

Polymerizations and Copolymerizations of *N*-(4-Substituted phenyl)itaconimides

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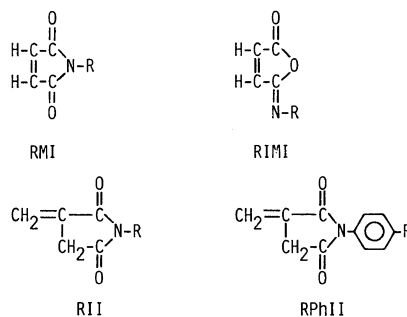
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ABSTRACT: Homopolymerizations of *N*-(4-substituted phenyl)itaconimide (RPhII) (R=H, CH₃, Cl, OCH₃, OCOCH₃, COOC₂H₅) were carried out at 60°C by using azobisisobutyronitrile (AIBN) as an initiator in tetrahydrofuran. The initial rate of the polymerization was $R_p = k[AIBN]^{0.5-0.6} [RPhII]^{1.0-1.3}$, where k is rate constant. The overall activation energies (E) and frequency factors (A) for RPhII were $E = 16.1-20.9$ kcal mol⁻¹, $A = 3.1 \times 10^7-5.6 \times 10^{10}$ s⁻¹. Also, radical copolymerizations of RPhII (M₁) with styrene (M₂) were carried out at 60°C in tetrahydrofuran in order to clarify the substituent effect on the copolymerization. Hammett's equation, $\log (1/r_2) = \rho\sigma$, was applied to this copolymerization and a linear relationship was obtained for $\rho = -0.33$. Further observation showed that the Q_1 values of the monomers are inversely proportional to σ -constants of the substituents.

KEY WORDS Polymerization / *N*-(4-Substituted phenyl)itaconimide / Initial Rate / Overall Activation Energy / Copolymerization / Styrene / Monomer Reactivity Ratio / Hammett's Equation /

As studies on syntheses and polymerizations of unsaturated dibasic acid and its derivatives, the author has synthesized various types of *N*-substituted maleimides (RMI) and *N*-substituted isomaleimides (RIMI), and studied their polymerization reactivities.¹⁻⁶ The results indicate that the values obtained for the activation energy (E) and the frequency factor (A) in the polymerization of RMI are generally higher than those for vinyl compounds independent of a homogeneous or a heterogeneous system in the polymerization. It was also demonstrated that the order (n) of the monomer concentration in the free radical homopolymerization rate equation becomes greater than 1 although the polymerization is homogeneous, and that the order (m) of the initiator concentration becomes 0.5—1.0.

As a continuation of the previous study, the author has studied *N*-(4-substituted phenyl)itaconimides (RPhII), which are unsaturated dibasic acid derivatives. Many studies have been reported on the polymerizations of itaconic acid and its derivatives.⁷⁻¹² Some types of *N*-alkylitaconimide (RII) have also been synthesized and briefly



Scheme 1

copolymerized by Akashi.¹³ However, RPhII have not yet been either synthesized or polymerized.

Six types of RPhII, *i.e.*, *N*-phenylitaconimide (PhII); *N*-(4-methylphenyl)itaconimide (MPhII), *N*-(4-chlorophenyl)itaconimide (ClPhII), *N*-(4-methoxyphenyl)itaconimide (MOPhII), *N*-(4-ethoxycarbonylphenyl)itaconimide (ECPhII), and *N*-(4-acetoxycarbonylphenyl)itaconimide (AOPhII) were synthesized, and their homopolymerization rate equations were studied, E and A values were also

obtained. In addition, copolymerizations with styrene (ST) were carried out, and the monomer reactivity ratios (r_1 , r_2), and Q_1 , e_1 values were calculated. To make a comparison with the polymerization parameters for RMI obtained so far, we tried to find out whether or not these RPhII have the usual characteristics. Also, in order to clarify the substituent effect on the copolymerization, Hammett's equation, (eq 1) was applied to this copolymerization, and the results are discussed.

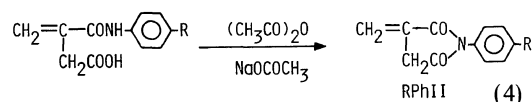
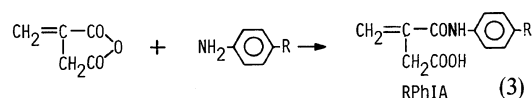
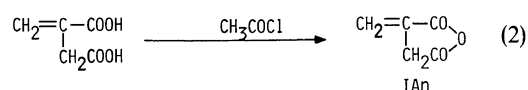
$$\log(1/r_2) = \rho\sigma \quad (1)$$

where ρ is the polar reaction constant, σ is the polar substituent constant.

EXPERIMENTAL

Syntheses of Monomers

The six types of RPhII were synthesized following processes (2), (3), and (4), according to the method of Akashi,¹³ or Mehta *et al.*¹⁴



R: H, (PPhII); Cl, (ClPhII); CH₃, (MPhII); OCH₃, (MOPhII); COOC₂H₅, (ECPHII); OCOCH₃, (AOPhII)

Scheme 2

N-(4-Substituted phenyl)itaconamic Acid (RPhIA). Itaconic anhydride (IAN) was dissolved in anhydrous ethyl ether. An anhydrous ethyl ether solution containing the first amine 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%).

RPhII. RPhIA was dissolved in acetic anhydride and the ring-closing reaction was carried out by dehydration in the presence of sodium acetate to produce RPhII. The product was recrystallized twice from ethanol.

RPhII were identified by elemental analyses, IR and NMR spectra. Table I gives the yields, melting

points, molecular weights, and results of the analyses of the RPhII monomers and polymers.

Comonomer, Initiator, and Solvent

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

Polymerization Methods

Homopolymerization. All homopolymerizations were carried out in a sealed tube. The required weight of monomer was added to the tube and the necessary amount of THF containing a certain amount of AIBN was then added. While the above ingredients were cooled with a freezing mixture, nitrogen was introduced into the tube by the usual method, and the tube was then sealed. The homopolymerizations took place while shaking this mixture, with the thermostat set at a specified temperature. After a certain period of time, the contents were poured from the tube into a large amount of methanol so as to precipitate the polymer. The precipitate was filtered, thoroughly washed with methanol, and dried under reduced pressure to obtain the polymer.

Copolymerization. The copolymerizations of RPhII with ST were carried out using AIBN as the initiator. The method of copolymerization was similar to that described above. The composition of each copolymer was calculated from the analysis for nitrogen.

Molecular-Weight Measurements

The number-average molecular weight of each homopolymer was measured in chloroform with a Hitachi Model 115 Molecular Weight Apparatus.

Viscosity Measurements

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

Softening-Point Measurements

These measurements were carried out according to the general method for melting-point determination in a fused-salt bath consisting of a mixture of

Table I. Melting points, yields, molecular weights, and elemental analyses of monomers (M) and polymers (P)

Sample	mp	Yield ^a	M_w	H/%		C/%		N/%	
	°C			%	Calcd	Found	Calcd	Found	Calcd
PhII (M)	110—112	40	—	4.85	4.72	70.58	70.12	7.48	7.09
PhII (P) ^b	—	70	11×10^3	4.85	5.02	70.58	70.98	7.48	7.39
ClPhII (M)	131—132	55	—	3.64	3.51	59.61	59.71	6.32	6.30
ClPhII (P) ^c	—	65	10×10^3	3.64	4.01	59.61	60.24	6.32	6.59
MPhII (P)	125—126	40	—	5.51	5.44	71.63	71.07	6.96	6.89
MPhII (P) ^d	—	73	8.5×10^3	5.51	5.68	71.63	72.07	6.96	6.74
ECPhII (M)	129—130	58	—	5.05	5.04	64.86	65.25	5.40	5.51
ECPhII (P) ^e	—	84	11×10^3	5.05	4.58	64.86	65.00	5.40	5.42
MOPhII (M)	107—109	38	—	5.10	5.10	66.35	66.09	6.45	6.40
MOPhII (P) ^f	—	83	12×10^3	5.10	5.52	66.35	66.93	6.45	6.38
AOPhII (M)	150—152	45	—	4.52	4.52	63.67	64.09	5.71	5.60

^a Yields of monomers are based on RPhIA.

^b [PhII], 3.26×10^{-1} mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹; temp, 60°C; time, 2 h.

^c [ClPhII], 4.01×10^{-1} mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹; temp, 60°C; time, 2 h.

^d [MPhII], 5.42×10^{-1} mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹; temp, 60°C; time, 2 h.

^e [ECPhII], 3.86×10^{-1} mol l⁻¹; [AIBN], 1.00×10^{-2} mol l⁻¹; temp, 60°C; time, 2 h.

^f [MOPhII], 3.69×10^{-1} mol l⁻¹; [AIBN], 3.00×10^{-2} mol l⁻¹; temp, 60°C; time, 1.5 h.

potassium nitrate and sodium nitrate.

RESULTS AND DISCUSSION

Homopolymerization

In the homopolymerizations of the five RPhII, all systems were homogeneous throughout.

The polymerization of each monomer was carried out at a constant monomer concentration and a constant polymerization temperature (60°C) in the presence of an AIBN initiator, for various periods of time. The polymerization curves were drawn on the basis of these results. From the slope of each curve, being initially linear, the initial rate of polymerization, R_p , could be found. The R_p was measured at various AIBN concentrations. When the logarithms of these R_p and AIBN concentrations were plotted, the lines shown in Figure 1 were obtained. The m were measured from the slopes of these lines. And the results are shown in Table II.

Polymerizations were carried out at 60°C at various monomer concentrations. The concentration of the initiator AIBN was constant. R_p was calculated from the time-conversion relationship. According to the same procedure for determining m , the relation between $\log R_p$ and $\log [M]$, (where $[M]$ is the monomer concentration), was plotted in

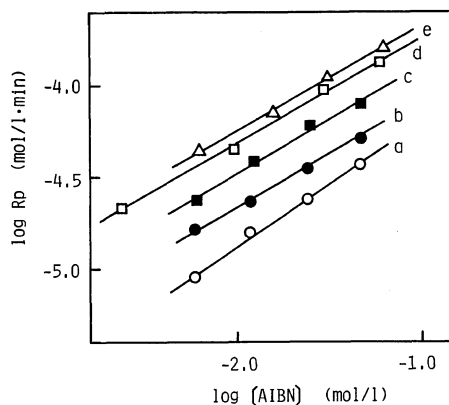


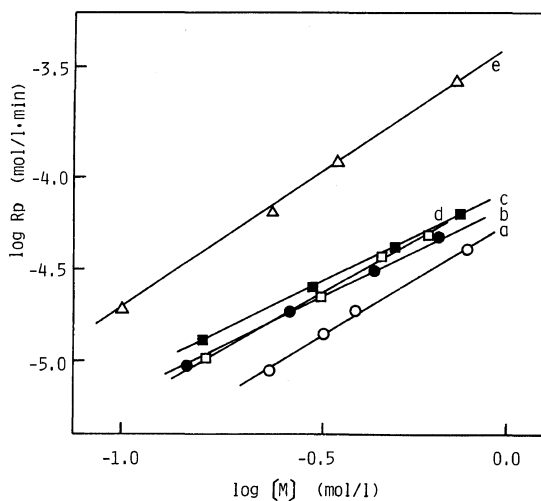
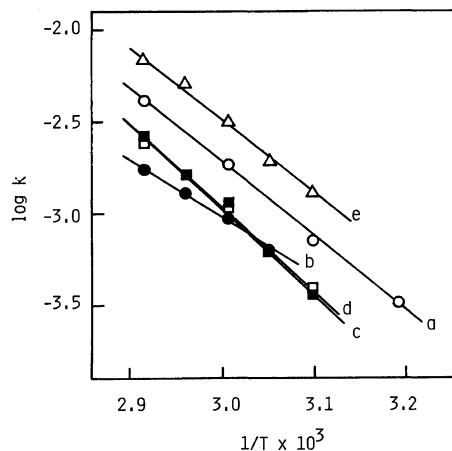
Figure 1. Effect of the AIBN concentration on the rate of polymerization at 60°C: a (○), [PhII], 3.21×10^{-1} mol l⁻¹; b (●), [ClPhII], 2.71×10^{-1} mol l⁻¹; c (■), [MPhII], 2.99×10^{-1} mol l⁻¹; d (□), [ECPhII], 3.86×10^{-1} mol l⁻¹; e (△), [MOPhII], 3.69×10^{-1} mol l⁻¹

Figure 2. n was obtained from the slope of this line. The results are shown in Table II.

As shown in Table II, m is about 0.5, indicating that RPhII satisfy the ordinary 1/2 power rule, and that the bimolecular termination occurs in the polymerization. The author¹⁻³ reported that in the homopolymerization rate equation of RMI, m is

Table II. Rate equations (R_p), rate constants (k), overall activation energies (E), and frequency factors (A) for the radical polymerizations of RPhII

Monomer, M	$R_p = k [\text{AIBN}]^m [\text{M}]^n$		k (at 60°C)	E kcal mol ⁻¹	A s ⁻¹	Reference
	m	n				
PhII	0.6	1.2	1.58×10^{-3}	19.5	9.9×10^9	—
CIPhII	0.5	1.1	8.83×10^{-4}	16.1	3.1×10^7	—
MPhII	0.5	1.0	1.28×10^{-3}	20.1	1.7×10^{10}	—
ECPhII	0.5	1.2	1.08×10^{-3}	20.9	5.6×10^{10}	—
MOPhII	0.5	1.3	2.58×10^{-3}	18.6	4.2×10^9	—
PhMI ^a	0.8	1.2	—	25.2	8.3×10^{14}	15
NMI ^b	0.55	1.6	8.25×10^{-5}	24.4	8.5×10^{11}	1
FMI ^c	0.64	2.1	1.62×10^{-2}	26.4	3.4×10^{15}	2
<i>n</i> -HMI ^d	0.80	2.5	9.91×10^{-4}	22.8	9.5×10^{11}	3
AEMI ^e	0.60	2.1	9.00×10^{-4}	31.3	3.1×10^{17}	17
MMA ^f	0.5	1.0	—	19.9	3.7×10^9	16

^a *N*-Phenylmaleimide.^b *N*-1-Naphthylmaleimide.^c *N*-2-Fluorenylmaleimide.^d *N*-*n*-Hexylmaleimide.^e *N*-Acetoxyethylmaleimide.^f Methyl methacrylate.**Figure 2.** Effect of the monomer concentration on the rate of polymerization at 60°C: a (○), PhII, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; b (●), CIPhII, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; c (■), MPhII, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; d (□), ECPhII, [AIBN], $1.00 \times 10^{-2} \text{ mol l}^{-1}$; e (△), MOPhII, [AIBN], $3.00 \times 10^{-2} \text{ mol l}^{-1}$.**Figure 3.** Relationship between $\log k$ and $1/T$ for the polymerization of RPhII initiated by AIBN at various temperatures: a (○), [PhII], $3.21 \times 10^{-1} \text{ mol l}^{-1}$, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; b (●), [CIPhII], $2.71 \times 10^{-1} \text{ mol l}^{-1}$, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; c (■), [MPhII], $2.99 \times 10^{-1} \text{ mol l}^{-1}$, [AIBN], $2.50 \times 10^{-2} \text{ mol l}^{-1}$; d (□), [ECPhII], $3.86 \times 10^{-1} \text{ mol l}^{-1}$, [AIBN], $1.00 \times 10^{-2} \text{ mol l}^{-1}$; e (△), [MOPhII], $3.69 \times 10^{-1} \text{ mol l}^{-1}$, [AIBN], $3.00 \times 10^{-2} \text{ mol l}^{-1}$.

0.6—0.9, and is thus of a considerably higher order than 0.5. In RMI, both the monomolecular and bimolecular terminations may occur simultaneously. However, RPhII did not show this tendency.

As shown in Table II, n is about 1.0—1.3. It seems

Table III. Radical copolymerization of RPhII (M_1) with ST (M_2) in THF at 60°C

Monomer	M_1 in monomer	Time	Conversion	N-Analysis	M_1 in copolymer	η_{sp}/c^a
	mol%	min	%	%	mol%	
PhII ^b	20.0	40	6.7	4.3	42.9	0.29
	40.1	15	4.0	4.5	45.6	
	50.2	15	6.1	4.8	49.9	
	60.0	15	7.6	5.0	52.8	
	80.0	13	8.8	5.4	59.1	
ClPhII ^b	19.9	20	4.9	3.8	41.5	0.25
	37.2	15	6.7	4.1	46.4	
	49.3	15	6.8	4.2	48.2	
	60.0	15	9.9	4.4	51.8	
	80.7	10	7.1	5.2	68.5	
MPhII ^b	14.4	15	2.6	3.6	35.7	0.23
	40.0	15	5.9	4.6	50.2	
	49.0	10	7.3	4.6	50.2	
	60.0	10	6.1	4.9	55.2	
	78.8	10	8.2	5.4	64.2	
ECPhII ^c	20.3	60	8.4	3.1	35.1	0.25
	41.9	60	7.5	3.6	44.5	
	50.5	60	8.8	3.7	46.6	
	58.0	60	8.7	3.9	51.0	
	79.8	60	9.0	4.2	58.3	
AOPhII ^c	20.3	15	4.3	2.9	30.5	0.27
	40.5	15	6.8	3.5	40.2	
	50.5	15	4.4	4.1	51.9	
	61.2	15	4.5	4.0	49.8	
	79.3	15	7.6	4.6	63.7	

^a C, 0.1 g dl⁻¹ in THF at 30°C.

^b [AIBN], 2.5×10^{-2} mol l⁻¹; THF, 5 ml; $M_1 + M_2$, 2.0 g.

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

that an ordinary radical addition reaction occurred in MPhII. In the case of PhII, ClPhII, ECPhII, and MOPhII, the reason for these higher orders seems to arise from the "cage effect," as pointed out in the polymerization of RMI.¹⁻³

Thus, polymerization was carried out at constant monomers and AIBN concentrations, at various temperatures. From these results, the R_p 's were obtained, and have been substituted in the rate equations shown in Table II for calculating the rate constants (k). Figure 3 shows the relationship between $\log k$ and $1/T$. From the slope of this straight line, E was obtained. Using the Arrhenius' equation, A was calculated. These values were shown in Table II. In order to compare these results with

those of RMI, the polymerization parameters of RMI and MMA which is an ordinary vinyl compound, are also shown in Table II. As the table indicates, the E and A for RPhII are $E = 16.1-20.9$ kcal mol⁻¹, $A = 3.1 \times 10^7-5.6 \times 10^{10}$ s⁻¹. The E and A for RPhII measured by the author are similar to those found for MMA. These values, however, when compared with those of RMI, are considerably small. The reason for this may be that, in the case of RMI, the double bond of the reaction site is placed in five-membered ring containing a nitrogen atom, but in RPhII, this double bond is placed outside the five-membered ring. Consequently, the influence of the carbonyl groups on the double bond may be smaller in RPhII than in

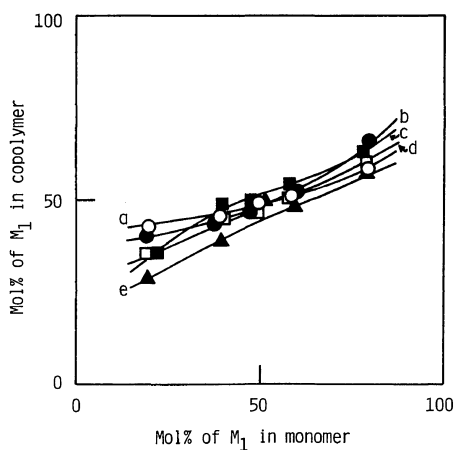


Figure 4. Copolymer composition curves of RPhII (M_1) and ST (M_2) in THF at 60°C: a (○), PhII-ST; b (●), CIPhII-ST; c (■), MPhII-ST; d (□), ECPHII-ST; e (▲), AOPhII-ST.

RMI. In conclusion, the fact that the E and A for RPhII are smaller than those for RMI is explained in terms of the differences in structure of the two monomers.

Copolymerization

The copolymerizations of RPhII (M_1) with ST

(M_2) were carried out at 60°C by using AIBN as the initiator. The polymerizations were homogeneous throughout. The results of the polymerizations are shown in Table III. The copolymer-composition curves obtained from the above results are shown in Figure 4. Table III and Figure 4 indicate that the copolymerization of RPhII with ST occurred readily. It is known that the copolymerization of maleic anhydride with ST or that of RMI with ST is practically an alternating type process. In the RPhII-ST system, however, it was found that the molar fraction of RPhII in the copolymer tends to increase as that of RPhII in the prepared monomer feed increases.

The monomer reactivity ratios (r_1 , r_2) were obtained by using the Fineman-Ross method or the Integration method. By these values, assuming Q_2 and e_2 of ST to be $Q_2=1$ and $e_2=-0.8$,¹⁸ the Q_1 and e_1 of RPhII were calculated. The copolymerization parameters are shown in Table IV. In Table IV, the Q_1 and e_1 values of RMI are also shown and that each Q_1 value of RPhII is higher than any RMI value. The e_1 values of RPhII are also high because of the polarization of the carbonyl groups. However, these values are lower than those of RMI perhaps as a result of the difference in structure between RMI and RPhII.

Table IV. Monomer reactivity ratios (r_1 , r_2) for RPhII (M_1) and ST (M_2), and Q_1 , e_1 values for RPhII

M_1	r_1	r_2	$1/r_2$	Q_1^a	e_1^a	σ	Ref
PhII	0.12 ± 0.03	0.14 ± 0.03	7.69	1.5	1.2	0.00	—
CIPhII	0.32 ± 0.03	0.19 ± 0.05	5.26	1.0	0.74	0.23	—
MPhII	0.23 ± 0.03	0.15 ± 0.05	6.67	1.6	1.0	-0.17	—
ECPHII	0.12 ± 0.04	0.24 ± 0.03	4.17	0.92	1.1	0.45	—
AOPhII	0.15 ± 0.07	0.25 ± 0.08	4.00	0.94	1.0	0.31	—
PhMI ^b	0.66	0.02	—	0.74 ^c	1.75 ^c	—	15
NMI ^d	0.0	0.15	—	0.75 ^c	2.0 ^c	—	1
FMI ^f	—	—	—	0.43 ^c	1.82 ^c	—	2
<i>n</i> -HMI ^g	0.08	0.0	—	0.56 ^c	1.43 ^c	—	3

^a Calculated by assuming that Q_2 and e_2 values of ST were 1.0 and -0.8, respectively;¹⁸ The errors of Q_1 , e_1 values are ± 0.1 .

^b *N*-Phenylmaleimide.

^c Calculated by assuming that Q_2 and e_2 values of vinyl acetate were 0.026 and -0.22, respectively.¹⁸

^d *N*-1-Naphthylmaleimide.

^e Calculated by assuming that Q_2 and e_2 values of methyl methacrylate were 0.74 and 0.4, respectively.¹⁸

^f *N*-2-Fluorenylmaleimide.

^g *N*-*n*-Hexylmaleimide.

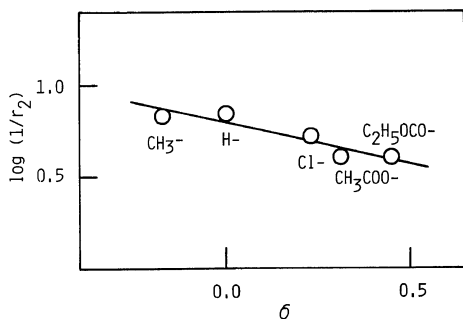


Figure 5. The correlation between relative reactivities of RPhII ($1/r_2$) toward attack of a polystyryl radical and σ -constants.

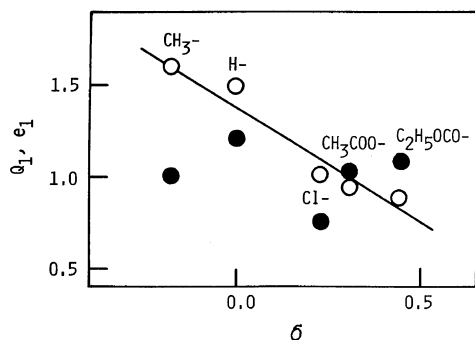
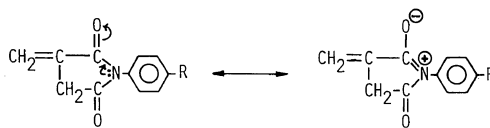


Figure 6. The correlation between the Q_1 or e_1 values of RPhII and σ -constants: (○), Q_1 value; (●), e_1 value.

The effect of the substituents on the radical copolymerization of RPhII (M_1) with ST (M_2) was investigated. When the relative reactivities ($1/r_2$) of RPhII toward an attack by polystyryl radicals were plotted using Hammett's equation (eq 1), $\log(1/r_2) = \rho\sigma$, a linear relationship in which $\rho = -0.33$, with 0.04 of a standard deviation was obtained, as shown in Figure 5. The negative ρ -value suggests that the relative reactivity ($1/r_2$) of RPhII toward an attack by polystyryl radicals tends to increase as the electron-donative nature of the substituents in RPhII becomes greater.

The relationship between the Q_1 or e_1 values of RPhII and the σ -constants of the substituents in RPhII is shown in Figure 6. Figure 6 indicates that the Q_1 values of RPhII are inversely proportional to the σ -constants of the substituents. In other words, the Q_1 values of RPhII also increase as the electron-donative nature of the substituents in RPhII becomes greater. Now, in order to explain the

reason for these results, the author proposes the following resonance structure.



Scheme 3

Owing to the mobile lone electron-pair of the nitrogen atom, the substituent, R, may affect the double bond of reaction site in RPhII. Consequently, as the conjugated system in RPhII becomes longer, the Q_1 values of RPhII may also become high.

It was found that the relative reactivity ($1/r_2$) of RPhII toward an attack by polystyryl radicals increases with an increase in the Q_1 values of RPhII. This is different to the case of copolymerizations of RMI with ST, in which the electron density of the double bond at reaction site in RMI takes on higher $\delta+$ since RMI has two carbonyl groups in the immediate neighborhood of the double bond. Consequently, the e values of RMI are high. In addition, the relative reactivity of RMI toward an attack by polystyryl radicals tends to increase with an increase in the e values of RMI. The relative reactivity of RMI toward an attack by polystyryl radicals is affected not by the Q values but by the e values of RMI. In the case of RPhII, however, the electron density of the double bond at reaction site has a lower $\delta+$ than that in RMI since RPhII has one carbonyl group in the immediate vicinity of the double bond. Thus, though a polystyryl radical has a nucleophilic nature, *i.e.*, the e value of ST is -0.8 , the relative reactivity ($1/r_2$) of RPhII toward an attack by polystyryl radicals may be affected not by the e_1 values but by the Q_1 values of RPhII.

Inoue *et al.*¹⁹ have reported that the ρ value is -0.13 in the copolymerization of *N*-(substituted phenyl)methacrylamide with acrylonitrile, and that this may be understandable in consideration of the electrophilic nature of acrylonitrile. Generally, the ρ value is positive in the nucleophilic nature of the attacking radical. However, this value is negative in the electrophilic nature of the attacking radical.

In the case of RPhII, however, in spite of the nucleophilic nature of a polystyryl attacking radical, the ρ value is negative. It is difficult to explain this

on the basis of the nucleophilic or electrophilic nature of the attacking radical. But, in this study, (1) the e values for RPhII are large and positive. Thus, there is little electrostatic mutual repulsion between RPhII and ST. (2) The e values for RPhII are independent of the polar character (σ -constants) of the substituents. (3) The Q values for RPhII increase with an increase in the electron-donative nature of the substituents. This tendency can be explained on the basis of resonance structures, as described above. In conclusion, the reactivities of RPhII depend not on the e values but on the Q values of RPhII.

In the case of N -(substituted phenyl)methacrylamide, the Q values are independent of the polar character (σ -constants), and the e values decrease slightly with an increase in the electron-donative nature of the substituents. That is, the relative reactivities of N -(substituted phenyl)methacrylamide toward an attack by polyacrylonitrile radicals depend not on the Q values but on the e values. Accordingly, because of different contributions from the Q and e values, the ρ value of RPhII may be negative, in spite of the nucleophilic nature of ST.

In comparison with the ρ value of -0.13 for N -(substituted phenyl)methacrylamide, the ρ value of -0.33 for RPhII is considerably large, perhaps as a result of the different characteristics of RPhII and N -(substituted phenyl)methacrylamide. (1) Both Q and e values of RPhII are much higher than those ($Q=0.36-0.38$; $e=-0.02--0.08$) of N -(substituted phenyl)methacrylamide. (2) With respect to the steric hindrance in the copolymerizations, there is also more steric hindrance in RPhII than that in N -(substituted phenyl)methacrylamide. As a result of these various interactions, it may be concluded that the ρ value for RPhII is negative and larger than that of N -(substituted phenyl)methacrylamide.

Properties of the Polymers

Table I shows the results of elemental analyses of polymers. The results in Table I and the IR spectra of RPhII polymers and monomers show that there is little difference between the monomers and polymers. Accordingly, it was concluded that normal addition polymerizations take place in RPhII. It was found that the number-average molecular weights of the homopolymers are about 10×10^3 .

The reduced viscosities and the softening points

Table V. Reduced viscosities and softening points of RPhII polymers

Polymer	Softening point	
	°C	
Poly(PhII) ^b	263—285	0.23
Poly(CIPhII) ^c	250—276	0.19
Poly(MPhII) ^d	269—280	0.20
Poly(ECPhII) ^e	265—291	0.25
Poly(MOPhII) ^f	255—278	0.27

^a c , 0.1 g/dl⁻¹ in THF at 30°C.

^b [PhII], 1.63 mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹.

^c [CIPhII], 2.01 mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹.

^d [MPhII], 2.71 mol l⁻¹; [AIBN], 1.51×10^{-2} mol l⁻¹.

^e [ECPhII], 1.58 mol l⁻¹; [AIBN], 1.00×10^{-2} mol l⁻¹.

^f [MOPhII], 1.84 mol l⁻¹; [AIBN], 3.00×10^{-2} mol l⁻¹.

are shown in Table V. As shown in Table V, there is no large difference among the five RPhII with respect to reduced viscosities. Also, their softening points 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.¹⁻³ The polymers obtained by the author also showed high softening points.

All the polymers and copolymers were white powders. The five types of homopolymers were soluble in organic solvents such as THF, dioxane, chloroform, N,N -dimethylformamide, or N,N -dimethyl sulfoxide. The solubility of RPhII-ST copolymers had a similar tendency.

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