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The Reactivities of Nuclear-Substituted Phenyl Methacrylates in Radical Copolymerization with Styrene

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In order to clarify the effects of the alkyl substituents on the reactivities of methacrylate monomers toward the attack of a radical, the copolymerizations of a series of nuclear-substituted phenyl methacrylates with styrene were investigated. From the results, the monomer reactivity ratios and the Alfrey-Price Q and e values were determined. It was found that the relative reactivities toward the polystyryl radical were not correlated with the ordinary Hammett equation, but a linear relationship was obtained with a modified Hammett equation which contained a term of the resonance contribution by the substituents. Accordingly, it was considered that the reactivities of substituted phenyl methacrylates depend on both polar and resonance effects caused by the substituents.

In previous papers,[1-3] we have found that the relative reactivities ($1/r_1$) of alkyl methacrylates and acrylates (M_2) toward a polystyryl radical are dependent on the polar substituent constants (σ^*) of the alkyl groups, but not on their steric substituent constants (E_s) in the modified Taft equation (1):

$$\log(1/r_1) = \rho^*\sigma^* + \delta E_s$$

where ρ^* and δ are the constants which give the susceptibility of a given reaction series caused by polar and steric effects of the substituents respectively. In these cases, the findings indicate that the reactivities are subsject to the polar effect of the alkyl substituents, but not to their steric effects.

In order to evaluate the substituent effect, the correlation between the relative reactivities of nuclear-substituted phenyl methacrylates toward the polystyryl radical and Hammett's σ constants of the substituents were investigated in the present study. In the case of nuclear-substituted phenyl methacrylates, the steric effects by the substituents should be similar, because all of the substituents lie across the benzene ring.

The nuclear-substituted phenyl methacrylates used in this study have the following substituents (X): p-OCH_3, p-CH_3, H, p-Cl, m-Cl, p-$COCH_3$, m-NO_2, and p-NO_2.

Experimental

Preparation of Substituted Phenyl Methacrylates (X-PhMA). The Schotten-Baumann reaction of methacrylyl chloride with the corresponding phenols was used to prepare X-PhMA. Then the resulting monomers were purified by fractional distillation under reduced pressure (for PhMA, p-CH_3-PhMA,

TABLE 1. PHYSICAL CONSTANTS FOR X-PhMA MONOMERS*

X in X-PhMA	Bp °C/mmHg	Mp °C	n_D^{20}
p-OCH_3		61.0—62.0 (63)	
p-CH_3	81.0—82.0/2		1.5108**
H	73.5—74.0/3 (83—84/4)		1.5152 (1.5156)
p-Cl	93.0—94.0/2 (113—114/6)		1.5299 (1.5292)
m-Cl	91.0—92.0/2		1.5301
p-$COCH_3$		90.5—92.0	
m-NO_2		59.0—60.0	
p-NO_2		95.5—96.0 (95)	

* Values in parentheses indicate the reference values of Kumanodani.[4]
** Date at 25°C.

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[1] T. Otsu, T. Ito and M. Imoto, *J. Polymer Sci.*, **B3**, 113 (1965).

[2] T. Otsu, T. Ito and M. Imoto, *ibid.*, **C** (16), 2121 (1967).

[3] T. Otsu, T. Ito, T. Fukumizu and M. Imoto, This Bulletin, **39**, 2257 (1966).

TABLE 2. RESULTS OF COPOLYMERIZATIONS OF X-PhMA (M_2) WITH STYRENE (M_1) AT 60°C

X in X-PhMA	$[M_2]$ in Comonomer, mole fraction	Time min	Conversion %	C(%) in Copolymer	$[m_2]$ in Copolymer, mole fraction
H	0.076	60	2.5	86.92	0.212
	0.242	60	3.4	83.41	0.379
	0.582	60	5.2	79.78	0.584
	0.748	60	9.0	77.96	0.703
p-CH_3	0.095	60	2.8	86.25	0.241
	0.191	60	3.7	83.90	0.358
	0.337	60	4.5	81.64	0.487
	0.482	60	5.9	81.20	0.514
	0.739	45	7.7	78.52	0.698
p-OCH_3	0.119	60	3.3	82.69	0.263
	0.301	40	3.3	78.35	0.423
	0.399	40	4.3	76.41	0.505
	0.500	40	2.8	75.05	0.571
	0.602	20	3.6	74.55	0.597
	0.705	15	3.8	73.27	0.662
	0.800	60	10.4	72.64	0.731
p-Cl	0.100	60	3.4	6.65b)	0.235
	0.195	60	4.3	9.13b)	0.352
	0.344	60	5.6	10.84b)	0.443
	0.490	45	5.6	12.27b)	0.529
	0.744	45	9.3	13.89b)	0.638
m-Cl	0.099	60	1.4	7.18b)	0.260
	0.251	100	1.2	10.12b)	0.403
	0.400	100	1.4	11.75b)	0.498
	0.502	100	1.3	12.32b)	0.533
	0.650	65	1.6	13.45b)	0.608
	0.802	100	1.9	14.64b)	0.696
p-$COCH_3$a)	0.121	90	5.6	82.23	0.295
	0.276	90	7.6	78.17	0.456
	0.467	70	8.0	76.66	0.543
	0.693	60	10.6	74.67	0.654
	0.835	60	13.5	72.82	0.775
m-NO_2a)	0.125	240	2.2	3.76c)	0.325
	0.270	240	1.3	3.94c)	0.422
	0.457	240	1.4	4.57c)	0.523
	0.690	240	5.3	5.35c)	0.672
	0.834	240	9.6	5.60c)	0.741
p-NO_2a)	0.123	100	1.1	3.16c)	0.307
	0.276	100	2.4	3.93c)	0.411
	0.456	100	3.1	4.51c)	0.502
	0.690	90	2.6	5.05c)	0.597
	0.833	70	3.6	5.32c)	0.650

a) Copolymerized in 50 vol% benzene solution.
b) Chlorine % in the copolymers.
c) Nitrogen % in the copolymers.

p-Cl-PhMA, and *m*-Cl-PhMA), or by recrystallization from ethanol (for *p*-OCH_3-PhMA, *p*-$COCH_3$-PhMA, *p*-NO_2-PhMA, and *m*-NO_2-PhMA). These purifications were repeated until the absorptions of the unreacted phenols disappeared in the IR spectra.

Table 1 shows the physical constants of these methacrylate monomers. The boiling points, melting points, and refractive indices of PhMA, *p*-OCH_3-PhMA, *p*-Cl-PhMA, and *p*-NO_2-PhMA were all in good agreement with the reported values.4) The results of the

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4) T. Kumanodani, *Kobunshi*, **11**, 917 (1962).

elementary analyses of the other methacrylate monomers were as follows:

p-CH_3-PhMA: Found: C, 75.02; H 7.14%. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%.

p-$COCH_3$-PhMA: Found: C, 70.28; H, 6.23%. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H 5.98%.

m-Cl-PhMA: Found: C, 61.07; H, 4.82%. Calcd for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61%.

m-NO_2-PhMA: Found: N, 6.78%. Calcd for $C_{10}H_9O_4N$: N, 6.76%.

Other Materials. The styrene used as a reference monomer was purified by a usual method. The α, α'-azobisisobutyronitrile (AIBN) used as the radical initiator was purified by recrystallization from ethanol. The benzene, methanol, and other solvents were also purified by ordinary methods.

TABLE 3. MONOMER REACTIVITY RATIOS FOR STYRENE (M_1) - X-PhMA (M_2) COPOLYMERIZATIONS, AND Q_2, e_2 VALUES FOR X-PhMA

X in X-PhMA	σ-Values of X	E_R-Values of X	r_1	r_2	$1/r_1$	Q_2*	e_2*
p-OCH_3	−0.268	0.11	0.28	0.60	3.57	1.23	0.53
p-CH_3	−0.170	0.03	0.30	0.70	3.33	1.23	0.45
H	0.000	0.00	0.30	0.60	3.33	1.17	0.51
p-Cl	0.226	0.10	0.22	0.45	4.55	1.35	0.72
m-Cl	0.373	0.08	0.21	0.40	4.76	1.36	0.77
p-$COCH_3$	0.516	0.21	0.15	0.49	6.67	1.82	0.82
m-NO_2	0.710	0.35	0.18	0.36	5.56	1.47	0.86
p-NO_2	0.778	0.41	0.19	0.22	5.26	1.27	0.98

* Calculated by assuming that $Q_1=1.0$ and $e_1=-0.8$ for styrene (M_1).

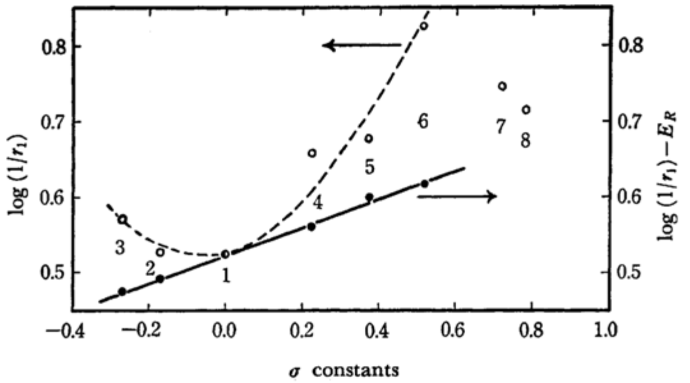

Fig. 1. Correlation between relative reactivities of X-PhMA and Hammett σ constants: 1 PhMA, 2 p-CH_3-PhMA, 3 p-OCH_3-PhMA, 4 p-Cl-PhMA, 5 m-Cl-PhMA, 6 p-$COCH_3$-PhMA, 7 m-NO_2-PhMA, 8 p-NO_2-PhMA.

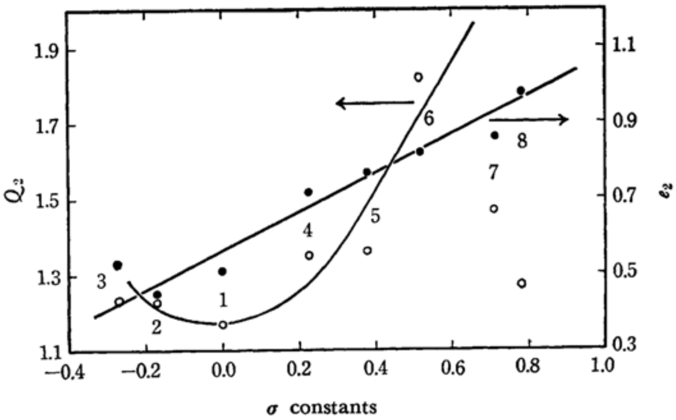

Fig. 2. Correlation between Q_2, e_2 values of X-PhMA and Hammett σ constants: the numbers are the same as those indicated in Fig. 1.

Copolymerization Procedure. The copolymerizations of X-PhMA (M_2) with styrene (M_1) were carried out in a glass tube with AIBN (6.1×10^{-3} mol/l) in bulk or in a benzene solution at 60°C. The resulting copolymers were precipitated in a large amount of methanol, and then reprecipitated from benzene and methanol. Most of the copolymerizations were continued up to 10% conversion. The composition of the copolymers was determined by nitrogen analysis for the copolymers of *p*- and *m*-NO_2-PhMA, by chlorine analysis for the copolymers of *p*- and *m*-Cl-PhMA, and by carbon analysis for the other copolymers. The monomer reactivity ratios were calculated by the method described by Fineman and Ross.⁵⁾

Results and Discussion

The results of the copolymerization of X-PhMA (M_2) with styrene (M_1) at 60°C are shown in Table 2. From the results of this table, the monomer reactivity ratios (r_1 and r_2) and the Q_2 and e_2 values for X-PhMA were calculated to be as given in Table 3.

As can be seen from Table 3, the relative reactivities ($1/r_1$) of X-PhMA toward the attack of the polystyryl radical increase with the introduction of the substituents (X) in PhMA. The relation obtained is shown in Fig. 1, which the $\log (1/r_1)$ of X-PhMA is plotted *vs.* the σ-constants of the ordinary Hammett equation (2):

$$\log (1/r_1) = \rho\sigma \tag{2}$$

where σ is the Hammett substituent constant and ρ is a reaction constant. As may be understood from this figure, no linear relationship between the $\log (1/r_1)$ and the σ constants is observed. Since the nitro group has been known to inhibit the radical polymerization, the values for NO_2-PhMA may include a rather large error. If these values are eliminated, the concave curve indicated by the dotted line is obtained. The value for *p*-OCH_3-PhMA was reconfirmed from a duplicate experiment.

It is well known that the resonance effect as well as the polar effect caused by the substituent is impotat in many radical reactions, as has already been pointed out by Alfrey and Price,⁶⁾ and Bamford and his co-workers.⁷⁾ Recently, one of the present authors proposed the following modified Hammett equation (3) for radical reactions:⁸,⁹⁾

$$\log (1/r_1) = \rho\sigma + \gamma E_R \tag{3}$$

where E_R is the resonance substituent constant (see Table 3) and γ is a reaction constant.

When Eq. (3) was applied in this case, a good linear relationship with $\rho=0.21$ and $\gamma=1.0$, except for the values for NO_2-PhMA, was obtained, as is also shown in Fig. 1. Accordingly, it may be expected that both polar and resonance effects of the substituents are important in considering the radical reactivities of X-PhMA.

Figure 2 shows the correlation of the Q_2 and e_2 values of X-PhMA with the σ-constants of their substituents. The Q_2 values are not linearly correlated with the σ-constants as well as in Fig. 1, but they are correlated with the resonance substituent constants (E_R), as Fig. 3 shows. Although the spectroscopic data of X-PhMA have been described in a previous paper,¹⁰⁾ no exact explanation of such a resonance effect is possible at the present time. From Fig. 2 it may be observed that the e_2 values show a straight-line relationship.

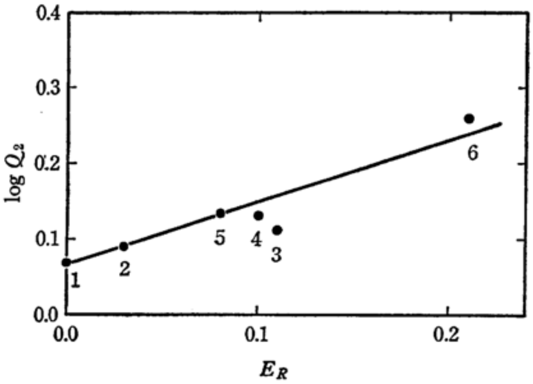

Fig. 3. Correlation between Q_2 values of X-PhMA and E_R constants: the numbers are the same as those indicated in Fig. 1.

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7) C. H. Bamford, A. D. Jenkins and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959); **59**, 530 (1963).

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9) T. Otsu and T. Yamamoto, *J. Soc. Org. Synth. Chem., Japan*, **23**, 643 (1965).

10) T. Otsu, T. Ito and M. Imoto, *J. Polymer Sci.*, **A1(4)**, 733 (1966).