Solvent Effect on Radical Polymerization of Phenyl Acrylate

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ABSTRACT

The radical polymerization of phenyl acrylate (PhA) 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 PhA with aromatic solvents had the same trend as that for PMA. The solvent effect on PhA was somewhat larger than that on PMA, indicating that the steric hindrance of methyl group of the latter is important. 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 complex formation.

INTRODUCTION

We previously reported that the trend in aromatic solvent effect on the polymerization rate constant of phenyl methacrylate (PMA) or methyl methacrylate (MMA) is opposite to that observed for vinyl benzoate (VBz) or vinyl acetate (VAc) [1–5]. 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 PMA or MMA, since the nature of the propagating radical of methacrylates is similar to that of acrylate.

The effect of steric hindrance on the polymerization rate and rate constants in the α-carbon position is also interesting. Therefore, the propagating rate constant for the radical polymerization of phenyl acrylate (PhA) having no methyl group in the α-carbon position 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 PhA in various aromatic solvents and compare the results for PMA.

EXPERIMENTAL METHODS

Preparation of Monomer and Other Reagents

Phenyl acrylate was prepared as described previously [6]. That is, acryloyl chloride was prepared by refluxing a mixture of thionyl chloride and acrylic acid, followed by distillation. Phenyl acrylate (PhA) was prepared by reacting acryloyl chloride with phenol in a 5% sodium hydroxide aqueous solution. The crude PhA was washed with 5% NaOH aqueous solution until the washed solution was colorless. It was then dried over anhydrous magnesium sulfate and distilled three times under reduced pressure, bp 60°C/2 mmHg. The monomer was characterized by analytical elemental analysis, IR, and NMR. Gas chromatography showed the purity of PhA to exceed 99.9%. Initiators 2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobiscyclohexane-carbonitrile (ACN) were purified as described previously [1–6]. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used as an inhibitor; it was recrystallized as described previously [1–6].

Polymerization Procedure

Photosensitized polymerization was carried out with ACN as an initiator to eliminate as much thermal decomposition as possible. The light source was a 250-W high-pressure mercury lamp filtered at 365 nm. Toshiba filters UV-D36C, UV-31, and IRA-25S were placed closer to the light source. The radical lifetime was determined by the rotating sector method as described previously [1–8]. Rates of initiation were determined by the inhibition method with DPPH. The rate of polymerization at 30 ± 0.005°C was measured in a vacuum-sealed dilatometer. The ampule containing PhA, benzene as solvent, and AIBN was evacuated several times on a high vacuum system and finally sealed off. Densities of monomer and monomer-polymer mixture were measured in a pycnometer at 30.0°C in order to calculate the

TABLE 1. Polymerization Rate of Phenyl Acrylate in Various Solvents at 30°C

Solvent	$R_p \times 10^{4,a,b}$ mol·L^{-1}·s^{-1}	$R_i \times 10^8$, mol·L^{-1}·s^{-1}	$k_p^2/k_t \times 10$ L·mol^{-1}·s^{-1}
⟨O⟩–OCH$_3$	1.74	2.10	3.60
⟨O⟩	1.47	2.13	2.53
⟨O⟩–F	1.32	2.11	2.06
⟨O⟩–Cl	1.86	2.24	3.86
⟨O⟩–Br	2.39	2.28	6.26
⟨O⟩–CN	3.56	2.37	13.37

[a]From dilatometer method, thermally initiated polymerization rate.
[b][AIBN] = 0.10 mol·L^{-1}, [phenyl acrylate] = 2.00 mol·L^{-1}.

rate of polymerization from dilatometer measurements. At complete conversion the polymerization of PhA was found to have a volume contraction of 23.6% [6].

RESULTS AND DISCUSSION

Rates of polymerization (R_p) of PhA in various solvents at 30°C are presented as Table 1. The largest R_p in benzonitrile is 2.4 times as large as the smallest in fluorobezene. Moreover, rates of polymerization of PhA having no methyl group in the α-carbon position were much larger than those of PMA in various solvents. These phenomena show that the steric hindrance of methyl group in the α-carbon position is important. The pattern of variation of the polymerization rate for PhA with solvent is in accordance with that for PMA or MMA and was opposite to that for VAc or VBz [1–5]. The dependence of the polymerization rate (R_p) on the initiator and monomer concentration at 30°C was investigated and found to be proportional to the square root of the initiator concentration and to the monomer concentration, which is in good agreement with the general orders of a radical polymerization.

In order to clarify the cause of the different polymerization rates in various solvents, elementary rate constants were determined by inhibition and by the intermittent illumination method. The former method is used to derive the k_p^2/k_t values. DPPH was used as an inhibitor to determine the rate of initiation (R_i). The results are listed in Table 1. R_i values are hardly affected by the solvents, indicating that the decomposition rate of AIBN was not influenced by the aromatic solvents. The value of k_p^2/k_t can be derived by using

$$\frac{k_p^2}{k_t} = \frac{R_p^2}{R_i[M]^2} \tag{1}$$

It can be seen from Table 1 that the observed variation in the polymerization rate arises from a variation of k_p^2/k_t.

In order to obtain the individual k_p and k_t values, the average lifetime (τ) of the propagating radicals was determined by the rotating sector method. The k_p/k_t value can be derived by using

$$\frac{k_p}{k_t} = \frac{R_p\tau}{[M]} \tag{2}$$

In Table 2 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. The largest k_p value is 2.6 times as large as the smallest one. The solvent effect on k_p values for PhA is larger than that observed for PMA (Fig. 1), indicating that steric hindrance of the methyl group in the α-carbon position is important.

In previous papers [1–5] the cause of the solvent effect was 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 solvent is best explained by the formation of a donor–acceptor complex [1–5]. In order to check the possibility of complex formation of the propagating radical with solvents, we calculated the delocalization stabilization (ΔE) for the complex formation of the radical with aromatic solvents by using Fukui's method [9, 10]. Since the radical of MMA was found to be electron-poor [5], the radical of PhA is likely to become an electron acceptor rather than a donor to aromatic rings. The correlation between k_p values and delocalization stabilization in various solvents is shown in Figure 2 [2]. A good linear relationship was obtained. This fact can be explained by the complexed radicals between propagating radicals and aromatic solvents being too stable to add the monomer. So the complex formation leads to a decrease of k_p value.

When the reversible charge-transfer complex of the propagating radical with solvent is considered, a correlation of k_t with delocalization stabilization for com-

TABLE 2.   Mean Lifetime of the Propagating Radical of Phenyl Acrylate and Derived Rate in Various Solvents at 30°C

Solvent	$R_p \times 10^4$, mol·L^{-1}·s^{-1}	τ,[a] s	(k_p/k_t) $\times 10^4$	$k_p \times 10^{-2}$, L·mol^{-1}·s^{-1}	$k_t \times 10^{-6}$, L·mol^{-1}·s^{-1}
⟨O⟩—OCH₃	9.36	1.30	6.08	5.92	0.974
⟨O⟩	8.32	1.27	5.28	4.79	0.907
⟨O⟩—F	7.89	1.15	4.54	4.54	1.000
⟨O⟩—Cl	9.76	1.25	6.10	6.33	1.308
⟨O⟩—Br	12.43	1.35	8.11	7.72	0.952
⟨O⟩—CN	17.20	1.31	11.27	11.86	1.052

[a][2,2′-Azobis cyclohexane carbonitrile] $= 1 \times 10^{-3}$ mol·L^{-1}, [phenyl acrylate] $= 2.00$ mol·L^{-1}.
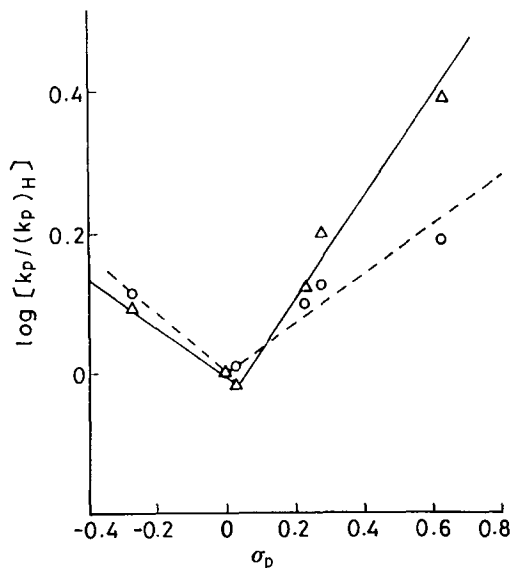
FIG. 1.   Correlation of k_p values for phenyl acrylate and phenyl methacrylate with Hammett's σ_p of solvents: ($\triangle$) phenyl acrylate; ($\bigcirc$) phenyl methacrylate; $(k_p)_H$, propagation rate constant in benzene.
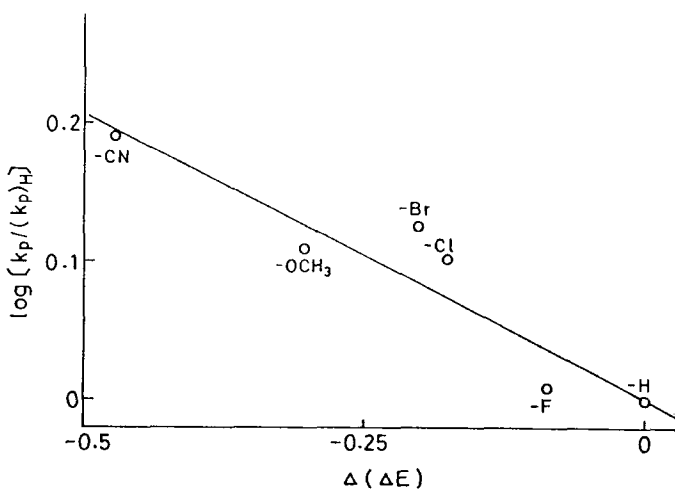
FIG. 2.   Correlation between k_p values and delocalization stabilization in various solvents: $(k_p)_H$, propagation rate constant in benzene.

plex formation will be expected, but no correlation was found. The termination rate constant is not significantly affected by the aromatic solvents [1-5].

CONCLUSIONS

Solvent effects on the radical polymerization of phenyl acrylate were studied in comparison with that of phenyl methacrylate (PMA). It was found that steric hindrance of the methyl group of PMA is important in radical polymerization. Variation in k_p values with solvents is explained by formation of an electron donor-acceptor complex. The termination rate constant is not significantly affected by the aromatic solvents.

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