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The Critical Miscibility Composition of Styrene-Acrylonitrile-Methyl Methacrylate Terpolymers

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ABSTRACT

Ternary statistical copolymers composed of styrene, acrylonitrile, and methyl methacrylate were synthesized and fractionated by a precipitational method. For a given polymer concentration, the volume fraction of nonsolvent, i.e., methanol, at the precipitation point, γ, increases in the order: polystyrene < acrylonitrile-styrene and acrylonitrile-methyl methacrylate binary copolymers < ternary copolymers. The γ values in methanol-dimethylformamide (DMF) mixture are larger than those in methanol-butanone, indicating that DMF is a better solvent for the terpolymer. A linear relation was obtained between the reciprocal limiting viscosity number and γ values of fractions. The dependence of γ on the terpolymer composition could not be established exactly in these systems. The temperature coefficient of γ, $d\gamma/dT$, increases with the MMA content and decreases with the styrene content in terpolymers both in butanone and in DMF mixtures.

The solution properties of binary copolymers have been discussed for the systems styrene and acrylonitrile [1-3] and acrylonitrile and methyl methacrylate [4]. In the present paper we extended this work to a terpolymer system composed of styrene (S), acrylonitrile (AN), and methyl methacrylate (MMA). Polymerization kinetics of terpolymerization has been studied theoretically [5-7] and examined numerically using a computer [8, 9]. The relation between the monomer reactivity ratios and the terpolymer composition of the S-AN-MMA terpolymer has been studied [10, 11].

A pair of solvent and nonsolvent for the fractional precipitation of a polymer sample is often chosen empirically. The fractionation of copolymers usually depends not only on the molecular weight, but also on the copolymer composition. We have fractionated the binary copolymers under various conditions (see Table 1). In the case of ternary copolymers we shall discuss the multicomponent fractional system by considering the phase diagram. The theta temperature ϑ was identified by Flory [12] as the critical miscibility temperature for infinite molecular weight considering the chemical potentials for equilibrium between two phases in a binary system. For equilibrium between two liquid phases in a system of three components, the limiting critical composition γ_ϑ is analogeous to the ϑ point in a two-component system. At the limiting critical point, the second coefficient in the virial expansion of the osmotic pressure becomes zero. In this paper this limiting critical composition is obtained experimentally and its relation to the terpolymer composition is discussed.

TABLE 1. Fractionation Conditions of the Binary Copolymers at 30°C

Polymer	Composition mole fraction		Solvent	Nonsolvent	Ref.
AN-S copolymer (Co-1) azeotrope	AN	0.383	Chloroform	Methanol	1-3
AN-S copolymer (Co-2)	AN	0.626	DMF	"	1-3
AN-MMA copolymer azeotrope	AN	0.48	Acetone	"	4
Polystyrene			Toluene	"	3
Polymethyl methacrylate			Acetone	"	4

EXPERIMENTAL

Materials

Polymerization conditions of the binary copolymers were shown in Table 1. The monomer mixtures of different ratios, shown in Table 2, were diluted with the same volume of DMF. Terpolymerization was carried out at 60° C under nitrogen atmosphere, α,α'-azobisisobutyronitrile (AIBN) being used as an initiator. Conversion was determined by precipitation with methanol every hour.

TABLE 2. Terpolymerization Condition at 60° C

Terpolymer No.	Monomer feeds mole fraction S	Monomer feeds mole fraction AN	Monomer feeds mole fraction MMA	Initiator conc, $c \times 10^{-2}$ (mole %)	Reaction time (min)	Yield (wt%)	Rate const, $k \times 10^3$ (min^{-1})
T1	0.263	0.455	0.282	0.486	300	53.7	1.96
T2	0.642	0.308	0.050	0.534	347	44.8	1.72
T3	0.167	0.284	0.549	0.538	411	55.4	2.03
T4	0.147	0.693	0.160	0.467	420	68.6	2.95
T5	0.516	0.295	0.189	0.535	480	48.2	1.57
T6	0.147	0.527	0.326	0.463	480	70.4	2.42
T7	0.55	0.15	0.30	0.580	420	37.3	1.20
T8	0.62	0.20	0.18	0.565	482	41.7	1.29

Fractionation

Fractionations of the binary copolymers were described previously. Fractional precipitation of terpolymers was carried out in 5 wt% solutions in butanone with methanol as nonsolvent. Twenty fractions were obtained for each terpolymer. The reprecipitation yield of the fractionation is 92-97% by weight. The phase diagram for the system composed of solvent-nonsolvent-polymer is shown in a triangular coordinate system. The volume fraction of nonsolvent in solvent mixture at the precipitation point, γ, for a given polymer concentration was determined by titration at constant temperature. The precipitation point was determined as the average of the concentrations at appearance of turbidity due to one drop of methanol and disappearance of the cloud on adding solvent.

Viscosity

The viscosity of the solutions was measured at 35°C with an Ubbelohde capillary viscometer; kinetic energy corrections were negligibly small. Butanone and DMF were used as solvents for viscosity measurements. The limiting viscosity number is determined by use of the Huggins equation. Figure 1 shows Huggins' plots for

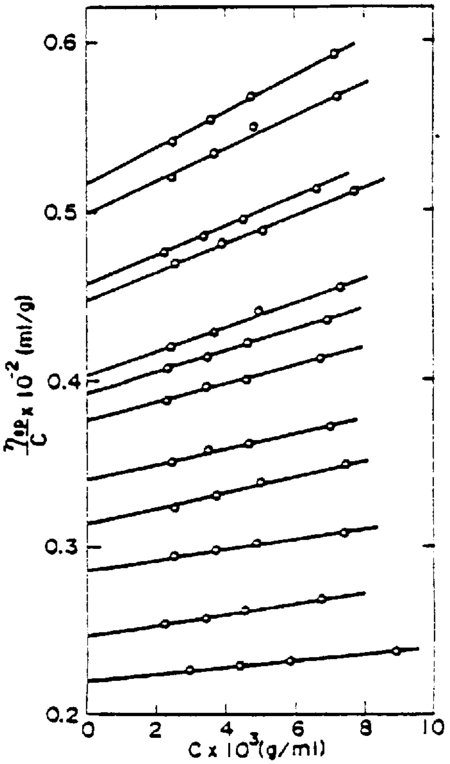

FIG. 1. The relationship of the reduced viscosity η_{sp}/c vs concentration c for fractions of T5. Curves from top to bottom are for F-2, F-4, F-6, F-8, F-10, F-12, F-14, F-16, F-18, F-20, F-22, and F-24.

fractions of T5, for example. The limiting viscosity number decreases with fraction number.

IR Spectrum

IR absorption of the polymer film was measured using a Hitachi-215 Spectrometer. The absorption maxima at 2250, 1730, and 1603 cm^{-1} are assigned to AN, MMA, and S components, respectively. A typical IR spectrum for T5 F-8 is indicated in Fig. 2.

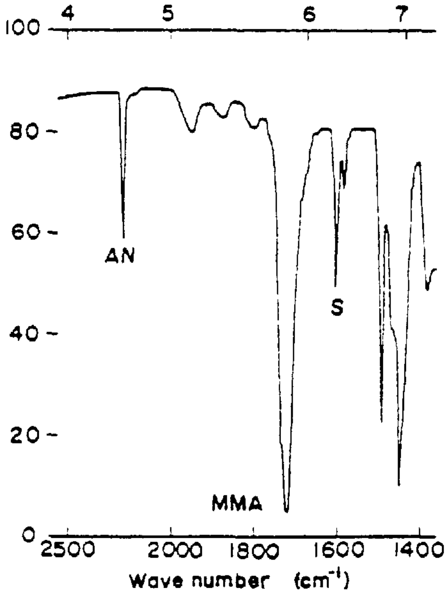

FIG. 2. IR spectrum for the S-AN-MMA terpolymer, T5 F-8.

RESULTS AND DISCUSSION

Terpolymerization

As a result of the kinetic analysis of terpolymerization, the first-order reaction rate constant (k) is determined from the slope of the lines plotted in Fig. 3 according to

$$\log c = \log c_0 - \frac{k}{2.303} t \qquad (1)$$

The concentration (c) is expressed by the total weight of the unreacted monomers in unit volume of solution instead of by the usual expression in mole/liter. Figure 3 shows that the rate constant increases with the AN content and decreases with the MMA content of the monomer feeds. The effect of AN on the rate constant is more significant than that of MMA.

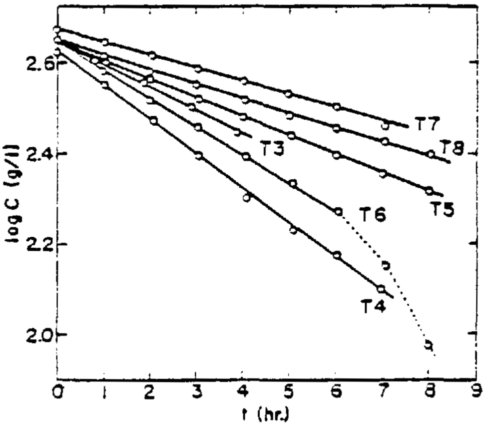

FIG. 3. Relationship between unreacted monomer concentration and terpolymerization time.

Composition of Terpolymer

Ham [11] has introduced the concept of "partial azeotrope," which corresponds to the condition that the relative monomer composition M_1/M_2 or M_1/M_3 does not change in the course of terpolymerization. The solid line in Fig. 4 shows a "partial azeotrope" having constant M_S/M_{MMA} according to Eq. (2), and the dotted line shows the constant M_S/M_{AN} monomer ratio by Eq. (3), using the following values of reactivity ratios: $r_{12} = 0.41$, $r_{21} = 0.04$, $r_{31} = 0.46$, $r_{13} = 0.52$, $r_{23} = 0.15$, and $r_{32} = 1.22$.

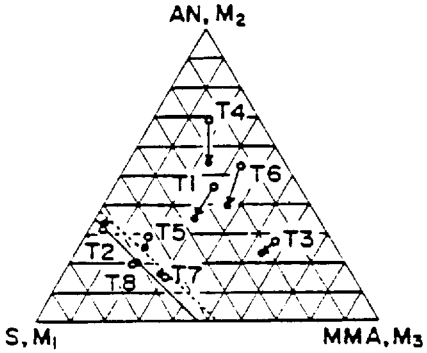

FIG. 4. Terpolymer compositions obtained by IR (●) and monomer feeds at the beginning of the terpolymerization (○). (——) Constant M_1/M_3 in monomer and terpolymer, and (···) constant M_1/M_2 in monomer and terpolymer.

$$\frac{M_1}{M_2} = \frac{(M_3/M_2)(1/r_{21}r_{13} - 1/r_{12}r_{23}) + (1/r_{12})(1/r_{21} - 1)}{(1/r_{21})(1/r_{12} - 1)} \tag{2}$$

$$\frac{M_1}{M_3} = \frac{(M_2/M_3)(1/r_{12}r_{31} - 1/r_{13}r_{32}) + (1/r_{13})(1/r_{31} - 1)}{(1/r_{31})(1/r_{13} - 1)} \tag{3}$$

where M_1 is for S, M_2 is for AN, and M_3 is for MMA.

According to Ham's idea that most ternary systems exhibiting "near azeotropic" behavior contain at least two binary azeotropic systems, the present terpolymers T2, T7, and T8 should behave as "near azeotropes." The terpolymers T7 and T8 were polymerized from the constant monomer feeds ratios M_1/M_2 and M_1/M_3, respectively, so as to get the "partial azeotropes." Therefore, the composition of terpolymers was calculated from IR data by keeping the mole ratios AN/S of T7 and MMA/S of T8 equal to the monomer feed ratios, as shown in Table 3 and Fig. 4. The composition of terpolymer approaches the two lines representing "partial azeotropes."

Fractionation

The integral curves of the fractionation were obtained as function of γ, and representative data are shown in Fig. 5, where terpolymer

TABLE 3. The Composition of Terpolymers Calculated from IR data

Polymer No.	Mole fraction		
	S	AN	MMA
T1	0.37	0.35	0.27
T2	0.62	0.34	0.04
T3	0.23	0.23	0.54
T4[a]	0.29	0.52	0.18
T4[b]	0.21	0.55	0.23
T5	0.56	0.25	0.19
T6	0.23	0.40	0.37
T7	0.57	0.16	0.27
T8	0.61	0.20	0.19

[a] Without the upper part of the curve in Fig. 6.

[b] Unfractionated sample.

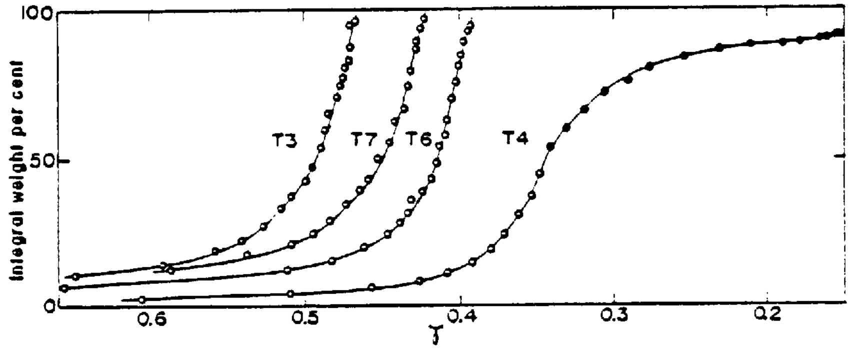

FIG. 5. Fractionation curves of terpolymers against the volume fraction of nonsolvent in solvent mixture: molecular weight fractionation (○), and composition fractionation (●).

T4 indicates an inflection point. The integral curves plotted against the limiting viscosity number are shown in Fig. 6. Figure 6 proves that the fractionations were due mainly to the molecular weight except for one case (T4).

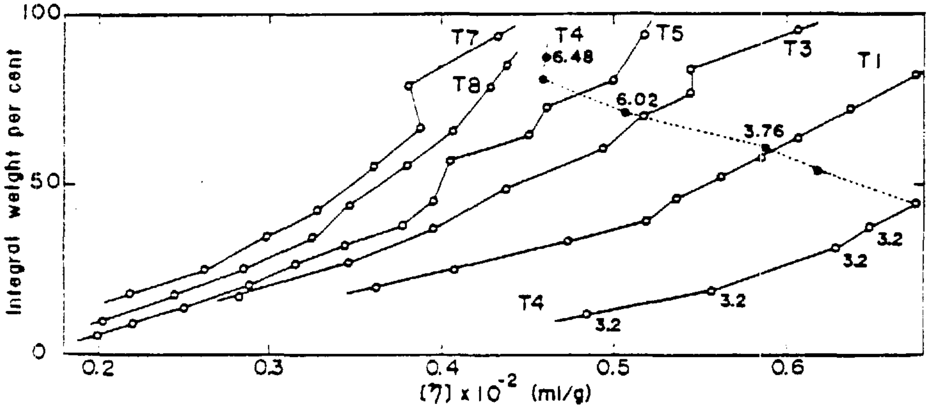

FIG. 6. Fractionation curves of terpolymers: numbers beside the T4 curve are the absorbance ratios D_{2250}/D_{1603} of IR; $[\eta]$ measured in butanone at 35° C; molecular weight fractionation (○), and composition fractionation (●).

The absorbance ratios D_{2250}/D_{1603} and D_{1730}/D_{1603} of the IR spectrum were used to eliminate the film thickness effect and to compare the relative compositions of AN and MMA in terpolymer fractions. The above ratios are constant to all fractions of a terpolymer except T4 within the experimental errors of IR spectroscopy. The ratio D_{2250}/D_{1503} for T4, written beside the curve for T4 in Fig. 6, changes for fractions. The AN content distribution curve was obtained from the analytical IR data and is shown in Fig. 7. At the initial stage of terpolymerization the products are of relatively uniform composition, corresponding to the sharp peak of the distribution curve at the lower concentration of AN. At later stages the composition of the products moves to higher concentrations, producing a long tail of the curve. T4 was precipitated first during fractionation due to the composition difference at the tail of the distribution curve, and it was fractionated according to the difference in molecular weight. Polyacrylonitrile (PAN) is not soluble in butanone, so the AN-rich T4 polymer is poorly soluble in butanone. DMF is a good solvent for PAN, but the DMF-methanol-T4 system did not cause a marked phase separation at room temperature. Hence DMF was not useful for fractionation in this case. The γ value determined during the course of fractionation depends on the polymer concentration. Although empirical relationships between γ and polymer concentration have been reported [13, 14], it is rigorous to get the phase diagram by changing the

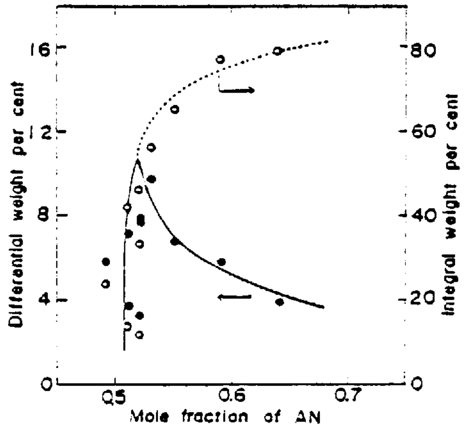

FIG. 7. The AN-content distribution curve for T4: integral weight per cent (○), and differential weight per cent (●).

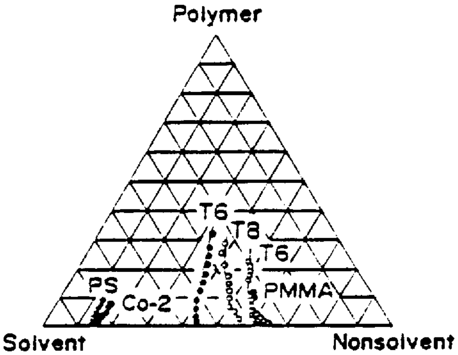

FIG. 8. Phase diagram for solvent-nonsolvent-polymer system: in butanone-methanol (●), in DMF-methanol (○).

polymer concentration at constant temperature. The phase diagrams at 35° C are shown in Fig. 8. The AN-S copolymer gives the curve close to that of PS, and the terpolymers have curves similar to PMMA. The copolymerization improves the solubility of polystyrene but not that of polymethyl methacrylate, both in DMF and butanone.

Values of 0.333 to 0.413 are obtained for γ at 35° C for the terpolymers

TABLE 4. The Volume Fraction of the Precipitant in Solvent Mixture, γ, at 35°C and the Temperature Coefficient of γ, $d\gamma/dT$

Polymer No.	γ_0 in butanone	γ in DMF	$d\gamma/dT \times 10^3$ in butanone	$d\gamma/dT \times 10^3$ in DMF
T1	0.398	0.641	2.24	1.56
T2	0.371	0.626	1.44	0.83
T3	0.413	0.628	3.08	2.23
T4		0.554		1.83
T5	0.386	0.624	1.98	1.13
T6	0.360	0.633	2.73	1.67
T7	0.349	0.577	2.16	1.60
T8	0.333	0.591	1.56	0.97
Co-1	0.144	0.245	0	0
Co-2	0.165	0.547	0.65	0.73
PS	0.143	0.234	0.33	1.48
PMMA	0.576	0.633	4.00	3.27

in the butanone-methanol system and 0.554 to 0.641 in the DMF-methanol system for a polymer concentration of 5 wt% in solution. The γ values in DMF-methanol are larger than those in butanone-methanol, indicating that DMF is a better solvent for terpolymer. The γ values for both DMF-methanol and butanone-methanol increase in the order shown in Table 4: PS < Co-1 < Co-2 < Terpolymer ≤ PMMA.

The Critical Miscibility Composition

The critical temperature (T_c) for two-component systems composed of solvent and polymer is determined from phase equilibrium experiments, and depends on the molecular weight (M):

$$\frac{1}{T_c} = \frac{1}{\theta}\left(1 + \frac{b}{M^{0.5}}\right) \tag{4}$$

where the theta temperature ϑ is the critical miscibility temperature in the limit of infinite molecular weight, and b is a constant. It is assumed that the dependence of γ on the molecular weight can be treated by

$$\gamma_c = \gamma_\theta \left(1 + \frac{1}{M^{0.5}}\right) \tag{5}$$

where γ_θ is identified as the critical miscibility composition for the infinite molecular weight and at infinite polymer dilution, and γ_c is that for the isothermal critical point (or plait point) of the three-component phase diagram as shown in Fig. 9.

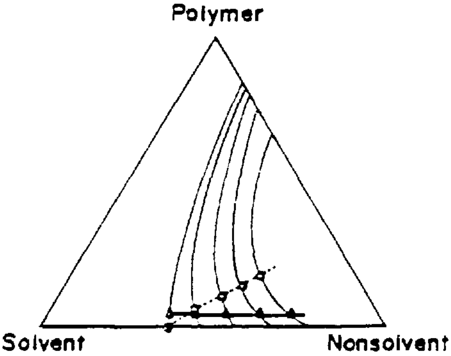

FIG. 9. Phase diagram of the three-component system: γ_c (○) is the isothermal critical point, γ_ϑ (●) is the critical miscibility composition, γ (▲) is the measurable point at the constant polymer concentration, and γ_0 (△) is the extrapolated point to the infinite molecular weight.

In treating the experimental data, Eq. (5') is useful:

$$\gamma = \gamma_0 \left(1 + \frac{b'}{M^{0.5}}\right) \tag{5'}$$

where γ_0 is γ for infinite molecular weight. The relation between γ_0 and the measurable γ value is also shown in Fig. 9. If the experimental values obtained in dilute solutions of polymers of various molecular

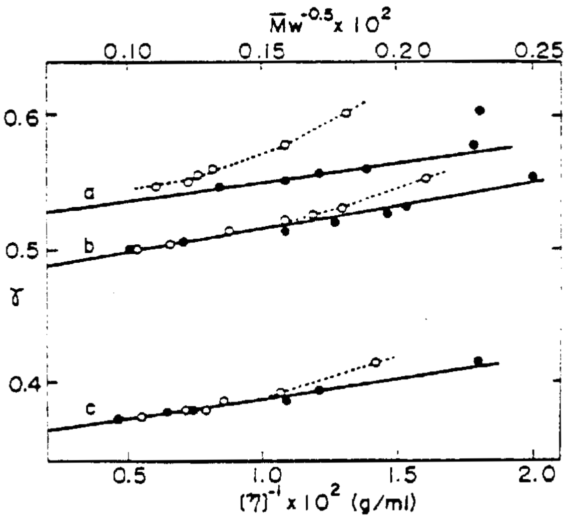

FIG. 10. The relationship of γ with limiting viscosity number (○) or molecular weight (●): (a) Co-2 AN (0.626 mole fraction)-S copolymer in DMF-methanol, (b) Co-1 AN (0.383 mole fraction)-S azeotrope in chloroform-methanol, and (c) AN (0.48 mole fraction)-MMA azeotrope in acetone-methanol.

weights are extrapolated to infinite molecular weight, the assumption that $\gamma_\theta = \gamma_0$ is useful.

The molecular weight of a terpolymer obtained by light scattering is affected by the distribution of the composition as in the case of binary copolymers [15]. The theoretical basis must be given at first to obtain the true molecular weight of a terpolymer. The relations between the limiting viscosity number $[\eta]$ determined in butanone and the true molecular weight ($\overline{M}_w$) were obtained for some binary copolymers [1, 2, 4]. The limiting viscosity number measured in butanone at 30°C is proportional to $M^{0.62}$ for the AN-S binary copolymer azeotrope [2] and to $M^{0.52}$ for the AN-MMA binary azeotrope [4]. The dependence of the γ value on molecular weight or on $[\eta]^{-1}$ is indicated in Fig. 10. As far as azeotropic copolymers are concerned, the limiting viscosity number measured in butanone can be used in place of $M^{0.5}$ in Eq. (5'). The dependence of γ on $[\eta]^{-1}$ for AN-S-MMA terpolymers, is shown in Fig. 11. The data deviate from a linear relationship in the region of relatively smaller molecular weights. The

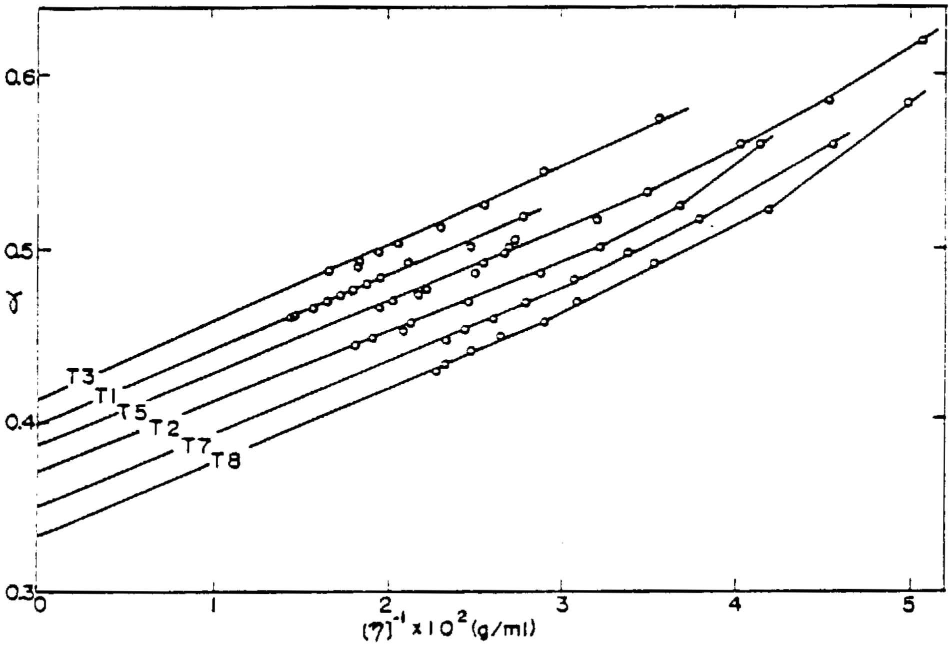

FIG. 11. Dependence of γ on the reciprocal limiting viscosity number $[\eta]^{-1}$: γ obtained in butanone-methanol mixture at 35° C, and $[\eta]$ measured in solution of butanone at 35° C.

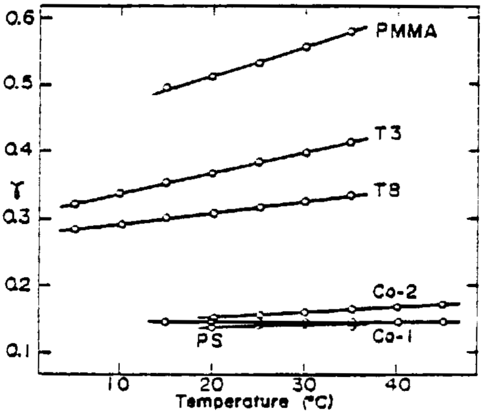

FIG. 12. The dependence of γ on temperature in a mixture of butanone and methanol.

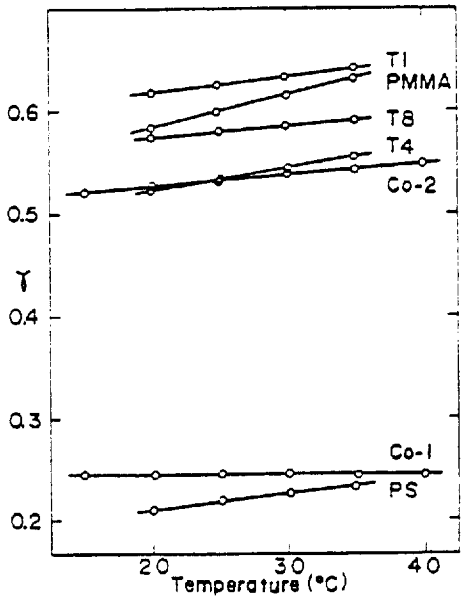

FIG. 13. The dependence of γ on temperature in a mixture of DMF and methanol.

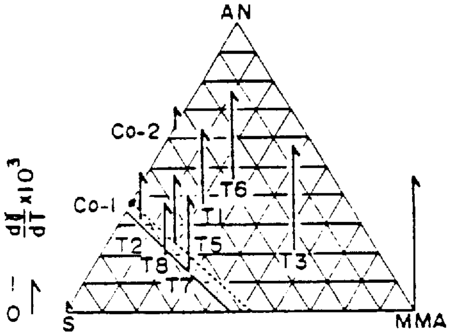

FIG. 14. The relation of the temperature coefficient of γ, $d\gamma/dT$, to the terpolymer composition for a butanone-methanol solution.

extrapolated γ_0 values and the constant b' do not indicate a distinct influence of the terpolymer composition at 35°C. The γ_0 values obtained by the plot against $[\eta]^{-1}$ for copolymers other than the azeotropes are estimated with some errors, as proved by the curve Co-2 in Fig. 10. The relationship of γ_0 values to the terpolymer composition would be clear if it was plotted against the true molecular weight.

The linear relation of γ values to temperature is obtained for the butanone-methanol system in Fig. 12 and for the DMF-methanol system in Fig. 13. The coefficient $d\gamma/dT$ indicates a reverse tendency to that for γ. That is, γ is larger in DMF solution than in butanone, but $d\gamma/dT$ is smaller in DMF than in butanone. The larger value of $d\gamma/dT$ in butanone means that the solubility of terpolymer is more sensitive to temperature in butanone than in DMF. The critical miscibility composition defined in Eq. (5) has a correlation with temperature. At the theta temperature of a binary system composed of polymer and solvent (e.g., DMF or butanone), the critical composition γ_g becomes zero. In the limit of $\gamma_g = 1$, the hypothetical theta temperature would be attained for a system of polymer and nonsolvent. The temperature coefficient gives a measure of the solvent power difference between solvent and nonsolvent for a given polymer. The dependence of $d\gamma/dT$ on the terpolymer composition is shown in Figs. 14 and 15 on triangular coordinates and is also expressed in Fig. 16. The binary copolymer Co-1 takes the minimum value of zero in these experiments. The solubility of PMMA and terpolymers decreases effectively with decreasing temperature. On

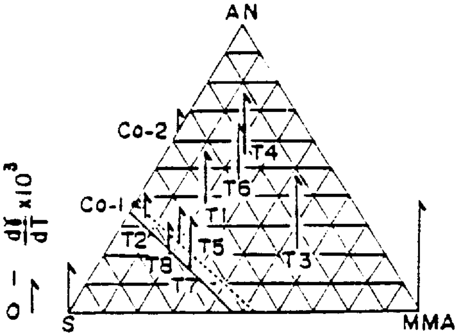

FIG. 15. The dependence of the temperature coefficient of γ, $d\gamma/dT$, on the terpolymer composition for a DMF-methanol solution.

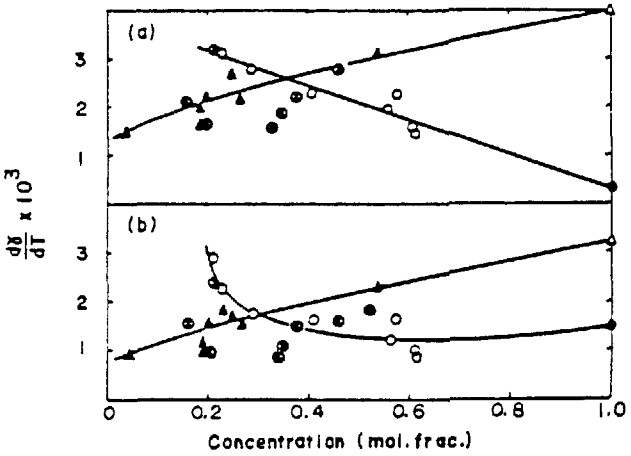

FIG. 16. The relation of the terpolymer composition to the coefficient dγ/dT: (a) butanone-methanol solution, (b) DMF-methanol solution; styrene concentration in terpolymer (○), MMA concentration in terpolymer (▲), polystyrene (●), PMMA (△), and AN concentration in terpolymer (⊗).

the other hand, the solubility of Co-1 or polystyrene does not increase with temperature. It is concluded from Fig. 16 that dγ/dT increases with MMA content and decreases with styrene content in terpolymer.

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REFERENCES

[1] Y. Shimura, J. Polym. Sci., Part B, 2, 403 (1963).
[2] Y. Shimura, Ibid., Part A-2, 4, 423 (1966).
[3] Y. Shimura-Kambe, J. Phys. Chem., 72, 4104 (1968).
[4] Y. Shimura, Bull. Chem. Soc. Japan, 40(2), 273 (1967).
[5] D. R. Crude and R. G. Lacombe, J. Polym. Sci., Part A-1, 8, 1373 (1970).

[6] G. E. Ham and R. D. A. Lipman, J. Macromol. Sci.—Chem., A1(6), 1005 (1967).
[7] R. K. S. Chan and V. Meyer, Ibid., A1(6), 1089 (1967).
[8] H. J. Harwood et al., J. Polym. Sci., Part C, 25, 23 (1968).
[9] C. Toci, Eur. Polym. J. 6, 161 (1970).
[10] J. Aoyagi and I. Shinohara, Kogyo Kagaku Zasshi, 74, 784 (1971).
[11] G. E. Ham, J. Macromol. Chem., 1, 93 (1966).
[12] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York, 1953, p. 545.
[13] D. R. Morey and J. W. Tamblyn, J. Appl. Phys., 16, 419 (1952).
[14] H. G. Elias, Makromol. Chem., 33, 140 (1959).
[15] W. Bushuk and H. Benoit, Can. J. Chem., 36, 1616 (1958).