Reactivities of Alkyl *N*-(4-Substituted phenyl) itaconamates in the Radical Copolymerizations with Styrene or Methyl Methacrylate

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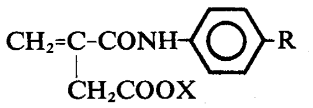
Abstract

The radical copolymerizations of alkyl *N*-(4-substituted phenyl) itaconamates (ARPhIA) (alkyl group: X, **I**, X=CH_3; **II**, X=C_2H_5; **III**, X=n-C_3H_7; **IV**, X=n-C_4H_9; nuclear-substituent: R, **a**, R=OCH_3; **b**, R=CH_3; **c**, R=H; **d**, R=Cl; **e**, R=$COOC_2H_5$) (M_1)



with styrene (ST) (M_2), methyl methacrylate (MMA) (M_2), or vinyl acetate (VAc) (M_2) were carried out at 60°C, using azobisisobutyronitrile as an initiator in tetrahydrofuran in order to clarify the polymerization behavior of ARPhIA and the substituent effects on the copolymerizations. From the results obtained, the monomer reactivity ratios (r_1, r_2) and the Q_1 and e_1 values were determined. It was found that the relative reactivities ($1/r_2$) of itaconamates **I**, **II**, and **III** toward the attack of a polystyryl radical could be correlated not only by the polar substituent constants (σ) of the nuclear-substituents, R, but also by the resonance substituent constants (E_R) in the modified Hammett equation: $\log(1/r_2)=\rho\sigma+\gamma E_R$. According to the above equation, the ρ and γ values were obtained as $\rho=0.16$, $\gamma=2.0$ in the itaconamate **I** and ST; $\rho=0.09$, $\gamma=1.5$ in the itaconamate **II** and ST; $\rho=0.13$, $\gamma=1.5$ in the itaconamate **III** and ST system. While, the ρ and γ values were obtained as $\rho=0$, $\gamma=0.5$ in the itaconamate **II** and MMA; $\rho=-0.06$, $\gamma=0.4$ in the itaconamate **III** and MMA system; *i.e.*, the relative reactivities of ARPhIA toward the attack by a poly (MMA) radical could be slightly affected both by the polar character of the nuclear-substituent, R, and by the resonance character. The radical reactivities were found to be also affected by the ester groups, X. It was observed, however, that both the Q_1 and e_1 values for ARPhIA were independent of Hammett's σ-substituent constants and that the number-average molecular weights (M_n) of the ARPhIA copolymer were not affected by the σ-constants or E_R-constants. M_n for the copolymer was found to be as $1.1\times10^4-1.6\times10^4$.

Introduction

In order to clarify the polymerization reactivities of unsaturated dibasic acid and its derivatives, we investigated *N*-substituted maleimide (RMI)[1-4], *N*-(4-substituted phenyl) isomaleimide (RPhIMI)[5-7], *N*-(4-substituted phenyl) itaconimide (RPhII)[8], and *N*-substituted citraconimide (RCI)[9,10].

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In this paper, alkyl *N*-(4-substituted phenyl) itaconamate (ARPhIA), an unsaturated dibasic acid derivatives, was studied. Various types of itaconic acid derivatives were synthesized and polymerized. However, ARPhIA has not yet been synthesized or polymerized. Twenty two types of ARPhIA; *i.e.*, methyl, ethyl, *n*-propyl, and *n*-butyl *N*-(4-methoxyphenyl) itaconamate (**Ia**, **IIa**, **IIIa**, and **IVa**); methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-hexyl *N*-(4-methylphenyl) itaconamate (**Ib**, **IIb**, **IIIb**, **IVb**, and **Vb**); methyl, ethyl, *n*-propyl, and *n*-butyl *N*-phenylitaconamate (**Ic**, **IIc**, **IIIc**, **IVc**); methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-hexyl *N*-(4-chlorophenyl) itaconamate (**Id**, **IId**, **IIId**, **IVd**, and **Vd**); methyl, ethyl, *n*-propyl, and *n*-butyl (*N*-(4-ethoxycarbonylphenyl) itaconamate (**Ie**, **IIe**, **IIIe**, and **IVe**) were synthesized and their homopolymerization reactivities were investigated. In addition, the copolymerizations of ARPhIA (M_1) with styrene (ST) (M_2), methyl methacrylate (MMA) (M_2), or vinyl acetate (VAc) (M_2) were carried out, and the monomer reactivity ratios, r_1 and r_2, and Q_1 and e_1 values for ARPhIA were calculated. Furthermore, in order to clarify the substituent effects on the copolymerizations, the modified Hammett equation (eq 1)[11] was applied to these copolymerizations, and the results are discussed.

$$\log(1/r_2) = \rho\sigma + \gamma E_R \qquad (1)$$

where ρ is the polar-reaction constant, σ is the polar-substituent constant, γ is the resonance-reaction constant, and E_R is the resonance-substituent constant. In a reaction in which the resonance effect brought on by the substituents is not important, *i.e.*, when $\gamma = 0$, eq 1 comes to be equal to the ordinary Hammett equation (eq 2)[12].

$$\log(1/r_2) = \rho\sigma \qquad (2)$$

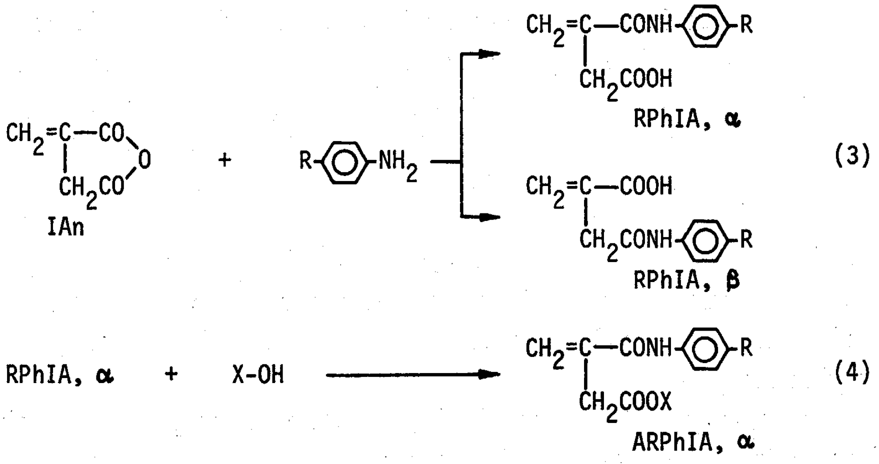
Experimental

Syntheses of ARPhIA Monomers

The twenty two types of ARPhIA monomers were synthesized, according to following processes (3) and (4) in Scheme 1, and by a method similar to that described by Crombie *et al.*[13] and Nagai *et al.*[14]

N-(4-Substituted phenyl) itaconamic Acid (RPhIA), (α, β isomer). Itaconic anhydride (IAn) was dissolved in anhydrous ethyl ether. An anhydrous ethyl ether solution containing the primary arylamine was added for 1 hour. The solution was stirred with a magnetic stirrer at 0–5°C for 2–3 hours to produce RPhIA. (Yield, 70–80%).

It can be considered that there are two different structures in RPhIA, α, β isomers, as illustrated in Scheme 2. However, either α or β of RPhIA should be prepared since the NMR spectrum of the product in the ether solution after filtration of RPhIA indicates an active methylene peak at the same position as RPhIA before and after recrystallization. In addition, the NMR spectrum of *N*-(4-chlorophenyl) itaconamic acid, RPhIA (R = Cl), in Scheme 2, indicates an active methylene peak at 3.42 (s) ppm when NMR spectra were taken by a Hitachi R–24 NMR spectrometer in deuterium dimethyl sul-

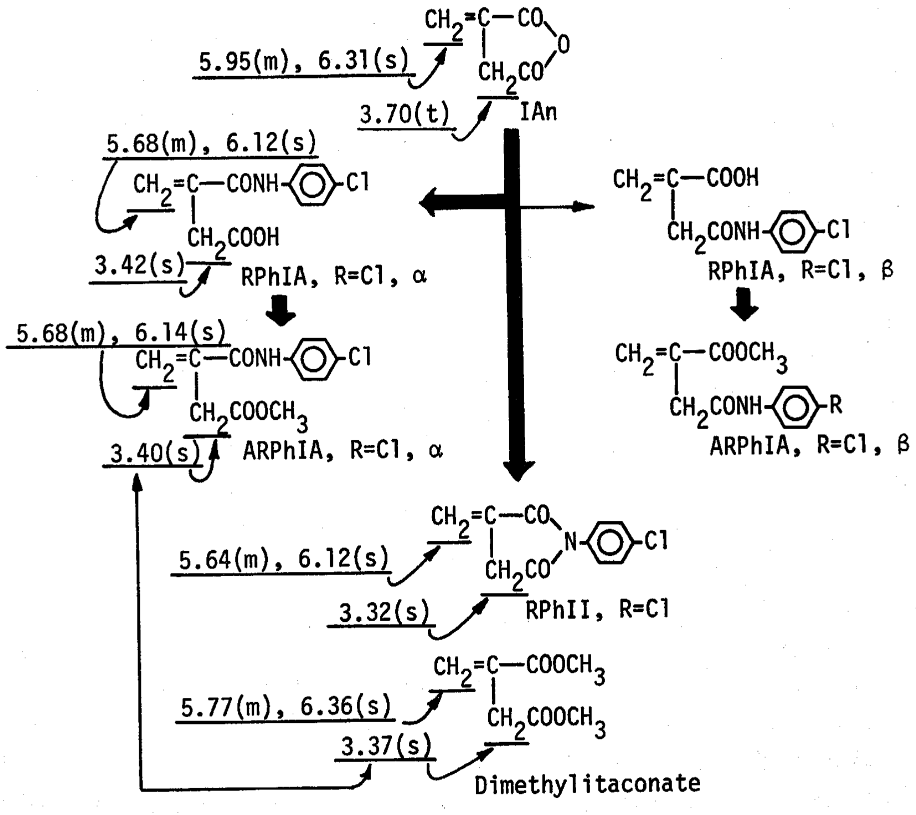


I, X=CH_3; II, X=C_2H_5; III, X=n-C_3H_7; IV, X=n-C_4H_9; V, X=n-C_6H_{13}.

a, R=OCH_3; b, R=CH_3; c, R=H; d, R=Cl; e, R=$COOC_2H_5$.

Scheme 1

foxide (DMSO-d_6), using TMS as the internal standard. Then the NMR spectrum of α type of methyl *N*-(4-chlorophenyl) itaconamate (**Id**) indicates an active methylene peak at 3.40 (s) ppm. On the other hand, the NMR spectrum of dimethyl itaconate



Scheme 2

indicates an active methylene peak and a methylene peak of the double bond of reaction site at 3.37 (s) ppm and 5.77 (m), 6.36 (s) ppm, respectively, as shown in Scheme 2.

Considering that the NMR spectrum of dimethyl itaconate indicates an active methylene peak at the same position as that of α type of ARPhIA, RPhIA should have only α type structure. If RPhIA has the structure of β type in Scheme 2, the NMR spectrum of β type of ARPhIA will indicate the methylene peak of double bond of reaction site at the similar position to that of dimehyl itaconate. Judging from the results of NMR spectra described above, we can regard the α type structure as RPhIA. Akashi *et al.*[15] also supported the structure of α type in RPhIA from the reactivity of IAn with arylamine.

ARPhIA. A mixture of 0.1 mol of RPhIA, 1.0 mole of the primary alcohol, and *ca.* 1.5 m*l* of acetyl chloride was heated under reflux at 40–50°C, until the RPhIA was dissolved completely. Furthermore, the heating was continued for 2 hours. After the reaction was over, the contents were poured into a large amount of ice water to precipitate the ARPhIA. The crude ARPhIA was recrystallized twice from methanol.

ARPhIA was identified by elemental analysis, IR, and NMR spectra. Table I gives the yields and the results of the analysis of each ARPhIA monomer.

Material

Table I. Yields, melting points, and elemental analyses of ARPhIA.

Monomer			Yield[a]	mp	C/%		H/%		N/%	
	X	R	%	°C	Calcd	Found	Calcd	Found	Calcd	Found
Ia	CH_3	OCH_3	12	123–124	62.6	62.7	6.0	6.2	5.6	5.6
Ib	CH_3	CH_3	38	124–125	66.9	66.9	6.5	6.5	6.0	6.1
Ic	CH_3	H	40	130–131	65.7	65.5	6.0	5.8	6.4	6.5
Id	CH_3	Cl	33	114–115	56.8	57.0	4.8	4.8	5.5	5.6
Ie	CH_3	$COOC_2H_5$	21	124–125	61.8	61.8	5.8	5.6	4.8	4.5
IIa	C_2H_5	OCH_3	12	93–95	63.8	63.9	6.5	6.5	5.3	5.6
IIb	C_2H_5	CH_3	44	102–103	68.0	67.6	6.9	6.8	5.7	5.7
IIc	C_2H_5	H	36	74–75	66.9	66.3	6.5	6.5	6.0	6.1
IId	C_2H_5	Cl	31	98–99	58.3	58.1	5.3	5.0	5.2	5.3
IIe	C_2H_5	$COOC_2H_5$	38	99–100	62.9	63.0	6.2	6.4	4.6	4.5
IIIa	n-C_3H_7	OCH_3	22	82–84	64.9	65.0	6.9	7.1	5.1	4.9
IIIb	n-C_3H_7	CH_3	25	88–89	68.9	69.0	7.3	7.4	5.4	5.6
IIIc	n-C_3H_7	H	33	62–63	68.0	67.4	6.9	6.8	5.7	5.8
IIId	n-C_3H_7	Cl	51	95–96	59.7	59.6	5.7	5.7	5.0	5.1
IIIe	n-C_3H_7	$COOC_2H_5$	19	96–98	63.9	63.9	6.6	6.8	4.4	4.1
IVa	n-C_4H_9	OCH_3	15	76–77	66.0	66.1	7.3	7.5	4.8	4.5
IVb	n-C_4H_9	CH_3	19	92–94	69.8	70.0	7.7	7.6	5.1	5.0
IVc	n-C_4H_9	H	20	70–71	68.9	69.3	7.3	7.5	5.1	4.8
IVd	n-C_4H_9	Cl	20	81–83	60.9	61.4	6.1	6.4	4.7	4.3
IVe	n-C_4H_9	$COOC_2H_5$	18	92–94	64.9	65.3	7.0	7.0	4.2	4.1
Vb	n-C_6H_{13}	CH_3	17	64–66	71.3	71.5	8.3	8.0	4.6	4.5
Vd	n-C_6H_{13}	Cl	15	69–71	63.1	63.4	6.8	6.8	4.3	4.0

[a] based on *N*-(4-substituted phenyl) itaconamic acid.

Azobisisobutyronitrile (AIBN) was used as the initiator and tetrahydrofuran (THF), as the solvent. In order to purify these compounds, commercial-quality AIBN was recrystallized and the THF was dehydrated with sodium metal and distilled before use. The ST, MMA, and VAc monomers were purified by the usual methods just before use.

Homopolymerization Procedure

All homopolymerizations of ARPhIA (3.5×10^{-1} mol l^{-1} – 1.2 mol l^{-1}) were carried out in THF (5 ml) at 60°C in a sealed tube in the presence of AIBN (3.0×10^{-2} mol l^{-1}), by using the same technique as described in the earlier paper[8]. In this study, however, petroleum ether was used as the precipitant and the homopolymers were purified by reprecipitating from the THF solution into a large amount of ethyl ether.

Copolymerization Procedure

The copolymerization of ARPhIA (M_1) with ST (M_2), MMA (M_2), or VAc (M_2) was carried out in THF at 60° in a sealed-glass tube in the presence of 3.0×10^{-2} mol l^{-1} of AIBN, by using the same technique as described in the previous papers[9,10]. After copolymerization for a given time, the tube was opened, and its contents were poured into a large amount of petroleum ether to precipitate the copolymer.

The composition of the copolymer was determined from carbon or nitrogen analysis. The monomer reactivity ratio, r_1 and r_2, were determined by the method of Fineman and Ross[16] or by that of Mayo and Lewis[17].

Molecular Weight Measurement

The molecular weights of the polymers and copolymers were measured at 50°C with a Shimadzu LC–3A belonging to a gel permeation chromatography (GPC) with a UV (254 nm) detector. THF was used as a solvent, and Shimadzu polystyrene-gels HGS–40–20–15 (each one of $7.9\phi \times 300$ mm) was used as a column system. The concentration of sample was *ca.* 5 mgd l^{-1}, and the flow rate was 1.2 m$l$min^{-1}. The number-average (M_n), the weight-average (M_w), the Z-average (M_z) molcular weight, and the degree of polydispersion (M_w/M_n) were calculated with Shimadzu Cromatopac C–E4A, according to the following equations (5), (6), and (7).

$$M_n = \frac{\Sigma H_i}{\Sigma(H_i/M_i)} \tag{5}$$

$$M_w = \frac{\Sigma(M_i H_i)}{\Sigma H_i} \tag{6}$$

$$M_z = \frac{\Sigma(M_i^2 H_i)}{\Sigma(M_i H_i)} \tag{7}$$

where H_i is the height of the GPC peak, and M_i is the molecular weight at the H_i peak.

Softening Points and Viscosities Measurements

The softening points were measured with a Mitamura Riken Kogyo MEL-TEMP by the standard melting point method[18]. The reduced viscosity of the copolymer was measured in THF at 30°C, using an Ostwald viscometer.

Results and Discussion

Homopolymerizations of ARPhIA

All homopolymerizations of ARPhIA were carried out in 5 m*l* of THF at 60°C in the presence of 3.0×10^{-2} mol l^{-1} of AIBN for 92 hours. In the homopolymerizations of twenty two types of ARPhIA, all systems were homogeneous throughout. It was found that the conversion of each copolymer was only 3–30% and that M_n is between 1200 and 2600; *i.e.*, all the homopolymers are oligomers of which the degree of polymerization are about 6–10. The fact that the ARPhIA homopolymers are oligomers may be attributable to the chain transfer reaction. That is, both the hydrogen atom of the amide group in ARPhIA and the active methylene group may behavior as inhibitors in the chain transfer mechanism. In addition, considering that the itaconamates **IV** and **V** could give less homopolymers than itaconamates **I**, **II**, and **III**, the steric character of bulky ester groups, X, in ARPhIA may not be negligible.

Copolymerizations of ARPhIA with ST

ARPhIA (M_1) was copolymerized with ST (M_2) at 60°C, using AIBN as the initiator. These copolymerizations were homogeneous throughout. In the copolymerizations of itaconamate **Vb** or **Vd** with ST, however, no copolymer could be obtained. The results of the copolymerizations are summarized in Table II. Four types of copolymer-composition curves in the **Ib**–ST, **Ie**–ST, **IIc**–ST, and **IIIc**–ST systems are shown in Figure 1. The composition curves of other copolymers are similar to those

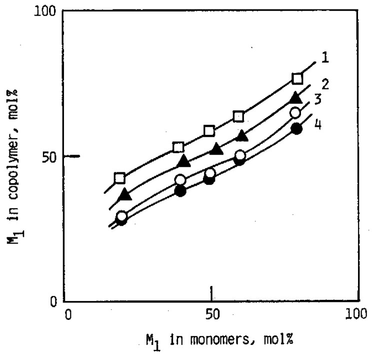


Figure 1 Copolymer-composition curves for the copolymerizations of ARPhIA (M_1) with ST (M_2) in THF at 60°C: 1 (□), **Ie**–ST; 2 (▲), **Ib**–ST; 3 (○), **IIc**–ST; 4 (●), **IIIc**–ST.

indicated in Figure 1. From Table II and Figure 1, it is observed that the molar fraction of ARPhIA in the copolymer tends to increase with increasing in the molar fraction of ARPhIA in the monomer mixture, and that the rates of copolymerization in *ca.* 50 mol% of ARPhIA in a monomer feed are greatest for most of the systems. It is known that the copolymerization of ST with maleic anhydride, RMI, or RCI is practically an alternating type process. In the case of the ARPhIA-ST sytem, however, no such observation could be made.

Table II. Results of the radical copolymerizations of ARPhIA (M_1) with ST(M_2) in THF at 60°C[a].

ARPhIA (M_1)	M_1 in monomer, mol%	Polymerization time, hr	Conversion, %	C-analysis %	M_1 in copolymer mol%
Ia	23.7	2.5	12.0	74.6	38.1
	40.0	2.5	14.5	71.8	48.3
	50.0	2.5	16.3	70.3	54.5
	60.0	2.5	15.0	69.5	58.0
	80.0	2.5	11.5	67.1	70.1
Ib	21.0	2.0	5.5	81.1	26.1
	41.4	5.0	12.0	76.2	43.6
	51.4	14.0	21.0	75.4	47.0
	61.4	14.0	11.2	74.4	51.6
	80.0	14.0	8.0	72.4	62.1
Ic	19.9	2.5	4.6	79.8	29.5
	40.0	6.0	12.5	76.2	42.1
	50.0	6.0	16.8	75.7	44.2
	59.9	22.0	8.9	74.1	50.6
	80.0	22.0	4.5	70.0	71.0
Id	20.6	1.0	1.2	73.9	32.4
	40.9	1.5	4.0	69.6	41.0
	50.9	1.5	3.2	68.4	51.4
	60.9	6.0	10.1	66.8	56.8
	80.0	30.0	1.4	63.9	62.1
Ie	20.0	1.8	2.7	72.1	41.5
	39.9	1.7	9.7	69.3	52.4
	49.9	2.2	14.1	68.0	58.5
	60.0	2.3	14.0	67.1	63.1
	80.1	2.5	9.3	64.9	76.2
IIa	20.0	1.5	7.4	74.5	29.0
	40.0	2.3	10.0	71.9	47.5
	50.0	2.0	8.8	70.5	53.4
	60.0	1.8	8.5	67.9	54.6
	80.0	1.7	4.5	65.6	68.6

Table II. Continued

ARPhIA (M_1)	M_1 in monomer,	Polymerization time,	Conversion,	C-analysis	M_1 in copolymer
	mol%	hr	%	%	mol%
IIb	20.7	2.5	7.5	79.1	33.2
	40.0	9.0	12.4	76.4	44.3
	51.0	3.5	9.0	75.7	47.6
	60.0	55.0	2.5	74.6	52.8
	80.0	60.0	1.2	73.5	59.2
IIc	20.0	2.0	6.1	79.3	31.8
	40.1	2.0	11.4	76.4	43.0
	50.3	2.0	12.2	74.9	49.3
	60.2	2.0	12.6	74.3	52.2
	79.0	2.0	7.7	72.3	62.2
IId	19.8	2.0	9.8	72.8	34.4
	39.5	2.0	10.1	69.9	42.9
	49.7	2.0	8.2	69.3	45.0
	59.8	2.0	7.1	67.4	51.4
	79.2	30.0	6.4	66.9	53.6
IIe	20.0	5.8	3.0	73.5	30.6
	39.9	6.0	6.7	70.1	40.3
	50.1	8.2	26.1	69.3	43.0
	59.8	8.0	10.4	68.5	45.9
	79.9	11.0	9.2	66.0	55.9
IIIa	20.0	2.3	4.5	74.9	31.9
	40.1	2.3	7.6	72.0	41.5
	50.0	2.0	5.4	71.2	52.0
	60.0	2.0	5.8	70.9	56.1
	80.0	2.0	3.0	66.6	60.4
IIIb	20.1	3.0	6.5	79.5	32.4
	40.1	6.0	7.1	77.4	41.0
	50.2	11.0	7.0	75.3	51.4
	59.5	72.0	3.7	74.5	56.3
	80.0	80.0	2.1	72.8	66.8
IIIc	20.1	4.0	10.1	80.3	29.2
	40.0	12.0	12.0	77.8	38.3
	50.1	12.0	16.2	76.8	42.6
	60.0	36.0	12.4	75.5	48.7
	79.2	72.0	2.7	73.4	59.8
IIId	20.0	3.0	4.1	74.7	30.1
	40.0	5.0	3.6	71.5	39.5
	49.8	18.0	2.1	71.1	40.6
	60.1	60.0	7.0	68.8	48.9
	80.0	120.0	4.8	66.5	58.0

Table II. Continued

ARPhIA (M_1)	M_1 in monomer,	Polymerization time,	Conversion,	C-analysis	M_1 in copolymer
	mol%	hr	%	%	mol%
IIIe	20.2	7.8	12.2	74.1	36.6
	40.0	10.0	24.6	71.8	45.9
	50.0	8.0	17.1	70.1	53.7
	60.0	8.0	14.1	64.9	57.7
	79.8	96.0	7.4	68.2	65.1
IVa	20.0	7.0	6.3	76.4	35.2
	40.0	1.5	3.3	72.4	52.4
	50.0	1.0	2.1	71.1	59.8
	60.0	1.0	1.7	70.2	65.0
	69.7	1.0	1.2	69.4	70.7
IVb	20.0	4.7	13.6	78.0	39.6
	40.0	2.0	8.6	76.4	47.8
	49.9	2.0	11.4	75.5	52.6
	59.8	1.5	1.7	74.9	52.2
	69.9	1.5	1.4	74.1	61.4
IVc	20.0	192.0	1.6	76.5	45.4
	39.9	22.0	4.9	75.5	50.4
	50.0	35.0	3.2	74.4	56.9
	60.1	35.0	2.9	73.6	61.5
	70.0	192.0	1.2	72.8	66.8
IVe	20.0	24.0	4.9	74.9	34.7
	39.9	48.0	13.3	71.4	49.9
	49.9	25.0	9.1	70.0	57.4
	59.9	110.0	3.5	69.2	62.3
	69.6	192.0	2.1	67.7	72.8

[a] [AIBN], 3.0×10^{-2} mol l^{-1}; THF, 5 ml; M_1+M_2, 1.5 g.

Based on the results of Table II, the monomer reactivity ratios (r_1, r_2) were determined according to either the method described by Fineman and Ross[16] or that by Mayo and Lewis[17]. The Q_1 and e_1 values for ARPhIA were then calculated, according to the method of Alfrey and Price[19], assuming that $Q_2=1.0$, $e_2=-0.8$ for ST[20]. These results are shown in Table III, along with the Hammett's σ-substituent constants and E_R-constants of the substituents in the modified Hammett equation (eq 1). From Table II, it is obvious that a difference of 1% in the carbon analysis for the copolymer corresponds to about a 5% difference in the composition for the copolymer. Accordingly, if the error of carbon analysis is about 0.3%, the results, *i.e.*, r_1, r_2, Q_1, e_1 values, and ρ, γ values which will be mentioned later, may contain a little error. This error is shown in Table III.

In order to guide a correlation between the relative reactivities ($1/r_2$) and the nature

Table III. Monomer-reactivity ratios (r_1, r_2) for ARPhIA (M_1) and vinyl monomer (M_2), Q, e values of ARPhIA.

ARPhIA			ST (M_2)			MMA (M_2)			VAc (M_2)		Q_1^a	e_1^a	σ^b of R	E_R^c of R
M_1	X	R	r_1^d	r_2^d	$1/r_2$	r_1^e	r_2^e	$1/r_2$	r_1^f	r_2^f				
Ia	CH_3	OCH_3	0.41	0.26	3.85	—	—	—	—	—	1.16	0.70	−0.27	0.11
Ib	CH_3	CH_3	0.16	0.30	3.33	—	—	—	5.65	0.00	0.83	0.94	−0.17	0.03
Ic	CH_3	H	0.18	0.39	2.56	—	—	—	3.65	0.00	0.69	0.84	0.00	0.00
Id	CH_3	Cl	0.18	0.38	2.38	—	—	—	—	—	0.71	0.84	0.23	0.10
Ie	CH_3	$COOC_2H_5$	0.58	0.15	1.21	—	—	—	—	—	1.91	0.76	0.45	0.16
IIa	C_2H_5	OCH_3	0.34	0.33	3.03	0.43	1.31	0.76	—	—	0.93	0.68	−0.23	0.11
IIb	C_2H_5	CH_3	0.26	0.38	2.63	0.63	1.43	0.69	—	—	0.78	0.72	−0.17	0.03
IIc	C_2H_5	H	0.21	0.45	2.22	0.47	1.32	0.76	5.76	0.00	0.65	0.73	0.00	0.00
IId	C_2H_5	Cl	0.16	0.35	2.86	0.36	1.24	0.81	—	—	0.73	0.90	0.23	0.10
IIe	C_2H_5	$COOC_2H_5$	0.20	0.23	4.35	0.48	1.21	0.83	—	—	1.07	0.95	0.45	0.16
IIIa	n-C_3H_7	OCH_3	0.40	0.38	2.63	0.40	1.03	0.97	—	—	0.88	0.57	−0.27	0.11
IIIb	n-C_3H_7	CH_3	0.19	0.54	1.85	0.72	0.78	1.28	—	—	0.58	0.73	−0.17	0.03
IIIc	n-C_3H_7	H	0.18	0.50	2.00	0.15	1.13	0.88	—	—	0.50	0.76	0.00	0.00
IIId	n-C_3H_7	Cl	0.31	0.39	2.56	0.31	1.26	0.79	—	—	0.79	0.66	0.23	0.10
IIIe	n-C_3H_7	$COOC_2H_5$	0.40	0.26	3.85	0.53	1.00	1.00	—	—	1.16	0.70	0.45	0.16
IVa	n-C_4H_9	OCH_3	0.69	0.12	8.33	—	—	—	—	—	2.35	0.78	−0.27	0.11
IVb	n-C_4H_9	CH_3	0.31	0.19	5.26	—	—	—	—	—	1.37	0.88	−0.17	0.03
IVc	n-C_4H_9	H	0.49	0.12	8.33	—	—	—	—	—	2.17	0.88	0.00	0.00
IVe	n-C_4H_9	$COOC_2H_5$	0.61	0.20	5.00	—	—	—	—	—	1.57	0.65	0.45	0.16

[a] Q_1, e_1 values calculated from the copolymerizations with ST.

[b] Hammett's σ-constants.

[c] E_R-constants in the modified Hamett equation: $\log(1/r_2) = \rho\sigma + \gamma E_R$.

[d] With an error of ±0.07. [e] With an error of ±0.17. [f] With an error of ±0.51.

of the substituents in ARPhIA, we attempted to plot the present results with the modified Hammett equation (eq 1). As shown in Figure 2–(i), in the case of the copolymerization of itaconamate **I** with ST, the ordinary Hammett plots did not give a linear relationship. However, by assuming that $\gamma = 2.0$ in eq 1, the plots of $[\log(1/r_2) - 2.0E_R]$ against σ-constants were found to give a good linear relationship where ρ is 0.16 with 0.04 of a standard deviation, as shown in Figure 2–(i). This result strongly suggests that the relative reactivities of itaconamate **I** toward the attack of a polystyryl radical are affected not only by the resonance but also by the polar character of the nuclear-substituent, R.

In the case of the copolymerizations of itaconamate **II** or **III** with ST, the similar tendencies could be observed. That is, the ρ and γ values were obtained as $\rho = 0.09 \pm 0.06$, $\gamma = 1.5 \pm 0.06$ in the itaconamate **II** with ST; $\rho = 0.13 \pm 0.05$, $\gamma = 1.5 \pm 0.05$ in the itaconamate **III** with ST, as shown in Figure 2–(ii), (iii).

Figure 2 indicates that the relative reactivities, $1/r_2$, of ARPhIA toward the attack by a polystyryl radical slightly increase with an increase in the electron-withdrawing nature of the nuclear-substituent, R.

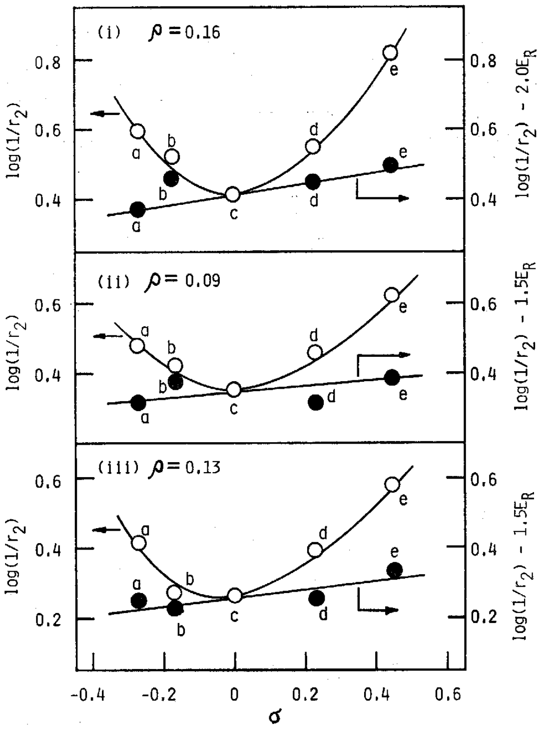
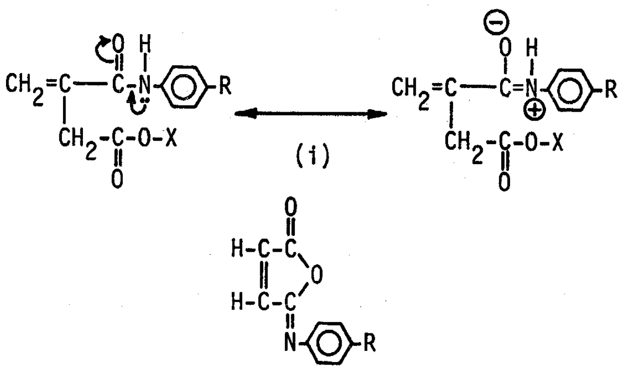


Figure 2 Correlations between the relative reactivities ($1/r_2$) of ARPhIA toward the attack of a polystyryl radical and σ-constants of the nuclear-sbustituents in ARPhIA: (i) I–ST; (ii) II–ST; (iii) III–ST; a, OCH_3; b, CH_3; c, H; d, Cl; e, $COOC_2H_5$.

The fact that the ρ value in these three reactions are positive can be understood as due to the nucleophilic nature of a polystyryl attacking radical. It was found, however, that this polar effect of the nuclear-substituent, R, was a very little. On the other hand, it is interesting to note that the resonance character of the nuclear-substituents, R, can greatly influence the radical reactivities of ARPhIA. It is very difficult to explain this large dependence. In the copolymerization of RPhIMI with ST, however, we reported[5,6] that the radical reactivities can be affected not by the polar but by the resonance character of the nuclear-substituents. That is, in this study, the conjugated system in ARPhIA may become longer owing to the mobile lone electron-pair on the nitrogen atom, as shown in Scheme 3–(i). Consequently, the reaction site in ARPhIA can completely conjugate the nuclear-substituent, R, as well as RPhMI shown in Scheme 3. Thus, the resonance character of the nuclear-substituent, R, may easily affect the reaction site, as described in previous papers[5,6].

Considering that neither ρ nor γ of itaconamates **I**, **II**, and **III** are constant, respectively, the radical reactivity of ARPhIA may depend on the nature of ester group, X, in ARPhIA. In fact, the homopolymerization reactivity of ARPhIA could be affected by the ester group, X, as described in *homopolymerizations of ARPhIA*. However, it is very difficult to determine quantitatively the radical reactivity to the alkyl groups since no ARPhIA monomers of which ester groups are t-butyl, s-butyl, β-chloroethyl,



RPhIMI

Scheme 3

benzyl, and phenyl could be prepared owing to the steric hindrance of its alkyl ester group. When the nature of ester substituents in a series of reaction are determined, we will generally estimate this effect according to the Taft equation (eq 8)[21].

$$\log(1/r_2)=\rho^*\sigma^*+\delta E_S \tag{8}$$

where σ^* is the polar-substituent constant of the alkyl groups, E_S is the steric-substituent constant of the alkyl groups, and ρ^* and δ are constants, giving the susceptibility of a given reaction series caused by polar and steric influences of the substituents, respectively. In our monomers, ARPhIA, the σ^*-substituent constants of four alkyl ester groups were so near that we could not determine the ρ^* and δ values for ARPhIA.

Copolymerizations of ARPhIA with MMA

The results of copolymerizations of ARPhIA (M_1) with MMA (M_2) are shown in Table IV. The copolymerizations were homogeneous throughout. Five types of copolymer-composition curves in the **IIa**–MMA, **IIb**–MMA, **IIc**–MMA, **IIIb**–MMA, and **IIIc**–MMA systems are shown in Figure 3. The composition curves of other copolymers are similar to those indicated in Figure 3. Table IV and Figure 3 indicate that the molar fraction of ARPhIA in the copolymer also tends to increase with an increase in the molar fraction of ARPhIA in the monomer mixture; *i.e.*, the composition curves are similar to those of "an ideal copolymerization type" which is along the azeotropic line.

When the relative reactivities ($1/r_2$) of itaconamate **II** toward the attack by a poly (MMA) radical were plotted against σ-constants in the modified Hammett equation (eq 1), no linear relationship between relative reactivities and σ-constants of the substituents could be observed, as shown in Figure 4–(i).

On transforming eq 1, [$\log(1/r_2)-\gamma E_R$] (where $\gamma=0.5$) was plotted against σ-constants. This plot, shown in Figure 4–(i), clearly indicates that the ρ value is almost zero, with 0.17 standard deviation.

While, in the copolymerizations of itaconamate **III** with MMA, the ρ and γ values were obtained as $\rho=-0.06\pm0.15$, $\gamma=0.4\pm0.15$, as shown in Figure 4–(ii).

Table IV. Results of the radical copolymerizations of ARPhIA (M_1) with MMA (M_2) in THF at 60°C^a.

ARPhIA	M_1 in monomer,	Polymerization time,	Conversion,	N-analysis	M_1 in copolymer
M_1	mol%	hr	%	%	mol%
IIa	20.0	1.7	16.3	1.8	16.3
	40.0	2.0	13.5	2.6	26.7
	50.1	2.2	10.6	3.2	36.5
	60.8	2.2	8.1	3.7	46.5
	80.0	5.0	10.6	4.5	67.7
IIb	19.8	2.5	10.0	2.0	18.3
	39.9	3.5	10.7	3.3	36.0
	49.8	14.0	8.1	3.7	43.4
	59.9	50.0	3.4	4.1	51.1
	80.0	96.0	1.8	4.7	65.5
IIc	20.0	2.0	12.2	2.0	17.3
	38.9	2.0	11.1	3.0	30.5
	49.8	2.0	9.6	3.6	38.7
	62.9	2.0	8.7	4.0	46.6
	79.5	2.0	1.8	4.8	63.7
IId	19.7	4.0	30.7	1.8	16.1
	39.6	4.0	10.7	2.8	30.5
	51.4	12.0	3.6	3.6	45.8
	59.5	24.0	1.4	3.5	43.6
	79.2	72.0	2.5	4.4	64.3
IIe	20.1	6.5	16.1	1.7	16.2
	40.1	6.3	14.7	2.7	31.9
	50.0	4.0	5.7	3.1	39.4
	60.1	6.4	11.9	3.5	51.4
	79.9	10.5	16.1	4.0	69.1
IIIa	20.0	1.5	21.6	2.3	23.2
	40.0	2.2	10.3	3.1	36.5
	50.0	2.3	7.9	3.3	40.5
	60.0	2.7	4.9	3.6	47.3
	80.1	23.0	21.6	4.3	68.1
IIIb	18.4	3.5	28.3	2.1	19.2
	37.7	3.5	17.5	3.4	40.0
	47.7	3.5	8.8	3.8	48.1
	57.7	6.5	9.7	4.4	64.4
	77.6	56.0	2.5	5.2	94.0
IIIc	19.1	3.5	18.6	1.8	15.4
	38.4	3.5	7.8	2.7	27.3
	48.5	6.0	12.1	3.2	35.0
	58.6	6.7	6.7	3.6	40.4
	78.7	24.0	2.1	4.1	50.8

Table IV. Continued.

ARPhIA	M_1 in monomer,	Polymerization time,	Conversion,	N-analysis	M_1 in copolymer
M_1	mol%	hr	%	%	mol%
IIId	20.0	3.0	19.7	1.7	16.0
	39.9	5.0	2.8	2.6	28.3
	50.0	24.0	6.2	3.1	36.0
	60.0	120.0	1.4	3.5	44.8
	80.0	240.0	1.1	4.2	65.5
IIIe	20.0	2.0	9.9	2.0	20.8
	39.9	2.2	2.2	2.8	35.0
	49.9	9.0	9.3	3.1	45.1
	60.1	14.0	4.8	3.4	52.0
	79.9	96.0	3.1	3.9	71.7

[a] [AIBN], 3.0×10^{-2} mol l^{-1}; THF, 5 ml; M_1+M_2, 1.5 g.

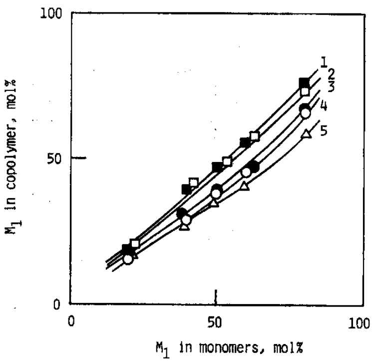


Figure 3. Copolymer-composition curves for the copolymerizations of ARPhIA (M_1) with MMA (M_2) in THF at 60°C: 1 (■), IIIb-MMA; 2 (□), IIb-MMA; 3 (●), IIc-MMA; 4 (○), IIa-MMA; 5 (△), IIIc-MMA.

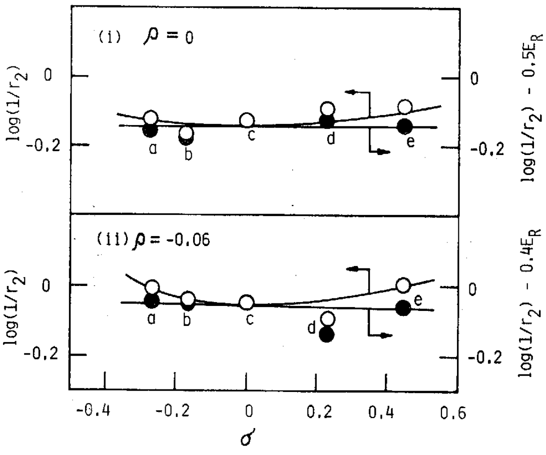


Figure 4. Correlations between the relative reactivities ($1/r_2$) of ARPhIA toward the attack of a poly(MMA) radical and σ-constants of the nuclear-substituents in ARPhIA: (○), II-MMA; (●), III-MMA; a, OCH_3; b, CH_3; c, H; d, Cl; e, $COOC_2H_5$.

These findings tend to strongly suggest that the relative reactivities of ARPhIA toward the attack by a poly (MMA) radical can be slightly affected both by the polar character of the nuclear-substituent, R, and by the resonance character. This fact differs from that of the copolymerizations of ARPhIA with ST. Particularly, the ρ value for the poly (MMA) radical is -0.06–0; *i.e.*, opposite in sign for the polystyryl attacking radical. The reason for this may be understandable from the fact that the poly (MMA) attacking radical has electrophilic nature in contrast to polystyryl attacking radical. On the other hand, the γ value (0.4–0.5) for the poly (MMA) radical is much smaller than that (1.5) for the polystyryl radical. The reason for this cannot be clearly explained. In the case of RPhIMI, however, we reported[6] that the ρ and γ values were obtained as $\rho=-0.5$, $\gamma=0.5$ in the poly (methyl acrylate (MA)); $\rho=0$, $\gamma=2.0$ in the polystyryl radical. Yamada *et al.*[22] also reported that the linear relationship with $\rho=-0.18$ was obtained in the case of the copolymerization of *N*-alkyl maleimide with MMA. In their report, the γ value was not described. But, judging from the modified Hammett equation (eq 1), the γ value seems to be almost zero. Considering that the *Q* value[20] for MMA, MA, and ST are 0.74, 0.6, and 1.0, respectively, these results may be related to the *Q* values for the attacking radical. That is, if the *e* values for the monomers, *e.g.*, unsaturated dibasic acid derivatives, attacked by the radical are positively great, the resonance character (γ value) of the substituent in the monomer may tend to increase with increasing of the *Q* value for the attacking radical. However, since there have been a few data for the unsaturated dibasic acid derivatives so far, we cannot describe a certain conclusion in this paper.

Copolymerizations of ARPhIA with VAc

The results of copolymerizations of **Ib**, **Ic**, or **IIc** (M_1) with VAc (M_2) are shown in Table V. The copolymerizations were homogeneous throughout. The copolymer-composition curves obtained from the above results are shown in Figure 5. Table V and Figure 5 indicate that the resulting copolymer always tends to contain much more ARPhIA than VAc, regardless of the composition of the monomer mixture. This tendency could not be detected in the ARPhIA-ST or ARPhIA-MMA system.

Table V. Results of the radical copolymerizations of ARPhIA (M_1) with VAc (M_2) in THF at 60°C[a].

ARPhIA	M_1 in monomer,	Polymerization time,	Conversion,	N-analysis	M_1 in copolymer
M_1	mol%	hr	%	%	mol%
Ib	20.0	2.0	3.3	5.1	66.8
	39.7	2.0	9.2	5.7	86.3
	49.4	2.0	7.9	5.7	86.3
	60.1	2.0	7.2	5.8	90.2
	79.3	2.0	2.3	5.9	93.4
Ic	22.0	6.0	7.3	5.5	70.1
	42.9	6.0	11.2	5.9	82.0
	53.0	6.0	13.6	5.9	82.0
	62.7	6.0	14.5	6.0	87.2
	80.0	6.0	3.0	6.2	92.8
IIc	20.7	16.0	3.7	5.3	73.6
	40.0	16.0	5.4	5.5	80.9
	50.0	16.0	4.5	5.7	86.7
	59.9	16.0	4.8	5.8	90.6
	79.5	16.0	6.8	5.8	90.6

[a] [AIBN], 3.0×10^{-2} mol l^{-1}; THF, 5 ml; M_1+M_2, 1.5 g.

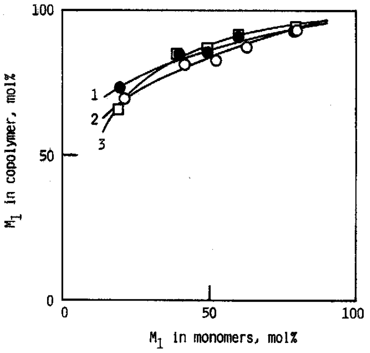


Figure 5. Copolymer-composition curves for the copolymerizations of ARPhIA (M_1) with VAc (M_2) in THF at 60°C: 1 (●), **IIc**–VAc; 2 (○), **Ic**–VAc; 3 (□), **Ib**–VAc.

As can be seen from Table III, all r_1 are always much greater than r_2, and all r_2 are nearly zero. These findings could be explained from the Q_1 values. It has been known[22] that a conjugative monomer ($Q > 0.2$) has high reactivity as a monomer, but low reactivity as its radical. In contrast to this, a non-conjugative monomer ($Q < 0.2$) has low reactivity as a monomer, but high reactivity as its radical. In this study, ARPhIA is a conjugative monomer, as shown in Table III, while VAc is a non-conjugative monomer ($Q_2 = 0.026$)[20]. Accordingly, the fact that the r_1 values are more than 1, and that the r_2 values are less than 1; *i.e.*, the r_2 are rather than zero could be understandable.

Q, e Values for ARPhIA

The Q_1 and e_1 values for ARPhIA are shown in Table III. It was found that the Q values for ARPhIA are between 0.50 and 2.35, and that all the ARPhIA monomers are conjugative monomers. The e values for ARPhIA were found to be between 0.65 and 0.94.

The e values of vinyl monomers are known to be proportional to the Hammett σ-constants of their substituents[23], however, no linear relationship between the e_1 value for ARPhIA and σ-constants was observed. It is possible to expect that the Q_1 values for ARPhIA are correlated with E_R-constants. However, the Q_1 values for ARPhIA were also found to be independent of E_R-constants of the nuclear-substituents. This problem can be attributed to the Q, e-theory described by Alfrey-Price[19]. That is, the hindrance is neglected completely in this theory. When the Q and e values for ARPhIA are determined, the steric hindrance of 1, 1-disubstituted ethylene structure cannot be neglected.

Properties of the Copolymers

The softening points, the reduced viscosities, and the molecular weights of the ARPhIA-ST, the ARPhIA-MMA, and the ARPhIA-VAc copolymers are shown in Table VI. As shown in Table VI, there is no large difference among the ARPhIA

Table VI. Softening points, reduced viscosities, and molecular weights for the ARPhIA copolymers.

Copolymer[a]	Softening point,	η_{sp}/c[b]	Molecular weights ($\times 10^{-3}$)			M_w/M_n
	°C	$dl g^{-1}$	M_n	M_w	M_z	
Ic–ST	199–245	0.29	13.3	17.7	23.4	1.33
Id–ST	203–251	0.14	12.4	19.0	57.5	1.52
IIc–ST	168–209	0.19	16.7	23.4	32.0	1.40
IId–ST	190–234	0.16	21.5	31.5	45.6	1.47
IIIa–ST	182–214	0.17	12.4	16.0	20.2	1.29
IIIb–ST	167–207	0.15	11.0	14.7	18.1	1.33
IIIc–ST	193–244	0.18	15.2	18.9	23.3	1.25
IIId–ST	178–209	0.16	10.7	15.2	40.2	1.42
IIIe–ST	181–222	0.19	12.6	16.2	20.5	1.29
IIIa–MMA	182–211	0.16	12.7	16.1	20.3	1.27
IIIb–MMA	170–211	0.14	16.2	23.0	32.3	1.41
IIIc–MMA	182–219	0.18	14.6	20.7	26.1	1.42
IIId–MMA	169–209	0.21	13.9	19.4	28.8	1.39
IIIe–MMA	171–204	0.19	14.3	18.2	22.3	1.27
Ib–VAc	175–206	0.08	8.2	10.1	12.5	1.48
Ic–VAc	164–209	0.08	7.3	11.6	18.3	1.60
IIc–VAc	178–209	0.10	4.4	5.9	7.2	1.35

[a] Copolymers obtained from ARPhIA (*ca.* 50 mol% in monomers) and ST, MMA, or VAc in Tables II, IV, and V.

[b] c, 0.1 g dl^{-1} in THF at 30°C.

copolymers with respect to the softening points. The reduced viscosities of the ARPhIA-VAc copolymers are found to be less than those of ARPhIA-ST and ARPhIA-MMA copolymers. The similar tendency is also observed in respect to the M_n, M_w, and M_z of ARPhIA copolymers. That is, the M_n is found to be as $10.7 \times 10^3 - 21.5 \times 10^3$ in the ARPhIA-ST copolymers; $13.9 \times 10^3 - 16.2 \times 10^3$ in the ARPhIA-MMA copolymers; $4.4 \times 10^3 - 8.2 \times 10^3$ in the ARPhIA-VAc copolymers. In addition, the degree of polydispersion (M_w/M_n) are present in between 1.25 and 1.60; *i.e.*, the each ARPhIA copolymer is found to be the mono-dispersion system.

All the copolymers were white powders. All the copolymers were soluble in an organic solvent such as THF, dioxane, chloroform, *N*, *N*-dimethylformamide, or dimethyl sulfoxide.

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