

Free radical polymerization in the presence of nonsolvents. II. Methyl methacrylate*

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The polymerization of methyl methacrylate (MMA) in methanol and in θ mixtures formed from MMA—methanol, MMA—2-butanol, MMA—*n*-hexane, and MMA—*n*-octane at 30°C was studied. The obtained values of the ratios $k_p/(k_t)^{0.5}$ from stationary and k_p/k_t from the nonstationary kinetics of polymerization were discussed from the point of view of the effects of the preferential solvation and the polymer coil size on the kinetics of the polymerization in the system MMA—precipitant for poly(methyl methacrylate).

Была изучена полимеризация метилметакрилата (ММА) в метаноле и в θ смесях ММА—метанол, ММА—2-бутанол, ММА—*n*-гексан и ММА—*n*-октан при 30°C. Полученные значения отношений $k_p/(k_t)^{0.5}$ из стационарной и k_p/k_t из нестационарной кинетики полимеризации были обсуждены с точки зрения влияния преобладающей сольватации и размеров полимерных частиц на кинетику полимеризации в системе ММА — осадитель поли(метилметакрилата).

For regulation of free radical polymerization the knowledge of factors influencing the rate constants of the elementary steps is indispensable. There are many examples in the literature discussing the effect of solvent and other additives on the course of polymerization [1—6]. In this connection most interesting and stimulating were studies concerning the regulation of the rate constant for propagation and termination reactions. Nowadays the old concept [7] that the rate constants for propagation and termination reactions are specific for a given monomer is no more valid. Complexing of monomer and/or monomer radical can lead to significant change of the rate constant for propagation [8, 9]. Similarly the rate constant for termination can be varied by changing the viscosity of the polymerization system [10, 11].

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In our previous paper [12] the kinetics of polymerization in the system styrene—precipitant for polystyrene and in θ systems formed from styrene and various precipitants for polystyrene were studied. It was found that in these systems the kinetic behaviour of the polymerization was greatly influenced by the effects of preferential solvation and the polymer coil size. In all these systems the preferentially absorbed component was the monomer — styrene. In this connection it seemed interesting to study the system in which inversion of preferential solvation occurred, *i.e.* the system in which in certain monomer concentration region it is solvent (precipitant) that is preferentially absorbed while in the other concentration range of the monomer the preferentially absorbed component is the monomer. To meet this requirement one can choose the system methyl methacrylate—methanol. For comparison with the results obtained by styrene polymerization [12] also θ systems formed from methyl methacrylate—precipitant for poly(methyl methacrylate) were studied.

Experimental

Chemicals

Methyl methacrylate was freed from inhibitor by gradual shaking with 10% solution of sodium hydroxide, sulfuric acid, sodium carbonate, and finally with distilled water. After drying with anhydrous calcium chloride MMA was distilled under nitrogen.

Alcohols and hydrocarbons were of anal. grade (Lachema, Brno). They were dried with calcium chloride and distilled under reduced pressure of nitrogen before use.

2,2'-Azoisobutyronitrile (Koch and Light Ltd.) was crystallized from ethanol; m. p. 103°C.

Procedures

The equipment and full details on photoinitiated polymerization, viscosity measurements of reaction solutions and the composition of θ mixtures were described previously [12]. Poly(methyl methacrylate) was separated from polymerization solutions by precipitation with large excess of *n*-hexane. The precipitated polymer was dried to constant weight *in vacuo* (50°C, 700 Pa).

The viscosity average molecular weight of poly(methyl methacrylate) was calculated [13] from the limiting viscosity number in toluene at 30°C according to the equation

$$[\eta] = 7.0 \times 10^{-5} M_v^{0.71} \quad ([\eta] \text{ in dl g}^{-1}) \quad (1)$$

The values of the viscosity average molecular weights were transformed to number average molecular weights in the manner outlined in [14] on condition that the ratio between termination by combination and disproportionation was 0.45 [15,16]. The ratio

$K = k_p/(k_t)^{0.5}$ of the rate constant for propagation k_p and the rate constant for termination k_t , was obtained from the equation

$$\begin{aligned} 1/P_n = 0.5(1 + \lambda)k_{t0}R_p/k_p^2[\text{MMA}]^2\eta_{\text{mix}} + C_M + \\ + C_s[S]/[\text{MMA}] + C_i[I]/[\text{MMA}] \end{aligned} \quad (2)$$

where P_n is the number average polymerization degree, λ is the ratio of the rate constant for termination by disproportionation and the rate constant for termination (disproportionation and combination), k_{t0} is the rate constant of termination at a viscosity of 1 mPa s ($k_{t0} = k_t\eta_{\text{mix}}$), R_p is the rate of polymerization [$\text{mol dm}^{-3} \text{s}^{-1}$], η_{mix} is the viscosity of the reaction system [mPa s], S solvent (precipitant of the polymer), I initiator (2,2'-azoisobutyronitrile), C_M , C_s , and C_i are the transfer constants for methyl methacrylate, solvent, and initiator, respectively.

In the evaluation of the ratio K from eqn (2) for C_M the value 1.17×10^{-5} was used [17]. The third term of the right side of eqn (2) was calculated from the published data [18] on C_s for individual alcohols (methanol 2×10^{-5} , 2-butanol 2.59×10^{-5}). These values of C_s refer to temperature 60°C, relevant data for 30°C were not available. But an error introduced by using data for 60°C is very small, because the value of $1/P_n$ is about two orders of magnitude greater than the sum of the second, third, and fourth term of the right side of eqn (2). For the same reason for *n*-hexane and *n*-octane the value of $C_s = 1.8 \times 10^{-4}$ was used [17], though it referred to *n*-heptane and temperature 50°C. For calculating the fourth term of eqn (2) the value 2×10^{-2} for C_i was used [19]. The reported values of the ratio K are arithmetic means of at least three measurements. The error of measurements of the ratio K at 95% confidence level was less than $\pm 4\%$.

The determination of the radical life-time τ and the calculation of k_p/k_t from nonstationary kinetics were carried out according to the known procedure for rotating sector measurements [20].

Results

The dependence of the rate of photoinitiated polymerization of MMA on the MMA concentration in a mixture with methanol is presented in Fig. 1. The slope of the line in Fig. 1 equals 1. On this basis one can assume that the ratio K should be a constant for all reaction mixtures indicated in Fig. 1. However, it was found that the ratio K calculated by means of eqn (2) changes with the composition of the reaction system (Table 1).

The variation of the ratio K and the limiting viscosity number $[\eta]$ of poly(methyl methacrylate) of the given molecular weight ($M_n = 6.1 \times 10^4$) with molar concentration of methyl methacrylate in methanol is given in Fig. 2.

Results obtained in the polymerization of methyl methacrylate in θ systems under stationary and nonstationary kinetics (rotating sector measurements) are compiled in Table 2.

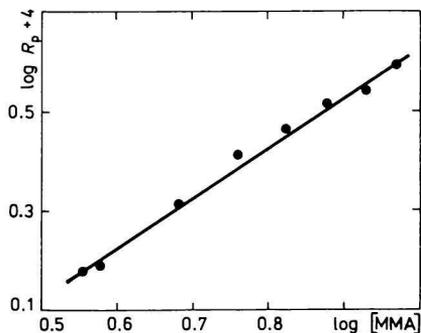


Fig. 1. Dependence of the log of MMA polymerization rate [$\text{mol dm}^{-3} \text{s}^{-1}$] on the log of MMA concentration [mol dm^{-3}] in methanol. Concentration of AIBN $5 \times 10^{-3} \text{ mol dm}^{-3}$; intensity of the incident light of the wavelength 365 nm, $I_0 = 8.48 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$; temperature 30°C .

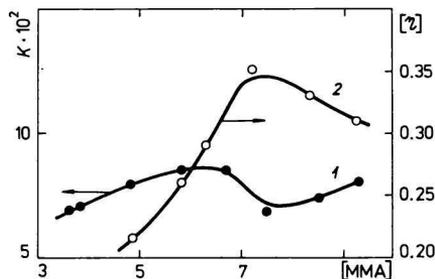


Fig. 2. Dependence of the ratio K (from Table 1) (curve 1) and of the limiting viscosity number $[\eta]$ in $[\text{dl g}^{-1}]$ (curve 2) of poly(methyl methacrylate) having number average molecular weight $M_n = 6.1 \times 10^4$ in the mixture MMA—methanol on molar concentration of methyl methacrylate; temperature 30°C .

Table 1

Polymerization of methyl methacrylate in methanol photoinitiated ($\lambda = 365 \text{ nm}$) by 2,2'-azoisobutyronitrile [$5 \times 10^{-3} \text{ mol dm}^{-3}$] Temperature 30°C

MMA mol dm^{-3}	$K \cdot 10^{2a}$	K/K_{bulk}^b
9.28	8.0	1.00
8.60	7.4	0.92
7.50	6.8	0.85
6.70	8.4	1.05
5.80	8.4	1.05
4.80	7.8	0.97
3.82 ^c	7.0	0.87
3.60 ^d	6.9	0.86

a) $K = k_p / (k_t)^{0.5} [\text{dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}]$.

b) Ratio of the constant K for MMA polymerization in mixtures with methanol and the constant K for bulk MMA polymerization.

c) θ Mixture.

d) Only slight turbidity of the reaction system was observed during polymerization.

Table 2

Polymerization of methyl methacrylate in θ system photoinitiated ($\lambda = 365$ nm)
by 2,2'-azoisobutyronitrile [5×10^{-3} mol dm $^{-3}$]
Temperature 30°C

θ System ^a	MMA mol dm $^{-3}$	η_{mix}^b	$K \cdot 10^{2c}$	$k_p/k_t \cdot 10^6$	k_p dm 3 mol $^{-1}$ s $^{-1}$	$k_t \cdot 10^{-6}$ dm 3 mol $^{-1}$ s $^{-1}$
Methanol	3.82	0.50	7.0	24.0	204	8.5
2-Butanol	3.20	0.99	5.7	27.7	117	4.2
<i>n</i> -Hexane	6.89	0.42	6.1	18.6	200	10.7
<i>n</i> -Octane	6.95	0.49	6.2	18.8	204	10.9

a) Formed from MMA and diluent indicated.

b) Viscosity of the reaction mixture in mPa s at 30°C.

c) $K = k_p/(k_t)^{0.5}$, dm $^{3/2}$ mol $^{-1/2}$ s $^{-1/2}$

Discussion

Contrary to expectations [12] the polymerization rate of photoinitiated polymerization of MMA in methanol is approximately linearly related to MMA concentration. Although in this polymerization system and under condition used complications arising from primary radical termination [21] were not observed, such phenomena like preferential solvation and polymer coil size are expected to play an important role. As was shown in several papers [22—24] the effect of the preferential solvation and polymer coil size on the course of polymerization invalidates the relationships derived for "ideal" kinetics of polymerization [7]. It was also shown that the polymer coil size influences the rate constant for termination [25]. Therefore comparison of kinetic parameters found for various monomer—solvent systems without considering these factors is not possible.

The "quasi" linear relation between R_p and [MMA] shows at first sight that the effects of preferential solvation and polymer coil size are probably not very important. Inspecting more closely the dependence given in Fig. 1, it is however evident that the experimental points can be divided into two groups. The line which suits well the experimental points for "high" concentration of MMA [>6 mol dm $^{-3}$] in the reaction system has a slope of 0.80. For "low" concentration of MMA [<6 mol dm $^{-3}$] the slope of the line is 1.18.

Only as a rough approximation these two groups of experimental points can be connected by one line with the slope equal to 1 (as was done in Fig. 1). Consequently, the ratio K cannot be considered to have a constant value for all reaction systems studied. As was shown by some authors [22] in system where preferential solvation occurs the linear dependence between polymerization rate and monomer

concentration can be obtained if "coil" instead of "average" monomer concentration is used.

Therefore, it is necessary to use "coil" monomer concentration in order to see if other effects (beside preferential solvation) simultaneously influence the ratio K .

Unfortunately quantitative data on preferential solvation in the system poly(methyl methacrylate)—MMA—methanol have not been published yet. The studies on preferential solvation of the system poly(methyl methacrylate)—benzene—methanol have shown that at low concentrations of methanol in the system, preferentially solvated by polymer coil is methanol, though this is a precipitant for poly(methyl methacrylate) [26, 27]. Benzene is preferentially absorbed only if the volume fraction of methanol in the mixture with benzene is greater than 0.17 [27].

Owing to the similarity between benzene and methyl methacrylate with respect to poly(methyl methacrylate) (*cf.* values of solubility parameters 18.74 and 18.88 $J^{1/2} \text{ cm}^{-3/2}$, respectively) the course of preferential solvation similar to that in the system poly(methyl methacrylate)—benzene—methanol can also be expected in the system poly(methyl methacrylate)—MMA—methanol.

As was already indicated polymerization rate and degree of polymerization (for a given monomer, rate of initiation, and temperature) are determined by the monomer concentration in the polymer coil (where the reaction occurs) and not by the average concentration of monomer in the reaction system. When using the average concentration of the monomer in the reaction system instead of the concentration of the monomer in polymer coil for calculation of kinetic parameters (*e.g.* ratio K) the values thus obtained are lower (if solvent is preferentially absorbed) or higher (if monomer is preferentially absorbed) relative to values of kinetic parameters of the reaction system where no preferential solvation occurs.

The observed decrease of the values of the ratio K with dilution of the reaction system with methanol (down to $[\text{MMA}] \approx 7.5 \text{ mol dm}^{-3}$) as well as the subsequent increase of the values of K (for $6.5 \text{ mol dm}^{-3} \leq [\text{MMA}] \leq 7.5 \text{ mol dm}^{-3}$) can be explained by the use of "average" (incorrect) instead of a "coil" (correct) MMA concentration for calculation of the ratio K by means of eqn (2). That is, in the system poly(methyl methacrylate)—MMA—methanol preferential solvation could be responsible for the observed inconstancy of the values of the ratio K .

The plot of the limiting viscosity number of poly(methyl methacrylate) on concentration of MMA in the reaction system (Fig. 2, curve 2) shows an increase of the polymer coil size in the region of MMA concentrations between $9.28\text{--}7.00 \text{ mol dm}^{-3}$

On increasing the polymer coil size the rate constant for termination k_t increases, too [24]. That is, the ratio K should decrease with dilution of the reaction system with methanol in the given region of MMA concentrations.

Thus, preferential solvation and the change of polymer coil size with dilution of the reaction system with methanol exert the same effect on the value of the ratio K

(Fig. 2, curve 1) in systems where $[\text{MMA}]$ is between 9.28 and 7.5 mol dm^{-3}

On lowering MMA concentration in the reaction system below 7.3 mol dm^{-3} the polymer coil size begins to decrease (limiting viscosity number falls) and the ratio K increases and reaches maximum at about $[\text{MMA}] = 6.5 \text{ mol dm}^{-3}$

For MMA concentrations below 6.0 mol dm^{-3} the ratio K slowly decreases down to the θ point of the poly(methyl methacrylate) in the system MMA—methanol.

The decrease of the ratio K for concentrations of MMA below 6 mol dm^{-3} cannot be explained either by the effect of preferential solvation or by the effect of polymer coil size. In this concentration region preferentially absorbed is MMA (in analogy with the system PMMA—benzene—methanol), thus the calculated ratio K should increase (when using “average” MMA concentration). The polymer coil size should exert the same effect on the ratio K , too (decrease of $[\eta]$ is accompanied by decrease of k_i). The reason for the observed decrease of the ratio K (instead of an increase) for MMA concentrations below 6.0 mol dm^{-3} is not clear.

For θ systems irrespective of the chemical structure of the precipitant (possible formation of hydrogen bonds between oxygen atom of MMA and hydroxyl group of alcohol) the ratio K undergoes no substantial change.

The same seems to be true for k_p/k_i . The effect of preferential solvation is most pronounced in θ systems [28]. Because the “coil” MMA concentration is higher than the “average” MMA concentration in the reaction system, the ratios K and k_p/k_i are to some extent overestimated (if “average” MMA concentration is used for calculation). In systems with weaker precipitants, *i.e.* in systems where preferential solvation is not so pronounced, the error arising from the use of average MMA concentration is, of course, smaller in comparison with the systems with strong precipitants [28, 29].

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