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Intrinsic Viscosities and Huggins' Constant for Ethylene-Propylene Copolymers. 1. Effect of the Correlations of Orientations in the Pure Components or in the Solutions on the Solvent Quality. Viscosities in Linear Alkanes and Three Highly Branched Alkanes

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ABSTRACT: Intrinsic viscosities of three ethylene-propylene copolymers (33, 63, 75%, mole percent of ethylene) have been measured at 25 °C in the series of linear alkanes and three branched alkanes 2,2,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane, and 2,2,4,4,6,8,8-heptamethylnonane. Intrinsic viscosities are lower in branched alkanes than in linear alkanes for the 63 and 75% samples. The 33% sample is, on the contrary, more expanded in branched alkanes. Intrinsic viscosities depend very little on chain length for the branched alkanes for the three samples while they do in linear alkanes particularly for the 33% sample. Results are interpreted in terms of correlations of orientations between the alkanes and the ethylene sequences of the polymer. Correlations of orientations are possible without regard to the solvent chain length in the 75% sample which has a distribution of ethylene sequences of different lengths. On the other hand, the short ethylene sequences of the 33% sample correlate more easily with the short alkanes. The presence of a low free-volume component in the solution makes correlations of orientations possible even with short-chain molecules. The Huggins' constant *k'* seems to be higher for ethylene-rich copolymers in linear alkanes than in the other systems. Correlations of orientations between solvent and polymer increase the solvent quality.

Intrinsic viscosity measurements[1] of copolymers of ethylene and propylene have shown that branched hexadecane was a better solvent than linear hexadecane for copolymers rich in propylene and that linear hexadecane was a better solvent for copolymers rich in ethylene. The difference in intrinsic viscosity in the two alkanes was found to be a linear function of the ethylene content so that these measurements could be used as a method of ethylene content determination. Intrinsic viscosities of the same copolymers in *n*-octane and in a branched octane had indicated that these two alkanes were not as suitable as the longer ones for composition determination. Consequently, it was thought worthwhile to make more extensive intrinsic viscosity measurements in order to establish more clearly the effect of solvent size and shape on the solubility of these copolymers.

EP copolymers are used commercially as additives to oils. They act as viscosity improvers or as agents to lower the pouring points of oils and these properties depend rather critically on the amount of ethylene present in the copolymer. From this, one could expect some different behavior particularly at low temperatures of the samples of dissimilar composition. The Huggins' constant *k'* has been obtained in the present work as a first step to predict the effect of the solvent shape on the viscosities at moderate concentrations (2%) used in the oil mixtures.

Correlations of Orientations in Long Chains. A way to approach the understanding of the behavior of the EP copolymers is to recognize their likeness to linear and branched alkanes. Extensive thermodynamic studies of linear and branched alkanes (or alkane-like molecules) have shown that the heats are very sensitive to the shape of the molecule mixed.[2-6] The results were interpreted in terms of the presence of orientational order between the molecules in the liquid state, e.q., linear alkanes and mixtures of linear alkanes, and the lack of this order in liquids of globular, isotropic molecules. Long linear alkanes such as *n*-hexadecane lose most of their correlations of orientations at room temperature when mixed with globular molecules. These results have been confirmed by

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depolarized Rayleigh scattering.[4,7] Order in the *n*-alkanes increases with the size of the molecule but is quite small in heptane at 25 °C. In other chain-like molecules such as SnR_4 and NR_3[6] (R represents an alkyl group), order exists for shorter chains because the free volume is lower than that of the alkane of the same chain length. The effect of correlations of orientations must be to stabilize the liquid or the solution so that the disorientation contribution to the excess free energy, when an ordered compound is mixed with a nonordered one, must be positive.[8] A few measurements[9-11] have been made, up to the present, to confirm this possibility and they indicate that, due to the entropy–enthalpy compensation, the effect of the correlation of orientations on the free energy is smaller than on the heats. Indication of the importance of correlations of orientations on solubilities has been seen on the phase diagram of *cis*-polybutadiene in the alkanes:[12] *n*-C_7 is a good solvent up to the lower critical temperature (~150 °C) while the 2-methylhexane is a solvent with a range of 40 °C only, for low molecular weights, between the Θ temperature and the lower critical temperature. The difference must come from correlations of molecular orientations between the polymer and the solvent possible in *n*-C_7 solutions but less probable in 2-methylhexane solutions. Another example is the good solvent quality of heptamethylnonane for poly(dimethylsiloxane) while linear hexadecane is a Θ solvent near room temperature for PDMS.[13] In the latter case, the destruction of correlations of molecular orientations of *n*-C_{16} by the polymers diminishes the stability of the solution. Intrinsic viscosity measurements of the EP copolymers were made to ascertain the influence on the free energy of mixing of correlations of orientations between the alkane-like segments of polyethylene and the alkane solvents. Heats of mixing measurements at infinite dilution of atactic polymers[14] in branched and linear alkanes are indicative of correlations of orientations of the polymer segments with the linear alkanes if the polymer contains a high enough percentage of ethylene.

The advantage of three copolymers of different composition is to simulate alkanes which combine different chain lengths with the same free volume since the three copolymers have about the same expansion coefficients. This is not the case for the different *n*-alkanes in the series.

Intrinsic viscosities have been measured in two types of compounds: (A) the series of linear alkanes from *n*-C_6 to *n*-C_{17} (except C_{11}, C_{13}, and C_{15}), and (B) three highly branched alkanes in C_8, 2,2,4-trimethylpentane, in C_{12}, 2,2,4,6,6-pentamethylhepatne, and in C_{16}, 2,2,4,4,6,8,8-heptamethylnonane.

Experimental Section

Polymers. The copolymers were the same as those used in previous work.[1] There were three samples, 33, 63, and 75%, the composition being expressed in mole percent of ethylene. Their origin is reported in ref 1.

Solvents. They were obtained from the Chemical Sample Co. (Columbus, Ohio) or Aldrich Chemical Co. (Milwaukee) and were used without purification.

Viscosities. Intrinsic viscosities were measured in an Ubbelhode viscosimeter at 25 °C in a bath regulated to 0.01 °C. The initial solution concentration was 0.2 g/dL. In the case of very good solvents (cyclo-C_6, *n*-C_6), the initial concentration used in other systems was already too high to give a linear $(t - t_0)/t_0c$ plot and had to be reduced to 0.1 g/dL.

Accuracy and Reproducibility. A good dissolution was the most important factor in the reproducibility of the [η] and the *k*′. The usual plots of $(t - t_0)/t_0c$ and $(\ln t/t_0)/c$ were made. If the extrapolation of the two lines at zero concentration differed by more than 0.002 dL/g, the measurements was repeated. In all cases, the $t - t_0/t_0c$ line had a positive slope while $(\ln t/t_0)/c$ had a negative one, but smaller in absolute value than the positive slope. *k*′ was calculated from the $t - t_0/t_0c$ line and from the usual expression:[15]

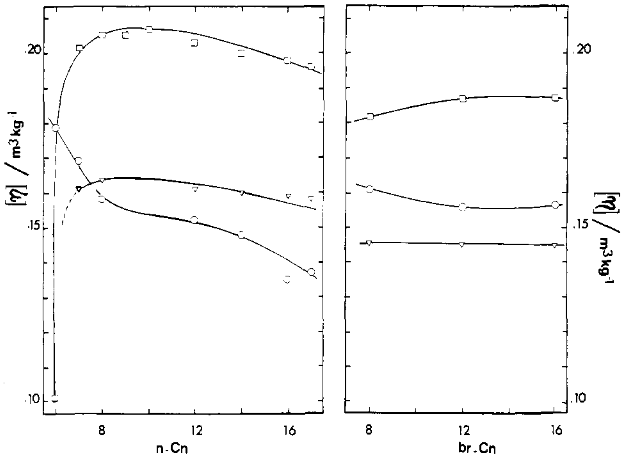

Figure 1. Intrinsic viscosities [η] in dL g⁻¹ for three samples of ethylene–propylene copolymers 75% (▽), 63% (□), and 33% (○) vs. the number of carbon atoms *n* of the solvent: (a) in linear alkanes; (b) in three branched alkanes C_8 (2,2,4-trimethylpentane), C_{12} (2,2,4,6,6-pentamethylheptane), and C_{16} (2,2,4,4,6,8,8-heptamethylnonane).

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

It was found that reproducibility in [η] was much easier to achieve than that of *k*′. This means that two successive experiments on the same system could give the same [η] but quite different *k*′ values. In these cases, another solution was made with special care to achieve a good dissolution. Eventually, the position of the point on the *k*′ vs. [η] graph helped in choosing the more likely value.

As there are few systematic determinations of *k*′ in the literature, these details would appear to be useful.

Linear and Branched Alkanes. On Figure 1a,b are plotted the intrinsic viscosities of the three samples in the linear and the branched alkanes vs. the carbon atom number of the alkane. Three characteristic features indicate the following: First the intrinsic viscosities are higher in linear than in branched alkanes for the two copolymers rich in PE, i.e., the 63 and 75% samples. On the contrary, the high propylene content polymer "prefers" the branched alkanes.

The second feature concerns the chain-length dependence of the intrinsic viscosities. For the three samples in the *branched* alkanes, the [η] are almost independent of chain length. On the other hand, these three samples have a different alkane chain length dependence in the *linear* alkanes. The 75% sample has about the same intrinsic viscosity in any alkane while there is a large dependence on chain length for the 33% sample, the 63% having an intermediate dependence. The third point concerns the intrinsic viscosities in the lower alkanes, which increase rapidly for one sample while the ethylene-rich sample is no longer soluble in *n*-C_6 at 25 °C due to a higher free volume difference between polymer and solvent.

Expansion of the Coil and Solvent Quality. An approximate relation between the viscosity, the molecular weight, and the solvent quality is due to Stockmayer and Fixman.[16]

$$[\eta] = \eta_\Theta + 0.51\phi_0 M \frac{2v^2}{N_0} \frac{(\frac{1}{2} - \chi)}{V_1}$$

or

$$[\eta] = \eta_\Theta + 0.653 \times 10^{-2} \frac{M}{V_1} (\tfrac{1}{2} - \chi)$$

Here V_1 is the molecular volume of the solvent, *M* is the polymer molecular weight, N_0 is the Avogadro's number, *v* is the polymer specific volume, ϕ_0 is a constant, and χ is the polymer–solvent interaction parameter. The first term corresponds to the coil dimension in a Θ solvent, $\eta_\Theta = K_\Theta M^{1/2}$, and the second term gives a quantitative expression showing that the polymer coil is more

Table I
Intrinsic Viscosities and Huggins' Constant at 25 °C for the Three Ethylene-Propylene Copolymers in the Series of Linear Alkanes and Three Highly Branched Alkanes in C_8, C_{12}, and C_{16}

solvent	75% E, 25% P M_v = 109 000		63% E, 37% P M_v = 248 000		33% E, 67% P M_v = 173 000[a]		no. on Figure 1 in part 2 and symbol
	[η], dL g^{-1}	k'	[η], dL g^{-1}	k'	[η], dL g^{-1}	k'	
linear alkanes							
hexane	ins		1.02	0.10	1.79		1
heptane	1.61	0.46	2.07	0.45	1.69	0.40	2
octane[b]	1.64	0.45	2.05	0.42	1.58	0.48	3
nonane			2.05	0.46			4
decane			2.07	0.50			5
dodecane	1.61	0.46	2.03	0.49	1.52	0.46	6
tetradecane	1.60	0.48	2.00	0.50	1.48	0.50	7
hexadecane[b]	1.59	0.49	1.98	0.43	1.35	0.42	8
heptadecane	1.58	0.38	1.96	0.50	1.37	0.48	9
highly branched alkanes							
2,2,4-trimethylpentane[b]	1.45	0.45	1.82	0.49	1.61	0.43	10
2,2,4,6,6-pentamethylheptane	1.45	0.49	1.87	0.50	1.56	0.48	11
2,2,4,4,6,8,8-heptamethylnonane[b]	1.45	0.58	1.87	0.43	1.56	0.34	13
toluene[d,e]	1.48	0.49	1.81	0.45	1.52	0.28	14
tetrahydrofuran[e]	1.25	0.44	1.53	0.60	1.43	0.40	15
MCT5[c]			2.02	0.18			12

[a] In ref 1, this sample was characterized by M_v = 140 000 which was a mistake. [b] From ref 1. [c] Commercial oil. [d] As in ref 1 to obtain the molecular weight. [e] Measured in order to have k' values in bad solvents (Figure 1, part 2).

expanded in a small size solvent due to the larger combinatorial entropy as well as in a good solvent (χ small). Usually, from measurements of the intrinsic viscosities in a Θ solvent (η_Θ), the χ parameter can be calculated by subtraction with [η] using the accepted value of ϕ_0. This has not been done here for two reasons. First, the Θ conditions are difficult to obtain for crystalline or partially crystalline polymers. We have obtained very low intrinsic viscosities in benzene[13] of the 75% sample (0.5 dL g^{-1}) but it is possible that this value is inferior to η_Θ. At low temperature, or in a bad solvent, the crystalline part of the copolymer (probably the ethylene sequences) may form crystalline regions held in solutions by the propylene sequences. Second, it is difficult to find reasonable χ values with the simple eq 1 which exaggerates the effect of solvent volume.

For example, from the small difference in the experimental intrinsic viscosities in n-C_8 and n-C_{16} for the 75% sample (0.06) the corresponding difference in χ can be calculated to be 0.2 without any assumptions on η_Θ (after using a typical χ value of 0.4). It has appeared worthwhile to us to stress the qualitative results rather than to use more elaborate formulas to obtain χ from [η] for solvents with a large difference in volume.

Since the solvents and polymers are made up of CH_2 and CH_3 groups only, the force-field contribution to the χ parameter should be minimal[17] and about the same for all the alkane systems. Another contribution to the χ parameter comes from the difference in free volume between the polymer and the solvent.[18] This contribution diminishes the solubility of the polymer and consequently the expansion of the coil.

The effect of the free-volume difference on viscosities could be seen on the intrinsic viscosities of polyisobutylene[19] in the n-alkanes series, [η] diminishing either for the volatile solvents (free-volume effect) or for the long-chain alkanes (diminution of the combinatorial entropy). Since the EP copolymers are less rigid, and expand more than PIB, the free volume contribution is less important except for the more volatile solvents ($n \leq 7$). Indeed, in the branched alkane series, the fact the [η] hardly changes between the branched octane and branched hexadecane indicates either a small free-volume contribution or a not very probable exact compensation between the effect of V and that of the free-volume contribution in χ.

Since both the force field or chemical contribution to χ and the free-volume contribution to χ do not seem to change between C_8 and C_{16} in the branched alkanes, the observed variation in [η] for the *linear* alkanes over the same interval of solvent volume is associated with "*different values of the contribution coming from the correlation of molecular orientations between the polymer and the solvent*".

Difference between the Linear and Branched Alkanes. The results of the present work complement those on the hexadecanes. Here again, the long linear alkanes are better solvents than branched alkanes for ethylene-rich copolymers (▽ and □ in Figure 1a,b) because the linear alkanes fit their orientations with those of the ethylene segments in the polymer chain while the branched alkanes disturb the correlations which exist between the polymer segments. For the three samples $[\eta]_{\text{lin}} - [\eta]_{\text{br}}/M$ can be calculated for alkanes between approximately C_{10} and C_{17} as in the case of the hexadecanes and found to be a regular function of the copolymer composition. The important parameter in the solubility is indeed the length of the ethylene sequences which increases with the ethylene percentage. The value of $([\eta]_{\text{lin}} - [\eta]_{\text{br}})$ changes sign for the propylene-rich sample (○).

Effect of Linear Alkane Chain Length on [η]. The intrinsic viscosities of the 75% sample depend little on the chain length of the solvent because the copolymer rich in ethylene contains long ethylene sequences. Due to the actual distribution of short and long sequences in the polymer chain, the average correlations of orientations or solvent quality do not vary significantly with the solvent chain length.

The less long ethylene sequences of the 63% sample correlate better with the shorter alkanes, hence the increase in the intrinsic viscosity for the lower alkanes. The effect of the alkane chain length is more important for the 33% sample. At the two extremes of the range of chain length, two effects contribute to increase or decrease the solvent quality. On the long alkane side, the low viscosity may be due not only to the lack of correlations of molecular orientations between the long chains of the solvent and those of the polymer but also to the disturbance of the orientational order of the solvent by the nonordered polymer. On the short alkane side, the order of solvent quality between the branched and linear alkane is inversed for n-C_7 and 2,4-dimethylpentane. This can be explained by the short segments of the ethylene part of the copolymer fitting their orientations with the shorter alkanes and by the absence of correlations of orientations in the pure shorter alkanes. The two possibilities are not contradictory since a relatively short ethylene sequence embedded in a polymer chain has less mobility and consequently more chance of correlations of orientations than the short alkane which has a large free volume. It is to be noted that [η] increases further for n-C_6.

The free-volume effect not favorable to the solubility can be seen with the lower alkanes but not to the same extent for the three samples. The effect is larger for the 75% copolymer since the intrinsic viscosity starts to diminish for n-C_7 and is not measurable in n-C_6 which is no longer a solvent. For the two other samples, the favorable effect of a small size solvent (larger combinatorial entropy and correlation of orientations with short sequences) wins for n-C$_7$ since $[\eta]$ increases but not for n-C$_6$ (63% $[\eta] = 1.02$). Intrinsic viscosities in the lower alkanes are in agreement with the expansion coefficient of the three samples following the order $\alpha(33\%) > \alpha(63\%) > \alpha(75\%)$. Table I in part 2 gives some physicochemical data on the two homopolymers and on the copolymers. The lower critical solubility temperatures (LCST) of polyolefins in the alkanes are mainly a function of the polymer expansion coefficient, the more expanded state of polypropylene compared to polyethylene being reflected by its higher LCST. The following data are for PP[20] and PE, respectively: in n-C$_5$ 397 and 353, in n-C$_6$ 441 and 406, and in n-C$_7$ 483 and 449 K.

The Bothorel *J* Parameter.[7] Details are given in ref 4 on the comparison of orientational order obtained on alkanes by Rayleigh scattering measurements and by thermodynamical data. We intend to obtain indirectly values of the J parameter for the different copolymers by measuring heats of transfer.

Huggins' Constant for the Three Copolymers. Table I lists the k' values for all the systems. It is not easy to answer the question whether the shape of the solvent and the composition of the copolymer have an effect on the k' since molecular weight and solvent quality are changing from one system to another. Values of k' are high, between 0.45 and 0.50 although the values expected for good solvents are near 0.3. This is surprising particularly for the linear alkanes which should be good solvents for the 75% due to the similarity of segment shape. By comparison tetrahydrofuran, a bad solvent because of its polarity, does not have a significantly higher k' value. If the high k' values are associated with formation of pairs of molecules even in dilute solution, one should conclude that the linear alkanes favor these associations even in a moderately good solvent. These associations may exist more frequently in ethylene-rich polymers. To obtain a qualitative answer to this question k' has been plotted against $([\eta]/[\eta](\mathrm{THF}))M^{-1/2}$. The division by $[\eta](\mathrm{THF})$ is to compare polymers of approximately the same solvent quality, while the $M^{-1/2}$ factor corrects for molecular weight difference between the samples. In our graph, the k' values fall on three curves, the highest being indeed the 75% and the lowest the 33%. The apparently erratic values for the highly branched alkanes are left unexplained here. More discussion will be given in part 2 on k' in sterically branched alkanes and cyclic alkanes, the values of which are undoubledly lower than those for the n-alkanes (part 2, Figure 1).

This work presents evidence that correlations of orientations in the solution increase the polymer–solvent solubility. Variation of the solubility with the chain length of the linear alkane depends on the distribution in the length of ethylene sequences. Correlations of orientations may be more prevalent in solutions than in the pure solvent due to the lowering of the free volume of the solvent by the polymer.

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