Macromolecules **1990**, *23*, 2519-2524

(11) Cabane, B.; Dubois, M.; Duplessix, R. *J. Phys. (Paris)* **1987**, *48*, 2131.
(12) Martin, J. E.; Keefer, K. D. *Phys. Rev. A* **1986**, *34*, 4988.
(13) Martin, J. E.; Wilcoxon, J.; Adolf, D. *Phys. Rev. A* **1987**, *36*, 1803.
(14) Patton, E. V.; Wesson, J. A.; Rubinstein, M.; Wilson, J. C.; Oppenheimer, L. E. *Macromolecules* **1989**, *22*, 1946.
(15) Martin, J. E.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 373.
(16) Adam, M.; Delsanti, M.; Durand, D. *Macromolecules* **1985**, *18*, 2285.
(17) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3*, 297.
(18) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 2620.
(19) Rubinstein, M.; Colby, R. H.; Gillmor, J. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 81.
(20) Ulrich, D. R. *J. Non-Cryst. Sol.* **1988**, *100*, 174.
(21) Bechtold, M. F.; Mahler, W.; Schunn, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3623.
(22) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *J. Phys. (Paris)* **1987**, *48*, 1809.
(23) de Gennes, P.-G. *C. R. Acad. Sci., Ser. B* **1978**, *286*, 131.
(24) Zabolinski, J. G.; Bergman, D. J.; Stauffer, D. *J. Stat. Phys.* **1986**, *44*, 211.
(25) Herrmann, H. J.; Derrida, B.; Vannimenus, J. *Phys. Rev. B* **1984**, *30*, 4080.
(26) Gauthier-Manuel, B.; Guyon, E.; Roux, S.; Gits, S.; Lefaucheux, F. *J. Phys. (Paris)* **1987**, *48*, 869.
(27) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980.
(28) Hair, D. W.; Niertit, F. J.; Hodgson, D. F.; Amis, E. J. *Rev. Sci. Instrum.* **1989**, *60*, 2780.
(29) Schrag, J. L.; Johnson, R. M. *Rev. Sci. Instrum.* **1971**, *42*, 224.
(30) Hair, D. W.; Amis, E. J. *Macromolecules* **1989**, *22*, 4528.
(31) Keefer, K. D. In *Better Ceramics Through Chemistry I*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Mater. Res. Soc. Proc. 32; North-Holland: New York, 1984; p 15.
(32) Schaefer, D. W.; Keefer, K. D. In *Better Ceramics Through Chemistry II*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Mater. Res. Soc. Proc. 73; North-Holland: New York, 1986; p 277.
(33) Bailey, J. K.; Mecartney, M. L. In *Better Ceramics Through Chemistry III*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Mater. Res. Soc. Proc. 121; North-Holland: New York, 1988; p 367.
(34) Kozuka, H.; Kuroki, H.; Sakka, S. *J. Non-Cryst. Sol.* **1988**, *100*, 226.
(35) Sacks, M. D.; Sheu, R.-S. *J. Non-Cryst. Sol.* **1987**, *92*, 383.
(36) Winter, H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367; **1987**, *31*, 683.
(37) Chambon, F.; Winter, H. *Polym. Bull.* **1985**, *13*, 499.
(38) Holly, E. E.; Venktaraman, S. K.; Chambon, F.; Winter, H. H. *J. Non-Newtonian Fluid Mech.* **1988**, *13*, 17.
(39) Hodgson, D. F.; Hair, D. W.; Amis, E. J. Unpublished results.
(40) Colby, R. H.; Coltrain, B. K.; Salva, J. M.; Melpolder, S. M. In *Fractal Aspects of Materials: Disordered Systems*; Hurd, A. J., Weitz, D. A., Mandelbot, B. B., Eds.; Materials Research Society: Pittsburgh, 1987.

Molecular Structures and Solution Viscosities of Ethylene–Propylene Copolymers

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ABSTRACT: Dilute solution studies on ethylene–propylene (EP) copolymers in hydrocarbon solvents at −10 to +50 °C showed that highest viscosities were obtained in methylcyclohexane and lowest in toluene and tetralin (tetrahydronaphthalene). The copolymers contained 58–80 mol % ethylene; their $\bar{M}_w$ values were 148 000 to 322 000 and only those with 80% ethylene contained crystallinity. The solvating power of aliphatic solvents for amorphous copolymers, as measured by viscosity, decreased slowly with rise in temperature while that of the aromatics improved slightly to 20 °C and then remained constant or gradually diminished. The low-temperature solubility of partially crystalline copolymers was poorer in most solvents, improved rapidly to 20 °C, and then changed little with temperature. Linear double logarithmic plots of $[\eta]$ against $\bar{M}_w$ were obtained for all EPs in methylcyclohexane, but the Mark–Houwink equation did not describe low-temperature data in toluene. Equivalent hydrodynamic volumes were calculated. Behavior of partially crystalline copolymers in poor solvents at low temperatures is explained by ordering of the longer ethylene sequences into aggregates or partially ordered domains.

Introduction

There are only scattered reports in the literature on dilute solution properties of ethylene–propylene copolymers[1-8] and just a few of them address the effect of temperature on solution behavior.[5-8] This is rather surprising in view of the extensive commercial applications of EP copolymers. One of their important applications is in motor oils where they modify the viscosities of the oils and extend the temperature range over which they can be used. The purpose of our work is to gain a better picture of polymer–solvent interactions of EP copolymers in hydrocarbon solvents and increase our understanding of their behavior in the temperature range useful for motor oils. With this in mind, we investigated the effect of aliphatic and aromatic hydrocarbon solvents on the solution viscosity of EP copolymers in the temperature range of −10 to +50 °C using five copolymers differing in such key properties as molecular weight, ethylene to propylene ratio, length of ethylene sequences, and crystallinity.

Experimental Section

The ethylene–propylene copolymers were prepared with a soluble Ziegler–Natta catalyst composed of an alkylaluminum halide and a vanadium salt. Molecular weights and polydispersity were obtained by means of gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 135 °C utilizing a Waters 150 C

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Table I
Molecular Characteristics of Ethylene–Propylene Copolymers

			NMR			FTIR	DSC	X-ray
EP copolymer	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	ethylene, mol %	$\bar{N}$	E_n	CH_2/CH_3	T_m, °C	crystallinity, %
EP-1	148	2.9	60	4.2	0.35	2.0		
EP-2	252	3.5	58	3.9	0.30	2.1		
EP-3	192	3.4	70	4.8	0.56	5.1		
EP-4	207	3.6	80	6.5	0.62	7.9	45	8.4
EP-5	322	4.1	80	6.1	0.65	7.5	43	5.2

GPC instrument equipped with five columns (1×10^6, 1×10^5, 1×10^4, 1×10^3, and 500 Å).

A Perkin-Elmer DSC-7 differential scanning calorimeter was used at a heating rate of 10 °C/min to determine melting points (T_m) while crystallinities were obtained from wide-angle X-ray scattering measurements (WAXS) on a Scintag Pad V diffraction system. Ethylene contents, mean number of ethylene units in sequences of 3 or more, $\bar{N}$, and the fraction of ethylene sequences containing 3 or more ethylenes, $E_n \geq 3$, were determined by using the method of Randall[9] and Johnston et al.[10] from ^{13}C NMR data obtained in *o*-dichlorobenzene on a Varian VXR-300 spectrometer.

All viscosity measurements were made with Ubbelohde viscometers in a bath controlled to within ±0.01 °C of the desired temperature. The initial solutions ranged in concentration from 0.4 to 1.0 g/dL, depending on copolymer molecular weight. Measurements for each solution were run as many as eight to ten times. Densities of the solvents at the different temperatures were measured with a Mettler/Paar DMA 45 Digital Density Meter and EP concentrations were corrected for the change of solvent density with temperature. No kinetic energy corrections were made because the flow times of the solvents were at least 100 s.[11] Since the $\bar{M}_w$ values were not too high and intrinsic viscosities of most EP samples were below 3.00 dL/g, the effect of shear rate was negligible.[12]

Methylcyclohexane, tetralin, and hexane were obtained from Aldrich Chemical and toluene and isooctane (2,2,4-trimethylpentane), from Burdick and Jackson Co. All solvents were of high purity and were used as received.

Results and Discussion

Copolymer Characterization. Important factors that affect intrinsic viscosity of copolymers include, in addition to those which are pertinent for homopolymers, chemical composition, homogeneity, and length of sequences of chemically identical monomer units.[5,13] The significant characteristics of the EP copolymers used in this study are listed in Table I. As shown, weight-average molecular weights range from 148 000 to 322 000 and molecular weight distributions, P_d, are 2.9–4.1. EP-1 and EP-2 contain, respectively, 60 and 58 mol % ethylene; EP-3 contains 70% ethylene; and EP-4 and EP-5 contain 80% ethylene. In both EP-1 and EP-2, the mean number of ethylene units in sequences of 3 or more and the fraction of these sequences are similar ($\bar{N}$ = 4.2 and 3.9; E_n = 0.35 and 0.30). For EP-3, $\bar{N}$ and E_n are 4.8 and 0.56, respectively. Both these values are, however, considerably larger for EP-4 and EP-5 ($\bar{N}$ = 6.5 and 6.1; E_n = 0.62 and 0.65). Judging by DSC scans, the copolymers with 58–70 mol % ethylene are completely amorphous while those with 80% have small crystalline fractions characterized by broad melting peaks around 43–45 °C. Wide-angle X-ray diffraction shows that EP-4 and EP-5 contain, respectively, 8.4 and 5.2% of crystalline material. The ratio of CH_2 to CH_3 groups[14] was found to be about 2 for EP-1 and EP-2, 5.1 for EP-3, and 7.9 and 7.5, respectively, for EP-4 and EP-5.

Relative Viscosities. Viscosity studies were carried out in five hydrocarbon solvents using the copolymers characterized in Table I. They were selected to be representative of different types of base oil components. Thus, hexane and isooctane are representative of paraffinic components; methylcyclohexane is representative of a naphthenic component, toluene, representative of an aromatic component, and tetralin, representative of a complex aromatic–naphthenic component.

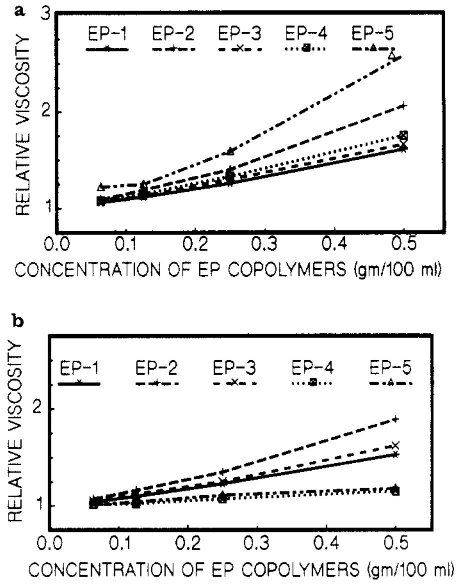

Figure 1. Relative viscosities of EP copolymers in toluene: (a) 20 °C; (b) -10 °C.

Parts a and b of Figure 1 illustrate how the various factors affecting viscosity can change in relative importance with temperature. Shown here are the relative viscosities (efflux times of solutions/efflux time of solvent) for solutions of EPs as a function of copolymer concentration in toluene at −10 and +20 °C. At 20 °C, as well as at higher temperatures, relative viscosities increase with molecular weight and concentration of the copolymers regardless of composition. At −10 °C, however, the situation is very different. Here, the viscosities of the partially crystalline EP-4 and EP-5 are lower than those of the samples with 58–70% ethylene even though EP-5 has the highest molecular weight and the molecular weight of EP-4 exceeds those of EP-1 and EP-3. These data reveal that molecular weight is the predominant factor which governs the solution viscosities of the EP copolymers in toluene at high temperatures; however, as temperature is lowered, parameters related to copolymer composition and structure such as ethylene content, size and number of ethylene sequences, and crystallinity gain in importance. Figure 2 shows the relative viscosities of solutions of EP-5 in all five solvents at 20 °C. Results at other temperatures and for the other copolymers are similar. It is apparent that methylcyclohexane is thermodynamically the best solvent.

Intrinsic Viscosities, Huggins Constants, and Equivalent Hydrodynamic Volumes. Intrinsic viscosities were obtained from the equation[15]

$$\eta_{sp}/c = [\eta] + K_1[\eta]^2 c \qquad (1)$$

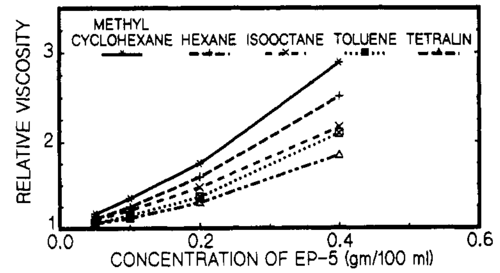

Figure 2. Relative viscosities of solutions of EP-5 in various solvents at 20 °C.

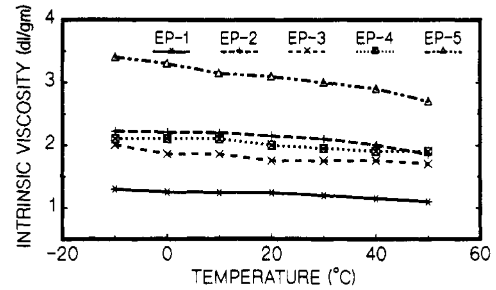

Figure 3. Intrinsic viscosities of EP copolymers in methylcyclohexane at various temperatures.

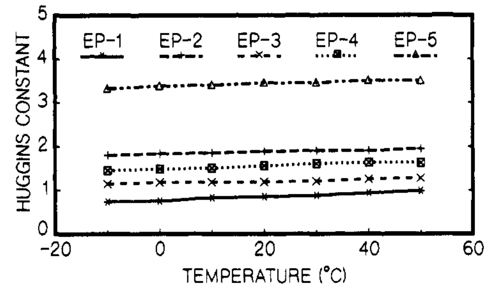

Figure 4. Huggins constants, K_1, for EP copolymers in methylcyclohexane at various temperatures.

by extrapolating plots of η_{sp}/c versus c to infinite dilution while Huggins constants, K_1, were calculated from the slopes of the plots. In the equation η_{sp} is the specific viscosity (the relative increment in solution viscosity over that of the solvent), η_{sp}/c, the reduced viscosity, $[\eta]$, the intrinsic viscosity, and c, the polymer concentration.

Figure 3 shows the temperature dependence of the intrinsic viscosities in methylcyclohexane. For all cases, they decrease slightly as the temperature is raised from -10 to 50 °C, indicating that solubility and polymer-solvent interaction are poorer at the higher temperature. The biggest $[\eta]$ decrease, about 20%, is obtained for EP-5. Huggins constants in methylcyclohexane are shown in Figure 4. As reported for other systems,[7,16-18] $[\eta]$ and K_1 change in opposite directions with an increase in temperature.

Intrinsic viscosity data were used to calculate the equivalent hydrodynamic volumes, V_e, a measure of the size of a polymer molecule at infinite dilution where polymer coils behave essentially like hard spheres and refuse to interpenetrate.[19,20] The following equation of Flory[19] was used to obtain V_e

$$V_e = \bar{M}[\eta]/\upsilon N \qquad (2)$$

where $\bar{M}$ is the molecular weight, N, Avogadro's number, and υ, a shape factor. For spheres, υ is equal to 2.5.[21] Equivalent hydrodynamic volumes for the copolymers in methylcyclohexane are given in Table II. At any given temperature, the values grow with increasing molecular weights; they decrease, however, by about 15-20% between -10 and 50 °C, indicating slightly reduced polymer-solvent interaction with rising temperature.

Table II
Equivalent Hydrodynamic Volumes, $10^{18}V_e$ (cm³/molecule), in Methylcyclohexane

temp, °C	EP-1	EP-2	EP-3	EP-4	EP-5
-10	12.3	39.2	24.9	26.5	76.3
0	11.8	38.8	23.1	26.5	74.0
10	11.7	38.8	23.1	26.5	70.7
20	11.7	37.9	21.8	25.3	69.5
30	11.4	37.0	21.8	24.7	67.3
40	10.9	35.3	21.8	24.0	65.1
50	10.4	32.6	21.2	24.0	60.6

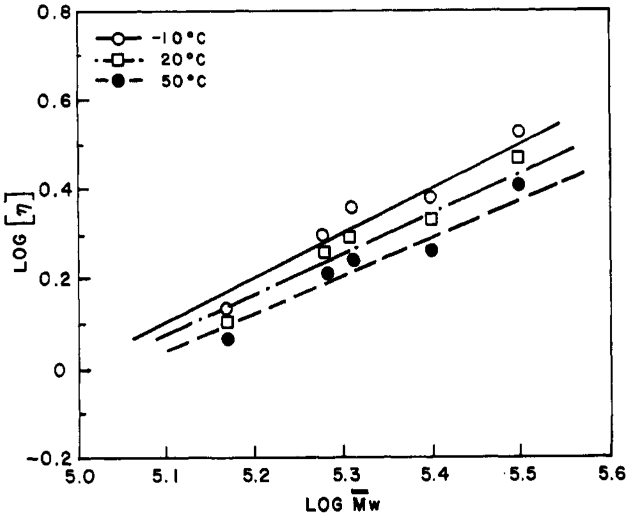

Figure 5. Double-logarithmic plots of $[\eta]$ against $\bar{M}_w$ for EP copolymes in methylcyclohexane.

Table III
Mark-Houwink Constants, K and a, in Methylcyclohexane and Toluene

temp, °C	10^4K, dL/g		a	
	methylcyclohexane	toluene	methylcyclohexane	toluene
10	0.80	3.50	0.82	0.66
20	0.92	1.10	0.81	0.76
30	1.00	0.80	0.80	0.79
40	1.04	0.79	0.80	0.79
50	1.10	0.78	0.79	0.80

For homopolymers and copolymers of identical composition and structure, weight-average molecular weights are frequently related to $[\eta]$ by using the Mark-Houwink expression

$$[\eta] = K\bar{M}_w^{\,a} \qquad (3)$$

where K and a are constants. Figure 5 shows the double-logarithmic plots of intrinsic viscosity against $\bar{M}_w$ in methylcyclohexane at -10, 20, and 50 °C. In spite of significant differences in the compositions and structures of the copolymers (Table I), a reasonably good linear fit is obtained at all temperatures. The parameters K and a are shown in Table III. The values for the parameter a (0.79-0.82), which is a measure of polymer-solvent interaction, are consistent with values reported for good solvents.[6,13,19] The fact that they decrease very slightly between 10 and 50 °C from 0.82 to 0.79 is in agreement with the already discussed weakening polymer-solvent interaction with rising temperature.

Intrinsic viscosities in toluene are given in Figure 6. While the values for the amorphous samples, EP-1 to EP-3, change only modestly with temperature, this is not the case for the partially crystalline samples with 80%

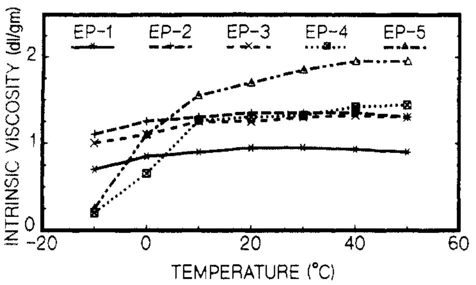

Figure 6. Intrinsic viscosities of EP copolymers in toluene at various temperatures.

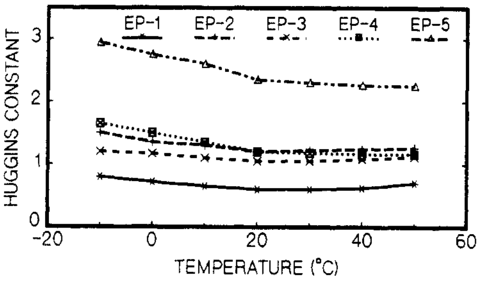

Figure 7. Huggins constants, K1, for EP copolymers in toluene at various temperatures.

Table IV
Equivalent Hydrodynamic Volumes, $10^{18} V_e$ (cm^3/molecule), in Toluene

temp, °C	EP-1	EP-2	EP-3	EP-4	EP-5
-10	6.6	19.4	12.5	2.5	5.6
0	8.1	22.1	13.7	8.2	24.7
10	8.5	22.9	15.6	15.9	29.2
20	9.0	23.8	15.6	16.4	38.2
30	9.0	23.8	16.2	16.7	41.5
40	8.8	23.8	16.5	18.0	43.7
50	8.5	22.9	16.2	18.2	43.7

ethylene. Here, the [η] values increase by over 500% between -10 and +10 °C. Such a rise in [η] with temperature has been interpreted as being indicative of an endothermal heat of mixing.[13,16] Figure 7 shows the corresponding Huggins constants. For the three amorphous samples, the changes are small; the values first decrease as the temperature rises and then increase slightly. The changes for EP-4 and EP-5 are larger, with the values falling as the temperature increases. The equivalent hydrodynamic volumes in toluene are listed in Table IV. Again, the biggest changes are for the same copolymers. For instance, the value for EP-5 increases by over 600% between -10 to +50 °C, with most of the increase occurring below 20 °C, while that for EP-1 increases by only 28%. These results are consistent with poor solvent–polymer interaction for the partially crystalline copolymers at low temperatures which improves upon heating while the interaction for the amorphous materials is not particularly sensitive to temperature.

The plots of the log [η] against log $\bar{M}_w$ in toluene at -10, 20, and 50 °C are shown in Figure 8. Comparison with Figure 5 shows that the behavior in toluene, a poor solvent, is quite different for the partially crystalline samples from that in methylcyclohexane, a considerably better solvent. Reasonably good straight lines are obtained at 20 and 50 °C. However, at -10 °C the data points for both crystalline copolymers, EP-4 and EP-5, are nowhere near the straight line. It should also be noted from Table III that the values for the parameter a in toluene increase from 0.66 at 10 °C to 0.80 at 50 °C, indicating considerably improved polymer–solvent interaction as the temperature rises.

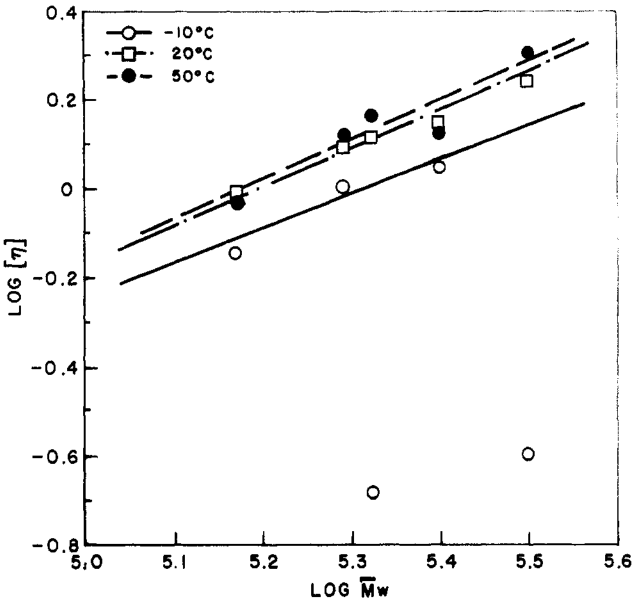

Figure 8. Double-logarithmic plots of [η] against $\bar{M}_w$ for EP copolymers in toluene.

Viscosity measurements and calculations, analogous to those described above for all copolymers in methylcyclohexane and toluene, were also obtained for EP-1, EP-2, and EP-5 in hexane, isooctane, and tetralin. Intrinsic viscosities, Huggins constants, and equivalent hydrodynamic volumes in hexane are shown in Table V. Viscosity–temperature behavior of EP-1 and EP-2 in hexane is similar to that in methylcyclohexane, with [η] decreasing slowly with temperature. Viscosity of EP-5 increases appreciably between -10 and 10 °C and then falls off as the temperature is raised further. In isooctane, [η] values or EP-1 and EP-2 decrease gradually from 1.10 and 1.70 dL/g to 0.80 and 1.30 dL/g when the temperature rises from -10 to 50 °C. For EP-5, [η] rises from 0.45 to 1.85 dL/g between -10 and 10 °C and then changes only slightly to 1.75 dL/g upon further warming to 50 °C. Hexane and isooctane are thus good solvents for EP-1 and EP-2 but poor ones for EP-5 at low temperatures. In tetralin, the intrinsic viscosites of EP-1 and EP-2 are essentially constant between -10 and 50 °C, with values of 0.90–1.00 and 1.10–1.15 dL/g, respectively. In contrast, the intrinsic viscosity of EP-5 rises rapidly from 0.70 dL/g at -10 °C to 2.10 dL/g at 20 °C and does not change much thereafter. The Huggins constants for the copolymers in hexane, isooctane, and tetralin again change in opposite direction from the [η] values. In hexane and isooctane, the equivalent hydrodynamic volumes of EP-1 and EP-2 decrease by about 25 % from -10 to 50 °C while that of EP-5 increases by about 90% in hexane and 300% in isooctane. It is interesting to note that although EP-1 and EP-5 have comparable V_e values in isooctane of 10.4 × 10^{-18} and 9.6 × 10^{-18} cm^3/molecule at -10 °C, the V_e of EP-1 decreases by 15% as the temperature is increased to 10 °C but increases by more than 300% for EP-5. The V_e values of EP-1 and EP-2 in tetralin do not change much with temperature but increase by about 200% for EP-5 between -10 and 20 °C.

General Comments. Intrinsic viscosities and the parameters that can be calculated from them provide a convenient tool for comparative study of a series of related materials in a group of solvents. Our data show very clearly the considerable effect of the structure of the solvent on the solubility of the EP copolymers. They also demonstrate unambiguously the unexpected importance of very small amounts of copolymer crystallinity, particularly on

Table V
Intrinsic Viscosities, $[\eta]$, Huggins Constants, K_1, and Equivalent Hydrodynamic Volumes, V_e, of EP-1, EP-2, and EP-5 in Hexane

	EP-1			EP-2			EP-5		
temp, °C	$[\eta]$, dL/g	K_1	$10^{18}V_e$, cm^3/molecule	$[\eta]$, dL/g	K_1	$10^{18}V_e$, cm^3/molecule	$[\eta]$, dL/g	K_1	$10^{18}V_e$, cm^3/molecule
−10	1.05	0.52	10.0	1.70	1.54	30.0	1.20	5.12	26.9
0	1.05	0.53	10.0	1.65	1.52	29.1	2.20	4.85	49.4
10	0.90	0.56	8.5	1.55	1.54	27.3	2.30	4.53	51.6
20	0.93	0.63	9.0	1.50	1.55	26.5	2.20	4.32	49.4
30	0.75	0.69	7.1	1.35	1.60	23.8	2.10	4.26	47.1
40	0.73	0.65	7.1	1.30	1.67	22.9	2.05	4.30	46.0
50	0.74	0.62	7.1	1.25	1.66	22.1	2.00	4.28	45.3

the viscosities in poorer solvents at low temperatures.

Of the five solvents investigated, methylcyclohexane is the best and tetralin the poorest. The differences in solvating power are most obvious below 10 °C; above that, the distinctions between good and poor solvents are less striking. In methylcyclohexane, polymer–solvent interaction decreases with increasing temperature for all samples, both amorphous and partially crystalline. In toluene and tetralin, much poorer solvents, solubility improves rapidly for the partially crystalline materials at low temperature and then remains constant or changes only slightly; for the totally amorphous materials it changes little over the entire temperature range. Holly[22] found from swelling studies of cross-linked EP rubber that aliphatic solvents become poorer and aromatic solvents improve with temperature between 25 and 100 °C. On the other hand, Arlie et al.,[6] who examined the solubility of an EP copolymer with 57 mol % ethylene which was presumably amorphous, reported that its intrinsic viscosities in dodecane, dodecylcyclohexane, and dodecylbenzene all decrease as the temperature is raised from 0 to 100 °C.

The effect of copolymer structure on solubility is most pronounced in the four poorer solvents in which the two partially crystalline samples behave very differently from the three amorphous ones. Both the intrinsic viscosities of EP-4 and EP-5 and their equivalent hydrodynamic volumes decrease steeply as the temperature is lowered below 10 °C. No such decrease is observed for EP-1, EP-2, and EP-3; the $[\eta]$ and V_e values for the amorphous copolymers with 60 and 70% ethylene show relatively little variation with temperature. This sharp increase in the endothermal nature of the systems with the partially crystalline EPs is characteristic of solutions approaching their Θ temperatures;[19] it is, therefore, very likely that at the lowest temperature in this study, −10 °C, these solutions are close to their Θ temperatures. Above 10 °C structure and crystallinity become secondary to molecular weight in their effect on solution behavior. In the best solvent, methylcyclohexane, the viscosity of all solutions is influenced primarily by copolymer molecular weights and the effects of composition, structure, and crystallinity, if any, are minor. Particularly striking here is the fact that straight lines are obtained in the plots of log $[\eta]$ versus log $\bar{M}_w$.

While it is clear from our data that ethylene sequences sufficiently long to form even very small amounts of crystallinity are responsible for the rapid decrease in intrinsic viscosity at low temperature in poor solvents, the exact nature of their involvement has yet to be elucidated. It is likely that the events at low temperature are started by contraction of the copolymer chains as the solvent becomes poorer, leading to greater proximity of ethylene sequences. This could permit nucleation of the longer ethylene sequences into aggregates or partially ordered domains leading to additional volume contraction and further decrease in viscosity;[23] the copolymer is maintained in solution by the more soluble propylene sequences and shorter ethylene sequences not part of the ordered domains. A somewhat similar suggestion was made several years ago by Filiatrault and Delmas, who postulated that in a bad solvent or at low temperature the crystalline part of an EP copolymer, i.e., the ethylene sequences, forms crystalline regions held in solution by the more soluble propylene segments.[4] Support for the view that ordered aggregates are responsible for our observations is found in other work as well. It has been reported that intermolecular ordering phenomena are more evident in samples with higher ethylene content.[24] High $\bar{M}_w$ results on EP copolymers using light scattering have been attributed to crystallites or molecular aggregates.[5,25] A number of studies have shown that when block copolymers are dissolved in a hydrocarbon which is a bad solvent for one of the components, the copolymer molecules can associate to form micellar aggregates with the insoluble blocks comprising the micellar cores.[26–28] EP-4 and EP-5 could be viewed as block copolymers with the crystallizable polyethylene segments above a certain minimum length comprising the less soluble blocks.

It is thus recognized that in poor solvents at low temperature EP-4 and EP-5 may exist as dispersions rather than solutions. The data in this paper are treated, however, as though soluble portions of the EP copolymers solubilized the partially ordered domains from the longer ethylene sequences of EP-4 and EP-5 and the copolymers are actually in solution, even at −10 °C. This approach is based upon lack of any compelling experimental evidence at this time to the contrary and previous work on EP copolymers.[1–4,6] Results reported here as well as the work on polystyrene–poly(ethylene/propylene) block copolymers in hydrocarbon solvents[26–28] show that the question of when EP copolymers are in solution and when in dispersion is far from clear-cut and needs further examination.

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References and Notes

(1) Delmas, G.; Daviet, V.; Filiatrault, D. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1629.
(2) Filiatrault, D.; Phuong-Nguyen, H.; Delmas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 763.
(3) Filiatrault, D.; Delmas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 773.
(4) Filiatrault, D.; Delmas, G. *Macromolecules* **1979**, *12*, 65, 69.
(5) Morimoto, M.; Okamoto, Y. *J. Appl. Polym. Sci.* **1972**, *16*, 2795.
(6) Arlie, J. P.; Denis, J.; Parc, G. K. *Inst. Pet., Tech. Pap.* **1975**, 75-006.
(7) Maderek, E.; Wolf, B. A. *Angew. Makromol. Chem.* **1988**, *161*, 157.
(8) Mays, J. W.; Fetters, L. J. *Macromolecules* **1989**, *22*, 921.
(9) Randall, J. C. *Polymer Sequence Determination, C-13 NMR Method*; Academic Press: New York, 1977.
(10) Johnston, J. E.; Bloch, R.; Ver Strate, G. W.; Song, W. R. U.S. Patent 4,507,515, 1985.

(11) Flory, P. J. *J. Am. Chem. Soc.* **1943**, *65*, 372.
(12) Fox, T. G., Jr.; Fox, J. C.; Flory, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 1901.
(13) Bohdanecky, M.; Kovar, J. *Viscosity of Polymer Solutions*; Elsevier Publishing: New York, 1982.
(14) Ham, G. E. *High Polymers*; Interscience: New York, 1964.
(15) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716.
(16) Schott, N.; Will, B.; Wolf, B. A. *Makromol. Chem.* **1988**, *189*, 2067.
(17) Schmidt, J. R.; Wolf, B. A. *Macromolecules* **1982**, *15*, 1192.
(18) Herold, F. K.; Wolf, B. A. *Mater. Chem. Phys.* **1986**, *14*, 311.
(19) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(20) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(21) Einstein, A. *Ann. Phys.* **1906**, *19*, 289; *34*, 591.
(22) Holly, E. D. *J. Polym. Sci., Part A* **1964**, *2*, 5267.
(23) Kapuscinski, M. M.; Sen, A.; Rubin, I. D. Presented at the 1989 SAE Fuels & Lubricants Meeting, Baltimore, Sept 1989, SAE Paper No. 892,152.
(24) De Candia, F.; Russo, R.; Vittoria, V. *J. Macromol. Sci.* **1980**, *B18*, 257.
(25) Rietveld, B. J.; Scholte, Th. G. *Macromolecules* **1973**, *6*, 468.
(26) Price, C.; Stubbersfield, R. B. *Eur. Polym. J.* **1987**, *23*, 177.
(27) Higgins, J. S.; Blake, S.; Tomlins, P. E.; Ross-Murphy, S. B.; Staples, E.; Penfold, J.; Dawkins, J. V. *Polymer* **1988**, *29*, 1968.
(28) Price, C.; Hudd, A. L.; Stubbersfield, R. B.; Wright, B. *Polymer* **1980**, *21*, 9.

Rheooptical Study of Isotropic Solutions of Stiff Polymers

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ABSTRACT: Stresses and birefringences are measured for isotropic solutions of poly(γ-benzyl L-glutamate) as functions of shear rate and time at concentrations ranging from dilute to concentrated. The Doi theory and other Landau-de Gennes theories for rigid molecules predict a pretransitional rise in the stress-optical ratio *C*—that is, the ratio of birefringence to stress—as the concentration approaches the value at which a first-order liquid-crystalline transition occurs. This predicted rise occurs because of critical slowing down as the concentration approaches the spinodal before being cutoff by the first-order transition. Our measurements of *C* for PBLG show a rise of this kind by a factor of 3.5. Kinetic rod-jamming effects in our data can be distinguished from the thermodynamic critical slowing down by combined use of stress and birefringence. The Doi theory also predicts a nonlinear coupling between the shearing field and the excluded-volume potential that causes curves of steady-state shear viscosity versus shear rate at different concentrations to cross, an effect seen in our measurements. We find violations of the stress-optical rule in that the measured values of *C* depend not only on molecular weight and concentration but also on shear rate and time after start-up and cessation of shearing. These latter dependencies can be explained by modest levels of polydispersity in molecular weight.

I. Introduction

The thermodynamics, molecular dynamics, and rheology of straight rigid polymers in solution are strongly dependent on concentration and molecular weight. If the aspect ratio of the rodlike molecules is high (100 or more) and the distribution of molecular weights is not too broad, four regimes of concentration can be discerned, as discussed by Doi and Edwards;[1] see Figure 1. In the dilute and semidilute regimes, the average distance between neighboring rods is so large compared to the rod diameter that they can be regarded as line particles. The semidilute regime is distinguished from the dilute in that in the former molecules are unable to rotate freely without interference from surrounding rods, and in the latter they can. Scaling arguments show that rotational interference becomes significant when

$$\nu L^3 \approx \beta \tag{1}$$

where ν is the number of molecules per unit volume of solution, L is the molecular length, and β is a dimensionless constant that experiments show to be roughly 30.[1]

When the concentration becomes high enough that

$$\nu b L^2 \approx 1 \tag{2}$$

then the rod diameter b is large enough compared to the distance between neighboring rods that excluded volume can no longer be neglected, and the solution is considered concentrated.[1] When excluded-volume effects are modest, the solution remains isotropic at equilibrium, though orientational correlations are present because of packing constraints. At higher concentrations, orientation-dependent excluded-volume effects become so strong that the rods spontaneously orient into a nematic liquid-crystalline phase.

In what follows, we briefly survey the status of theory for the rheology of dilute and semidilute solutions of rigid-rod polymers. We then detail some predictions of the Doi theory for concentrated isotropic solutions of these polymers. Attempts to apply this theory to the liquid-crystalline regime have been hindered by the orientational inhomogeneities (or defects) present in real liquid-crystalline samples and unaccounted for in the theory. The potential of the Doi theory to describe concentrated isotropic solutions, which have no defects, has not heretofore been assessed and is one motivation for the present work.

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