A_sD_1$$

With increase of polymer concentration c changes in R, D_r, D_1 are observed. To simplify the problem, we discuss θ—conditions and we assume D_r is equal to macromolecular self-diffusion coefficient D. In the moderate concentration range, where Equation (3) is valid, K_t is given as follows[31]:

$$\ln K_t = \ln K_t(o) + \frac{Q_1}{T - T_g} + a_2\sqrt{x[\eta]} \quad (14)$$

(at $x[\eta] > 1$), a_1, a_2 = numerical coefficients.

In the moderate x-range, Equation (14), the main factor belongs to the third term $x[\eta]$. When $T_g \rightarrow T(\Delta T > o)$ the second terms is the controlling one. Thus the K_t dependence on M is specific. In the low x range K_t is independent of M, Equation (13), in the moderate x range K_t is affected by M, in the high x range molecular weight dependence may exist ($T_{gp} < T$) or not ($T_{gp} > T$). For some systems (small $x[\eta]$ and ΔT values) "latent" gel effects are manifested.

Analysis of the experimental data available in the literature show the validity of Equation (14).

Equation (14) may be used for estimation of the polymerization kinetics and molecular-weight distributions in different industrial processes. It should be mentioned, that the numerical coefficients in Equation (14) differ from that in the diffusion theories of macromolecular mobility discussed here. It is probably due to imperfection in the Smoluchowski formula as well as to simplification of the gel effect mechanisms. Nevertheless, this approach can predict several peculiar effects in radical polymerization at high degrees of conversion.

3.2 K_t Dependence on Radical Molecular Weight

Substitution of Equation (3) into the Smoluchowski expression, allows separation of the influence of radical molecular weight M_r from that of the surrounding macromolecules:

$$K_t(x) = K_t(o)\frac{D_1(x)}{D_1(o)}\left[e^{-127\sqrt{x[\eta]}} + \frac{1}{1.843N^{0.5}}\right] \quad (15)$$

The first term in the brackets is governed by molecular weight of surrounding macromolecules (M_m), the second one—by macroradical length $N(M_r)$. Equation (15) predicts, that for some concentration intermolecular hydrodynamic interactions do not affect the termination rate constant. The value of K_t is controlled only by the radical length and relaxation state of the polymerization system.

The dependence $K_t(N)$ on N is considered in the form of a power law N: $K_t \sim n^{-d}$. Then d will change with x from 0 to 0.5 and even more, while the temp of the functional changing $d(x)$ will be governed by the molecular weight of the surrounding macromolecules.[29] Analysis showed,[30] that during PMMA and ST polymerization d changes from 0 to 0.45, while the polymer concentration increases from 0 to 0.4 Figure 5.

3.3 Distribution Function on Macromolecules Chain Lengths

Representation of K_t (Equations 14 and 15) allows solutions of Equation (6).[26] For the distribution function of the chain lengths (weight averaged function) one obtains:

$$f_w(n) = \frac{2d_1 n + d_2\sqrt{n}}{\nu} e^{\{-d_1 n - d_2\sqrt{n}\}} \tag{16}$$

where $d_1 \cdot 2\nu = 1 + \bar{K}^{-1} \cdot e^{-1.27\sqrt{x[\eta]}}$; $d_2\nu = 1.083/4\bar{K}$; $\bar{K} = e^{-1.27\sqrt{x[\eta]}} + 1.92/\sqrt{2\nu}$ where ν is the instantaneous averaged length of the kinetic chain: $\nu = V/V_{in}$. In the low concentration range $\bar{k} \sim 1$, expression (16) asymptotically approaches the well-known Flory's distribution function ($P_w/P_n = 2$). In the moderate concentration range, the $K_t(M_r)$ dependence on M_r leads to significant broadness of instantaneous MWD ($P_w/P_n = 5$). Meanwhile, the distribution function is unimodal in contrast to the results, presented in References 20 and 22. Bimodality of instantaneous MWD, obtained in References 20 and 22 is the consequence of assumed relations for the diffusion coefficients.

The distribution function Equation (16) has its maximum in the region of $n_m \sim \nu$ (low concentration range) and $n_m \sim 1.8\ \nu$ (high concentration range).

3.4 Dependence of C_m, C_s on Polymer Concentration

K_m, K_s and K_p are determined not only by the components ability to react but also their mobility. Then it is reasonable to expect a weak dependence of the ratio $C_m = K_m/K_p$ and $C_s = K_s/K_p$ on polymer concentration.

A direct method for estimation of any reaction contribution in polymerization process has been proposed, in particular transfer to the monomer and to the S-agent.[32] Determination of C_m and C_s at every stage of conversion showed, that

$$C_m/C_m(o) = C_s/C_s(o) = 1 - ax \tag{17}$$

where $a = 0.5$; $C_m(o)$, $C_s(o)$ represent C_m and C_s values at $x = 0$. Thus, C_m and C_s produce very weak dependence on conversion and are completely independent of molecular weight.

3.5 Dependence of K_p and V_{in} on Concentration

The general interpretation of the propagation and initiation rate constant dependences on conversion is based on the conception of the "cell effect."[33] Besides the direct cell effect the indirect one must also be taken into account. The latter consists of hindrance of the chemical reaction in the cell proper, i.e. the formation of intermediate complex of reacting components in the cell. Formation time of this complex is governed by the time of rebuilding the cell, i.e. by the mobility of medium elements. In this case the rate constant of the chemical reaction is expressed by

$$K = \frac{K(o)}{1 + \left(\frac{\nu_1 K(o)}{\nu}\right)\tau} \tag{18}$$

where $K(o) = K$ at $\tau \to 0$, τ is the relaxation time of molecular motion, ν is the cell volume, ν_1 is the frequency factor ($\nu_i \sim 10^{13}$ s).

Using these concepts the following expression has been derived for the propagation rate constant K_p[34]:

$$K_p = K_p(o)\frac{(1-\varphi)^{2/3}}{1 + C_1 \frac{D_1(o)}{D_1(\varphi)}} \tag{19}$$

where $K_p(o) = K_p$ at $\varphi = 0$, $D_1(\varphi)$, $D_1(o)$ is the self-diffusion coefficients of the monomer at φ and $\varphi = 0$.

$$C_1 = \left(\frac{\nu_1 K_p(o)}{\nu}\right)\frac{\beta e^2}{6D_1(o)}$$

here 1 has the dimensions of the elementary unit, characterizing molecular rebuilding of the complex, β is a numerical coefficient ($\beta \sim 1$).

The dependence of K_p on concentrations is defined mainly by the factor C_1, i.e. by the value of $K_p(o)$ and D_1. Estimation gives $C_1 = 10^{-2} \div 10^{-3}$. For simple cell effect model $C_1 = 0$.

In Figure 6, the calculated function $K_p/K_p(o)$ versus φ at various C_1 are presented. It can be seen that the K_p curves decay with increase in φ, especially in the range $\varphi > 0.5$. At $\varphi = 0.8$ K_p falls only three–four times ($C_1 = 0$) and fifty times (C_1

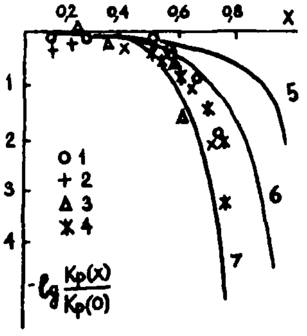

FIGURE 6 The propagation rate constant as a function of conversion in the process of radical polymerization: MMA at 22°C (1, 2), at 0°C (3) and vinylacetate at 20°C (4). Points represent experimental data.[38,39] Curves correspond to estimation according to Equation (19) at $A = 3$, $C = 0$ (5) and 10^{-2} (6, 7); $d = 0.8$ (6); 1.1 (7).

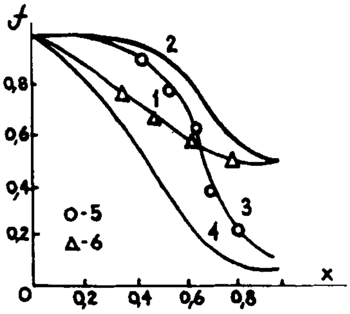

FIGURE 7 The efficiency of initiation plotted versus conversion. Curves correspond to calculation according to Equation (20) at $A = 3$; $q = 0.8$; $Q = 0.1$ (1, 4); 0.01 (2, 3); $q = 5$ 10 (2); 5 10 (1); 1 10 (3); $1 \cdot 10^{-2}$ (4). Points represent experimental data.[39]

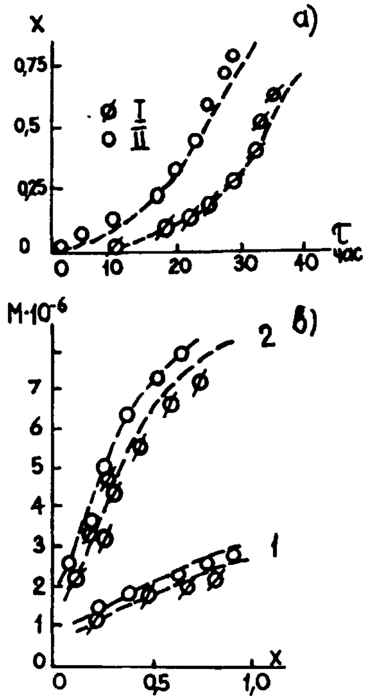

FIGURE 8 The conversion plotted versus time (a) of bulk-polymerization of MMA at 20°C in the presence of dicycloperoxicarbonate 0.003 mol/liter. The molecular-weight functions M_n (1), M_w (2) plotted versus conversion (b). Points correspond to the process in the instrument of periodical action (I), in the ampule (II). Solid line represents result of calculation according to Equation (16) in account of conversional dependences K_p, and f Equation (19, 20). Dashed line—according to Equation (16) in account of inhibition Equation (22).

$= 10^{-2}$). Moreover, at high values of $K_p(o)$ ($\sim 10^3$), the dependence of K_p on concentration is more pronounced. Experimental data for MMA and VA are also plotted in this figure.[35–37] Good correlation between theoretical and experimental curves is clearly observed.

The initiation rate is governed by initiator efficiency f and decomposition constant

K_d. It is important to notice, that the initiation process is often influenced by the by-side chemical reactions.[38] When side reactions are absent, the K_d dependence on φ will be described by Equation (19) at C_1 10^{-5}. In this case the dependence of K_d on φ is practically not observed. Experimental data confirms a weak decrease of K_d with polymer concentration.[39]

Using these concepts the equation for the initiator efficiency f was derived[34]:

$$f = \frac{\dfrac{D_1(\varkappa)}{D_1(o)} + q}{\dfrac{D_1(\varkappa)}{D_1(o)} + Q} \tag{20}$$

where q and Q are governed by the process parameters and radical concentration N_r in the cell ($N_r \sim 3$ mol/liter), (Figure 7)

$$q = \left(\frac{\nu_1 K_p(o)}{\nu}\right)^{0.5} \frac{\beta l^2}{6D_1(o)}; \qquad Q = q + \frac{K_p(o)N_2 l^2}{D_1(o)} \tag{21}$$

3.6 Practical Application of These Methods

The computer programs based on the above approach has been used to estimate the K_t dependence on x, M, T_g, M_r. A good correlation between experiment and theory, has been shown for MMA polymerization processes with strong autoacceleration. Similar calculations have been performed for polyvinylchloride and polyvinylacetate.

4. PECULIARITIES OF CHEMICAL REACTIONS WITH RADICAL POLYMERIZATION AT HIGH CONVERSIONS

4.1 Kinetic Schemes for Free Radical Polymerization in Industrial Conditions

Applications of the theoretical approach for free radical polymerization at high degrees of conversions has worked relatively well in laboratory and common industrial conditions. However, wider application of the computer program has shown significant discrepancies between theoretical and experimental results, in some industrial situations. For this reason, a more precise definition of the kinetic scheme has been carried out.

In Figure 8, the results of MMA bulk-polymerization in an industrial reactor are plotted. Calculated values of M_n, M_w are also shown and exceed the experimental values over a wide conversion range. At the same time comparison between theoretical and experimental results in the laboratory showed good correlation. It illustrates the problems of carrying out the process in industrial conditions.

Investigation of MMA polymerization kinetics[40] pointed out the influence of

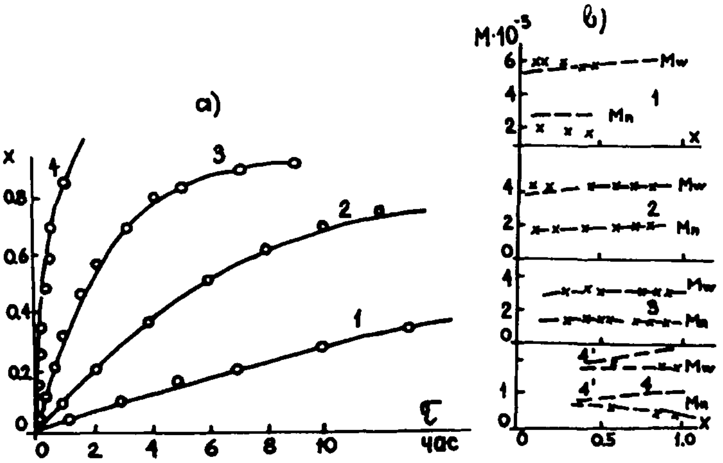

FIGURE 9 The conversion plotted versus time (a) of bulk-polymerization of styrene. The molecular-weight functions M_n (1), M_w (2) plotted versus conversion (b). Points correspond to experimental data.[10] Labels correspond to different polymerization temperatures in grades C: 100 (1), 120 (2), 140 (3), 170 (4). Curves represent theoretical model estimations. Dashed lines 4 (l) represent calculations without taking in account the reaction of olygomer initiation and transfer.

admixtures found in monomer. Taking the latter into account, new reactions have been derived which more precise define the kinetic scheme[41]:

$$\frac{d[Z]}{dt} = -\beta Y_o[Z](K_Z + K_{mZ}) - K_{11}[S_Z][Z] + \beta K_{1l}[O_2]Y_o;$$

$$\frac{d[O_2]}{dt} = -\beta K_{1l}[O_2]Y_o; \quad \frac{d[S_z]}{dt} = -\beta K_{SZ}[S_Z]Y_o - K_{11}[S_Z][Z];$$

$$\frac{dY_o}{dt} = 2fK_d[T] + K_{th}M^n - \beta K_t Y_o^2 + -\beta K_Z[Z]Y_o$$

$$+ \beta K_{t1}[O_2]Y_o - \beta K_{SZ}[S_Z]Y_o \qquad (22)$$

Here K_Z, K_{mZ}, K_{SZ} are the rate constants of inhibition, chain transfer for inhibitor and stabilizator; K_{11} is the rate constant for the reaction of inhibitor (Z) with stabilizator molecule (S_Z), K_{1t} being the rate constant of the reaction of inhibitor formation. $[Z]$, $[S_Z]$, $[O_2]$ are inhibitor, stabilizator and oxygen concentrations. These reactions depend on the polymerization temperature. Good correspondence of the calculated results with experimental data has been observed (Figure 9).

Bulk thermoinitiated styrene polymerization on an industrial scale has been modified in a similar way. The calculated and experimental data are plotted on Figure 10. It can be seen, that in the moderate and high conversion ranges the calculated values exceed experimental values. At the same time good accordance is observed for lower conversions ($x < 30\%$) as well as for laboratory samples. In experiments, set to definition of the scheme,[42,43] the presence of unsaturated bi-

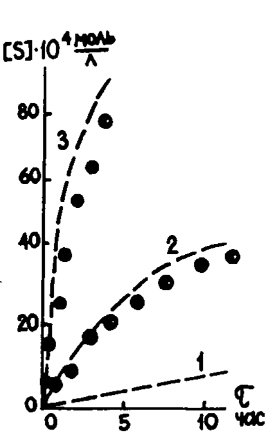

FIGURE 10 The influence of temperature on the rate of formation of olygomer fractions. Labels correspond to different polymerization temperatures (in grades C): 100 (1), 120 (2), 180 (3). Points represent the experimental data.[10] Dashed lines represent estimations according to Equation (23).

and trimers (diphenylbutene and threephenylhexene) have been observed. The rate constants of the by-product formation in the polymerization process have been estimated.[44] MWD of polystyrene have been investigated.[45] The decrease in M suggests chain transfer on the by-products. The rate constant for the latter is 2.4 $10 \cdot \exp\{-7068/RT\}$.[45]

The additional reaction may be expressed as follows:

$$\frac{d[OL]}{dt} = -K_{sol}[OL]Y_o + K_{ol}[M]^2 \qquad (23)$$

where K_{sol} is the rate constant for chain transfer to oligomer, K_{ol} is the rate constant of oligomer inhibition, and $[OL]$ is its concentration. K_{ol} is equal to 6.8 10 exp($-32900/RT$) and $K_{sol} < K_{ol}$ at the same T, since the accumulation of these products in polymerization system is observed. The higher the polymerization temperature and degrees of conversion, the larger will be the $[OL]$ values and this speciality explains discrepancies in the theoretical and experimental data (Figure 10).

4.2 The Formation of Microinhomogeneities in Polymerizating Medium

In gel effect theories the homogeneity of the polymerization medium is assumed. Usually, space-homogeneous solution of the system of kinetic equations for the functions V and R_i is searched. V and R_i functions determine the conversion and concentrations of radicals with polymerization degree $i = 1, 2, \ldots$ at t time after the start of polymerization. However, in the gel effect region microinhomogeneities have been observed,[10,11] which can have considerable effects on the biradical termination rate constants. A radical, trapped in the fluctuation, can live for a long time. It is equivalent to the existence in the reaction of additional monomolecular terminations. Consider the solution of the system of equations for microinhomogeneous medium.[46] From a mathematical point of view the instability (microinhomogeneity formation) is connected with bifurcation in the solution of kinetic equations system, governing the polymerization process. Searching for the bifurcation moment, small perturbation of homogeneous solutions have been considered. This depends on the space coordinates of the polymerization medium. The diffusional transfer of radicals with different chain length S, is controlled by their self-diffusion coefficients D_s. Diffusional transfer, which is controlled by the cooperative diffusion coefficient D_k, also has to be taken into account. Let us substitute the perturbed solution in the ordinary system of equations and linearize the systems for small perturbations for r_s, Y_o, x. Allowing for the diffusion terms and termination constants dependence vs conversion, the linearized system of equations can be expressed as follows:

$$\frac{\partial r_s}{\partial t} = K_p(r_{s-1} - r_s) - r_s \sum_{j=1}^{\infty} K_{js}(X_o) \cdot R_{oj}^{(o)} - R_{os}^{o} \sum_{j=1}^{\infty} K_{js}(X_o) r_j$$

$$+ -\varkappa \sum_{j=1}^{\infty} \frac{\partial K_{js}(X_o)}{\partial X_o} + D_s(\varkappa_o)\Delta r_s;$$

$$\frac{\partial x}{\partial t} = K_p(1 - x)y - K_p Y_o \varkappa + D_k(x_o)\Delta x; \quad y(Q, t) = \sum_{s=1}^{\infty} r_s(Q_1 t) \tag{24}$$

In Equation (24) the terms responsible for possible instability are those, involving $\partial K_{ij}/\partial x_o$. Since $\partial K_{ij}/\partial x_o < 0$ these terms turn out to be positive.

Arbitrary perturbation of a homogeneous distribution of radical concentrations may be divided in two terms:

$$r_s(Q, t) = \frac{R_{os}^{(o)}(t)}{Y_o} y(Q, t) + \rho_s(Q, t) \tag{25}$$

The first term characterizes the fluctuations of concentration of radicals without changing the shape of their length distribution. The second one, on the contrary, characterizes the shape fluctuations of this distribution without changing the radical concentrations ($\Sigma\, \rho_j = 0$). Let the initial perturbation, at moment t be such, that all $\rho_j = 0$. During the relaxation process of this perturbation Equations (24), radical molecular weight distribution will change so, that at $t > t_o$ $\rho_j \neq 0$. However, as was mentioned already, radical redistribution in increasing conversion fluctuation proceeds in such a way, that it leads to an additional decrease in the termination rate. Therefore, if we search only for conditions of instability, terms with ρ_j may be neglected at $t > t_o$.

Substituting (25) at $\rho_j = 0$ in system (24) and adding all equations except the latter one, we obtain a closed set of two differential equations for $x(a, t)$ and $y(a, t)$. After Fourier-transformation on space coordinates $x(a, t) > x_*(\mathbf{q}, t)$ and $y(a, t) > y_*(\mathbf{q}, t)$, ($\mathbf{q}$ = wave-vector), the system may be represented as follows:

$$\frac{dy_*}{dt} = -A_{11}y_* + A_{12}X_*; \quad \frac{dx_*}{dt} = A_{21}y_* - A_{22}X_* \tag{26}$$

Coefficients $A_{\alpha\beta}(1 < \alpha\beta < 2)$ of the system (26) are positive functions alterating in a limited range of time. They are determined by space-homogeneous solutions of kinetic equations system

$$A_{11} = 2k_t Y_o + q^2 D; \quad A_{12} = -\sum \frac{\partial K_{tij}}{\partial x_o} R_{oi}^{(o)} \cdot R_{oj}^{(o)};$$

$$A_{21} = K_p(1 - x_o); \quad A_{22} = K_p Y_o + q^2 D_k \tag{27}$$

here K_t and D are average termination constant and self-diffusion coefficient of the radicals, respectively:

$$K_t = \langle K_t \rangle_o$$

$$D = Y_o^{-1} \sum_i D_i R_{oi} \tag{28}$$

Equation (26) is the consequence of Equation (24) at the initial moment to, when the perturbation occurs and all ρ (a, t_o) are equal to 0.

Let us suppose, that all coefficients of the system (26) are time independent. In this case this system will be characterized by positive Liapunov factor and will be unstable, if the following inequality holds[47]:

$$A_{12}A_{21} > A_{11}A_{22} \tag{29}$$

More detailed analysis shows, the dependence of coefficients $A_{\alpha\beta}$ on time does not lead to significant change in the result (29).

Condition (29) has its simplest representation in the absence of diffusion processes ($D = D_k = 0$). Formally, this condition coincides with that of instability in the polymerization system with infinite sizes, assuming $q = 0$. Then from (29) it follows:

$$-\sum \frac{\partial K_{ij}}{\partial x} R_{oi}^{(o)} R_j^{(o)} > \frac{2}{1 - x} \sum K_{ij} R_i^{(o)} R_j^{(o)} \tag{30}$$

Thus, the termination "constants" K_{ij} produce a strong dependence on conversion, so that reversible fluctuations are formed. If all K_{ij} produce symbate dependence on conversion, i.e. $\lambda = -\partial \ln K_{ij}/\partial x$ does not depend on i and j,‡ then condition (30) is simplified as follows:

$$\lambda = -\frac{\partial \ln K_t}{\partial x} > \frac{2}{1 - x} \tag{31}$$

‡This condition holds at moderate concentration range ($c[\eta] < 20$, where c is polymer concentration, $[\eta]$ is intrinsic viscosity).

Few direct experimental results for the dependence of the averaged termination constants on conversion show, that as x changes from 0–5% to 35–45% at bulk polymerization, K_t value may be reduced: for PMMA—approximately at two orders of magnitudes, for PS—approximately at one order and for PVA—approximately in three times.

When Equation (31) is valid, it is possible to estimate the minimal size of the inhomogeneities forming the minimal value of Λ corresponds to maximal $q(\Lambda \sim q^{-1})$, when the inequality (31) turns to the equality.[48] Let us take into account, that $D_k > D$, $K_t >> K_p$ and polymerization rat: $V = dx/dt$. Then, from the instability condition one can estimate Λ:

$$\Lambda \sim \left(\frac{D_k}{\lambda V}\right)^{0.5} \tag{32}$$

Typical values for PMMA and PS: $\lambda = 1 \div 10$, $D_k = (10 \div 10)$ ms, $V = (10^{-3} \div 10^{-2})s^{-1}$ depending on temperature.

Therefore, typical values are $\Lambda \sim 10 \div 100$ m, that fit the experimental estimations.[8] When the polymerization rate decreases, the size of inhomogeneities formed increases according to (32).

The more complete conditions for instability can be determined by taking into account the possible chain transfer reactions and the rate dependence of all the elementary reactions.

Thus, for the first time, the criteria for the formation of space inhomogeneities in homophase free radical polymerization, have been formulated and can serve as a basis for improvement of the gel effect theory.

4.3 Kinetics of Chain Transfer on Macromolecule and Long Chain Branched Macromolecules Formation

One of peculiarities of free radical polymerization at high conversions is the increased probability of kinetic chain transfer to the macromolecule. This leads to the formation of long chain branched macromolecules.[5]

The chain transfer reaction to polymer may be expressed as:

$$R_{r,b} + P_{s,m} \xrightarrow{K_{tp}} P_{r,b} + R_{s,m+1} \tag{33}$$

here R_{rb} is the radical with length "r," carrying "b" branches, P_{sm} is the "dead" polymer chain, consisting of s—monomers and m branches, K_{tp} = rate constant of kinetic chain transfer to the polymer. Using the standard approach one can generate equations for the moments[49]:

$$K_t Y_o^2 = K_T T$$

$$(C_d + 2C_r)Y_n Y_o - (1 - x)[(Y + 1)_n - Y_n]$$

$$+ C_m Y_n M_o(1 - x) + C_p(xY_n - Y_o Q_{n+1}) = 0$$

$$(1 - x)Y_o \frac{dQ_n}{dx} = C_d Y_n Y_o + C_r[Y + Y]_n + C_m Y_n M_o(1 - x)$$

$$+ C_p(xY_n - Y_o Q_{n+1})$$

$$C_t H_n Y_o - (1 - x)[(H + 1)_n - H_n] + C_m H_n M_o(1 - x)$$

$$+ C_p[xH_n - Y_o A_{n+1} + Q_{n+1}] = 0$$

$$Y_o(1 - x) \frac{dA_n}{dx} = C_d H_n Y_o + C_r[H + Y]_n M_o$$

$$+ C_m H_n M_o(1 - x) + C_p[xH_n - A_{n+1} Y_o] \quad (34)$$

here $H_n = \Sigma_{b=0} \Sigma_{r=0} br^n R_{r,b}$; $A_n = \Sigma_{b=0} \Sigma_{r=0} b_r^n P_{r,b}$; $C_p = K_{tp} K_p$; $C_{dn} = K_{dn}/K_p$; $C_m = K_m/K_p$; $C_t = C_d + C_r$, where "n" means the moment of the termination rate constant. The last two equations determine the moments changes for "living" and "dead" long chain branched macromolecules. Number-averaged and weight-averaged number of branches are evaluated as:

$$B_n = \frac{A_o}{Q_o}; \qquad B_w = \frac{A_1}{Q_1} \quad (35)$$

Equations for several first moments are expressed as follows:

$$\frac{dQ_o}{dx} = C_m + \frac{C_{do} + C_{ro}}{1 - x} Y_o; \quad \frac{dQ_2}{dx} = 1 + \frac{2Y_1}{Y_o} + \frac{2C_{r2} Y_1^2}{(1 - x)Y_o}$$

$$\frac{dQ_3}{dx} = 1 + \frac{3Y_2}{Y_o} + \frac{3Y_1}{Y_o} + \frac{6C_{r3} Y_1 Y_2}{(1 - x)Y_o}; \quad A_o = -C_p[\ln(1 - x) + x]$$

$$\frac{dA_1}{dx} = \frac{H_o}{Y_o} + \frac{C_{r1} H_o Y_1}{(1 - x)Y_o} + \frac{C_p Q_2}{1 - x}$$

$$C_1 Y_1 = Y_o \left(1 + \frac{C_{p2} Q_2}{1 - x}\right); \qquad C_2 Y_2 = Y_o \left(1 + \frac{2Y_1}{Y_o} + \frac{C_p Q_3}{1 - x}\right);$$

$$C_1 H_o = Y_o C_p(A_1 + M_o x); \qquad C_2 H_1 = Y_o \left[\frac{C_p(A_2 + Q_2)}{1 - x} + \frac{H_o}{Y_o}\right] \quad (36)$$

where $C_i = C_m + C_{di}$.

The solution of Equation (34) can be carried out on the computer. If the rate constants of chemical reactions are known, the solution of (34) gives quantitative values of MWD for the products in the low conversion range.

It should be pointed, that the transition from a system of differential equations for material balance to the system for the moments H_n, is not elementary from the mathematical point, as it seems to be at the first glance.

In low conversion range, the analytical solutions may be obtained. For the radical termination by disproportionation:

$$\frac{1}{P_n} = C_m - \frac{C_d Y_o}{M_o} \frac{\ln(1 - x)}{x} \simeq \frac{1}{P_{no}} \left(1 + \frac{C_d Y_o P_{n,o}}{M_o} x + \cdots\right)$$

and the number-averaged molecular weight does not depend on the chain transfer reaction to polymer and P_w:

$$P_w = 2P_{n,o}(1 + 0.5b_1 P_{n,o} x) \quad (37)$$

where $P_{no}^{-1} = C_m C_d Y_o / M_o$; $b_1 = 2C_m + C_d Y_o / M_o + C_p$; $Y_o = V_{in}^{0.5} K_p / K_d^{0.5}$ at $x \neq 0$, P_w depends on the rate constant for transfer to polymer. The numbers of branching, are defined by:

$$B_n = -C_p P_n \left(1 + \frac{\ln(1 - x)}{x}\right) \simeq C_p \times P_n$$
$$B_w = C_p P_w x \quad (38)$$

and the averaged branch length is $\ln = P_n/1 + B_n$.

For recombination termination we have:

$$\frac{1}{P_n} = \frac{1}{P_{no}}\left(1 + \frac{x}{2}\right); \quad P_w = \frac{3}{2} P_{n,o}\left(1 + \frac{P_{n,o} b_{2x}}{2}\right) \quad (39)$$

where $P_{n.o}^{-1} = C_r Y_o M_o^{-1}$; $b_2 = 2C_p + 1 - 2/P_{n,o}$

Applications of this approach to calculation of the molecular characteristics of branched polystyrene,[50,51] polyethylene,[52] and polyvinylacetate[53] have been considered.

Analysis of the above relations shows, that the conversion influences the formation of long chain branched molecules in a very complicated manner. From Equation 37 as x increases the value of the second factor may raise (change of the kinetic scheme) or fall (decrease of the biradical termination rate constant). The problem of the influence of conversion and diffusion mobility on such processes needs further study.

References

1. C. P. Gladushev and V. A. Popov, "The Radical Polymerization at High Conversions," Russia, Moscow, Science, 1974, 242 p.

2. S. A. Volfson and N. S. Enikolopyan, "Calculations of High Efficiency Polymerization Processes," Russia, Moscow, Chemistry, 1980, 312 p.
3. P. De Gennes, "Scaling Ideas in Polymer's Physic," Russia, Moscow, Piece, 1982.
4. V. P. Budtov, *Makromolec. Chem.*, **188**, 23553 (1987).
5. V. P. Budtov, "Physical Chemistry of Polymer's Solution," Russia, St. Petersburg, Chemistry, 1992, p. 382.
6. V. P. Budtov, S. J. Kogan and N. G. Podoseyonova, *Reports of the Academy of Science*, Russia, **309**, 883 (1988).
7. V. P. Budtov, The Success of Chemistry, 1989.
8. V. P. Budtov, *Makromolec. Compounds, Russia*, **A28**, 2578 (1986).
9. N. G. Podoseyonova and V. P. Budtov, *Makromolec. Compounds, Russia*, **A19**, 1643 (1977).
10. S. J. Kuchanov, A. J. Dyachkov and V. P. Zubov, *Makromolec. Compounds, Russia*, **293**, 653 (1987).
11. A. A. Levinsky, S. U. Menshov, A. J. Dyachkov and V. P. Zubov, *Makromolec. Compounds, Russia*, **A29**, 1917 (1987).
12. S. W. Benson and J. North, *J. Amer. Chem. Soc.*, **84**, 935 (1962).
13. G. Horie, J. Mita and H. Kambe, *J. Polym. Sci.*, **6**, 2663 (1968).
14. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **114**, 883 (1976).
15. M. Stickler and G. Meyerhoff, *Makromolec. Chem.*, **179**, 2729 (1978).
16. S. J. Kuchanov and B. S. Povolotchky, *Reports of the Academy Science*, Russia, **227**, 1147 (1976).
17. B. W. Brooks, *Proc. Royal Soc.*, **A3**, 183 (1977).
18. K. Ito, *J. Polym. Sci., Pol. Chem. Ed.*, **13**, 401 (1975).
19. S. K. Soh and D. C. Sundberg, *J. Polym. Sci., Pol. Chem. Ed.*, **20**, 1299 (1982).
20. H. Boots, *J. Polym. Sci., Pol. Phys. Ed.*, **20**, 1695 (1982).
21. E. B. Brun, V. A. Kaminsky and G. P. Gladushev, *Reports of the Academy Sci., Russia*, **278**, 134 (1984).
22. V. A. Kaminsky, E. B. Brun and V. A. Ivanov, *Reports of the Academy Sci., Russia*, **282**, 923 (1985).
23. De Gennes, *J. Chem. Phys.*, **76**, 3316 (1982).
24. N. G. Podoseyonova and V. P. Budtov, "News of the High Schools, Chemistry and Chemical Technology," Russia, **31**, 3 (1988).
25. V. P. Budtov, N. G. Podoseyonova and E. G. Zotikov, *Makromolec. Compounds, Russia*, **A23**, 15535 (1981).
26. S. J. Kogan and V. P. Budtov, *Makromolec. Compounds, Russia*, **A32**, (1989).
27. N. G. Podoseyonova and V. P. Budtov, *Makromolec. Compounds, Russia*, **A23**, 1461 (1981); **A30**, 364 (1988).
28. N. G. Podoseyonova, E. G. Zotikov and V. P. Budtov, *Makromolec. Compounds, Russia*, **A25**, 43 (1983).
29. J. Boqunjoko and B. Brooks, *Makromolec. Chem.*, **B184**, 1603 (1983).
30. V. P. Budtov, B. V. Revnov and N. G. Podoseyonova, *Makromolec. Compounds, Russia*, **A30**, 263 (1988).
31. V. P. Budtov and N. G. Podoseyonova, *Makromolec. Compounds, Russia*, **B28**, 363 (1986).
32. V. P. Budtov, N. G. Podoseyonova and G. D. Ballova, *J. Appl. Chemistry, Russia*, 2055 (1980).
33. S. Ja. Lebedev, *Reports of the Academy Sci.*, Russia, **281**, 633 (1985).
34. B. V. Revnov, N. G. Podoseyonova, S. S. Ivanchev and V. P. Budtov, *Makromolec. Compounds, Russia*, **A30**, 184 (1988).
35. G. Meyerhoff, R. Sac and M. Konloumbris, *Polymer Preprints*, **26**, 293 (1985).
36. H. Melville, *Electrochem.*, **60**, 276 (1954).
37. P. Handlin and H. Melville, *J. Polym. Sci.*, **43**, 201 (1960).
38. S. S. Ivanchev, "The Radical Polymerization," 1984, St. Petersburg, Chemistry, Russia, p. 270.
39. E. G. Denisov, S. S. Ivanchev, L. A. Zberchik and H. B. Zolotova, *News of the Acad. Sci., Chemistry*, Russia, 1700 (1968).
40. N. N. Tvorogov and U. A. Matveeva, *Makromolec. Compounds, Russia*, **A18**, 347 (1976).
41. N. G. Podoseyonova, *Thesis, Inst. of the Acad. Sci.*, Russia, 1992.
42. N. G. Podoseyonova, I. V. Soloveyova *et al.*, *J. Appl. Chemistry, Russia*, **62**, 2343 (1989).
43. V. M. Bulatova, E. A. Volkova, E. I. Egorova and N. G. Podoseyonova, *Plastmass, Russia*, 31 (1977).
44. V. M. Bulatova, L. M. Barbolina *et al.*, In the book "Synthesis and Properties of Polymer," Russia, St. Petersburg, ONPO "Plastpolymer," 1985, pp. 45–54.
45. N. G. Podoseyonova, E. G. Zotikov *et al.*, "Chemical Industry," Russia, 31 (1989).
46. S. S. Ivanchev, M. J. Gandelsman and V. P. Budtov, *Reports of the Acad. Sci.*, Russia, **303**, 395 (1988).

47. D. P. Merkin, "Introduction in the Theory of Stability of Motion," Russia, Moscow, Sci., 1987, p. 286.
48. G. Nikolis and N. Prigojin, "Itself of the Organization in Unequilibrium System," Russia, Moscow, Piece, 1979, 328 p.
49. S. J. Kogan and V. P. Budtov, in the book "Polymerization Kinetics and Molecular Properties of Polymers," Russia, St. Petersburg, ONPO "Plastpolymer," 1982, p. 131.
50. W. Graessley and H. Mittelhausez, *J. Polym. Sci.*, **A2**, 5, 431 (1967).
51. V. P. Budtov, E. L. Ponomoreva and V. M. Beljaev, *Makromolec. Compounds, Russia*, **A22**, 2152 (1980).
52. V. P. Budtov, V. M. Beljaev and G. A. Otradina, *Makromolec. Compounds, Russia*, **A21**, 31 (1979).
53. N. M. Domareva, V. P. Budtov and L. J. Godunova, *Makromolec. Compounds, Russia*, **B15**, 604 (1973).