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Radical Copolymerizations of *N*-(4-Substituted phenyl)citraconimide with Styrene or Methyl Methacrylate

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ABSTRACT: The radical copolymerizations of *N*-(4-substituted phenyl)citraconimide (RPhCI, R= –H, –OCH_3, –CH_3, –Cl, –$OCOCH_3$, –$COOC_2H_5$) (M_1) with styrene (ST) (M_2) or methyl methacrylate (MMA) (M_2) were carried out at 60°C, using azobisisobutyronitrile as the initiator in tetrahydrofuran. The purpose of this was to clarify the substituent effect on the copolymerizations. The modified Hammett equation, $\log(1/r_2)=\rho\sigma+\gamma E_R$, was applied to these copolymerizations and linear relations were obtained for $\rho=0.18$, $\gamma=0$ in the RPhCI–ST system and $\rho=0$, $\gamma=0.4$ in the RPhCI–MMA system. A non-linear correlation between e_1 values of RPhCI and σ constants of the substituents was found to exist. It was also found that the Q_1 values of RPhCI were independent of the E_R constants of the substituents.

KEY WORDS Copolymerization / *N*-(4-Substituted phenyl)citraconimide / Styrene / Methyl Methacrylate / The Modified Hammett Equation / *e* Value / *Q* Value / *ρ* Value / *γ* Value /

In order to clarify the polymerization reactivities of an unsaturated dibasic acid and its derivatives, the author made an investigation of *N*-substituted maleimide (RMI),[1-4] *N*-(4-substituted phenyl)isomaleimide (RPhIMI),[5-7] and *N*-(4-substituted phenyl)itaconimide (RPhII).[8]

In this paper, *N*-(4-substituted phenyl)citraconimide (RPhCI), an unsaturated dibasic acid derivative, was studied. Various types of *N*-alkylcitraconimide were synthesized and briefly copolymerized by Mehta *et al.*[9] or Paesschen *et al.*[10] However, RPhCI has not yet been synthesized or polymerized.

Six types of RPhCI; *i.e.*,
N-phenylcitraconimide (PhCI), *N*-(4-methoxyphenyl)citraconimide (MOPhCI), *N*-(4-methylphenyl)citraconimide (MPhCI), *N*-(4-chlorophenyl)citraconimide (ClPhCI), *N*-(4-acetoxyphenyl)citraconimide (AOPhCI), and *N*-(4-ethoxycarbonylphenyl)citraconimide (ECPhCI) were synthesized and their homopolymerization reactivities were investigated. In addition, the copolymerizations of RPhCI (M_1) with styrene (ST) (M_2) or methyl methacrylate (MMA) (M_2) were carried out, and the monomer-reactivity ratios (r_1, r_2) and Q_1, e_1 values for RPhCI were calculated. Furthermore, in order to clarify the substituent effect on the copolymerizations, the modified Hammett equation (eq 1)[11] was applied to these copolymerizations, and the results are discussed.

$$\log(1/r_2)=\rho\sigma+\gamma E_R \tag{1}$$

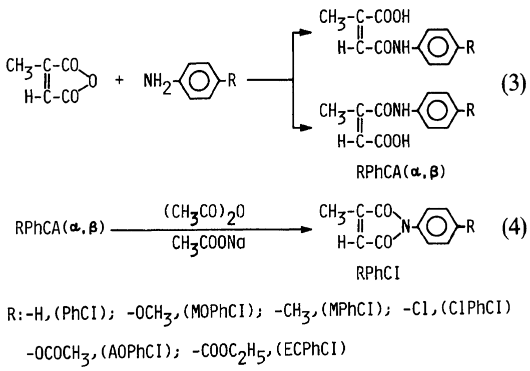
where ρ is the polar-reaction constant, σ is the polar-substituent constant, γ is the resonance-reaction constant, and E_R is the resonance-substituent constant. In a reaction in which the resonance effect brought on by the substituents is not important, *i.e.*, when $\gamma=0$, eq 1 comes to be equal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

$$\log(1/r_2)=\rho\sigma \tag{2}$$

EXPERIMENTAL

Syntheses of Monomers

The six types of RPhCI were synthesized according to following processes (3) and (4) in Scheme 1, and by a method similar to that described by Mehta *et al.*[9]



Scheme 1.

N-(4-Substituted phenyl)citraconamic acids (RPhCA), (α, β isomers). A solution of 0.2 mol of the first aryl amine in 200 ml of anhydrous ethyl ether was added dropwise over 0.5 hour to a well-stirred solution of 0.2 mol of citraconic anhydride[13] (CAn) in 300 ml of anhydrous ethyl ether at 0—5°C. A precipitate of RPhCA was formed immediately on addition of the amine. The reaction mixture was stirred for 1 hour longer. The precipitate was collected and washed with ether. About an 80% yield of a crude mixture of RPhCA isomers was obtained.

RPhCI. A mixture of 0.1 mol of the mixture of isomeric RPhCA, 6 g of anhydrous sodium acetate, and 100 ml of acetic anhydride was heated with stirring until the internal temperature reached 90—95°C. Heating and stirring were continued for 2—3 hours. This reaction was mildly exothermal. After cooling, the reaction mixture was poured into ice water and stirred for 4 hours. Free acid was neutralized with sodium carbonate and the product was extracted with ether. After washing with sodium bicarbonate and drying over potassium carbonate, evaporation of the ether layer gave the RPhCI. The product was recrystallized twice from methanol.

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

Materials

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

Copolymerization Procedure

All copolymerizations of RPhCI (M_1) with ST (M_2) or MMA (M_2) were carried out in THF in a sealed glass tube in the presence of AIBN (3.0×10^{-2} mol l^{-1}) at 60°C. After the solution of monomers, containing the required amount of AIBN, was charged into the polymerization tube, it was degassed under vacuum by ordinary freezing and thawing techniques. Nitrogen was introduced into the tube by the usual method; the tube was then sealed off. Copolymerizations were performed on shaking the tube in a thermostat maintained at 60°C. Following copolymerization for a given period of time, (the conversion was lower than about 10%), the tube was opened, and its contents were poured into a large amount of methanol to precipitate the copolymer. The resulting copolymer was purified by reprecipitating from the THF

Table I. Melting points, yields, and elemental analyses of RPhCI

Monomer	mp	Yield[a]	H/%		C/%		N/%	
	°C	%	Calcd	Found	Calcd	Found	Calcd	Found
PhCI	94—96	20	4.84	4.80	70.53	70.85	7.47	7.43
MOPhCI	125—126	25	5.10	5.04	66.35	66.37	6.45	6.27
MPhCI	111—112	21	5.50	5.47	71.62	71.48	6.96	6.90
ClPhCI	115—116	15	3.63	3.46	59.60	59.60	6.31	6.30
AOPhCI	134—135	20	4.52	4.34	63.67	63.60	5.71	5.47
ECPhCI	76—77	41	5.05	5.02	64.85	64.95	5.40	5.36

[a] Based on *N*-(4-substituted phenyl)citraconamic acids.

solution into a large amount of methanol. The precipitate was filtered, thoroughly washed with methanol, and dried under reduced pressure to obtain the polymer.

The composition of the resulting copolymers was determined by nitrogen analysis.

Viscosity Measurements

The reduced viscosity of the copolymer was measured in THF at 30°C, using an Ostwald viscometer.

Softening-Point Measurements

The softening points were measured with a Mitamura Riken Kogyo MEL-TEMP by the standard melting point method.[21]

RESULTS AND DISCUSSION

First, the radical homopolymerizations of RPhCI were carried out in THF in the presence of AIBN (3.0×10^{-2} mol l^{-1}) at 60°C. However, no homopolymers could be obtained. It has been

Table II. Radical copolymerizations of RPhCI (M_1) with ST (M_2) in THF at 60°C

Monomer[a] M_1	M_1 mol% in monomer	Time	Conversion	N-analysis	M_1 mol% in copolymer
		min	%	%	
PhCI	19.8	60	5.0	3.86	37.2
	39.8	80	6.8	4.34	43.5
	49.8	100	7.5	4.55	46.3
	59.5	120	8.2	4.59	46.9
	80.2	120	5.4	4.76	49.3
MOPhCI	20.1	30	4.7	3.35	34.1
	40.2	30	6.4	3.40	34.8
	49.1	40	7.1	3.75	40.0
	59.5	50	8.0	3.80	40.7
	79.4	60	8.1	4.45	51.6
MPhCI	19.9	30	3.6	3.49	34.2
	40.4	30	4.9	3.75	37.7
	50.1	30	5.0	3.86	39.2
	59.9	45	6.9	4.30	45.5
	78.2	45	7.4	4.68	51.5
ClPhCI	19.6	30	6.3	3.56	34.2
	39.6	30	9.8	4.10	46.4
	50.1	25	6.3	4.17	47.7
	59.2	35	8.6	4.39	51.6
	79.8	45	8.8	4.49	53.5
AOPhCI	20.2	30	4.7	3.34	37.4
	39.6	30	5.7	3.82	46.0
	48.6	30	6.5	3.91	47.8
	59.4	30	7.2	3.80	45.6
	79.7	30	7.4	4.14	52.6
ECPhCI	20.5	30	6.4	3.29	38.4
	39.9	30	7.8	3.66	45.7
	49.9	35	8.9	3.69	46.3
	59.3	35	8.7	3.73	47.1
	75.1	45	7.5	3.86	50.0

[a] [AIBN], 3.0×10^{-2} mol l^{-1}; THF, 5 ml; $M_1+M_2=2.0$ g.

reported that RMI can be homopolymerized under the same conditions.[1-4] Consequently, the fact that the homopolymerizations of RPhCI did not occur can be understood as due to the steric hindrance of α-methyl groups in RPhCI.

Copolymerizations of RPhCI with ST

RPhCI (M_1) was copolymerized with ST (M_2) at 60°C, using AIBN as the initiator. These copolymerizations were homogeneous throughout. The results of the copolymerizations are summarized in Table II. The copolymer composition curves obtained from the above results are shown in Figure 1. From Table II and Figure 1, it is observed that the rates of copolymerizations in *ca.* 50 mol% of RPhCI in a monomer mixture are greatest for most of the systems. In addition, from Figure 1, it is obvious that all the copolymerizations of RPhCI with ST are virtually alternating-type processes, as is the case for those of ST with maleic anhydride or RMI. This may be attributed to the charge-transfer complex of RPhCI and ST.

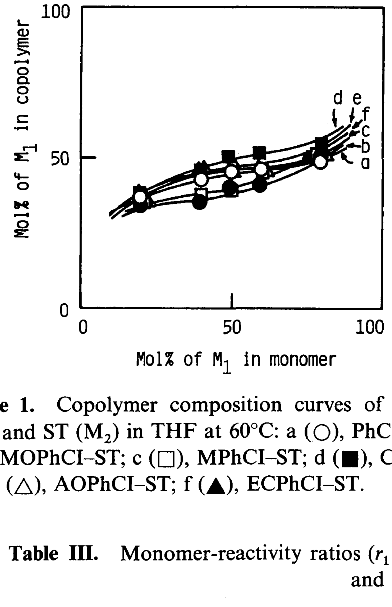


Figure 1. Copolymer composition curves of RPhCI (M_1) and ST (M_2) in THF at 60°C: a (○), PhCI–ST; b (●), MOPhCI–ST; c (□), MPhCI–ST; d (■), ClPhCI–ST; e (△), AOPhCI–ST; f (▲), ECPhCI–ST.

In the copolymerizations of ST with maleic anhydride, the solution became colored when the monomers were mixed, and the formation of the charge-transfer complex was identified by UV spectra.[20] However, in this study, such phenomena were not observed. Yamada *et al.*[18] reported that in the case of RMI also, no such observation could be made.

In the case of the formation of the charge-transfer complex, generally, it is known[10,18] that e values are approximately equal, on the contrary, Q values are abnormally great in comparison with Q and e values calculated from the copolymerizations with another comonomer instead of ST.

But in this study, it seems that the Q_1 values for RPhCI are great, but not abnormally so. In conclusion, this alternating-copolymerization reactivity may be attributable to the charage-transfer complex of ST and RPhCI; however, this cannot be confirmed experimentally.

Based on the results of Table II, the monomer-reactivity ratios (r_1 and r_2) were determined according to either the method described by

Table III. Monomer-reactivity ratios (r_1, r_2) for the RPhCI (M_1) and ST (M_2) or MMA (M_2) system, and Q_1, e_1 values for RPhCI

Monomer M_1	Monomer-reactivity ratios						Q_1^a	e_1^a	σ	E_R
	M_2=ST			M_2=MMA						
	r_1	r_2	$1/r_2$	r_1	r_2	$1/r_2$				
PhCI	0.004 ± 0.05	0.18 ± 0.04	5.60	0.012 ± 0.04	2.99 ± 0.05	0.33	0.54(0.51)[b]	2.3(2.2)[b]	0.00	0.00
MOPhCI	0.0 ± 0.04	0.21 ± 0.04	4.76	0.0 ± 0.03	2.69 ± 0.04	0.37	0.52[c]	2.0[c]	−0.27	0.11
MPhCI	0.0 ± 0.04	0.22 ± 0.04	4.55	0.0 ± 0.03	2.43 ± 0.04	0.41	0.55[c]	1.9[c]	−0.17	0.03
ClPhCI	0.09 ± 0.07	0.17 ± 0.05	5.88	0.0 ± 0.04	2.89 ± 0.06	0.35	1.18	1.2	0.23	0.10
AOPhCI	0.047 ± 0.05	0.17 ± 0.04	5.88	0.16 ± 0.04	1.79 ± 0.05	0.56	1.05(0.62)[b]	1.4(1.5)[b]	0.31	—
ECPhCI	0.014 ± 0.04	0.16 ± 0.04	6.25	0.0 ± 0.04	2.50 ± 0.04	0.40	0.87	1.7	0.45	0.16

[a] Calculated by assuming that Q_2 and e_2 values of ST were 1.0 and −0.8, respectively; with an error of ±0.12.

[b] Calculated by assuming that Q_2 and e_2 values of MMA were 0.74 and 0.4, respectively; with an error of ±0.08.

[c] Calculated from the method described by Nishiwaki *et al.*[17]; with an error of ±0.12.

Fineman and Ross[14] or that by Mayo and Lewis.[15] The Q_1 and e_1 values for RPhCI were then calculated, assuming that $Q_2=1.0$, $e_2=-0.8$ for ST. These results are shown in Table III, along with the σ constants of the substituents in the Hammett equation (eq 2) and E_R constants of the substituents in the modified Hammett equation (eq 1). From Table II, it is clear that a difference of 1% in the nitrogen analysis of the copolymer corresponds to about 15% of the composition in the copolymer. Accordingly, if the error from nitrogen analysis is about 0.3%, the results, *i.e.*, r_1, r_2, Q_1, e_1 values, and ρ, γ values to be mentioned later, may contain considerably more error, as indicated in Table III. As can be seen from Table III, the relative reactivities, $1/r_2$, of RPhCI toward an attack by polystyryl radicals increase with an increase in the electron-withdrawing nature of their substitutents.

When the relative reactivities, $1/r_2$, of RPhCI toward an attack by polystyryl radicals were plotted by the modified Hammett equation (eq 1), a linear relationship which, having $\rho=0.18$ with 0.13 standard deviation, was obtained, as shown in Figure 2. The fact that the ρ value in this reaction is positive can be understood as resulting from the nucleophilic nature of the polystyryl attacking radical. However, no linear relationship between relative reactivities and E_R constants in RPhCI was observed.

On transforming the modified Hammett equation (eq 1), $\log(1/r_2)-\rho\sigma$ (where $\rho=0.18$) was plotted with E_R constants. This plot, shown in Figure 3, clearly indicates that the γ value is nearly zero, *i.e.*, the relative reactivities of RPhCI do not correlate with the E_R constants of the substituents. The formula which has 0 of γ in the modified Hammett equation (eq 1) gives exactly the same values as the ordinary Hammett equation (eq 2). This suggests that perhaps the radical reactivities of RPhCI depend on the polar character, but not on the resonance character of the substituents.

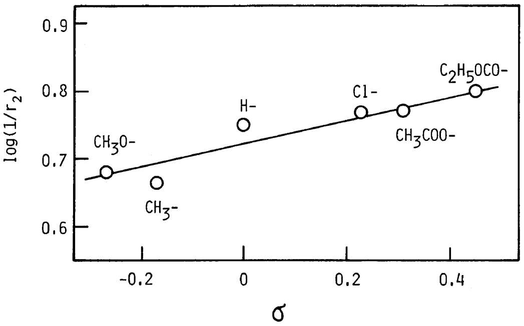


Figure 2. The correlation between the relative reactivities of RPhCI ($1/r_2$) toward attack of a polystyryl radical and σ constants of the substituents in RPhCI.

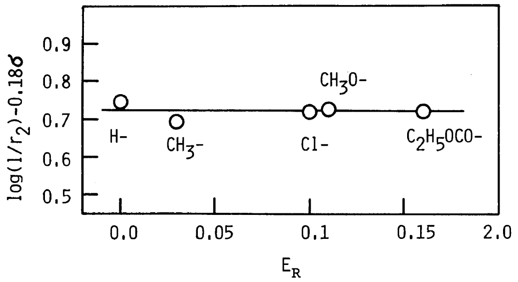


Figure 3. The correlation between $\log(1/r_2)-\rho\sigma$ and E_R constants of the substituents in RPhCI.

Copolymerizations of RPhCI with MMA

The results of the radical copolymerizations of RPhCI (M_1) with MMA (M_2) are shown in Table IV. The copolymerizations were homogeneous throughout. The copolymer composition curves obtained from the above results are shown in Figure 4. Table IV and Figure 4 indicate that the molar fraction of RPhCI in the copolymer also tends to increase with an increase in the molar fraction of RPhCI in the monomer mixture. However, it was found that the rates of the copolymerizations with MMA are smaller than those of ST. A possible reason for this may be that since the electron density of the double bond of reaction site in RPhCI is $\delta+$, *i.e.*, the e values for RPhCI are positively great as shown in Table III, ST which is more nucleophilic in nature than MMA may be able to easily attack the double bond in RPhCI.

In the case of the RPhCI and ST system, r_1 and r_2 were very small because of alternating copolymerization. Accordingly, it seems that the Q_1 and e_1 values for RPhCI contain considerable error. Since r_1 and r_2 were not zero only in the RPhCI–MMA and AOPhCI–MMA systems, the Q_1 and e_1 values could be determined as $Q_1=0.51$, $e_1=2.2$ for RPhCI; $Q_1=0.62$, $e_1=1.5$ for AOPhCI. When compared with the Q_1 and e_1 values calculated from the copolymerizations with ST, both e_1 values are nearly equal, on the contrary, the Q_1 value for AOPhCI was remarkably different. That is, with

Table IV. Radical copolymerizations of RPhCI (M_1) with MMA (M_2) in THF at 60°C

Monomer[a] M_1	M_1 mol% in monomer	Time	Conversion	N-analysis	M_1 mol% in copolymer
		min	%	%	
PhCI	20.9	60	8.8	0.99	7.5
	40.5	60	6.7	1.98	16.1
	50.3	75	5.2	2.44	20.6
	58.9	90	4.8	2.79	24.1
	78.7	90	1.8	3.83	35.9
MOPhCI	20.1	60	9.0	0.95	7.4
	39.8	60	4.6	1.05	8.2
	49.5	70	6.7	1.90	16.1
	60.2	90	9.1	2.50	22.6
	79.9	90	4.0	3.00	28.6
MPhCI	18.8	45	6.9	1.01	7.8
	40.5	45	5.1	1.95	16.2
	49.4	75	6.9	2.39	20.6
	60.3	75	5.0	2.92	26.4
	81.7	90	2.1	4.12	41.9
ClPhCI	19.5	30	4.5	0.98	7.7
	40.3	30	3.2	1.78	15.0
	50.1	60	2.6	2.26	20.1
	60.7	60	1.8	2.44	22.1
	80.3	90	2.9	4.00	43.9
AOPhCI	19.2	50	8.4	1.32	10.9
	39.9	60	9.8	2.34	22.1
	49.9	60	9.2	2.85	28.9
	59.9	90	7.4	3.51	39.4
	77.5	90	6.2	4.11	51.2
ECPhCI	19.9	20	3.5	1.01	8.2
	40.3	30	4.0	1.78	15.9
	47.4	60	6.8	2.09	19.6
	59.2	70	5.3	2.50	25.0
	79.5	80	3.2	3.30	37.7

[a] [AIBN], 3.0×10^{-2} mol l^{-1}; THF, 5 ml; $M_1+M_2=2.0$ g.

respect to at least the Q value, it may be considered that there is considerable error. However, these Q_1 values calculated from the copolymerizations with ST do not seem to be abnormally large in comparison with those for RMI,[1-4] RPhIMI.[5-7]

From Table III, it is clear that r_1 was zero in the case of the MOPhCI and ST or MMA system, and also in the case of the MPhCI and ST or MMA system. Thus, in these cases, the Q_1 and e_1 values were calculated by the method described by Nishiwaki *et al.*[17]

When the relative reactivities of RPhCI toward attack by a poly(methyl methacrylate) radical were plotted using the σ constants of the substituents 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 5.

On transforming eq 1, $\log(1/r_2)-\gamma E_R$ (where $\gamma=0.4$) was plotted with σ-constants. This plot, shown in Figure 5, clearly indicates that the ρ value is almost zero, with 0.06 standard deviation, *i.e.*, the

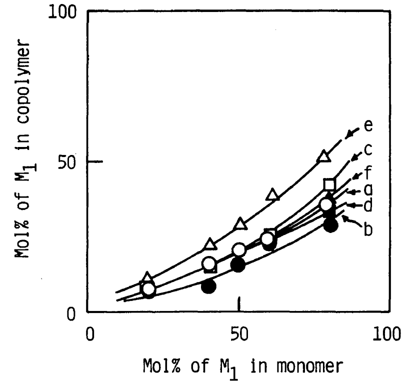


Figure 4. Copolymer composition curves of RPhCI (M_1) and MMA (M_2) in THF at 60°C: a (○), PhCI–MMA; b (●), MOPhCI–MMA; c (□), MPhCI–MMA; d (■), ClPhCI–MMA; e (△), AOPhCI–MMA; f (▲), ECPhCI–MMA.

relative reactivities of RPhCI do not correlate with the σ constants of the substituents. This suggests that the radical reactivities of RPhCI depend possibly on the resonance character, but not on the polar character of the substituents.

This finding differs from that of the copolymerizations of RPhCI with ST because of the difference of the e_2 value rather than the Q_2 value for the comonomer. That is, there is no large difference between ST ($Q_2=1.0$) and MMA ($Q_2=0.74$) with respect to the Q_2 values. On the other hand, the e_2 value for ST ($e_2=-0.8$) is different from that of MMA ($e_2=0.4$). Consequently, copolymerizations with ST may be affected by the polar character of substituents, while the resonance character may be important in the case of copolymerizations with MMA.

It is interesting to note that the substituents may slightly affect the double bond of the reaction site in RPhCI. These phenomena are not characteristic of RPhCI, and can be detected in imides containing the five-membered ring.[2-8,18,19] This may be due to the mobile lone electron-pair of the nitrogen atom in RPhCI, as described in previous papers.[2-4,8] The conjugated system in RPhCI may become longer owing to the mobile lone electron-pair on the nitrogen atom, as can be understood from the resonance structure as follows.

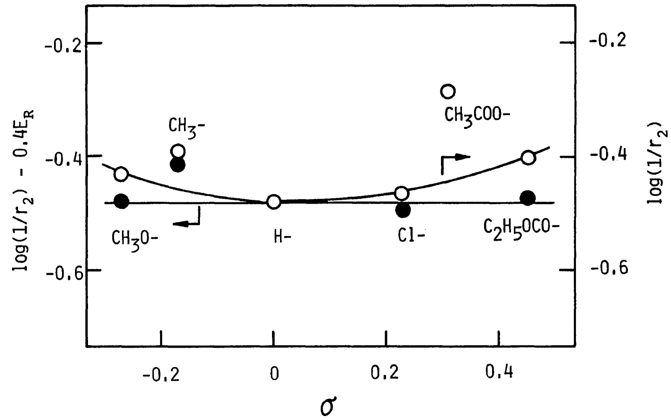
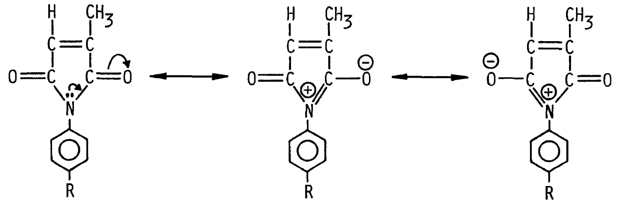


Figure 5. The correlation between the relative reactivities of RPhCI ($1/r_2$) toward attack of a poly(MMA) radical and σ constants of the substituents in RPhCI.



Scheme 2.

Table V. Softening points and reduced viscosities of copolymers for the RPhCI (M_1)–ST or MMA (M_2) systems

Copolymer[a] M_1	Softening points/°C		η_{sp}/c^b/dl g^{-1}	
	M_2=ST	M_2=MMA	M_2=ST	M_2=MMA
PhCI	182—238	156—208	0.20	0.13
MOPhCI	213—246	141—176	0.18	0.12
MPhCI	212—249	158—192	0.16	0.11
ClPhCI	225—278	155—188	0.29	0.10
AOPhCI	228—276	171—223	0.16	0.12
ECPhCI	188—249	160—211	0.21	0.13

[a] Copolymers obtained from RPhCI (*ca.* 50 mol% in monomers) and ST or MMA in Tables II and IV.
[b] *c*, 0.1 g dl^{-1} in THF at 30°C.

The *e* values of vinyl monomers are known to be proportional to the Hammett σ constants of their substituents[16]; however, no linear relationship between the e_1 value for RPhCI and σ constants was observed.

It has been reported that the *Q* values of monomers are proportional to the E_R constants in the modified Hammett equation (eq 1).[5,6] But, it was found that the Q_1 values for RPhCI are also independent of E_R constants of the substituents.

Properties of the Copolymers

The reduced viscosities and the softening points of the RPhCI–ST or the RPhCI–MMA copolymers are shown in Table V. As can be seen from Table V, the reduced viscosities of the RPhCI–ST copolymers are generally higher than those of the RPhCI–MMA copolymers. The softening points of the RPhCI–ST copolymers are also higher than those of the RPhCI–MMA copolymers. In addition, softening points of the copolymers are generally higher than those of ordinary vinyl polymers. It has been reported that the softening points of RMI are high because of the polarization of the carbonyl groups.[1–4,8] The copolymers obtained by the author also showed high softening points.

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

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