Vinyl Copolymerization. II. Copolymerization of Acrylonitrile with Styrene and Vinyl Acetate

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In the previous paper[1], an investigation of the rate of copolymerization of AN(acrylonitrile)-MM(methyl methacrylate) by the thermistor method[2] was reported. In this experiment, two pairs, i. e., AN-St (styrene) and VA (vinyl acetate)-AN have been chosen for rate measurement.

The procedure and the treatment of the experimental results are the same as those in previous paper[1]. For both of the copolymerization systems, the temperature was 20.0°C and the sensitizer for photopolymerization was 1, 1′-azobiscyclohexanecarbonitrile at a concentration of 7.56×10^{-3} mol./l. The necessary data for the calculation of the factor $1/\Delta t$, which is used for converting the rate of temperature increase into the rate of copolymerization, are shown in Table I.

TABLE I. VALUES OF CONSTANTS OF EACH MONOMER IN THE AN-St AND VA-AN SYSTEMS AT 20.0°C

	Copolymerization system	
	AN-St	VA-AN
Molecular weight, g./mol.		
M_1	53.06	86.05
M_2	104.14	53.06
Specific heat, cal./mol. °C		
H_1	26.53[3]	40.50[7]
H_2	43.31[4]	26.53[3]
Specific gravity, g./cc.		
S_1	0.8060[3]	0.9319[8]
S_2	0.9050[5]	0.8060[3]
Reactivity ratio		
r_1	0.04[6]	0.06[9]
r_2	0.41[6]	4.05[9]

Results and Discussion

Heat of Copolymerization.—The values of the rate of temperature rise, the rate of copolymerization, ΔH_c and $\Delta H_{12}+\Delta H_{21}$ are shown in Table II and III. Details of the meaning and calculation of these quantities were described in the previous paper[1].

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1) M. Suzuki, H. Miyama and S. Fujimoto, This Bulletin, **35**, 57 (1962).

2) H. Miyama, ibid., **29**, 711 (1956).

3) H. S. Davis and O. F. Wiedman, *Ind. Eng. Chem.*, 37, 482 (1945).

4) R. H. Boundy and R. F. Boyer, " Styrene ", Reinhold. New York (1952), p. 67.

5) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **67**, 1701 (1945).

6) F. M. Lewis, F. R. Mayo and W. F. Hulse, ibid., **67**, 1701 (1945).

7) W. I. Bengough and H. W. Melville, *Proc. Roy. Soc.*, **A225**, 330 (1954).

8) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 2610 (1949).

9) F. R. Mayo, F. M. Lewis, C. Walling and W. F. Hulse, ibid., **70**, 1523 (1948).

TABLE II. VALUES OF RATE OF TEMPERATURE RISE, RATE OF COPOLYMERIZATION, ΔH_c AND $\Delta H_{12}+\Delta H_{21}$ IN THE AN-St SYSTEM AT 20.0°C

Mole fraction of AN f_1	Rate of temp. rise 10^{-2} °C/sec.	Rate of copolymerization 10^{-4} mol./l. sec.	ΔH_c kcal./mol.	$\Delta H_{12}+\Delta H_{21}$ kcal./mol.
1.0	1.83	4.61	16.03 ($=\Delta H_{11}$)	
0.94	0.65	1.57	16.48	33.75
0.88	0.59	1.40	16.67	33.60
0.72	0.51	1.19	16.81	33.67
0.64	0.50	1.13	17.29	34.63
0.54	0.50	1.10	17.62	35.66
0.30	0.40	0.85	17.92	37.10
0.16	0.29	0.65	16.99	34.30
0	0.20	0.45	16.73 ($=\Delta H_{22}$)	
				Av. 34.67

TABLE III. VALUES OF RATE OF TEMPERATURE RISE, RATE OF COPOLYMERIZATION, ΔH_c AND $\Delta H_{12}+\Delta H_{21}$ IN THE VA-AN SYSTEM AT 20.0°C

Mole fraction of VA f_1	Rate of temp. rise 10^{-2} °C/sec.	Rate of copolymerization 10^{-4} mol./l. sec.	ΔH_c kcal./mol.	$\Delta H_{12}+\Delta H_{21}$ kcal./mol.
1.0	2.03	3.96	22.49 ($=\Delta H_{11}$)	
0.87	0.56	1.22	19.81	40.45
0.63	0.78	1.84	18.08	38.98
0.42	0.88	2.18	17.00	35.51
0.32	0.97	2.37	17.00	35.45
0.23	0.98	2.38	17.28	40.40
0.07	1.30	3.04	17.29	58.80*
0	1.90	4.56	16.80 ($=\Delta H_{22}$)	
				Av. 38.15

* Note: This value is omitted in calculating the average value of $\Delta H_{12}+\Delta H_{21}$ because of its large deviation.

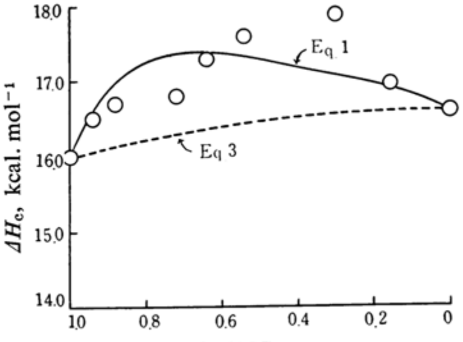

Fig. 1. Variation of ΔH_c with f_1 in the AN-St system.
○ experimental values
Note: f_1 is a mole fraction of AN in the feed.

By using these results and Alfrey's equation[10], the heat of copolymerization ΔH_c can be expressed as follows:

$$\Delta H_c = 1.02\left[1-(1-3.93F_1F_2)^{1/2}\right] + 16.03F_1 + 16.73F_2 \quad \text{for AN-St} \qquad (1)$$

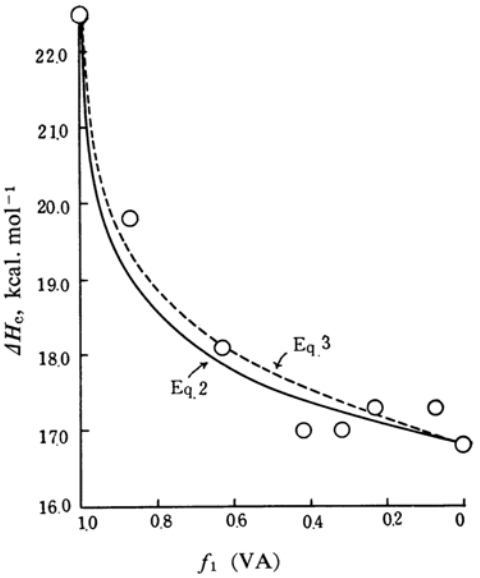

Fig. 2. Variation of ΔH_c with f_1 in the VA-AN system.
○ experimental values
Note: f_1 is a mole fraction of VA in the feed.

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[10] T. Alfrey, *J. Polymer Sci.*, **4**, 222 (1949).

$$\Delta H_c = -0.76\,[1-(1-3.03F_1F_2)^{1/2}] + 22.49F_1 + 16.80F_2 \quad \text{for VA-AN} \quad (2)$$

As shown in Figs. 1 and 2, the values of ΔH_c in Tables II and III agree with the full lines expressing Eqs. 1 and 2. The dashed lines in these figures are drawn according to the following equation:

$$\Delta H_c = F_1\Delta H_{11} + F_2\Delta H_{22} \quad (3)$$

Rate of Copolymerization.—In Tables IV and V, the values of $1/\Delta t$, the rate of copolymerization and ϕ are shown, the details of calculation of which were shown in the previous paper[1].

TABLE IV. VALUES OF $1/\Delta t$, THE RATE OF COPOLYMERIZATION AND ϕ IN THE AN-St SYSTEM AT 20.0°C

Mole fraction of AN f_1	$1/\Delta t$ 10^{-2} mol./l. °C	Rate of copolymerization 10^{-4} mol./l. sec.	ϕ_{exp}
1.00	2.53	4.48	
0.94	2.37	1.54	19
0.88	2.30	1.38	28
0.72	2.27	1.18	53
0.64	2.26	1.06	77
0.54	2.24	1.05	76
0.30	2.23	0.78	120
0.16	2.22	0.62	186
0	2.26	0.50	
			Av. 80

TABLE V. VALUES OF $1/\Delta t$, THE RATE OF COPOLYMERIZATION AND ϕ IN THE VA-AN SYSTEM AT 20.0°C

Mole fraction of VA f_1	$1/\Delta t$ 10^{-2} mol./l. °C	Rate of copolymerization 10^{-4} mol./l. sec.	ϕ_{exp}
1.00	1.95	4.97	
0.87	2.27	1.41	11
0.63	2.38	1.83	19
0.42	2.41	2.19	49
0.32	2.41	2.34	83
0.23	2.39	2.70	103
0.07	2.39	3.01	488*
0	2.40	4.08	
			Av. 53

* Note: This value is omitted in calculating the avevage value of ϕ because of it's large deviation.

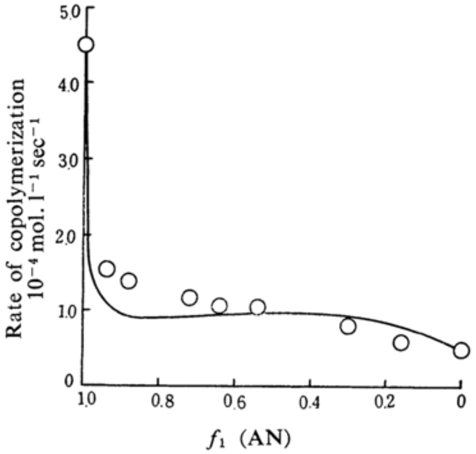

Fig. 3. Variation of rate of copolymerization with f_1 in the AN-St system.

○ experimental values
— Walling's equation with $\phi=80$

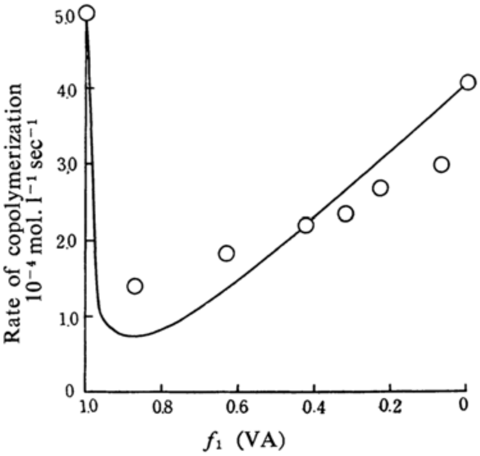

Fig. 4. Variation of rate of copolymerization with f_1 in the VA-AN system.

○, experimental values
—, Walling's equation with $\phi=15$

As shown in Figs. 3 and 4, the theoretical curves obtained by substituting $\phi=80$ and $\phi=53$ (average values of ϕ_{exp}) into Walling's equation[11] agree with the experimental values. However, in order to explain the non-constancy of ϕ, the application of Arlman's[12] equation to these data must be considered. In the AN-St system, the curve shown in Fig. 5 was constructed by using Arlman's equation. The value of χ[1,12] is 0.05, and the corresponding value of ϕ_n[1,12] is 266. By using termination constants k_{taa} and k_{tbb} of each monomer alone, normal cross-termination constant k_{tbba} and constant k_{taba} of the cross-termination reaction having a penultimate unit are calculated[1]. These values are shown in Table VI.

Here, we took the values of k_{taa} and k_{tbb} at 25°C because the termination constant of AN is known only at 25°C and no activation energy

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[11] F. M. Lewis and C. Walling, *J. Am. Chem Soc.*, **71**, 747 (1949).

[12] J. Arlman and H. W. Melville, *Proc. Roy. Soc.*, **A203**, 301 (1950).

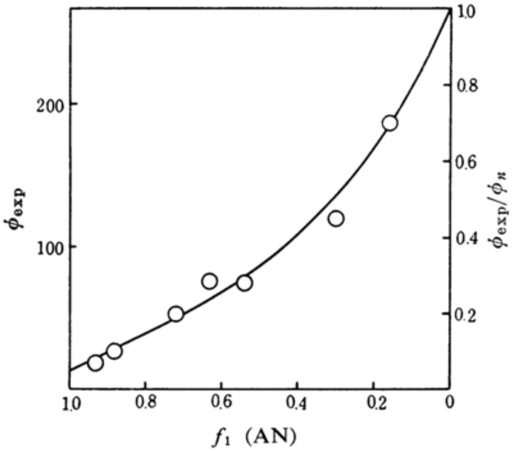

Fig. 5. Variation of ϕ_{exp} and ϕ_{exp}/ϕ_n with f_1 in the AN-St system.

○ experimental values
— Arlman's equation with $\chi=0.05$ and $r_2=0.41$

TABLE VI. VALUES OF k_{taa}, k_{tbb}, k_{tbba} AND k_{taba} FOR AN-St SYSTEM AT 25°C

$k_{taa}=1.22\times10^7$ 13) $k_{tbb}=2.79\times10^6$ 14)
$k_{tbba}=1.55\times10^9$ $k_{taba}=7.75\times10^7$

is available. From the results of Table VI, it is obvious that in the AN-St system, termination constants for mixed radicals are larger than those for homogeneous radicals and that the ratio of the normal cross-termination constant to the constant of the cross-termination having a penultimate unit is 20.

On the other hand, in the VA-AN system, the application of Arlman's equation was impossible. As explained in the case of the St-VA system[15], this seems to be due to the large difference between the reactivity ratios of the two monomers, which difference causes a large error limit in the calculated values of ϕ.

Summary

Rates of copolymerization of AN-St and VA-AN for various mixing ratios of the two monomers were measured by the thermistor method. The heat of copolymerization, which was obtained by comparing the results of the thermistor method with those of the usual analytical method, agrees very well with Alfrey's equation. Also, the non-constancy of ϕ in the AN-St system can be explained by Arlman's theory; it is concluded that the termination constants for mixed radicals are larger than those for homogeneous radicals and, furthermore, that the ratio of a normal cross-termintion constant to a constant of the cross-termination having a penultimate unit is 20.

However, in the VA-NA system, the application of Arlman's equation was impossible because the large difference between the reactivity ratios of the two monomers causes a large error limit in the calculated values of ϕ.

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13) W. I. Bengough, *J. Polymer Sci.*, **28**, 476 (1958).

14) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* **A193**, 309 (1948).

15) M. Suzuki, H. Miyama and S. Fujimoto, *J. Polymer Sci.*, 37, 533 (1959).