

NOTE

## Syntheses and Polymerizations of Alkyl *N*-(4-Substituted phenyl)itaconamates

Tsutomu OISHI, Minoru FUJIMOTO, and Tadashi KIMURA\*

Department of Industrial Chemistry, Technical College, Yamaguchi University,  
2557 Tokiwadai, Ube, Yamaguchi 755, Japan.

(Received September 8, 1981)

**KEY WORDS** Radical Polymerization / Radical Copolymerization / Alkyl *N*-(4-Substituted phenyl)itaconamate / Styrene / Methyl Methacrylate / Monomer Reactivity Ratio /  $Q$ ,  $e$ -Value / The Modified Hammett Equation /

In order to clarify the polymerization reactivities of an unsaturated dibasic acid and its derivatives, we investigated *N*-(4-substituted phenyl)itaconimide<sup>1</sup> and *N*-substituted citraconimide.<sup>2,3</sup> In this paper, alkyl *N*-(4-substituted phenyl)itaconamate (ARPhIA), an unsaturated dibasic acid derivative, was studied. Various types of itaconic acid derivatives were synthesized and polymerized. However, ARPhIA has not yet been synthesized or polymerized. Nineteen types of ARPhIA were synthesized, and their homopolymerization reactivities were investigated. In addition, the copolymerization of ARPhIA ( $M_1$ ) with styrene (ST) ( $M_2$ ) or methyl methacrylate (MMA) ( $M_2$ ) was carried out, and the monomer reactivity ratios,  $r_1$  and  $r_2$ ,  $Q_1$  and  $e_1$  values for ARPhIA were calculated. Furthermore, in order to clarify substituent

effects on the copolymerization application was made of a modified Hammett equation (eq 1),<sup>4</sup> and the results are discussed.

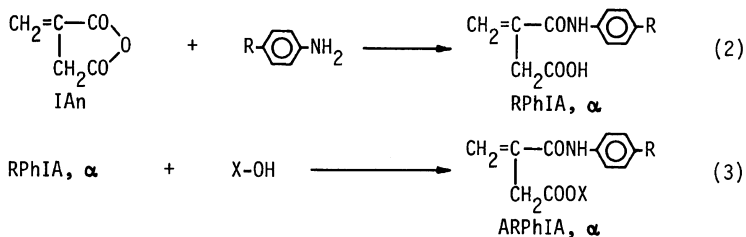
$$\log (1/r_2) = \rho\sigma + \gamma E_R \quad (1)$$

where  $\rho$  is the polar-reaction constant,  $\sigma$  is the polar-substituent constant,  $\gamma$  is the resonance-reaction constant, and  $E_R$  is the resonance-substituent constant.

### EXPERIMENTAL

#### ARPhIA Monomers and Other Materials

The nineteen types of ARPhIA monomers were synthesized, according to following processes (2) and (3) in Scheme 1, and by a method similar to that described by Crombie *et al.*<sup>5</sup> and Nagai *et al.*<sup>6</sup>



I, X=CH<sub>3</sub>; II, X=C<sub>2</sub>H<sub>5</sub>; III, X=*n*-C<sub>3</sub>H<sub>7</sub>; IV, X=*n*-C<sub>4</sub>H<sub>9</sub>; V, X=*n*-C<sub>6</sub>H<sub>13</sub>.  
a, R=OCH<sub>3</sub>; b, R=CH<sub>3</sub>; c, R=H; d, R=Cl; e, R=COOC<sub>2</sub>H<sub>5</sub>.

Scheme 1.

\* Present address: Ube Technical College, Tokiwadai, Ube, Yamaguchi 755, Japan.

ARPhIA was identified by elemental analysis IR and NMR spectra. Table I gives the yield and melting point of each ARPhIA monomer.

ST, MMA, azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), and petroleum ether were purified by the usual methods.

#### Homopolymerization and Copolymerization Procedure

All homopolymerizations of ARPhIA ( $3.5 \times 10^{-1}$  mol  $l^{-1}$ — $1.2$  mol  $l^{-1}$ ) were carried out in THF (5 ml) at  $60^\circ\text{C}$  in a sealed glass tube in the presence of AIBN ( $3.0 \times 10^{-2}$  mol  $l^{-1}$ ), using the same technique as described in an earlier paper.<sup>1</sup> In this study, however, petroleum ether was used as the precipitant.

The copolymerization of ARPhIA ( $M_1$ ) with ST ( $M_2$ ) or MMA ( $M_2$ ) was carried out in THF at  $60^\circ\text{C}$  in a sealed-glass tube in the presence of  $3.0 \times 10^{-2}$

mol  $l^{-1}$  of AIBN, using the same technique described in the previous papers.<sup>2,3</sup>

The composition of the copolymer was determined from carbon and nitrogen analysis. The monomer reactivity ratios,  $r_1$  and  $r_2$ , were determined by the method of Fineman and Ross<sup>7</sup> or by that of Mayo and Lewis.<sup>8</sup>

#### Measurement

The GPC analysis of the polymers was carried out with a Shimadzu LC-3A instrument, provided with a computing data processor.

## RESULTS AND DISCUSSION

All homopolymerizations of ARPhIA were carried out in 5 ml of THF at  $60^\circ\text{C}$  for 92 hours. It was found that the conversion of each homopolymer was only 3–30% and that the number-average

**Table I.** Yields, melting points of ARPhIA monomers, and monomer reactivity ratios ( $r_1$ ,  $r_2$ ) for ARPhIA ( $M_1$ ), ST ( $M_2$ ), and MMA ( $M_2$ ), and the  $Q$  and  $e$  values of ARPhIA

$M_1$	ARPhIA monomer		Monomer reactivity ratio				$Q_1^d$	$e_1^d$
	Yield <sup>a</sup>	mp	ST ( $M_2$ )		MMA ( $M_2$ )			
			$r_1^b$	$r_2^b$	$r_1^c$	$r_2^c$		
%	$^\circ\text{C}$							
Ia	12	124	0.41	0.26	—	—	1.16	0.70
Ib	38	125	0.16	0.30	—	—	0.83	0.94
Ic	40	131	0.18	0.39	—	—	0.69	0.84
Id	33	115	0.18	0.38	—	—	0.71	0.84
Ie	21	125	0.58	0.15	—	—	1.91	0.76
IIa	12	95	0.34	0.33	0.43	1.31	0.93	0.68
IIb	44	103	0.26	0.38	0.63	1.43	0.78	0.72
IIc	36	75	0.21	0.45	0.47	1.32	0.65	0.73
IId	31	99	0.16	0.35	0.36	1.24	0.73	0.90
IIe	38	100	0.20	0.23	0.48	1.21	1.07	0.95
IIIa	22	84	0.40	0.38	0.40	1.03	0.88	0.57
IIIb	25	89	0.19	0.54	0.28	1.11	0.58	0.73
IIIc	33	63	0.18	0.50	0.15	1.13	0.50	0.76
IIId	51	96	0.31	0.39	0.31	1.26	0.79	0.66
IIIe	19	98	0.40	0.26	0.53	1.00	1.16	0.70
IVa	15	77	0.69	0.12	—	—	2.35	0.78
IVb	19	94	0.31	0.19	—	—	1.37	0.88
IVc	20	71	0.49	0.12	—	—	2.17	0.88
IVe	18	94	0.61	0.20	—	—	1.57	0.65

<sup>a</sup> Based on *N*-(4-substituted phenyl)itaconamic acid.

<sup>b</sup> An error of  $\pm 0.07$ .

<sup>c</sup> An error of  $\pm 0.17$ .

<sup>d</sup> Calculated from copolymerization with ST.

molecular weight ( $M_n$ ) was between 1200 and 2600; *i.e.*, all the homopolymers were oligomers whose degree of polymerization ranged from about 6–10. This fact may be attributable to the chain transfer reaction. Based on the results of the copolymerization of ARPhIA ( $M_1$ ) with St ( $M_2$ ), the monomer reactivity ratios ( $r_1, r_2$ ) were determined. The  $Q_1$  and  $e_1$  values for ARPhIA were then calculated, according to the method of Alfrey and Price,<sup>9</sup> assuming that  $Q_2=1.0$ ,  $e_2=-0.8$  for ST.<sup>10</sup> These results are shown in Table I.

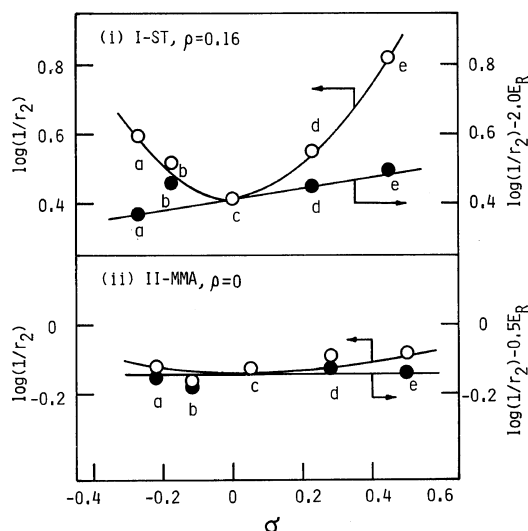
As shown in Figure 1(i), in the case of the copolymerization of itaconamate I with ST, ordinary Hammett plots did not give a linear relationship. However, assuming that  $\gamma=2.0$  in eq 1, the plots of  $[\log(1/r_2)-2.0E_R]$  against  $\sigma$ -constants were found to give a good linear relationship where  $\rho$  is 0.16 with 0.04 of a standard deviation, as shown in Figure 1(i). This result strongly suggests that the relative reactivities of itaconamate I toward polystyryl radical attacks are effected not only by resonance but also by the polar character of the nuclear-substituent, R. In the case of the copolymerization of itaconamate II or III with ST, similar tendencies could be observed. That is, the  $\rho$  and  $\gamma$  values were obtained as  $\rho=0.09\pm 0.06$ ,  $\gamma=$

$1.5\pm 0.06$  in the itaconamate II with ST and as  $\rho=0.13\pm 0.05$ ,  $\gamma=1.5\pm 0.05$  in the itaconamate III with ST. These results indicate that the relative reactivities,  $1/r_2$ , of ARPhIA toward an attack by a polystyryl radical slightly increase with an increase in the electron-withdrawing nature of the nuclear-substituent, R.

When the relative reactivities ( $1/r_2$ ) of itaconamate II toward an attack by a poly(MMA) radical were plotted against  $\sigma$ -constants in the modified Hammett equation (eq 1), a linear relationship between relative reactivities and  $\sigma$ -constants of the substituents could not be observed, as is evident from Figure 1(ii). In transforming eq 1,  $[\log(1/r_2)-\gamma E_R]$  (where  $\gamma=0.5$ ) was plotted against  $\sigma$ -constants. This plot, shown in Figure 1(ii), clearly indicates that the  $\rho$  value is almost zero, with 0.17 standard deviation. But in the copolymerization of itaconamate III with MMA, the  $\rho$  and  $\gamma$  values were obtained as  $\rho=-0.06\pm 0.15$ ,  $\gamma=0.4\pm 0.15$ . These findings strongly suggest that the relative reactivity of ARPhIA toward an attack by a poly(MMA) radical can be slightly effected both by the polar character of the nuclear-substituent, R, and the resonance character. This is at variance with the copolymerization of ARPhIA with ST. With respect to the  $\rho$  value, the reason for this may be that the poly(MMA) attacking radical has an electrophilic nature in contrast to the polystyryl attacking radical. But with respect to the  $\gamma$  value, no satisfactory explanation has yet been presented.

As can be seen from Table I, the  $Q$  values for ARPhIA are in between 0.50 and 2.35, and 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  $\sigma$ -constants of their substituents<sup>11</sup>; however, no linear relationship between the  $e_1$  value for ARPhIA and  $\sigma$ -constant has been observed. It may be reasonable 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.

$M_n$  could be calculated as  $10.7 \times 10^3 - 21.5 \times 10^3$  in the ARPhIA-ST copolymers and as  $13.9 \times 10^3 - 16.2 \times 10^3$  in the ARPhIA-MMA copolymers. In addition, there is a degree of polydispersion ( $M_w/M_n$ ) between 1.25 and 1.60; *i.e.*, each ARPhIA copolymer is in accordance with the monodisper-



**Figure 1.** Correlation of relative reactivity ( $1/r_2$ ) of ARPhIA toward an attack of a polystyryl radical or a poly(MMA) radical and  $\sigma$ -constants of the nuclear-substituents in ARPhIA: (i) I-ST; (ii) II-MMA. a, OCH<sub>3</sub>; b, CH<sub>3</sub>; c, H; d, Cl; e, COOC<sub>2</sub>H<sub>5</sub>.

sion system.

*Acknowledgements.* The authors wish to express their sincere appreciation to Professor Hiromu Murata of Hiroshima University for his helpful comments and encouragement. The authors are also very grateful to Mr. I. Seo, Mr. K. Yamamoto, Mr. S. Oda, and Mr. O. Nomura for their assistance in carrying out the experiments.

#### REFERENCES

1. T. Oishi, *Polym. J.*, **12**, 719 (1980).
2. T. Oishi, *Polym. J.*, **12**, 799 (1980).
3. T. Oishi, *Polym. J.*, **13**, 57 (1981).
4. T. Yamamoto and T. Otsu, *Chem. Ind. (Milan)*, 787 (1967).
5. L. Crombie, H. E. Hancock, Jr., and R. P. Liinstead, *J. Chem. Soc.*, **1953**, 3496.
6. S. Nagai and K. Yoshida, *Kobunshi Kagaku*, **17**, 77 (1960); *ibid.*, **17**, 79 (1960).
7. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).
8. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1954 (1944).
9. T. Alfrey, Jr., and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
10. G. E. Ham, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1964, p 695.
11. J. Furukawa and T. Tsuruta, *J. Polym. Sci.*, **36**, 275 (1959).