Solvent Effect on Radical Polymerization of Methyl Methacrylate

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ABSTRACT: The radical polymerization of methyl methacrylate (MMA) in various aromatic solvents was studied under the same conditions as that of phenyl methacrylate (PMA) reported previously. The propagation-rate constants (k_p) and termination-rate constants (k_t) were determined by intermittent illumination methods. The variation in the k_p values for MMA with aromatic solvents had the same trend as that for PMA, although the solvent effect on the former values was somewhat smaller than that on the latter. Variation in k_p values with solvents can be explained by the formation of an electron donor-acceptor complex and is correlated with the delocalization stabilization of the complex formation. The dependence of k_p value on the monomer concentration supports the view that a propagating radical complexed with a solvent is in the dormant state. A study of temperature dependence on k_p and k_t values was also carried out in benzene and activation energy of these values determined to be 5.0 ± 0.8 and 0.38 ± 0.10 kcal mol⁻¹, respectively.

KEY WORDS Methyl Methacrylate / Radical Polymerization / Polymerization Rate / Elementary Rate Constant / Initiation Rate / Solvent Effect / Delocalization Stabilization /

We previously reported that the trend in aromatic solvent effect on the polymerization-rate constant of phenyl methacrylate (PMA) ($e=0.73$) is opposite to that observed for vinyl benzoate ($e=-0.55$).¹⁻³ This opposite effect is explained in terms of a donor-acceptor complex formation between the propagating radical and the π -system of the solvents.

If a complex formation occurs, the same solvent effect will be observed on the rate constant in the polymerization of methyl methacrylate (MMA), since the nature of the propagating radical of MMA is similar to that of PMA. Although Bamford *et al.*,^{4,5} Burnett *et al.*,⁶ and Yamamoto *et al.*⁷ have independently measured the rate constants in the polymerization of MMA in aromatic solvents, the experimental conditions in each case were different from that for PMA^{1,2} with respect to monomer concentrations and temperature. In order to compare the aromatic-solvent effect on the polymerization of MMA with that of PMA, results obtained under the same conditions must be used,

since different laboratories frequently show different values for the rate constant even for the same polymerization.⁸ Therefore, the propagation-rate constant for the radical polymerization of MMA in aromatic solvents was determined under the same conditions as that for PMA.^{1,2}

In this paper, we report the results of the determination of rate constants for MMA in various aromatic solvents and discuss the cause for the solvent participation in the polymerization. In addition, we mention the monomer concentration and the temperature dependence on k_p for MMA in benzene.

EXPERIMENTAL

MMA, aromatic solvents, 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobiscyclohexanecarbonitrile (ACN), and 1,1'-diphenyl-2-picrylhydrazyl (DPPH) were purified as previously described.²

The rate of polymerization (R_p), the rate of initiation (R_i), and radical lifetime (τ) were de-

terminated as described in a previous paper.² Monomer and initiator concentrations were completely the same as described in the PMA polymerization.²

Experimental error for the rate constants was estimated in the same method as previously described.²

The intrinsic viscosity of the polymer was determined in benzene at 30°C with an Ostwald viscometer.

A Varian A-60 nuclear magnetic resonance (NMR) spectrometer was used with tetramethylsilane as the internal reference (5% solution).

A Neac-2200 computer was used for making the calculations involved in the LCAO MO method.

RESULTS

Determination of k_p and k_t

The rate dependence on initiator and monomer concentration was determined at $30 \pm 0.001^\circ\text{C}$ for both the initiator and photosensitized polymerization. Typical examples of the results obtained in benzene are shown in Figures 1 and 2. Also, it was confirmed with other solvents that the rates of polymerization were proportional to the monomer concentration and to the square root of the initiator concentration. These results suggest that degradative chain transfers or unimolecular terminations are not important in the polymerization.

In order to determine the elementary rate constants, the initiation rates (R_i) were determined by the inhibition method using DPPH as an

Figure 1. Dependence of the polymerization rate on monomer and initiator concentrations in thermal-initiated polymerization at 30°C ; solvent, benzene; (a), [monomer], 2.00 mol l^{-1} ; (b), [2,2'-azobisisobutyronitrile], 0.1 mol l^{-1} .

inhibitor in all solvents. The effect of the addition of DPPH on the initiated polymerization and the correlation between the obtained duration of inhibition and the concentration of the inhibitor in benzene are shown in Figures 3 and 4. Similar

Figure 2. Dependence of the polymerization rate on monomer and initiator concentrations in photosensitized polymerization at 30°C ; solvent, benzene; (a), [monomer], 2.00 mol l^{-1} ; (b), [2,2'-azobiscyclohexanecarbonitrile], $3.0 \times 10^{-3} \text{ mol l}^{-1}$.

Figure 3. Inhibition effect of DPPH in the polymerization of methyl methacrylate in benzene at 30°C ; [methyl methacrylate], 2.00 mol l^{-1} ; [2,2'-azobisisobutyronitrile], 0.1 mol l^{-1} ; [DPPH]: a, 0; b, 0.456 ; c, 0.798 ; d, $1.14 \times 10^{-4} \text{ mol l}^{-1}$.

Figure 4. Relationship between inhibitor concentration and induction period.

Table I. Initiator polymerization rate and initiation rate in various solvents at 30°C

Solvents	$R_p \times 10^5$ ^a	$R_i \times 10^8$ ^{a,b}	$(k_p^2/k_t) \times 10^3$
	mol l ⁻¹ s ⁻¹	mol l ⁻¹ s ⁻¹	mol l ⁻¹ s ⁻¹
-OCH ₃	1.77 ± 0.09 (3) ^c	1.09 ± 0.07 (3) ^c	71.19
1.45 ± 0.08 (4)	1.09 ± 0.04 (3)	4.82
-F	1.40 ± 0.08 (3)	1.15 ± 0.05 (3)	4.26
-Cl	1.58 ± 0.05 (3)	1.08 ± 0.05 (3)	5.78
-CN	2.03 ± 0.07 (4)	1.09 ± 0.06 (3)	9.45

^a [AIBN], 0.10 mol l⁻¹; [monomer], 2.00 mol l⁻¹.^b Inhibitor, DPPH.^c Run number.

behavior was observed in initiator polymerizations using other solvents.

R_i can be calculated from Figure 4, the values of k_p^2/k_t being derived from R_i and the rate of initiator polymerization. These results are shown in Table I.

The mean lifetime of the propagating radical was determined by the rotating sector method at 30 ± 0.001°C. Figure 5 shows the variation in the rate of polymerization with illumination time. The mean lifetime of the growing chain was determined to be 0.47 s. In Table II, the rate of the photo-sensitized polymerization, the lifetime, and derived values of k_p/k_t are shown together with k_p and k_t , obtained by combining the values of k_p/k_t and k_p^2/k_t . Since the number of the measurements of the k_p and k_t values was too few to permit estimation of the standard deviation, the relative precision of these values was estimated by the amount of deviation from the mean in three or four runs, that of the k_p

Figure 5. Determination of the average life-time of propagating radicals from methyl methacrylate in benzene at 30°C: $\bar{R}_p$, rate of overall polymerization at intermittent illumination; R_p^s , rate at stationary state under continuous irradiation; t , intermittent illumination time (s), ratio of dark to light = 3; [2,2'-azobiscyclohexanecarbonitrile], 3.00×10^{-3} mol l⁻¹; [methyl methacrylate], 2.00 mol l⁻¹.**Table II.** Rate constants in various solvents at 30°C

Solvents	$R_p \times 10^5$ ^a	τ	$(k_p/k_t) \times 10^5$	k_p	$k_t \times 10^{-7}$
	mol l ⁻¹ s ⁻¹	s		mol l ⁻¹ s ⁻¹	mol l ⁻¹ s ⁻¹
-OCH ₃	6.16 ± 0.10 (3) ^b	0.46 ± 0.04 (3) ^b	1.42 ^c	506 ± 48 (3) ^b	3.56 ± 0.39 (3) ^b
5.11 ± 0.12 (4)	0.42 ± 0.03 (4)	1.07	450 ± 33 (4)	4.20 ± 0.30 (4)
-F	4.67 ± 0.10 (3)	0.41 ± 0.05 (3)	0.95	448 ± 47 (3)	4.72 ± 0.66 (3)
-Cl	5.42 ± 0.09 (3)	0.43 ± 0.04 (3)	1.16	498 ± 39 (3)	4.29 ± 0.47 (3)
-CN	6.87 ± 0.13 (3)	0.45 ± 0.03 (3)	1.54	614 ± 43 (3)	3.99 ± 0.33 (3)
C ₆ D ₆	5.20 ± 0.09 (2)	0.40 ± 0.03 (2)	1.04	456 ± 29 (2)	4.38 ± 0.20 (2)

^a [2,2'-Azobis(cyclohexanecarbonitrile)], 3.00×10^{-3} mol l⁻¹; [Monomer], 2.00 mol l⁻¹.^b Run number.^c Mean value.

values being less than 10% and that of the k_t values less than 15%. Limits for the error in k_p and k_t were estimated by the following formula in which all deviations of individual measurements were taken into account:

$$\left| \frac{\Delta k_p}{k_p} \right| = \left| \frac{\Delta R_p}{R_p} \right| + \left| \frac{\Delta R_i}{R_i} \right| + \left| \frac{\Delta \tau}{\tau} \right| + \left| \frac{\Delta W_m}{W_m} \right| + \left| \frac{\Delta W_c}{W_c} \right|$$

$$\left| \frac{\Delta k_t}{k_t} \right| = \left| \frac{\Delta R_i}{R_i} \right| + 2 \left| \frac{\Delta \tau}{\tau} \right| + \left| \frac{\Delta W_c}{W_c} \right|$$

where W_m and W_c are weights of monomer and initiator, respectively. The limits for error of k_p and k_t were estimated to be around 12% and 20%, respectively. Accordingly, the variation in k_p with solvents is beyond the limit of error, indicating that there is indeed a solvent effect on the propagating process.

The termination-rate constants were approximately correlated with the reciprocal viscosities of

the polymerization system, as shown in Figure 6. The viscosities of the polymerization system were calculated from the viscosities of the constituents, assuming a linear relation of viscosity to the volume composition.

The monomer-concentration dependence and the temperature dependence of k_p were determined in

Figure 6. Correlation of k_t values with viscosity of polymerization systems.

Table III. Effect of the monomer concentration on rate constants in benzene at 30°C

Monomer concn.	$R_p \times 10^5$ ^a mol l ⁻¹ s ⁻¹	$R_i \times 10^8$ ^{a,b} mol l ⁻¹ s ⁻¹	$k_p^2/k_t \times 10^3$ mol l ⁻¹ s ⁻¹	$k_p/k_t \times 10^5$ ^c	k_p mol l ⁻¹ s ⁻¹	$k_t \times 10^{-7}$ mol l ⁻¹ s ⁻¹
1.0 (10.0) ^d	0.79 ± 0.04 (3) ^e	1.06 ± 0.03 (3) ^e	5.89 ^f	1.38 ^f	427 ± 38 (3) ^e	3.09 ± 0.37 (3) ^e
2.0 (8.81)	1.45 ± 0.08 (4)	1.09 ± 0.04 (3)	4.82	1.07	450 ± 33 (4)	4.20 ± 0.30 (4)
3.0 (7.62)	2.29 ± 0.09 (3)	1.19 ± 0.04 (3)	4.90	1.08	454 ± 36 (3)	4.20 ± 0.46 (3)

^a [AIBN], 0.10 mol l⁻¹; [Monomer] = 2.00 mol l⁻¹.

^b Inhibitor, DPPH.

^c From rotating sector method.

^d Solvent concentration.

^e Run number.

^f Estimation from mean values.

Table IV. Temperature dependence of rate constants in benzene

Temp °C	$R_p \times 10^5$ ^a mol l ⁻¹ s ⁻¹	$R_i \times 10^8$ ^{a,b} mol l ⁻¹ s ⁻¹	$k_p^2/k_t \times 10^3$ mol l ⁻¹ s ⁻¹	$k_p/k_t \times 10^5$ ^c	k_p mol l ⁻¹ s ⁻¹	$k_t \times 10^{-7}$ mol l ⁻¹ s ⁻¹
20	0.379 ± 0.034 (3) ^d	0.160 ± 0.008 (3) ^d	2.24 ^e	0.744 ^e	301 ± 36 (3) ^d	4.05 ± 0.54 (3) ^d
30	1.45 ± 0.08 (4)	1.09 ± 0.04 (3)	4.82	1.07	450 ± 33 (4)	4.20 ± 0.30 (4)
40	4.28 ± 0.29 (3)	5.65 ± 0.21 (3)	8.11	1.36	596 ± 71 (3)	4.38 ± 0.72 (3)

^a [AIBN], 0.10 mol l⁻¹; [Monomer], 2.00 mol l⁻¹.

^b Inhibitor, DPPH.

^c From rotating sector method.

^d Run number.

^e Estimation from mean values.

Table V. The chemical shift of olefinic proton for methacrylate monomers in various solvents^{a,b}

Methyl methacrylate			<i>t</i> -Butyl methacrylate		
	δH_a	δH_b	$\Delta\delta H^c$	δH_a	δH_b	$\Delta\delta H^c$
	Hz	Hz	Hz	Hz	Hz	Hz
–OCH ₃	363.5	319.0	44.5	363.0	318.0	45.0
–H	365.0	314.0	51.0	364.5	312.5	52.0
–F	364.5	321.0	43.5	364.5	320.0	44.5
–Cl	363.0	320.5	42.5	363.0	319.2	43.8
–Br	363.5	321.5	42.0	363.0	320.0	43.0
–CN	365.0	331.0	34.0	364.0	328.7	35.3

^a Tetramethylsilane was used as an internal reference.^b In 5% solution.^c Data of reference 2.

benzene and are shown in Tables III and IV. Table III suggests that k_p is likely to decrease with an increase in the solvent concentration. From the Arrhenius plot of k_p and k_t the activation energies were calculated to be 5.0 ± 0.8 and 0.38 ± 0.10 kcal mol^{–1}.

The Interaction of Monomer with Solvents

The interaction between monomer and solvent was estimated by the difference in chemical shifts ($\Delta\delta$) of β -olefinic protons of MMA.^{9,10} The results are shown in Table V along with data of *t*-butyl methacrylate (*t*-BMA). Since the mean deviation of the difference was less than 1 Hz, the observed difference is far beyond the experimental error, indicating that there is some interaction between monomer and solvent. Since the solvent dependence of the chemical shift of MMA was almost the same as that of *t*-BMA having bulky ester groups, the interaction between the carbonyl or alkoxy group and the solvent molecule does not seem important. The chemical shift of the olefinic proton in the *cis* position from ester group was scarcely influenced by the ratio of benzene to cyclohexane, but the chemical shift of the *trans* olefinic proton goes down field as the ratio increases (Table VI). This result shows that the *trans* olefinic proton (H_b) interacts with an aromatic ring. In order to estimate the extent of this interaction, NMR spectra were taken

Table VI. The chemical shift of the *trans* olefinic proton (H_b) of methyl methacrylate at various concentration of benzene^{a,b}

Solvent	[Benzene]	H_b	Δ^c
	mol l ^{–1}	Hz	Hz
Cyclohexane	0	324	
Benzene 50%	5.56	316	8
Benzene 70%	7.68	314	10
Benzene 90%	9.92	312	12

^a [MMA], 9.0×10^{-2} mol l^{–1}.^b Cyclohexane used as internal reference.^c $\Delta = H_b$ (Cyclohexane) – H_b (Benzene).

for several ratios of benzene to cyclohexane at a constant concentration of MMA ([MMA], 9.0×10^{-2} mol l^{–1}), since cyclohexane is considered an inert solvent. The stability constant (K) was estimated by using the following equation.¹¹

$$\frac{1}{\Delta} = \frac{1}{K \cdot \Delta_0 \cdot [D]_0} + \frac{1}{\Delta_0}$$

where Δ is the observed shift for the *trans* olefinic proton in the system relative to that in cyclohexane, Δ_0 represents the shift of the pure interacting species relative to that in cyclohexane, and $[D]_0$ is the concentration of benzene. This result is shown in

Figure 7. Plot of $1/\Delta$ against $1/[D]_0$ for the complex of MMA with benzene, cyclohexane being used as the internal reference.

Figure 7, indicating $K=0.06 \text{ l mol}^{-1}$. In addition, $\Delta H=0 \text{ kcal mol}^{-1}$ was found from the temperature dependence of K , suggesting that the interaction between monomer and solvent did not influence the k_p values.

Molecular-Orbital Calculation

In order to check the possibility of the complex formation of the propagating radical with solvent molecules, we calculated the delocalization stabilization (ΔE) for the complex formation by Fukui's method^{12,13} which was successfully used for the silver complex. The parameters for simple LCAO MO calculation are shown in Table VII.^{14,15} The interaction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a donor and an acceptor was taken into account in the calculation. Since the location of the radical on the center of the aromatic ring of the solvents nullifies the HO-LU overlapping because of the symmetry of the coefficients of atomic orbital in frontier orbitals, the radical was assumed to lie above one of the C=C bonds. The delocalization stabilization was calculated by the following formula.¹³

$$-\Delta E = \frac{(C_r^{\text{LU}} + C_s^{\text{LU}})^2 (d_N^{\text{SO}})^2}{\epsilon_N - \epsilon_{\text{LU}}} \gamma^2 \beta^2 + \frac{(C_r^{\text{HO}} + C_s^{\text{HO}})^2 (d_N^{\text{SO}})^2}{\epsilon_{\text{HO}} - \epsilon_N} \gamma^2 \beta^2$$

where ϵ_{HO} and ϵ_{LU} are the energies of HOMO and LUMO of the solvent, ϵ_N is the energy of the nonbonding molecular orbital of the propagating radical ($\epsilon_N = \alpha + 0.162\beta$), and $\gamma\beta$ is the resonance integral between the radical and the r th and s th atoms of the aromatic molecule. Notation C_r^{HO} and

Table VII. k_p Value and delocalization stabilization^a

Solvents	$k_p \times 10^{-2}$	$\Delta E, -\gamma^2, \beta$
	$\text{l mol}^{-1} \text{ s}^{-1}$
-OCH ₃	5.06	0.732
4.50	1.048
-F	4.48	1.040
-Cl	4.98	0.866
-CN	6.14	0.507

^a The same parameters for simple LCAO MO calculation as reference 2.

C_s^{HO} , and C_r^{LU} and C_s^{LU} are the coefficients of the r th and s th carbon atomic orbitals in HOMO and LUMO of the solvent in which the r th and s th carbon atoms are adjacent to each other. Notation d_N^{SO} is the coefficient of the carbon atomic orbital of the propagating radical in the nonbonding molecular orbital.

The first term indicates stabilization resulting from the electron donation of the propagating radical to the LUMO π -orbital of the solvent and the second term, that from the electron donation of the π -electron of the solvent to the nonbonding orbital of the radical. Since the radical of MMA was found to be electron-poor,¹⁶ the radical of MMA is likely to become an electron acceptor rather than a donor to aromatic rings. According to our theory, the complex formation generally takes place in a way such that the overlap of HOMO of the donor and LUMO of the acceptor becomes maximum.^{12,14,17,18} Accordingly, the complex formation is considered to occur at site such that the second term is maximum and thus the absolute value of the sum of coefficient of adjacent atomic

Figure 8. Correlation between delocalization stabilization and Hammett's σ_p of solvents.

Figure 9. Correlation of k_p values for methyl methacrylate and phenyl methacrylate with Hammett's σ_p of solvents: —○—, phenyl methacrylate; —●—, methyl methacrylate; $(k_p)_H$, propagating-rate constant in benzene.

orbitals of HOMO of solvent is largest, as shown in Ag^+ -aromatic compounds.¹³ The results of the calculation for the above-mentioned location are shown in Table VII and Figure 8. Variation in these values with solvent is almost consistent with the experimental results in Figure 9.

DISCUSSION

Since the rate of initiation seems to be virtually independent of the solvents used, the influence of the solvent to rate of initiation is too small to be taken into account. (Table I)

The largest k_p value is 1.4 times as large as the smallest one as shown in Table II. The solvent effect has the same trend as Bamford's result although the former is somewhat larger than the latter.^{4,5} The difference in the k_p values is beyond the experimental error, indicating that there is indeed solvent participation in the propagating process. Although the solvent effect on k_p for MMA is a little smaller than that observed for PMA, the trend of the solvent effect is quite similar in both system. (Figure 9)

The solvent effect on k_p must be discussed in terms of the following five points. 1. Change in the monomer reactivity by the interaction of the monomer with solvents. 2. Polarity and the polarizability of the medium. 3. Chain-transfer reaction with solvents. 4. Selective solvation of monomer with the polymer. 5. Reversible complex formation of the propagating radical with the aromatic ring of the solvent.

First, the solvent effect on k_p may be explained by the change of the reactivity of the monomer brought

Table VIII. The relation between the k_p value and the number-average degree of polymerization

Solvents	k_p	P_n^a	P_n^b
<chem>c1ccccc1OC</chem>	506	1878	1933
<chem>c1ccccc1</chem>	450	1406	1582
<chem>c1ccccc1F</chem>	448	1359	1447
<chem>c1ccccc1Cl</chem>	498	1563	1741
<chem>c1ccccc1C#N</chem>	614	2167	2216

^a From $[\eta]$, using the relation shown by Bamford *et al.*⁴

^b From kinetic chain length.

on by solvation, because the NMR study shows that there is an interaction between the monomer and solvents. However, since the enthalpy of the interaction is negligibly small and the change of the interaction with solvents indicates the same pattern as that of vinyl acetate whose k_p values change oppositely with solvent,¹⁹ solvation of the monomer is ruled out. (Table V)

Second, if these solvent effects result mainly from the polar participation of solvent in the transition state of the propagation reaction, variation in k_p with solvents should be correlated with the polarity or the polarizability of the solvent.²⁰ No correlation could be as found between k_p and $1/\epsilon$ or $(\epsilon-1)/(2\epsilon+1)$, where ϵ is the dielectric constant of the solvent. Accordingly, the direct polar participation of solvent in k_p is also ruled out.

Third, rate retardation through chain transfer to the solvents is considered, because the solvent effect on k_p might possibly be caused by the difference in chain transfer to the solvent and/or the reinitiation rates by the resulting solvent radicals. However, the chain-transfer reaction to aromatic solvents used has been reported too small to warrant consideration.⁴ If so, the observed number-average degree of polymerization will be almost in accordance with that calculated from the kinetic chain length (v_n), using the following relation:

$$P_n = \frac{2(1+y)}{2+y} v_n$$

where y is the ratio of combination to disproportionation, taking $y=0.47$.²¹ This relation is shown in Table VIII, indicating that the transfer reaction to solvent and/or reinitiation by the resulting solvent radical is not important for the solvent effect.

Furthermore, the fact that k_p in deuterated benzene is nearly the same as that in benzene permits the chain-transfer reaction to be neglected in the polymerization. (Table II)

Fourth, the selective solvation of the polymer with the monomer or solvent was consideration as a cause of the solvent effect. The observed k_p value is likely to be smaller in solvent which has larger solvation to the polymer, because the concentration of the monomer near the propagating polymer radical becomes smaller in the solvent. The selective solvation of the polymer to solvents or monomer was estimated by the difference in the solubility parameter between the polymer and solvent, the change of the difference in solvents being not consistent with that of the k_p value.²² In addition, the fact that solvent effect of k_p value for vinyl acetate (VAc),¹⁹ whose polymer has a solubility parameter similar to poly(MMA),²² is opposite to that for MMA indicates that the selective solvation with the polymer is not an important factor in the solvent effect.

Fifth, the reversible formation of a charge-transfer complex between the propagating radical and aromatic solvents must be considered.^{1,4,5} We have pointed out the validity of the concept that the solvent effect on k_p for PMA was caused mainly by the radical complex.^{1,2} Since MMA has a propagating radical similar to PMA, the same solvent effect will be observed in the rate constant. This expectation is the case. The relationship of k_p to Hammett σ_p values of substituents shows that the k_p values shift to large values by either donor or acceptor substituents (Figure 9). Since similar effects were found in some radical reactions in which aromatic rings directly or indirectly participate,²³⁻²⁷ the variation in k_p with σ_p also indicates that participation of the π -system of the solvent in the reactivity of the propagating radical must be taken into account. Accordingly, the radical complex between the propagating radical and solvents seems to be attractive for elucidating the solvent effect. The MO calculation which considers both the energy level and local electron density of frontier orbitals supports the possibility that variation in k_p with solvents is due to the complex formations with solvents. (Table VII and Figure 8)

A solvent effect for MMA smaller than that for PMA might possibly be due to the difference in complex stabilization, since the PMA radical was

found in the copolymerization data to be more electropositive than the MMA radical and thus is considered to have more electron-accepting ability.²⁸

The behavior of the propagating radical of PMA in aromatic solvents is assumed as follows.

where K_s and K_m are association constants for the above equilibria and k_{po} is a true propagation-rate constant independent of the polymerization medium. The observed propagation-rate constant (k_p) is represented by eq 2 on the assumption that the propagating radical complex with the aromatic ring is in a dormant state,

$$k_p = \frac{k_{po}}{1 + K_m[M] + K_s[S]} \quad (2)$$

Equation 2 may be represented by the solvent concentration as shown in eq 3.

$$k_p = \frac{k_{po}}{1 + K_m \left(\frac{1000d_m}{M_m} \right) + \left(K_s - K_m \frac{d_m M_s}{d_s M_m} \right) [S]} \quad (3)$$

where d_m and d_s are monomer and solvent densities and M_m and M_s are their molecular weights, respectively. Therefore, if this mechanism is correct and K_s is not equal to $K_m d_m M_s / d_s M_m$, then the observed k_p value will depend on the concentration of the solvent. The fact that the k_p value decreased with an increase in the solvent concentration seems to support this mechanism. The activation energies of k_p and k_t seem almost the same as those reported in the bulk polymerization ($E_p = 4.4 \text{ kcal mol}^{-1}$ and $E_t = 0.0 \text{ kcal mol}^{-1}$),²⁹ indicating that the temperature dependence of these values is not influenced by the complex formation of propagating radicals.

When it is assumed that the monomer complexation is neglected the observed k_p is represented by eq 4.

$$k_p = \frac{k_{po}}{1 + K_s[S]} \quad (4)$$

From the plot of $1/k_p$ against $[S]$, K_s was estimated

Figure 10. Plot of the reciprocal of the k_p value against solvent concentration; solvent, benzene.

to be $3.1 \times 10^{-2} \text{ l mol}^{-1}$ (Figure 10), indicating that the fraction of the complexed radical is about one fifth of the propagating radical at $[S] = 8.8 \text{ mol l}^{-1}$. Since radical complexation with the monomer might not be neglected, the above K_s values may still have some ambiguity.

The influence of the complex formation on the termination-rate constant also should be taken into account. The following termination processes are considered in the polymerization.

When the fraction of the complexed radical is α , the observed termination-rate constant (k_t) is shown in the following formula.

$$k_t = k_{11}(1-\alpha)^2 + 2k_{12}\alpha(1-\alpha) + k_{13}\alpha^2$$

Since the complexed radical is considered to be less reactive, the rate constants decrease in the order: $k_{11} > k_{12} > k_{13}$. Therefore, when α is considerably smaller than 1, k_t is likely to be affected mainly by k_{11} , being linearly correlated with the reciprocal viscosity. This view reasonably explains the influence of solvents on k_t for MMA in the present polymerization systems whose K_s values are considered to be smaller than 3.1×10^{-2} . When α becomes larger, a deviation from the linear correlation is presumed. This was shown to be the case in the polymerizations of vinyl acetate, whose K_s values were much larger.¹⁹

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