PROPERTIES OF DILUTE SOLUTIONS OF ETHYLENE–PROPYLENE–DIENE TERPOLYMERS IN BENZENE AND TOLUENE

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Commercial samples of ethylene–propylene–diene terpolymers (EPDM) and their fractions were characterized by osmometry (number-average molecular weight, second virial coefficient), viscometry (intrisic viscosity) and ^{1}H NMR spectrometry (mole fraction of propylene monomeric units). The results were analyzed in terms of the two-parameter theory of polymer solutions. Theta temperatures and polymer–solvent interaction parameters were estimated and correlated with composition. Existence of organized structures is indicated by high values of the reduced partial molar entropy parameter ψ. The increase in ψ with increasing content of ethylene units is assigned to their association. The results lend support to the previous study on the Huggins viscosity coefficient of EPDM.

Although ethylene–propylene copolymers (EPM) and ethylene–propylene–diene terpolymers (EPDM) have long been used in practice as elastomers, additives to oils and polymer blends[1], there exists scarce information on their solution properties and derived molecular characteristics. Baldwin and Ver Strate[2] and Cesca[3] critically reviewed the papers published until the seventies, and pointed out the problems existing at that time. Though the knowledge has since improved[4–17], many unsolved questions persist.

One of them is the association of copolymer molecules in solutions[1]. Sen and Rubin[11] demonstrated it by light-scattering of dilute (0.1%) solutions of an EPM sample (mole fraction of propylene units $x_p = 0.2$) in methylcyclohexane and tetrahydronaphthalene. Association was also indicated by unusually high values of the Huggins viscosity coefficient of EPDM terpolymers in benzene and toluene[13]. The anomaly was especially large at $x_p = 0.19$ and almost vanished at $x_p = 0.49$.

The intrinsic viscosities for these terpolymers are reported in this paper. Their analysis is based on the assumption that the effect of intermolecular association is eliminated by extrapolation to infinite dilution. Since, however, the tendency to association is strong, it must be admitted that association persists on the intramolecular level even at infinite dilution. Hence, the parameters derived on this basis are to be regarded as apparent ones. Indeed, their values are outside the usual range and may be interpreted as an indication of intramolecular ordering.

THEORETICAL BACKGROUND

The analysis of the intrinsic viscosity data rests on the two-parameter theory, specifically, on the Yamakawa–Tanaka equation[18]

$$\alpha_\eta^3 = 1 + 0.346\Phi_{0,\infty}(B/K_0)M^{1/2} \ , \qquad (1)$$

where α_η^3 is the viscosity expansion factor

$$\alpha_\eta^3 \equiv [\eta]/[\eta]_\Theta = [\eta]/K_0M^{1/2} \qquad (2)$$

and $[\eta]_\Theta$ corresponds to the state unperturbed by the excluded-volume effect. Equation (*1*) is an empirical modification of the theoretical equation devised by Burchard[19] and Stockmayer and Fixman[20]. The viscosity constant $\Phi_{0,\infty}$ corresponds to the limit of random coil in the non-draining regime ($\Phi_{0,\infty} = 2.5 \ . \ 10^{21}$ g^{-1} if $[\eta]$ is expressed in dl g^{-1}; ref.[21]). The K_0 constant is related to the unperturbed mean-square end-to-end distance $\langle R^2\rangle_0$ in the random coil limit (subscript ∞)

$$K_0 = \Phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2} \qquad (3)$$

and B is characteristic of the excluded-volume interaction of chain segments, depending on the polymer–solvent system and temperature. In the vicinity of the theta temperature (where the second virial coefficient vanishes) the latter dependence is assumed to be[18]

$$B = B_0(1 - \Theta/T) \ , \qquad (4)$$

where B_0 is a constant independent of temperature.

Equations (*1*) to (*4*) are currently used to test the applicability of the theory to polymeric systems. A straightforward application to EPDM is impeded by the fact that we were not able to determine the weight-average molecular weight $\overline{M}_w$ by light scattering while the number-average values $\overline{M}_n$ are not suitable for the correlation of the intrinsic viscosity data for non-uniform polymers. To circumvent this obstacle we combine Eqs (*1*) to (*4*) to obtain

$$\alpha_\eta^3 = 1 + 0.346\Phi_{0,\infty}(B/K_0^2)\,[\eta]_\Theta \tag{5a}$$

or

$$\alpha_\eta^3 = 1 + 0.346\Phi_{0,\infty}(B/K_0^2)\,(1 - \frac{\Theta}{T})\,[\eta]_\Theta \tag{5b}$$

and plot α_η^3 vs $[\eta]_\Theta$ (toluene) or vs $(1 - \Theta/T)\,[\eta]_\Theta$ (benzene).

When calculating the viscosity expansion factor α_η^3 at different temperatures we take into consideration the temperature effect on K_0. The quotient d ln K_0/dT is not known for EPDM, and only one value (d ln K_0/dT = –1.5 . 10^{-3} K^{-1}) is available for EPM (x_p = 0.4; ref.[22]). Since approximately the same value has been reported for polyethylene[21], we employ it to correct the K_0 and $[\eta]_\Theta$ values of EPDM. Since the highest temperature (50 °C) is only 20 to 30 °C above the Θ temperatures, an inaccuracy in d ln K_0/dT has no serious effect on the results.

To convert B/K_0^2 into B and B_0/K_0^2 into B_0 we need to know the K_0 values. Anticipating the conclusions of Appendix, we employ the empirical formula (*A-7*) with K_0^{PE} = 3.6 . 10^{-3} dl g^{-1} for polyethylene[21] to calculate the K_0 values for EPDM copolymers.

The parameter B is related to the Flory–Huggins parameter χ of free energy of dilution[18,23] by

$$B = (2\bar{v}^2/V_1 N_A)(1/2 - \chi)\ , \tag{6}$$

where

$$1/2 - \chi = \psi - \kappa\ . \tag{7}$$

Here, ψ and κ are, respectively, the entropy-of-dilution and heat-of-dilution parameters (at infinite dilution), $\bar{v}$ is the partial specific volume of polymer, and V_1 is the molar volume of solvent. It is useful to write[23]

$$1/2 - \chi = \psi(1 - \Theta/T)\ . \tag{8}$$

Equation (*8*) is similar to Eq. (*4*) and, likewise, is valid only for temperatures close to Θ. It follows from Eqs (*6*) to (*8*) that

$$\psi = (N_A V_1/2\bar{v}^2)B_0 \tag{9}$$

$$\kappa = \psi\Theta/T \ . \tag{10}$$

By means of these equations the B and B_0 values are converted into χ, ψ and κ.

The ψ parameter is the reduced partial molar entropy of dilution[23]

$$\psi = 1/2 + \lim\,(\overline{\Delta S}{}_1^{R}/R\phi_2^2) \ , \tag{11}$$

where ϕ_2 is the polymer volume fraction. The first term in Eq. (*11*) corresponds to the lattice combinatory contribution,

$$\lim_{\phi_2 \to 0}\,(\overline{\Delta S}{}_{1,\mathrm{comb}}^{R}/R\phi_2^2) = 1/2 \ , \tag{12}$$

the second term is the reduced partial molar entropy.

With copolymers the χ parameter consists of three components corresponding to various types of interaction (AA, BB, AB) between monomeric units[24,25] (A, B):

$$\chi = \chi_A x_A + \chi_B x_B - \chi_{AB} x_A x_B \ . \tag{13}$$

Equations formally similar to Eq. (*13*) can be written for the parameters ψ and κ. If there is no preference for attractive or repulsive interaction of chemically dissimilar units, then $\chi_{AB} = 0$, and the dependence of χ on the copolymer composition should be linear. Preference for repulsive interaction ($\chi_{AB} > 0$) is indicated by negative deviations from linearity, and vice versa.

The correlations of the interaction parameters B or χ with the terpolymer composition are completed by the values for atactic polypropylene. They were estimated from the slopes of the plots of $[\eta]/M^{1/2}$ vs $M^{1/2}$ made with the data reported by Danusso and Moraglio[26] (benzene) and Inagaki et al.[27] (toluene). In the latter paper, the $\overline{M}_w$ values were obtained by light scattering. In the former, the viscosity-average molecular weights, $\overline{M}_\eta$, were calculated from the intrinsic viscosities in toluene by means of the relation $[\eta] = KM^a$, calibrated by M_w.

In correlations with the composition of terpolymers, the presence of diene units is not taken into consideration. In principle, they could change the stoichiometry, the sequence distribution and the polymer–solvent interaction. However, these effects do not seem relevant with the samples studied, probably because the content of diene units is low.

EXPERIMENTAL

Polymer samples and fractions. Commercial samples (Table I) of terpolymers of ethylene, propylene and a small amount of diene monomer (ethylidenenorbornene and dicyclopentadiene) were used. Samples C, D and E were fractionated by precipitation from 1% hexane solution with a mixture of methanol and acetone (30/70 v/v) as precipitant. Fractionation was carried out in the usual manner and 5 to 11 fractions were thus obtained. The original samples and their fractions were characterized by viscometry (intrinsic visosity $[\eta]$), osmometry (number-average molecular weight $\overline{M}_n$ and second virial coefficient A_2), ^{1}H NMR spectrometry (mole fraction of propylene units x_p) and DSC. As indicated by DSC, copolymers B, C, E with $x_p > 0.3$ were amorphous while those with $x_p = 0.19$ displayed some crystallinity (melting endotherms at 308 and 310 K with samples A and D, respectively).

Solutions in benzene and toluene (analytical grade, Lachema Brno) of samples B, C, E and their fractions were prepared by shaking overnight the weighed amount of copolymer with the solvent (containing 0.1 wt.% of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) as stabilizer) at 30 °C and were kept at 25 °C. Viscosity of these solutions was constant in time and the intrinsic viscosities were reproducible within ±0.01 dl g^{-1}.

Samples A and D swelled at normal temperature in both solvents, and complete dissolution could be achieved only by heating to 50 °C. Solutions of sample D thus prepared were stable at 25 °C. If solutions of sample A were kept at 25 °C, their viscosity slowly increased with time. If they were

TABLE I
Characterization of EPDM samples

Sample[a]	x_p[b]	$\overline{M}_n \cdot 10^{-3}$			$A_2 \cdot 10^{-4}$, mol cm^3 g^{-2}			$[\eta]$, dl g^{-1}	
		T	B	H	T	B	H	T	B
A	0.19	–	86	–	–	0.3	–	1.80	1.26
B	0.38	78	91	–	8.3	1.9	–	1.62	1.15
C	–	55.6	–	–	9.2	–	–	–	–
D	0.20	77.5	–	76	8.0	–	7.8	1.69	–
E	–	91.2	–	–	8.5	–	–	1.99	–

[a] Data for samples A, B from ref.[13]; [b] mole fraction of propylene units. Abbreviations for solvents: T toluene at 25 °C, B benzene at 30 °C, H n-heptane at 25 °C.

kept at 35 °C and quickly cooled to a lower temperature immediately before measurement the viscosity was constant in time and the [η] values were obtained with a reproducibility of ±0.03 dl g^{-1}.

Osmometry. The osmotic pressure was measured with a Hewlett–Packard High Speed Membrane Osmometer, Model 502, with cellulose membranes Schleicher & Schüll SS 08. The number-average molecular weight, $\overline{M}_n$, was calculated according to the equation

Table II
Characteristics of EPDM fractions

Fraction[a,b]	$\overline{M}_n \cdot 10^{-3c}$	$A_2 \cdot 10^{-4c}$, mol cm^3 g^{-2}	[η][d], dl g^{-1}	
			T	B
C-1 (0.29)	92 (91[d])	8.0 (0.8[d])	1.89	1.11
C-2	85	7.4	1.89	1.23
C-3	91	9.0	1.95	1.24
C-4	84	7.8	1.80	1.28
C-5	82	8.1	1.79	1.24
C-6	83	8.2	–	–
C-7	75	7.8	1.78	1.23
C-8	77	8.4	–	–
C-9	74	8.5	–	–
C-10 (0.48)	53	8.9	1.37	1.01
C-11	17.3	10	0.55	0.49
D-1 (0.18)	158 (160[e])	10.3 (7.5[e])	2.18	1.43[e]
D-2	129	7.2	2.08	1.52[e]
D-3	102	7.4	1.70	1.22[e]
D-4	74.3	7.6	1.37	1.00[e]
D-5 (0.21)	38 (45[f])	9.8 (–0.9[e], 15[f])	0.88	0.72[e] (0.98[f])
E-1 (0.28)	142	7.4	2.09	1.29
E-2 (0.29)	125	8.1	1.99	1.27
E-3 (0.31)	115	7.9	2.13	1.45
E-4 (0.39)	96	7.8	2.13	1.39
E-5	110	8.1	2.16	1.44
E-6 (0.49)	76	8.5	1.68	1.19

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[a] Data for fractions C-1 and C-10 from ref.[13]; [b] values in parentheses are mole fractions x_p of propylene units; [c] measurement in toluene at 25 °C; [d] at 25 °C, T toluene, B benzene; [e] benzene at 30 °C; [f] n-heptane at 25 °C.

$$(\pi/c)^{1/2} = (RT/\overline{M}_n)^{1/2}\,(1 + 0.5\,A_2\,\overline{M}_n c)\ ,$$

where π is the osmotic pressure, c the polymer concentration in g cm^{-3}, R the gas constant, T the temperature in K and A_2 the second virial coefficient.

Viscometry. Viscosity measurements were made in Ubbelohde capillary viscometers adapted for subsequent dilution. The flow times were recorded opto-electrically using a home-made apparatus. The temperature was kept constant within 0.03 °C. The dimensions of viscometers were such that viscometric corrections were negligible. The concentration was chosen so that the relative viscosity η_r (i.e., ratio t/t_0 of flow times of solution and solvent) was between 1.1. and 1.8. The intrinsic viscosity [η] and the Huggins coefficient k_H were estimated by the Heller methods[28] (triple plot of c/η_{sp},

TABLE III
Intrinsic viscosity [η] (dl g^{-1}) of EPDM fractions in benzene

Temperature, °C	E-2	E-3	E-4	E-5	D-2	D-3	B
25	1.27	1.45	1.39	1.44	–	–	1.18
28	1.37	1.54	–	1.51	1.59[a]	–	1.21
30	1.41	1.54	1.55	1.58	1.54[a]	1.23	1.23
32	1.47	1.59	1.56	1.62	1.54	1.28	1.27
35	1.53	1.65	1.61	1.69	1.64	1.33	1.31
40	1.64	1.77	1.68	1.76	1.77	1.44	1.41
50	1.80	1.99	1.89	1.96	1.98	1.59	1.48

[a] At 28.8 °C.

TABLE IV
Intrinsic viscosity of EPDM-A in benzene and toluene

Temperature °C	[η], dl g^{-1}		Temperature °C	[η], dl g^{-1}		Temperature °C	[η], dl g^{-1}	
	B	T		B	T		B	T
25	0.895	1.75	31	1.34	–	44	1.52	–
26	1.12	–	32	1.31	–	45	1.54	–
27	1.16	–	35	1.35	1.83	48	1.61	–
28	1.21	–	38	1.45	–	50	1.60	1.88
30	1.26	1.80	40	1.46	1.86	–	–	–

$c/\ln \eta_r$ and $(c/2)(1/\eta_{sp} + 1/\ln \eta_r)$ vs c where $\eta_{sp} = \eta_r - 1$). Advantages of this method over the more usual one (η_{sp}/c and $\ln \eta_r/c$ vs c) were discussed elsewhere[13,29]. The [η] values were corrected for the variation of solvent density with temperature. The results are collected in Tables I to V.

Specific volumes of terpolymers were obtained as mole averages of the polyethylene and polypropylene data[6] (v_{sp} = 1.169 and 1.165 cm^3 g^{-1}) and were corrected for the effect of temperature ($\alpha \cdot 10^3$ = 0.752 and 0.80 K^{-1}).

RESULTS AND DISCUSSION

Fractionation of EPDM

Although the same solvent–nonsolvent system was used with all EPDM samples, the fractionation proceeded according to the molecular weight only with samples containing the lowest amount of propylene units (samples A and D). The $\overline{M}_n$ values of fractions of sample D cover a rather broad range (Table II) whereas the x_p values are almost the same. Similarly, the intrinsic viscosities of fractions of sample A are between 2.4 and 0.94 dl g^{-1} (toluene at 25 °C) while the propylene content is 0.18 ± 0.01. On the contrary, fractionation of samples C and E proceeded according to both factors (Table II).

Fuchs[30] has recommended the system tetrachloromethane–ethyl acetate for the fractionation of EPM copolymers according to the molecular weight. We applied this system to terpolymer C and obtained five fractions with similar intrinsic viscosities (1.6 to 1.8 dl g^{-1} in toluene at 25 °C) but with large differences in x_p (0.28 to 0.55).

It is actually impossible to give a satisfactory account of these results but it is felt that they are related to differences in the sequential arrangement of comonomer units.

TABLE V
Intrinsic viscosity [η] (dl g^{-1}) of EPDM-A in benzene and toluene

Temperature °C	A-1		A-2		A-3		A-4	
	B	T	B	T	B	T	B	T
25	gel	2.42	–	2.22	1.02	1.46	–	0.94
28	1.53	–	1.49	–	–	–	–	–
29.6	1.60	–	1.53	–	1.10	–	0.75	–
30	1.63	–	1.53	–	1.12	1.47	0.76	–
32	1.73	–	1.64	2.32	–	1.49	–	0.98
35	1.82	1.51	1.69	–	1.20	–	0.81	–
40	2.01	–	1.81	–	–	–	–	–
50	2.27	2.64	2.00	2.45	1.34	1.55	0.89	1.02

Correlation of [η] and $\overline{M}_n$

In Fig. 1 the intrinsic viscosity in toluene at 25 °C is plotted against the number-average molecular weight. Data points for fractions D1 to D5 display no scatter and can be fitted by straight line *1* with slope $\nu = 0.67$. Most data points for non-fractionated samples and for the other fractions are situated above line *1*, indicating higher polydispersity.

Line *1* is nearly parallel to line *2* fitting data points for EPM ($x_p = 0.27$) in toluene at 30 °C reported by de Chirico (cf. ref.[3]). This is the only correlation for this system which is based on the absolute determination of $\overline{M}_w$ by light scattering. Since the correlation of [η] vs $\overline{M}_n$ for EPDM in toluene at 25–50 °C only slightly depends on the copolymer composition and temperature, one can assess the polydispersity index $\overline{M}_w/\overline{M}_n$ by comparing the experimental data for EPDM with line *2*. One obtains $\overline{M}_w/\overline{M}_n \approx 1.7$ for fractions of sample D and $\overline{M}_w/\overline{M}_n \approx 2$ for the other fractions and the original samples.

Solutions of EPDM in Benzene

The values of the second virial coefficient (Table I) show that benzene at 25–30 °C is a poor solvent of EPDM terpolymers with $x_p \leq 0.19$ and a better one for those with $x_p \geq 0.4$. The theta temperatures Θ for EPDM samples are obtained by a procedure involving two steps. The first step is the estimation of the intrinsic viscosity $[\eta]_\Theta$ at theta conditions. For sample A the $[\eta]_\Theta$ value is calculated from [η], $\overline{M}_n$ and A_2 at 30 °C by means of the semiempirical equation derived by Krigbaum[31]

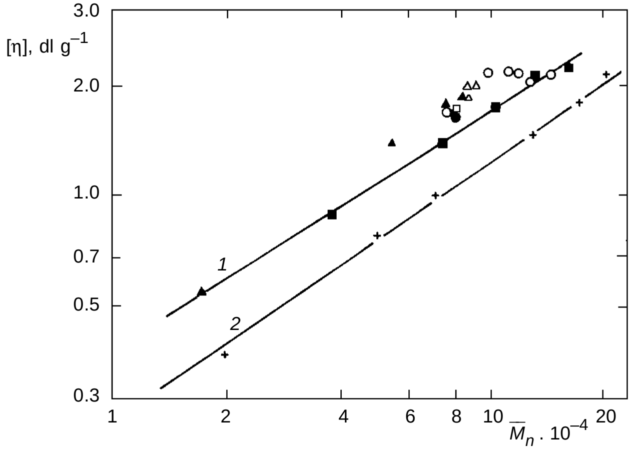

FIG. 1

Plot of [η] of EPDM in toluene at 25 °C against $\overline{M}_n$. Data points: fractions D ■, C ▲, E ❍; non-fractionated samples A Δ, B ●, D ❒. Line *1* drawn through points for D; line *2* fits data of [η] vs $\overline{M}_w$ for EPM ($x_p = 0.27$) (ref.[3])

$$[\eta]_\Theta = [\eta] - 5\ .\ 10^{-3} A_2 M\ . \qquad (14)$$

For sample B and fractions C-10 and B-5 the $[\eta]_\Theta$ values are obtained by extrapolating to $A_2\overline{M}_n = 0$ in the plots of $[\eta]$ vs $A_2\overline{M}_n$ (Fig. 2).

The second step is the extrapolation to $[\eta]_\Theta$ of the plots of $[\eta]$ vs T (Fig. 3). Theta temperatures thus obtained (Table VI) are plotted against x_p in Fig. 4*a* along with those reported for ethylene–propylene copolymers (EPM)[3,15]. The dependence is not significantly affected by the presence of diene units in EPDM (2–5 mole %) and is smooth enough for theta values for other copolymers and terpolymers to be estimated by interpolation.

In Fig. 5 the viscosity expansion factors are plotted according to Eq. (*5b*). The scatter of points is small and data for various terpolymers form a single composite dependence

TABLE VI

Θ-temperatures and $[\eta]_\Theta$ values of EPDM samples in benzene

Variable	A	B	C-1	C-10	D-5
Θ, °C	29.5[a]	20.5[a]	26[b]	19[b]	29[b]
$[\eta]_\Theta$, dl g^{-1}	1.24[c]	1.09[d]	–	1.01[d]	0.72[d]

[a] Estimated by interpolation or extrapolation to $[\eta]_\Theta$ of plots in Figs 2 and 3; [b] approximate values obtained by interpolation in Fig. 4; [c] estimated according to Eq. (*14*); [d] estimated from Fig. 2.

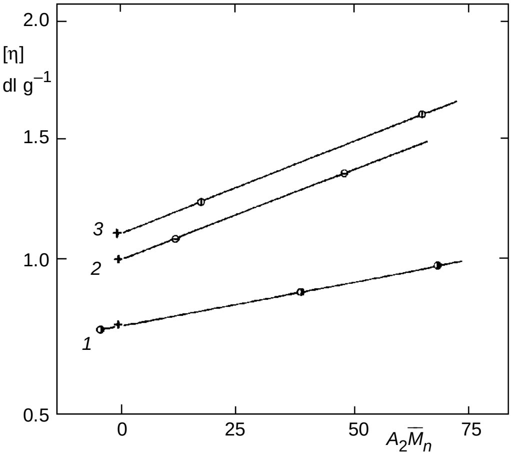

FIG. 2

Plot of $[\eta]$ vs $A_2\overline{M}$ for EPDM in several solvents. Data points: samples D5 (*1*), C-10 (*2*), B (*3*). Values of $[\eta]_\Theta$ are denoted by crosses

(Fig. 6). Hence, the value of $B_0/K_0^2 = 5.4 \,.\, 10^{21}$ derived from the initial slope is almost invariant with respect to the terpolymer composition ($0.18 \leq x_p \leq 0.4$ and $0.02 \leq x_d \leq 0.05$). The B values deduced from it increase and the B_0 values decrease with increasing content of propylene monomeric units (Fig. 4*b*).

Solution of EPDM in Toluene

The intrinsic viscosities in toluene are higher than those in benzene. The plots of α_η^3 vs $[\eta]_\Theta$ according to Eq. (*5a*) in Fig. 7 for fractions with $x_p = 0.19$ at three temperatures are linear and their slopes increase with increasing temperature. Plots for terpolymers with $x_p = 0.29$ and 0.38 comprise only two data points each but are clearly above line *1* corresponding to $x_p = 0.19$.

The B and χ values for $0.19 \leq x_p \leq 0.38$ at 25 °C (Fig. 8) are almost independent of composition. This is in line with Fig. 9 where the molecular-weight dependence of the second virial coefficient displays no significant effect of composition. Anyway, the solvent power of toluene for EPDM is lower than for atactic polypropylene (cf. Fig. 8).

Sen and Rubin[11] have recently studied solutions of EPM copolymers in toluene over a broader temperature range (–10 to 50 °C). They have found that the intrinsic viscosity at 20–50 °C only slightly depends on temperature (similarly to the present results) but starts decreasing strongly with decreasing temperature below 10 °C.

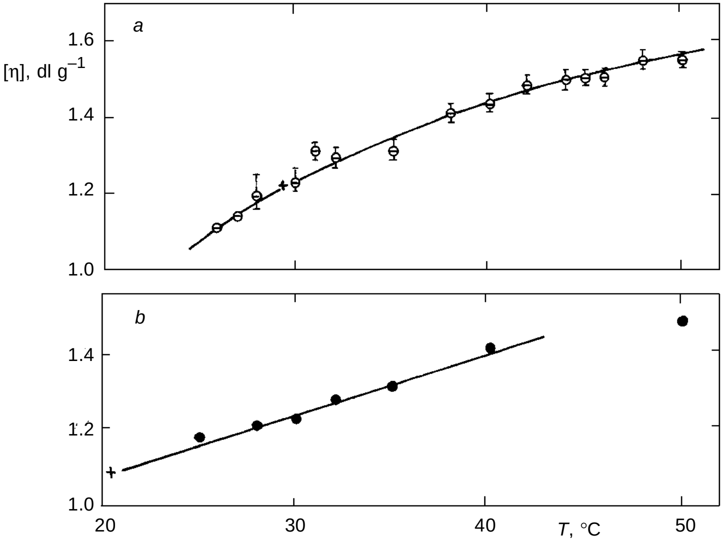

FIG. 3

Estimation of $[\eta]_\Theta$ by extrapolating the dependences of $[\eta]$ vs T to theta temperature. Data points: sample A (*a*) (with denoted error limits of duplicate and triplicate estimation), sample B (*b*)

Polymer–Solvent Interaction Parameters

The data plotted in Figs 4 and 8 cover too narrow a range of copolymer composition and the values of parameters for homopolymers are not known[32]. Therefore, only a qualitative analysis is possible. Unlike the copolymers studied so far, the present system offers a possibility of distinguishing entropic and enthalpic contributions to the copolymer–solvent interaction.

The dependence in Figs 4*b* and 4*c* might be fitted by straight lines. However, a linear dependence of κ vs x_p must be excluded as it would extrapolate to a negative κ value for polypropylene in contradiction to the positive heat of mixing found by Ochiai et al.[33]. A non-linear dependence of ψ vs x_p is also more probable. With $\chi = 0.443$ and $\kappa > 0$ for polypropylene we obtain $\psi \geq 0.05$, which is a reasonable value.

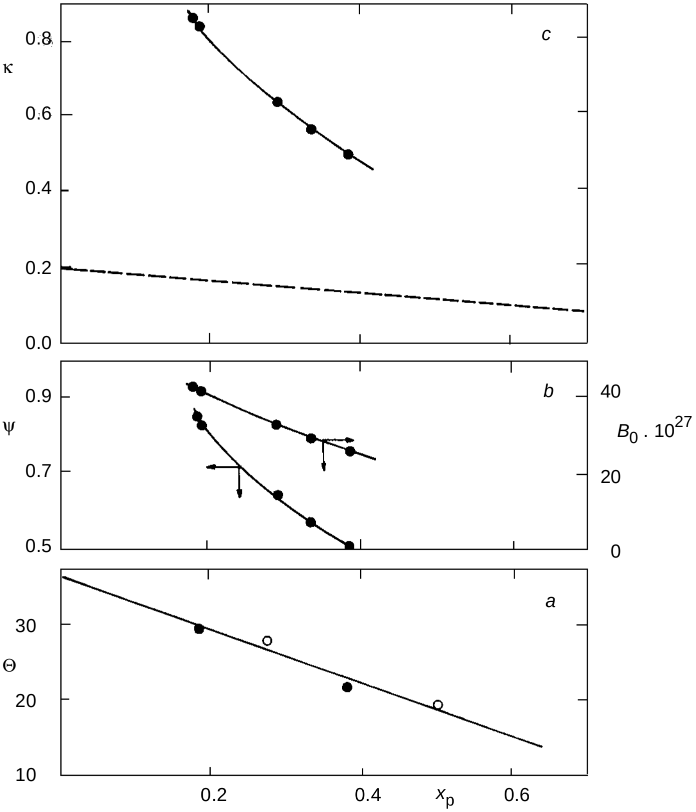

FIG. 4

Dependence of thermodynamic parameters of EPDM in benzene on terpolymer composition. *a* Θ-temperature, *b* ψ and B_0 parameter, *c* κ parameter at 30 °C. Dashed line calculated with Eq. (*15*). Data points: ● this paper, ❍ refs[3,15]

With most polymers investigated so far[23], the ψ parameter was lower than 1/2 because the second term in Eq. (*11*) was negative and opposed the combinatory term. With solutions of EPDM in benzene the ψ values are higher than 1/2 and the difference from 1/2 is of such magnitude that it cannot be due to inaccuracy of measurements or evaluation of data.

Positive values of (ψ – 1/2) are indicative of an order within the coils of EPDM molecules swollen by the solvent. Dissipation of the order with dilution (i.e., with expanding the coil dimensions) is reflected in the entropy of dilution enhanced above the lattice combinatory contribution. The decrease in (ψ – 1/2) with increasing x_p can be understood, assuming that ordered regions are due to sequences of ethylene units. The shorter these sequences are, the lower is the local order and, consequently, (ψ – 1/2).

As shown by Fig. 4*b* the ψ parameter is close to 1/2 at $x_p \approx 0.4$ and probably would decrease below it at a higher content of propylene units. In other words, the residual partial molar entropy would be negative with such copolymers and with polypropylene as it indeed is with other hydrocarbons such as natural rubber, polyisobutylene, polystyrene, etc.[23].

It is generally assumed that approximate values of κ for nonpolar polymers can be obtained from the solubility parameters of the solvent δ_s and polymer δ_p

$$\kappa = (V_1/RT)(\delta_p - \delta_s)^2 \quad . \qquad (15)$$

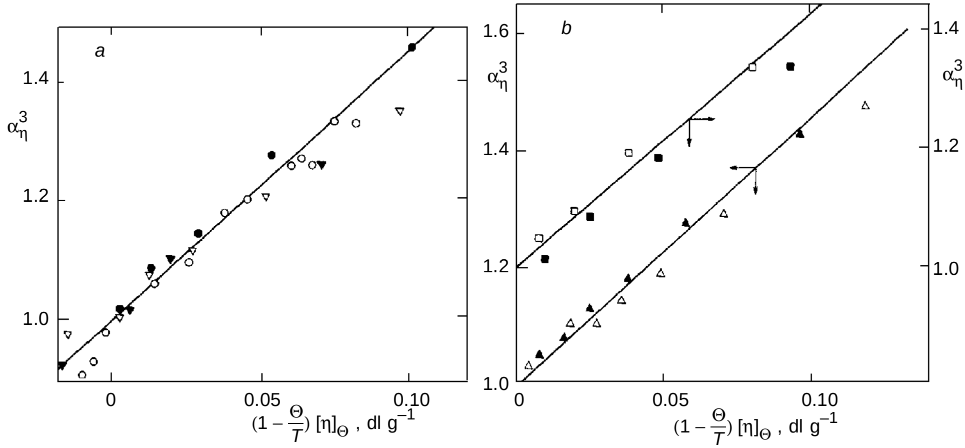

FIG. 5
Plots of the viscosity expansion factor for EPDM in benzene according to Eq. (*5b*). *a* A ❍, A-1 ●, A-2 ∇, A-4 ▼; *b* D-2 ■, D-3 ❐, E-2 ▲, E-3 ∆

Van Krevelen[34] reports an interval of δ_p values for polyethylene (15.7–17.1 $J^{1/2}$ $cm^{-3/2}$) and polypropylene (16.8–18.8 $J^{1/2}$ $cm^{-3/2}$). Substituting their arithmetic means for δ_p and setting δ_s = 18.7 $J^{1/2}$ $cm^{-3/2}$ for benzene, we obtain κ = 0.2 and 0.045 for polyethylene and polypropylene, respectively. These data are included into Fig. 4*c*. The dashed line connecting them corresponds to the case where the cross term κ_{AB} is zero. The experimental values are significantly higher. (They correspond to unrealistic values of δ_p for copolymers, e.g., 13.9 or 23.5 $J^{1/2}$ $cm^{-3/2}$ at x_p = 0.19.) Though Eq. (*15*) yields only approximate κ's, the differences $\Delta\kappa$ of experimental and calculated values are too high to be ascribed to this inaccuracy.

The differences $\Delta\kappa$ decrease with increasing x_p and seem to vanish at $x_p \geq 0.6$, i.e., with copolymers with prevalence of propylene units. They are very high with copolymers where the sequences of ethylene units are, on average, longer than those of propylene units. It may be concluded that the anomalies are related to the length of ethylene sequences and have the same reason as those of the ψ parameter: they contain heat contributions needed for dissipation of ordered structures.

These results lend support to the conclusions deduced from high values of the Huggins viscosity coefficient[13]. The association monitored by the Huggins coefficient is intermolecular whereas the interactions derived from the intrinsic viscosities indicate that an order of ethylene units exists also on the intramolecular level. In such case, polymer chains would have physical intramolecular loops. If a certain fraction of monomeric units participated in these loops, the chain dimensions and the intrinsic viscosity would be lower than in absence of association. Intramolecular loops would be destroyed by heating and the intrinsic viscosity would approach the value corresponding to random coils without order. In consequence of this effect, the dependences of [η] vs *T* would be steeper and the slopes of plots in Figs 5 and 6 would be higher than in the absence of any organization. Therefore, the B_0 and ψ values would be merely effec-

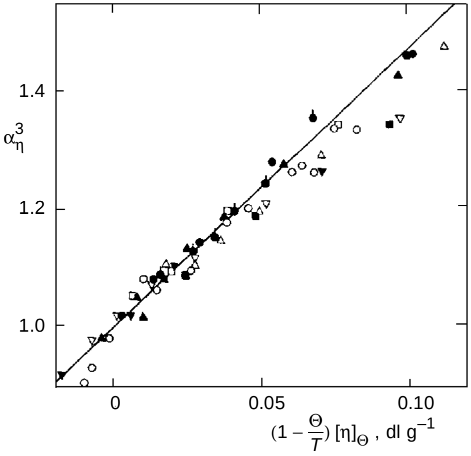

FIG. 6
Composite plot of the viscosity expansion factor for EPDM in benzene according to Eq. (*5b*). For notation of points see Fig. 5

tive (or apparent) values containing contributions corresponding to the destruction of intramolecular association.

Kuhn and Majer[35] theoretically calculated the effect of intramolecular rings formed by covalent bonds on the intrinsic viscosity. If the ring formation is a random process the average size of the ring (expressed by the number s_r of statistical segments) is

$$s_r = (2^{3/2}/3)N^{1/2} \;, \tag{16}$$

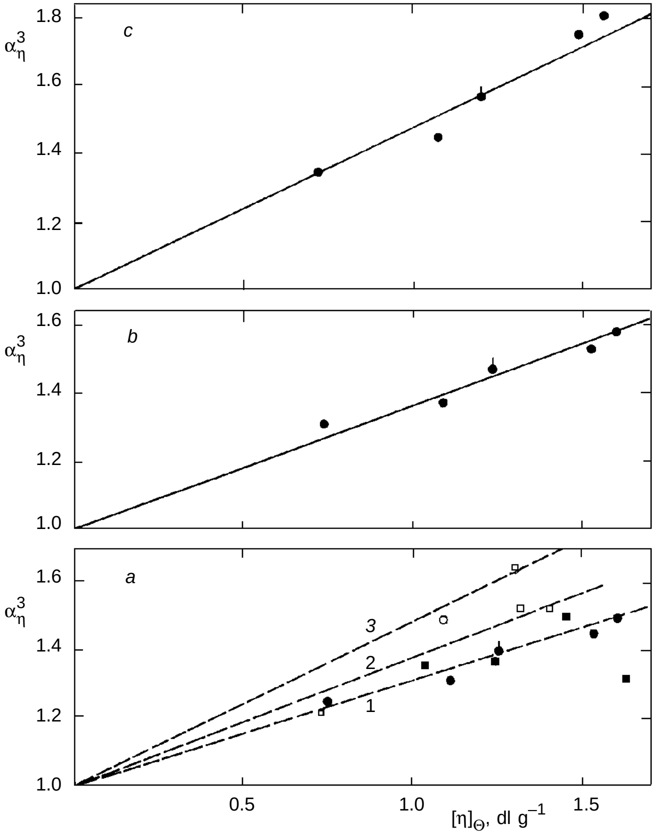

FIG. 7

Plot of the intrinsic viscosity according to Eq. (*5a*) for EPDM in toluene. Temperature (°C): 25 (*a*), 35 (*b*), 50 (*c*). Lines *1* to *3* in *a* for x_p: 0.18–0.2, 0.29, 0.39, respectively. For notation of points, see Fig. 1. Pips denote data for non-fractionated samples where N is the number of statistical segments per chain. The intrinsic viscosity of such chains is lower than that of the linear molecules at the same N, the ratio $g'_{0,\mathrm{r}}$ being approximately (under theta condition)

$$g'_{0,\mathrm{r}} \equiv [\eta_\mathrm{r}]_\Theta/[\eta_\mathrm{l}]_\Theta \approx 1 - m_\mathrm{r}(2/N)^{1/2} \ , \qquad (17)$$

where subscripts r and l with $[\eta]_\Theta$, respectively, denote chains with and without rings.

If, e.g., $N = 10^3$ the average size is $s_\mathrm{r} \approx 30$. If one or two rings are formed (number of rings $m_\mathrm{r} = 1, 2$) the intrinsic viscosity is decreased by 4.5 and 9%, respectively.

It is a question whether intramolecular association is a random process. To the extent that the results of the above calculation may be applied to physical loop formation, its effect on [η] may be significant, and may be particularly relevant for the temperature dependence of [η] if loops are destroyed by heat.

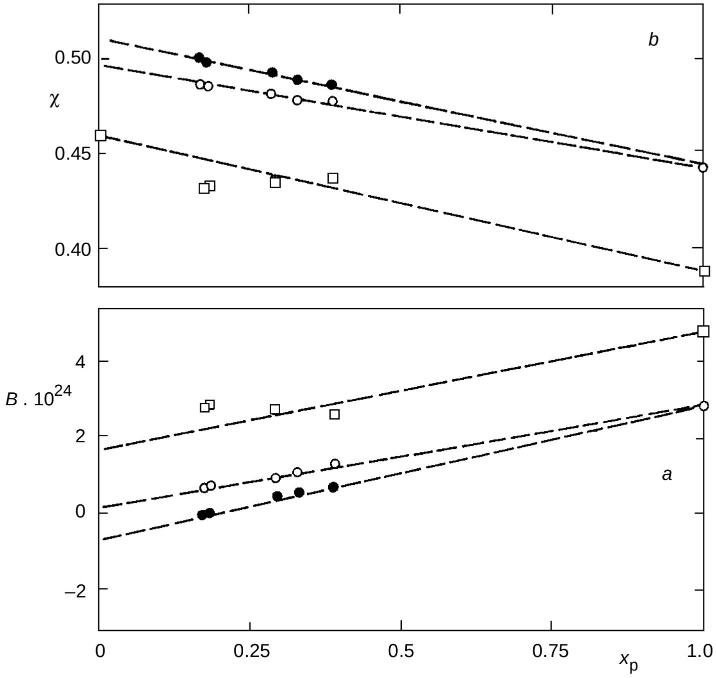

FIG. 8
Dependence on terpolymer composition of the interaction parameters B (*a*) and χ (*b*) for EPDM. Data points: ● ○ benzene at 30 and 35 °C, respectively, □ toluene. Values at $x_\mathrm{p} = 1$ from refs[26,27], the value for $x_\mathrm{p} = 0$ in toluene from ref.[32]

We are actually not in state to assess these effects and to estimate how much the ψ values are affected by intramolecular association. In any case, high values of ψ are an indication of some vestiges of order in molecules of EPDM elastomers dissolved in benzene at normal temperatures.

Interaction Parameters of Polyethylene

By extrapolating the dependences of the interaction parameter on x_p (Fig. 8) to $x_p = 0$, we can assess the values for polyethylene. For solutions in toluene we obtain $\chi = 0.46$ which agrees with the value obtained from measurements of sorption[32]. By applying the same treatment to the data for benzene (Fig. 8) we obtain $\chi = 0.52$ and 0.498 at 30 and 35 °C, respectively. These data show that the theta temperature is close to 35 °C. Extrapolation of the dependence of Θ vs x_p yields $\Theta = 36$ °C. Significantly lower values would be deduced from sorption measurements[32] which have given $\chi = 1/2$ at 25 °C. However, the difference may be due to different regimes in measurements of sorption (high polymer concentration, crystalline state) and viscosity (dilute solutions, random coil conformation).

These data explain the insolubility of polyethylene in these solvents at normal temperature, whereas insolubility in toluene is due exclusively to the high melting temperature of the polymer; this factor along with high interaction parameter are responsible for insolubility in benzene.

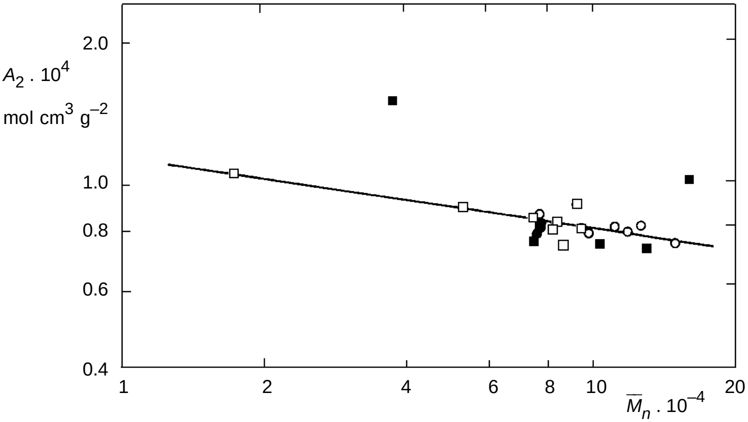

FIG. 9
Molecular-weight dependence of the second virial coefficient A_2 for EPDM terpolymers in toluene at 30 °C. Sample fractions: B ●, C ❐, D ■, E ❍

APPENDIX

The Dependence of the Constant K_0 on the Composition of EPM Copolymers

The K_0 constant is related to the conformational characteristic referred to as the characteristic ratio C_∞ and defined by the equation[21]

$$C_\infty = (\langle R^2 \rangle_0 / nl^2)_\infty \qquad (A\text{-}1)$$

as the ratio of the unperturbed mean-square end-to-end distance $\langle R^2 \rangle_0$ of the real chain and a freely jointed one (nl^2) in the random coil limit. The symbol n stands for the number of main chain bonds of length l each. From Eqs (*A-1*) and (*3*) we obtain

$$C_\infty = (K_0/\Phi_{0,\infty})^{2/3}\,(M_0/2\,l^2)\ , \qquad (A\text{-}2)$$

where M_0 is the mean molecular weight per main chain unit.

In general[36], the characteristic ratio of EPM copolymers depends on the probability p_2 of occurrence of propylene units, on the probability p_r of isotactic placement of these units, and on the chemical sequence distribution governed by the product of reactivity ratios r_1r_2. The values of r_1r_2 = 10, 1 and 0.01 correspond, respectively, to block, statistical and alternating copolymers.

Mark[36] has carried out theoretical calculations for EPM copolymers differing in p_2,p_r and r_1r_2. Since the sequences of propylene units in EPDM are probably atactic we employ only the results for $p_r = 0.5$ (atactic placement of propylene units). In this case the dependences of C_∞ vs p_2 have a shallow minimum at $p_2 = 0.8$ and are practically invariant with respect to $1 \le r_1r_2 \le 0.01$. The K_0 values (Fig. A-1, curve *1*) were calculated from the C_∞ values corresponding to $p_r = 0.5$ and $r_1r_2 = 1$ taking account of the variation of M_0 with composition. The dependence of K_0 vs w_p is almost linear.

Scholte et al.[17] have introduced a simple assumption that the EPM molecules may be treated as polymethylene chains with randomly distributed short branches (methyl groups) and that the ratio g of the radii of gyration of branched and linear chains may be expressed by

$$g \equiv \langle S^2 \rangle_{0,\mathrm{b}} / \langle S^2 \rangle_{0,\mathrm{l}} = 1 - \frac{1}{3} w_\mathrm{p}\ . \qquad (A\text{-}3)$$

This leads to

$$K_0^{\mathrm{EPM}} \approx K_0^{\mathrm{PE}}(M_0^{\mathrm{E}}/M_0^{\mathrm{EPM}})^{3/2}\,(1 - w_{\mathrm{p}}/3)^{3/2}\ . \qquad (A\text{-}4)$$

The K_0 values calculated on this basis (Fig. A-1, curve *2*) are lower than those represented by curve *1* by 10 to 20%.

There are very few experimental data in literature to check these dependences. For alternating EPM copolymers ($p_{\mathrm{r}} = 0.5$, $w_{\mathrm{p}} = 0.60$), May and Fetters[15] estimated K_0 from the intrinsic viscosities and weight-average molecular weights in the temperature range from 5 to 60.9 °C. By interpolation for 30 °C we obtain $K_0 = 1.98 \,.\, 10^{-3}$ dl g^{-1}. De Chirico (cf. ref.[3]) measured the intrinsic viscosities in toluene and isooctane of fractions with $w_{\mathrm{p}} = 0.37$. The plot of $[\eta]/M_{\mathrm{w}}^{1/2}$ vs $M^{1/2}$ according to Burchard–Stockmayer–Fixman[31,32] extrapolates to $K_0 = 2.5 \,.\, 10^{-3}$ dl g^{-1}.

Brückner et al.[37] studied fractions of two copolymers ($w_{\mathrm{p}} = 0.29$ and 0.62) in ethyl phenyl ether at $\Theta = 89$ and 79 °C, respectively, and obtained $K_{0,n} \,.\, 10^3 \equiv [\eta]_\Theta/\overline{M}_n^{1/2} \,.\, 10^3$ to be 2.85 and 2.11 dl g^{-1}. Approximate values for 30 °C ($K_{0,n} \,.\, 10^3 = 3.1$ and 2.3 dl g^{-1}) are calculated assuming $\mathrm{d}\ln K_0/\mathrm{d}T = -1.5 \,.\, 10^{-3}\ \mathrm{K}^{-1}$ (ref.[21]). These values are located above curve *1* in Fig. A-1. However, since the number average molecular weights were used in the work quoted, the $K_{0,n}$ values should be corrected for polydispersity[38]

$$K_0 = K_{0,n}/q_{\mathrm{n}}\ . \qquad (A\text{-}5)$$

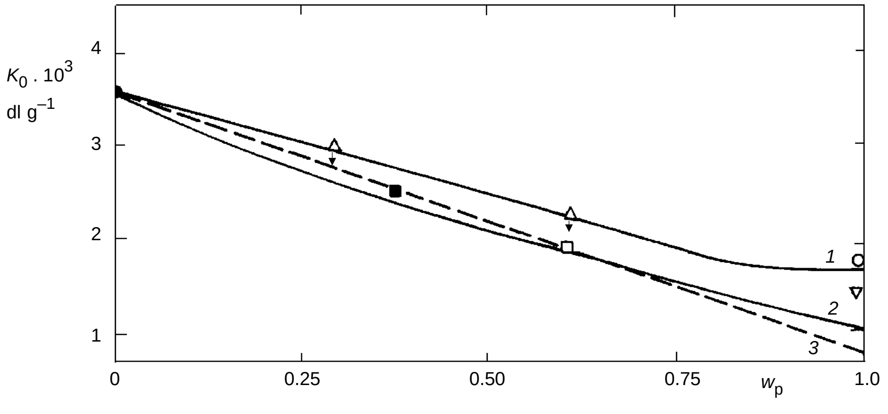

FIG. A-1

Dependence of the viscosity constant K_0 on composition of EPM copolymers at 30 °C. Data points: ● polyethylene[21], ❍ ∇ atactic polypropylene[26,27], ❐ EPM (ref.[15]), ■ EPM (extrapolated by means of the Burchard–Stockmayer–Fixman method[19,20] from data in isooctane[3]), Δ EPM (ref.[37]). Lines: *1* theoretical[36], *2* theoretical[17], *3* fit by Eq. (*A-7*). Arrows with Δ denote the K_0 values after an approximate correction for polydispersity (see the text)

Assuming the Schulz–Zimm function to describe the molecular weight distribution, the correction factor q_n is

$$q_n = h^{1/2}\Gamma(h+1)/\Gamma(h+1.5) \ , \tag{A-6}$$

where $1/h = (\overline{M}_w/\overline{M}_n) - 1$.

Unfortunately, the polydispersity of fractions has not been reported. Assuming, rather arbitrarily, $(\overline{M}_w/\overline{M}_n) = 1.25$, we obtain $q_n = 1.09$. As shown by arrows in Fig. A-1, this correction shifts the data points to the proximity of straight line *3* drawn through the values for polyethylene and two copolymers. It is slightly (5%) above curve *2* and can be fitted by the equation

$$K_0^{\mathrm{EPM}} = K_0^{\mathrm{PE}}(1 - 0.778w_p) \ . \tag{A-7}$$

There is little agreement in the K_0 values for atactic polypropylene at 30 °C. The recent value obtained by Mays et al.[15] is lower by about 15% than that estimated by Inagaki et al.[27]. Fortunately, the difference, though significant, is of no consequence for the present work.

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