Investigation of Solutions and Gels of Poly(4-methyl-1-pentene) in Cyclohexane and Decalin by Viscosimetry, Calorimetry, and X-ray Diffraction. A New Crystalline Form of Poly(4-methyl-1-pentene) from Gels

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ABSTRACT: Comparison is made of solution and gel properties of crystalline poly(4-methyl-1-pentene) (P4M1P) in cyclohexane (A) and decalin (B). Heats of mixing and viscosities have been measured in A at 65 °C and viscosities in B at 135 °C. The difference between $[\eta]$ in A (6.5 dL g^{-1}) and B (2.8 dL g^{-1}) points to a different molecular state of the polymer chain in the two solvents, specifically a statistical coil in B and possibly a helix or association of helices in A. ΔH(dissolution) of P4M1P at infinite dilution in A (32 J g^{-1}) is found to have almost the same value as ΔH(fusion). However, ΔH(dissolution) decreases when the polymer volume fraction increases and reaches a plateau of 15 J g^{-1} above $\phi_2 = 0.10$. This is indicative of a highly cohesive gel. Wide-angle X-ray diffraction patterns were taken on P4M1P swollen at room temperature and also at various temperatures between 20 and 110 °C on gels obtained after cooling a solution made at 125 °C. The gel in B has the same X-ray pattern as the pure crystalline polymer (form I) while a new crystalline pattern (form II) is observed in A up to 100 °C. After drying of the cyclohexane or cyclopentane gels, form II persists, a feature observed recently on isotactic polystyrene. The new pattern is characterized by a displacement toward lower angles of the two lower 2θ diffraction peaks (2θ displacement = 1°). DSC on form II indicates that it transforms to form I around 90 °C, with a ΔH(transition) of 6 J g^{-1}.

Introduction

The study of dilute-solution properties of poly(4-methyl-1-pentene) (P4M1P) has been limited, as for other crystalline polymers, to high-temperature regions due to a lack of solubility at lower temperatures. Unperturbed dimensions[1] were obtained on fractions in θ solvents above 175 °C and viscosity–molecular weight relationships have been established in a good solvent, decalin, at 135 °C.[1,2] Recently,[3] however, fractions of partially isotactic P4M1P have been obtained by precipitation from solution below 70 °C. The existence of gels at low polymer concentration ($\phi_2 > 0.015$) in the nonpolar volatile solvents cyclohexane and cyclopentane and their stability over a wide temperature interval[4] (30–50 °C) prompted us to study and compare the dilute-solution properties and gels in two solvents, cyclohexane and decalin. In the present work, calorimetry and viscosity measurements have been made on dilute solutions and X-ray diffraction patterns have been obtained from gels. The intriguing X-ray data of Wilkes and Lehr,[5] suggesting order in the polymer melt at 266 °C, provided another reason to investigate the P4M1P gels by X-ray diffraction.

Apparatus and Techniques

Heats of Mixing. An adiabatic microcalorimeter (Setaram, Lyon, France) equipped with a revolving mechanism is used. The cell is identical with those made for previous work on heats of mixing of atactic polymers.[8] The calibration constant is measured by the Joule effect and verified by mixing two liquids for which the heats of mixing are known.

From a dilute solution in cyclohexane, washer-like disks of about 0.2-mm thickness are made and dried for 60 min at 135 °C and for 24 h under vacuum at room temperature. The polymer disks (1–5) are pinned on the holder at about 1–2-mm intervals at the bottom of the cell. Mercury is used to separate the polymer and the solvent during equilibrium. The turning over of the calorimeter brings the solvent into contact with the polymer and starts the dissolution, which takes place in about 60 min. The final concentration is calculated from the respective weight of the polymer and the solvent. In the present work, heats of mixing are measured at 65 °C. Five points have been added on Figure 1, using samples annealed at 120 °C for 1 day whose form (I) has been checked by X-ray measurements. Visual examination of the content of the cell at the end of the experiment indicates that it is a gel similar to that obtained in a glass tube where the observation is easier.[6]

Viscosities. An Ubbelhode viscosimeter is used with a temperature-controlled oil bath. For the decalin solutions, the highest concentration is made by dissolving, in the viscosimeter, a weighted amount of polymer, the other concentrations being obtained by dilution in the viscosimeter. For the cyclohexane solutions, the four concentrations are made at the same time, in different viscosimeters, and the flow times are measured simultaneously after allowing the polymer to dissolve for 2 days at 65 °C. Flow times taken 24 h after the measurement indicate a small diminution, due probably to some degradation, but the general trend of the viscosity curves is not changed if the lower times are used.

X-ray Diffraction Measurements. Technique I: Room Temperature. Wide-angle X-ray diffraction (WAXD) patterns are obtained with a Norelco diffractometer, using filtered Kα radiation and operating in parafocus geometry. The short time needed to scan the sample (~20 min) has the advantage of not allowing the gel to dry, even in volatile solvents such as cyclohexane and cyclopentane.

The polymer (P4M1P (B)) is ground at dry ice temperature to obtain a coarse powder. Samples for study are prepared by mixing in a sealed vessel 10 g of P4M1P and 22 g of solvent. In all instances, the polymer did not fully dissolve at room temperature, even after 1 year of immersion. At the same time, some highly fluid dilute solution is found to exist between the swollen polymer particles, solution that could be decanted simply by tilting the vessel. The vessel was kept sealed, being open only to take gel samples for measurements.

The polymer volume fraction of the gel which is mounted on sample holders and measured immediately after being taken out of the vessel is not known exactly due to the presence of the dilute phase but must be between 0.4 and 0.5.

Technique II: Temperature Scans in Glass Capillaries. A 3-cm-long capillary (i.d. = 1 mm) is completely filled with the original P4M1P (A) beads (about 0.2 mm in diameter). Afterward, the extremities are minced to prevent the polymer from running out of the tube. Upon immersion in the solvent, the gradual filling

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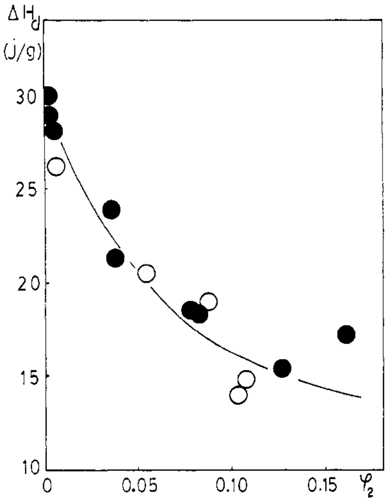

Figure 1. ΔH(dissolution) in J g^{-1} of P4M1P in cyclohexane at 65 °C vs. the polymer volume fraction, ϕ_2, at the end of the experiment. ΔH(dissolution) at infinite dilution is quite comparable to ΔH(fusion) (40 J g^{-1}) measured directly by DSC at 240 °C on the pure polymer. Samples annealed (●) at 100 °C during 1 h and (○) at 120 °C during 24 h.

of the thin tube can be followed visually and when it is completed, the capillary is sealed with epoxy resin. The polymer concentration is about 50% by volume, X-ray diagrams are obtained on flat films with a Picker Nuclear apparatus (Cu Kα source). The exposure time is 35 min. The temperature of the sample is maintained by a gentle flow of air regulated to the desired temperature. The tube conducting the air is 10 mm in diameter and is situated 3 mm above the capillary. The temperature is measured by calibration with a thermocouple in the same position as the capillary, the accuracy of the temperature being estimated at ±2.5 °C. To ascertain dissolution, the capillary is placed for 4 h in an over at 125 °C but the different temperature cycles are made directly in the X-ray apparatus.

Materials and Solvents

Materials. Two P4M1P samples were used having probably the same origin. P4M1P (A) was obtained directly from ICI Co. while P4M1P (B) was from Aldrich (catalog no. 19,100-0, melt index 8). The commercial P4M1P is known to contain a small amount (<5%) of polyoctene or polyhexene. P4M1P (A) has the following characteristics: [η] in decalin[6] at 135 °C is equal to 2.8 dL g^{-1}, which corresponds[1] to M_v = 350000. The heat of fusion at 240 °C is found to be 40 ± 1 J g^{-1} with a Perkin-Elmer DSC II apparatus. This value is higher than the literature one[7] found for pure P4M1P (32.4 J g^{-1}) and must be indicative of a higher crystallinity. All measurements were made on P4M1P (A) except the X-ray diffraction patterns obtained by technique I below, for which P4M1P (B) was used.

Solvents. These were of reagent grade or better and were used without purification. *cis*-Decalin was used for the temperature dependence of the WAXD patterns and a commercial mixture was used for the other experiments.

Results and Discussion

Heats of Mixing. Figure 1 gives the value of ΔH(dissolution) in J g^{-1} for P4M1P in cyclohexane at 65 °C vs. ϕ_2, the polymer volume fraction at the end of the experiment. The measured heat is, in fact, the sum of two contributions, the heat of fusion of the polymer and the heat of mixing of the liquid polymer with the solvent. However, as the heats of mixing of atactic polyolefins in nonpolar solvents have been found[8] to be small (<2 J g^{-1}) or negative (>−1 J g^{-1}), the measured heat represents mainly the heat of fusion of the polymer. Indeed, the value of ΔH(dissolution) extrapolated at $\phi_2 = 0$ is equal to 30 ± 1 J g^{-1}, a value quite comparable to the heat of fusion (40 J g^{-1}) obtained directly on the pure polymer at 240 °C. (The somewhat lower value obtained by calorimetry at 65 °C may be due to the molecular state of the polymer not being identical in the dilute solution at 65 °C and in the molten polymer.) Whether the polymer conformation is a statistical coil, a helix or a group of a small number of helices cannot be decided from these measurements alone. But the measurements do indicate that the energetic state of the polymer chain is very similar to that in the molten polymer. Wilkes and Lehr[5] have found X-ray evidence of some order in the pure polymer melt at 266 °C. They associate it tentatively with the presence of groups of four ordered helices. As the final polymer concentration increases , a gel in cyclohexane is formed which keeps about half the cohesive energy of the crystal since ΔH(dissolution) appears to tend toward a constant value of 15 ± 2 J g^{-1} in the limits of the experimental data ($\phi_2 < 0.15$).

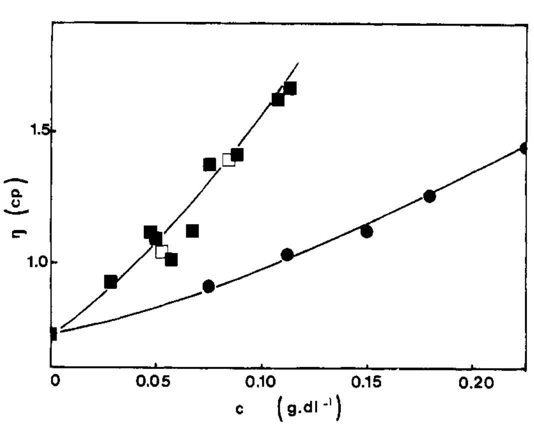

Figure 2. Absolute viscosity in cP of the solution vs. the polymer concentration, c, in cyclohexane at (■) 65 and (□) 70 °C and decalin (●) at 135 °C. The different rate of increase of the viscosity with c may be indicative of a different state of the polymer chain in the two solvents.

Viscosities. The change in the state of the solution seen in Figure 1 between $\phi_2 = 0$ and $\phi_2 = 0.15$ should be detected by other properties. In Figure 2 the increase of the solution viscosity in cyclohexane with increase in the polymer concentration, c, is shown and compared to that observed in decalin at 135 °C. The data in Figure 2 can be used to obtain [η], which is found to be 6.5 ± 1.5 dL g^{-1} with a Huggins' constant of $k' = 1.0 \pm 0.5$. This high value, compared to 2.8 obtained in decalin at 135 °C, indicates that the polymer is readily dissolved since crystalline microgels in the solution give usually a small intrinsic viscosity. For instance, [η] of P4M1P in hexadecane, below the gel temperature, is found to be between 0.8 and 1.0 dL g^{-1}. The increase in [η] from decalin to cyclohexane is due to an aggregated state of the molecules, probably an ordered aggregated state consisting of a few helices.

The effect of the solvent on the conformation of a crystalline polyolefin was observed on low molecular weight syndiotactic polypropylene.[9] The association in benzene below 65 °C was followed by osmotic pressure and viscosity measurements and related to the presence of helices identified by the 868-cm^{-1} band in the IR spectra of the solution.

The presence of order in dilute cyclohexane solutions of P4M1P fits in with the X-ray results presented later on more concentrated solutions at the same temperature. Although viscosity mesurements have not been made up to the same concentration as the heats ($\phi_2 = 0.0015$ instead of 0.16), the rapid increase of the viscosity with c occurring in cyclohexane solutions of P4M1P corresponds to the onset of the highly cohesive gel seen by calorimetry.

X-ray Diffraction Patterns. Additional information on the solution properties in cyclohexane was sought by

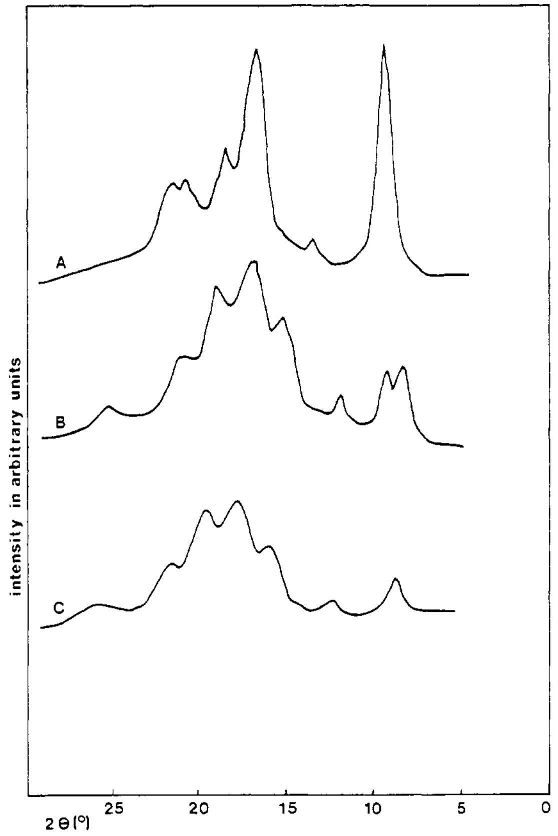

Figure 3. WAXD pattern (technique I) of pure P4M1P swollen in cyclohexane at room temperature: curve A, P4M1P as received; curve B, soaked 1 day; curve C, soaked 1 year.

X-ray analysis of the solutions. However, in order to obtain enough resolution, more concentrated solutions were made which then form a gel. Since the polymer is visibly swollen in some solvents at room temperature, X-ray scattering patterns were first taken at room temperature (technique I). In view of the results obtained and in order to continue our studies at 65 °C, other measurements were carried out at higher temperatures.

Technique I: Polymer–Solvent Systems at Room Temperature. Immersion in Cyclohexane. In Figure 3 are shown the WAXD patterns of P4M1P II as received (curve A) and in cyclohexane after different soaking times. Curves B anc C correspond respectively to 24-h and 1-year immersion.

Interesting changes, such as the shift of the low-2θ peaks, are seen to occur as the swelling of the polymer proceeds. It is worth noticing that two peaks coexist in curve B, indicating that the new crystalline form has not had enough time (in 24 h) to form from the initial on (curve A). Other solvents were tried which have the characteristic of being either good solvents (decalin) or large free-volume solvents (CS_2) or both, like cyclopentane. WAXD patterns taken on these gels indicate that at room temperature all have the usual crystalline P4M1P pattern (form I) except cyclopentane. In the latter solvent, a new pattern (form II) was observed so similar to curve (C) of Figure 3 that it has not been reproduced. In cyclopentane, a 1-week immersion time seems to be sufficient to obtain the form II pattern without a trace of the usual one. In perfluorocyclohexane, perfluorocyclopentane, and nitromethane, no change of the polymer crystalline structure was found.

Technique II: Temperature Variation of the WAXD Patterns. Measurements at higher temperatures appeared necessary in order to ascertain the dissolution of the polymer, particularly in decalin, and to investigate the possible existence of form II at higher temperature.

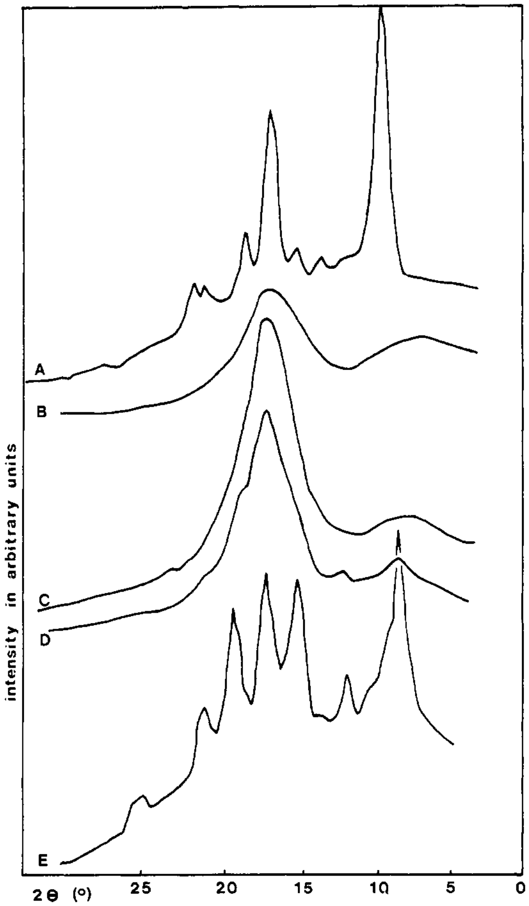

Figure 4. WAXD patterns (technique II) of P4M1P in cyclohexane at different temperatures: curve A, pure polymer annealed; curve B, gel at 83 °C; curve C, gel between 83 and 38 °C; curve D, gel below 38 °C; curve E, P4M1P dried from the gel, showing the new structure.

Gels in Cyclohexane. WAXD patterns were taken between 83 and 23 °C and compared with that of annealed P4M1P (curve A in Figure 4). There was a 2-h interval between the different temperatures except for that between 83 and 68 °C, where it was 12 h. Three types of patterns occur upon cooling, indicative of an increasing order at lower temperature: the high-temperature one (B), showing two broad peaks similar to that obtained on the melt of crystalline and amorphous P4M1P,[5] the intermediate one (C) between 68 and 38 °C, and the crystalline structure (D) below 38 °C, analogous to that already found by technique I (Figure 3). After 1 week at room temperature, this pattern is persistent. A heating treatment similar in programming to the cooling one confirmed the existence of form II and its range of stability with temperature. Form II can be obtained either by ordering a more disordered structure (cooling the gel from 83 to 38 °C) or by disordering a more ordered one (swelling the pure polymer by a high free-volume solvent at room temperature). This reversibility is a criterion for defining a state of equilibrium. Reasonably, the time necessary to reach the equilibrium is shorter at higher temperature, i.e., by technique II. Under the conditions of the experiments, the structure or mixed structures giving the high-temperature and intermediate patterns (C) appear to be at equilibrium since their appearance is reversible. The peak at $2\theta = 17.3°$ is more intense and narrower in the intermediate pattern than in that at high temperature and its intensity relative to that of the other maximum is constant up to 68 °C. The appearance of form II on cooling can be

Table I
Values of the Position of the Peaks and Corresponding Distances of the Diffracting Planes in the Usual (Form I) and the New (Form II) Structures of P4M1P

form I			form II	
2θ, deg	d_{hkl},[a] Å	d_{hkl},[b] Å	2θ, deg	d_{hkl},[a] Å
9.5	9.3	9.25	8.6	10.2
13.5	6.6	6.60	12.0	7.4
15.1	5.9	5.75	15.2	5.8
16.7	5.3	5.389 5.281	17.3	5.1
18.4	4.8	4.85	19.2	4.6
21.0	4.2	4.29 4.19	21.1	4.2
			24.5	3.6

[a] This work. [b] Reference 10.

seen visually since the capillary becomes at this point turbid. A crystalline pattern, different from that of the initial polymer, is obtained (curve E of Figure 4) upon drying (at room temperature, under vacuum for 16 h) the cyclohexane gel of the previously analyzed capillary. One can recognize the same crystalline pattern in the gel state (curve C of Figure 3 and D of Figure 4) and in the dry state if allowance is taken of the peak broadening due to the solvent. The conditions necessary for the obtention of form II are not quite precise yet but it seems easy to obtain form II when well-dissolved concentrated cyclopentane and cyclohexane solutions are slowly cooled and evaporated.

In Table I, the 2θ and d_{hkl} values are listed for forms I and II. The third column gives the d_{hkl} obtained by Keller.[10] In form II, the spacings corresponding to the smaller angles are larger by 0.8–0.9 Å while the others are smaller by 0.1 and 0.2 Å.

The crystalline structure of P4M1P (form I) has been studied by several workers and determined with great refinement.[10–14] Another crystalline form of P4M1P has been prepared by heat treatment under high pressure.[15] Although no structural parameters were published, it is unlikely that the present form II is similar to the high-density one due to the quite different experimental conditions.

For another branched polyolefin, poly[(*S*)-4-methyl-1-hexene] (P4M1H) a crystalline modification has been obtained[12,16] by evaporation of solutions. The general features of the X-ray patterns of P4M1P and P4M1H crystalline modifications are alike. This could be expected since the usual structures of the two polymers are similar[12] and can cocrystallize over a range of mixed composition.[17] The cell dimension determination of the crystalline modification obtained from gels is in progress in this laboratory, using the X-ray fiber analysis.

Differential scanning calorimetry was performed on form II. The DSC trace shows two endotherms, one whose maximum is at 90 °C, corresponding to a heat of 6 J g^{-1} (with a scanning speed of 10 °C min^{-1}), and the other at the usual melting point of form I, 240 °C, with a heat of fusion of 40 J g^{-1}. X-ray patterns of form II, annealed at 100 °C, were identical with those of form I. These results indicate that a crystal–crystal transformation occurs from II to I at 82 °C. The transformation is not reversible in the solid state. Similar irreversibility was encountered by Karasz, Bair, and O'Reilly[18] in their extensive thermodynamic measurements of P4M1P. They found a peak in C_P whose temperature and existence depends on thermal history imparted to the sample. Their X-ray diffractometer tracings of the powder and of the annealed sample are indicative of the presence of small amounts of another polymorph in the polymer "as received", which could be form II. However, the temperature at which the sample has to be annealed to transform the polymorph into the usual form I is much higher than that which has been obtained in the present work. Although it is possible that the transformation temperature of form II into form I varies with its concentration in the sample, it is not possible to have a definite conclusion about the identity of the two isomorphs.

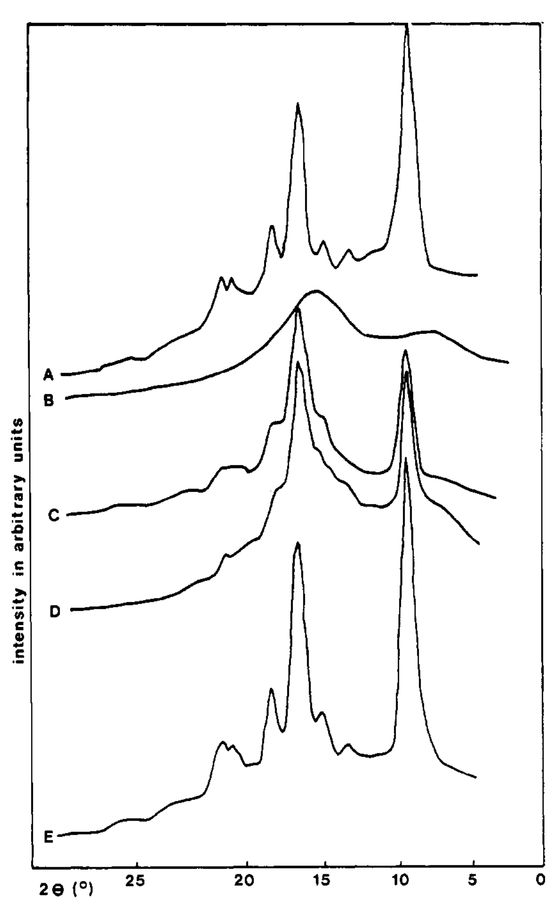

Figure 5. WAXD patterns (technique II) of P4M1P in decalin at different temperatures: curve A, pure polymer annealed; curve B, gel at 105 °C; curve C, gel at 100 °C; curve D, gel at 25 °C; curve E, P4M1P dried from the gel.

***cis*-Decalin.** A simple explanation of the absence of form II in decalin at room temperature could be that its domain of stability in this solvent is at higher temperature. The search for the novel pattern was achieved by successive cycles of slow heating and slow cooling of a decalin solution between the temperature corresponding to the pattern typical of a high temperature (curve B of Figure 5 at 105 °C) and that characteristic of a lower one (curves C and D). No new pattern could be found. The gel pattern appears to change without intermediates from the crystallike structure to the high-temperature one. Interestingly, the decalin gel is transparent even at room temperature when it has a crystallike pattern.

These studies have shown that the solvent in which form II occurs, cyclohexane, is also the solvent in which intrinsic viscosity is indicative of helices in solution. One can wonder if the existence of form II is a necessary condition for the stability of helices in solution. The stability of form II in the gel up to the boiling point of the solvent is a favorable indicator of its stability in dilute solution. Viscosities and X-ray patterns in other solvents could give more information on this point. Cyclooctane was chosen because its physicochemical properties are intermediate between those of cyclohexane and decalin. The value of [η] for P4M1P in this solvent has been shown[6] to be constant between 60 and 90 °C and then diminish over a 15 °C temperature interval form 6.1 to 3.0 dL g^{-1} near the value in decalin at 135 °C. X-ray patterns are currently being obtained on P4M1P gels in cyclooctane to compare the information drawn from dilute- and concentrated-solution techniques.

The above results in which the solvent can have an influence in determining the polymer conformation not only in solution but in the dried state are similar to what has been found recently on solutions and gels of isotactic polystyrene in decalin.[19] The general character of this solvent effect is worth examining on other polymer solvent systems.

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Note Added in Proof. Several papers relating Japanese work on another modification[20a–c] of P4M1P escaped our attention during preparation of the present article. In a later publication,[20d] a revised version of the present comment of the Karasz, Bair, and O'Reilly work and a reindexation of the modifications anterior to the present one will be made.

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Crystalline Morphology of Isothermally Crystallized Branched Polyethylene

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ABSTRACT: The crystalline morphology, or supermolecular structure, of well-characterized whole polymers and fractions of branched polyethylene was systematically studied as a consequence of and during isothermal crystallization. Small-angle laser light scattering was the principal technique used, and this work necessitated a delineation of the isothermal crystallization range and a careful preliminary study of the overall crystallization kinetics under these conditions. Molecular weight, molecular weight distribution, and branching content were the principal constitutional variables investigated. Although both whole polymers and fractions respond in a similar manner to these variables, the whole polymers display a greater propensity to form spherulites after isothermal crystallization and cooling. Molecular weight fractionation is ruled out from being of any significance here, and the effect is attributed to the accessible crystallization range. Major control of spherulitic structure and size observed at room temperature can be obtained from both the extent of crystallization and the morphological form developed at the isothermal crystallization temperature. Under favorable conditions the latter can lead to "macronuclei" for spherulite formation.

Introduction

We have previously reported studies of the crystalline morphology of isothermally crystallized molecular weight fractions of linear polyethylene as well as the rapid nonisothermal crystallization of both linear and branched fractions and whole polymers.[1–4] Small-angle light scattering (SALS) was the principal technique used, augmented when necessary by optical and electron microscopy. For similar crystallization conditions it was found that the morphology, or supermolecular structure, of the linear polyethylenes is strongly influenced by molecular weight and is also extremely sensitive to polydispersity.[1,2,5] Molecular weight fractions with molecular weights less than about 2×10^6 can develop rodlike morphology under appropriate crystallization conditions, while it is also possible to establish conditions under which organized morphological forms are not observed, although the characteristic lamella crystallites are present. For

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