

Reactivities of *N*-Alkylcitraconimides in the Radical Copolymerizations with Styrene or Methyl Methacrylate

Tsutomu OISHI

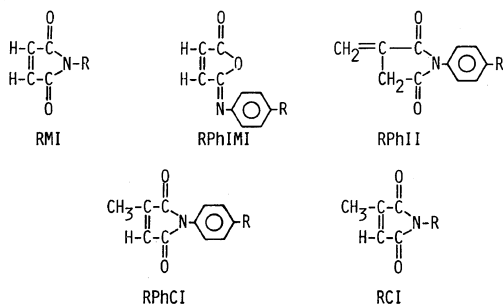
Department of Industrial Chemistry, Technical College,
Yamaguchi University, Tokiwadai, Ube 755, Japan.

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ABSTRACT: The radical copolymerizations of *N*-alkylcitraconimide (RCI: R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇, *n*-C₄H₉, *i*-C₄H₉, *t*-C₄H₉, *n*-C₆H₁₃, C₆H₅CH₂) (M₁) with styrene (ST) (M₂) or methyl methacrylate (MMA) (M₂) were carried out at 60°C, using azobisisobutyronitrile as the initiator in tetrahydrofuran in order to clarify the substituent effect on the copolymerizations. From the results obtained, the monomer reactivity ratios and the Q_1 and e_1 values were determined. It was found that the relative reactivities ($1/r_2$) of RCI toward attack of a polystyryl radical could be correlated only by the polar-substituent constant (σ^*) of the alkyl group in RCI, not by the steric-substituent constant (E_s) in Taft's equation: $\log (1/r_2) = \rho^* \sigma^* + \delta E_s$. According to the above equation, the ρ^* and δ values were obtained as 0.34 and 0, respectively, in the RCI-ST system. On the other hand, in the RCI-MMA system, both the ρ^* and δ values were 0; that is, neither the polar nor the steric character of alkyl group in RCI contributed to the relative reactivities ($1/r_2$) of the RCI toward attack of a poly(MMA) radical. It was also observed that both the Q_1 and e_1 values for RCI were independent of Taft's σ^* -substituent constant.

KEY WORDS Copolymerization / *N*-Alkylcitraconimide / Styrene / Methyl Methacrylate / Monomer-Reactivity Ratio / Q , e Value / Taft Equation /

In order to clarify the polymerization properties of unsaturated dibasic acid and its derivatives, we investigated *N*-substituted maleimide (RMI),¹⁻⁴ *N*-(4-substituted phenyl)isomaleimide (RPhIMI),⁵⁻⁷ and *N*-(4-substituted phenyl)itaconimide (RPhII).⁸



Scheme 1.

In a previous paper,⁹ it has been reported that the relative reactivities ($1/r_2$) of *N*-(4-substituted phenyl)citraconimide (RPhCI) toward an attack from a polystyryl radical were correlated only by the

polar-substituent constant (σ) of the alkyl group in the Yamamoto and Otsu equation 1¹⁰:

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

where E_R is the resonance-substituent constant, and ρ and γ are reaction constants. It was observed that the relative reactivities ($1/r_2$) of RPhCI toward an attack by a poly(methyl methacrylate) (MMA) radical were correlated only by the resonance-substituent constant (E_R). According to eq 1, it was found that linear relations were obtained for $\rho = 0.18$, $\gamma = 0$ in the RPhCI-styrene (ST) system and $\rho = 0$, $\gamma = 0.4$ in the RPhCI-MMA system.

As a continuation of the previous study, the author investigated the relative reactivities ($1/r_2$) of *N*-alkylcitraconimide (RCI) toward an attack of a polystyryl radical or a poly(MMA) radical, according to Taft's equation 2¹¹:

$$\log (1/r_2) = \rho^* \sigma^* + \delta E_s \quad (2)$$

where σ^* is the polar-substituent constant of the alkyl groups relative to methyl group, E_s is the

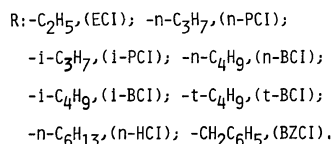
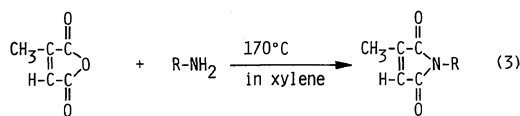
steric-substituent constant of the alkyl groups, and ρ^* and δ are constants giving the susceptibility of a given reaction series caused by polar and steric influences of the substituents, respectively.

Certain types of RCI have been synthesized and briefly copolymerized by Mehta *et al.*¹² or Paesschen *et al.*¹³ However, no attempt to investigate the correlation between the structure and the reactivities of RCI in radical copolymerizations has been made so far. RCI used in this study are as follows: *N*-ethylcitraconimide (ECI), *N*-*n*-propylcitraconimide (*n*-PCI), *N*-isopropylcitraconimide (*i*-PCI), *N*-*n*-butylcitraconimide (*n*-BCI), *N*-isobutylcitraconimide (*i*-BCI), *N*-*t*-butylcitraconimide (*t*-BCI), *N*-*n*-hexylcitraconimide (*n*-HCI), and *N*-benzylcitraconimide (BzCI). The copolymerization parameters for *N*-methylcitraconimide (MCI) obtained by Paesschen *et al.*¹³ and those for *N*-phenylcitraconimide (PhCI) obtained by the author in the previous paper⁹ were also used.

EXPERIMENTAL

Syntheses of Monomers

Eight types of RCI were synthesized following process (3), according to a method similar to the one described by Coleman *et al.*¹⁴



Scheme 2.

RCI. Citraconic anhydride¹⁵ and xylene were mixed at 80°C and the first alkylamine was added at 80–90°C. Equimolar amounts were used. A mixture was refluxed at 170°C for 24 hours, and then xylene was distilled off. The residue was distilled under reduced pressure to obtain the crude product. The crude RCI were then redistilled under reduced pressure.

RCI were identified on the basis of the results of elemental analyses, infrared (IR) spectra, and

nuclear magnetic resonance (NMR) spectra. Table I gives the yields and the results of the elemental analyses of the RCI monomers.

Materials

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 and MMA monomers were purified by the usual methods just before use.

Copolymerization Procedure

All copolymerizations of RCI (M₁) with ST (M₂) or MMA (M₂) were carried out in THF in sealed glass tubes 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, the tube was degassed under vacuum by the ordinary freezing and thawing technique. Nitrogen was introduced in the tube by the usual method, and then the tube was sealed off. Copolymerizations were performed on shaking the tube in a thermostat maintained at 60°C. After copolymerization for a given period of time, allowing a conversion lower than about 10%, the tube was opened, and its contents poured into a large amount of methanol to precipitate the copolymers. The resulting copolymer was purified by reprecipitating it from the THF solution into a large amount of methanol. The precipitate was filtered, thoroughly washed with methanol, and dried under reduced pressure to obtain the copolymer.

The composition of the resulting copolymer was calculated from nitrogen contents observed by elemental analysis.

RESULTS AND DISCUSSION

The radical homopolymerizations of RCI were carried out in THF in the presence of AIBN (3.0 × 10⁻² mol l⁻¹) at 60°C for 50 hours. However, no homopolymers could be obtained. It has been reported¹⁻⁴ that RMI can be homopolymerized under the same conditions. Accordingly, the fact that no homopolymerizations of RCI occurred can be understood as due to the steric hindrance of α -methyl groups in RCI. This can be seen in the case

Table I. Boiling points, yields, and elemental analyses of RCI

Monomer	bp	Yield %	C/%		H/%		N/%	
	°C (mmHg)		Calcd	Found	Calcd	Found	Calcd	Found
ECI	97—98 (21)	20	60.42	60.75	6.52	6.40	9.80	10.07
<i>n</i> -PCI	113—114 (37)	37	62.73	62.14	7.24	7.55	9.14	9.11
<i>i</i> -PCI	107—109 (59)	59	62.73	62.58	7.24	7.19	9.14	9.31
<i>n</i> -BCI	124—126 (22)	65	64.65	64.59	7.84	7.90	8.38	8.39
<i>i</i> -BCI	120—121 (29)	57	64.65	64.55	7.84	8.00	8.38	8.50
<i>t</i> -BCI	112—113 (32)	25	64.65	64.24	7.84	7.68	8.38	8.54
<i>n</i> -HCI	159—160 (23)	79	67.66	67.82	8.78	8.75	7.25	7.33
BzCI	187—188 (64)	64	71.63	71.52	5.51	5.49	6.96	7.20

of RPhCI.

Copolymerizations of RCI with ST

RCI (M_1) were copolymerized with ST (M_2) at 60°C by using AIBN as the initiator. The copolymerizations were homogeneous throughout. The results of the copolymerizations are summarized in Table II. Four types of copolymer-composition curves in the ECI-ST, *n*-PCI-ST, *t*-BCI-ST, and BzCI-ST systems are shown in Figure 1. The composition curves in the *i*-PCI-ST, *n*-BCI-ST, *i*-BCI-ST, and *n*-HCI-ST systems are similar to those indicated in Figure 1. From Table II, it can be observed that the rate of copolymerization of *i*-PCI with ST increases with an increase in the concentration of *i*-PCI in the monomer mixture, but that the rate of *n*-BCI decreases. In addition, it was found that in the ECI, *n*-PCI, *i*-BCI, *t*-BCI, *n*-HCI, or BzCI and St systems, the rates showed no constant tendencies.

These various tendencies may be attributed to the formation of the charge-transfer complex of RCI and ST. Figure 1 indicates that nearly all copolymerizations of RCI with ST were of the alternating-type processes, as well as those of ST with maleic anhydride, RMI, or RPhCI. This may be also attributed to the charge-transfer complex of RCI and ST.

In the case of the copolymerization of ST with maleic anhydride, coloration of the solution could be observed when the monomers were mixed, and the formation of the charge-transfer complex was identified by ultraviolet (UV) spectra.²² In this study, these phenomena could not be observed, and neither in RPhCI.⁹ Yamada *et al.*¹⁷ reported that no such observations could be made in the case of RMI

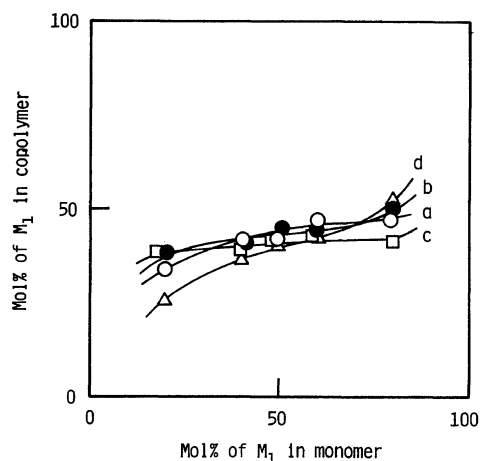


Figure 1. Copolymer-composition curves of RCI (M_1) and ST (M_2) in THF at 60°C: a (○), ECI-ST; b (●), *n*-PCI-ST; c (□), BzCI-ST; d (△), *t*-BCI-ST.

either.

In the formation of the charge-transfer complex, it is known^{13,17} that e values generally are relatively equal; however, Q values are abnormally large in comparison to the Q and e values calculated from the results of the copolymerizations with another comonomer instead of ST. In this study, however, it seems that the Q_1 values of RCI are not abnormally large, and this will be discussed in detail later. The alternating copolymerization may be attributable to the charge-transfer complex of ST and RCI. However, no confirmation of this could be made by the experiments. Based on the results of Table II, the monomer-reactivity ratios (r_1 and r_2) were determined according to the method described by Fineman and Ross,¹⁶ and Alfrey-Price²⁰ Q_1 and e_1

Table II. Radical copolymerizations of RCI (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	%	%	
ECI	20.2	30	2.9	4.10	33.9
	40.2	30	2.5	5.00	42.5
	49.6	60	8.3	5.00	42.5
	60.1	60	9.1	5.50	47.4
	79.8	90	9.2	5.50	47.4
<i>n</i> -PCI	20.7	30	2.9	4.40	38.7
	41.1	30	3.6	4.70	41.8
	51.0	45	5.6	5.00	45.1
	60.1	50	6.3	5.00	45.1
	80.1	55	5.6	5.50	50.7
<i>i</i> -PCI	20.0	120	8.0	3.92	33.9
	40.0	120	8.8	4.52	41.7
	50.3	120	8.5	4.72	42.1
	58.5	120	9.7	4.96	44.6
	80.0	120	9.8	5.31	48.5
<i>n</i> -BCI	19.4	60	8.1	4.14	37.8
	40.1	60	7.7	4.73	44.7
	50.0	60	7.1	4.83	45.9
	60.2	60	6.9	5.01	48.1
	80.1	60	5.5	5.45	53.7
<i>i</i> -BCI	19.7	30	3.3	3.64	32.4
	40.0	40	2.6	4.15	37.9
	49.9	45	5.9	4.70	44.3
	59.7	50	2.6	5.15	49.8
	79.8	60	5.2	5.50	54.3
<i>t</i> -BCI	19.7	30	1.2	3.00	25.8
	39.1	30	1.6	4.15	37.9
	50.4	45	2.1	4.50	41.9
	60.7	60	3.4	4.65	43.7
	79.8	120	3.7	5.40	53.0
<i>n</i> -HCl	20.2	60	5.4	3.35	31.9
	40.8	60	6.1	3.92	39.2
	49.7	60	5.0	4.19	42.8
	60.0	60	5.9	4.04	40.8
	80.0	60	4.9	4.64	49.4
BzCI	18.3	60	5.7	3.38	38.1
	40.0	60	7.8	3.91	39.9
	80.1	60	6.5	3.96	42.6
	59.2	60	7.6	4.16	43.5
	80.1	60	5.8	4.05	41.9

^a [AIBN], 3.0×10^{-2} mol l⁻¹; THF, 2 ml.

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

Monomer	Monomer-reactivity ratios						Q_1	e_1	σ^*	E_s
	$M_2 = \text{ST}$		$M_2 = \text{MMA}$		$1/r_2$					
M_1	r_1	r_2	r_1	r_2	r_1	r_2				
MCI ^a	0.24	0.14	0.15	3.24	0.31	0.31	0.95	1.05	0.00	0.00
ECl	0.0 ± 0.05	0.24 ± 0.05	0.0 ± 0.04	2.56 ± 0.04	0.39	0.39	0.51 ^b	1.83 ^b	-0.100	-0.07
<i>n</i> -PCI	0.02 ± 0.04	0.27 ± 0.04	0.0 ± 0.04	2.60 ± 0.05	0.38	0.38	0.61	1.46	-0.115	-0.36
<i>i</i> -PCI	0.003 ± 0.05	0.031 ± 0.04	0.21 ± 0.04	2.91 ± 0.04	0.34	0.34	0.39	1.85	-0.170	-0.42
<i>n</i> -BCI	0.05 ± 0.05	0.21 ± 0.06	0.04 ± 0.04	2.68 ± 0.05	0.37	0.37	0.88	1.32	-0.130	-0.39
<i>i</i> -BCI	0.07 ± 0.06	0.32 ± 0.06	0.0 ± 0.04	2.53 ± 0.06	0.40	0.40	0.66	1.14	-0.125	-0.93
<i>t</i> -BCI	0.0 ± 0.04	0.46 ± 0.04	0.06 ± 0.04	2.83 ± 0.05	0.35	0.35	0.44 ^c	1.73 ^c	-0.300	-1.54
<i>n</i> -HCl	0.02 ± 0.03	0.43 ± 0.04	0.0 ± 0.04	2.21 ± 0.05	0.45	0.45	0.40	1.42	—	—
BzCl	0.0 ± 0.05	0.24 ± 0.06	0.0 ± 0.04	2.41 ± 0.06	0.41	0.41	0.80 ^b	1.26 ^b	0.215	-0.38
PhCl ^d	0.004 ± 0.05	0.18 ± 0.04	0.01 ± 0.04	2.99 ± 0.05	0.33	0.33	0.63	1.89	0.600	1.24

^a See ref 13.^b Q_1 , e_1 values calculated from the method described by Nishiwaki *et al.*²¹^c Q_1 , e_1 values calculated from the copolymerizations with MMA.^d See ref 9.

values for RCI were then calculated by assuming that $Q_2=1.0$, $e_2=-0.8$ for ST. These results are shown in Table III, in which the Taft's σ^* constants and E_S constants of alkyl group in RCI are also indicated. From Table II, it is obvious that a difference of 1% in the nitrogen analysis for the copolymer corresponds to about a 10% difference in the composition for the copolymer. Accordingly, if the error of nitrogen analysis is about 0.3%, the results, *i.e.*, r_1 , r_2 , Q_1 , e_1 values, and ρ^* , δ values which will be mentioned later, may contain considerable error. This error is shown in Table III. As can be seen from Table III, the relative reactivities ($1/r_2$) of RCI toward attack of a polystyryl radical increase with an increase in the electron-withdrawing nature of their substituents.

In order to follow the correlation between the relative reactivities ($1/r_2$) and the nature of alkyl groups in RCI, we attempted to plot the present results with the Taft equation 2, which was derived

from hydrolysis of a series of aliphatic esters by acid or base.¹¹

When the relative reactivities ($1/r_2$) of RCI toward an attack by a polystyryl radical were plotted on the Taft equation 2, a linear relationship having $\rho^*=0.34$, with 0.08 standard deviation, was obtained, as shown in Figure 2. The fact that the ρ^* value in this reaction is positive can be understood as due to the nucleophilic nature of a polystyryl attacking radical. However, no linear relationship between the relative reactivities ($1/r_2$) and E_S constants in RCI was observed.

By transforming the Taft equation 2, $\log(1/r_2) - \rho^*\sigma^*$ (where $\rho^*=0.34$) was plotted with E_S constants. This plot, shown in Figure 3, clearly indicates that the δ value is nearly zero, *i.e.*, the relative reactivities of RCI do not correlate with E_S constants of the substituents. This result might suggest that the radical reactivities of RCI depend on the polar character of the alkyl groups, but not on the steric character of these groups.

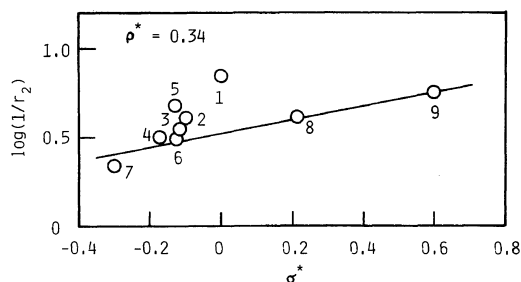


Figure 2. Correlation between the relative reactivities ($1/r_2$) of RCI toward an attack by a polystyryl radical and σ^* constants of alkyl groups: 1, CH_3 ; 2, C_2H_5 ; 3, $n\text{-C}_3\text{H}_7$; 4, $i\text{-C}_3\text{H}_7$; 5, $n\text{-C}_4\text{H}_9$; 6, $i\text{-C}_4\text{H}_9$; 7, $t\text{-C}_4\text{H}_9$; 8, $\text{C}_6\text{H}_5\text{CH}_2$; 9, C_6H_5 .

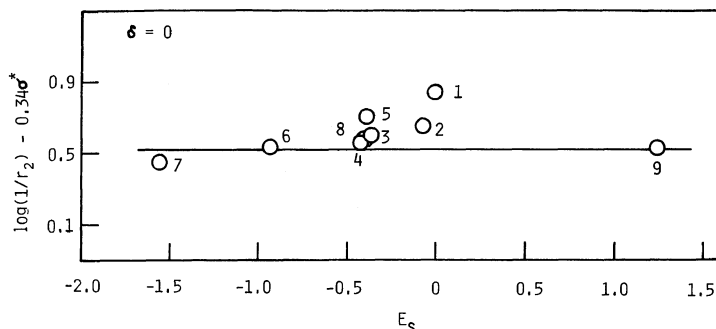


Figure 3. Correlation between $\log(1/r_2) - \rho^*\sigma^*$ and E_S constants of alkyl groups: 1, CH_3 ; 2, C_2H_5 ; 3, $n\text{-C}_3\text{H}_7$; 4, $i\text{-C}_3\text{H}_7$; 5, $n\text{-C}_4\text{H}_9$; 6, $i\text{-C}_4\text{H}_9$; 7, $t\text{-C}_4\text{H}_9$; 8, $\text{C}_6\text{H}_5\text{CH}_2$; 9, C_6H_5 .

Copolymerizations of RCI with MMA

The results of radical copolymerizations of RCI (M_1) with MMA (M_2) are shown in Table IV. The copolymerizations were homogeneous throughout. Four types of copolymer-composition curves in the ECI-MMA, *n*-PCI-MMA, *t*-BCI-MMA, and BzCI-MMA systems are shown in Figure 4. The composition curves in the *i*-PCI-MMA, *n*-BCI-MMA, *i*-BCI-MMA, and *n*-HCI-MMA systems are similar to those indicated in Figure 4. Table IV and Figure 4 indicate that the molar fraction of RCI in the copolymer also tends to increase with an increase in the molar fraction of RCI in the

Reactivities of *N*-Alkylcitraconimides

 Table IV. Radical copolymerizations of RCI (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	%	%	
ECI	20.6	60	7.8	1.10	8.1
	40.6	60	4.8	1.50	11.2
	47.5	120	8.8	2.40	18.4
	59.6	120	5.1	2.90	22.5
	80.6	150	1.1	5.00	41.5
<i>n</i> -PCI	19.9	60	9.8	1.05	7.8
	40.3	60	7.8	1.50	11.4
	49.7	60	5.5	2.40	18.9
	60.2	60	4.9	2.50	19.8
	79.8	60	2.4	5.50	49.7
<i>i</i> -PCI	20.0	90	7.7	1.00	7.4
	39.1	90	6.5	2.55	20.2
	50.5	120	6.7	2.60	20.6
	59.9	120	4.9	3.90	32.7
	80.2	120	4.7	5.10	45.2
<i>n</i> -BCI	20.2	90	6.8	1.35	10.3
	40.2	90	4.5	1.95	15.4
	48.8	120	5.5	2.15	17.3
	60.4	120	3.2	3.50	30.5
	69.5	120	2.7	3.90	34.3
<i>i</i> -BCI	20.1	45	8.2	1.60	13.7
	40.1	45	5.3	1.75	14.9
	50.0	45	5.3	2.10	16.7
	60.0	45	3.7	3.45	29.5
	79.9	45	2.7	4.10	36.5
<i>t</i> -BCI	20.0	60	8.8	1.00	7.5
	40.1	60	5.2	2.10	16.7
	50.6	90	6.0	2.60	21.2
	59.8	90	4.3	3.40	29.0
	86.7	100	1.5	4.85	45.1
<i>n</i> -HCI	19.8	90	5.8	1.15	8.9
	40.4	90	5.3	2.10	17.5
	49.6	120	4.8	2.20	18.5
	59.3	120	3.7	2.60	22.6
	70.2	120	3.4	4.00	39.3
BzCI	20.0	90	6.7	1.10	8.5
	39.2	90	4.3	1.80	14.8
	50.3	120	5.4	2.45	21.3
	60.0	120	3.9	3.00	27.4
	80.1	120	3.7	4.15	42.3

^a [AIBN], 3.0×10^{-2} mol l⁻¹; THF, 5 ml.

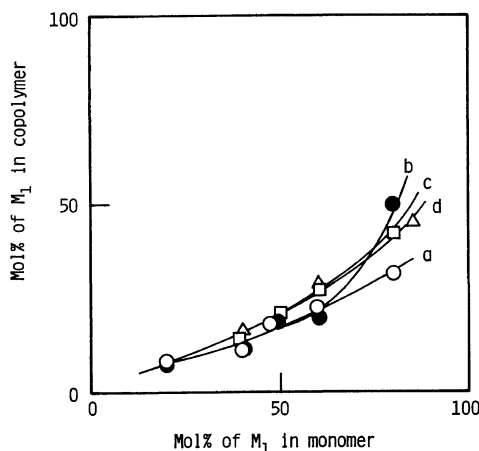


Figure 4. Copolymer-composition curves of RCI (M_1) and MMA (M_2) in THF at 60°C: a (○), ECI-MMA; b (●), *n*-PCI-MMA; c (□), BzCI-MMA; d (△), *t*-BCI-MMA.

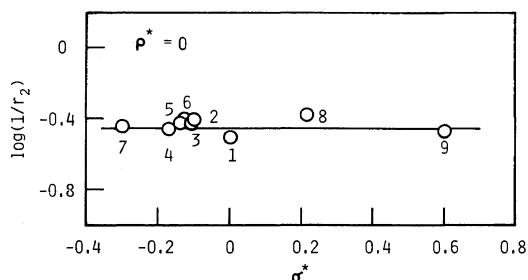


Figure 5. Correlation between the relative reactivities ($1/r_2$) of RCI toward an attack by a poly(MMA) radical and σ^* -constants of alkyl groups: 1, CH_3 ; 2, C_2H_5 ; 3, *n*- C_3H_7 ; 4, *i*- C_3H_7 ; 5, *n*- C_4H_9 ; 6, *i*- C_4H_9 ; 7, *t*- C_4H_9 ; 8, $\text{C}_6\text{H}_5\text{CH}_2$; 9, C_6H_5 .

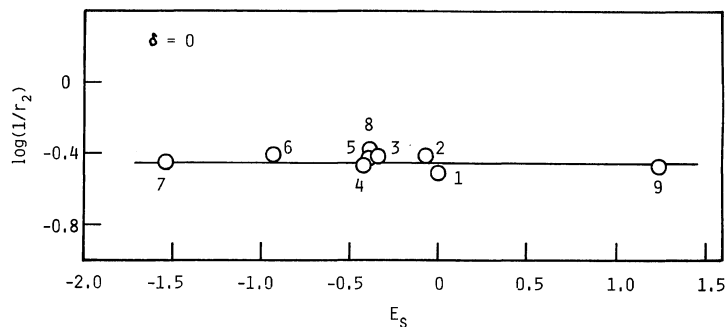


Figure 6. Correlation between $\log(1/r_2) - \rho^*\sigma^*$ and E_s constants of alkyl groups: 1, CH_3 ; 2, C_2H_5 ; 3, *n*- C_3H_7 ; 4, *i*- C_3H_7 ; 5, *n*- C_4H_9 ; 6, *i*- C_4H_9 ; 7, *t*- C_4H_9 ; 8, $\text{C}_6\text{H}_5\text{CH}_2$; 9, C_6H_5 .

monomer mixture.

When the relative reactivities ($1/r_2$) of RCI toward an attack by a poly(MMA) radical were plotted with σ^* constants in the Taft equation 2, a linear relationship having $\rho^* = 0$, with 0.04 standard deviation, was obtained, as shown in Figure 5.

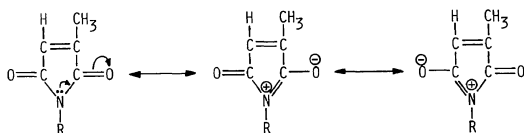
The relative reactivities ($1/r_2$) were plotted with E_s constants. This plot, shown in Figure 6, clearly indicates that the δ value is nearly zero. These findings tend to strongly suggest that neither the polar nor the steric character of the alkyl groups contributes to the relative reactivities of RCI toward an attack from a poly(MMA) radical.

These facts differ from those for the copolymerizations of RCI with ST. The reasons for the difference between $\rho^* = 0.34$ in the RCI-ST system

and $\rho^* = 0$ in the RCI-MMA system may be as follows. (i) The electron density of the double bond of a reaction site in RCI is $\delta+$, i.e., the e_1 values for RCI are positively great, as shown in Table III. Accordingly, ST, which has a more nucleophilic nature than MMA, may be able to attack easily the double bond. (ii) There is no large difference between ST ($Q_2 = 1.0$) and MMA ($Q_2 = 0.74$) with respect to the Q_2 value. On the other hand, the e_2 value for ST ($e_2 = -0.8$) is greatly different from that of MMA ($e_2 = 0.4$). Consequently, copolymerizations with ST may be affected by the polar character of the alkyl groups. In the case of the copolymerizations of RCI with MMA, these polar effects may not be important.

The fact that the polar character of alkyl groups

plays an important role only in the copolymerizations with St can be seen also in the case of RPhCI, as described in the previous paper.⁹ It is interesting to note that the substituent may slightly affect the double bond of the reaction site in RCI. These phenomena are not characteristic of RCI, but can be recognized in imides containing five-membered rings.^{2-8,17,18} That is, the conjugated system in RCI may become longer owing to the mobile lone electron-pair on the nitrogen atom, as can be seen from the following resonance structure.



Scheme 3.

In both the RCI-ST and the RCI-MMA system, the δ values were nearly zero. That is, it was found that there is little contribution from the steric character of alkyl groups in the copolymerizations of RCI. The reason for this is that the double bond of the reaction site is very far from the substituent (R). It can be conclusively demonstrated that the steric hindrance of an α -methyl group in RCI is more important than that of alkyl groups of the substituents from the standpoint of steric hindrance.

The e values for vinyl monomers are known to be proportional to the σ constants of their substituent.¹⁹ Accordingly, it is thought that the e values for RCI may perhaps be involved in the σ^* constants of monomer substituents. However, no linear relationship between e_1 values for RCI and σ^* constants was observed. This is consistent with the case of RPhCI. This problem can be attributed to the Q, e theory described by Alfrey-Price.²⁰ That is, the steric hindrance is neglected completely in this theory. When the Q and e values for RCI are determined, the steric hindrance of the α -methyl group in RCI cannot be neglected. In addition, the characteristics of the imides containing five-membered rings are also not likely to be negligible. These characteristics are as follows. (i) Because of the cyclic structure containing a 1,2-disubstituted ethylene structure, there is some steric hindrance. (ii) There is a strain in the five-membered ring containing the nitrogen atom.

Both the Q_1 and e_1 values were also independent of E_s constants of alkyl groups in RCI. This

tendency could also be seen in the case of RPhCI.

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