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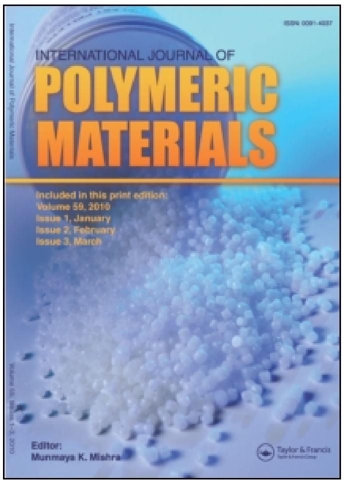

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Influence of Diffusional Mobility of Polymerization System Components on the Rate Constants of Free Radical Polymerization

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The rate constants of free radical polymerization are influenced by the diffusional mobility of the components of the polymerization system. A comprehensive study was undertaken to determine whether the existing theories of diffusion mobility can be used to quantitatively predict the rate constant changes of the main chemical reactions of free radical polymerization.

KEY WORDS Rate constants, free radical polymerization, diffusional mobility theory.

INTRODUCTION

A number of papers dealing with the quantitative theory of free radical polymerization at high conversion had recently appeared. The growing interest of scientists is due to the following reasons. First, through a great number of industrial polymerization processes are carried out at high conversions of the monomer,[1,2] the problem of technological optimization of the process still remains unsolved. Next, considerable success in understanding the behaviour of the polymer concentrated solutions and melts has been achieved. Especially good results in description of molecular motion of different components in such complicated system as the solution of chain macromolecule have been obtained.[3–5] Finally, the new molecular-weight-distribution measurements in polymers have been carried out,[6–10] as well as new methods of investigation of the peculiarities of kinetics have been proposed.[11–13]

Let us define the subject of the present work. The polymerization rate V and average polymerization degree Pn of the macromolecule at low conversions are given by the following equations:

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

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

where $[M]$, $[S]$ are the concentrations of the monomer and of chain transfer S-agent, K_m, 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. $V_{in} = fxk_dx[I]$, where f is the initiator efficiency, $[I]$ is the initiator concentration, K_d is the initiator decomposition rate.

Thus, we have to examine the dependence of K_p, K_t, C_m, C_s, K_d, f on polymerization process conditions, i.e. on polymer concentration and its molecular weight.

It is known, that free radical polymerization of methylmethacrylate (MMA) is accompanied by strong increase both in polymerization rate and in polymer molecular weight (MW). This effect contradicts the classical free radical polymerization scheme and is referred to as gel effect (autoacceleration). This phenomena is associated with the decrease of radical mobility at high polymer concentrations in polymerization system.[1] Thus the bimolecular termination rate constant K_t is to depend both on conversion and on molecular weights of radical and "dead" polymer chains. This makes the traditional approach of estimating the radical process, based on the method of molecular-weight distribution moments [MWD], incorrect.[6]

Moreover, the change of mobility of polymerization system components affects also the rate constants of other chemical reactions. However, these effects should be described by equations, different from that for K_t.

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

However, it is insufficient for the full account of radical polymerization. Indeed, at the same conversions and media viscosities, gel effect is manifested in some systems (MMA) and is absent in the others (styrene) ("evident" and "latent" gel effect).[9] It depends upon the concrete correlation between chemical reactions rate constants.

In some recent papers[10,11] the idea of microinhomogeneity formation during the polymerization process, and its probable influence on the rate constant of chemical reactions has been suggested.

Therefore for the quantitative prediction of the process behaviour in wide conversion range one must know not only the kinetic model, but also the physical properties of polymerization media must be known. The latter govern the intensity of molecular motion and the rate outlay of reagents. Consequently, this influence is propagated on molecular-weight-distribution (MWD) and on the quality of the formed product.

1. Brief Review of Publications

The problem of free radical polymerization account is the subject of many experimental and theoretical works. The main efforts in experimental studies have been directed to receive the empirical correlations between the rate constants, molecular weight distribution parameters and conversions. Considerable success in this field

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has been achieved: the complicated character of molecular weight (M) versus conversion $\{x\}$ dependence has been established, the influence of the monomer type, initiator concentration and polymerization temperature on the dependence of M on x has been determined.

However, some experimental facts remained unexplained: the absence of acceleration in styrene polymerization for example. The question of shape of MWD curve is also unsolved, because some theories propose a bimodal MWD curve.

In considerable number of experimental researches efforts were made to determine the polymerization system parameters, as well as the process parameters, which govern the change of rate constants with x. It was found that such parameters are viscosity of the reaction media (η), molecular weights of the "dead" polymer (M_m) and radical (M_r), conversions, polymerization temperature, initiator concentration, free volume (V_f) (see for example References 12–17). Attempts were made to describe them by means of empirical equations. But these empirical equations with numerous coefficients hold only in the fixed conditions of the process.

Therefore it is hard to use them in practice for quantitative predictions of kinetic behaviour of the processes, as well as of molecular-weight-distribution formation.

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Theoretical studies[18-22] were mainly directed to work out a model taking in account the rate constants versus conversion and radical length dependence. Only in recent years the works,[6] dealing with the general solution of the system of differential equations of material balance for polymerization system have appeared. They already take into account the dependence of rate constant on conversion and radical molecular weight. Usually two assumptions are made to account for the K_t versus x and M dependence, such as: (1)—identity of the molecular motion mechanisms for macromolecules and radicals, (2)—correctness of Smoluchowski equation for the analysis of radical reactions in chain macromolecules. According to de Gennes,[23] the validity of the latter assumption is equivalent to $t_\eta \gg R^2D^{-1}$; where R = square radius of gyration and D = diffusion coefficient of the macromolecule, respectively, t_η = radical lifetime. This inequality holds always in radical polymerization, because the radical lifetime makes up 1–10 s, $R^2 \cdot D^{-1} \sim 10^{-2}$–$10^{-5}$ s.

Thus the relation of byradical termination rate constant vs radical length and media properties is

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

where D_{ij} is the selfdiffusion coefficient and R_{ij} the average square radius of i and j macroradicals, z = a numerical coefficient. These assumptions allow to use the well-known dependence of selfdiffusion coefficient D on concentration and M to describe the $K_t(x, M)$ dependence.

For the first time, this approach was used in the works.[18-20] However, the lack of exact theory of dependence of macromolecular selfdiffusion coefficient on concentration forced the authors to use empirical relations between D and c, M. Functional representations D vs c and M depend upon c and M ranges.[8] Thus, in dilute solution, according to Einstein-Stockes diffusion theory D_i/D_1† $\sim i^{-0.5}$, in semidilute

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

solution the Rouse-model gives $D_i/D_1 \sim i^{-1} \cdot c^{-0.5}$ $(i < i_e)$ and reptation model leads to $D_i/D_1 \sim i^{-2} c^{-7/4}$ $(i > i_e)$, i_e parameter gives the scale of entanglements and characterises the range of transition to reptile diffusion mechanisms. Moreover i_e depends also on c and M. As a result, the relations obtained contain some empirical parameters, which depend on c and M values, as well as on the experimental conditions and on the chosen type of functional representation $D = f(c, M)$ used. Naturally, it reduces the practical significance of this approach.

Another defect on this approach arises from the fact, that investigators, discussing K_t dependence on x and M, make no difference between molecular weights M of the radical itself and the medium ("dead" macromolecules, matrice), in which this radical moves. But M_m of the medium is conditioned by prehistory of the polymerization process whereas M_r is conditioned by instantaneous values of reagents concentrations. That is why the results of quantitative calculations carried out without taking into account such discrepancy in M-values, can not be really precise.

A theory of diffusion mobility of macromolecules in concentrated solutions was suggested recently.[4,5,7,8] It was shown, that D depends on c, M_m, M_r parameters 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 = 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 in much more large-scale range.

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

$$D_1(\varphi) = D_1(0)e^{(A\varphi/1-a\varphi)} = A_1 e^{(A_s/T-T_{gs})-(A_p/T-T_{gp})} \tag{4}$$

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

The recent revue[2] touches up the problem of solutions of differential equations systems. It is also emphasized in Reference 2, that the necessity of taking into account K_t vs radical length dependence, makes the computer method of direct numerical or analytical integration of the systems 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.

Thus, in spite of the great number of experimental and theoretical works, 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 can not be found experimentally. The direct task of chemical kinetics with termination rate constant, depending on the radical length, still has no adequate method of solution. Besides,

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separate influence of the macroradical length and of "dead" macromolecules on the termination rate constant of the radical, has not yet been carried out.

2. Experimental Methods and Main Results

2.1 Method of "derivatives" of MWD moments. The method of "derivatives" of MWD moments of polymerization products, described in References 24 and 25 was used. The latter gives the opportunity to study in peculiarities the radical polymerization without any assumptions on K_t versus conversion and radical length dependence. Moreover, this method is the only one of experimental study of $K_t - M_r$ relation.

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

$$Q_0 = x/P_n; \qquad Q_1 = x; \qquad Q_2 = xP_w; \qquad \text{etc.} \tag{5}$$

where P_w = weight averaged degree of polymerization. The MWD moments Q_i are connected with rate constants of chemical reactions. If the Q_i versus x and M relation is known, one might determine the relation of the corresponding constants versus these parameters (the inverse task of chemical kinetics). On the contrary, if the dependence of rate constants on x and M is known the dependence Q_i on these values may be calculated (the direct task of chemical kinetics).

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

$$\begin{aligned} \frac{dY_0}{dt} &= V_{\text{in}} - \int K_{tij} R_i R_j \, di \, dj \\ \frac{dY_n}{dt} &= K_p[M][(Y+1)_n - Y_n] - \lambda Y_n - \int K_{tij} R_i R_j i^n \, di \, dj \\ \frac{dQ_n}{dt} &= \lambda Y_n + \int K_{tij} R_i R_j i^n \, di \, dj \end{aligned} \tag{6}$$

where λ characterises all the processes of transfer: $K_m[M] + K_s[S]$; $(Y + 1)_n = Y_n + nY_{n-1} + \cdots + 1$ etc., K_{tij} = 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 concrete functional relation $K_t(i, j)$ is given, the system of equations is also solvable, but the result fully depends on the type of this function $K_{tij}(ij)$.

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

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

It led to a simple enough relations for Q_n if an assumption of radicals quasistationary conditions still holds on ($dY_n/dt = 0$). Moreover, the corresponding moment is associated with that of biradical termination rate constant. It is possible to apply already worked out techniques of polymerization kinetics analysis.

Let us define‡:

$$C = \frac{\lambda}{K_p[M]}; \qquad A_0 = \frac{\langle K_t\rangle_0 Y_0}{K_p[M]}; \qquad Y_0^2 = \frac{V_{in}}{\langle K_t\rangle_0}; \qquad \delta_i = \frac{\langle K_t\rangle_i}{\langle K_t\rangle_0} \tag{8}$$

Then system (6) is as follows:

$$\begin{gathered} \frac{1-x}{M_0}\frac{dQ_0}{dx} = C + A_0; \qquad \frac{1}{2M_0(1-x)}\frac{dQ_2}{dx} = \frac{1}{C + A_0\delta_1}; \\ \frac{1}{6M_0(1-x)^2}\frac{dQ_3}{dx} = \frac{1}{(c + A_0\delta_1)(c + A_0\delta_2)} \end{gathered} \tag{9}$$

It should be emphasized, that the equations obtained (9) differ from the traditional ones only by $\delta_i \neq 1$ values. Thus, once determining value, one might use the set (9) for solving any problems of polymerization kinetics, even without knowing the precise relations $K_{tij}(ij)$. Besides using Equations (9) possible errors in solution of the direct and inverse problems may be predicted.

It should be also pointed, that equation for Q_0 does not contain δ_i. As a result, the Q_0 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 higher in taking into account the $K_t(i, j)$ versus i, j relation. The same is right also for M_w, M_z.

Experimental data analysis, made by the author, led to the universal relation for δ_1 and δ_2:

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

Theoretical estimations carried out on several models, represented in References 6 and 26 and 21 and 22 showed, that δ_1 must decrease from 1 to 0.16, when conversion increases. Moreover, calculations, carried out in References 6 and 26, pointed to equality $\delta_1 = \delta_2$, that fits experimental results.

Experimental data analysis, concerning molecular-weight-distribution (M_n, M_w, M_z)

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‡The designations proposed differ from that, used later[21] but the final results are equal.

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versus x relation, allows to determine different average moments K_t. In this case, the zero moment ($\langle K_t\rangle 0$) has simple physical interpretation and coincides with the standard K_t value, which is traditionally defined from the kinetics of the process by equation:

$$\langle K_t\rangle_0 = \frac{V^2}{V_{\text{in}}(K_p[M])^2} \tag{11}$$

2.2 *Experimental methods and samples studied.* The method of gel-permeation chromatography (GPC) for molecular-weight-distribution studies was used as a basic one. Experimental techniques, as well as methods of interpretation are fully described in References 27 and 28. All this provided high "reproducibility" of experimental results. The set of relations used gave the possibility: (1)—to choose GPC-experimental conditions, (2)—to control the correctness of molecular-weight-distribution experimental data in the macromolecular weight range $10^2 \div 10^7$.

Polymerization conditions were chosen according to modern point of view on the dependence of macromolecular thermal motion in solutions on concentration.[4,7] Thus, the dependence of 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} ($-70° \div 100°$C). To fit these conditions, the homologous raw of alkylmethacrylates was chosen, because the polymerization products of the latter are characterized by permanently decreasing values T_{gp} when their side-chain length increases. $c\cdot[\eta]$ value defines the forces, which distort the velocity field of macromolecular brownian motion. In low $c[\eta]$ range the segmental hydrodynamic interaction of the macromolecule plays the role of this force. With $c[\eta]$ increase intramolecular segmental hydrodynamic interaction weakens due to so-called "screening" effect, 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 investigation was carried out in different conditions. Processes in the presence of initiator, differing by C-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 of samples studied and conditions of their polymerization. All this gave the possibility to vary T and $x[\eta]$ parameters in wide ranges.

2.3 *Experimental results on* $K_t/K_p^2(x, \text{M})$ *dependence.* Experimental results are shown in Figures 1–3 for the following parameters: degree of polymerization, rate of the process, propagation and termination rate constants ratio.

The results in the figures are plotted in such a way, that only one parameter varies during experimental series. It allows to separate the influence of different parameters, such as, polymerization temperature, initiator concentration, length of alkyl group,

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§Here and forward the product $x[\eta]$ means $xv^{-1}[\eta]$.

TABLE I

Polymerization condition of investigated polymers

N, sample	Monomer type	T, °C	Initiator	Concentration, mol/liter 10^2	$K_d \cdot 10^5$ 1/s	$P_w \cdot 10^{-3}$
1	AMA-1	60	PL	1.0	0.5	6
2	AMA-2	60	PL	1.0	0.5	6
3	AMA-8	60	PL	1.0	0.5	8.2
4	MMA	50	DAA	1.5	0.25	12.0
5	MMA	70	DAA	1.5	0.5	6
6	MMA	90	DAA	1.5	33.5	3
7	MMA	70	DAA	0.5	5	6
8	MMA	70	DAA	1.5	5	3
9	MMA	70	PB	5.0	5	2.3
10	Styrene	45	DAA	5.0	0.15	8
11	Styrene	45	DAA	2.0	0.1	4
12	Styrene	60	PB	2.0	0.17	1.9
13	Styrene	70	DAA	1.7	5	1.1
14	Styrene	70	DAA	5.7	5	0.5
15	Styrene	70	PB	0.7	0.5	4.5
16	Styrene	70	PB	1.5	0.5	3
17	Styrene	90	PB	2.6	6.4	2.5
18	Styrene	90	PB	6.4	6.4	1.4
19	Styrene	90	TBPB	1.0	0.5	1.5
20	Styrene	90	TBPB	4.0	0.5	2.2
21	Styrene	80	TBPB	1.0	0.13	2.2
22	Styrene	100	TBPB	3.7	1.8	2.25
23	Styrene	100	TBPB	1.2	1.8	2.85
24	Styrene	100	Thermoinitiation		$1.8 \cdot 10^{-6}$	6
25	Styrene	120	Thermoinitiation		$1.2 \cdot 10^{-5}$	3.7
26	Styrene	150	Thermoinitiation		$1.4 \cdot 10^{-4}$	3
27	Styrene	180	Thermoinitiation		$1.3 \cdot 10^{-3}$	2
28	Styrene	200	Thermoinitiation		$4.6 \cdot 10^{-3}$	1.8

PL—lauric peroxide, DAA—dinitrylasobutyric acid, PB—benzoylperoxide, TBPB—three butilperbensoate.

TABLE II

Initiator parameters

Initiator	Half-termination time range, h	Concentration initiator range, mol/l 10^2
PB	0.10–100	2–0.3
TBPB	10–100	10–1
PL	20	1
DAA	1–15	0.5–5

K_p of the monomer on the polymerization degree and process rate as well as on the K_t/K_p^2 value.

It may be seen, that the degree of polymerization and the rate of the process may be constant or may increase or decrease with increase of conversion; so the concrete behaviour of the system fully depends on the values of parameters mentioned above. Meanwhile, the decrease of K_t/K_p value with conversion takes place in the whole temperature range studied. Biradical termination rate constant K_t decreases with x in

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TABLE III

Monomer and polymer main parameters

	Main parameters							
							Polymer	
Monomer	$K_\eta \cdot 10^4$	a_η	M_0	$K_p \frac{\mathrm{L}}{\mathrm{MOL \cdot S}}$	$K_1 \cdot 10^6$	C_m	T_{gp} °C	$M_w \cdot 10^{-5}$
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 whole conversion range and polymerization conditions. The degree of its decrease depends on initiator concentration, on polymerization temperature and on the length of alkyl groups. Thus, according to the autoacceleration theory all the processes at high x increase become more complicated due to diffusion control of radical termination reaction.

Now, let us consider the effect of temperature and macromolecular weight on the dependence K_t on x. Nonlinear dependence K_t versus x is well observed and the influence of process conditions depends on conversion range. Thus, polymerization temperature does not affect the ratio of propagation and termination rate constants in low conversion range, but they differ hundred and even more times at high conversion. The same conclusion may be drawn if the length of alkyl radical is varied. At the same time initiator concentration affects the constants 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. Thus, now it becomes clear, that numerous attempts made by investigators to describe the functional relation K_t/K_p^2 vs conversion failed because of its multiformity.

In this work an effort is made to generalize the experimental results by revealing and forming the relation of termination and propagation rate constants vs conversion system. If we compare the processes, that lead to polymer formation with similar M, then the dependence of K_t/K_p^2 value on conversion has linear generalization in $\lg(K_t/K_p^2) \sim \Delta T$ coordinates (see Figures 1, 3). If we compare the 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 $D(c)$ relation (see Equation (3) and Section 1) one obtains for K_t/K_p^2:

$$\ln \frac{K_t(x)}{K_p^2(x)} \cdot \frac{K_p^2(0)}{K_t(0)} = -\frac{220}{T - T_{gs}} + \frac{220}{T - T_{gp}(x)} + 0.38\sqrt{x[\eta]} \qquad (12)$$

This equation has a more general meaning than the common empirical one. It holds in a wide range of parameters variations, 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 obtained product ($[\eta]$) and on the state of polymerization system (T_g).

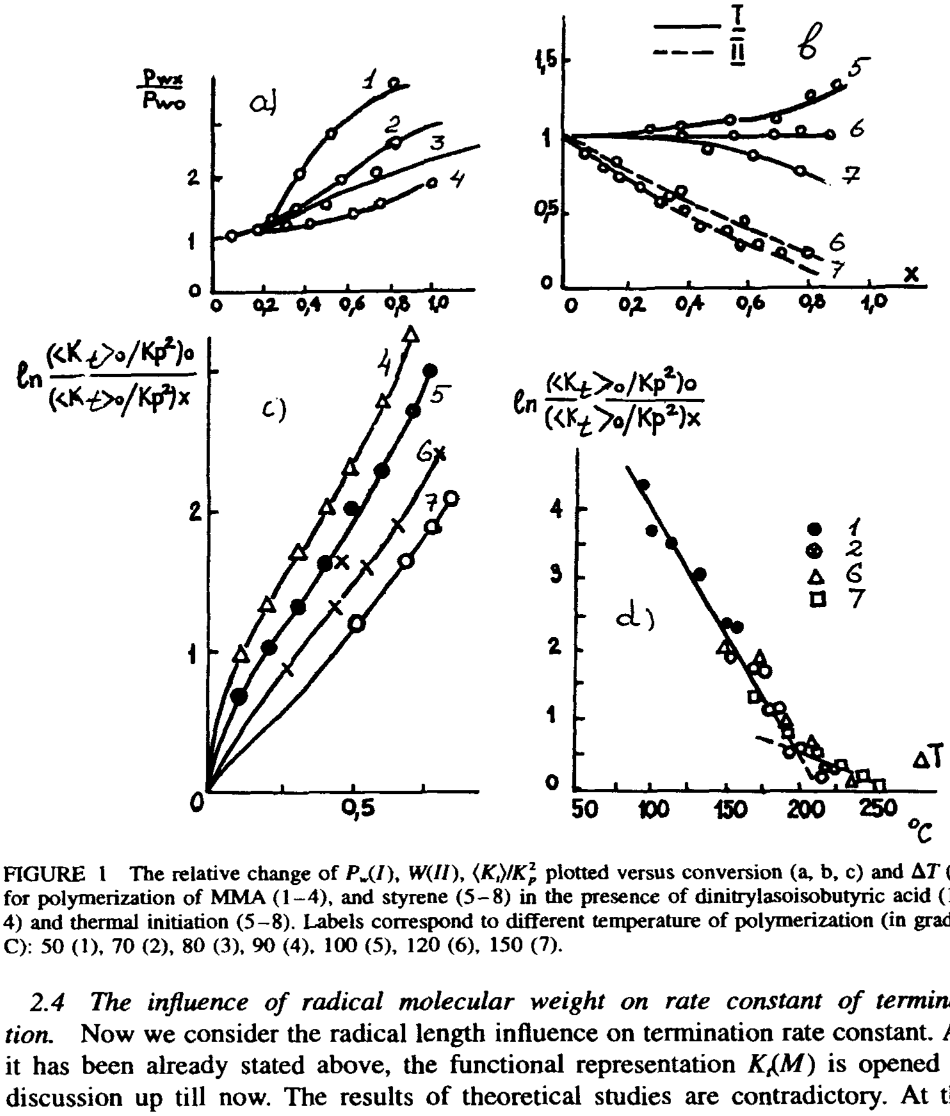

FIGURE 1 The relative change of $P_w(I)$, $W(II)$, $\langle K_t\rangle/K_p^2$ plotted versus conversion (a, b, c) and ΔT (d) for polymerization of MMA (1–4), and styrene (5–8) in the presence of dinitrylasoisobutyric acid (1–4) and thermal initiation (5–8). Labels correspond to different temperature of polymerization (in grades C): 50 (1), 70 (2), 80 (3), 90 (4), 100 (5), 120 (6), 150 (7).

2.4 The influence of radical molecular weight on rate constant of termination. Now we consider the radical length influence on termination rate constant. As it has been already stated above, the functional representation $K_t(M)$ is opened to discussion up till now. The results of theoretical studies are contradictory. At the same time due to small number and wide discrepancy of experimental results, the conclusion about relation $K_t(M)$ and its concrete type can not be drawn out. It is not surprising, because experimental relations observed can be affected not only by radical length, but also by molecular weight of the polymer, surrounding the moving radical. As a rule, the discussion of termination rate constant on molecular weight and conversion relation is carried out without taking into account the difference between the molecular weight of the radical and that of the media, where this radical moves. At the same time M_m is defined by the prehistory of polymerization process and not by instantaneous values of reagents concentration.

The kinetics of polymerization in styrene and methylmethacrylate with independently varied M_m and M_r values was studied.[29,30] This process can be carried out practically if the polymerization of monomer is made in solution of its own poly-

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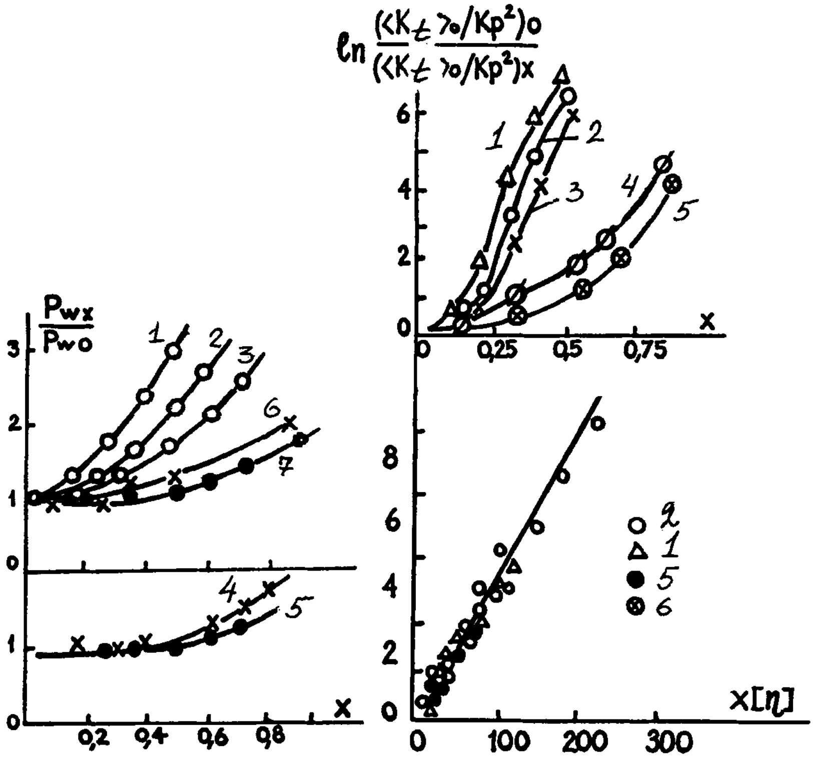

FIGURE 2 The relative change of P_w, $\langle K_t\rangle/K_p^2$ plotted versus conversion and $x[\eta]$ for polymerization of MMA-I (1–3), styrene (4–7) at 45°C (4, 5); 70°C (1–3) and 90°C (6, 7). Figures correspond to different concentration in ((mol/liter) 100) of dinitrylasoisobutyric acid 0.5 (1),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

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mer.[29] In this case variation c and M of its own polymer 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 reciprocal to initiation polymerization rate.

Thus, not only the power law of $K_t(M_r, x)$ relation was established, but also the exponent in this relation was obtained in this paper.

If the dynamics of changing of the moments dQ_0/dx, dQ_2/dx, dQ_3/dx is known, the set (9) may be used for solving the reverse problem—i.e. δ_1 and δ_2 determination at any conversions. Estimate results of the latter 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. As one can see, 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 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 at constant x. Thus, δ_1 and δ_2 change does not exceed 30%, while M increases three times. The main reason of δ_1, δ_2 changes is due to polymer concentration increase. In the first approximation, δ_1, δ_2 versus x relation follows linear representation:

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

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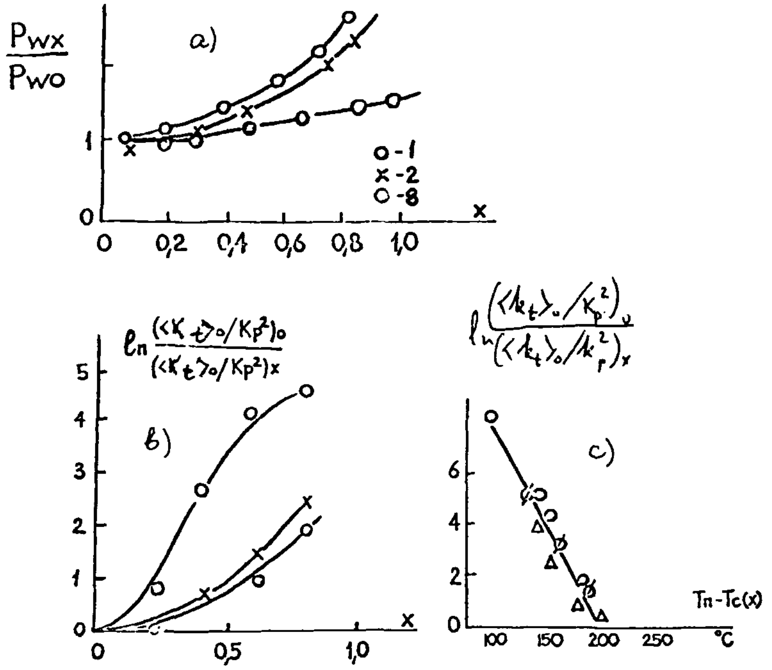

FIGURE 3 The relative change of P_w (a), $\langle K_t\rangle/K_p^2$ (b) and (c) plotted versus X and T. Figures correspond to different length of the alkyl radical.

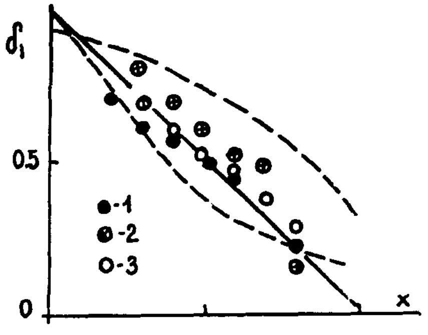

FIGURE 4 The δ_1 is plotted versus conversion for polymerization of MMA at 70°C in the presence of dinitrylasoisobutyric acid. Labels correspond to different concentration of initiator in mol/l 100: 0.5 (1), 1.5 (2), 5 (3). Curves represent estimations according to Equation (13).

Here a is an empirical parameter equal to 1 with disproportionation and to 1/2 with recombination.

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

3. Model Account of Diffusion Mobility Influence on the Rate Constants of Chemical Reactions

3.1 Biradical termination rate constant K_t dependence on concentration and molecular weight. According to Smoluchowski equation, $K_t(0)$ is defined only by segment size A_s and D_1 (θ-conditions) in low polymer concentration range:

$$K_t(0) = zA_s \cdot D_1 \qquad (13)$$

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

$$\frac{1}{K_t} = \frac{1}{ZDR} + \frac{1}{Z^1 D_1 A_s} \qquad (14a)$$

and in low conversion range K_t is given by

$$K_t = \frac{ZZ^1}{(Z + Z^1)} A_s \cdot D_1$$

With increase of polymer concentration c (conversion x), the 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. Moderate concentration range, where Equation (3) is valid, will be discussed. Then K_t is given as follows[31]:

$$\ln K_t = \ln K_t(0) + \frac{a_1}{T - T_g} + a_2\sqrt{x[\eta]} \qquad (14)$$

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

In the moderate x-range, as is seen from Equation (14) the main role belongs to the third term $x[\eta]$. When $T_g \rightarrow T$ ($\Delta T \rightarrow 0$) the second term is the basic one. Thus, K_t dependence on M is specifical. In the low x range K_t is independent of M (see 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 effect is manifested.

Analysis of experimental data available in the literature as well as obtained by the authors showed the validity of Equation (14). 34 systems, differing by monomers, initiators, polymerization temperatures and polymer glass-transition temperatures have been analysed.

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

3.2 K_t dependence on radical molecular weight. Substitution of Equation (3) to Smoluchowski expression, permits one to separate the influence of radical molecular weight M_r from that of the surrounding macromolecules:

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$$K_t(x) = K_t(0)\frac{D_1(x)}{D_1(0)}\left[e^{-1.27\sqrt{x[\eta]}} + \frac{1}{1.843N^{0.5}}\right] \qquad (15)$$

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

The dependence $K_t(N)$ on N is considered in the form of 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 functional changing $d(x)$ will be governed by the molecular weight of surrounding macromolecules. The necessary experiments have been carried out in Reference 29. Analysis of the latter[30] showed, that during PMMA and ST polymerization d changes from 0 to 0.45, while polymer concentration increases from 0 to 0.4.

3.3 Distribution function on macromolecules lengths. K_t representation (Equations 14, 15) permits to solve Equation (6).[26] Then for the distribution function on lengths (weight averaged function) one obtains:

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

where

$$d_1\cdot 2\nu = 1 + \bar{K}^{-1}\cdot e^{-1.27\sqrt{x[\eta]}}; \qquad d_2\nu = \frac{1.083}{4\bar{K}}; \qquad \bar{K} = e^{-1.27\sqrt{x[\eta]}} + \frac{1.92}{\sqrt{2\nu}}$$

ν is instantaneous averaged length of kinetic chain: $\nu = V/V_{\text{in}}$. In low concentration range $\bar{k} \sim 1$, and expression (16) asymptotically approaches the well-known Flory's distribution function ($P_w/P_n = 2$). In moderate concentration range, the account of $K_t(M_r)$ 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 diffusion coefficients.

Distribution function (see 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 reactionary ability, but also by the mobility of reacting low-molecular-weight components. Then it is reasonable to expect weak dependence of their ratio $C_m = K_m/K_p$ and $C_s = K_s/K_p$ on polymer concentration.

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

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$$C_m/C_m(0) = C_s/C_s(0) = 1 - ax \tag{17}$$

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

3.5 Dependence of K_p and V_{in} on concentration. The general interpretation of propagation and initiation rate constant dependences on conversion is based on the conception of "cell effect." In Reference 33 it was emphasized, that besides direct cell effect the indirect one must be taken into account. The latter consists of chemical reaction hindrance in the cell proper, i.e. the formation of intermediate complex of reacting components in the cell is assumed. Formation time of this complex is governed by the time of rebuilding of the cell i.e. by the mobility of medium elements. In this case the rate constant of chemical reaction is expressed by

$$K = \frac{K(0)}{1 + \left(\dfrac{V_1 K(0)}{v}\right)\tau} \tag{18}$$

where $K(0) = K$ at $\tau \rightarrow 0$, τ = relaxation time of molecular motion, v = cell volume, V_1 = frequency factor ($V_1 \sim 10^{13}$ s).

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

$$K_p = K_p(0)\frac{(1 - \varphi)^{2/3}}{1 + C_1\dfrac{D_1(0)}{D_1(\varphi)}} \tag{19}$$

where $K_p(0) = K_p$ at $\varphi - 0$, $D_1(\varphi)$, $D_1(0)$ = self-diffusion coefficients of the monomer at φ and $\varphi = 0$ ($C_1 = (V_1 K_p(0)/v)\beta l^2/6D_1(0)$). Here l being the dimension of elementary unit, characterizing molecular rebuilding of the complex, β = numerical coefficient ($\beta \sim 1$).

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

In Figure 5, calculated functions $K_p/K_p(0)$ versus φ at various C_1 are presented. It can be seen, that K_p curves decay with increase 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 ($C_1 = 10^{-2}$). Moreover, at high values $K_p(0)$ (10), dependence of K_p on concentration is more pronounced. Experimental data[35–37] for MMA and VA are also plotted in this figure. 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 initiation process is often influenced by the by-side chemical reactions.[38] When the by-side chemical reactions are absent, K_d dependence on φ will be described by Equation (19) at C_1 10^{-5}. In this case dependence K_d on

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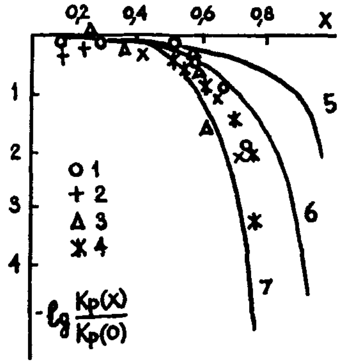

FIGURE 5 The propagation rate constant as a function of conversion in the process of radical polymerization: MMA at 22°C (1, 2), at 0°C (3) and vinylacetate at 20°C (4). Points represent experimental data.[18,19] Curves correspond to estimation according to Equation (19) at $A = 3$, $C = 0$ (5) and 10^{-2} (6, 7); $a = 0.8$ (6); 1.1 (7).

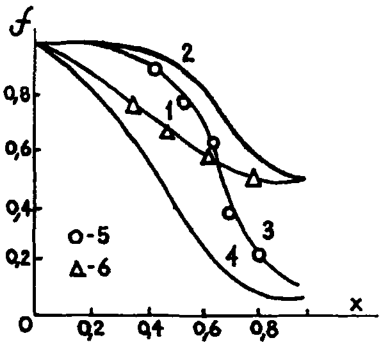

FIGURE 6 The efficiency of initiation plotted versus conversion. Curves correspond to calculation according to Equation (20) at $A = 3$; $a = 0.8$; $Q = 0.1$ (1, 4); 0.01 (2, 3); $q = 5$ 10 (2); 5 10 (1); 1 10 (3); 1 10 (4).

φ practically is not observed. Experimental data confirm weak decrease of K_d with polymer concentration.[39]

Using these conceptions the equation relation of initiator efficiency f was derived in Reference 34:

$$f = \frac{\dfrac{D_1(x)}{D_1(0)} + q}{\dfrac{D_1(x)}{D_1(0)} + Q} \tag{20}$$

where q and Q are governed by mentioned process parameters and radical concentration N_r in the cell ($N_r \sim 3$ mol/liter) (Figure 6).

$$q = \left(\frac{V_1K_p(0)}{v}\right)^{0.5} \frac{\beta l^2}{6D_1(0)}; \qquad Q = q + \frac{K_p(0)N_rl^2}{D_1(0)} \tag{21}$$

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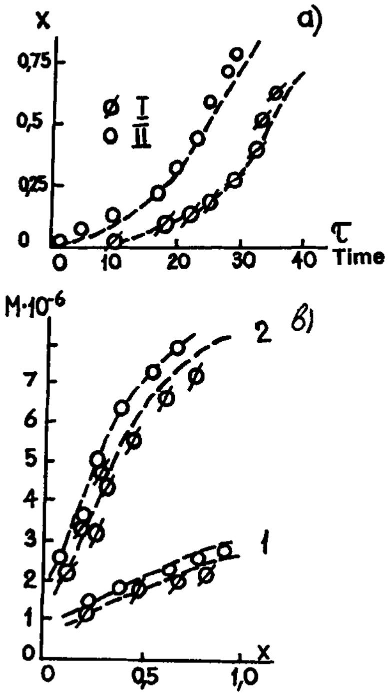

FIGURE 7 The conversion plotted versus time (a) of bulk-polymerization of MMA at 20°C in the presence of dicycloperoxicarbonate 0.003 mol/liter. The molecular-weight functions M_n (1), M_w (2) plotted versus conversion (b). Points correspond to the process in the instrument of periodical action (I), in the ampoule (II).

3.6 Practical application of these methods. Using of derived methods for solution of reverse problem of radical polymerization it is possible to describe the influence of changing state on the following evolution of radical polymerization process. Termination rate constant dependence on radical length is experimentally observed. The system of Equations (5) is obtained to describe quantitatively this influence.

The whole complex of results has practical application. Presented approach gives a possibility to use obtained equations for solving the direct task. In this case the process kinetics and molecular weight distribution moments of different orders can be calculated by known values of component concentration.

The computer program has been worked out for producing these estimations by the system of equations and with account of K_t dependence on x, M, T_g, M_r. Adequacy of computed and experimental results has been proved for MMA polymerization processes with strong autoacceleration. Analogous adequacy has been proved using literary experimental data for polyvinylchloride and polyvinylacetate in solution. Good adequacy of the estimation, as well as the absence of "fit" parameters in the algorithm, make possible to apply it for solution of specific kinetic problems in gel effect range not only in laboratory conditions (in ampoules), but also in the industrial reactors.

4. Peculiarities of Chemical Reactions with Radical Polymerization at High Conversions

4.1 Peculiarities of kinetic schemes for free radical polymerization in industrial conditions. Theoretical approach of free radical polymerization at high conversions has been relatively well proved in laboratory conditions and common industrial reactors. However, precise and wide application of the computer program has showed the significant discrepancy between theoretical and experimental results, obtained in some industrial conditions. By this reason a more precise definition of kinetic scheme has been carried out.

On Figure 7 the results of MMA bulk-polymerization process in the industrial reactor are plotted. Calculated values M_n, M_w are also presented here and, as it can be seen, they exceed experimental ones in the wide conversion range. At the same time the comparison between the theoretical and experimental results in the laboratory ones showed good correlation. It indicates the peculiarities of the running process in these industrial conditions.

The independent investigation of MMA polymerization kinetics[40] pointed out the influence of admixtures found in monomer. Taking the latter into account, the new reactions have been worked out[41] for more precise definition of the kinetic scheme:

$$\begin{aligned}
\frac{d[Z]}{dt} &= -\beta Y_0[Z](K_z + K_{mz}) - K_{11}[S_z][z] + \beta K_{1t}[O_2]Y_0; \\
\frac{d[O_2]}{dt} &= -\beta K_{1t}[O_2]Y_0; \\
\frac{d[S_z]}{dt} &= -\beta K_{sz}[S_z]Y_0 - K_{11}[S_z][Z]; \\
\frac{dY_0}{dt} &= 2fK_d[T] + K_{th}M^n - \beta K_t Y_0^2 + -\beta K_z[Z]Y_0 + \beta K_{t1}[O_2]Y_0 - \beta K_{sz}[S_z]Y_0
\end{aligned} \tag{22}$$

Here K_z, K_{mz}, K_{sz} are the rate constants of inhibition and chain transfer on inhibitor and stabilizator; K_{11} is rate constant of interaction reaction of inhibitor (Z) with stabilizator molecule (S_z), K_{1t} being rate constant of the reaction of inhibitor formation. $[Z]$, $[S_z]$, $[O_2]$ are inhibitor, stabilizator and oxygen concentrations. The significance of the reactions, mentioned above, essentially depends on polymerization temperature. Good adequacy of calculated results with experimental data have been observed (Figure 7). More precise kinetic scheme, presented above, have been used to ground the new method of technological process optimization: as a result the time process was reduced and homogeneity of the block increases.

The scheme of bulk thermoinitiated styrene polymerization on the industrial plant has been modified by the similar way. The calculated and experimental data are plotted on Figures 8 and 9. It can be seen, that at moderate and high conversion range (reactor cascade of periodical action) calculated values exceed experimental one. At the same time good accordance is observed for lower conversions ($x < 30\%$)

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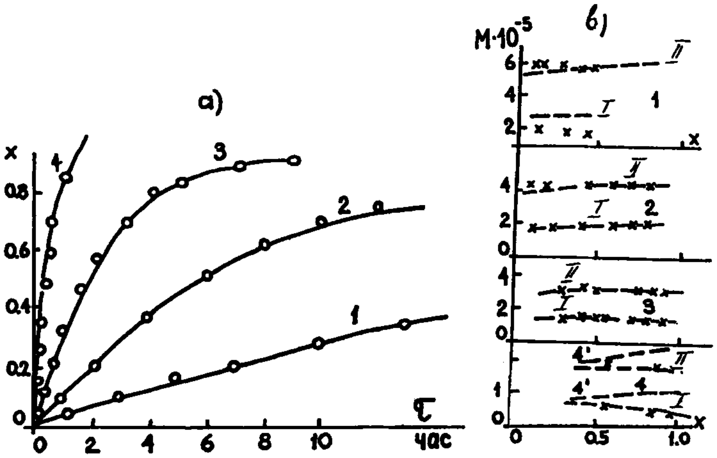

FIGURE 8 The conversion plotted versus time (a) of bulk-polymerization of styrene. The molecular-weight functions M_n I, M_w II plotted versus conversion (b). Points correspond to experimental data.[10] Labels correspond to different polymerization temperatures in grades °C: 100 (1), 120 (2), 140 (3), 170 (4). Curves represent theoretical model estimations. Dashed lines 4′ represent calculations without taking in account the reaction of olygomer initiation and transfer.

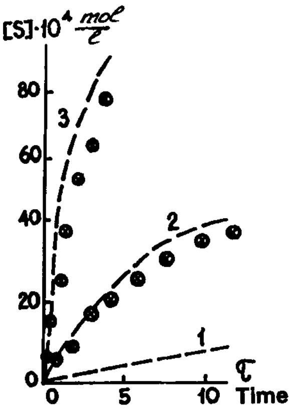

FIGURE 9 The influence of temperature on the rate of formation of olygomer fractions. Labels correspond to different polymerization temperatures (in grades °C): 100 (1), 120 (2), 180 (3). Points represent the experimental data.[10] Dashed lines represent estimations according to Equation (23).

as well as for laboratory samples. In special experiments, set up for precise definition of the scheme,[42,43] the presence of nonsaturated bi- and threemers (diphenylbutene and threephenylhexene) has been observed. Rate constants of by-product formation in the polymerization process have been estimated in Reference 44. MWD of polystyrene have been investigated in Reference 45 by special introduction of these products (i.e., dymere fraction). The observed decrease in M permitted to suppose the presence of the reaction of chain transfer on this by-products. Rate constant of the latter is $2.4\ 10 \cdot \exp\{-7068/RT\}$.[45]

The additional reaction may be expressed as following:

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$$\frac{d[\mathrm{OL}]}{dt} = -K_{SOL}[\mathrm{OL}]\cdot Y_0 + K_{\mathrm{OL}}[M]^2 \tag{23}$$

where K_{sol} is the rate constant of chain transfer on the olygomer, K_{0l} is the rate constant of olygomer inhibition, [OL]—its concentration. K_{0l} is equal to $6.8\cdot 10\ \exp(-32900/RT)$. So far as $K_{sol} < K_{0l}$ at some T, the accumulation of these products in polymerization system is observed. The higher are polymerization temperature and conversion, the larger will be [OL] value. It is just the reason, why the role of the chain transfer reaction is increased. This speciality explains the discrepancy of the theoretical and experimental data, presented in Figures 8 and 9.

4.2 The formation of microinhomogeneities in polymerizating medium. In gel effect theories the homogeneity of polymerization medium is assumed. Usually, space-homogeneous solution of kinetic equations system 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 moment after polymerization start. However, in gel effect region microinhomogeneities have been observed,[10,11] which can considerably affect on the biradical termination rate constants. The radical, trapped in the fluctuation, can live for a long time. It is equivalent to the existence of reaction of additional monomolecular termination. In this case, let us consider the solution of the system of equations in the microinhomogeneous medium.[46] From mathematical point of view the instability (microinhomogeneity formation) is connected with bifurcation in the solution of kinetic equations system, governing the polymerization process. For searching the bifurcation moment, according to well-known algorithm, the small perturbation of homogeneous solution have been considered. It depends on space coordinates of polymerization medium points. Moreover, the diffusional transfer of radicals with different chain length S, which is controlled by their self-diffusion coefficients D_s have been taken into account. Diffusional transfer of conversion, which is controlled by cooperative diffusion coefficient D_k, also had to be taken into account. Let us substitute the perturbed solution in the ordinary system of equations and linearize the differenced system on small order perturbations for r_s, Y_0, x. With account of diffusion terms and termination constants dependence vs conversion, the linearized system of equations can be expressed as following:

$$\begin{aligned}\frac{\partial r_s}{\partial t} &= K_p(r_{s-1} - r_s) - r_s \sum_{j=1}^{\infty} K_{js}(x_0)\cdot R_{0j}^{(0)} - R_{0s}^{0} \sum_{j=1}^{\infty} K_{js}(x_0) r_j \\ &\quad + -\varkappa \sum_{j=1}^{\infty} \frac{\partial K_{js}(x_0)}{\partial x_0} + D_s(\varkappa_0)\Delta r_s; \\ \frac{\partial x}{\partial t} &= K_p(1 - x)y - K_p Y_0 \varkappa + D_k(\varkappa_0)\Delta x; \qquad Y(a, t) = \sum_{s=1}^{\infty} r_s(a, t)\end{aligned} \tag{24}$$

In the system (24) the terms responsible for possible instability are those, involving $\partial K_{ij}/\partial x_0$. Since $\partial K_{ij}/\partial x_0 < 0$ these terms turn out to be positive. Arbitrary perturbation of homogeneous distribution of radical concentrations may be divided in two terms:

$$r_s(a, t) = \frac{R_{0s}^{(0)}(t)}{Y_0} y(a, t) + \rho_s(a, t) \tag{25}$$

The first term characterizes the fluctuations of summarized 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 summarized radical concentrations ($\Sigma\ \rho_j = 0$). Let initial perturbation, given at moment t, is such, that all $\rho_j = 0$. During relaxation process of this perturbation (Equations (24)), radical molecular weight distribution will change so, that at $t > t_0$ $\rho_j \neq 0$. However, as it was already mentioned, radical redistribution in increasing conversion fluctuation proceeds in such a way, that it leads to additional decrease in termination rate. Therefore, if we search only sufficient conditions of instability, terms with ρ_j may be neglected at $t > t_0$.[¶]

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

$$\begin{aligned} \frac{dy_*}{dt} &= -A_{11}y_* + A_{12}x_* \\ \frac{dx_*}{dt} &= A_{21}y_* - A_{22}x_* \end{aligned} \tag{26}$$

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

$$\begin{aligned} A_{11} &= 2K_tY_0 + q^2D; \qquad A_{12} = -\sum \frac{\partial K_{tij}}{\partial x_0} R_{0i}^{(0)} \cdot R_{0j}^{(0)}; \\ A_{21} &= K_p(1 - x_0); \qquad A_{22} = K_pY_0 + q^2D_k \end{aligned} \tag{27}$$

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

$$\begin{aligned} K_t &= \langle K_t \rangle_0 \\ D &= Y_0^{-1} \sum_i D_i R_{0i} \end{aligned} \tag{28}$$

The system (26) is the consequence of the system (24) only in the initial moment to, when the perturbation is carried in and all $\rho(a, t_0)$ are equal 0. However, at the

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[¶] This statement may be grounded in more details.

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same time the condition of instability of the system (26) is time, the sufficient condition of instability of the investigated system (24).

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 instable, if the following inequality holds[47]:

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

More detailed analysis shows, that dependence of coefficients $A_{a\beta}$ on time does not lead to significant change in the result drawn out (29). So, the inequality (29) determines the searched sufficient condition of polymerization medium instability relatively local fluctuations of the conversion and radical concentration.

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

$$-\sum \frac{\partial K_{ij}}{\partial x} R_{0i}^{(0)} \cdot R_j^{(0)} > \frac{2}{1 - x} \sum K_{ij} R_i^{(0)} \cdot R_j^{(0)} \tag{30}$$

Thus, termination "constants" K_{ij} had to produce rather strong dependence on conversion, so as the unreversable fluctuation can be 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 to the next one:

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

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

When sufficient condition of instability (31) is valid, it is possible to estimate the minimal size of the forming inhomogeneities. Minimal value Λ corresponds to maximal $q(\Lambda \sim q^{-1})$, when inequality (31) turns to equality.[48] Let us take into account, that $D_k > D$, $K_t >> K_p$ and polymerization rate $V = dx/dt$. Then, from the general condition of instability one can receive the following estimation for 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 $(10^{-1} \div 10)$ μ^2/s, $V = (10^{-3} \div 10^{-2})$ s^{-1} (conditioned by temperature). Therefore, typical values are $\Lambda \sim 10 \div 100$

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

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μ, that fit experimental estimations.[8] When the polymerization rate decreases, the size of forming inhomogeneities increases according to (32).

So, the more complete conditions of instability can be determined in the limits of the formalism worked out taking into account the possible reactions of chain transfer in the system and rate dependence of all elementary reactions on conversion.

Thus, for the first time, criteria, determining the formation of space inhomogeneities at homophase free radical polymerization, have been formulated. The latter one can serve as a basis for the improvement of general gel effect theory at free radical polymerization.

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

Reaction of chain transfer to polymer may be expressed as following:

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

Here R_{rb} is radical with length "r," carrying "b" branches, P_{sm} is "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 receive equations for the moments[49]:

$$K_t Y_0^2 = K_T \cdot T$$

$$(C_d + 2C_r)Y_n Y_0 - (1 - x)[(Y + 1)_n - Y_n]$$
$$+ C_m Y_n M_0(1 - x) + C_p(xY_n - Y_0 Q_{n+1}) = 0$$

$$(1 - x)Y_0 \frac{dQ_n}{dx} = C_d Y_n Y_0 + C_r[Y + Y]_n$$
$$+ C_m Y_n M_0 (1 - x) + C_p(xY_n - Y_0 Q_{n+1}) \tag{34}$$

$$C_t H_n Y_0 - (1 - x)[(H + 1)_n - H_n] + C_m H_n M_0(1 - x)$$
$$+ C_p[xH_n - Y_0 A_{n+1} + Q_{n+1}] = 0$$

$$Y_0(1 - x) \frac{dA_n}{dx} = C_d H_n Y_0 + C_r[H + Y]_n M_0$$
$$+ C_m H_n M_0(1 - x) + C_p[xH_n - A_{n+1} Y_0]$$

Here $H_n = \Sigma_{b=0} \Sigma_{r=0} br^n R_{\mathrm{r,b}}$; $A_n = \Sigma_{b=0} \Sigma_{r=0} br^n P_{\mathrm{r,b}}$; $C_p = K_{\mathrm{tp}}/K_p$; $C_{dn} = K_{dn}/K_p$; $C_{rn} =$

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K_{rn}/K_p; $C_i = C_d + C_r$. "n" means the moment of the termination rate constant. The rest designation—see in Equations (1) and (2). 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:

$$B_n = \frac{A_0}{Q_0}; \quad B_w = \frac{A_1}{Q_1} \tag{35}$$

Equations for several first moments are expressed as follows:

$$\frac{dQ_0}{dx} = C_m + \frac{C_{d0} + C_{r0}}{1 - x} Y_0$$

$$\frac{dQ_2}{dx} = 1 + \frac{2Y_1}{Y_0} + \frac{2C_{r2}Y_1^2}{(1 - x)Y_0}$$

$$\frac{dQ_3}{dx} = 1 + \frac{3Y_2}{Y_0} + \frac{3Y_1}{Y_0} + \frac{6C_{r3}Y_1Y_2}{(1 - x)Y_0}$$

$$A_0 = -C_p[\ln(1 - x) + x] \tag{36}$$

$$\frac{dA_1}{dx} = \frac{H_0}{Y_0} + \frac{C_{r1}H_0Y_1}{(1 - x)Y_0} + \frac{C_pQ_2}{1 - x}$$

$$C_1Y_1 = Y_0\left(1 + \frac{C_{p2}Q_2}{1 - x}\right); \quad C_2Y_2 = Y_0\left(1 + \frac{2Y_1}{Y_0} + \frac{C_pQ_3}{1 - x}\right)$$

$$C_1H_0 = Y_0C_p(A_1 + M_0x); \quad C_2H_1 = Y_0\left[\frac{C_p(A_2 + Q_2)}{1 - x} + \frac{H_0}{Y_0}\right]$$

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

The solution of the system (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 of the products in the low conversion range.

It should be pointed, that transition from the system of differential equations of material balances to the system for the moments H_n, A_n is not so elementary from the mathematical point, as it seems to be at the first glance. This circumstance lead the author,[50] discussing the polymerization of vinylacetate to the false formula (Equation A-2, p. 451), and, consequently, made impossible the application of theoretical relations obtained there.

In low conversion range, the analytical solutions may be received. For the radical termination in the reaction of disproportionation we receive:

$$\frac{1}{P_n} = C_m - \frac{C_dY_0}{M_0}\frac{\ln(1 - x)}{x} \approx \frac{1}{P_{n0}}\left(1 + \frac{C_dY_0P_{n,0}}{M_0}x + \cdots\right)$$

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

$$P_w = 2P_{n,0}(1 + 0.5b_1P_{n,0}\cdot x) \tag{37}$$

where $P_{n0} = C_m + C_dY_0/M_0$; $b_1 = 2C_m + C_dY_0/M_0 + C_p$; $Y_0 = V_{\text{in}}^{0.5}K_p/K_d^{0.5}$.

At $x \neq 0$ P_w depends on rate constant transfer to polymer. For the number of branching, we receive

$$\begin{aligned} B_n &= -C_pP_n\left(1 + \frac{\ln(1-x)}{x}\right) \simeq C_pxP_n \\ B_w &= C_pP_wx \end{aligned} \tag{38}$$

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

For recombination termination we have:

$$\frac{1}{P_n} = \frac{1}{P_{n,0}}\left(1 + \frac{x}{2}\right); \quad P_w = \frac{3}{2}P_{n,0}\left(1 + \frac{P_{n,0}b_2x}{2}\right) \tag{39}$$

where $P_{n,0}^{-1} = C_rY_0M_0^{-1}$; $b_2 = 2C_p + 1 - 2/P_{n,0}$.

Some applications of these approaches and peculiarities of molecular characteristics of branched molecules of polystyrene, polyethylene,[52] polyvinylacetate[53] are illustrated.

The analysis of the relations obtained shows, that conversion influence in the case of long chain branched molecules formation is very complicated. Thus, from Equation (37) one can see, that with x increase, the value of the second factor may raise (the changes of kinetic scheme) or fall (the decrease of biradical termination rate constant). Thus, the problem of the influence of conversion and diffusion mobility in such processes needs further study.

CONCLUSION

The results stated above, indicate that, excluding the material of long chain branched macromolecules formation, the existing theories of diffusion mobility of the components in polymerization medium permit to predict quantitatively the change of rate constants of the main chemical reactions of radical polymerization. Moreover, the form of these relations for every rate constants is special. The establishment of biradical termination constant dependence on the radical molecular weight lead to the necessity of new conceptions. However, it does not lead to considerable complication of the solution scheme, as it was firstly predicted. On the basis of the relations obtained, the computer program of kinetics and MWD of the polymer have been worked out. This scheme may be used not only for estimations of the product characteristics, but also as the method of industrial processes analysis.

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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, "Skaling Idea in the 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, S-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, 58, 1748.
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. Compound, 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," S-Petersburg, Chemistry, Russia, p. 270, 1984.
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, S-Petersburg, ONPO "Plastpolymer," 1985, pp. 45–54.

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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, S-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).

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