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Heat of Formation of Poly(4-methylpentene-1) Gels

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ABSTRACT: Heats of gel formation have been measured for poly(4-methylpentene-1) (P4MP1) gels, in order to investigate the molecular origin of their cohesive junctions. The latter, which were previously found to be noncrystalline, are stable in cyclopentane (c-C$_5$) and cyclohexane (c-C$_6$) more than 50 °C above the dissolution temperature T_D of the chain-folded crystals. Heats have been measured between 25 and 75 °C below or above T_D depending on the solvent. Below T_D, at 25 °C, the heats (in this case, heats of swelling) have been obtained in linear, branched, and cyclic alkanes. Above T_D, the polymer–solvent interacting parameter in solution, h^E(interaction), can be calculated. For $\phi_p < 0.02$ the final state is a pseudosolution containing aggregates, while for $\phi_p > 0.02$ it is a gel. The main features are the following: (1) h^E(interaction) is *exothermic* and can be almost as large as the endothermic heat of fusion. (2) h^E(interaction) is concentration dependent, reaching a plateau for $\phi_p = 0.20$. (3) A sharp variation of h^E(interaction) is noted when the final state changes from a solution to a gel. (4) h^E(interaction) diminishes when T increases and extrapolates to 0 at the gel–solution transition (110 °C). The sign of h^E(interaction) and its variation with ϕ_p are characteristic of an association between the polymer chains either in the pseudosolution or in the gel. These results support the previously proposed model of junctions consisting of cohesive associations of regularly spiraled helices, stabilized by solvent.

Introduction

Thermoreversible gels may exist in nonpolar systems if the macromolecule has a "copolymeric" character due to differences in chemical nature or stereoregularity. This allows the cohesive regions to coexist in the solvent with the solution-like regions of random coils which give the gel its elasticity. The participation of the same chain in successive ordered and disordered regions is a requirement of the gel state.[1]

During the last decade, the conditions required for forming gels from solutions of several isotactic polymers have been discovered, initiating a surge of effort toward the understanding of their molecular origin. It is generally proposed that gelation is due to different modes of crystallization of the same chains in a given solvent—namely, fringed micellar crystallization, responsible for the cohesive regions, and the usual chain-folding crystallization. A gel is formed if, under special conditions of solvent quality, temperature, and thermal history, fringed micellar crystals are present and stable—but not chain-folded crystals. If gels of stereoregular polymers share the common feature of being quite unexpected, the prerequisites for their occurrence are varied, involving either stirring, quenching at high supercooling, or changing the solvent quality. Recent investigations have revealed new features related to conformation of the chain (isotactic polystyrene (iPS)[2–4]), polymer crystallizability (polyethylene (PE),[5] poly(vinyl chloride) (PVC),[6] poly(*p*-chlorostyrene) (PCS)[7]), and effect of molecular weight and stirring on gelation (PE and polypropylene (PP)[8]). Gels of atactic polystyrene have also been investigated.[9]

This work, which follows a previous one[10] on the characterization of gels of a highly isotactic branched polyolefin, poly(4-methylpentene-1) (P4MP1), investigates the nature of the cohesive junctions through measuring the heat of formation of the gels.

Characteristic Features of P4MP1 Gels. P4MP1 has been studied[11] both in its nascent state (sample N) and after slow recrystallization from the melt (sample M). At the dissolution temperature of the chain-folded crystals, T_D, sample M forms a solution, while sample N experiences gelation at polymer volume fractions higher than about 0.02. However, the M solutions turn to clear gels on isothermal standing at higher temperature than the crystallization temperature of the chain-folded crystals. P4MP1 gels exhibit high thermal stability, since the gel–solution transition (or solation) temperature, T_S, is observed in cyclopentane and cyclohexane at 110 °C, well above the solvent boiling point. The results are consistent with the existence in N, but not in M, of a certain organization which is, in turn, the precursor of network junctions. In a solvent, the junctions can be destroyed by raising the temperature and re-formed on cooling after a suitable thermal history. With enough time, the polymer chains in the solutions of sample M can acquire the necessary characteristics to form a gel. If so, they also acquire the organization precursor of the gel since the polymer sample obtained after drying the gel again gives a gel at the dissolution temperature, as does sample N.

P4MP1 Solutions. Dilute-solution properties at high temperature in good solvents have indicated that the P4MP1 molecules are in the expected statistical coil conformation.[12] In cycloalkanes, on the other hand, solutions of this highly crystalline polymer (T(fusion) = 240 °C) are stable below 100 °C, even as low as room temperature in c-C$_5$. The solutions are actually pseudosolutions containing aggregates which display high intrinsic viscosities. In c-C$_6$, the disappearance of the aggregates when the temperature increases has been followed by measurements of intrinsic viscosities. The latter diminishes abruptly from about 8 to 0.8 dL g^{-1} at 98 °C but it is a slow process which takes several days.[10]

Nature of the Junctions. Since neither a sizable X-ray crystallinity of the gels between T_D and T_S nor any heat effect at T_S can be detected, the junctions in P4MP1 gels are unlikely to be fringed micellar crystals. If the inherent high cohesion of crystals is not at the origin of the junctions, the cohesion in the gels could originate from a

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specific polymer–polymer interaction when the chains have a helicoidal conformation. The presence of helices in solution has been proved[13] with poly(4-methylhexene-1), an optically active polymer similar to P4MP1. A three-step mechanism, operating in solution, has been proposed[10] for the formation of the junctions: (1) conformational change, in solvents of small molecular volume, at low temperature, of the P4MP1 chains from statistical coils to helices; (2) solvent-induced lengthening, at low temperature, of the helical segments spiraled in a given screw sense (the chain, originally formed of short alternatively right- and left-handed sequences, now contains some longer, relatively rigid, rodlike portions); (3) self-association, stabilized by the solvent, of the longer rodlike segments.

The origin of the properties of the nascent polymer might be that it retains, from the conditions of polymerization, a certain portion of longer, regularly screwed helices. The latter transform into alternatively spiraled shorter sequences after melting and recrystallization. Consequently, the nascent polymer, because of the presence of both arrangements, gives a gel at dissolution while the melted polymer gives a solution. Sample M has to go through the rather slow process of one-sense spiralization and association to be able to form a gel while avoiding the formation of chain-folded crystals.

The above model invokes the well-known principle[1] that relatively weak forces such as van der Waals forces may give cohesive structures if they act cooperatively. A minor change in the length of the spiralized portions may actuate the cooperativity of weak forces between the helices and in turn their association.

Molecular Shape and Association in Solution. Analysis of thermodynamic data and Rayleigh scattering[14] in liquids and solutions is a sensitive way to investigate the loose molecular structure of nonpolar systems, and in particular the effect of molecular shape on this structure. Differences in heats of mixing of linear and branched alkanes[14,15] reveal correlations of molecular orientation (i.e., weak associations) between anisotropic molecules. These studies show the great influences of regularity of the molecular shape on such correlations of orientations. For example, a methyl group introduced along the chain of a linear hydrocarbon drastically reduces the correlations of orientations between these molecules in the liquid state. In the same fashion, irregularity introduced into the chain by a change in the sense of spiraling is likely to reduce the possibility of association between chains.

Because of its sensitivity, calorimetry appears to be a good way to investigate the gel junctions and to obtain more information for developing a molecular model of them. Calorimetry has also been used successfully to measure the heat and free energy of association of molecules interacting to form complexes such as the proteins and their ligands.[16]

Heats have been measured in alkanes and cycloalkanes in three temperature ranges: (1) at 25 °C, below T_D, in a series of alkanes; (2) in the vicinity of T_D, when the polymer is only partially dissolved, at 25 °C in c-C_6 and at 75.3 °C in c-C_8 and n-C_7; (3) above T_D, between 25 and 73 °C in c-C_5 and c-C_6. At temperatures where some or all of the polymer is dissolved, the heats have been measured as a function of the volume fraction.

The extent of the dissolution of the polymer has been determined by following the swelling of P4MP1 as a function of temperature. Results are reported in three cycloalkanes between 10 and 75 °C.

Experimental Section

Solvents. These were purchased from the Chemical Sample Co. (Columbus, OH). They were of reagent grade or better and were used without further purification.

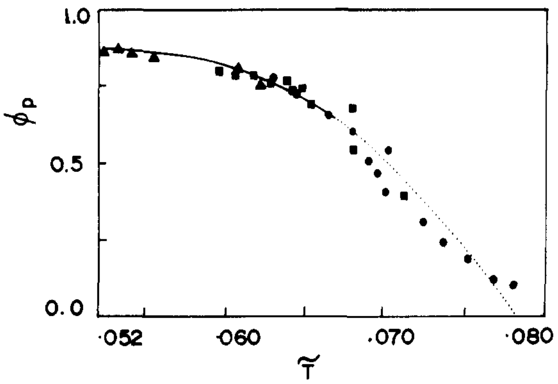

Figure 1. Equilibrium swelling ϕ_p, of P4MP1 strips in three cycloalkanes between 10 and 75 °C plotted against the solvent reduced temperature, $\tilde{T}$: (●) c-C_5, (■) c-C_6, (▲) c-C_8.

Polymer. A commercial ICI P4MP1 sample (Welwyn Garden, Hertforshire, England) was used throughout this work. It is a nascent (or as-polymerized) polymer made of small (probably hollow) globules of 0.2-mm average diameter. Its intrinsic viscosity in Decalin is 2.8 dL g^{-1} at 135 °C, which corresponds to M_v = 360 000.[10] From ^{13}C NMR results it was concluded that the polymer is a pure homopolymer which contains more than 95% isotactic dyads.[10]

Preparation of Films of Nascent Polymer. Since the globules are not easy to handle in the calorimetric cell, a film was prepared by mild heat treatment to avoid the loss of its nascent character. A mixture of highly swollen polymer and solvent was made in c-C_6, by stirring the two components for a short time at a temperature of about 75 °C and pouring on a flat surface. After annealing overnight under vacuum at 125 °C, the dried film was cut into small disks (diameter, 8–10 mm, weight 6–12 mg). This procedure did not modify the junctions since gels made from the disks had the same T_S as the initial polymer.

The crystallinity, w_c, of the disks was somewhat higher than that of the initial polymer, as indicated by the heat of fusion (respectively, 47 and 40 J g^{-1}). In the following, w_c is taken as 0.75, which is in the middle of the range of values obtained by different techniques (0.70–0.80).[11]

Calorimeter. The Setaram apparatus (Lyon, France), which can be regulated between room temperature and 95 °C, was used as described in previous work.[15–18]

Swelling Measurements. For isotropic swelling, the equilibrium volume fraction, ϕ_p(equil), of a thin polymer strip, the length of which has changed from l_0 to l in the solvent, can be calculated as $\phi_p(\text{equil}) = [1 + ((l - l_0)/l_0)]^{-3}$. The polymer volume fraction, ϕ_p, has the usual definition

$$\phi_p = (m_p/d_p)(m_p/d_p + V_S)^{-1} \qquad (1)$$

where m_p and d_p are the mass of the polymer and its density and V_S is the volume of the solvent.

Results and Discussion

A. Swelling. Figure 1 shows the variation of the equilibrium volume fraction ϕ_p(equil) vs. the reduced temperature for three cyclic alkanes over a temperature range of 10–75 °C. (A reduced temperature, indicative of the state of dilation of a compound, can be calculated by dividing the actual temperature by a reducing parameter, which can be the boiling temperature or another temperature derived from the expansion coefficient.[14–18]) The curve can be divided into three regions, without sharp dividing lines between them:

For ϕ_p(equil) > 0.8, the swelling which hardly depends on T corresponds to the interaction of the amorphous part with the solvent.

For ϕ_p(equil) < 0.8, the swelling increases rapidly because of the gradual dissolution of the chain-folded crystals. About 30 °C higher than the start of the dissolution, all the crystals disappear at around T(reduced) = 0.70–0.072.

For ϕ_p(equil) < 0.40–0.50, the solution is made of aggregates which are stable until the solation temperature T_S.

Other swelling data[19] obtained in a variety of solvents follow a curve comparable to that of Figure 1 when plotted against ϕ_p(equil).

B. Heat Effects. B.1. Generalities. Heats of Solution ($\phi_p < 0.02$) and of Gel Formation ($\phi_p > 0.02$). The heat evolved when a crystalline polymer is mixed with a solvent is made of two contributions which, in the present systems, can be written as

$$h(\text{exptl}) = h(\text{fusion}) + h(\text{mixing}) \qquad (2)$$

where h(fusion) is the heat of fusion of the crystal and h(mixing) is the heat of mixing the molten polymer with the solvent. The former is a known quantity, which does not change with ϕ_p, while h(mixing) does.

Heats of Mixing for Polymeric Systems. For polymer solutions, h(mixing) = h^E is conveniently expressed as a function of the polymer (ϕ_p) and solvent (ϕ_S) volume fractions:

$$h(\text{mixing}) = h^E = (m_p/d_p + V_S)\phi_p\phi_S h^E(\text{interaction})$$

or

$$h^E = m_p/d_p(1 - \phi_p)h^E(\text{interaction}) \qquad (3)$$

For high molecular weights, h^E(interaction) is measured at infinite dilution. Because of the high viscosity of polymer solutions, h^E(interaction) can be obtained over the entire concentration range only for low molecular weights. In the present work h^E(interaction) has been obtained for $0 < \phi_p < 0.16$. By comparison with mixtures of nonpolar small molecules, one would expect h^E(interaction) to vary regularly and not greatly with ϕ_p. Heats of dilution of atactic polymers[20] have been shown to increase or decrease only slightly over the concentration range investigated in the present work.

In eq 1, the two contributions will be expressed per gram of polymer. Using eq 3 in eq 2, one finds

$$h(\text{exptl})/m_p = h(\text{fusion}) + d_p^{-1}(1 - \phi_p)h^E(\text{interaction})$$

The parameter of interest in this study, h^E(interaction), in J cm^{-3}, will be given by

$$h^E(\text{interaction}) = ((h(\text{exptl})/m_p) - h(\text{fusion}))d_p(1 - \phi_p)^{-1} \qquad (4a)$$

In cases of partial dissolution, a more detailed expression must be used to calculate h^E(interaction), to take into account the fact that only the amorphous and dissolved polymer interacts with the solvent

$$h^E(\text{interaction}) = ((h(\text{exptl})/m_p) - h^\circ(\text{fusion})(1 - m(\text{amorph})/m_p))d_p(1 - \phi_p)^{-1} \qquad (4b)$$

with

$$m_p = m(\text{amorph}) + m_c(\text{dissolv}) = 0.25m_p(\text{total}) + (h_T(\text{fusion})/h^\circ(\text{fusion}))m_p(\text{total})$$

$$h^\circ(\text{fusion}) = h(\text{fusion})/w_c$$

Here m_p(total) is the total amount of polymer, h°(fusion) the heat of fusion of the totally crystalline polymer, h_T(fusion) the heat of fusion of the partially soluble sample and m_p the quantity used to calculate ϕ_p.

Equation 4 will be used differently in the three temperature regions defined above:

(1) At $T < T_D$, $m_p = 0.25m_p$(total) since m_c(dissolv) = 0, h^E(interaction) can be measured only at one value of ϕ_p, the polymer concentration in the amorphous phase, that corresponding to the equilibrium swelling, ϕ_p(equil) at the temperature of the measurement. In the 0.91–0.98 range of ϕ_P(equil), found in the series of the linear alkanes (between heptane and hexadecane), ϕ_p will vary between 0.72 and 0.92. (Figures 2 and 3).

(2) At T in the vicinity of T_D, the two terms in eq 4b contribute to m_p. Here h^E(interaction) is measured for $0 < \phi_p < 0.075$ (Figure 4).

(3) $T > T_D$, m_p and ϕ_p have their usual definitions and h^E(interaction) is obtained for $0 < \phi_p < 0.16$ (Figures 5 and 6).

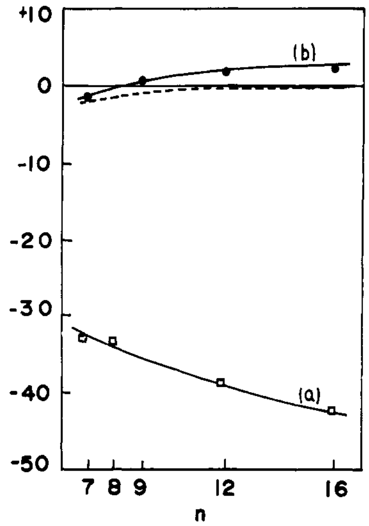

Figure 2. h^E(interaction), at 25 °C in J per cm^3 of the amorphous polymer (m(amorph) = 0.25m_p) in the series of linear alkanes, (for which T_D is higher than 25 °C) plotted against the alkane carbon atom number of the solvent (curve a). For comparison, the heats of atactic polypropylene are given (curve b).

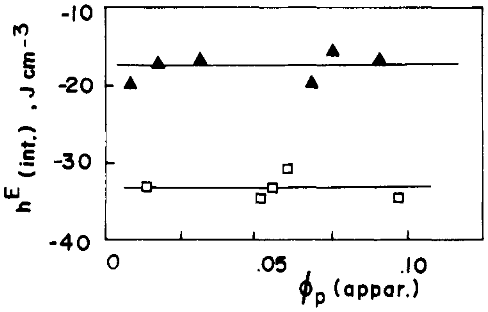

Figure 3. h^E(interaction), at 25 °C, in J per cm^3 of the amorphous polymer obtained from the heats of swelling in n-heptane (□) and c-C$_8$ (▲) (for which T_D is higher than 25 °C) plotted against ϕ_p(appar).

B.2. Heat Effects at $T < T_D$. Heats of Swelling. Comparison with the Heats of Mixing of Atactic Polyolefins. In the left-hand part of Figure 1, at low T, the polymer crystals are not dissolved so that the only contribution to h^E(exptl) is h(mixing) of the solvent with the amorphous part of the polymer. One could expect h(mixing) to be similar in origin and magnitude to that found with nonpolar, amorphous polymers such as polyisobutylene, polypropylene (PP), polybutene-1, etc.[21]

To illustrate the difference between the thermodynamic behavior of P4MP1 and the other polymers, h^E(interaction) with the linear alkanes is plotted in Figure 2, for P4MP1 (curve a) and for PP (curve b). It is clear that the h^E(interaction) values obtained from the heats of swelling of P4MP1 in this alkane series do not bear any similarity to those obtained with PP (or polyisobutylene or polybutene-1). The molecular effect which causes the aggregates and the gel is manifest in a quite unambiguous way

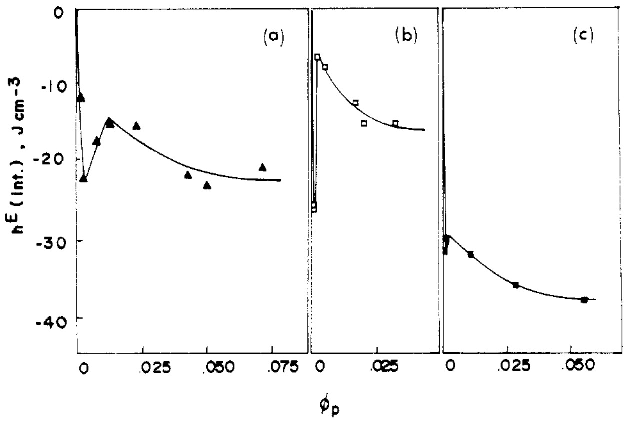

Figure 4. Concentration dependence of h^E(interaction) in three solvents at the onset of the dissolution of the chain-folded crystals: (a) c-C_8 (▲) and (b) n-C_7 (□) at 75.3 °C; (c) c-C_6 (■) at 25 °C. The ϕ_p(equil) are similar (0.75–0.77) in these solvents.

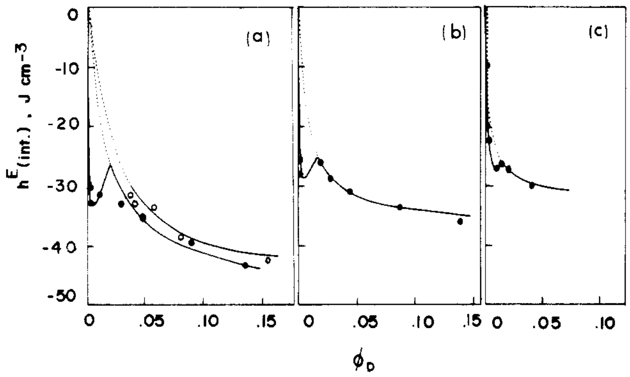

Figure 5. Concentration dependence of h^E(interaction) above T_D in c-C_5: (a) at 25 °C, (b) at 40 °C, and (c) at 45 °C. h^E(interaction), in the gel region only, at 30 °C has been added in Figure 5a. The limit between the pseudosolution and the gel corresponds to $\phi_p = 0.02$. The curves in the gel region in Figures 5 and 6 are fitted to the experimental points through eq 5.

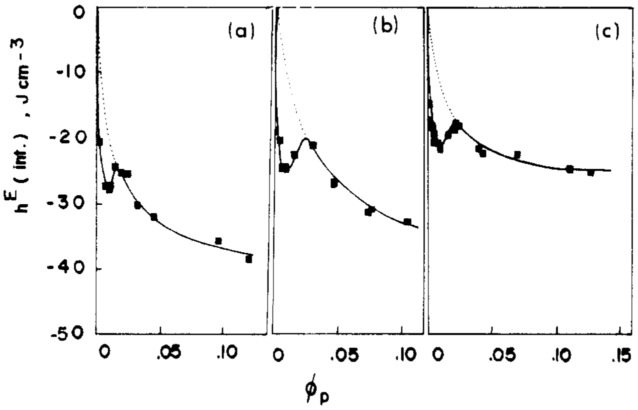

Figure 6. Concentration dependence of h^E(interaction), above T_D, in c-C_6: (a) at 50 °C, (b) at 65 °C, and (c) at 70 °C. As in the c-C_5 systems, the gel and pseudosolution regions are seen to have different cohesion.

in the heats of swelling. The large negative h^E(interaction) indicates association or ordering in solution. It is interesting to note the effect of molecular shape on swelling and h^E(interaction). For example, the experimental heats in J g^{-1} at 25 °C from which the h^E(interaction) are calculated are respectively for three octanes -2.0_4 (n-C_8), -2.5_4 (2,2,4-trimethylpentane), and -1.8_6 (cyclooctane). The effect is more remarkable for longer alkanes since the heats are very small (between −0.2 and 0) for the heavily branched pentamethylheptane and heptamethylnonane while they are −2.00 and −0.95 for n-dodecane and n-hexadecane. On the other hand, the heats of swelling are the same (-1.8_8) in *cis*- and *trans*-Decalin.

Effect of Solvent Excess at $T < T_D$ on h^E(interaction). In Figure 3 h^E(interaction) is seen for c-C_8 and n-C_7 to be independent of ϕ_p(appar) as could be expected since ϕ_p(equil) is not affected by the amount of solvent around the swelling polymer. The h^E(exptl) are −2.7 and −1.8 J g^{-1} for n-C_7 and c-C_8, respectively.

B.3. Heat Effects at the Onset of Dissolution. B.3a. Heats of P4MP1 Partially Dissolved in n-C_7 and c-C_8 at 75 °C. The interest of these results stems from the fact that because of the small amount of crystalline polymer dissolved in n-C_7 and c-C_8 at 75 °C, the endothermic heat coming from the fusion can be separated from the exothermic heat of interaction, enabling one to determine the amount of polymer dissolved. In c-C_8 and n-C_7, the endothermic heats at infinite dilution are respectively 7 and 1 J per gram of total polymer, indicating that 15% (7/47) and 2% (1/47) of the polymer are dissolved. In Figure 4, a and b, h^E(interaction) has been calculated and plotted against ϕ_p.

B.3b. Heats of P4MP1 Partially Dissolved in c-C_6 at 25 °C. In this system, the large exothermic heat does not permit the separation of the two contributions directly. However, the amount of polymer dissolved has been taken to be the same as in c-C_8 since the ϕ(equil) are the same in these two solvents. In Figure 4c h^E(interaction) has been plotted vs. ϕ_p. As the general profile of h^E(interaction) is similar to those obtained when the polymer is totally dissolved (Figures 5 and 6), commentaries on the results in Figure 4 will be postponed. One can note meanwhile that, even in cases of partial solubility, h^E(interaction) is concentration dependent and shows an unexpected behavior at high dilution.

Change of Crystalline Modification during Swelling. It has been reported previously[17] that a new crystalline modification (V) is formed slowly upon immersion of P4MP1 (I) in c-C_5 and c-C_6. One can wonder if the enthalpy associated with this transformation, h(I→V), could be part of the heat of swelling. The problem did not arise for c-C_8 and the linear and branched alkanes, whose heats have been given above, since no spontaneous change of modification has been observed at 25 °C.

Swelling in c-C_6. The more negative values of h^E(interaction) in c-C_6 compared to c-C_8 and n-C_7 may reflect either a stronger interaction (due to the lower temperature and the smaller molecular shape) or alternatively the contribution of the heat of solid–solid transformation from modification I to modification V, h(I→V), found[17] to be 6 J g^{-1}. The appearance of a "tail" in the calorimetric curve seems to support the presence of a slower evolution of heat than that coming from the swelling of the amorphous part of the polymer. However, a quantitative separation of the contributions is not feasible because of the incompleteness of the solid–solid transformation during the time of the calorimetric experiment.

Swelling in c-C_5. The solid–solid transformation will not be discussed since in this solvent measurements were made only above T_D. However, it is timely to note at this point an observation made in c-C_5 gels. The clear gel obtained by isothermal dissolution at 25 °C becomes turbid after a few days, and crystals of modification V are recovered in the tube. This recrystallization of the polymer previously dissolved at 25 °C implies that the new species formed has a dissolution temperature higher than that of the original polymer. This rise of T_D may have two origins; either the smaller solubility of modification V or the greater degree of crystallinity of the crystals (either I or V) when they are formed from the gel, compared to those of the initial polymer.

B.4. Heat Effects at $T > T_D$. Heats of P4MP1 Totally Dissolved in c-C_5 and c-C_6 between 25 and 70 °C. The heats have been measured in c-C_5 at 25, 30, 40, and 45 °C. The dependence of h^E(interaction) on ϕ_p is reported for $0 < \phi_p < 0.15$ at 25, 40, and 45 °C in Figure 5a–c and only in the gel region in Figure 5a at 30 °C. For the c-C_6 systems, h^E(interaction) is given in the same range of polymer concentration, at 50, 65, and 70 °C in Figure 6a–c.

The main features of the results are the following: (1) The h^E(interaction) are large and exothermic. (2) The h^E(interaction) are strongly dependent on the polymer concentration. (3) For a given system, the h^E(interaction) become less negative as the temperature is raised; also, the minimum in the pseudosolution region is less accentuated. (4) The h^E(interaction) in the pseudosolution region are consistently larger than expected from the extrapolation of the gel curve. (5) The change in h^E(interaction) from the pseudosolution to the gel is sharp.

Features 1–3 were expected from considerations of the characteristics of a heat of association and of the stability of the junctions with temperature. On the other hand, the finding that the cohesion of the junctions in the pseudosolution is stronger than that prevalent in the gel is new.

The P4MP1 gels would not be then the result of the accumulation in solution of a greater number of cohesive junctions but would occur through a definite change in the state of aggregation of the chains as indicated by the change in h^E(interaction) between the pseudosolution and the gel.

Heat of Gel Formation ($\phi_p > 0.02$). The experimental results suggest an interaction which tends toward a plateau as the polymer concentration increases. Over the range of polymer concentrations investigated, it is reasonable that the number and quality of the junctions in the gel, expressed per gram of polymer, be constant. A detailed model involving the number of chains taking part in a junction as well as the amount of solvent molecules participating in the cohesive region would be necessary to develop a quantitative expression for the variation of h^E(interaction) with ϕ_p. Instead, by analogy with the expression used to describe the heat of interaction for protein–ligand systems,[16] the following equation will be used:

$$h^E(\text{interaction}) = A\phi_p(B + \phi_p)^{-1} \qquad (5)$$

(It would be more precise to write h^E(interaction) as the sum of two terms, one which is the usual parameter for the mixing of two liquids and has a finite value at $\phi_p = 0$ and the other characterizing the interaction between the chains. However, as the latter is so much larger than the former, only the polymer–polymer interaction term is kept in eq 5.) Here A (negative) is the heat of the maximum interaction and B (positive) the value of ϕ_p for which h^E(interaction) = $A/2$. Stronger interactions are characterized by low B's and large A's. The six curves in the gel region are obtained by fitting eq 5 to the experimental points. The dotted line, which extrapolates to $\phi_p = 0$ and h^E(interaction) = 0, corresponds to the heat expected for a dilute solution with the same type of junction as the gel.

Variation of the Gel Cohesive Energy with Temperature. In Figure 7 the A values for c-C_5 and c-C_6 have been plotted against the temperature. They are seen to extrapolate to 0 at about the temperature of solution of the gels, 110 °C in these two solvents. The standard method to linearize eq 5

$$h^E(\text{interaction})^{-1} = A^{-1} + (B/A)\phi_p^{-1}$$

has been used to calculate A and B.

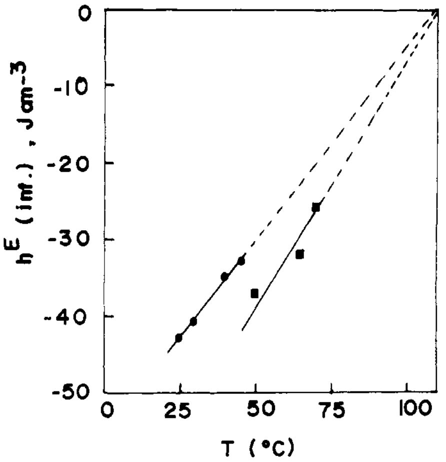

Figure 7. Variation with temperature of h^E(interaction) at the plateau. The parameter A, in eq 5, characteristic of the interaction between the chains in c-C_5 (●) and c-C_6 (■) is plotted as a function of T. A extrapolates to 0 at T_S (110 °C), the temperature of solation of the gel in these solvents.

Heat of Aggregate Formation ($\phi_p < 0.02$). The rapid diminution of h^E(exptl) with ϕ_p is indicative of a strong polymer–solvent and polymer–polymer–solvent interaction heat. The latter can be several times as exothermic as the one in the gel phase (seen from the difference between the dotted line and the curve). When ϕ_p approaches the concentration at which a gel occurs, the organization in the pseudosolution changes to the less cohesive one which is stable in the gel, causing the h^E(interaction) curve to increase between about $\phi_p = 0.01$ and $\phi_p = 0.02$. One should note here that, in previous results[17] in c-C_6, the anomalous behavior of the heats had not been observed since no measurements had been taken in just the right interval ($0.01 < \phi_p < 0.02$).)

An equation similar to eq 5 could be used to describe the interaction in the pseudosolution and to obtain other A and B parameters. The low B values which would fit the equation indicate that, even in very dilute solution, the polymer segments are aggregated. This aggregation leads to molecular association and a highly temperature-dependent apparent molecular weight, as indicated by intrinsic viscosity data.

Variation of the Aggregate Cohesive Energy with Temperature. Inspection of Figure 6a–c indicates that, in c-C_6, the interaction diminishes gently with temperature but stays higher than in the gel. However, since in the present system the intrinsic viscosity is known to have at 98 °C a low value characteristic of a true solution,[10] the loss of the junctions in the dilute region and in the gel seems to occur around the same temperature. One should nevertheless be cautious about measurements of molecular size in solvents near T_S because it has been observed that the pseudosolution junctions are very slow to disappear, much slower than in the gel.

In c-C_5, the difference in the two regions vanishes above 55 °C (value obtained by extrapolating the data of Figure 5a–c). Intrinsic viscosity or light scattering data would tell whether the pseudosolution has become a true solution at this temperature or whether the junctions are now identical with those of the gels.

Type of Transition in the Junctions. A molecular model of the junctions in the two regions, which would explain unambiguously the difference in their cohesiveness, cannot be drawn from the present calorimetric data alone. Some speculation can be presented which may be confirmed or demolished by further studies. An intramolecular transition of the helix-coil type between the dilute and concentrated regions would give the right difference of h^E(interaction). However, such an explanation has to be dismissed on two grounds: a gel is unlikely to occur through the association of statistical coils; furthermore, an increase of concentration, at a given temperature, would be expected to displace the equilibrium conformation toward the helix and not the other way around since the helices can form a more compact and ordered solution than the coils. The process must be more complex and involve not one but several molecules.

In the transition from the pseudosolution to the gel, two changes are expected to occur in the junctions, one concerning the length of the one-sense spiraled helix and the other the number of polymer chains involved in the assembly. The length of the one-sense spiraled helix may diminish when the gel is formed in order to accommodate the junctions formed in the other parts of the chain. Because of cooperativity of the forces between the helices, a small reduction in length may cause a sizable diminution of the overall cohesion. The latter, as expressed per gram of polymer, will also diminish if more chains concur to form the gel junctions from the pseudosolution aggregates. The sharpness of the variation of h^E(interaction) with ϕ_p between the dilute and gel regions indicates that the number of chains involved does not vary regularly when ϕ_p increases but stabilizes rapidly to another value which minimizes the overall free energy. X-ray results taken above the P4MP1 melting point have been interpreted by Wilkes and Lehr[22] as indicating the presence in the melt or ordered structures involving the association of four interpenetrating helices. Such interpenetration may also occur in the presence of solvent, but must depend on the number of chains associating. The final cohesion has to depend critically on the extent of interpenetration. Another factor may be of importance in the change of the cohesion between the two types of junctions and is related to different possible types of helices in solution. Although information on these can be obtained only with similar polymers endowed with an asymmetric carbon,[13] the fact that four crystalline modifications can be obtained[23] from the cyclic alkanes depending on the standard parameters (temperature, concentration, thermal history) may be an indication of an easy change in solution between one type of helix and another.

In conclusion, one can stress the fact that large exothermic interaction heats and their dependence on polymer concentration gives quite definite support to the model of solvent-induced chain association as the origin of the cohesive noncrystalline junctions in the P4MP1 gels. The change in quality of the junctions from the dilute to the gel phase makes worthwhile the investigation of other gels in order to analyze the generality or specificity of this effect. Studies, by other techniques, of changes in the helices at the onset of the formation of the gel may help in developing a detailed molecular model of the junctions.

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