Macromolecules

Heats of Mixing at Infinite Dilution of Atactic Polymers. 1. Effect of Correlations of Orientations in the Solvents or in the Polymers

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ABSTRACT: Heats of mixing at infinite dilution h_∞^E have been measured at 25 °C in linear and three highly branched alkanes in C_8, C_{12}, and C_{16} for nine atactic polymers: (A) four polymers made of segments having side groups, polypropylene, polyisobutylene, polybutene-1 and poly(dimethylsiloxane), (B) two polymers with linear segments, polybutadiene and polypentenamer, and, (C) three copolymers with different proportions of linear (ethylene) and branched (propylene) segments. Orientational order in polymers and solutions is investigated. h_∞^E is larger with the linear alkanes than with the branched alkanes for the type A polymers while the h_∞^E are in the opposite order for the type B polymers. Ethylene-rich copolymers of class C have an order of heats similar to that of the B type while the propylene-rich copolymer belongs to class A. These results are interpreted as indicative of the presence of some orientational order in class B polymers which can be preserved in a solution of ordered solvents. Class A polymers are order destroyers of the long alkanes. The X_{12} parameter of the Flory equation of state theory is calculated and found unexpectedly negative for eight systems. Interpretation of an exothermic non-free-volume contribution to the heats is given in terms of steric hindrance of the very substituted branched C_{16} or in the case of the n-C_{12} and n-C_{16} solutions of increased order of the solvent in solution with the low free-volume ordered polymer.

The early result in polymer solution thermodynamics of exothermic heats[1] in nonpolar systems was puzzling for several years. The theoretical work of Prigogine[2] was instrumental in understanding an important contribution to the thermodynamics of polymer–solvent systems, the contribution due to the difference of state of expansion between the polymer and the solvent. This contribution to the heats of mixing is exothermic and can be calculated from equation of state theories. In polymer–solvent systems where the solvent is similar to the polymer in chemical nature, the combination of a large negative heat due to free volume differences with a small positive one caused by the difference in force field makes the total heats negative, a rare occurrence in nonpolymeric, nonpolar systems. In order to test quantitatively the free-volume theory, Patterson and Delmas[3] have measured the heats of mixing at infinite dilution (h_∞^E) of polyisobutylene in linear alkanes. In this early work, the parameter characterizing the alkane consisted of a number of segments while in the subsequent Flory theory[4] the less ambiguous expansion coefficient α_s was used.

A common feature of the h_∞^E values in the series of the linear alkanes obtained with different atactic polymers (PIB, PDMS) was the regular increase of the heats with solvent chain length over the whole range of measurable heats at 25 °C, i.e., from n-C_5 to n-C_{16}. The h_∞^E which was initially exothermic became endothermic for the longer alkanes. However, the slope of the heats vs. the carbon atom number was different from one polymer to another. The first explanation of this trend was the gradual disappearance of the exothermic contribution to the heats when the alkane chain became longer, leaving only the positive contribution for the longer alkanes. However, a quantitative comparison of the dependence of the heats on temperature or on the chain length with that calculated from the equation of state theories was not very successful.[5,6] It was shown too that end effects in the alkane could not be responsible for the observed variation.[7]

The next step in the understanding of the heats of the atactic polymers in the linear alkanes came from experimental and theoretical work on mixtures of branched and linear alkanes. Patterson et al.[7-9] and our group[10-13] showed that a shape-specific effect was occurring in mixtures of long alkanes, namely the destruction of correlation of molecular orientations in the n-alkanes by mixing with a nonordered component. Studies of correlations of orientations in small molecules have been made calorimetrically and by Rayleigh scattering[8,9] on the same systems. They indicate that linear alkanes or mixtures of linear alkanes have correlations of molecular orientations. Branched alkanes or other isotropic globular molecules do not have these orientations. The mixing of an ordered liquid with a nonordered one destroys the order of the ordered liquid, the destruction being accompanied by an endothermic heat.

Analysis of the heats of polybutene-1[13] in the n-alkane series as well as those of poly(dimethylsiloxane)[6] and polyisobutylene[3] shows that these polymers act in the alkane solution as order breakers of the alkane. Furthermore, it was found that very similar heats (or X_{12} values) are obtained with the linear alkane as a second component if the order breaker is either polybutene-1 or a small molecule such as 3,5-dimethylpentane, whose shape is similar to that of the polybutene-1 segment.

Previous work on heats of mixing of atactic polymers was carried out in order to test the theories of free volume using the linear alkane series to obtain a range of values of the difference ($\alpha_p - \alpha_s$) of the polymer and the solvent expansion coefficients. Globular molecules, like the branched alkanes, should be more suited for this purpose than linear alkanes since little or no heat of disordering of the solvent is expected to be added to the negative heat due to the free volume difference.

In part 1, heats have been measured in linear alkanes and in three highly branched, nonordered alkanes, 2,2,4-trimethylpentane (br-C_8), 2,2,4,6,6-pentamethylheptane (br-C_{12}), and 2,2,4,4,6,8,8-heptamethylnonane (br-C_{16}), as solvents. In order to obtain a more complete picture of order–disorder relationships, two kinds of atactic polymers were chosen. Polymers A comprised the compounds made of branched segments, polyisobutylene (PIB), polypropylene (PP), polybutene-1 (PBu-1), poly(dimethylsiloxane) (PDMS), which are expected to be order breakers of an ordered solvent. Polymers B consisted of the macromolecules made of linear segments of polybutadiene (PBD) and polypentenamer (PPmer), which could have some degree of order. Polymers C are three copolymers of ethylene and propylene which are expected to be order

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breakers if rich in propylene and to have some order if rich in ethylene. In part 2, heats of the same polymers have been measured in other alkanes or hydrocarbons known to be sterically hindered.

Experimental Section

Heats of Mixing. Apparatus. A tilting Tian-Calvet calorimeter was used as in previous work.[13] The atactic polymer deposited as a film (30 to 80 mg) on the surface of a spiral container dissolves faster than when it is in the shape of a small ball. In this way, the length of time for the complete dissolution is quite similar to that of the mixing of two liquids.

Reproducibility. Three to six runs were made, and the experimental values of $h_\infty{}^E$ were averaged. The greatest difference between these values varied between 5 and 20% for the smallest $h_\infty{}^E$ and 2 to 10% for the largest heats.

Materials. Polyisobutylene. This sample Bh 505C was graciously given to us by Dr. G. J. Wilson of Polysar (Sarnia, Ontario, Canada). The molecular weight obtained by viscosity was 4500. The heats with this sample were quite comparable with those obtained previously on other samples.[3]

Polybutene-1 and Polypropylene. The atactic polymer was extracted from the isotactic ones according to the procedure described in ref 13. The molecular weight was about 20 000 for PBu-1 and 6000 for PP as measured by intrinsic viscosities.

Polybutadiene. The *cis*-1,4-polybutadiene used was a low molecular weight fraction obtained as in ref 15.

Polydimethylsiloxane. The polymer was a commercial sample, Dow Corning DC 200, of 20 000 molecular weight used in previous work.[16]

Polypentenamer. The sample M_v = 50 000 was kindly given to us by Dr. Ofstead (Goodyear Tire and Rubber Co., Akron, Ohio).

Ethylene–Propylene Copolymers. These were three random copolymers of the following compositions, 75, 63, and 33%, expressed in mole percent of ethylene. The origin of these samples is given in ref 17.

Solvents. The three branched alkanes in C_8, C_{12}, and C_{16} and the linear alkanes were purchased from the Chemical Sample Co. (Columbus, Ohio). They were used without purification.

Theory. The heats of mixing at infinite dilution were obtained from the experimental heats, the polymer volume fraction, ϕ_2, and the density, d_2, by the relation:

$$h_\infty{}^E = h_{\exp}{}^E d_2/(1 - \phi_2) \qquad (1)$$

Table II shows $h_\infty{}^E$ for the different systems.

From equation of state theories[5,13] the heat of solution of a polymer at infinite dilution is given by:

$$\frac{h_\infty{}^E}{P_2{}^* v_{2\mathrm{sp}}{}^*} = \frac{s_2 X_{12}}{s_1 P_2{}^*}[\tilde{U}(\tilde{T}_1) - \tilde{T}_1 \tilde{C}_p(\tilde{T}_1)] + [\tilde{U}(\tilde{T}_1) - \tilde{U}(\tilde{T}_2) - (\tilde{T}_1 - \tilde{T}_2)\tilde{C}_p(\tilde{T}_1)] \qquad (2)$$

In this equation, $\tilde{U}(\tilde{T})$ is the reduced energy, $\tilde{T}_1$ and $\tilde{T}_2$ are the reduced temperatures of the two components, and $\tilde{C}_p$ is the configurational heat capacity. $P_2{}^*$ is the pressure reduction parameter of the polymer, and $v_2{}^*$ is the volume reduction parameter. s_1 and s_2 are the surface-to-volume ratios of the components;[4] X_{12}, like the parameter ν^2 used in other expressions, is a parameter related to the difference in force field between solvent and polymer. Using the van der Waals model, $\tilde{U} = -1/\tilde{V}$, in eq 2, one obtains:

$$\frac{h_\infty{}^E}{P_2{}^* v_2{}^*{}_{\mathrm{sp}}} = \frac{s_2 X_{12}(1 + \alpha_1 T)}{s_1 P_2{}^* \tilde{v}_1} + \left[\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}_1}\right) - \frac{\alpha_1 T}{\tilde{v}_1}\left(1 - \frac{T_1{}^*}{T_2{}^*}\right)\right] \qquad (3)$$

where α_1 represents the thermal expansion coefficient of the solvent and $T^* = T/\tilde{T}$. In this simple model applied widely by Flory, the reduced volume of a pure component can be calculated by $\tilde{v}^{1/3} = ({}^4/{}_3\alpha T + 1)/(\alpha T + 1)$ and the reduced temperature by $\tilde{T} = \tilde{v}^{-1}(1 - \tilde{v}^{-1/3})$, while $\tilde{v}_2 = v_{2\mathrm{sp}}/v_2{}^*{}_{\mathrm{sp}}$. As an example, α(PDMS) = 0.887×10^{-3} K^{-1} so that $\tilde{v}$(PDMS) = 1.2240, and $v_2{}^*$ = 0.843 from d(PDMS) = 0.969 cm^3 g^{-1}. The symbol $h_{\mathrm{f.v.}}{}^E$ will be used later as an abbreviation for the second term of the right-hand side of eq 3. To obtain the X_{12} parameter from the experimental heats in eq 3, the parameters α, P^*, and s are necessary.

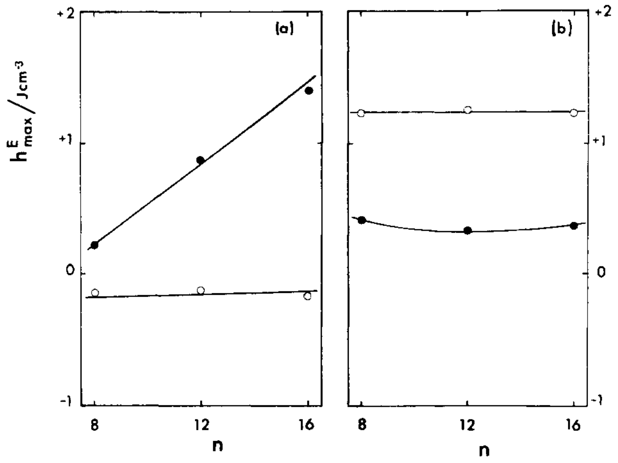

Figure 1. Comparison of the heats of a nonordered, order-breaker compound (a) in linear (●) and branched (○) alkanes with those of an ordered compound (b) in linear (●) and branched (○) alkanes. SnBu$_4$ (ref 10) and SnLaur$_4$ (ref 11) are examples of (a) and (b), respectively; n is the atom carbon number of the alkane.

Equation of State Parameters for the Pure Materials. The densities, expansion coefficients, and pressure reduction parameters can be found in ref 4b for PIB, in ref 13 for PBu-1, in ref 15 for PBD, in ref 6 and 16 for PDMS, and in ref 18 for PP. A mole average of the d and P^* data of PP and PE has been used for the EP copolymers.[19]

Solvents. The same data for the linear alkanes and 2,2,4-trimethylpentane have been obtained from the literature.[20] Values of the thermal pressure coefficients needed to obtain P^* for br-C_{12} and br-C_{16} are quoted in ref 21. Physicochemical data for polymers and solvents are given in Table I.

Calorimetric Test of Order in a Liquid. Measurements of heats of mixing of ordered and nonordered liquids have indicated that the comparison of $H_M{}^E$ in branched and linear alkanes (if the liquid is soluble in alkanes) gives a clear enough picture of the correlation of orientations. In small molecule mixtures, the comparison of heats between systems is usually made on $H_M{}^E$, the maximum value of the heats made over all the concentration range.

Figure 1 is a schematic representation of the heats vs. the number of carbon atoms of the alkane. Figure 1a is the profile expected if the liquid is an order breaker: (1) the heats are larger for the linear alkanes than for the branched alkanes and (2) they increase regularly with the chain length of the alkane with linear alkanes while they do not depend on the alkane size with branched alkanes. For an ordered liquid (Figure 1b), the profile is inversed: the heats are smaller in the linear alkane series than in the branched due to the fitting of the order of the two components. The larger heats with the branched alkanes correspond to the disturbance or destruction of the ordered liquid by the nonordered branched alkane.

The purpose of the present work was to make the heat test on atactic polymers and to conclude if their order–disorder ability was in line with what one could have expected from the shape of their segment.

Results and Discussion

Table II gives the values of $h_\infty{}^E$, X_{12}/s_1, and $h_{\mathrm{f.v.}}{}^E$ for all the systems. In Figures 2 and 3, $h_\infty{}^E$ has been plotted against the carbon atom number of the alkanes. Points for the linear alkanes (Figures 2a and 3a) and the branched alkanes (Figures 2b and 3b) have been plotted side by side to see clearly the differences between isomers of different shape. The characteristic features of the results are the following:

(1) For the branched polymers (Figure 2), $h_\infty{}^E$ is larger with the linear alkanes than the branched alkanes. Furthermore, $h_\infty{}^E$ increases with the chain length of the alkane for linear alkanes while it does not depend strongly

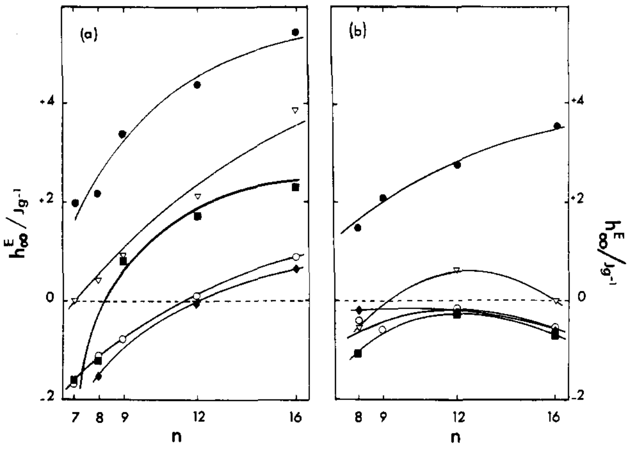

Figure 2. h_∞^E in J g^{-1} for four atactic branched polymers and one ethylene–propylene copolymer in (a) linear and (b) branched alkanes vs. the atom number of the alkane: (●) PDMS, (▽) PBu-1, (■) PP, (○) PIB, and (♦) Cop 33% E.

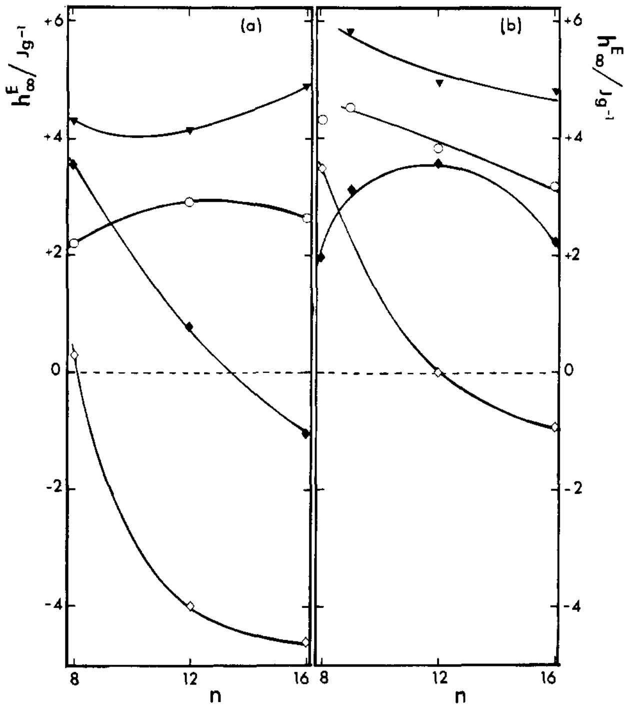

Figure 3. h_∞^E in J g^{-1} for two linear polymers and two ethylene–propylene copolymers in (a) linear and (b) branched alkanes vs. the alkane carbon atom number: (▼) PBD, (○) PPmer, (♦) Cop 63% E, and (◇) Cop 75% E.

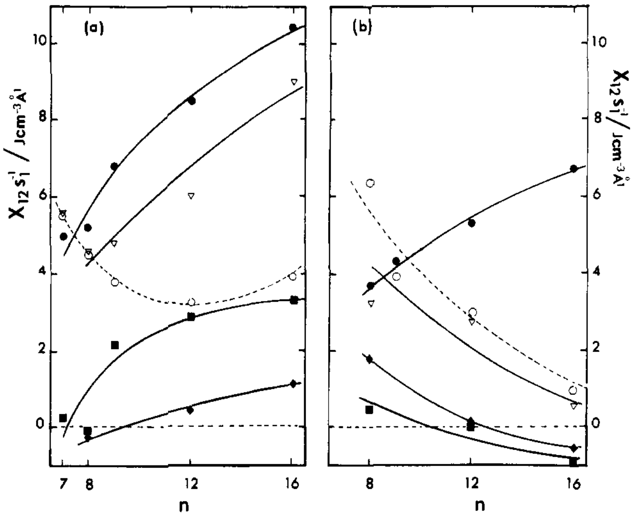

Figure 4. $X_{12}s_1^{-1}$ for the branched polymers and Cop 33% E in (a) linear and (b) branched alkanes vs. the alkane carbon atom number: (●) PDMS, (▽) PBu-1, (■) PP, (○) PIB, and (♦) Cop 33% E. The increase of X_{12} for more volatile alkanes, particularly large for PIB, must be due to an overestimation of the free volume term when solvent and polymer have large expansion coefficient differences. X_{12} is negative for PP and Cop 33% E with the sterically hindered br-C$_{16}$.

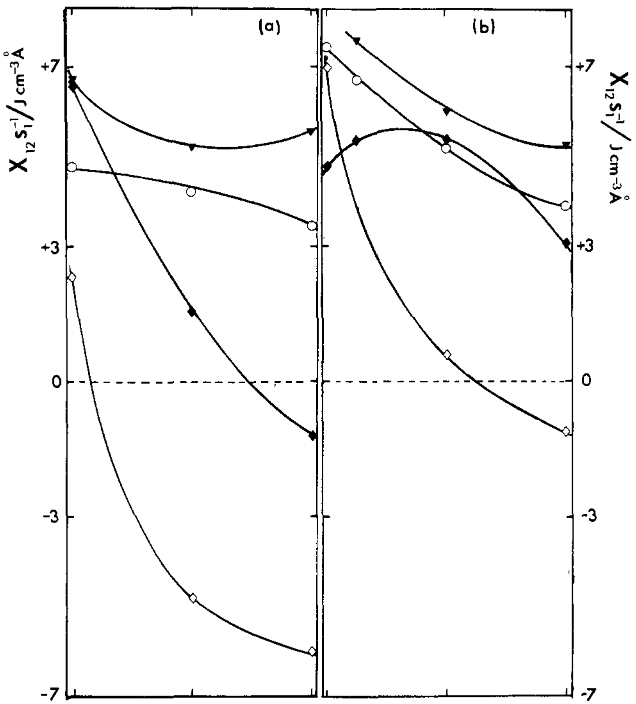

Figure 5. $X_{12}s_1^{-1}$ for the linear polymers and Cop 63% E and Cop 75% E in (a) linear and (b) branched alkanes vs. the alkane carbon atom number: (▼) PBD, (○) PPmer, (♦) Cop 63% E, and (◇) Cop 75% E. X_{12} is unexpectantly large and negative for the copolymers in long alkanes and should correspond to the creation of order in solution.

on the size of the solvent for branched alkanes. These atactic polymers with branched segments act as order breakers of the linear alkanes.

(2) For the two linear homopolymers (Figure 3) PPmer and PBD, h_∞^E for the branched alkanes is larger than for the linear alkanes, and there is no significant increase of h_∞^E for the longer alkanes. This is interpreted as an indication of some fitting of the orientational order between the polymer segments and the solvent.

(3) The two copolymers rich in ethylene have h_∞^E which diminishes very rapidly with alkane chain length. This must correspond to a greater facility for the long chains to be ordered. The negative value of h_∞^E (and of $X_{12}s_1^{-1}$ on Figure 5) for four systems may be indicative of a creation of order in solution.

X_{12} Parameter. The X_{12} parameter of eq 3 corresponds to the experimental h_∞^E from which the free volume term has been deduced. Since the free-volume contribution does not vary too much from one system to another except in very volatile solvents (not studied here), one would expect the trends of X_{12} to be very similar to those of h_∞^E. Figures 4 and 5 show that it is indeed the case. For the order-breaker polymers, X_{12} is larger with linear alkanes than with branched alkanes and increases with the chain length of the linear alkanes. For the linear polymers, the order is reversed, while for the copolymers, X_{12} diminishes with linear alkane chain length as does h_∞^E. The X_{12} values for

Table I: Parameters for the Pure Compounds

compd	$d_{298\ \mathrm{K}}$, g cm^{-3}	$10^3\alpha_{298\ \mathrm{K}}$, K^{-1}	V^*, cm^3 mol^{-1}	P^*, J cm^{-3}	$s = S/V$, Å^{-1}
heptane	0.6795	1.252	114.63	430	1.01
octane	0.6985	1.155	127.83	433	0.99
nonane	0.7138	1.090	141.67	436	0.98
dodecane	0.7450	0.980	183.72	455	0.94
hexadecane	0.7699	0.901	239.69	463	0.90
2,2,4-trimethylpentane	0.6880	1.190	129.08	370	0.81
2,2,4,4-tetramethylpentane	0.7156	1.075	141.90	376	0.79
2,2,4,6,6-pentamethylheptane	0.7414	0.969	184.29	393	0.82
2,2,4,4,6,8,8-heptamethylnonane	0.7819	0.857	238.04	399	0.77
PIB	0.9170	0.555	1.129	447	0.58
PBu-1	0.8700	0.700	1.284	418	0.47
PDMS	0.9692	0.887	0.843	353	0.60
PPmer	0.8888	0.702	0.951	497	0.90
PBD	0.9050	0.685	1.144	502	1.00
PE	0.855	0.752	0.979	484	0.80
PP	0.858	0.806	0.966	470	0.70
Cop 33% E	0.856	0.780	0.973	475	0.77
Cop 63% E	0.857	0.772	0.973	489	0.74
Cop 75% E	0.858	0.765	0.973	481	0.73

Table II: Heats of Mixing at Infinite Dilution of Nine Polymers with Linear and Branched Alkanes at 298 K

	order-breaker polymers (2)														
	PIB			PBu-1			PP			PDMS			Cop 33% E (67% P)		
solvent (1)	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	$h_\infty^{E\,a}$, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}
heptane	−1.7	5.5	−4.9	+0.0	5.5	−2.6	−1.6	0.3	−1.8	+1.9	5.0	−0.7			
octane	−1.1	4.5	−3.7	+0.4	4.7	−1.8	−1.2	−0.1	−1.2	+2.4	5.2	−0.4	−1.6	−0.3	−1.3
nonane	−0.8	3.8	−3.0	+0.9	4.8	−1.4	+0.8	2.2	−0.8	+3.3	6.8	−0.2			
dodecane	+0.2	3.3	−2.0	+2.1	6.0	−0.7	+1.7	2.9	−0.3	+4.4	8.5	−0.1	−0.1	+0.4	−0.4
hexadecane	+0.9	3.9	−1.3	+3.9	9.0	−0.4	+2.3	3.4	−0.1	+5.5	10.4	−0.0	+0.7	+1.0	−0.2
2,2,4-trimethylpentane	−0.4	6.4	−4.1	−0.5	3.3	−2.1	−1.0	0.4	−1.4	+1.4	3.7	−0.5	−0.2	+1.8	−1.6
2,2,4,4-tetramethylpentane	−0.6	3.9	−2.9							+2.1	4.3	−0.2			
2,2,4,6,6-pentamethylheptane	−0.1	3.0	−1.9	+0.6	2.8	−0.7	−0.2	0.0	−0.3	+2.7	5.3	-0.0_4	−0.3	+0.1	−0.4
2,2,4,4,6,8,8-heptamethylnonane	−0.5	1.0	−1.0	+0.1	0.6	−0.2	−0.7	−1.0	-0.0_3	+3.5	6.8	-0.0_1	−0.5	−0.6	−0.1

	ordered or potentially ordered polymers											
	PPmer			PBD			Cop 63% E (37% P)			Cop 75% E (25% P)^b		
solvent	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}	h_∞^E, J g^{-1}	$X_{12}s_1^{-1}$, J cm^{-3} Å	$h_{\mathrm{f.v.}}^E$, J g^{-1}
octane	+2.2	4.8	−2.1	+4.3	6.7	−2.3	+3.6	6.6	−1.4	+0.3	+2.3	−1.5
dodecane	+2.9	4.2	−0.8	+4.2	5.3	−1.0	+0.8	1.6	−0.4	−4.0	−4.8	−0.5
hexadecane	+2.6	3.5	−0.4	+4.9	5.6	−0.5	−1.1	−1.2	−0.2	−4.6	−6.0	−0.2
2,2,4-trimethylpentane	+4.3	7.5	−2.4	ins			+1.9	4.9	−1.7	+3.5	+7.0	−1.8
2,2,4,4-tetramethylpentane	+4.5	6.7	−1.5	+5.8	7.5	−1.6	+3.2	5.4	−0.9			
2,2,4,6,6-pentamethylheptane	+3.8	5.2	−0.8	+5.0	6.0	−0.9	+3.6	5.4	−0.4	0.0	+0.6	−0.4
2,2,4,4,6,8,8-heptamethylnonane	+3.2	3.9	−0.3	+4.8	5.3	−0.3	+2.2	3.1	−0.1	−0.9	−1.1	−0.1

[a] From ref 13. [b] After substracting the small heat of fusion of this copolymer (see part 2).

the PIB system are seen in Figure 4a,b to be larger than those for the PP systems and to increase considerably for the lower alkanes. As it is not likely to correspond to a physical effect, it is believed to be due to the overestimation of the free-volume term for systems with large differences in expansion coefficient (α(PIB) = 0.55×10^{-3} K^{-1}, while it is around 0.7×10^{-3} for the other polymers). For this reason, the points corresponding to $X_{12}s_1^{-1}$ for the PIB systems have been joined by a dotted line. The graphs for X_{12} have been submitted although they give no more information than h_∞^E because it is an accepted way of presenting the results. Furthermore, comparison with small molecule systems can be carried out on X_{12} but not on h_∞^E. Negative X_{12} values which appear for eight systems will be discussed later.

Order–Disorder Contribution to the Heats at Infinite Dilution. The experimental heats of mixing, h_∞^E, are the result of various contributions. These contributions are associated with the many ways a solvent and an atactic polymer can be dissimilar. The difference in force fields gives rise to the positive contribution h_{chem}^E, while in the expansion coefficient it is denoted by the negative term $h_{\text{f.v.}}^E$. The diversities in "structure" or "order" between the polymer and the solvent correspond to the positive h_{dis}^E contribution. In a formal way, one can write the experimental heat as the sum of these three contributions even if it is not proven that they are additive and independent.

$$h_\infty^E = h_{\text{chem}}^E + h_{\text{dis}}^E + h_{\text{f.v.}}^E \qquad (4)$$

In eq 3, the first term with X_{12} includes both h_{chem}^E and h_{dis}^E. The difference in heats between two isomers of unlike shape can give information on the contribution which is sensitive to the shape h_{dis}^E. It is reasonable to assume that the free-volume and force-field contributions are very similar in two isomers, one a linear and the other a branched alkane, so that:

$$\Delta_H = h_\infty^E(\text{lin}) - h_\infty^E(\text{br}) \simeq h_{\text{dis}}^E \qquad (5)$$

In Figure 6, Δ_H has been plotted versus the carbon atom number of the solvent for the different polymers.

A positive sign of the difference Δ_H (i.e., larger heats with the linear alkane) is an indication of destruction of orientational order of the *long alkane* by the atactic polymer. This is the case of five polymers with branched segments PP, PBu-1, PDMS, and PIB and the 33% E copolymer EP when they are mixed with long alkanes in C_{12} and C_{16}. The extent of the destruction of orientational order appears to be different for these five polymers, but it may rather be due to other contributions not identical between the linear and the branched alkane. This is the case of PIB whose large steric hindrance produced by the two methyl groups causes special effects (cf. part 2). The disorientation of the alkane chains may be less extensive in a solution of the 33% E copolymer because of the presence of the ethylene segments which align themselves partially with the solvent. PP and PBu-1 give very similar values of the difference as could be expected from their segment shape. The positive slope of Δ_H vs. n is in agreement with orientational order increasing with the chain length of the alkane. PDMS appears to be a less efficient order breaker, but again it may be due to the nonvalidity of the assumptions that eq 5 can be substituted for eq 4. h_{chem}^E may be different for the branched and linear alkanes because of the slightly polar character of the PDMS segment.

A value of Δ_H near 0 means that the disordering contribution is negligible or that compensation of the different terms in eq 4 makes it appear so. Δ_H is near 0 for n-octane with the order-breaker polymers PP and PBu-1, since at 25 °C orientational order is small for n-octane.

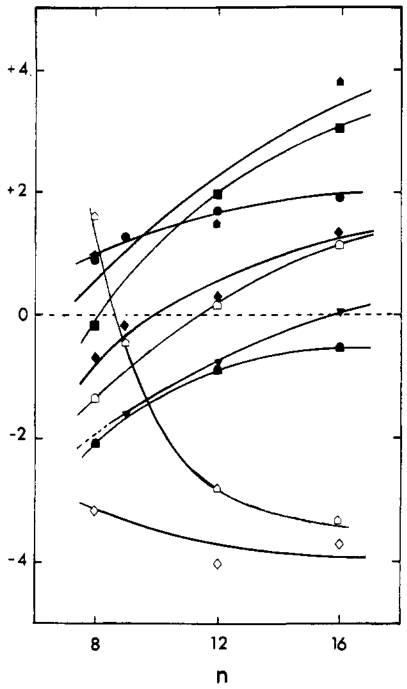

Figure 6. $\Delta_H = h_\infty^E(\text{lin}) - h_\infty^E(\text{br})$ for the nine polymers vs. the alkane carbon number. A positive Δ_H corresponds to an order-breaker polymer and a negative Δ_H corresponds to an "ordered" polymer. The large negative Δ_H values obtained for the copolymers with n-C_{12} and n-C_{16} indicate the ordering of the solvent by the low free volume copolymers: (♦) PBu-1, (■) PP, (●) PDMS, (♦) PIB, (▼) PBD, (●) PPmer, (○) Cop 33% E, (◇) Cop 63% E, and (◇) Cop 75% E.

A negative sign of Δ_H (i.e., larger heats with the branched alkane than the linear alkane) is an indication of orientational order *in the polymer* being destroyed by the globular solvent, the linear solvent fitting its chains with those of the polymer. In this category, there are PBD and PPmer on the one hand and the two ethylene-rich copolymers on the other. The alignment of the polymer segments of PBD and PPmer seems to be easier with short chain alkanes like octane. Due to the presence of a double bond every four and five bonds in these polymers, one would not expect a longer range order. In solutions of longer alkanes like hexadecane, PBD and PPmer must act partially as order breakers and partially as ordered polymers so that the average Δ_H is small. The 63 and 75% ethylene copolymers have long ethylene sequences. From the large negative values of Δ_H with long chain alkanes, it can be reasonably concluded that they fit their long chains better with long alkanes than with short ones. It is interesting to note that the 33% sample is an order-breaker polymer when in solution with a long alkane ($\Delta_H > 0$), and it fits the orientations of its ethylene sequences when mixed with a short linear alkane (n-C_8). This is not in contradiction with the finding that there is little orientational order in short chain alkanes at 25 °C. Orientational order depends as much on free volume as on chain length only. The low free volume of the copolymer is favorable to orientational order in solution between the short ethylene sequences of the copolymer and the short alkanes.

Δ_H being an experimental quantity does not depend on any parameters used to calculate $X_{12}s_1^{-1}$ or $h_{\text{f.v.}}^E$. The free-volume term and $X_{12}s_1^{-1}$ depend much more on the difference of expansion coefficients of the two components than on the surface to volume ratio parameter and the pressure reduction parameter P^*. The error in $H_{\mathrm{f.v.}}{}^E$ comes from some incertitude in the expansion coefficient of some of the atactic polymers and from the model used. In the systems presented here, the differences in $h_\infty{}^E$ from one system to another are large enough so that the general interpretation does not depend on the exact value of the calculated parameters.

Negative X_{12} Parameters and Ordering of the Solution. A negative value of the X_{12} parameter is found for eight systems, four with an order-breaker polymer (PP and Cop 33%) in solution with br-C_{16} and n-C_8 and four with linear alkanes (Cop 63% E and 75%). These negative values mean that there is another negative contribution to the heats other than that of the free volume, which is not explicit in eq 5. In the systems involving br-C_{16}, this contribution must be the steric hindrance contribution found to occur in nonpolar systems with alkanes substituted on the same carbon atom or on neighboring carbon atoms[9,22] and with other compounds.[23] In the case of polymer solutions, the calorimetric study of this contribution is considered in part 2. The negative value of X_{12} obtained with the two ordered polymers in the n-alkanes is quite unexpected and interesting. The origin of these values can be understood if one appreciates that two factors contribute to the extent of correlation of orientations, namely the fit of the molecular segments of similar shape and the low free volume of the mixture. With small molecule mixtures, the effect of the shape has been investigated more extensively than the effect of free volume. However, it has been found (either by raising the temperature or by using an order breaker of different volatility) that orientational order of n-C_{16} for instance drops quite fast when the free volume of the surrounding molecules increases. Using a polymer as the second component lowers considerably the free volume of the solvent. If the polymer and the solvent can fit their segments, as is the case with the high ethylene content copolymers and the linear alkanes, then the solution will indicate an increased order of the ordered alkane as shown by negative heats or negative X_{12}. The large negative Δ_H values for these systems have the same origin. It is our intention to perform other measurements on the same systems such as excess heat capacity and heats at higher concentrations in order to support this hypothesis.

The order–disorder contribution could have been discussed from data on the X_{12} parameter or from differences in the X_{12} parameter between the linear and the branched alkanes. The same qualitative results would have been obtained.

Orientational Order and Free Energy. Intrinsic viscosities $[\eta]$ have been measured in linear and branched alkanes for the copolymers[19] and some homopolymers[25] in order to know the effect of orientational order and steric hindrance on the free energy of mixing or on the quality of a solvent. It has been found on these systems that at infinite dilution of polymer, correlations of orientations between solvent and polymer lower the free energy. Other measurements[24] indicate that, for nonpolymeric systems, there is a partial compensation between the enthalpic and entropic contributions at the concentration of the maximum of G^E so that the overall effect is smaller than on the heats alone or at infinite dilution. $\Delta_{[\eta]}$ values can be calculated for the viscosities in a similar way as in eq 5 and compared to Δ_H. If the $\Delta_{[\eta]}$ are very small whatever the values of Δ_H, it means that there is an enthalpic–entropic compensation in the order–disorder contribution. If $\Delta_{[\eta]}$ are of the opposite sign of Δ_H, it means that the enthalpic term corresponding to orientational order is dominant in the free energy (the opposite sign comes from the fact that a lower free energy corresponds to a higher intrinsic viscosity). This happens in the copolymer systems since eight out of nine $\Delta_{[\eta]}$ have the opposite sign to Δ_H. It is not meaningful to compare the variation of $\Delta_{[\eta]}$ and Δ_H with alkane chain length for all the systems since the combinatorial entropy (not necessarily the same for the branched and the linear alkane) influences $\Delta_{[\eta]}$ and not Δ_H.

References and Notes

(1) (a) H. Tompa, "Polymer Solutions", Butterworths, London, 1956, Chapter 5; (b) H. Daoust, C. Walters, and M. Rinfret, *Can. J. Chem.*, **39**, 1087 (1960).
(2) I. Prigogine (with the collaboration of A. Bellemans and V. Mathot). "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.
(3) G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **57**, 79 (1962).
(4) (a) B. E. Einchinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968); (b) ibid., **64**, 2051 (1968).
(5) D. W. Dreifus and D. Patterson, *Trans. Faraday Soc.*, **67**, 631 (1971).
(6) P. Tancrède, D. Patterson, and V. T. Lam, *J. Chem. Soc., Faraday Trans. 2*, **71**, 985 (1975).
(7) V. T. Lam, P. Picker, D. Patterson, and P. Tancrède, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1465 (1974).
(8) P. Tancrède, P. Bothorel, and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, **73**, 29 (1977).
(9) P. Tancrède, P. Bothorel, P. de Saint-Romain, and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, **73**, 15 (1977).
(10) S. Turrell and G. Delmas, *J. Chem. Soc., Faraday Trans. 1*, **70**, 572 (1974).
(11) G. Delmas and Ng. T. Thanh, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1172 (1975).
(12) G. Delmas and P. Purves, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1828 (1977).
(13) G. Delmas and P. Tancrède, *Eur. Polym. J.*, **9**, 199 (1973).
(14) H. Phuong-Nguyen and G. Delmas, *Macromolecules*, following paper in this issue.
(15) G. Delmas and P. de Saint-Romain, *Eur. Polym. J.*, **10**, 1133 (1974).
(16) R. S. Chahal, W. P. Kao, and D. Patterson, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1834 (1973).
(17) G. Delmas, V. Daviet, and D. Filiatrault, *J. Polym. Sci.*, **14**, 1629 (1976).
(18) O. Griffin-Lewis, "Physical Properties of Linear Homopolymers", Springer-Verlag, New York, 1968.
(19) (a) D. Filiatrault and G. Delmas, *Macromolecules*, **12**, 65 (1979); (b) *ibid.*, **12**, 69 (1979).
(20) R. R. Dreisbach, *Adv. Chem. Ser.*, (1959).
(21) R. Philippe, G. Delmas, and M. Couchon, *Can. J. Chem.*, **56**, 370 (1978).
(22) R. Philippe, G. Delmas, and H. Phuong-Nguyen, *Can. J. Chem.*, **56**, 2856 (1978).
(23) G. Delmas and Ng. T. Thanh, *J. Phys. Chem.*, **81**, 1730 (1977).
(24) M. Couchon and G. Delmas, *Can. J. Chem.*, **56**, 2472 (1978).
(25) H. Phuong-Nguyen and G. Delmas, to be published.