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Solution Properties of the Methyl Methacrylate-Acrylonitrile Copolymer

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Short-range interactions between chain units of random copolymers in solution may be influenced by the characters of the pendant side groupes or, more precisely, by the dipole moment of the substituent. In those experiments the steric factor was derived for a random copolymer composed of methyl methacrylate and acrylonitrile from the relation between the limiting viscosity number and the molecular weight. Mark-Houwink relations were obtained in N, N'-dimethylformamide (DMF) and in methyl ethyl ketone (MEK) at 30°C for the copolymer containing 0.48 mol fraction of acrylonitrile, and for polymethyl methacrylate (PMMA) for the sake of comparison:

$$[\eta] = 4.61 \times 10^{-4} M^{0.65} \quad \text{for the copolymer in DMF}$$
$$[\eta] = 1.70 \times 10^{-4} M^{0.65} \quad \text{for PMMA in DMF}$$
$$[\eta] = 1.26 \times 10^{-3} M^{0.52} \quad \text{for the copolymer in MEK}$$

With the Stockmayer-Fixman expression, these correlations become, respectively:

$$[\eta] = 213 \times 10^{-5} M^{1/2} + 12.4 \times 10^{-7} M$$
$$[\eta] = 78.2 \times 10^{-5} M^{1/2} + 5.05 \times 10^{-7} M$$
$$[\eta] = 163 \times 10^{-5} M^{1/2} + 1.05 \times 10^{-7} M$$

The unperturbed mean square end-to-end distance, $\langle L^2 \rangle_0$, determined from the first term of the latter expressions, together with the $\langle L^2 \rangle_{0f}$ value calculated by assuming the completely free rotation, gives the steric factor of $\sigma = (\langle L^2 \rangle_0 / \langle L^2 \rangle_{0f})^{1/2}$ 2.59 ± 0.10 from the DMF solution; this factor is larger than that for polymethyl methacrylate (2.11 ± 0.08),, and that for polyacrylonitrile ($2.20 + 0.05$). The steric parameter derived from the MEK solution is 2.37 ± 0.05 for this copolymer; this value does not agree with the value obtained from the DMF solution. In both cases, it may be concluded that the dimensions of the copolymer between acrylonitrile and methyl methacrylate are influenced by the electrostatic interactions between nitrile groups of acrylonitrile units and methoxy-carbonile and/or methyl groups of methyl methacrylate units. The second virial coefficient in MEK obtained from the light scattering measurements also has a larger value for this copolymer than for polymethyl methacrylate. This tendency of copolymers to show a larger second virial coefficient seems to be an essential characteristic of some copolymers.

In a preceding paper¹⁾ it was shown that the steric parameters²,³⁾ for styrene-acrylonitrile copolymers and for constituent homopolymers have similar values. The σ parameter is defined

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1) Y. Shimura, *J. Polymer Sci.*, Part A-2 **4**, 423 (1966).

2) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, **C1**, 137 (1963).

3) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, **3**, 244 (1963).

as follows:

$$\sigma^2 = \langle L^2\rangle_0 / \langle L^2\rangle_{0f} \quad (1)$$

where $\langle L^2\rangle_0$ is the real mean square end-to-end distance of the polymer chain in the unperturbed state, and where $\langle L^2\rangle_{0f}$ is the hypothetical dimension for a chain in which the internal rotation about the carbon-carbon bond of the chain backbone is completely free. In this system, even though the properties of homopolymers in solution are very different from each other, the copolymers composed of acrylonitrile (AN) and styrene (S) shows the same steric parameter; *i. e.*, the hindrance to free rotations of chain backbone is found to be of the same order. It was concluded that the dimensions of random AN-S copolymres do not suffer from the influence of the alternation tendency between styrene units with phenyl side-groups of a larger molar volume and acrylonitrile units with nitrile groups responsible to the significant electrostatic interactions.

In this paper the copolymer between acrylonitrile and methyl methacrylate (MMA) will be discussed; the latter has a pendant group of a larger dipole moment than styrene. It will be found that the short-range interactions between the $-CN$ group in AN and $-COOCH_3$ and/or $-CH_3$ groups in MMA increase the mean square end-to-end distance in the unperturbed state.

The paper will also discuss the long-range interactions with relation to the second virial coefficient, A_2, obtained from light-scattering measurements, and on the Huggins constant, k', in *N, N'*-dimethylformamide (DMF) and methyl ethyl ketone (MEK) solution. The second virial coefficient of the AN-MMA copolymer is found to show a seemingly larger value than PMMA in both solvents.

Experimental

Materials. The methyl methacrylate monomer was washed successively with a saturated aqueous solution of sodium hydrogensulfite, 5% solution of sodium hydroxide, and 20% solution of sodium chloride. After having been dried with sodium sulfate anhydride, it was purified by distillation under a nitrogen atmospheric pressure.

Copolymerization with monomer feeds of AN 274 cc and MMA 179 cc were carried out at 60°C under a nitrogen atomosphere, using 0.05% benzoyl peroxide as an initiator. Polymerization was terminated at a low conversion of about 6% in order to suppress the distribution in composition. The yield of the copolymer was about 24 g for each batch.

According to the theory of random copolymerization,[4] the composition of the copolymer was calculated to be 47 mol% for AN, with a ratio of monomer feeds and the monomer reactivity ratios $r_1=0.15$, $r_2=1.20$.[5] The composition obtained from elementary analysis was 48.0 mol%. Considering the low conversion of copolymerization, the composition heterogeneity is within one percent.

Fractional precipitation of the copolymer were carried out from a 0.5% acetone solution at 30°C, using methanol as the non-solvent. The γ-values, *i. e.*, the volume fractions of the non-solvent at fractionation ranged from 0.371 to 0.518. The yields of each fractions were about 0.7—2.0 g.

Methyl methacrylate was polymerized under a nitrogen atmosphere at 68°C, using α-α'-azo-bis-isobutylonitrile as an initiator, and fractionated with an acetone and methanol system. The γ-values ranged from 0.500 to 0.690.

These fractions were refined by reprecipitation, dried in a vacuum, and stored in a desiccator with silica gel until they were measured.

Differential Refractive Index Increment. The differential refractive index increment, d*n*/d*c*, where *n* is the refractive index and *c* is the weight concentration of the solution, was measured in methyl ethyl ketone (MEK) and dimethylformamide (DMF) with a Brice-Phoenix differential refractometer. All the fractions of the copolymer show the same value of the differential refractive index increment. That is, $(dn/dc)_{MEK}=0.116$ and $(dn/dc)_{DMF}=0.066$. This means that the fractionation is based only on the molecular weight and not on the copolymer composition. Both in MEK and DMF the values of d*n*/d*c* for the copolymer agree with those calculated from the composition and from the d*n*/d*c* value for homopolymers, as is shown in Fig. 1.

The values for PMMA are $(dn/dc)_{MEK}=0.113$ and $(dn/dc)_{DMF}=0.059$.

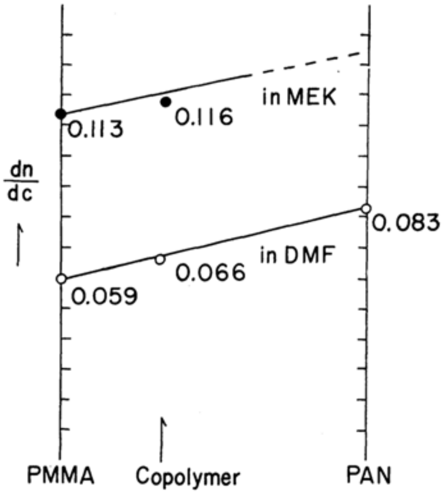

Fig. 1. Relation of the differential refractive index increment with the polymer composition.

Light Scattering. All measurements of the light scattering of copolymer solutions were performed in MEK, because the absolute scattering from a MEK solution is more intence than that from DMF, as has been known from the values of d*n*/d*c*. Each solution

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[4] T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[5] F. M. Lewis, F. R. Mayo and W. F. Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1945).

was purified by centrifugation at 20000 G for 1 hr. Light-scattering measurements were carried out at 30°C with a Brice-Phoenix (Type 1000-D) photometer over the angular range from 45° to 135° with a cylindrical cell and with light of 436 mμ. The weight-average molecular weight and the second virial coefficient were determined from a Zimm plot. A typical Zimm plot is shown in Fig. 2. The molecular weight obtained from the MEK solution coincided with the value given by the DMF solution. This means that these copolymer fractions do not have a distribution in composition which may cause trouble in obtaining the true molecular weight.[6-9] It may be concluded that, for the present samples, the true molecular weight will be given by the treatment applicable to the homopolymers.[10,11]

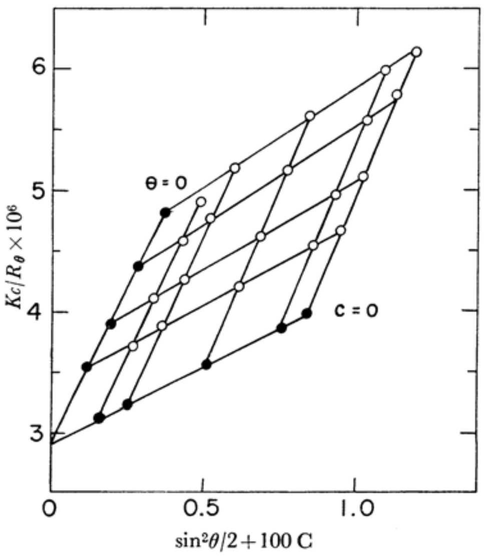

Fig. 2. Zimm plot for the acrylonitrile-methyl methacrylate copolymer fraction (F-3.1) in methyl ethyl ketone.

Viscosity. The viscosity of the solutions was measured at 30°C with an Ubbelohde capillary viscometer, and corrected for kinetic energy effects. Since dimethyl formamide has been found[12] to be a common solvent for polyacrylonitrile, polymethyl methacrylate, and copolymers between them, DMF and MEK were used as solvents for the viscosity measurements. The limiting viscosity number and the Huggins constant were determined in the usual way.

Results and Discussion

Mark-Houwink Equation. In Fig. 3 the limiting viscosity number, $[\eta]$, is plotted against the weight-average molecular weight, M_w, for polymethyl methacrylate, polyacrylonitrile, and acrylonitrile - methyl methacrylate copolymer. According to the Mark-Houwink expression,

$$[\eta] = KM^{\alpha} \tag{2}$$

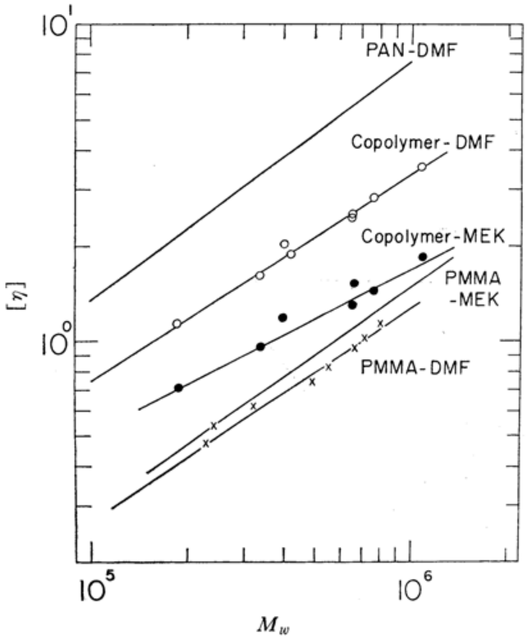

Fig. 3. Relationship of the limiting viscosity number with the molecular weight at 30°C.
○: Copolymer, containing 0.48 mole fraction of acrylonitrile in DMF
●: Copolymer, containing 0.48 mole fraction of acrylonitrile in MEK
×: Polymethyl methacrylate in DMF
Relations for polyacrylonitrile in DMF[13] and polymethyl methacrylate in MEK[14] at 25°C are drawn based on references.

the following relations were obtained:

For the AN-MMA copolymer in DMF at 30°C;

$$[\eta] = 4.61\times10^{-4}M^{0.65}$$

For PMMA in DMF at 30°C;

$$[\eta] = 1.70\times10^{-4}M^{0.65}$$

For the AN-MMA copolymer in MEK at 30°C;

$$[\eta] = 1.26\times10^{-3}M^{0.52}$$

Other relations for the parent homopolymers have already been published:

For PAN in DMF at 30°C;[13]

$$[\eta] = 2.09\times10^{-4}M^{0.76}$$

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[6] W. Bushuk and H. Benoit, *Can. J. Chem.*, **36**, 1616 (1958).
[7] M. Leng and H. Benoit, *J. Chim. Phys.*, **58**, 480 (1961).
[8] I. Mita, *ibid.*, **59**, 330 (1962).
[9] W. H. Stockmayer, L. D. Moore, J. M. Fixman and B. N. Epstein, *J. Polymer Sci.*, **16**, 517 (1955).
[10] H. Kambe, I. Mita and Y. Shimura, Rept. Aeronaut. Res. Inst., Univ. Tokyo, No. 381 (1964).
[11] Y. Shimura, I. Mita and H. Kambe, *J. Polymer Sci.*, **B2**, 403 (1964).
[12] Y. Shimura and H. Kambe, Reports on Progress in Polymer Physics in Japan, **9**, 103 (1966).

[13] H. Inagaki, K. Hayashi and T. Matsuo, *Makromol. Chem.*, **84**, 80 (1965).

For PMMA in MEK at 25°C;[14]

$$[\eta]=7.1\times10^{-5}M^{0.72}$$

The limiting viscosity numbers in DMF for the copolymer are just between those for PMMA and PAN. For the same molecular weight, the AN-MMA copolymer chain is more expanded beyond the free rotation dimensions than PMMA and less than PAN in a dimethylformamide solution.

The exponent, α, of the copolymer in MEK at 30°C indicates that there exists a θ-composition at a little richer composition than the 0.48 mol fraction of acrylonitrile at 30°C in methyl ethyl ketone.

Stockmayer-Fixman Equation. According to the Stockmayer and Fixman theory,[2] the limiting viscosity number, $[\eta]$, is related to the molecular weight as follows:

$$[\eta]=\Phi_0A^3M^{1/2}+0.51B\Phi_0M\cdots \tag{3}$$

where:

$$A=(\langle L^2\rangle_0/M)^{1/2}$$

Φ_0 is a universal constant, 2.87×10^{21} c. g. s.; $\langle L^2\rangle_0$ is the mean-square unperturbed displacement length, and B is a parameter representing the interactions between the polymer and the solvent. From this relationship, we can obtain some knowledge about the conformation of the AN-MMA copolymer. The plots according to Eq. (3) are shown in Fig. 4. With the method of least squares, the following results are obtained:

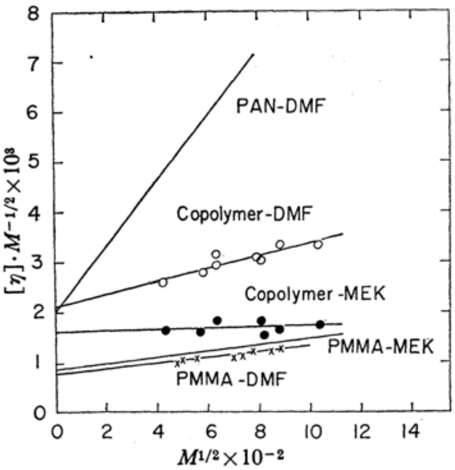

Fig. 4. Viscosity-molecular weight relation based on Stockmayer-Fixman equation.[2]
○: Copolymer, containing 0.48 mole fraction of acrylonitrile in DMF
●: Copolymer, containing 0.48 mole fraction of acrylonitrile in MEK
×: Polymethyl methacrylate in DMF
Relations for polyacrylonitrile in DMF[13] and polymethyl methacrylate in MEK at 25°C[14] are drawn by recalculation from references.

For the AN-MMA copolymer in DMF at 30°C;

$$[\eta]=213\times10^{-5}M^{1/2}+12.4\times10^{-7}M$$

For PMMA in DMF at 30°C;

$$[\eta]=78.2\times10^{-5}M^{1/2}+5.05\times10^{-7}M$$

For the AN-MMA copolymer in MEK at 30°C;

$$[\eta]=163\times10^{-5}M^{1/2}+1.05\times10^{-7}M$$

The relation for PAN in DMF at 30°C;[13]

$$[\eta]=205\times10^{-5}M^{1/2}+65\times10^{-7}M$$

and for PMMA in MEK at 25°C, recalculated from the literature;[14]

$$[\eta]=88\times10^{-5}M^{1/2}+6.07\times10^{-7}M$$

Steric Factor. The value of the steric factor, $\sigma^2=\langle L^2\rangle_0/\langle L^2\rangle_{0f}$, was also calculated. If the internal rotation of the carbon-carbon bond of the chain backbone is assumed to be completely free, the mean-square end-to-end distance divided by the degree of polymerization, $\langle L^2\rangle_{0f}/P$, is a constant independent of the substituent on the main chain.[15] From this constant, $\langle L^2\rangle_{0f}/P=9.471\times10^{-16}$, and the apparent molecular weight of copolymer unit, $\langle L^2\rangle_{0f}/M$ can be calculated. For the copolymer the $(\langle L^2\rangle_{0f}/M)^{1/2}$ value is 350×10^{-11}, while it is 308×10^{-11} for PMMA.

On the other hand, from the intercept of Fig. 4 we can obtain the mean-square unperturbed displacement length per molecular weight $(\langle L^2\rangle_0/M)^{1/2}$ for the DMF solution as 905×10^{-11} and 648×10^{-11} for the AN-MMA copolymer and PMMA respectively. The value estimated from the MEK solution for the copolymer is 829×10^{-11}; this is smaller than that obtained in DMF.

TABLE 1. CONSTANT A AND B AT 30°C

	$A\times10^8$ cm			$B\times10^{27}$ cm^3		
	from $[\eta]_{\mathrm{DMF}}$	from $[\eta]_{\mathrm{MEK}}$	from $A_{2\mathrm{MEK}}$	from $[\eta]_{\mathrm{DMF}}$	from $[\eta]_{\mathrm{MEK}}$	from $A_{2\mathrm{MEK}}$
Polyacrylonitrile[13]	0.89	—	—	4.44	—	—
AN-MMA copolymer	0.91	0.83	0.74	0.85	0.07_2	1.43
Polymethyl methacrylate	0.65	—	0.69	0.35	—	1.21
Polymethyl methacrylate[14,23]	—	0.67	0.67	—	0.41	1.34

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14) S. N. Chinai, J. D. Matlack, A. L. Resnick and R. J. Samuels, *J. Polymer Sci.*, **17**, 391 (1955).

15) "Principles of Polymer Chemistry," P. J. Flory pp. 415.

The ratio of these quantities gives σ. The value of σ becomes a measure of the hindrance to the free rotation about the carbon-carbon bond. Its value for the present copolymer is found to be 2.59±0.10 from DMF and 2.37±0.05 from MEK solution. For PMMA it is 2.11±0.08 from DMF; this value agrees with the values obtained in solvents with various dielectric constant.[3] The values of σ have been reported to be 2.09—2.27[3,13] for PAN; the value differed from sample to sample under the influence of the polymerization conditions. The values of σ for the copolymer are not consistent in the two solvents. As is indicated from the slopes of Figs. 3 and 4 and the B parameter listed in Table 1, the condition of the MEK solution at 30°C is similar in the θ-solvent for this copolymer. Accordingly, the σ-value of 2.37 in MEK nearly corresponds to the unperturbed state, and the value of 2.59 in DMF is due to the imperfect elimination of the perturbation effects by the solvent molecules. Systems showing behavior like this have also been reported to exist for polytetrahydrofuran[16] and polystyrene[17].

The greater σ value for the copolymer in all cases signifies that, in the unperturbed state, the copolymer is more extended than consistent homopolymers; that is, the conformation of the AN-MMA copolymer consists of more trans type bonding than in parent homopolymers. This is characteristic of the AN-MMA copolymer; it is different from the styrene-acrylonitrile copolymers, in which the values of σ are nearly constant, irrespective of the composition.[1,11]

For the composition of the AN-MMA copolymer, 0.48 mole fraction of AN, it is statistically[4] calculated using the monomer reactivity ratios, that the number-average sequence length of the acrylonitrile unit is 1.15, that that the of methyl methacrylate is 1.12, and that 87% of AN units in the copolymer molecules are bonded on both sides with MMA units.

Considering the above-mentioned facts, it can be concluded that the interactions between the nitrile groups of AN units and methoxycarbonyl groups and/or methyl groups pendant to the MMA unit make the copolymer longer. On the other hand, the molar volumes of the substituent to the homopolymers are 38 cc, 60cc and 89 cc for PAN, PMMA and PS respectively,[3] but the steric factor of the AN-MMA copolymer becomes larger, while that of the S-AN copolymer is the same as those for homopolymers. Therefore, the interactions affecting the displacement length of the AN-MMA copolymer in solution can not be attributed to the bulkiness of the substituent groups. Presumably, electrostatic interactions such as the dipole force must be acting upon its conformation.

Second Virial Coefficient. The second virial coefficient A_2 of polymer solutions depends on the molecular weight of the polymer. This relation is usually expressed by the following empirical formulas:

$$A_2 = CM^{-\alpha} \tag{4}$$

$$A_2 = a/M^{1/2} + b \qquad (5)^{18)}$$

The curves of the second virial coefficient versus the reciprocal of the square root of the molecular weight for PMMA and the AN-MMA copolymer in MEK are drwan in Fig. 5 according to Eq. (5). For the same molecular weight, the second virial coefficient of the copolymer is larger than that of PMMA in MEK. This is the same tendency as is found in the styrene-acrylonitrile copolymer system.[1]

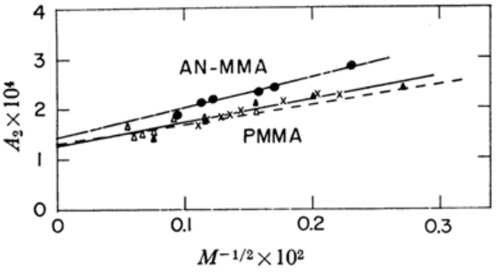

Fig. 5. Dependence of the second virial coefficient on the weight average molecular weight in methyl ethyl ketone at 30°C.
●: Copolymer, containing 0.48 mole fraction of acrylonitrile
×: Polymethyl methacrylate
▲: Polymethyl methacrylate, recalculated from Casassa *et al.*'s data[23] at 25°C
△: Polymethyl methacrylate, recalculated from Chinai *et al.*'s data[14] at 25°C

In order to obtain some theoretically explicable information, the combined expression[19] of the Casassa-Markowitz theory[20] about the second virial coefficient and Fixman's relation[2,21,22] representing the expansion coefficient caused by the long range excluded volume is used in place of Eq. 5:

$$A_2M^{1/2} = \Psi_\infty A^3 + 0.631\,\Psi_\infty BM^{1/2} \tag{6}$$

Ψ_∞ is a constant, 1.518×10^{23}. A and B are the

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[16] M. Kurata, H. Uchiyama and K. Kamada, *Makromol. Chem.*, **88**, 281 (1965).
[17] H. Bauman, *J. Polymer Sci.*, **B3**, 1069 (1965).
[18] H. Sotobayashi and K. Uberreiter, *Z. Electrochem. Ber. Bunsenges. Physik. Chem.*, **66**, 838 (1962); *J. Polymer Sci.*, **A2**, 1257 (1964).
[19] H. Yamakawa, *Kobunshi (Japan)*, **14**, 54 (1965).
[20] E. F. Casassa and H. Markovitz, *J. Chem. Phys.*, **29**, 493 (1958).
[21] M. Fixman, *ibid.*, **23**, 1656 (1955).
[22] M. Fixman, Doctoral Thesis, M. I. T. (1953).
[23] E. F. Casassa and W. H. Stockmayer, *Polymer*, **3**, 53 (1962).

same parameters as were defined in Eq. (3). According to Eq. (6) and Fig. 5, the *A* and *B* molecular parameters can be calculated as shown in Table 1. The values listed at the bottom of Table 1 are recalculated from the literature.[14,23]

The calculated values based on the limiting viscosity number were estimated from both DMF and MEK solutions, and *A* and *B* parameters derived from the second virial coefficient were obtained in the MEK solution. Therefore, the discrepancy of *B* in these results is a matter of course, reflecting the distinction of the solvent power. The larger *B* value in DMF for the AN-MMA copolymer means that the copolymerization with AN units produces more interaction with the solvent molecule (DMF) than does the MMA homopolymer, as may be expected empirically.

The second virial coefficients measured in DMF are as follows:

	$A_2\times10^4$	$M_w\times10^{-4}$
Polyacrylonitrile[13]	5.0	29.5
AN-MMA Copolymer (48 mol% of AN)	4.9	66.7
Polymethyl methacrylate	1.77	71.0

The A_2 value of the copolymer shows a relatively large value against the composition of the copolymer, even considering its molecular-weight dependence.

TABLE 2. SECOND VIRIAL COEFFICIENTS FOR SOME COPOLYMER-SOLVENT SYSTEMS

(1) Methyl methacrylate - methyl acrylate in methyl ethyl ketone[26]

	$A_2\times10^4$	$M_w\times10^{-4}$
Polymethyl methacrylate	1.1	74
C-1 (0.116 mol frac. MMA)	3.5	56
C-2 (0.195 mol frac. MMA)	3.2	68
C-3 (0.494 mol frac. MMA)	2.9	71
Polymethyl acrylate	1.2	68

(2) Styrene - methyl methacrylate in dioxane[27]

	$A_2\times10^4$	$M_w\times10^{-4}$
Polystyrene	2.8	92
Azeotropic copolymer	3.8	133
Polymethyl methacrylate	3.1	122

(3) Styrene - methyl methacrylate block copolymer in toluene at 25°C[28]

	$A_2\times10^4$	$M_n\times10^{-4}$
Polystyrene	3.1	34
B-1 (85% styrene)	3.01	39
B-2 (70% styrene)	3.17	30
B-3 (62% styrene)	3.24	23
B-4 (48% styrene)	3.46	19
B-5 (43% styrene)[29]	5.55	36
B-6 (35% styrene)[29]	4.24	37

TABLE 3. MOLECULAR WEIGHT, SECOND VIRIAL COEFFICIENT, AND THE LIMITING VISCOSITY NUMBER FOR FRACTIONS OF AN (48 MOLE %)-MMA COPOLYMER, AT 30°C

Fraction No.	$[\eta]_{\mathrm{DMF}}$	$[\eta]_{\mathrm{MEK}}$	$M_w\times10^{-4}$	$A_2\times10^4$, MEK
F-2	3.51	1.85	108.7	1.85
F-3.1	2.93	1.44	76.9	2.12
F-3.2	2.48	1.28	66.7	2.20
F-3.1.2	2.50	1.50	65.4	—
F-3.4.2	1.89	—	41.3	—
F-3.4	2.01	1.18	40.0	2.32
F-3.5	1.60	0.95	33.7	2.40
F-6	1.12	0.71	18.8	2.85

TABLE 4. MOLECULAR WEIGHT, SECOND VIRIAL COEFFICIENT, AND THE LIMITING VISCOSITY NUMBER FOR FRACTIONS OF POLYMETHYL METHACRYLATE, AT 30°C

Fraction No.	$[\eta]_{\mathrm{DMF}}$	$M_w\times10^{-4}$	$A_2\times10^4$, MEK
F-2	1.12	80.0	1.68
F-3	1.03	71.4	1.80
F-4	0.95	60.6	1.83
F-5	0.82	54.7	1.88
F-6	0.74	48.5	1.95
F-7	0.62	31.9	2.15
F-8	0.47	23.3	2.30
F-8.2	0.54	24.2	2.25

The *B* parameter of the AN-MMA copolymer derived from the limiting viscosity number in MEK is much smaller than that of PMMA in MEK, but the *B* parameter obtained from the second virial coefficient in MEK indicates an inclination for the copolymer containing AN units insoluble in MEK to have greater long-range interactions with the MEK molecule than does PMMA, though the absolute values contain some uncertainty arising from the application of Eq. (6).[19,24] In the case of the AN-S copolymer system in MEK, the second virial coefficient is also larger than those for parent homopolymers and varies with the composition of the copolymer.[1] If the second virial coefficient becomes zero, or if the lower consolute temperature is found in the solution of statistical copolymers, consisting of monomer units with different solution properties, such as AN-S and AN-MMA, we have no theory

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24) O. B. Ptitsyn, *Vysokomol. Soed.*, **3**, 1673 (1961).

25) R. Cleland and W. H. Stockmayer, *J. Polymer Sci.*, **17**, 473 (1955).

26) A. Kotera, T. Saito, Y. Watanabe and M. Ohama, *Makromol. Chem.*, **87**, 195 (1965).

27) W. H. Stockmayer, *J. Polymer Sci.*, **16**, 517 (1955).

28) J. R. Urwin and J. M. Stearne, *Makromol. Chem.*, **78**, 204 (1964).

29) H. Inagaki and T. Miyamoto, *ibid.*, **87**, 166 (1965).

from which a molecular image can be derived. In such a solution MEK is non-solvent for the one component (AN) of the copolymer; therefore, no increase in the long-range interactions can be expected.

The second virial coefficients of some copolymer-solvent systems are collected in Table 2. In all cases the copolymers give larger values than do the constituent homopolymers. If the larger virial coefficient of a copolymer were an essential character of a copolymer solution, it could be suggested that in the derivation of the dependence of the second virial coefficient on the molecular weight such as Eq. (6), the difference between the expansion coefficient caused by the polymer-solvent interactions and that by polymer-polymer interactions no longer be neglected.

About the A parameter, the results obtained from A_2 or $[\eta]$ are theoretically based on the unperturbed state. Therefore, the difference between values for the copolymer will be due to the experimental errors and, mainly, to the incomplete elimination of the perturbation effects by the solvent. The A parameter of PMMA becomes a constant independent of the solvents and the estimation methods. This may be because the solvent powers of MEK and DMF are of almost the same order. The conclusion presented in the "Steric Factor" section, that the trans conformations increase in AN-MMA copolymer, is consistent qualitatively with the results obtained from the second virial coefficient.

Huggins Constant. The Huggins constant, k', obtained from viscosity measurements in DMF at 30°C is 0.40 for PMMA, 0.30 for the AN-MMA copolymer, and 0.33 for PAN.[25] This increasing tendency for long range interactions between the copolymer and the solvent corresponds to the fact obtained with the second virial coefficient.

The Huggins constant, k', measured in MEK at 30°C is 0.42 for PMMA; the k' for the copolymer is larger than 0.45, but PAN is insoluble in MEK.

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