

## Solvent Effect on Radical Polymerization of Phenyl Methacrylate

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**ABSTRACT:** The radical polymerization of phenyl methacrylate has been studied in various aromatic solvents at 30 and 60°C, and the solvent effects on the polymerization rate were observed. In order to make clear the cause of the solvent effect, propagation rate constants ( $k_p$ ) and termination rate constants ( $k_t$ ) were determined by the intermittent illumination method. Values  $k_p$  increased in this order of solvents: benzene < fluorobenzene < chlorobenzene < anisole < bromobenzene < benzonitrile. The variation of  $k_p$  value for phenyl methacrylate with solvents was compared with that for vinyl benzoate. The cause of the solvent effect is discussed in terms of monomer solvation, polar effect of the propagating radical, chain transfer, and donor—acceptor complex between the propagating radical and solvents. The variation of  $k_p$  value with solvents is best explained by the formation of a donor—acceptor complex, and is correlated with delocalization stabilization for the complex formation.

**KEY WORDS** Phenyl Methacrylate / Radical Polymerization / Polymerization Rate / Elementary Reaction / Propagation Rate Constant / Termination Rate Constant / Initiation Rate / Solvent Effect / Delocalization Stabilization /

A number of papers have reported the solvent effect on the rate of radical polymerization of vinyl compounds, especially styrene and methyl methacrylate.<sup>1-13</sup>

Originally, the effects of aromatic solvents on the polymerization rate of methyl methacrylate was ascribed to solvent participation in the initiation reaction.<sup>1,2</sup> Henrici-Olivé, *et al.*,<sup>3-7</sup> have given forth a reasonable explanation of solvent effect on the polymerization rate of styrene and methyl methacrylate as due to the charge—transfer complex between the propagating radicals and aromatic solvents. Bamford and Brumby<sup>8</sup> have measured individual rate constants in the polymerization of methyl methacrylate in several aromatic solvents, indicating that both the propagation rate constant ( $k_p$ ) and the termination rate constant ( $k_t$ ) vary with the type of solvents. They explain the variation of  $k_p$  value with solvents as a result of a complex formed between the propagating

radical and the solvents. The  $k_t$  value was found to be approximately inversely proportional to the viscosity of the polymerization system. This fact has later been confirmed in the polymerization of methyl methacrylate in various solvents with a wide range of viscosity.<sup>9,10</sup> Minor solvent effect has been observed on the  $k_p$  values in various solvents.<sup>12,14,15</sup> Other investigations have cast doubt on the formation of a complex of propagating radicals, because the observed variation of  $k_p$  values was too small to be distinguished from the experimental error.<sup>16-18</sup> Therefore, whether or not there is any special interaction between the propagating radical and aromatic solvents still remains unsolved. A promising way to solve this problem may be to determine accurately the individual values of  $k_p$  and  $k_t$  in various solvents for vinyl compounds, of which the propagating radicals have opposite polarities. Vinyl benzoate and phenyl methacrylate were used, since it has been

reported that the propagating radical of vinyl benzoate is electron-rich<sup>19</sup> and that of methyl methacrylate electron-poor.<sup>20</sup>

The present authors previously<sup>21</sup> indicated that the trend in the solvent effect on the polymerization rate of phenyl methacrylate ( $e=0.73$ )<sup>22</sup> is opposite to that observed for vinyl benzoate ( $e=-0.55$ ).<sup>22</sup> This opposite solvent effect is explained as a reversible complex formation between the propagating radical and  $\pi$ -system of the solvents.

We will report here the details of the determination of the rate constants for phenyl methacrylate in various aromatic solvents by using the intermittent illumination method and discuss the cause of the solvent participation.

## EXPERIMENTAL

### Materials

Methacryloyl chloride was prepared by refluxing a mixture of thionyl chloride and methacrylic acid, followed by distillation.<sup>23</sup> Phenyl methacrylate was prepared in 70-% yield by the addition of methacryloyl chloride into phenol dissolved in an aqueous 5-% sodium hydroxide solution.<sup>24</sup> The crude ester was purified by washing with an aqueous 5-% sodium hydroxide solution, drying over anhydrous magnesium sulfate, and distillation under reduced pressure. The purity of the monomer was confirmed by gas chromatography to be a monopeak and was estimated to be more than 99.9% (1.5-m Apiezon grease on celite-545, 190°C). Solvents were purified by the usual method described in "Organic Solvent."<sup>25</sup> 2,2'-Azobis(isobutyronitrile) (AIBN), commercially available, was recrystallized twice from absolute ethyl alcohol. 2,2'-Azobis(cyclohexane-1-carbonitrile) (ACN) was prepared by Overberger's description<sup>26</sup> and recrystallized twice from absolute ethyl alcohol, mp 113–114°C. 1,1-Diphenyl-2-picrylhydrazyl (DPPH), commercially available, was recrystallized twice from benzene and obtained as a benzene complex,<sup>27</sup> mp 132–133°C.

### Polymerizations

The rate of polymerization at  $60 \pm 0.01^\circ\text{C}$  was gravimetrically determined. The gas from an ampoule containing phenyl methacrylate, solvent, and AIBN was removed several times in

a high vacuum system and sealed off. The polymer was precipitated with methanol, purified by reprecipitation of a benzene solution of the polymer with methanol, dried for about 24 hr at  $60^\circ\text{C}$  under vacuum, and weighed.

The rate of polymerization at  $30 \pm 0.001^\circ\text{C}$  was measured in a vacuum sealed dilatometer. AIBN was used as an initiator in thermally initiated polymerizations. Photosensitized polymerizations were carried out with ACN as an initiator to make thermodecomposition as small as possible. The light source was an Ushio 250-W high-pressure mercury lamp and filters (Toshiba UV-D1C, UV-31, and IRQ-80) for 3650 Å. The dilatometer consisted of a drum-shaped pyrex glass reaction vessel (11.32 ml) connected to a capillary of 1.38-mm inside diameter. The capillary is available in a length of 15.6 cm. Freshly distilled monomer, initiator and solvent were placed in an ampoule connected to the dilatometer. The ampoule was attached to a high vacuum system and subjected to repeated freezing, pumping, and thawing. The contents were transferred to the dilatometer, sealed off and placed in a double water thermostat regulated to  $\pm 0.001^\circ\text{C}$ . The thermostat bath was attached to both the front and rear with double windows of pyrex glass.<sup>28</sup>

The temperature of the thermostat was measured with a platinum resistance thermometer (Shimazu BDR-2) and recorded during the experiment. All experiments unless otherwise stated were performed at the same concentrations of initiator ( $3 \times 10^{-3}$  mol/l) and monomer (2 mol/l).

Rates of initiation were determined by the inhibition method, DPPH being used as an inhibitor.

Radical life-time was determined by the intermittent illumination method. A rotating sector was used for the illumination time shorter than 1 sec and an electric shutter with a ratio of dark to light of 3, was used for illumination longer than 1 sec. Use of this shutter ensured a square wave form of the incident light. The sector was made of a black-colored aluminum disk of 52-cm diameter with the dark to light period ratio of 3 and was driven by an induction motor of 200 W through a variable reduction gear. The rate of polymerization under

constant illumination ( $R_p^s$ ) was determined before and after the rate determination under intermittent illumination ( $\bar{R}_p$ ) so that a correction was possible for the slight reduction of  $R_p^s$  with time. In the rotating sector experiments, about ten rate experiments were possible with a single dilatometer.

Densities of monomer and monomer-polymer mixtures were measured in a pycnometer at 30.0°C in order to calculate the rate of polymerization from the dilatometer measurement. The volume contraction of complete conversion in the polymerization of phenyl methacrylate was found to be 17.2%. Viscosity of monomer was measured at 30.0°C with an Ostwald viscometer.<sup>29</sup> The viscosity of phenyl methacrylate was 2.29 cp.

A Varian A-60 NMR spectrometer was used with tetramethylsilane as an internal reference (5-% solution). A NEAC-2200 computer was used for the calculation of LCAO MO method.

## RESULTS

### Determination of $k_p$ and $k_t$

Rates of radical polymerization of phenyl methacrylate were determined in various solvents







at 30 and 60°C. These results are shown in Table I, which indicated similar solvent effects on the polymerization rate irrespective of the polymerization temperature and method for initiation.

The rate dependence on initiator and monomer concentrations were determined at 30°C in both thermally initiated and photosensitized polymerization. Typical examples of the results obtained in benzene solutions are shown in Figures 1 and 2. It was also found 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 polymerizations.

In order to determine the elementary rate constants, the initiation rates ( $R_i$ ) were determined by the inhibition method using DPPH as an inhibitor in all solvents. The effect of the addition of DPPH on the thermally initiated polymerization and the correlation between the obtained duration of inhibition and the concentration of the inhibitor are shown in Figures 3 and 4.

A similar behavior was observed in thermally

Table I. Polymerization rates of phenyl methacrylate in various solvents at 30 and 60°C

Solvents	Photosensitized <sup>a, b</sup>	Thermally initiated <sup>a, c</sup>	Thermally initiated <sup>d, e, f</sup>
	$R_p \times 10^4$ (30°C), mol/l sec	$R_p \times 10^5$ (30°C), mol/l sec	$R_p \times 10^5$ (60°C), mol/l sec
 -OCH <sub>3</sub>	1.88 ± 0.04(2) <sup>g</sup>	3.52 ± 0.03(2) <sup>g</sup>	4.42 ± 0.04(2) <sup>g</sup>
	1.70 ± 0.04(4)	3.04 ± 0.04(4)	3.59 ± 0.04(2)
 -F	1.47 ± 0.03(3)	2.90 ± 0.03(2)	3.39 ± 0.06(2)
 -Cl	1.71 ± 0.05(2)	3.40 ± 0.04(2)	3.99 ± 0.05(2)
 -Br	2.27 ± 0.08(2)	3.91 ± 0.03(2)	4.66 ± 0.03(2)
 -CN	2.37 ± 0.07(2)	4.36 ± 0.03(3)	5.33 ± 0.05(2)

<sup>a</sup> From dilatometrical method.

<sup>b</sup> [2,2'-azobis(cyclohexane-1-carbonitrile)] = 3.00 × 10<sup>-3</sup> M; [monomer] = 2.00 M.

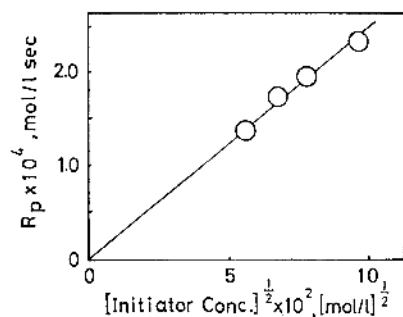
<sup>c</sup> [2,2'-azobis(isobutyronitrile)] = 0.10 M; [monomer] = 2.00 M.

<sup>d</sup> From gravimetric method.

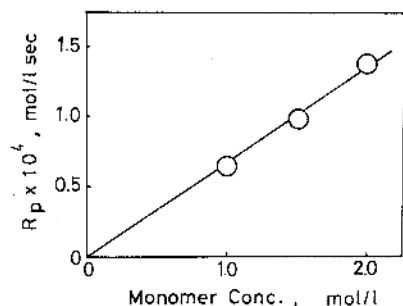
<sup>e</sup> [2,2'-azobis(isobutyronitrile)] = 5.0 × 10<sup>-3</sup> M; [monomer] = 1.00 M.

<sup>f</sup> Polymerization time, 3 hr.

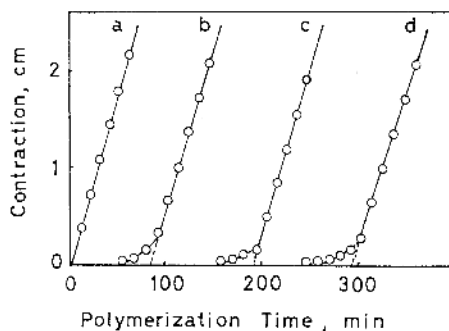
<sup>g</sup> The number of repeated runs.



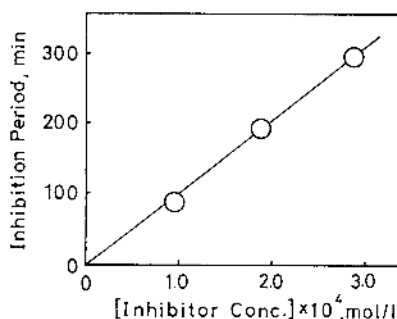
**Figure 1.** Dependence of the polymerization rate of phenyl methacrylate on monomer concentration in benzene at 30°C: [2,2'-azobis(cyclohexane-1-carbonitrile)]= $3.00 \times 10^{-3}$  mol/l.



**Figure 2.** Dependence of the polymerization rate of phenyl methacrylate on initiator concentration in benzene at 30°C: [phenyl methacrylate]=2.00 mol/l.









**Figure 3.** Inhibition effect of DPPH in the polymerization of phenyl methacrylate in benzene at 30°C: [phenyl methacrylate]=2.00 mol/l; [2,2'-azobis(isobutyronitrile)]=0.10 mol/l; [DPPH]=a) 0, b) 0.94, c) 1.88, d)  $2.82 \times 10^{-4}$  mol/l.



**Figure 4.** Relationship between inhibitor concentration and induction period.

**Table II.** Initiation rates and  $k_p^2/k_t$  values for phenyl methacrylate polymerization at 30°C in various solvents

Solvents	$R_i \times 10^8$ , <sup>a,b</sup> mol/l sec	$(k_p^2/k_t) \times 10^2$ , l/mol sec
 —OCH <sub>3</sub>	1.13 ± 0.03 (2) <sup>c</sup>	2.62
	1.55 ± 0.05 (3)	1.49
 —F	1.40 ± 0.03 (2)	1.50
 —Cl	1.31 ± 0.03 (2)	2.21
 —Br	1.18 ± 0.03 (2)	3.24
 —CN	1.25 ± 0.04 (2)	3.80

<sup>a</sup> [2,2'-azobis(isobutyronitrile)]=0.10 M;  
[monomer]=2.00 M.

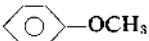


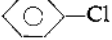
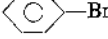
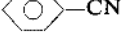
<sup>b</sup> Inhibitor=1,1-diphenyl-2-picryl hydrazyl.

<sup>c</sup> The number of repeated runs.

initiated polymerizations using other solvents. Since rates of polymerization after the consumption of DPPH were lower than that without an inhibitor in the case of photosensitized polymerizations, initiation rates are considered to be more accurate in thermally initiated polymerizations than in photosensitized polymerizations. Therefore, the determinations of  $k_p^2/k_t$  were carried out in the former polymerization at 30°C.  $R_i$  and  $k_p^2/k_t$  obtained in various solvents are shown in Table II. It can be seen from Table II that the initiation rates are scarcely affected by the solvents, the observed variation in the polymerization rate arising from a variation of  $k_p^2/k_t$ .

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**Table III.** Mean life-time of the propagating radical of phenyl methacrylate and derived rate constants in various solvents at 30°C

Solvents	$\tau^a$ , sec	$(k_p/k_t) \times 10^4$	$k_p \times 10^{-2}$ , l/mol sec	$k_t \times 10^{-6}$ , l/mol sec
 -OCH <sub>3</sub>	1.21 ± 0.08 (4) <sup>b</sup>	1.14	2.30	2.02
	1.00 ± 0.04 (8)	0.85	1.76	2.06
 -F	1.13 ± 0.06 (6)	0.83	1.80	2.16
 -Cl	1.15 ± 0.07 (6)	0.99	2.23	2.26
 -Br	1.21 ± 0.04 (4)	1.38	2.35	1.72
 -CN	1.18 ± 0.05 (4)	1.40	2.73	1.96

<sup>a</sup> [2,2'-azobis(cyclohexane-1-carbonitrile)] =  $3.00 \times 10^{-3}$  M; [monomer] = 2.00 M.

<sup>b</sup> The number of data for the determination of lifetime.

The mean life-time of the propagating radical was determined by the sector method at  $30 \pm 0.001^\circ\text{C}$ . Figure 5 shows the variation of the rate of polymerization with illumination time in a benzene solution. The mean life-time of the growing chain was determined by sliding the theoretical curve for lifetime of 1 sec over the plots of the experimental data until the best fit was attained. The mean deviation of the lifetime was estimated by the deviation of the experimental data from the slope part (illumination time 0.8 to 10 sec) of the theoretical curve. In Table III lifetimes and derived values of  $k_p/k_t$  are shown together with  $k_p$  and  $k_t$  obtained by combining values of  $k_p/k_t$  and  $k_p^2/k_t$ . Limits for accumulated error of  $k_p$  and  $k_t$  were estimated from the mean deviation of the rate and the lifetime to be around 15%.<sup>\*</sup> The variation of the  $k_p$  value with solvents is beyond the limit of error, indicating that there is indeed a solvent effect on the propagation process.

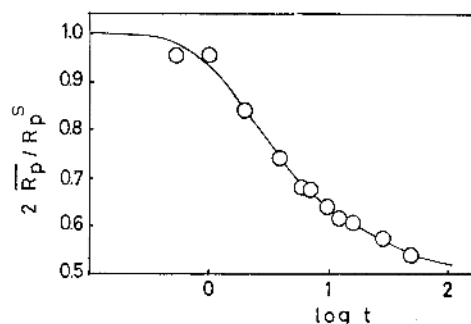
Termination rate constants were approximately correlated with the reciprocal viscosities of the polymerization system, as shown in Figure 6.

<sup>\*</sup> The limits for error were estimated by the following formula

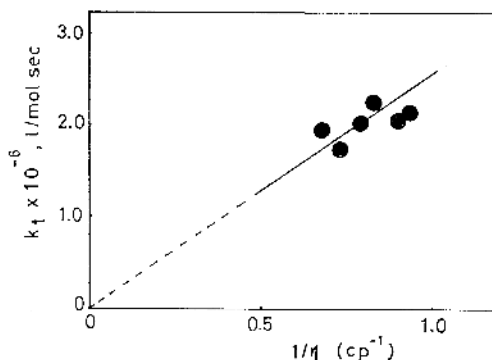
$$\left| \frac{\Delta k_p}{k_p} \right| = \left| \frac{\Delta R_p}{R_p} \right| + \left| \frac{\Delta R_i}{R_i} \right| + \left| \frac{\Delta \tau}{\tau} \right| + \left| \frac{\Delta W_m}{W_m} \right| + \left| \frac{\Delta W_c}{W_c} \right|$$

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

where  $W_m$  and  $W_c$  are weights of monomer and initiator, respectively.










**Figure 5.** Determination of the average life-time of propagating radicals from phenyl 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 (sec); [phenyl methacrylate] = 2.00 mol/l.



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

Table IV. The chemical shifts of olefinic protons for vinyl compounds in various solvents<sup>a, b</sup>

Solvents	Phenyl methacrylate				Vinyl benzoate			
	$\delta H_a$ , Hz	$\delta H_b$ , Hz	$\Delta\delta^c$ , Hz	$k_p$ , l/mol sec	$\delta H_a$ , Hz	$\delta H_b$ , Hz	$\Delta\delta^c$ , Hz	$k_p$ , l/mol sec
 —OCH <sub>3</sub>	376.5	328	48.5	230	297	270	27	106
	377	321	56	176	293	262	31	185
 —F	378	330	48	180	298	271	27	246
 —Cl	377	330	47	223	298	270	28	168
 —Br	377	331	46	235	298	271	27	
 —COOC <sub>2</sub> H <sub>5</sub>	380	338	42		305	280	25	69
 —CN	382	344	38	273	308	284	24	32.7

<sup>a</sup> Tetramethylsilane was used as an internal reference.

<sup>b</sup> In 5% solution.

<sup>c</sup>  $\Delta\delta = \delta H_a - \delta H_b$ .

The viscosities of the polymerization system were calculated from the viscosities of the constituents by assuming a linear relation of viscosity to volume composition.

The interaction between monomer and solvents was estimated by solvent effect on the difference of chemical shifts ( $\Delta\delta$ ) of  $\beta$ -olefinic protons of phenyl methacrylate.<sup>30,31</sup> The results are shown in Table IV along with data of vinyl benzoate. Since the mean deviation of the difference was less than 1 Hz in several experimental runs, the observed difference is far beyond the experimental error, indicating that there is some interaction between monomer and solvents. Since the solvent effect on the difference of chemical shifts shows the same pattern for both monomers, the interaction of monomer with solvents may be caused by the same mechanism.

#### Molecular Orbital Calculation

In order to check the possibility of the complex formation of the propagating radical with solvents, we calculated the delocalization stabilization ( $\Delta E$ ) for the complex formation of the radical with aromatic solvents by using

Fukui's method<sup>32,33</sup> which was successfully used for silver cation complex. The parameter for simple LCAO MO calculation are shown in Table V.<sup>34,35</sup> 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 solvents nullifies the HO—LU overlapping because of the symmetry of the coefficients of atomic orbitals in frontier orbitals, the radical was assumed to lie above one of the C—C bond. The delocalization stabilization is calculated by the following formula<sup>32</sup>

$$-\Delta E = \frac{(C_r^{LU} + C_s^{LU})^2 (d_N^{SO})^2}{\epsilon_N - \epsilon_{LU}} \gamma^2 \beta^2 + \frac{(C_r^{HO} + C_s^{HO})^2 (d_N^{SO})^2}{\epsilon_{HO} - \epsilon_N} \gamma^2 \beta^2 \quad (1)$$

where  $\epsilon_{HO}$  and  $\epsilon_{LU}$  are the energies of HOMO and LUMO of solvent,  $\epsilon_N$  is the energy of nonbonding molecular orbital of the propagating radical ( $\epsilon_N = \alpha - 0.064\beta$ ), and  $\gamma$  is the resonance integral between the radical and the  $r$ th and  $s$ th atoms

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

The first term indicates the stabilization from the electron donation of the propagating radical to LUMO  $\pi$ -orbital of solvent and the second term that from electron donation of the  $\pi$ -electron of solvent to the nonbonding orbital of the radical. Since the radical of methyl methacrylate was found to be electron-poor,<sup>20</sup> the radical of phenyl methacrylate is likely to become an electron acceptor rather than a donor to aromatic rings. One theory says that the charge-transfer interaction takes place according to the way in which the overlap of HOMO of the donor and LUMO of the acceptor become maximum.<sup>82,83,86,87</sup> The complex formation occurs at such a location that the second term is maximum and thus the absolute value of the sum of the coefficient of adjacent atomic

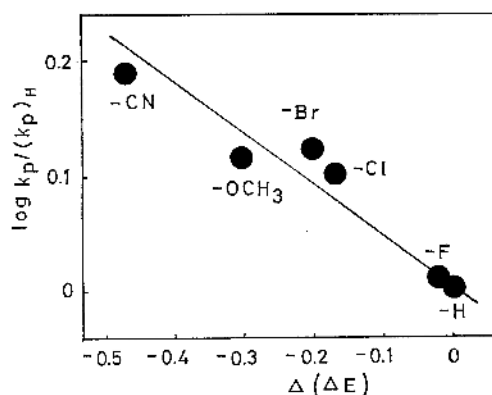
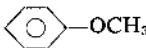


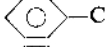
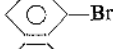



Figure 7. Correlation between  $k_p$  values and delocalization stabilization in various solvents:  $(k_p)_H$ , propagation rate constant in benzene.

orbital of HOMO is largest.

The results of the calculation obtained at the above-mentioned location are shown in Table V and Figure 7. The variation of these values with solvents is almost consistent with the experimental results, in which  $k_p$  is the smallest in benzene and  $k_p$  in anisole is larger than that in benzene.

Table V.  $k_p$  Value and delocalization stabilization<sup>a</sup>

Solvents	$k_p \times 10^{-2}$ , l/mol sec	$\Delta E$ , $-\gamma^2\beta$
	2.30	0.526
	1.76	0.827
	1.80	0.741
	2.23	0.655
	2.35	0.628
	2.73	0.359

<sup>a</sup> Anisole,<sup>84</sup>  $\alpha_{\text{OCH}_3} = \alpha + 0.5\beta$ ;  $\alpha_{\text{adj.C}} = \alpha$ ;  
 $\beta_{\text{C-OCH}_3} = 0.6\beta$ .  
 Fluorobenzene,<sup>84</sup>  $\alpha_{\text{F}} = \alpha + 2.1\beta$ ;  $\alpha_{\text{adj.C}} = \alpha + 0.2\beta$ ;  
 $\beta_{\text{C-F}} = 1.25\beta$ .  
 Chlorobenzene,<sup>84</sup>  $\alpha_{\text{Cl}} = \alpha + 1.8\beta$ ;  $\alpha_{\text{adj.C}} = \alpha + 0.18\beta$ ;  
 $\beta_{\text{C-Cl}} = 0.8\beta$ .  
 Bromobenzene,<sup>84</sup>  $\alpha_{\text{Br}} = \alpha + 1.4\beta$ ;  $\alpha_{\text{adj.C}} = \alpha + 0.14\beta$ ;  
 $\beta_{\text{C-Br}} = 0.7\beta$ .  
 Benzonitrile,<sup>85</sup>  $\alpha_{\text{N}} = \alpha + 0.8\beta$ ;  $\alpha_{\text{adj.C}} = \alpha + 0.08\beta$ ;  
 $\beta_{\text{C-N}} = \beta$ .

## DISCUSSION

Since the rate of initiation appears to be scarcely influenced by the nature of the solvents, the contribution of the rate of initiation to the solvent effect was not considered (Table II).

The largest  $k_p$  value is 1.6 times as large as the smallest one as shown in Table III. The difference in values for  $k_p$  is beyond the experimental error. The solvent effect on  $k_p$  values for phenyl methacrylate is smaller than that observed for vinyl benzoate, and these solvent effects are opposite in trend (Figure 8).

In order to make clear the cause of the solvent effect, let us discuss the influence of solvents on the  $k_p$  value from the following four points. First, the solvent effect on  $k_p$  might be explained by the change of the reactivity of the monomer with aromatic solvents, because NMR study shows that there is an interaction between the monomer and solvents. However, since the change of the interaction with solvents indicates the same pattern in both phenyl methacrylate and vinyl benzoate, it is not consistent with

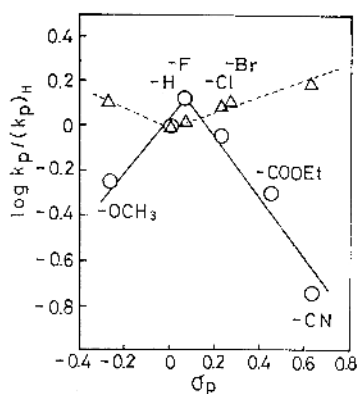


Figure 8. Correlation of  $k_p$  values for phenyl methacrylate and vinyl benzoate with Hammett's  $\sigma_p$  of solvents:  $\text{---}\Delta\text{---}$ , phenyl methacrylate;  $\text{---}\circ\text{---}$ , vinyl benzoate;  $(k_p)_H$ , propagation rate constant in benzene.

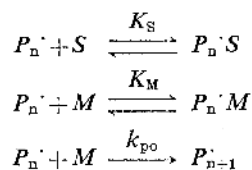
the solvent dependency of  $k_p$ . In addition, the interaction energy between monomer and solvent was estimated to be less than 0.1 kcal/mol from the largest  $\Delta\delta(\Delta\delta_{\text{benzene}} - \Delta\delta_x)$  value, indicating that its contribution to the solvent effect on the  $k_p$  value was less than 0.1%.

Second, if these solvent effect result mainly from the polar participation of solvent in the transition state of the propagation reaction, the variation of  $k_p$  with solvents should be correlated with the polarity or the polarizability of the solvent.<sup>38</sup> No correlation was found between  $k_p$  and  $1/\epsilon$  or  $(\epsilon-1)/(2\epsilon+1)$ , where  $\epsilon$  is a dielectric constant of solvent. Accordingly the direct polar participation of solvent in  $k_p$  is ruled out.

Third, rate retardation through chain transfer to solvents is considered, because the solvent effect on  $k_p$  might be caused by the difference in the chain transfer to solvents and/or the reinitiation rates by the resulting solvent radicals. Since available data for chain-transfer constants in the radical polymerization of phenyl methacrylate was not found in the reference, data for methyl methacrylate was used, which are reported to be almost zero at 25°C.<sup>8,39</sup> If the solvent effect is originated from a difference of reinitiation rate of the resulting solvent radical, the same solvent effect will be observed for both phenyl methacrylate and vinyl benzoate. The expectation is not consistent with our ex-

perimental results.<sup>21</sup> Accordingly, the effect of the chain transfer reaction on  $k_p$  could be ruled out.

Fourth, the reversible formation of charge-transfer complex between the propagating radical and aromatic solvents must be considered. Bamford, *et al.*,<sup>8</sup> have proposed that a small solvent effect on  $k_p$  for methyl methacrylate might be caused by the radical complex. Since a free radical has a low ionization potential and a high electron affinity, there is a high possibility of the complex formation of the propagating radical with aromatic solvents. The poly(methyl methacrylate) radical is electron-poor<sup>20</sup> and is able to become an electron acceptor from aromatic solvents. On the other hand, the poly(vinyl benzoate) radical is electron-rich<sup>19</sup> and can be an electron donor to aromatic solvents. It seems reasonable, therefore, to ascribe the opposite solvent effects for vinyl benzoate and phenyl methacrylate to the electron accepting property of phenyl methacrylate and the electron-donating property of vinyl benzoate in their propagating radicals. If the complexed radicals are too stable to add the monomer, the complex formation would lead to a decrease of  $k_p$  value. We must also take into account the complex formation with the aromatic ring and the vinyl group of monomer. The complex formation with the double bond is considered to be followed by the propagating reaction, the process being regarded as the propagation reaction. Since the complex formation with aromatic rings of monomer and solvents is considered to be a reversible process, the behavior of the propagating radical can be represented as follows



where  $K_S$  and  $K_M$  are association constants for above equilibria and  $k_{po}$  is a true propagation rate constant which is independent of the polymerization medium. The observed propagation rate constant ( $k_p$ ) is given by eq 2

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



A variation in  $k_p$  with aromatic solvents can be reasonably explained by these assumptions.

Since the propagating radical of phenyl methacrylate is electron-accepting and anisole is considered to be the most electron-donating, the  $k_p$  value in anisole seems to be abnormally large (Figure 8). However, the MO calculation, which considers both the energy level and local electron density of frontier orbitals, shows that the variation of  $k_p$  with solvents is reasonable (Table V and Figure 7). Although the result of MO method is not the direct evidence for the complex formation, we can consistently explain the solvent effect on  $k_p$  for both phenyl methacrylate and vinyl benzoate.<sup>21</sup>

A smaller solvent effect for phenyl methacrylate than that for vinyl benzoate might be due to difference in complex stabilization, since the phenyl methacrylate radical has steric hindrance by the methyl group and is more delocalized than vinyl benzoate. Therefore, the resonance integral between the phenyl methacrylate radical and aromatic solvents is possibly smaller than that between the vinyl benzoate radical and aromatic solvents.

Although the correlation between the  $k_t$  values and the reciprocal viscosities of the polymerization system cannot be made clear because of the narrow range of the viscosity, the  $k_t$  values seem to distribute near the straight line through the origin (Figure 6) and suggest that the termination reaction might be viscosity-controlled in phenyl methacrylate as well as in methyl methacrylate and styrene.<sup>40-43</sup>

When the reversible charge-transfer complex of the propagating radical with solvent is considered, the correlation of  $k_t$  with delocalization stabilization for complex formation will be expected, but no correlation was found. The complexed radical, being stable, might participate rarely in the propagation step, but readily in the termination step which is caused by the attack of much more reactive propagating radicals than the monomer.

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