Vinyl Copolymerization. I. Copolymerization of Acrylonitrile with Methyl Methacrylate

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In previous papers[1,2], investigations on the rate of copolymerization of VA (vinyl acetate)-MM (methyl methacrylate), St (styrene)-VA and MM-St by the thermistor method[3] were reported. Usually the rate of copolymerization is measured by weighing the copolymer's weight in the copolymerization system after a difinite time of reaction, but this method is not accurate because the concentration of each monomer changes during this definite period. On the other hand, the thermistor method can measure accurately the initial rate of copolymerization within ten seconds. In the VA-MM and St-VA systems, the large difference between the reactivity ratios of the two monomers caused a large error limit of ϕ, the ratio of the rate constant for "crossed" termination to the geometric mean of the rate constants of the chain termination of each monomer alone, so that we could not find any essential regularities in the variation of ϕ with successive mixing ratios. In the MM-St system, however, where the difference of the two reactivity ratios is not so large, we could determine the value of ϕ more precisely and obtain a concrete confirmation of Arlman's theory[4].

In this experiment, an AN (acrylonitrile)-MM pair was chosen for the rate measurement.

Experimental

The procedure and the treatment of the experimental results are almost the same as those described in detail in previous papers[1-3]. The temperature was 30.5°C and the fluctuation of the thermostat temperature was controlled within ±0.001°C. The sensitizer for photopolymerization was 1,1′-azobiscyclohexanecarbonitrile at a concentration of 7.56×10^{-3} mol./l.

The rate of polymerization was found by multiplication of the rate of temperature increase by the factor $1/\Delta t$ as follows[1,2]:

$$1/\Delta t=(S\times H)/(\Delta H_c\times M) \tag{1}$$

Here, M, H, S and ΔH_c are molecular weight, specific heat, specific gravity and heat of polymerization, respectively, of the copolymerization system. The quantities M, H and S are related by:

$$M=(M_1f_1+M_2f_2)/(f_1+f_2) \tag{2}$$

$$H=(H_1f_1+H_2f_2)/(f_1+f_2) \tag{3}$$

$$S=(M_1f_1+M_2f_2)S_1S_2/(S_2M_1f_1+S_1M_2f_2) \tag{4}$$

in which f's are the mole fractions of each monomer. According to Alfrey[4], ΔH_c is given by the following equation:

$$\Delta H_c=\frac{1-[1-F_2(1-F_2)(1-r_1r_2)]^{1/2}}{2(1-r_1r_2)}\times(\Delta H_{12}+\Delta H_{21}-\Delta H_{11}-\Delta H_{22})+F_1\Delta H_{11}+F_2\Delta H_{22} \tag{5}$$

in which F's are the mole frations of each monomer in copolymer, r's are the reactivity ratios of each monomer, and the suffixes 1 and 2 denote the values of each monomer. ΔH_{11}, ΔH_{12}, ΔH_{21} and ΔH_{22} are heats of copolymerization corresponding to the following four different chain-propagation processes between monomers (M_1 or M_2) and radicals (M_1^* or M_2^*).

$$-M_1^* + M_1 \rightarrow -M_1-M_1^* \qquad \Delta H_{11}$$
$$-M_1^* + M_2 \rightarrow -M_1-M_2^* \qquad \Delta H_{12}$$
$$-M_2^* + M_1 \rightarrow -M_2-M_1^* \qquad \Delta H_{21}$$
$$-M_2^* + M_2 \rightarrow -M_2-M_2^* \qquad \Delta H_{22}$$

Although the values of ΔH_{11} and ΔH_{22} can be measured for the polymerization of each monomer alone, nothing is known about the values of ΔH_{12} and ΔH_{21}. As described in previous papers[5,6], the values of $\Delta H_{12}+\Delta H_{21}$, and also ΔH_c, can be obtained by comparing the rate of temperature rise with the rate of copolymerization. The rate of the temperature rise was measured every minute for 15 min. by the thermistor method, and the rate of copolymerization was obtained from the results of

TABLE I. VALUES OF CONSTANTS OF EACH MONOMER IN AN-MM SYSTEM AT 30.5°C

$M_1=53.06$	$M_2=100$	g./mol.
$H_1=26.53$[7]	$H_2=49.00$[8]	cal./mol. °C
$S_1=0.7944$[7]	$S_2=0.9305$[9]	g./cc.
$r_1=0.18$[10]	$r_2=1.35$[10]	

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[1] M. Suzuki, H. Miyama and S. Fujimoto, *J. Polymer Sci.*, **32**, 445 (1958).

[1] Ibid., **37**, 533 (1959).

[3] H. Miyama, This Bulletin, **29**, 711 (1956).

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

[5] M. Suzuki, H. Miyama and S. Fujimoto, ibid., **31**, 212 (1958).

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[9] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949).

[10] F. M. Lewis and W. F. Hulse, ibid., **67**, 170 (1945).

TABLE II. VALUES OF RATE OF TEMPERATURE RISE, RATE OF COPOLYMERIZATION, ΔH_c AND $\Delta H_{12}+\Delta H_{21}$ AT 30.4°C

Mole fraction of AN f_1	Rate of temp. rise 10^{-3} °C/sec.	Rate of copolymerization 10^{-4} mol./l. sec.	ΔH_c kcal./mol.	$\Delta H_{12}+\Delta H_{21}$ kcal./mol.
0	5.60	1.87	13.65 ($=\Delta H_{22}$)	
0.15	5.00	1.70	13.22	23.17
0.29	5.15	1.65	13.86	28.31
0.41	5.27	1.65	14.00	29.11
0.52	5.31	1.60	14.35	29.18
0.62	5.53	1.58	14.92	29.96
0.79	7.05	2.01	14.53	27.75
0.94	13.10	3.26	16.25	31.38
1.00	23.94	5.68	16.75 ($=\Delta H_{11}$)	
				Av. 28.40

analysis in which the copolymerization system was dissolved in a mixture of acetone and dimethylformamide after the photocopolymerization had proceeded 15 min.

In Table I, the necessary data for the calculation of $1/\Delta t$ are shown.

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. Details of the calculation of ΔH_c and $\Delta H_{12}+\Delta H_{21}$ have been described in previous papers[5,6].

From the fact that the values of $\Delta H_{12}+\Delta H_{21}$ are almost constant in Table II, the application of Eq. 5 in this system seems reasonable. By substituting the average value 28.40 kcal./mol. of $\Delta H_{12}+\Delta H_{21}$, the values of ΔH_{11} and ΔH_{22} of Table II and the values of r_1 and r_2 of Table I in Eq. 5, ΔH_c can be expressed as follows:

$$\Delta H_c = -1.32\,[1-(1-3.03F_1F_2)^{1/2}] + 16.75F_1 + 13.65F_2 \qquad (6)$$

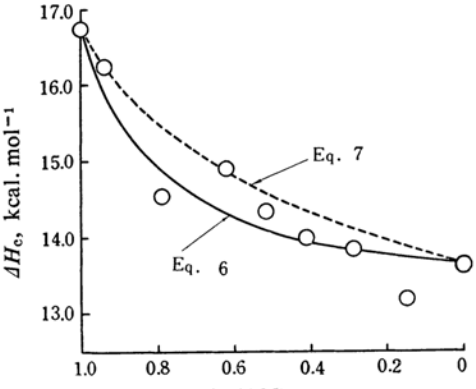

Fig. 1. Variation of ΔH_c with f_1.
○ Experimental values
Note: f_1 is a mole fraction of AN in the feed.

As shown in Fig. 1, the values of ΔH_c in Table II agree with the full line expressing Eq. 6. The dashed line in this figure is drawn by using the following equation:

$$\Delta H_c = F_1\Delta H_{11} + F_2\Delta H_{22} \qquad (7)$$

The results of calculation by using 6 and 7 give almost the same curve as shown in Fig. 1. Therefore, the application of 7 instead of 6 in this systems seem approximately correct.

Rate of Copolymerization. — In Fig. 2, the values of $1/\Delta t$ calculated from Eq. 1 are plotted against f_1, where Eq. 6 is used to obtain the value of ΔH_c. The values of the rate of polymerization as shown in Table III were calculated by a multiplication of the rate of temperature increase by this factor, $1/\Delta t$, where the rate of temperature increase was measured within 10 sec. of the instant polymerization starts by the thermistor method.

As shown in Fig. 3, the rate is minimum at the molar fraction of about 0.7 of AN. The

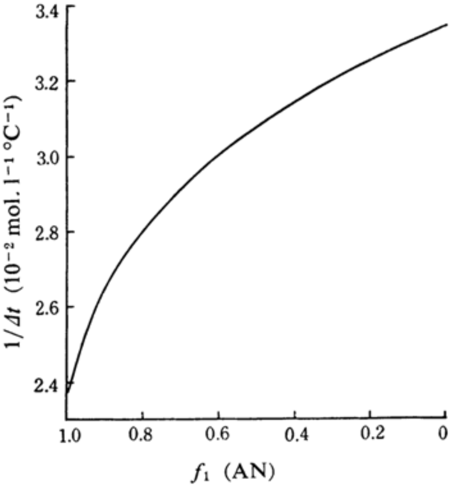

Fig. 2. Variation of $1/\Delta t$ with f_1.

TABLE III. VALUES OF THE RATE OF COPOLYMERIZATION AND ϕ VALUES

Mole fraction of AN f_1	Rate of copolymerization 10^{-4} mol./sec. l.	ϕ_{exp}
0	1.96	
0.15	1.72	24
0.29	1.69	18
0.41	1.69	16
0.52	1.68	15
0.62	1.66	14
0.79	1.83	10
0.94	2.51	6
1.00	4.94	
		Av. 15

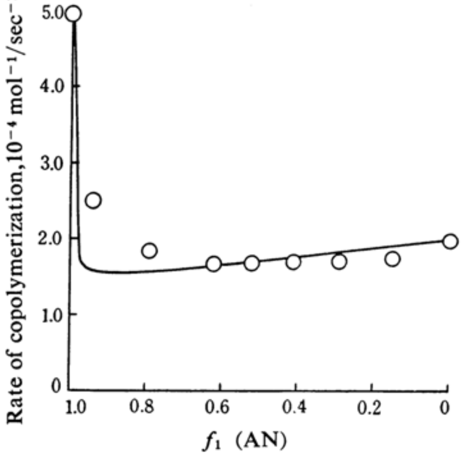

Fig. 3. Variation of rate of copolymerization with f_1.

○ Experimental values

— Walling's equation with $\phi=15$

rate of copolymerization is given by the following equation of Walling[11]:

$$V=\frac{(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2)I^{1/2}}{\left\{\begin{array}{c}(\delta_1^2r_1^2[M_1]^2+2\phi\delta_1\delta_2r_1r_2[M_1][M_2]\\+\delta_2^2r_2^2[M_2]^2)^{1/2}\end{array}\right\}} \tag{8}$$

The nomenclature of which is described in detail in Walling's paper[11] or in our previous papers[1,2]. Although ϕ in this equation should be constant, the values of ϕ calculated from Walling's equation (expressed as ϕ_{exp} in Table III) vary with the mole fraction of AN. The theoretical curve obtained by substituting $\phi=15$ (the average value of ϕ_{exp} in Table III) into Eq. 8 agrees with the experimental values as shown in Fig. 3. However, in order to explain the nonconstancy of ϕ, the application of Arlman's equation[12] to these data must be considered[2]. Arlman considered in his theory the following two cross-termination reactions:

$$\text{(I)} \qquad \sim\!\sim\!\sim\, \mathrm{BB}\cdot + \cdot\mathrm{A}\, \sim\!\sim\!\sim \qquad k_{\mathrm{tbba}}$$

$$\text{(II)} \qquad \sim\!\sim\!\sim\, \mathrm{AB}\cdot + \cdot\mathrm{A}\, \sim\!\sim\!\sim \qquad k_{\mathrm{taba}}$$

Reaction I is a usual cross-termination reaction, but in reaction II the existence of the penultimate unit A in the first free radical somewhat retards the termination reaction. Postulating these reactions, Arlman derived the equation:

$$(f_1\chi+r_2f_2)/(f_1+r_2f_2)=\phi_{\mathrm{exp}}/\phi_n \tag{9}$$

χ and ϕ_n are related by:

$$\chi=k_{\mathrm{taba}}/k_{\mathrm{tbba}}<1 \tag{10}$$

$$1/\phi_n=(k_{\mathrm{taa}}k_{\mathrm{tbb}})^{1/2}/k_{\mathrm{tbba}} \tag{11}$$

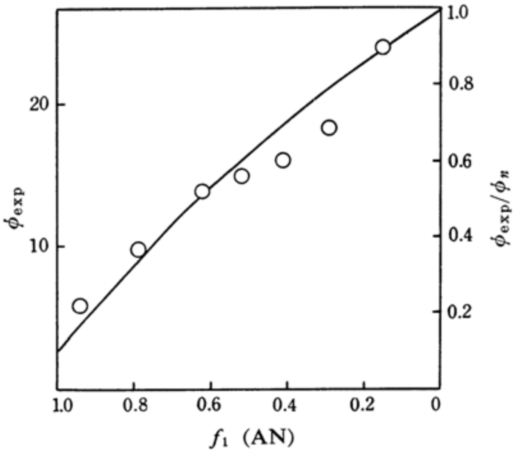

Fig. 4. Variation of ϕ_{exp} and $\phi_{\mathrm{exp}}/\phi_n$ with f_1.

○ Experimental values

— Arlman's equation with $\chi=0.1$ and $r_2=1.35$.

Here, k_{taa} and k_{tbb} are the termination constants of each monomer, and ϕ_{exp} is obtained from experimental data by a calculation according to Wallings' equation. Using Eq. 9, the curve shown in Fig. 4 was constructed; a χ with which the experimental and theoretical value in this figure agreed most satisfactorily was chosen. This value of χ is 0.1, and the corresponding value of ϕ_n is 27. Since k_{taa} and k_{tbb}, the termination constants of AN and MM, are known, k_{tbba} can be calculated by the substitution of these values and $\phi_n=27$ in Eq. 11. We took k_{taa} as 1.22×10^7 [13] and k_{tbb} as 2.32×10^7 [9] respectively at 25°C because no activation energy is available for the termination constant of AN, and, therefore, correction to the values for our polymerization temperature 30.5°C is impossible. The resulting value was $k_{\mathrm{tbba}}=4.55\times10^8$. From

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[11] F. M. Lewis and C. Walling, ibid., **71**, 747 (1949).

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

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

Eq. 10, using $\chi=0.1$, $k_{\mathrm{taba}}=4.55\times10^{7}$ was obtained. Therefore, the termination constants for mixed radicals are larger than those for homogeneous radicals, and furthermore, the rate constant of reaction I is about ten times as large as that of reaction II.

Summary

Rates of copolymerization, of AN-MM 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 can be explained by Arlman's theory. It is concluded that the termination constants for mixed radicals are larger than those homogenous radicals and, furthermore, that the rate constant for a normal cross-termination reaction is about ten times as large as that of the cross-termination reaction having a penultimate unit.

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