$\eta_0 J_e^0 \omega_0 = 0.6 \pm 0.2$ for all samples. The same value for $\eta_0 J_e^0 \omega_0$ was also observed for linear, star, and comb polymers.[18,28]

The moduli–frequency curves of the H-polymer melts are quite different from those of entangled narrow molecular weight linear polymers as shown in Figures 2 and 3. In fact, they resemble the curves for star and comb polystyrene melts.[18,28] This is also true of the corresponding relaxation spectra.[1] The $G''(\omega)$ curves of linear polymer melts are characterized by a single sharp maximum at the low-frequency end of the plateau region and a minimum at the higher frequencies of the plateau (see Figure 2). At the low end of the plateau region, branched polymers, including the H-polymers, have both G' and $G'' \propto \omega^{1/2}$ (Figures 2 and 3), suggesting that the longest relaxation processes are quite Rouse-like. At higher frequencies in the plateau region, $G''(\omega)$ shows a broad maximum that is most pronounced in the branched polymers with the largest enhancement of viscosity. It appears that the frequency of $[G''(\omega)]_{\max}$, $\omega_{\max}$, is a function of the molecular weight of the branch (arm) only and independent of the particular architecture of the branched polymer. This was already suggested by comparison of $\omega_{\max}$ in the two series of combs (τ_{br} in Figure 13 of ref 28).[28] Branched polymer melts have a set of short-time relaxation processes that involve branches or arms and that are independent of the long-time processes that dominate the zero-shear viscosity. The present Doi[14] and Graessley[9] theories for star melts do not explicitly foresee a maximum in $G''(\omega)$.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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Thermoreversible Gelation of Poly(4-methyl-1-pentene) in Cyclopentane and Cyclohexane

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ABSTRACT: The conditions for the occurrence of thermoreversible gelation of poly(4-methyl-1-pentene) (P4MP1) in cyclopentane and cyclohexane are investigated. The results depend on the history of the polymer sample and are described for a highly isotactic material, either in its nascent state (sample N) or after slow recrystallization from the melt (sample M). At the dissolution temperature of the chain-folded crystals, T_D, where sample M forms a solution, sample N experiences gelation at polymer volume fraction higher than 0.03. However, the M solutions turn to clear gels if left standing at an observation temperature higher than the chain-folding crystallization temperature. P4MP1 gels exhibit a high thermal stability since the gel–solution transition (or solation), T_S, is observed well above the solvent boiling point. The results are consistent with the existence in N but not in M of network junctions which can be destroyed and formed again in solution of any polymer sample after a suitable solvent and thermal history. Since neither a sizeable X-ray crystallinity of the gels between T_D and T_S nor any heat effect at T_S can be detected, the origin of the junctions in P4MP1 gels is discussed in terms of associations of polymer helical sequences, probably stabilized by a favorable interaction between the helices and the small-size cycloalkane solvent.

The P4MP1 gels, formed without either supercooling or stirring, belong to a new class of gels, different from those of other polyolefins, such as isotactic polystyrene or polyethylene.

In nonpolar polymer systems, the occurrence of thermoreversible gelation is associated with a certain co-

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polymeric character of the polymer. Due to the difference in chemical nature or stereoregularity, a fraction of the chains form ordered and cohesive domains in the solvent while the other, being in a random state, gives to the gel its elasticity.[1] The participation of the same chain to successive ordered and disordered regions is a requirement of the gel state.

The discovery of gels in solutions of polyethylene (PE)[2] and highly isotactic polymers such as isotactic polystyrene (iPS)[3,4] has shown that the two entities in presence are now different modes of crystallization of the same chains in a given solvent, namely fringed-micellar crystallization responsible for the cohesive regions and usual chain-folding crystallization. A gel is formed if for special conditions of solvent quality, temperature, and thermal history, fringed-micellar crystals are present and stable but not chain-folded crystals. In the case of iPS, wide-angle X-ray diffraction (WAXD) studies reported by Keller et al.[4] indicated that the polymer in the fringed-micellar junctions could have an extended conformation which had been predicted feasible previously by Sundararajan et al.[5] The last few years, gels have been prepared from PE,[2] atactic poly(vinyl chloride) (PVC),[6] isotactic poly(p-chlorostyrene) (PCS),[7] and isotactic polypropylene (PP).[8] Their investigation has revealed new features about polymer crystallizability (PVC and PCS), lateral orientation (PVC), polymorphism (iPS), and effect of molecular weight and stirring on the occurrence of gelation (PE and PP). Keller[9] has proposed recently a classification of thermoreversible gels obtained from crystallizable polymers. Gels of class 1 (e.g., gels of iPS or of high molecular weight PE) are formed under quiescent conditions and high supercooling, i.e., *below* the chain-folding crystallization temperature T_C. For the class 2 gels (e.g., PE and PP gels), gelation is induced by preceding stirring and occurs on cooling *above* T_C.

In this paper, the conditions for gelation of a highly isotactic polyolefin, poly(4-methyl-1-pentene) (P4MP1), in two cycloalkanes, cyclopentane (c-C_5) and cyclohexane (c-C_6) are described. The following investigation will reveal that P4MP1 gels belong to a different class since they are formed from a medium molecular weight sample without stirring initiation, but above the chain-folding crystallization temperature.

Experimental Section

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

Origin and Thermal History of the Polymer. A commercial ICI P4MP1 sample (Welwyn Garden, Hertfordshire, England) was used throughout this work. It is a nascent (as-polymerized) polymer made of small (probably hollow) globules of 0.2-mm average diameter. Solution and gel properties have been studied on two distinct materials: (1) the as-received polymer, labeled N (for nascent), and (2) sample M obtained from the melt. Melting was performed under vacuum during about 6 h and the sample was allowed to recrystallize slowly by turning off the oven heater.

Polymer Characterization. IR. IR absorption spectra were taken on a Perkin-Elmer 621 spectrophotometer in order to detect the eventual presence of ethylene segments quite frequently introduced in commercial P4MP1 by copolymerization with a long linear 1-alkene monomer. On 0.1-mm-thick samples, no absorption band was observed at 725 cm^{-1}, the wavenumber characteristic of CH_2–CH_2 sequences. Such was the case of a laboratory sample of homopolymer, given by Dr. Lehr (Goodrich Co., Brecksville, OH). On the other hand, a small absorption band is readily detected on another P4MP1 sample (ICI-Mitsui, trade name TPX RT20) known to contain less than 5% of linear units.

^{13}C NMR. Measurements were performed on a Bruker WH-400 multinucleic spectrometer (100.6 MHz) on a 10% solution in a tetrachloroethylene–deuterated benzene (4:1 by volume) mixture. Scans (904) were accumulated separated by a relaxation delay of 5 s. By comparing the spectrum obtained with that attributed to the completely isotactic polymer[10] it was concluded that the polymer is a pure homopolymer which contains more than 95% of isotactic dyads.

Differential Scanning Calorimetry. A Perkin-Elmer DSC-2C was used for the thermal analysis of P4MP1 (scanning rate, 20 K·min^{-1}) and its c-C_5 and c-C_6 gels (10 K·min^{-1}).

Crystallinity. The results of crystallinity determination by different methods are reported elsewhere.[11] The as-received sample N exhibits a latent heat of fusion ΔH_u^* of 45 ± 1 J·g^{-1}. When the sample is annealed at 220 °C overnight or slowly recrystallized from the melt, ΔH_u^* increases to 50 ± 2 J·g^{-1}. The X-ray crystallinities are 0.66 and 0.77 ± 0.05 for samples N and M, respectively.

Solution Properties. The dissolution temperature of the polymer, T_D, was measured by direct visual observation. At infinite dilution, T_D was determined by observing under the microscope the sudden change of shape of the globules. For the as-received polymer, T_D which varies from 13 °C for a small-size solvent like c-C_5 to 170 °C for n-hexadecane are reported for 25 solvents in ref 11 and 12. Intrinsic viscosities, determined in decalin at 135–140 °C for molecular weight characterization[13] and in cyclohexane between 70 and 140 °C to study the temperature stability of the network junctions at low concentration, were measured by using standard procedures[14] and sealed viscosimeters when necessary.

Results and Discussion

The striking result of this work is the following: on heating the as-received polymer (N) in c-C_6, a gel is formed at the dissolution temperature T_D, while at the same concentration, the previously melted sample M gives a fluid solution.

The occurrence of gelation at $T \geq T_D$ indicates that the "morphology" responsible for the gel junctions is already existent in sample N and that this morphology is destroyed by melting and not formed again in the applied conditions of recrystallization. A sample which gives a gel at the dissolution temperature will be referred to as a protogel.

Since the gels of other polyolefins are formed either by stirring or by supercooling a *solution*, the ability of forming a gel at the polymer dissolution seems to be a special feature of P4MP1.

Study of the Protogel Junctions. In order to gain information on the temperature stability, conditions of formation, and molecular nature of the junctions in c-C_5 and c-C_6 systems, the following investigations have been undertaken.

1. Solation and gelation temperatures of the gels have been measured at moderate concentrations (polymer volume fraction ϕ_2 between 0.02 and 0.16). The solation and gelation are the gel–solution and solution–gel transitions, respectively. In this part, it was necessary to define a criterion for a gel.

2. The stability of the junctions at low concentration has been studied as a function of temperature by intrinsic viscosity measurements.

3. Swelling and partial dissolution of samples N and M

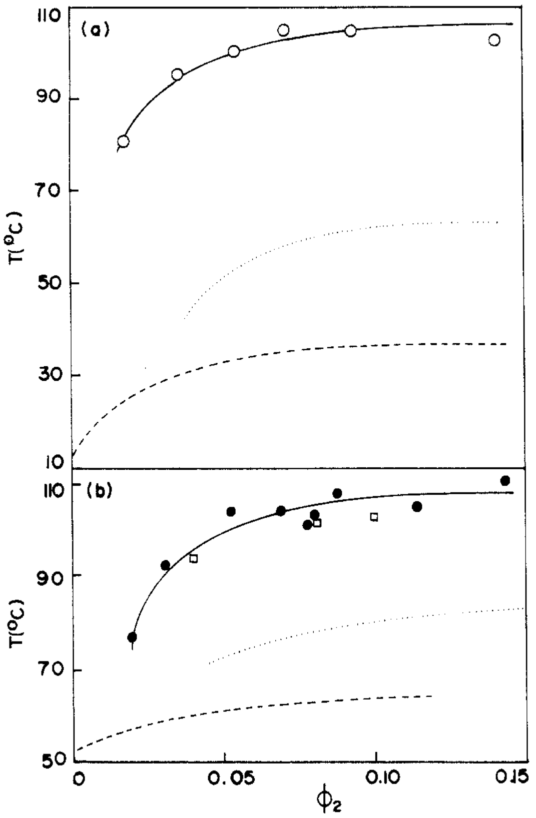

Figure 1. Solation temperatures T_S of sample N gels vs. the polymer volume fraction ϕ_2 in c-C_5 (a) and c-C_6 (b). The dissolution temperature T_D of the chain-folded crystals of samples M (···) and N (– – –) is also plotted vs. ϕ_2. □ represents solation temperatures for protogel obtained from M.

have been determined between 25 and 72 °C.

4. Heats of formation of gels have been measured between 25 and 72 °C.

The results of swelling measurements and calorimetry will be reported elsewhere.[15]

Thermal Stability of c-C_5 and c-C_6 Gels of Sample N. Mixtures of solvent and sample N were prepared in sealed glass tubes at polymer volume fraction $0.02 \le \phi \le 0.16$. The tube content was visually observed as a function of temperature. In c-C_6, there is first a temperature at which the polymer globules swell dramatically and ultimately disappear as a clear gel is formed. This temperature, T_D, is associated with the dissolution of chain-folded crystals, i.e., of polymer chains or parts of polymer chains not involved in the junctions. Upon further heating, the gel is dissolved at the solation temperature T_S.

In c-C_5, dissolution occurs below room temperature so that a transparent gel is obtained directly during the mixing if precautions are taken to avoid agglutination of the globules by introducing them in small amount at one time in the solvent.

Figure 1a,b shows the solation temperature of sample N gels as a function of ϕ_2 in c-C_5 and c-C_6, respectively. On the same graph, the dissolution temperature, T_D of the chain-folded crystals of sample M is plotted against ϕ_2 in both solvents. The dissolution temperature of sample N, measured at infinite dilution under the microscope and at finite concentration visually (as the transition from the two-phase polymer–solvent mixture to the gel), is also reported. The difference between $T_D(M)$ and $T_D(N)$ can be attributed to crystallinity differences.[11] The domain of existence of a clear gel free from chain-folded crystals should lie inside the temperature region limited by T_D and T_S. The $T_D(\phi_2)$ have been obtained by raising the temperature at 5 $°C \cdot h^{-1}$. The T_S curves have been found independent of the heating rate between 1 $°C \cdot day^{-1}$ and 5 $°C \cdot h^{-1}$. Several features of the gels are illustrated by Figure 1. The first is their unexpected stability with regard to the boiling point of the solvents. At $\phi_2 = 0.10$, the gel persists respectively 60 and 30 °C above the c-C_5 and c-C_6 boiling points. The concentration dependence of T_S is also more important for c-C_5 than for c-C_6.

Isothermal Gelation of Sample M Solutions. The second important result of this work is the finding that a clear gel is formed if a solution of M is left standing at 50 °C in c-C_5 and c-C_6. This final state does not depend on the thermal history of the polymer. Furthermore, upon subsequent heating, the gels formed at 50 °C experience solation at the same temperature as sample N gels.

To confirm the reversibility from M to N, the gel obtained isothermally from M is dried to test its protogel character by measurement of T_S. The T_S values noted (□) on Figure 1b in c-C_6 fall on the curve $T_S(\phi_2)$ so that one cannot make any distinction between protogels of different thermal history. The implications of this finding are that the gelation ability is no longer associated with a peculiar polymer sample. The particular "morphology", which is responsible for the cross-linked character of N and disappears upon melting, can be formed again in suitable temperature, solvent, and concentration conditions. The type and number of junctions in the original sample N and in the other protogels must be similar enough to lead to the same T_S.

Gelation and Solation Obtained by Temperature Cycles

The results presented until now, namely solation temperatures as a function of ϕ_2 and isothermal gelation of a M solution, do not depend on thermal history. This is no longer the case when successive heating and cooling cycles are imparted to the systems. Obtaining a gel by cooling a solution presents another difficulty. The gel exists above the dissolution temperature of the chain-folded crystals T_D, so that there was no ambiguity about the nature of the nonflowing mixture. On cooling a solution, a different degree of hysteresis in the formations of the gel and the chain-folded crystals may cause an overlapping of the gelation and crystallization temperature curves. As a consequence, a turbid nonflowing mixture may be a real gel where the polymer chains connecting the network junctions have experienced extensive chain-folding crystallization or a fine suspension of discrete polymer crystals where spatial phase separation has been prevented, or a mixture of both. To clarify the analysis, a test was decided to characterize a gel. The internal cohesion of a turbid gel (I) is superior to that of a rigid crystal suspension (II). So, in order to distinguish between I and II, the tube containing the system was submitted to a vigorous shaking. If the cohesion was kept, the system was considered as a real gel. If the mixture crumbles, it was not. In the latter case, crumbling was most generally followed by spatial phase separation of discrete polymer crystals, which confirms the validity of the shaking test.

The results are given for uniform cooling and heating rates of 5 $°C \cdot h^{-1}$. The systems submitted to the cycles were solutions of sample N after solation at 110 °C and of sample M after dissolution at T_D as indicated in Figure 1.

Cyclohexane Solutions. The N and M solutions become nonfluid on cooling at gelation (or apparent gelation) temperatures T_G given in Figure 2. The gelation temperatures are about 20 °C higher for N than for M. In a second heating cycle, the solation temperatures, noted $T_{S\text{-}2}$, have about the same values for M and N except in dilute

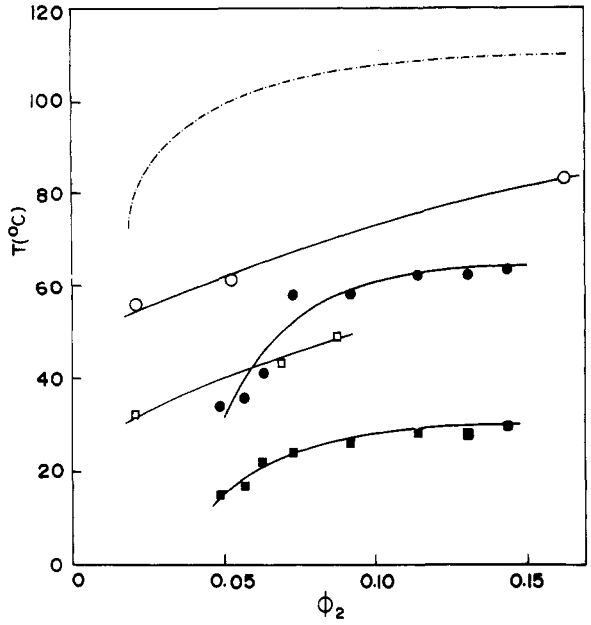

Figure 2. Cooling and heating cycles in $c\text{-}C_6$ mixtures. The gelation (□) and second solation ($T_{S\text{-}2}$) (○) temperatures are plotted vs. ϕ_2 for N (open) and M (full symbols) systems. For M systems, the second gelation and third solation temperatures are indistinguishable from those above. At the scanning rate of 5 °C·h^{-1} used here, crumbling gels are obtained, their weakness being emphasized by their low $T_{S\text{-}2}$, as compared to T_S(N) (–·–).

solution. A second cycle on M solutions indicates that T_G and $T_{S\text{-}2}$ are reproducible with a plateau at about 30 and 60 °C, respectively. This result shows that the junctions responsible for gel formation either from N or from M systems are not formed again in the given cooling conditions, so that the nonfluid mixture obtained at the gelation temperature is not very stable. Indeed, it becomes fluid about 50 °C lower than the initial N gel formed under isothermal conditions, whose solation temperatures have been reported for comparison (–·–·–).

Furthermore, the gels obtained from M or N at the second gelation are weak and do not pass the shaking test. The curves obtained may rather represent dissolution and crystallization temperatures of the polymer in these solvents. However, the large concentration dependence of $T_{S\text{-}2}$ may indicate that a mixture of gel and discrete polymer crystals is formed in these conditions.

Cyclopentane Solutions. Figure 3 gives T_G and $T_{S\text{-}2}$ for samples N and M in cyclopentane. The general features of Figure 2 are present in Figure 3 with important differences. As in $c\text{-}C_6$, a large hysteresis is observed between gelation and solation but the effects of temperature cycles are quite different. The stability of the more concentrated gels ($\phi \geq 0.10$), as evaluated from $T_{S\text{-}2}$, is not very different from that of sample N gels prepared at the polymer dissolution (–·–·–). Furthermore, the gels are very cohesive since they do not crumble upon shaking. This result implies that in $c\text{-}C_5$ the junctions are formed again when the temperature is lowered at the rate of 5 °C·h^{-1} so that their overall concentration and temperature dependence is comparable to that of the gel formed at the dissolution of sample N. In contrast, the nonflowing systems obtained at $\phi_2 \leq 0.05$ below room temperature are probably a mixture of gel and crystals.

This reversibility in the $c\text{-}C_5$ mixture is another indication of the difference between the two solvents. The junctions which resist larger solvent expansion in $c\text{-}C_5$ form also more easily at lower temperature.

Effect of the Maximum Heating and Observation Temperatures on Gelation. The final state of a system after cooling from a higher temperature than T_S will depend on several parameters such as the maximum temperature at which the solution has been held, T_{max}, the time spent at this temperature, the cooling rate, and the final temperature of observation of the system. At the solation temperature, enough junctions are dissipated to make the mixture flow. However, no measurements were performed at $T > T_S$ to ascertain an aggregate-free state of the solution. Such tests would be difficult to do at this concentration but are possible in the very dilute region as discussed later. Very likely, the solution contains, above T_S, some junctions which act as nuclei for the development of more junctions upon cooling. At constant cooling rate, a longer time at high temperature and/or a higher T_{max} may, by diminishing the number of nuclei, alter the gelation temperature or even the final state of the mixture. Finally, the final state of a system will obviously depend on the observation temperature, T_{obsd}, different states being likely obtained if T_{obsd} is higher or lower than the chain-folding crystallization temperature T_C.

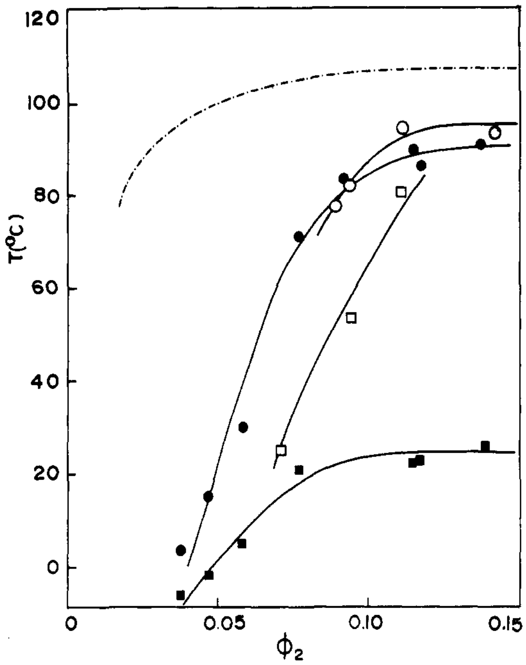

Figure 3. Cooling and heating cycles in $c\text{-}C_5$ mixtures. The gelation (□) and second solation ($T_{S\text{-}2}$) (○) temperatures are plotted vs. ϕ_2 for N (open) and M (full symbols) systems. At the scanning rate of 5 °C·h^{-1} used here, very cohesive gels are obtained, their solation temperature $T_{S\text{-}2}$ being not much lower than those of sample N (–·–). As in $c\text{-}C_6$, gelation and solation temperatures of sample M systems are very reproducible over several temperature cycles. The junctions form again faster than in $c\text{-}C_6$.

Tables I and II report the effect of heating the system at a temperature T_{max}, much higher than T_S, on the final state of the mixture after cooling and offer an illustration of the conditions of gelation described previously. The higher maximum temperatures in $c\text{-}C_5$ and $c\text{-}C_6$ (135 and 165 °C) have been chosen in order to correspond to identical states of expansion of the liquids. On the other hand, 110 °C is T_S for the gels and 85 °C is T_D for sample M at the highest ϕ_2. All systems were cooled rapidly from T_{max} to T_{obsd}. The results are explained as follows:

In $c\text{-}C_6$ (Table I). Systems 2 and 4 give a crumbling system because the observation temperature, 25 °C, is situated below T_c. The rapid cooling does not allow the junctions which were not previously present (system 4), or which have been destroyed by the high T_{max} (system 2), to be formed again. On the other hand, the observation at 50 °C of mixtures 3 and 5, submitted to the same T_{max} as systems 2 and 4, respectively, left time for the junctions

Table I
Effect of Thermal History on the Final State of the Mixtures for P4MP1–*c*-C_6 Systems at ϕ_2 = 0.10

	system				
	1	2	3	4	5
polymer[a]	N	N	N	M	M
T_D, °C		~60[b]		80[c]	80[c]
T_C, °C				~45	~45
T_{max}, °C[d]	110	165	165	85	85
T_{obsd}, °C[e]	25	25	50	25	50
initial state	clear rigid body	fluid solution	fluid solution	fluid solution	fluid solution
state after a few days[f]	white opaque rigid body	white opaque rigid body[g]	clear rigid body[h]	white opaque rigid body[g]	clear rigid body[h,i]
effect of shaking	none	crumbling	none	crumbling	none

[a] Sample M is prepared from sample N by slow recrystallization from the melt. [b] At T_D, a gel is formed. [c] At T_D, a fluid solution is formed. [d] The times left at T_{max} lie between 5 and 48 h. [e] All solutions are cooled rapidly from T_{max} to T_{obsd}. [f] No change is observed on further standing at T_{obsd} for a month. [g] Onset of turbidity prior to apparent gelation. [h] Drying of these gels gives polymer samples whose mixtures with *c*-C_6 (ϕ_2 = 0.10) experience gelation at T_D and solation at 110 °C. [i] In some cases, crystallization was observed instead of gelation. This irreproducibility could be related to slight differences between sample M from different melting batches. Work is currently pursued to determine the effect of thermal history parameters of the melting process on sample M properties.

Table II
Effect of Thermal History on the Final State of the Mixtures for P4MP1–*c*-C_5 Systems at ϕ_2 = 0.05 and 0.10

	system					
	1	2	3	4	5	6
polymer[a]	N	N	N	M	M	M
ϕ_2	0.05	0.05	0.10	0.05	0.10	0.10
T_D, °C	<25[b]	<25[b]		45[c]		
T_C, °C					~25	~25
T_{max}, °C[d]	110	135	135	85	85	85
T_{obsd}, °C[e]	25	25	50	25	25	50
initial state	clear rigid body[f]	fluid solution	fluid solution	fluid solution	clear rigid body[f]	fluid solution
state after a month	turbid rigid body	turbid rigid body	clear rigid body[g]	viscous solution	turbid rigid body	clear rigid body[g,h]
effect of shaking	none		none		none	none

[a] Sample M is prepared from sample N by slow recrystallization from the melt. [b] At T_D, a gel is formed. [c] At T_D, a fluid solution is formed. [d] The times left at T_{max} vary between 5 and 48 h. [e] All solutions are cooled rapidly from T_{max} to T_{obsd}. [f] Gelation occurs in a few minutes. [g] Gelation occurs in a few days. [h] Same remarks as for *c*-C_6 systems (footnote *i*, Table I). However, crystallization in *c*-C_5 at 50 °C was more scarce than in *c*-C_6 and gives rise to very large and flat crystals of modification V.[21] This phenomenon is currently studied.

to reappear without chain-folding crystallization. Consequently, a clear gel is formed. The lower T_{max} for system 1, as compared to system 2, allows some junctions to be kept after solation so that a gel, which becomes turbid due to subsequent chain-folding crystallization, is obtained at 25 °C. The maximum temperature may affect the kinetics of gelation but not the final state, provided T_{obsd} is higher than T_C.

In *c*-C_5 (Table II). The final state of *c*-C_5 systems is listed at two concentrations ϕ_2 = 0.05 and 0.10. In none of these, a crumbling system is obtained because at 25 or 50 °C, the crystal formation is less important than the junction formation. The latter is faster in *c*-C_5 than in *c*-C_6. At ϕ_2 = 0.05 a clear gel is formed in system 1 and only a viscous solution in 2 because the milder heat treatment left enough nuclei for the junctions in 1 to form a gel. The lack of gelation or crystallization in system 4 is due to the slowness of junction or crystal formation at low concentration (ϕ_2 = 0.05). A gel is obtained for all 10% mixtures whatever the polymer sample or the value of T_{max}. System 5 becomes turbid on standing because the observation temperature coincides with T_C.

DSC of the Gels. A mixture of sample N and *c*-C_6 (ϕ_2 = 0.15) was placed in a Perkin-Elmer high-pressure capsule and heated at 10 °C·min^{-1}, between −20 and 135 °C. The thermogram is characterized by only two endotherms corresponding to the fusion of *c*-C_6 (at 6 °C) and of the chain-folded polymer crystals at T_D around 45 °C, respectively. No discernible heat effect is observed around T_S. A similar curve is obtained in *c*-C_5. This result indicates that the heat content of the junctions may be too small to be measured since in the given experimental conditions, a heat effect of 1–2 J·g^{-1} of polymer could be detected if developed in a first-order transition. Measurements with a more sensitive calorimeter (DSC 111, Setaram, Lyon, France) are in progress. Alternatively, a sizable heat may not appear on the thermogram at T_S if the gel junctions are gradually destroyed on heating. Heats of gelation[15] in *c*-C_5 and *c*-C_6 between 25 and 72 °C seem to support the latter hypothesis.

WAXD of the Gels. Due to the volatility of the solvent, stretched gels for X-ray analysis could not be prepared without extensive polymer crystallization. WAXD measurements on unoriented *c*-C_5 and *c*-C_6 gels (ϕ_2 about 0.3) do not show[16] any crystallinity between T_D and T_S. This indicates that the gel junctions are either noncrystalline in nature or too scarce and/or small to be detected above the solvent amorphous halo.

Effect of Temperature on the Network Junctions in Dilute Cyclohexane Solutions. The intrinsic viscosities [η] of cyclohexane solutions of sample M and N have been measured in sealed viscosimeters as a function of temperature between 70 and 183 °C. The results, presented in Figure 4, reveal a considerable difference between the two polymer specimens. The solution of the nascent sample exhibits, up to 70 °C, an extremely high

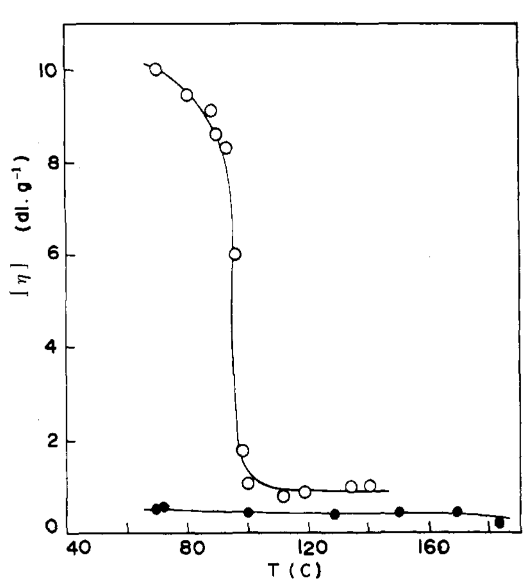

Figure 4. Intrinsic viscosity [η] of sample N (○) in c-C_6 as a function of temperature T between 70 and 140 °C. The rapid decrease of [η] at 98 °C is associated with the dissociation of polymer aggregates. The viscosity of sample M (●) is also reported for comparison.

intrinsic viscosity of 10 dL·g^{-1}. This value compares well with the result of previous measurements[16] at 65–70 °C in unsealed viscosimeters. On the contrary, a very low value of [η], about 0.5 dL·g^{-1}, is obtained for the sample M solution in the same temperature range. The high intrinsic viscosity of sample N indicates that the polymer is readily dissolved since crystalline microgels give usually a small [η] value. It reflects a highly aggregated state of the P4MP1 chains, probably involving the network junctions responsible for gelation at higher polymer volume fractions. At 98 °C, i.e., a temperature close to the solation temperature of more concentrated systems, a sudden drop of [η] to 1.0 dL·g^{-1} accompanies the destruction of the aggregates, which can also be followed isothermally as a function of time, as shown in Figure 5a. The intrinsic viscosity is then similar for both solutions of M and N and remains approximately constant up to 183 °C. On subsequent cooling, [η] does not increase again and the low value persists until it eventually falls sharply at low temperature (below 50 °C) as the polymer begins to crystallize. Even standing of the solutions at 50 °C for more than 3 weeks does not restore the original high [η] value. This behavior can be interpreted as follows. The high viscosities are understood in terms of molecular aggregation whose gelation is a manifestation at high concentration. The gel can be therefore associated with a certain critical concentration of junctions which are present at any concentration and are destroyed around 100 °C. The nonreversibility of the viscosity transition on cooling is undoubtedly due to the high dilution, which reduces the probability of intermolecular contacts necessary for the formation of junctions.

Molecular weight determinations on P4MP1 are usually performed on a decalin solution (commercial mixture of cis and trans isomers) at 130–135 °C, where the polymer has presumably a random-coil conformation.[13] In a previous work,[16] the intrinsic viscosity of a decalin solution of sample N was reported to be 2.8 dL·g^{-1} at 135 °C. This result, which is surprisingly higher than the value in cyclohexane above 100 °C, prompted us to carry out new measurements in decalin. The intrinsic viscosity of sample M is found to be 0.4 dL·g^{-1}, very much in line with the results in c-C_6. Furthermore, as shown in Figure 5b, [η] decreases constantly as a function of time for the sample N solution at 140 °C, suggesting that the value of 2.8 dL·g^{-1} at 135 °C is mainly due to the persistence during the time of the experiment of some network junctions at this temperature. This behavior is consistent with the phenomenology of P4MP1 sample N–decalin systems: at a volume fraction of 0.10, gels are formed upon heating at T_D = 119 °C, which then experience solation around 135 °C.

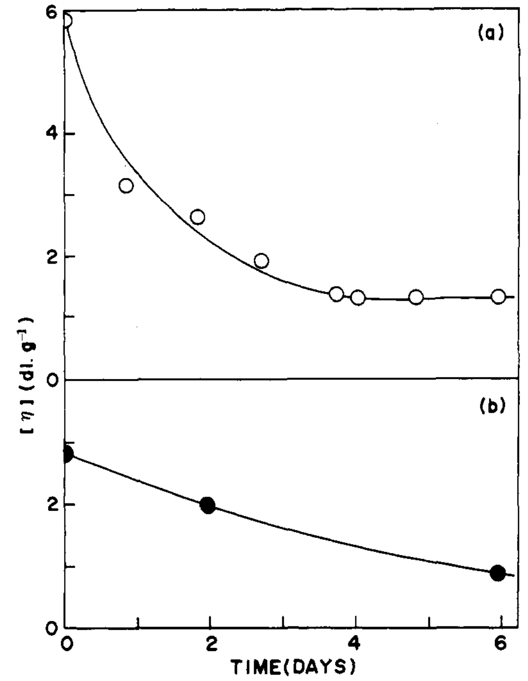

Figure 5. Intrinsic viscosity [η] of sample N in c-C_6 at 98 °C (a) and decalin at 140 °C (b), as a function of time. In both solvents, [η] decreases steadily up to a value of 0.9 dL·g^{-1}, similar to that directly obtained for sample M in the same conditions.

The consequence of the above observations in decalin on the validity of published viscosity–molecular weight relationships[13] is difficult to estimate, since it is not possible to know if, firstly, the polymerization conditions applied by the authors led to a protogel sample and, secondly, the fractionation and purification processes allowed this eventual protogel character to be kept. The fact still remains that the very low viscosity of sample M above T_D or of sample N above the [η] transition corresponds to a very low polymer molecular weight which is surprising for a commercial sample. The question therefore arises whether the heat treatments imparted to the sample either in solution (above 100 °C c-C_6 or 130 °C in decalin) or in the pure state (during the melting process) could have promoted some degradation of the polymer. The difference in the [η] values between samples M and N above the transition in c-C_6 or decalin (respectively 0.9 and 0.5 dL·g^{-1} for both solvents) is indeed indicative of some degradation promoted by melting and recrystallization. However, all viscosities are very stable in time, the flow times of solutions being constant within 0.1% at a given temperature over several days. This precludes any degradation in solution. In any case, the possible degradation of the polymer occurring during preparation of sample M is definitely not a hindrance to the formation of network junctions. Protogel specimens can be prepared from sample M (see Table II for instance). Preliminary measurements of intrinsic viscosity on such samples[17] are indicative of aggregations in solution, similar to that observed for sample N.

Degradation being precluded as the origin of the low [η] values, it should be admitted that the commercial sample N does have a low molecular weight. Other explanations involving for instance the onset at the viscosity transition of intramolecular interactions are in disagreement with (i) the persistence of low [η] at very high temperatures (up to 183 °C) where any interactions are presumably absent and (ii) the low intrinsic viscosity measured[17] for sample N in solvents where gels cannot be prepared, e.g., *n*-hexadecane or 2,2,4,4,6,8,8-heptamethylnonane.

To conclude, the intrinsic viscosity measurements revealed that the presence of junctions in the polymer drastically affects the properties in dilute solutions. It can be associated with very high value of [η], indicative of a highly aggregated state of the polymer. The junctions disappear over a very narrow temperature interval but this destruction is very slow, more than a week being necessary for its completion around the [η] transition temperature (Figure 5). The slowness of this destruction is at least as important in concentrated systems, with regard to the partial reversibility of gelation upon cooling from a higher temperature than T_S. As emphasized in Table I (comparison of systems 1 and 4), some junctions persist above T_S for a long enough time to allow the formation of a clear gel on cooling, even at a lower temperature than 50 °C.

Origin of the Protogel Character of Sample N. The globular form of the as-received sample N indicates that the polymer is in its nascent or as-polymerized form. Preliminary tests on P4MP1 samples of another origin (Mitsui), either homo- or copolymer but both in their nascent state, showed that they possess, as sample N, a definite protogel character. Therefore, the question arises why the nascent product of Ziegler–Natta polymerization should have a protogel character. The extensive studies of the morphology of nascent polyolefins including P4MP1, by Blais and Manley,[18] and the degradation of nascent polyethylene, by Willmouth and Keller,[19] have revealed that Ziegler–Natta polymers could have a composite extended-chain and chain-folded structure, the chain-folded lamella elements being held together by an extended-chain core. A model for nascent P4MP1 involving the extended-chain crystals as the physical cross-links, which confer a protogel character to the polymer, seems to be straightforward. This hypothesis must be consistent with the gradual loss of protogel character by annealing at lower temperatures than the polymer melting point. As a matter of fact, the solation temperature of a cyclohexane system ($\phi_2 = 0.10$) is only 85 °C when sample N was previously submitted to annealing at 150 °C overnight and no gelation occurs at all at T_D after annealing at 190 °C. This observation is in disagreement with the expected dependence of the melting point on the polymer macroconformation, extended chains being presumably more stable than chain-folded crystals.[20] On the other hand, the existence of any other macroconformation, different from chain-folding (extended chains or other), is not substantiated by differential scanning calorimetry. Most generally, there is, even at high heating rates, no significant difference between the DSC thermograms of sample M and protogel specimens prepared by various routes.[11] Therefore, any definite conclusion about the relevance of the above description of nascent polyolefins to sample N and its protogel property is, at present, precluded.

Gelation and Polymorphism. WAXD studies[16,21] revealed that P4MP1 recovered from c-C_5 and c-C_6 gels have crystalline conformations different from the usual modification I prepared from the melt. Furthermore, an extensive investigation[22] of the solid-state structure of P4MP1 crystallized from solutions and gels in a large variety of solvents has shown that as much as five different polymer modifications can be prepared. Because of their relevance to the question whether gelation and polymorphism are directly related phenomena (one being the consequence or a manifestation of the other), selected observations are presented here, which seem to preclude any direct relation:

(i) A change in thermal history induces in xylene solutions of sample N the formation of gels whose phenomenological behavior is similar (no crumbling by shaking, identical thermal stability) but from which different crystalline structures are recovered.[22b]

(ii) The P4MP1 polymorphic structures prepared by drying of the gels can also be obtained by crystallization accompanied with phase separation, in more dilute solutions in the same solvents.

(iii) A P4MP1 sample, recovered from a clear elastic gel of sample M in cyclopentane, formed by cooling the solution to 50 °C (Table II, system 6), exhibits protogel properties. Its structure, determined by WAXD under long exposures, is that of *pure* modification V. This sample has the same gelling ability after annealing at 150 °C, while, as reported in ref 21, its structure is again modification I. This result, and especially the observation that pure modification V has been recovered from the gel, precludes any interpretation of the gelation phenomenon involving differences in crystallizability and/or crystallization temperatures between the various P4MP1 polymorphs.

Although a direct relation between gelation and polymorphism is unlikely, the fact still remains that both phenomena are often observed simultaneously and have probably a common origin, namely the existence of helical conformations of the polymer in solution.

Helical Conformations of P4MP1 in Solution. Circumstantial evidence has been given in the literature that stereoregular polymers may have ordered conformations in solution. In carbon disulfide solutions[7] of iPS, isotactic polypropylene (iPP), and isotactic poly(*p*-chlorostyrene) (iPCS), the absorbed intensity at IR wavelengths characteristic of the helix conformation of the polymer chain was shown to increase when the temperature is lowered from 25 to −50 °C, without any simultaneous detectable change in the intensity of bands associated with the crystal (crystal bands). These helix bands can ultimately reach similar (iPS) or even larger (iPCS) intensities than those observed on the pure polymer. The authors concluded that the trans–gauche conformation of the chain, which generates the helix, is also stable in the noncrystalline state and attributed the variation of helix band intensities with temperature to changes in the average length of the helical chain portions. Similar observations were reported for syndiotactic polypropylene solutions in benzene.[23] While the intensity of a selected helix band of the polymer remains constantly low in carbon tetrachloride as the temperature is lowered, a significant increase is observed in benzene solution. The approach of Pino and co-workers[24] deals mainly with the solution conformation of a hypothetical isolated single chain. Their extensive work leaves little doubt about the existence in solutions of the most stereoregular polyolefins, of helical main-chain sections spiralized in both screw senses. The evidence presented by the authors is based on measurements of the molar optical rotation of stereoregular optically active polyolefins in solution and of its variation with temperature. The results are in good agreement with semiempirical calculations which point,[24] in the case of poly((*S*)-4-methyl-1-hexene) (P(*S*)4MH1), to a conformation in solution consisting at room temperature of left-handed sequences (about 22–28 monomeric units) alternated with right-handed sequences (average length, 2–3 monomeric units).

In the case of non-optically active polyolefins, like isotactic P4MP1, the same calculations predict the following picture: no screw sense is favored due to the absence of a chiral unit, and the amount of monomeric units included in left-handed and right-handed sequences must be the same. Indirect confirmation of these predictions was sought by synthesizing copolymers of chiral and nonchiral units. 4-Methyl-1-pentene units included in the left-handed helix of a copolymer with (*S*)-4-methyl-1-hexene or included in the right-handed helix of a copolymer with (*R*)-4-phenyl-1-hexene contribute remarkably (and by the same absolute value) to the molar optical rotation in solution.[25]

Effect of Temperature and Polymer Local Conformation on Associations in Solution. The dissolution temperatures T_D of P4MP1 have been found to be inversely proportional to the solvent molar volume for about 30 solvents[11] as predicted by the Flory–Huggins theory. The low molar volume solvents, in which the polymer form stable solutions at low temperature, displace the polymer conformation from the statistical coil prevalent at high temperature to the helix formed at lower temperature. The ordering in solution as the temperature is decreased may be visualized not only as the formation of helical sequences from statistical coil but also as the lengthening of the fraction of the chain spiralized in one screw sense. The infrared result in small-size solvents quoted above is an indication of this effect. The increased rigidity of the lengthened helical sequences will have an important effect on molecular association, as can be inferred from small-molecule mixtures.

In nonpolar liquids made of anisotropic molecules such as the linear alkanes, the correlations of molecular orientations equivalent to weak associations depend strongly, apart from the temperature, on the chain length and molecular shape. A small irregularity along the chain, such as a methyl group or a double bond for the small molecules or a kink in the helix for the macromolecule, reduces drastically the possibility of order in the system. Consequently, in P4MP1 solutions, any condition of solvent or temperature which increases the length of the regularly shaped helical part of the chain will, in the same time, increase the chances of association and be the starting point of the junctions.

Nature of the Junctions or Physical Cross-Links. The proposed model for the junctions has to be consistent with the following observations: (1) The high stereoregularity of the polymer chain, i.e., its great potential for regular spiraling. (2) The existence of a protogel character of the as-received polymer but not of the sample recrystallized from the melt. (3) The higher gel stability and easier gelation reversibility in c-C_5 than in c-C_6. (4) The disappearance of the protogel character at high temperature in solution but its slow reversibility from any polymer sample by keeping c-C_5 and c-C_6 solutions at higher temperature than T_D. (5) The lack of detection of some crystallinity in the gel and the absence of a latent heat of solation.

The following model appears to fit these results: protogel P4MP1 samples are composed of two types of crystals. Besides the familiar chain-folded crystals, they contain some fringed-micellar crystals which give rise to the gel junctions in the presence of a suitable solvent. The protogel character disappears after melting or annealing near the melting point, the fringed micelles being transformed into chain-folded crystals. In the presence of c-C_5 or c-C_6, the respective temperature stabilities of chain-folded and fringed-micellar crystals are reversed, since the dissolution temperature of nonprotogel samples is lower than the solation temperature of the gels. However, the apparent lack of crystallinity of the gels points to junctions arising from an ordered association between the solvent and the polymer chains which were involved in fringed micellar crystals, rather than from the persistence of pure fringed micellar crystals in solution above T_D.

In solutions of nonprotogel samples, as well as in solutions of protogel specimens heated at high temperature, gelation may occur on cooling (and ultimately a protogel polymer may be obtained upon drying) because of the transition from a random coil to a chain containing helical sequences, which lengthened as the temperature is lowered. The gel junctions form by intermolecular associations between several helical sections and the solvent. The limited participation of the polymer to these associations which leads to a gel rather than to complete phase separation may be due either to a drastic decrease of the chain mobility after the first junctions have been formed or to a low fraction of the polymer involved in long enough helices to engage in intermolecular associations. Gelation is a concentration- and temperature-dependent phenomenon because both parameters affect the kinetics of chain spiralization and the probability of contact between helical sequences. The dependence of the gel properties on the solvent, emphasized by the higher gel stability and easier gelation reversibility in c-C_5, indicates a possible inclusion of the solvent in the junctions, inclusion which is favored by the loose packing of P4MP1 helices and the small size of the cycloalkane solvents.

Heats of gelation in c-C_5 and c-C_6 between 25 and 72 °C[15] confirm the above description. Gelation is accompanied with an exothermic heat whose temperature and concentration dependences are consistent with the model of solvent helical sequences associations as the constituent of the P4MP1 gel junctions.

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Microstructure in Linear Condensation Block Copolymers: A Modeling Approach

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ABSTRACT: X-ray scattering, differential scanning calorimetry, and dielectric spectroscopy have been combined to model the microstructure in linear thermoplastic condensation block copolymers where one block is semicrystalline. The materials characterized were segmented polyether–esters which exhibit properties between those of elastomers and tough plastics. Quantitative analysis of experimental data was used to evaluate a set of explicit modeling assumptions, regarding the nature of the crystalline and amorphous phases as well as the nature of the interdomain boundaries. The data generally supported the modeling assumptions of sharp interfaces between phase domains, minimal disorder in the polyester crystallites, nearly complete mixing of the chemically dissimilar sequences in the amorphous domains, predominantly three-dimensional (rather than one-dimensional) organization of the crystal–amorphous superstructure, and decreased self-diffusion among the amorphous sequences immediately adjacent to the (001) surfaces of the polyester crystallites. Microstructural parameters such as phase composition, crystallite size, and intercrystallite distance statistics were determined from the modeling studies. Subaudio frequency dielectric spectroscopy appears to be a useful technique for investigating interdomain boundary zone properties. Certain questions remain unresolved, such as to what extent is the crystalline phase continuous.

Introduction

Where polymer microstructures are heterogeneous, particularly when distinct phases coexist, the relationships between intrinsic phase properties and macroscopic properties are dictated by the spatial arrangement of phase boundaries and the properties of these boundaries. This is certainly true for thermomechanical, electrical, optical, and transport properties. These relationships can be used to quantify the design and selection of block copolymers, blends, interpenetrating networks, and polymer–filler composites for specific applications. Difficulty in evaluating the germane structural parameters tends to limit the usefulness of this approach to material design.

For linear condensation block copolymers, where the blocks are typically short and polydisperse, measurement of the various microstructural attributes is particularly difficult. Phase domains whose typical dimensions are a few nanometers tend to be difficult to resolve by microscopy. Although density and diffraction contrast mechanisms exist in principle, the small sizes are beyond the resolution of conventional transmission electron microscopy. Phase contrast microscopy can be used although the images can easily be misinterpreted.[1] The inability to prepare suitably thin representative (of bulk morphologies) films is a practical barrier.[2] Nor are the intrinsic properties of phases and interfaces easily accessible. Relevant investigations must identify both phase compositions and properties. Interdomain boundary zones of finite thickness can be distinguishable from the domain interiors in terms of both chemical composition and constraints on molecular mobility, although the second of these need not imply the first.

Among this class of materials are the linear block copolymers formed with alternating segments of poly(tetramethylene terephthalate) (PTMT) and poly(tetramethylene oxide) (PTMO). The PTMT segments are capable of partial crystallization. In most published studies[3-6] the PTMO segments are derived from approximately 1000 molecular weight polydisperse α-hydro-ω-hydroxypoly(tetramethylene oxide) oligomers. PTMO crystallization appears to be suppressed during solidification of the undiluted polymer melts.

Differential scanning calorimetry (DSC) studies[5] of these segmented polyether–esters confirm that an amorphous phase of mixed chemistry coexists with a PTMT crystalline phase in samples prepared from undiluted melts. Broad thermal glass transitions and aging effects[7] suggest that the amorphous regions are not without some heterogeneous structure. Lilaonitkul et al. have shown that the thermal glass transition midpoints of the PTMO–PTMT systems

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