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Kinetics of Radical Polymerization. XLI. Kinetic Investigation of the Radical Polymerization of Methyl Methacrylate in Benzene and Bromobenzene

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ABSTRACT

The present paper deals with the radical polymerization kinetics of the systems MMA-AIBN-Bz-50°C and MMA-AIBN-BrBz-50°C. The rate of initiation and the $k_2/\sqrt{k_4}$ value were determined in a broad range of monomer concentrations. The initiation rate constant was found to be independent of the concentration of solvent and monomer. In the system MMA-Bz the $k_2/\sqrt{k_4}$ value does not change with dilution, while in the system MMA-BrBz it depends on the viscosity of the initial monomer-solvent mixture.

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Methyl methacrylate (MMA) is used in large scale by the plastics industry. The kinetics of its radical polymerization have been studied by several authors.

According to the investigations of Bagdasaryan [1] and Arnett [2], the rate of MMA polymerization in bulk is directly proportional to the square root of the initiator (azobisisobutyronitrile, AIBN) concentration, in accordance with the classical kinetical treatment. Arnett determined the exponent of the monomer in benzene solution within the mole fraction range of $\chi_{MMA} = 0.2$ to 1, and they obtained the theoretical value of 1 within the limits of experimental error.

Burnett et al. [3] reported some results different from the classical kinetical model when using the sysemt MMA-AIBN-Bz-60°C and low monomer concentration. In the system MMA-AIBN-BrBz-60°C they found that the rate of polymerization changes with the mole fraction of monomer along a maximum curve. As a possible explanation, they suggest that the initiation proceeds partly with the participation of solvent molecules. Henrici-Olivé [4] interpreted the results obtained for the system MMA-AIBN-BrBz with the theory of electron-donor-acceptor (EDA) complexes, which claims that the propagating radicals form complexes with the monomer or solvent molecules, but only the macroradical-monomer complexes take part in the chain propagation.

They determined the τ_s/τ_m values from their data and from those of Burnett [3]. The values were found to be nearly constant in the region in which they measured. It should be noted that the τ_s/τ_m values belonging to a monomer concentration lower than 20 vol% show a systematic deviation from those given in Ref. 4.

The effect of the solvent on the chain propagation reaction in the polymerization of MMA in aromatic solvents was investigated by Allen and Bateup [5] by the NMR technique. They found a slight interaction between MMA and benzene which, however, does not lead to a kinetic solvent effect. The interaction is negligible with chlorobenzene or bromobenzene, and it is therefore unlikely that the solvent effect appearing in the system MMA/BrBz would be correctly described by the model of Henrici-Olivé [4].

Bamford and Brumby [6] investigated the MMA polymerization initiated by AIBN in aromatic solvents at one monomer concentration (4.65 mol/L). They found the rate of initiation to be independent of the quality of solvent used, which contradicts the hypothesis of Burnett.

Fischer and co-workers [7] studied the polymerization of MMA at low temperature (0°C) and at 2 mol/L monomer concentration in different solvents, benzene among them. They found the rate constant of termination to be inversely proportional with the viscosity of the solution. They therefore interpreted the chain termination process by the diffusion theory of North, which is in agreement with the measurements of other authors [8, 9].

It can be seen from the above treatment that in spite of the detailed investigations carried out on MMA polymerization in solution, no adequate explanation of the solvent effect has been found.

A considerable deficiency is that the authors cited have carried out their experiments mainly at one single monomer concentration or in only a small part of the whole concentration region. This article gives an account of results obtained in the entire dilution ranges of the systems MMA-AIBN-Bz-50°C and MMA-AIBN-BrBz-50°C.

EXPERIMENTAL

Benzene (Bz) and azobisisobutyronitrile (AIBN) were purified as reported earlier [10, 12].

Methyl methacrylate (MMA, Fluka product) was extracted with 10% NaOH solution, washed with water until it gave a neutral reaction, and dried over $CaCl_2$. It was freshly distilled before use.

The original purification method of bromobenzene (BrBz) proved ineffective; therefore, the method of Mayo [11] was used.

The purity of the materials used was checked by measurements of the refractive index and melting point. Bz $n_D^{20} = 1.5011$, MMA $n_D^{20} = 1.4142$, BrBz $n_D^{20} = 1.5600$, AIBN mp = 103.5 - 104.0°C.

Polymerization kinetic measurements were carried out dilatometrically at 50°C.

The rate of initiation was determined by the inhibition method, using triphenyl verdazyl (TPV) as the stable free radical. TPV was synthesized and purified as given in Ref. 13.

Viscosities were measured in an Ubbelohde viscometer.

EXPERIMENTAL RESULTS AND THEIR EVALUATION

The initiation rates of the systems MMA-AIBN-Bz-50°C and MMA-AIBN-BrBz-50°C were determined by the inhibition kinetic method.

From the inhibition kinetics of polymerization, the following relationship is known

$$t_i = \frac{\mu}{2k_1f} \frac{z_0}{\bar{x}} \qquad (1)$$

where t_i is the length of the inhibition period, $2k_1f$ is the rate constant of initiation, z_0 is the initial inhibitor concentration, $\bar{x}$ is the average initiator concentration during the inhibition period, and μ is the

TABLE 1. Inhibition Kinetic Data of the Systems MMA-AIBN-BrBz and MMA-AIBN-Bz at 50° C

	$10^2 \times \frac{z_0}{\bar{x}}$	t_i (min)	$2k_1f \times 10^4$
MMA-AIBN-BrBz-50° C:			
$X_{\mathrm{MMA}} = 0.208$	1.529	85	1.80
	3.080	169.5	
	4.696	260	
	6.184	345.5	
	7.946	439	
$X_{\mathrm{MMA}} = 0.532$	1.541	88	1.78
	3.026	171.5	
	4.474	253.5	
	6.089	340	
	7.852	428.5	
$X_{\mathrm{MMA}} = 0.070$	1.516	87	1.76
	2.952	168	
	4.782	272	
	6.449	369	
	8.191	462	
$X_{\mathrm{MMA}} = 0.148$	1.510	86.5	1.75
	2.916	167	
	4.440	256	
	5.865	336.5	
	7.833	441.5	
$X_{\mathrm{MMA}} = 1.000$	1.592	88	1.80
	3.113	186.5	
	4.693	256	
	6.062	342	
	7.613	401	
MMA-AIBN-Bz-50° C:			
$X_{\mathrm{MMA}} = 0.515$	1.493	81.5	1.85
	2.939	165	
	4.883	265	
	6.389	330	
	7.991	425	
$X_{\mathrm{MMA}} = 0.278$	2.001	115	1.72
	5.554	332.5	
	7.678	450	
	9.776	553	
AIBN-Bz-50° C			1.53 [15, 16]

stoichiometric constant of the inhibitor. Since TPV is a stable free radical, its stoichiometric constant is unity.

Table 1 contains the data of initiation rate measurements for the systems MMA-AIBN-BrBz-50° C and MMA-AIBN-Bz-50° C. Figure 1 shows the t_i values obtained for the MMA-BrBz system plotted against $z_0/\sqrt{x}$ at different (but kept constant within each series) monomer concentrations. As can be seen, the rate constant of initiation in the MMA-BrBz system is independent of the monomer-solvent mixture, Its numerical value is $2\ k_i f = 1.78 \times 10^{-4}\ \text{min}^{-1}$.

The initiation rate constant of the MMA/Bz system does not change in the mole fraction region 0.25 - 1 within the limits of experimental

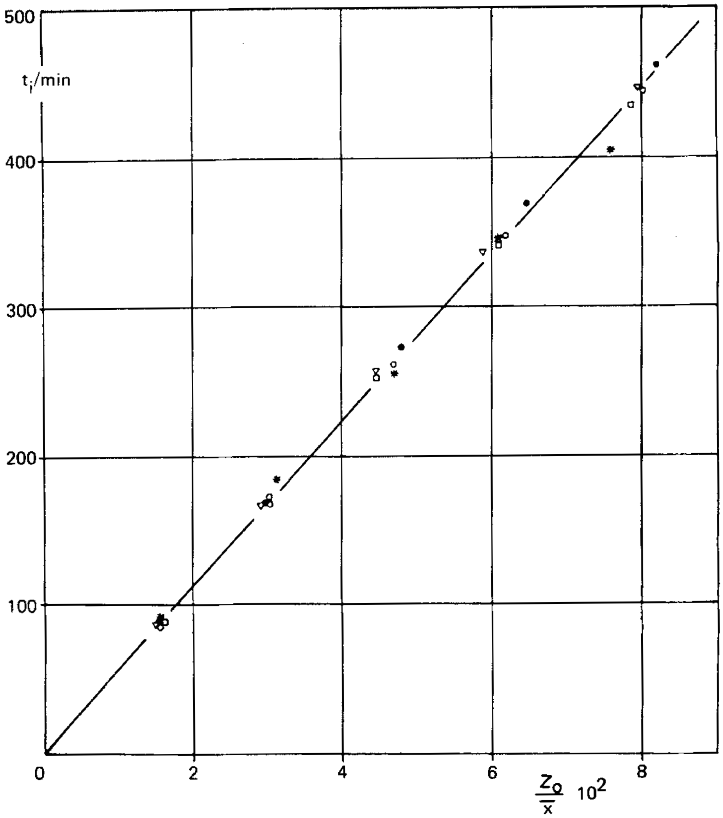

FIG. 1. The value of t_i plotted against $z_0/\sqrt{x}$ for the system MMA-AIBN-BrBz-50°C. χ_{MMA} = 0.072 (●), 0.1479 (▽), 0.208 (○), 0.532 (□), and 1.0 (*).

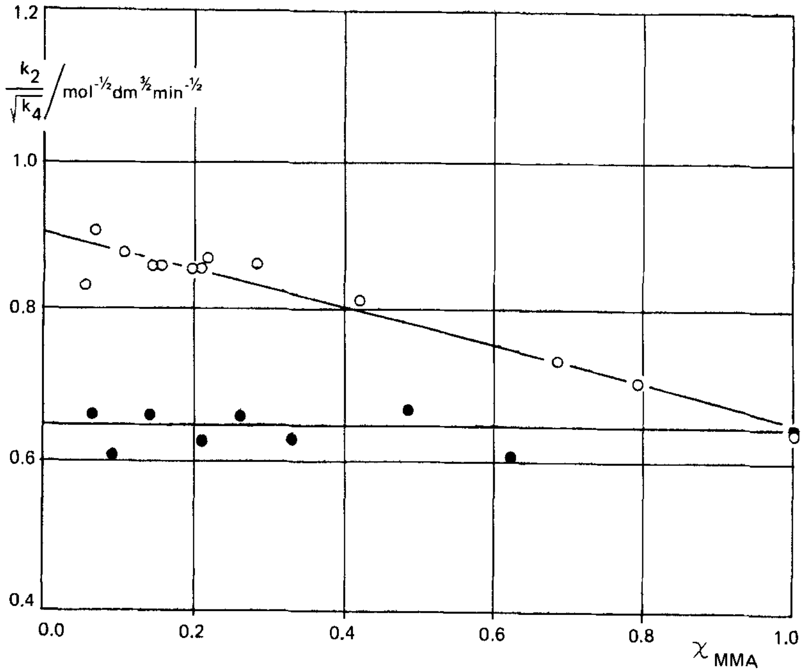

FIG. 2. The value of $k_2/\sqrt{k_4}$ plotted against the mole fraction of monomer for the systems MMA-AIBN-BrBz-50°C (○) and MMA-AIBN-Bz-50°C (●).

error, while it shows a slight decrease in the mole fraction region 0-0.25 (Table 1).

Later, the overall rate constant of polymerization was investigated over the entire range of monomer concentration:

$$W = dm/dt = K\sqrt{x}m \tag{2}$$

where

$$K = k_2\sqrt{2k_1f/k_4} \tag{3}$$

where x and m are the concentrations of initiator and monomer, respectively, and k_2 and k_4 are the rate constants of chain propagation and termination, respectively. The $k_2/\sqrt{k_4}$ ratios, which can be calculated if we know the K and $2k_1f$ values, are plotted against the mole fraction in Fig. 2. The $k_2/\sqrt{k_4}$ values are summarized in Table 2. It

TABLE 2. Polymerization Kinetic Data of the Systems MMA-AIBN-BrBz and MMA-AIBN-Bz at 50°C

x_{MMA}	$10^3 \times K$ ($mol^{-1/2} dm^{3/2} min^{-1}$)	$10^2 \times x_0$ (mol/dm^3)	$k_2/\sqrt{k_4}$ ($mol^{-1/2} dm^{3/2} min^{-1/2}$)	$10^4 \times \eta$ (Pa·s)
		MMA-AIBN-BrBz-50°C		
0.053	11.10	1.495	0.832	7.552
0.070	12.08	7.083	0.905	7.502
0.102	11.70	1.533	0.877	7.398
0.148	11.36	7.111	0.851	7.199
0.151	11.45	1.544	0.858	7.199
0.199	11.40	1.569	0.855	7.001
0.204	11.40	1.697	0.855	6.980
0.208	11.60	1.513	0.870	6.949
0.277	11.55	1.525	0.866	6.682
0.419	10.90	1.492	0.817	6.150
0.681	9.80	1.541	0.735	5.148
0.791	9.40	1.495	0.705	4.679
1.0	8.50	1.463	0.637	3.928

(continued)

TABLE 2 (continued)

x_{MMA}	$10^3 \times K$ $(mol^{-1/2} dm^{3/2} min^{-1})$	$10^2 \times x_0$ (mol/dm^3)	$k_2/\sqrt{k_4}$ $(mol^{-1/2} dm^{3/2} min^{-1/2}$	$10^4 \times \eta$ (Pa·s)
		MMA-AIBN-Bz-50°C		
0.065	8.787	1.447	0.659	
0.091	8.186	1.497	0.614	
0.136	8.830	1.490	0.662	
0.219	8.330	2.521	0.624	
0.258	8.816	1.489	0.661	
0.335	8.370	2.468	0.627	
0.481	8.973	1.517	0.673	
0.626	8.110	1.521	0.608	
1.0	8.641	1.504	0.648	

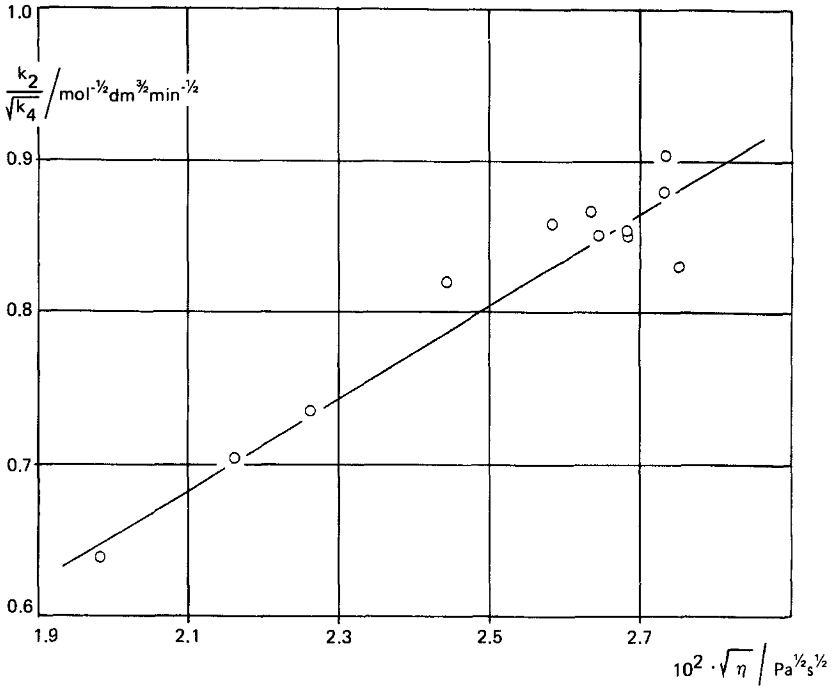

FIG. 3. The $k_2/\sqrt{k_4}$ values of the system MMA-AIBN-BrBz-50°C plotted against $\sqrt{\eta}$.

can be established from the results that in the system MMA-Bz the $k_2/\sqrt{k_4}$ values do not depend on the composition of monomer-solvent mixture. In the system MMA-BrBz the $k_2/\sqrt{k_4}$ values show a slight (~35%) increase with dilution.

It should be stressed that our studies extended to the region of low mole fractions, and the results fit the corresponding straight line quite well, within the limits of experimental error.

We note that in the same series of experiments in which the purity of the bromobenzene used was not satisfactory, we obtained at higher dilutions some results similar to the low K values published by Burnett et al. [3]. This observation explains the data obtained by Burnett.

Yokota and Itoh [14] modified the viscosity of the monomer-solvent mixture to correspond to the diffusion theory of North by considering the classical kinetic equation:

$$-dm/dt = k_2(2k_1f)^{1/2}(k_4{}^0)^{-1/2}\eta^{1/2}mx^{1/2} \qquad (4)$$

where η is the viscosity of the solvent mixture at the given temperature and k_4^0 is the rate constant of chain termination in a medium of unit viscosity.

In the system MMA-BrBz the $k_2/\sqrt{k_4}$ values are plotted against the square root of the viscosity in Fig. 3, while the numerical values can be found in Table 2.

Figure 3 shows that the value of this quotient is directly proportional to the square root of the viscosity within the limits of experimental error. This can be interpreted in terms of the diffusion theory of North and Reed [8, 9], which means that the solvent effect observed takes place in the chain termination reaction.

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