Intrinsic Viscosities and Huggins' Constant for Ethylene–Propylene Copolymers. 2. Effect of the Steric Hindrance of the Solvent on the Solvent Quality. Viscosities in Branched Alkanes, Cycloalkanes, Tetraalkyltin Compounds, *cis*- and *trans*-Bicyclo[4.4.0]decane, and Tetrahydronaphthalene

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Received August 3, 1978

ABSTRACT: The intrinsic viscosities of three ethylene–propylene copolymers (33, 63, 75%, mole percent of ethylene) have been measured in branched alkanes, cycloalkanes, *cis*- and *trans*-bicyclo[4.4.0]decane, tetrahydronaphthalene, and the SnR_4 (R = alkyl group) compounds. The solvents chosen represent striking examples of the large differences of steric hindrance among compounds of apparent similarity. The macromolecules were used as models of linear and branched alkanes to investigate the effect of the steric hindrance character of the solvent on the free energy of mixing. Steric hindrance is known to give an exothermic contribution to the heats and is found here to increase considerably the quality of the solvent. For example, with 2,4-dimethylpentane $[\eta] = 1.73$ whereas it is 2.37 dL/g^{-1} for the sterically hindered 2,3-dimethylpentane. Cyclopentane is recognized as being by far the best solvent for two samples. The Huggins' constant diminishes from 0.5 to 0.2 when the solvent quality increases. Large variations of k' in moderately bad solvents seem to reflect differences in shape and steric hindrance of the solvent. Due to its low cost in time and in the amount of material required, intrinsic viscosity measurements of EP copolymers may be a convenient way to study some properties of linear and branched alkanes.

In part 1, intrinsic viscosities[1] of three ethylene–propylene copolymers of different ethylene content were measured in linear alkanes and three highly branched alkanes. The relative values of $[\eta]$ in branched and linear alkanes and the variation of $[\eta]$ with the solvent chain length were interpreted in terms of correlations of molecular orientations between the solvent and the polymer or destruction of the correlations of an ordered component by a nonordered one. It was assumed that the correlations of orientations occurred almost exclusively between the segments of the CH_2 groups and not between those of the $-C(CH_3)HCH_2$ groups. Numerous results on mixtures of linear and branched alkanes showing the loss of orientational order, when methyl groups replace H atoms along the chain, support this simplification. The increase of intrinsic viscosities in systems where correlations of orientations are possible, compared to systems where they are not, is indicative of a stabilization of the solution or lowering of the free energy by the formation of order in the solution.

In this paper, another type of order formation will be investigated. It cannot be visualized as simply due to the correlations of orientations or good fitting of ethylene segments but it is related to the sterically hindered character of one of the molecules of the mixture. Another difference with the correlations of orientations is that in the former case the disorder was most often created by the mixing, while in the present case of the steric hindrance effect, order appears to be formed in the solution.

Calorimetric Evidence for the Steric Hindrance Effect. (a) Small Molecules. This effect was first noticed when some heats of mixing of nonpolar systems were obtained and discovered to be too negative[2] or positive but not large enough[3] to meet the expected value. Examples of such systems will be given below. To interpret formally the results, it was assumed that this type of molecule brings a negative contribution to the heats of mixing. Support for this hypothesis has been found in recent work since other systems consisting of molecules with structural features similar to those originally studied show again too small heats of mixing. To account for the negative sign of the steric contribution to the heats, it was named "condensation" contribution[3] or steric hindrance contribution.[4,5] Three types of molecules until now appear to produce this effect corresponding to the creation of order in the solution: (A) highly branched alkanes[3,4] whose substituents are on the same carbon atom or on neighboring carbon atoms; (B) tetrasubstituted alkyl derivatives[5] of Sn, such as $SnEt_4$ and $SnPr_4$, and, to a lesser extent, the trialkylamines,[9,11] (C) cyclic alkanes like cyclopentane[6] or other cyclic compounds such as *cis*- and *trans*-bicyclo[4.4.0]decane. Although these divisions were made for convenience, they may not have a molecular significance. For example, the compound 3,3-diethylpentane (class A) (or CEt_4) has structural features common with $SnEt_4$ (class B). On the other hand, the molecular mechanism which causes the exothermic contribution may be significantly different in the above classes even if it is related in all cases to the molecular shape. For systems having negative heats although they are not polar and do not have a large free volume contribution, one can find them in (A), n-C_8 + 3,3-diethylpentane (DEP) (−80 J/mol)[2], (B) $SnPr_4$ + heptamethylnonane (br-C_{16}) (−80 J/mol)[9] and, in (C) *trans*-bicyclo[4.4.0]decane + n-C_7 (−25 J/mol).[8] When the heat is positive, but too small, a comparative system with a nonsterically hindered component is needed to appreciate the steric hindrance contribution. In (A), one can quote the two following systems:[4] tridodecylamine + 2,3-dimethylpentane (160 J/mol) and tridodecylamine + 2,4-dimethylpentane (260 J/mol). Comparing these two values the steric hindrance contribution caused by the sterically hindered compound substituted in 2 and 3 would be about −100 J/mol since other contributions to the heat of mixing must be very similar for the two heptane isomers. The same effect is well documented on the systems with n-C_{16} + a series of branched nonanes.[3] In (B), $SnPr_4$ + n-C_{16}[9] has a H^E of only 266 J/mol while $SnEt_4$ and $SnBut_4$ with the same second component[10] have H^E of 333 and 354 J/mol respectively. In (C) one can quote the heats of toluene with cyclopentane (365 J/mol) while the heats are 610 ± 15 J/mol for the three higher cycloparaffins.[6] Examples of systems involving other sterically hindered

0024-9297/79/2212-0069$01.00/0

Table I
Date on the Pure Components

	d^{25},[a,c] g cm^{-3}	α, kK^{-1}	V^*,[b] cm^3 mol^{-1}	P^*, GPa	s/v,[d] nm^{-1}	$\eta^{25°}(s)$, mPa s	Z_g[e]	LCST[i] (PIB), K
class A								
2,4-dimethylpentane	0.6683	1.312	114.6	0.371[n]	8.5	0.385	2.00	403
br-C$_7$ 2,3-dimethylpentane	0.6909	1.209	112.5	0.385[n]	8.5	0.439	3.55	451
3,3-dimethylpentane	0.6891	1.218	112.7	0.415[n]	8.5	0.431	4.00	451
2,2,4,4-tetramethylpentane[a]	0.7156	1.075	141.9	0.376[f]	7.9	0.828		
br-C$_9$ 2,3,3,4-tetramethylpentane	0.7511	0.958	137.8	0.390[f]	7.9	0.913		
3,3-diethylpentane	0.7500	0.957	138.0	0.422[f]	7.8	0.765		
class B								
$SnMe_4$[g]	1.286	1.28	106.7	0.409	8.8	0.36[h]		
$SnEt_4$[g]	1.187	1.00	158.6	0.453	8.6	0.68[h]		
$SnPr_4$[g]	1.101	0.89	215.8	0.478	8.4	1.25[h]		
$SnBut_4$[g]	1.049	0.818	273.6	0.438	8.3	2.30[h]		
class C								
cis-bicyclo[4.4.0]decane[j]	0.8929	0.851	127.3	0.542	9.5	2.99		
trans-bicyclo[4.4.0]decane[j]	0.8659	0.865	130.9	0.504	8.8	1.92		
commercial mixture of cis and trans	0.8754					2.23		
tetrahydronaphthalene	0.9632	0.828		0.620		2.03		
cyclopentane[k]	0.7404	1.332	72.20	0.509	8.9	0.416[c]		461
cyclohexane[j]	0.7739	1.217	84.27	0.530	9.3	0.890		516
cycloheptane	0.8066	1.091	96.16	0.545[n]	9.5	1.35		572
cyclooctane[l]	0.8320	0.986	108.3	0.563	9.9	2.24		637
methylcyclohexane[m]	0.7650	1.132	100.7	0.458[c]	9.0	0.655		526
Polymers								
copolymer[o] 33% E	0.856	0.780	0.9729[r]	0.475	7.7			
copolymer 63% E	0.857	0.772	0.9732	0.489	7.4			
copolymer 75% E	0.858	0.765	0.9734	0.481	7.3			
polyethylene[p]	0.855	0.752	0.9792	0.484	8.0			
polypropylene[q]	0.858	0.806	0.9660	0.470	7.0			

[a] Reference 15. [b] From $V^* = V/\tilde{v}$ and $\tilde{v}^{1/3} = ((4/3)\alpha T + 1)/(\alpha T + 1)$. [c] Reference 16. [d] From standard models of the alkanes, see ref 8 and 17. [e] Reference 18. [f] Reference 8. [g] Reference 17. [h] Reference 19. [i] Reference 14. [j] Reference 20. [k] Reference 21. [l] Reference 22. [m] Reference 23. [n] Interpolated. [o] Obtained by mole average of the PP and PE data. [p] Reference 24. [q] Reference 25. [r] Core specific volume. [s] References 15 and 1b or this work. The unit is the same as the centipoise.

molecules (S.H.) can be found in previous work[11] or in the literature.[12]

Semiquantitative evaluation of the steric hindrance contribution has been made recently[11] and the values have been found to be proportional, for a given sterically hindered molecule, to the molar volume of the second component.

(b) Polymers. Heats of mixing of atactic polymers[13] which act as order breakers or which present some order themselves have been carried out using ordered, nonordered, and sterically hindered solvents. The results can be interpreted mainly in terms of steric hindrance of the solvent (classes A and C) but in one case it appears to be due to the steric hindrance of the polymer (polyisobutylene $(-C(CH_3)_2CH_2-)_n$).

Investigation of the effect of the steric hindrance contribution on the free energies has been made by vapor-pressure measurements on systems with heptane isomers,[4] one branched nonane,[2] and bicyclo[4.4.0]decane.[12] (Hereafter, the compound bicyclo[4.4.0]decane will be written by its common name, i.e., decalin.) It was found that the steric hindrance contribution to the entropy of mixing had about the same sign and magnitude as the heat contribution so that the total effect on the free energy at the concentration of the maximum is small.

Indirect measurements of the different solvent quality of various isomers include the determination of lower critical solubility temperatures (LCST) of polyisobutylene. It was found that the more sterically hindered (S.H.) 2,3-dimethylpentane had a LCST higher by 50 °C than that obtained with the 2,4-dimethylpentane.[14]

However, vapor pressure measurements are not very practical at room temperature for components of molecular weight higher than that of the heptane, and chemical potential measurements by light scattering[7] are possible only if the two components do not have the same refractive index. Therefore, other measurements related to the free energy of mixing were sought. The object of this work was to use intrinsic viscosities as a measure of the effect of steric hindrance on the free energies of mixing. Measurements were made in the following solvents. Class A: (1) two S.H. branched heptanes, 2,3-dimethylpentane and 3,3-dimethylpentane, and a non- or little-S.H. branched heptane, 2,4-dimethylpentane; (2) one S.H. branched nonane 2,3,3,4-tetramethylpentane and a non- or little-S.H. nonane, 2,2,4,4-tetramethylpentane. Class B: four SnR_4 derivatives, $SnMe_4$, $SnEt_4$, $SnPr_4$, $SnBut_4$. Class C: (1) a S.H. cyclic alkane, cyclopentane, and four non- or little-S.H. cycloalkanes, cyclohexane, cycloheptane, cyclooctane, and methylcyclohexane; (2) *cis*- and *trans*-decalin and their mixture (commercial) and tetrahydronaphthalene.

Physicochemical Data on the Pure Components. Table I gives some data on the compounds used as solvents. Some are directly measurable such as the density, d, and the expansion coefficient, α. Others are calculated from the van der Waals equation of state like the core volume V^* (or the volume at 0 K) and the pressure reduction parameters P^*.[24,26] The surface to volume ratio s/v has been obtained from standard models of the linear and branched alkanes.[26] In isomers with the same molecular weight and shape, d and P^* increase with the steric hindrance while α diminishes. One expression of this is the "conformational rule" which states that the isomer with the highest enthalpy also has the lowest molar volume. In the series, the trends of d and α are more influenced by molecular weight than by steric hindrance. However, in the SnR_4 series, the two compounds which give large negative contribution to the heats and which accordingly are supposed to be sterically hindered do have

Table II
Intrinsic Viscosities and Huggins' Constant at 25 °C for Three Ethylene-Propylene Copolymers in Three Classes of Differently Sterically Hindered Solvents

	polymer						
	75% E, 25% P M_v = 109 000		63% E, 37% P M_v = 248 000		33% E, 67% P M_v = 173 000[b]		no. on Figure 1, part 2
solvent	[η], dL g^{-1}	k'	[η], dL g^{-1}	k'	[η], dL g^{-1}	k'	
class A							
br-C_7 2,4-dimethylpentane	ins[a]		1.93	0.17	1.62	0.12	16
br-C_7 2,3-dimethylpentane	1.81	0.25	2.37	0.19	1.79	0.16	17
br-C_7 3,3-dimethylpentane	1.87	0.28	2.38	0.26	2.01	0.22	18
difference %			23		24		
br-C_9 2,2,4,4-tetramethylpentane	1.62	0.34	2.16	0.27	ins[a]		19
br-C_9 2,3,3,4-tetramethylpentane	2.02	0.37	2.58	0.34	1.26	0.26	20
br-C_9 3,3-diethylpentane	2.12	0.30	2.46	0.30	1.89	0.26	21
difference %	31		19				
class B							
$SnMe_4$	ins[a]		1.34	0.12	ins[a]		22
$SnEt_4$	1.66	0.37	2.02	0.43	1.74	0.29	23
$SnPr_4$	1.45	0.45	1.88	0.53	1.49	0.33	24
$SnBut_4$	1.23	0.58	1.64	0.54	1.42	0.32	25
difference %	35		23		23		
cis-bicyclo[4.4.0]decane	2.17	0.31	2.72	0.27	2.20	0.23	26
trans-bicyclo[4.4.0]decane	2.26	0.23	2.76	0.29	1.71	0.38	27
difference %	4		2		−30		
$10^7\{\cdot[\eta]_{trans} - [\eta]_{cis}\}/M$	8.26		1.61		−28.3		
cis and trans (commercial mixture)							
tetrahydronaphthalene					2.03	0.32	28
class C	1.57	0.44	1.81	0.62	1.32	0.58	29
cyclopentane	ins[a]		3.03	0.20	2.48	0.11	30
cyclohexane	2.14	0.28	2.58	0.37	2.17	0.27	31
cycloheptane	2.03	0.43	2.54	0.38	2.24	0.29	32
methylcyclohexane	2.03	0.46	2.65	0.37	2.33	0.25	33
cyclooctane	1.89	0.55	2.57	0.39	2.16	0.29	34
difference %			17		12		

[a] Insoluble at 25 °C. [b] In ref 30 this sample was characterized with a M_v of 140 000 which was a mistake.

high P^* values.[17] Some variation of P^* with molecular weight may be due to the inexactitude of the theory.[27] However, a large difference between isomers can have a physical significance. On the other hand, cyclopentane which appears to be an order maker in solution has a lower P^* than cyclohexane. But, in fact, it is more the ratio of $P^*/(s/v)$ than P^* which is indicative of the cohesive energy for molecules with different shape. Viscosities, measured on the isomers, have been reported in the sixth column. Sterically hindered molecules seem to have higher viscosities. However, a relation between viscosity and mobility of isomers should be done at the same reduced volume since the viscosities are very sensitive to the state of expansion of the liquid.

Degrees of steric hindrance arise from different conformations, the greater the steric hindrance, the greater the number of gauche conformations. Mann[18] was able to correlate the number of gauche arrangements Z_g reported in the penultimate column with the macroscopic properties of the various heptanes and nonanes. The difference between the isomers can be made clearer by building molecular models where 2,3,3,4-tetramethylpentane appears to have little molecular motion whereas in 2,2,4,4-tetramethylpentane, the two *tert*-butyl groups seem to librate more freely. The last column gives some experimental data on the lower critical solubility temperature of PIB in some isomers and in the cycloalkanes; PIB dissolved in the more sterically hindered and more cohesive 2,3 derivative has a higher LCST than PIB dissolved in the 2,4 derivative.

Results and Discussion

Table II gives the intrinsic viscosities and the k' values for the different systems. In Figure 1a–c, showing the curves k' vs. [η], the comparison of solvent quality for the various isomers or between the different classes can easily be made.

Steric Hindrance and Solvent Quality. Contrary to vapor-pressure measurements in small molecule mixtures, the intrinsic viscosities indicate without ambiguity an increase of the solvent quality or a lowering of the free energy for mixtures with a sterically hindered compound. An explanation of this difference may be the fact that intrinsic viscosities can only be measured in high concentration of the sterically hindered compound, while mixtures of small molecules are made over the whole concentration range. In fact, for the tridodecylamine mixtures, data could not be obtained at concentrations lower than $\phi_2 \sim 0.4$ for the sterically hindered compound (2). Steric hindrance effects may well be more pronounced in this region because for the system n-C_{16} + 3,3-diethylpentane, H^E is positive in n-C_{16}-rich solutions and negative at high concentrations of DEP.[3] The effect of steric hindrance on [η] is unexpectedly large; a semiquantitative evaluation of the effect can be made by taking as a reference the [η] value in the nonsterically hindered compound. The difference expressed in percentage as calculated in Table II varies between 10 and 30%. The negative sign of the steric hindrance contribution to G^E implies that the steric hindrance contribution to the entropy is less negative than that to the enthalpy.

Effect on the Different Copolymers. To obtain the steric hindrance effect, the shape of the polymer segment does not seem to be as important as it is in the correlations of orientations: From the percentage of difference shown in Table II, one observes some increase of the effect in the

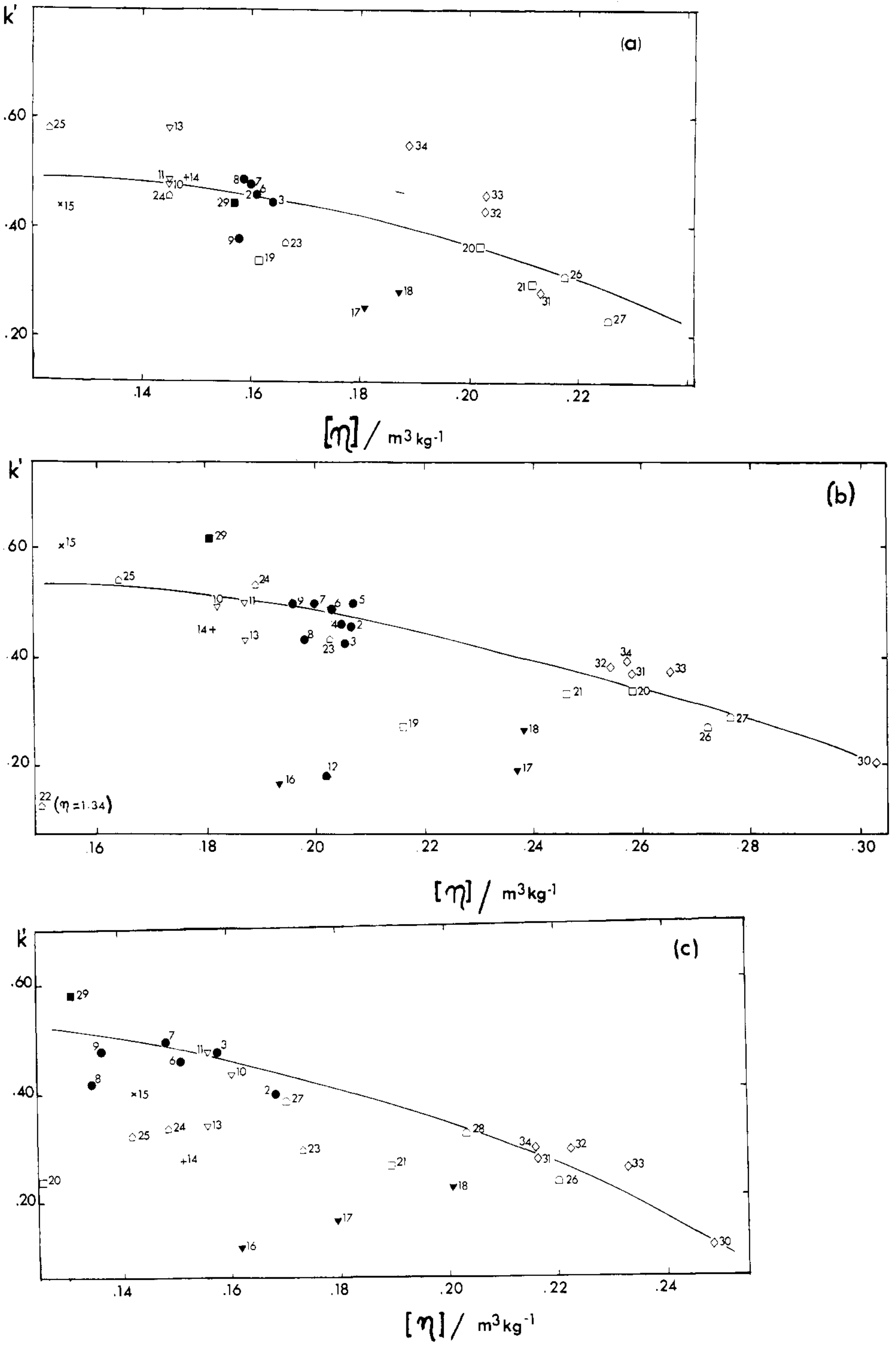

Figure 1. The Huggins' constant k' vs. the intrinsic viscosities $[\eta]$ in dL g^{-1} for the different solvents including the linear and highly branched alkanes of part 1: 1a/75%, 1b/63%, 1c/33%. The numbers refer to compounds listed in Table II and Table I of part 1.

ethylene-rich copolymers although the data are not complete with the 75% sample. Because the free-volume contribution is slightly higher for this sample, cyclopentane and 2,4-dimethylpentane are no longer solvents for the 75% copolymer. Figure 2 shows the $[\eta]$ in the branched heptanes (a) and branched nonanes (b) vs. the core volume of the isomer. Low core volumes, i.e., high steric hindrance, correspond to high intrinsic viscosities. Other isomers of intermediate core volume exist such as 2,2,3-trimethylpentane ($V^* = 113.9$ cm^3 mol^{-1}). They would probably give intermediate intrinsic viscosities. However, verification of this did not seem to justify the cost of these expensive isomers. Two results about the 33% sample are unexplained: it is insoluble in 2,2,4,4-tetramethylpentane and has a very low $[\eta]$ in 2,3,3,4-tetramethylpentane and it must be a very specific shape incompatibility, which will be investigated later.

***cis-* and *trans*-Decalin.** H^E of these isomers with the *n*-alkanes,[8] the cycloalkanes,[20,21] or atactic polymers[13] are more negative or less positive with the trans isomer. A similar difference is seen if the second component is a branched alkane although its magnitude is less.[8] From the H^E results one would then expect *trans*-decalin to be a better solvent. This is the case for the 75% E and 63% E samples but *trans*-decalin is unexpectedly a bad solvent for the propylene segments. It is possible that some correlations of orientations exist between the ethylene sequences and the flat, rigid *trans*-decalin in the other

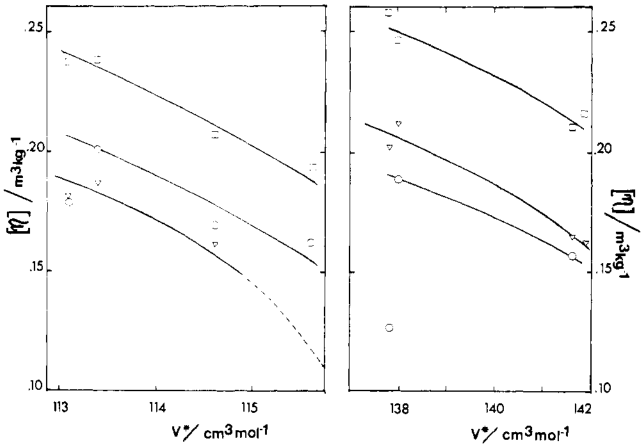

Figure 2. Intrinsic viscosities in dL g^{-1} of the three samples vs. (a) the core volume of the branched heptanes or (b) the core volume of the branched nonanes. A similar graph would be obtained with molar volumes: (▽) 75%, (□) 63%, (○) 33%.

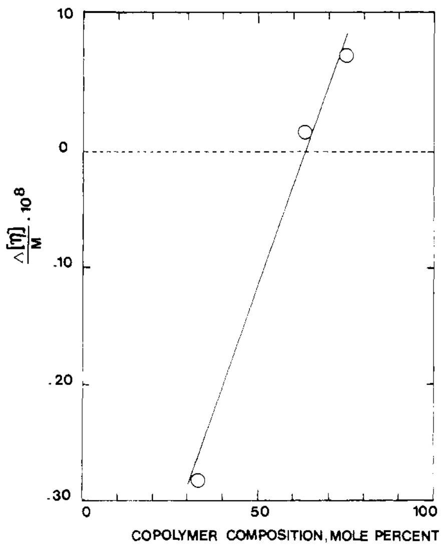

Figure 3. $\{[\eta](trans\text{-decalin}) - [\eta](cis\text{-decalin})\} \times 10^7/M$ vs. the polymer composition in mole percent of ethylene.

copolymers, but correlations are no longer possible with the short ethylene sequences of the ethylene part nor with the propylene segments of the 33% E sample. The commercial decalin gives an $[\eta]$ for the 33% E sample intermediary between those of the two isomers. If it is assumed that $[\eta]$ in the mixture is a mole average of the $[\eta]$ in the pure isomers, from the experimental $[\eta]$ in the mixture, one finds that the commercial mixture contains 63% of the cis isomer. If the same averaging is made on the refractive indexes of the pure components and compared to that of the mixture, the percentage of the cis isomer is found to be 60%. In Figure 3 the difference of intrinsic viscosity in *trans*- and *cis*-decalin is seen to be a linear function of the copolymer composition in the range investigated and could be used eventually for composition analysis.

Tetrahydronaphthalene. Heats of mixing of tetrahydronaphthalene with the series of linear and branched alkanes[31] show almost indentical values in these two series while small molecules usually give higher heats with the linear alkanes because of the additional heat of disordering the chains. The too low values in the linear alkanes were interpreted as an indication either of some correlations of orientations between tetrahydronaphthalene and the alkane chains or of a compensation between H^E (disorder) and a negative steric hindrance contribution. Tetrahydronaphthalene has a much lower solvent quality for the 33% sample as for the ethylene-rich copolymers. An explanation of this could be that the equally bad solvent quality due to chemical difference is partially compensated in the 75 and 63% but not in the 33% sample by favorable correlations of orientations between the solvent and the ethylene segments.

Tetraalkyltin Compounds. The intrinsic viscosities were expected to go through a maximum for $SnPr_4$ or $SnEt_4$ because heats of mixing of the series with the linear alkanes have shown a large steric hindrance effect for these two compounds compared to the methyl and butyl derivatives.[9,10] The large maximum can indeed be seen for the 63% sample. For the two other samples, the intrinsic viscosities increase by 35 and 23% between $SnBut_4$ and $SnEt_4$, but $SnMe_4$ is no longer a solvent. It is true that part of the reduced solvent quality for $SnMe_4$ and $SnBut_4$ may be due to, on one hand, increased volatility and, on the other hand, larger size of the molecule. However, these two effects would not give in the present range of size and expansion coefficients such a pronounced variation in solvent quality. For comparison, the intrinsic viscosities of PIB between *n*-heptane and *n*-hexadecane vary by less than 10%.

The Huggins' Constant. Figure 1a–c gives the general trend of k' vs. $[\eta]$ for the three samples. k' diminishes from 0.6 to 0.2 over a 1.4 dL g^{-1} range of $[\eta]$. The k' values for the globular SnR_4 molecules fall on the main curve of the alkanes and cycloalkanes. On the other hand, specific shape effects can be seen on some compounds having k' values situated quite outside the curve. Unexpectedly, low values are indeed obtained for the three branched heptanes and specially for 2,4-dimethylpentane. Although *n*-C_7 and 2,4-dimethylpentane give about the same $[\eta]$'s, k'(2,4-dimethylpentane) is much lower, less than 0.2, than k'(*n*-C_7), 0.4 to 0.5. As this effect is larger for the 33 and 63%, it may be related to the similarity of shape between the solvent substituted on the 2,4 carbons and the propylene segment. Intrinsic viscosity measurements on polypropylene could help us to understand the molecular mechanism behind these results. The low k' value for the 33% sample in 2,3,3,4-tetramethylpentane is as unexplained as its $[\eta]$. The MCT5 oil is a mixture of mainly polycyclic saturated compounds. It is worthwhile noting that like the branched C_7 and unlike other solvents, this oil combines a low value of $[\eta]$ with a low value of k' (point 12 and Table I of part 1).

Difference in the χ Parameter. The simple Stockmayer–Fixman equation between $[\eta]$ and χ is not suitable

$$[\eta] = K_\theta M^{1/2} + 0.51 \frac{\phi_0}{N_{\mathrm{av}}} \frac{2v^2M}{V}(\tfrac{1}{2} - \chi) \qquad (1)$$

for χ determination or comparison of χ between solvents of different molar volumes.[1] However, it can be used for evaluation of the difference in χ between isomers from the difference in $[\eta]$. With $K_\theta = 11.3 \times 10^{-4}$ (value for polybutene-1 at 24 °C[28]) together with $\chi = 0.336$ at 25 °C for the PIB + *n*-C_9 system[29] and $v = 1.16$ cm^3 g^{-1}, the value for the intrinsic viscosities of the copolymer of molecular weight 248 000 is calculated to be 2.03 dg L^{-1}. Agreement with the experimental value (2.05) for *n*-C_9 is fortuitous but it will give some confidence for the value obtained with the other nonanes. Using the same K_θ and eq 1 with the experimental $[\eta]$, the χ values are found respectively to be 0.275 for the sterically hindered compound and 0.321 for the 2,2,4,4-tetramethylpentane. Similar differences could be found for the other samples or the branched heptanes but some fitting is necessary between eq 1 and the experimental [η].

Solvent Quality for the Different Classes. For each sample the solvents are listed below in decreasing order of solvent quality: (75%) *trans*-decalin > *cis*-decalin > c-C_6 > S.H. br-C_9 > cycloalkanes > S.H. br-C_7 > *n*-alkanes not S.H. br-C_9 > tetrahydronaphthalene > highly branched alkanes > toluene > tetrahydrofuran > $SnBut_4$; (63%) cyclopentane > *trans*-decalin > *cis*-decalin > methyl c-C_6 > cycloalkanes > S.H. br-C_9 > S.H. br-C_7 > not S.H. br-C_9 > *n*-alkanes > not S.H. br-C_7 > highly branched alkanes > toluene > tetrahydronaphthalene > tetrahydrofuran > $SnBut_4$; (33%) cyclopentane > methyl c-C_6 > *cis*-decalin > cycloalkanes > br-C_9 S.H. br-C_7 > highly branched alkanes > *n*-alkanes > toluene > tetrahydronaphthalene > tetrahydrofuran > *n*-C_{16}, *n*-C_{17} > $SnBut_4$. It is to be noted that for two samples, cyclopentane is by far the best solvent. The order of the solvent quality is about the same for the three samples except for *cis*- and *trans*-decalin, tetrahydronaphthalene, and for the linear and branched alkanes where correlations of orientations between solvent and polymer are important.

This work illustrates the importance of the shape of the polymer and that of the solvent on the free energy of mixing. Large variations in [η] may be found in systems where the usual parameters influencing the solvent quality and chemical and free volume differences are apparently negligible.

Acknowledgment. We acknowledge the support of the Imperial Oil Company and of the Ministère de l'Education (Québec) for this work.

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Pressure Dependence of the Intrinsic Viscosity of Poly(dimethylsiloxane)–Cyclohexyl Bromide Solution

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ABSTRACT: The pressure dependence of the viscosity of solutions of poly(dimethylsiloxane) in cyclohexyl bromide was measured over the pressure range of 1 to 400 kg/cm^2 and the temperature range of 25 to 45 °C. The viscosity measurements at elevated pressure were carried out using the rolling-ball type viscometer, and the validity of this method was examined by comparison with the measurements by the Ubbelohde viscometer at atmospheric pressure. The intrinsic viscosity and the chain dimension increase with the increase of pressure. The interaction parameter, χ_1, was deduced from the coil expansion coefficients on the assumption of the fifth power rule for the expansion of the polymer molecules in the solution. χ_1 decreases with increasing pressure and in this system the solvent becomes better near the Θ temperature. The pressure coefficient of the Θ temperature calculated from the pressure and the temperature dependence of χ_1 agreed with the results obtained by high-pressure light-scattering measurement. Values of χ_1 were compared with those predicted from the Patterson theory and the new Flory theory for polymer solutions.

The importance of the effect of pressure on solution thermodynamics has been recognized by recent investigations,[1-12] and many interesting characteristics of the pressure effect have become evident. The new Flory theory[13,14] of polymer solutions based on the principle of corresponding states[15] emphasizes the importance of the free volume effect, and the pressure effect on the solution thermodynamic properties is of great interest. The

0024-9297/79/2212-0074$01.00/0