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(40) The data were obtained by scaling the results shown in Figure 1 to a temperature of 125 °C. We calculated the fractional free volume to be equal to 0.042 (the same value calculated for the low molecular weight matrices (see Appendix)) for higher molecular weight matrix chains at this temperature. The shift factor was obtained by scaling the data to results obtained for the diffusion of a $M = 110\,000$ molecular weight chain in a matrix of 2.0×10^6 at this temperature.

Further Morphological Studies of *trans*-1,4-Polyisoprene Crystallized from Solution

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ABSTRACT: Three fractions of *trans*-1,4-polyisoprene with $M_v = (1.4–5.9) \times 10^5$ were crystallized from amyl acetate solution at temperatures from 0 to 30 °C. Optical microscopy before drying and scanning electron microscopy after treatment in suspension with OsO_4 and drying were used to investigate these preparations. Changes in morphology with molecular weight and crystallization temperature were followed; curved lamellas, lamellar stacks, and spherulites were found. Scanning electron microscopy revealed features, such as lamellar interpenetration and curvature, branching, and twisting, either not seen or not seen clearly with optical microscopy. When stacks of curved lamellas are subjected to ultrasonic vibration, preferential fracture across the center portion of all the layers takes place.

Introduction

trans-1,4-Polyisoprene (TPI) can be crystallized in monoclinic (α)[1] or orthorhombic (β)[2] forms depending on the conditions used. Seeded crystallization from solution, a process that involves dissolution at elevated temperature, precipitation, redissolution at moderate temperatures, and crystallization at constant temperature, is found usually to yield overgrown α-form TPI lamellas.[3,4] On the other hand, direct crystallization from solution, consisting of dissolution at an elevated temperature followed by isothermal crystallization, leads to more complex structures, such as sheaves, spherulites, and curved lamellar aggregates, which can be in the α- or β-forms depending on the crystallization solvent and temperature.[5] The various structures resulting from direct crystallization from solution were previously studied in suspension prior to drying[5] with interference contrast optical microscopy. As is usually the case with optical micrographs, the magnification and contrast were low and therefore few details of the lamellar organization were visible. However, in that work transmission electron microscopy was successfully employed to view at much higher magnifications a preparation of curved lamellar aggregates that had been reacted with OsO_4 while in suspension prior to drying. Due to their overall thickness and complexity sheaves and spherulites are difficult to investigate by transmission electron microscopy. However, as shown below, it is possible to study these structures with scanning electron microscopy. In order to preserve the organization of these structures while in suspension prior to drying while enhancing the contrast, reaction with OsO_4 is carried out. That the overall appearance of these structures is not modified by the chemical treatment is evident by comparing interference contrast optical micrographs taken of them in suspension with scanning electron micrographs of similar fields taken after reaction and drying.

In the work presented here direct crystallization at 0–30 °C was carried out with fractions of synthetic *trans*-1,4-polyisoprene with viscosity-average molecular weights of 1.4×10^5, 2.6×10^5, and 5.9×10^5, extending the range of the previous study to higher molecular weights. Also in the present work the effects of ultrasonic vibration of sheave and spherulite structures, prior to OsO_4 treatment and drying, were investigated.

Experimental Section

Samples. Synthetic *trans*-1,4-polyisoprene (TPI) was obtained from Polychemicals, Inc. This was found earlier with gel permeation chromatography[6] to have $M_n = 3.5 \times 10^4$, $M_w/M_n = 4.8$, and a trans-1,4 content from carbon-13 NMR of 99%.

TPI fractions were obtained by fractional precipitation from toluene solution with methanol using the scheme shown in Figure 1. The three fractions P_5, P_6, and P_{15} were used. Viscosity-average molecular weights of 1.4×10^5, 2.6×10^5, and 5.9×10^5, respectively, were determined by solution viscosity measurements in toluene at 30 °C employing the relationship $[\eta] = 3.34 \times 10^{-2} M^{0.686}$. This relationship was determined by using molecular weight fractions with $M_w/M_n = 1.2–1.3$ prepared on a diatomaceous earth column and characterized by gel permeation chromatography earlier.[4,5]

Crystallization. Samples were prepared from 0.1 and 1% (w/v) amyl acetate solutions by the direct method. The polymer was dissolved in amyl acetate by heating to 90–95 °C for 30 min; the solution was cooled to 60 °C and then placed in a constant-temperature bath at one of the following temperatures: 0, 10, 20, or 30 °C for 1 h to 4 days. One preparation was obtained by a seeded crystallization.[5]

Optical Microscopy. After crystallization of the sample, a drop of the amyl acetate suspension was placed on a slide with a cover glass and viewed at room temperature with a Zeiss photomicroscope having interference contrast optics.

Scanning Electron Microscopy. The TPI–amyl acetate suspensions were mixed with OsO_4 for about 1 h and washed with fresh amyl acetate. A drop was placed on aluminum foil; the sample was dried and then coated with evaporated Au/Pd(80/20). For a number of the preparations the suspension was placed in an ultrasonic vibrator for 3 min prior to the chemical treatment. A Cambridge Stereoscan S4 scanning electron microscope was used for viewing these preparations.

Results

For TPI with $M_v = 1.4 \times 10^5$ direct crystallization at 20 °C from 1% amyl acetate was carried out for 1, 2, 3, 5, 24, and 48 h followed by treatment with OsO_4 before drying. For crystallization times up to 3 h relatively little precipitation occurs. A scanning electron micrograph of one

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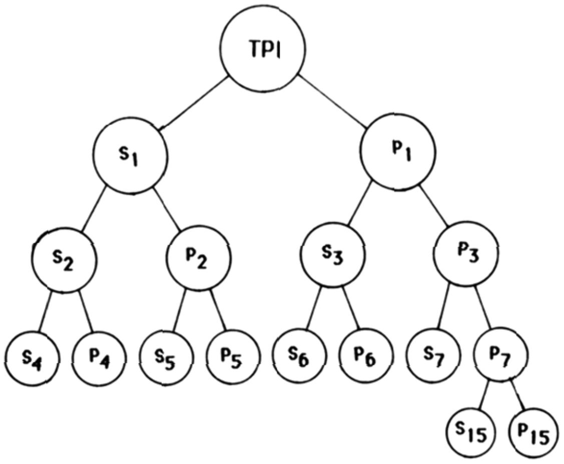

Figure 1. *trans-1,4-Polyisoprene fractionation scheme.*

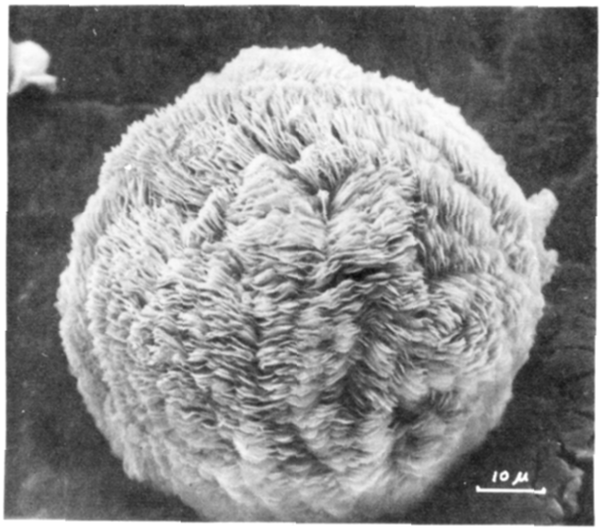

Figure 2. Scanning electron micrograph of TPI with $M_v = 1.4 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 3 h, treated in suspension with OsO_4, and coated with Au/Pd.

structure observed at 3 h of crystallization is given in Figure 2. This consists of a large number of curved lamellar ribbons, with considerable interlamellar penetration and branching being evident; the ribbon appears in groups of approximately parallel layers. A number of the lamellar ribbons viewed edge-on contain one or more bends. The principal structural type (>90%) found at longer crystallization times first appears at 5 h. Micrographs taken after 24 h are given in Figures 3 and 4. These are made up of 10 or more overgrown lamellar layers. The layers have some curvature along the sides and have flat or slightly rounded ends. Each layer is dished, with the center depth varying from one lamellar stack to another and from one face to another in a single stack. There also is considerable branching, twisting, and interlamellar penetration evident; a structure having considerable interlamellar penetration is shown in Figure 5. The sheavelike appearance can be observed under the optical microscope with unreacted material in amyl acetate suspension, but little detail is evident.[5] If scanning electron microscopy is carried out on unreacted, dried, and metal-coated samples, only poorly resolved structures are seen. When the lamellar stacks are subjected to ultrasonic vibration for 3 min, breakage occurs across the center portion of all the layers, resulting in two approximately equal-sized pieces, as is evident in Figure 6. In addition, the formation of a mosaic of cracks on the exposed layers also occurs. Crystallization from 0.1% amyl acetate solution at 20 °C yields structures similar to those obtained from 1% solution.

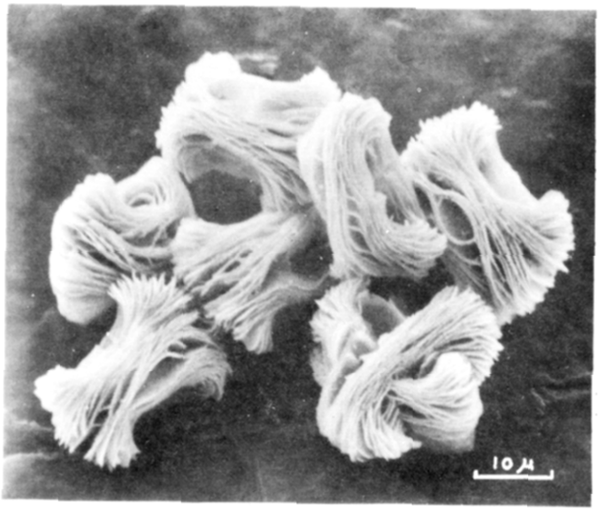

Figure 3. Scanning electron micrograph of TPI with $M_v = 1.4 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 24 h, treated in suspension with OsO_4, and coated with Au/Pd.

Figure 4. Same as Figure 3, but a different field.

Figure 5. Same as Figure 3, but a different field.

Crystallization from amyl acetate at 20 °C for 3 h of a TPI fraction with $M_v = 2.6 \times 10^5$ yielded some large lamellar bodies. After 24 h of crystallization, a mixture of

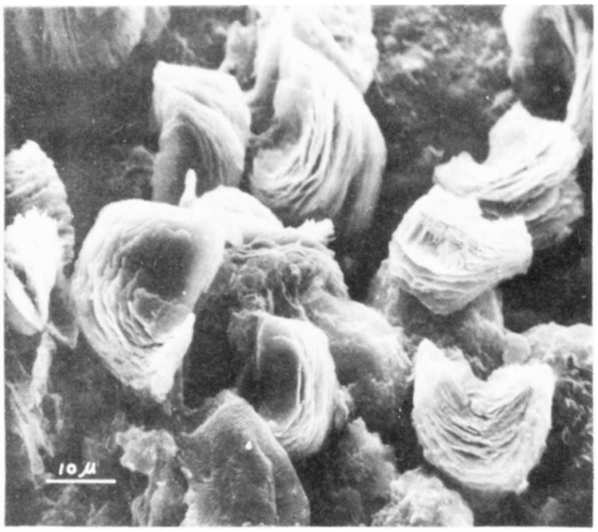

Figure 6. Scanning electron micrograph of TPI with $M_v = 1.4 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 24 h, ultrasonically vibrated for 3 min, treated in suspension with OsO_4, and coated with Au/Pd.

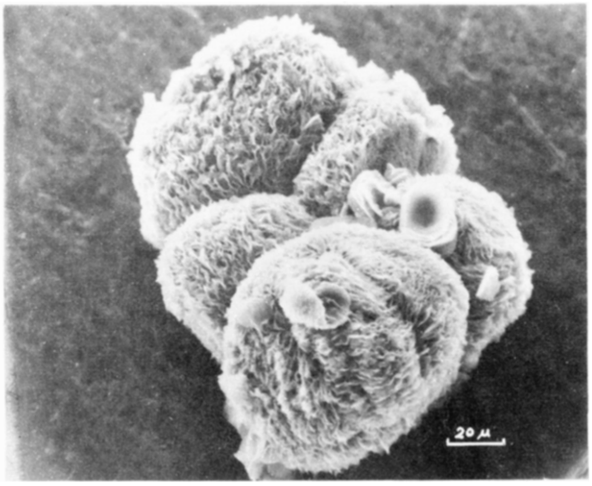

Figure 7. Scanning electron micrograph of TPI with $M_v = 2.6 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 24 h, treated in suspension with OsO_4, and coated with Au/Pd.

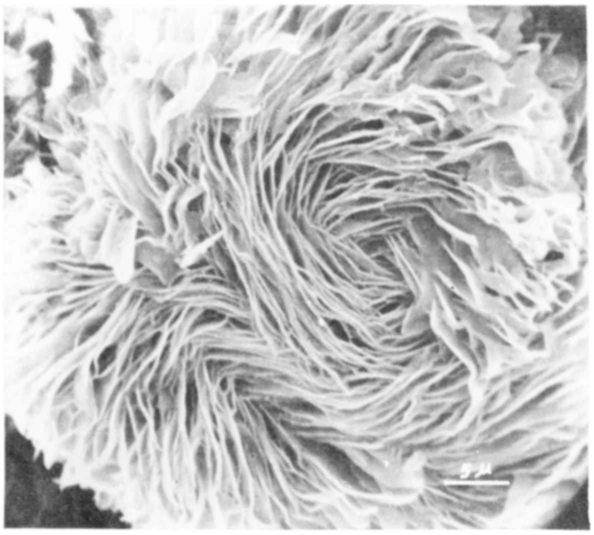

Figure 8. Scanning electron micrograph of TPI with $M_v = 2.6 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 2 days, treated in suspension with OsO_4, and coated with Au/Pd.

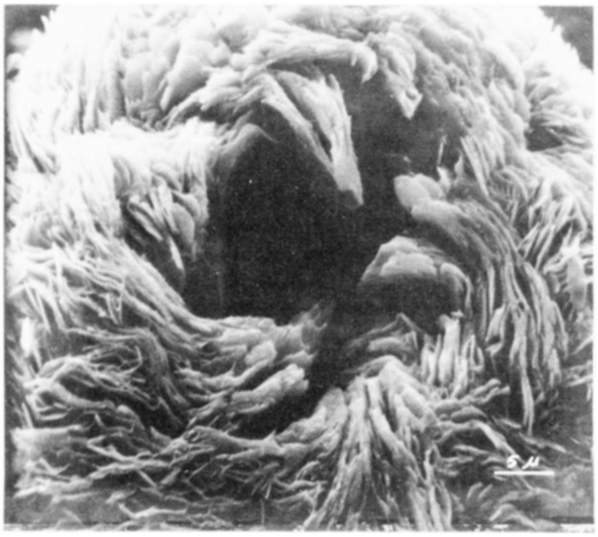

Figure 9. Scanning electron micrograph of TPI with $M_v = 2.6 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 24 h, ultrasonically vibrated for 3 min, treated in suspension with OsO_4, and coated with Au/Pd.

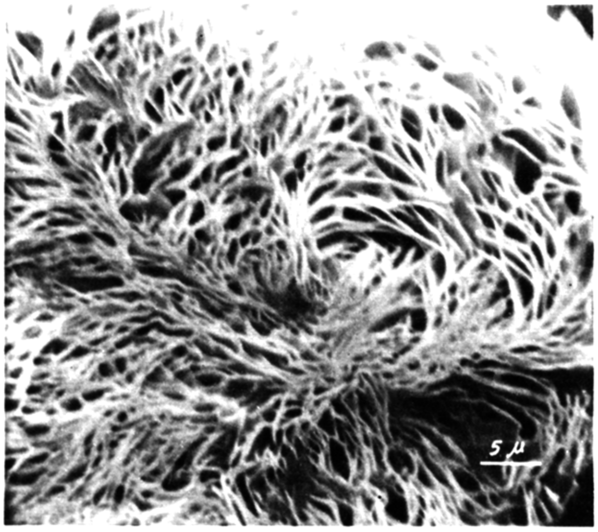

Figure 10. Scanning electron micrograph of TPI with $M_v = 2.6 \times 10^5$ crystallized from 0.1% amyl acetate solution at 20 °C for 2 days, treated in suspension with OsO_4, and coated with Au/Pd.

>60% stacks and <40% of the larger rounded objects containing creases or fissures are found; a group of the latter type and a few of the former are seen in Figure 7. Scanning electron micrographs taken after 2 days of crystallization show the organization of the lamellas making up the larger structures (Figure 8). The lamellas appear curved, twisted, irregular, and interpenetrating. When subjected to ultrasonic vibration, the rounded structures appear to fracture within the center, as shown in Figure 9. Crystallization from 0.1% amyl acetate solution at 20 °C leads to large rounded bodies, usually with one flattened area as well as lamellar stacks. A scanning electron micrograph taken of this flattened part is given in Figure 10; a network of lamellas with branching and interpenetration is clearly evident, although the separate layers are more widely spaced than for the structures grown from 1% solution.

A TPI fraction with $M_v = 5.9 \times 10^5$ crystallized from 1% amyl acetate at 20 °C for 3 h yielded spherulitic structures that apparently contain a small stack of lamellas at the center, as shown in Figure 11. These structures are more numerous, are more spherical in shape, are smaller, and at or near the surface have more curvature and twist, leading to a looser packing than in the rounded objects

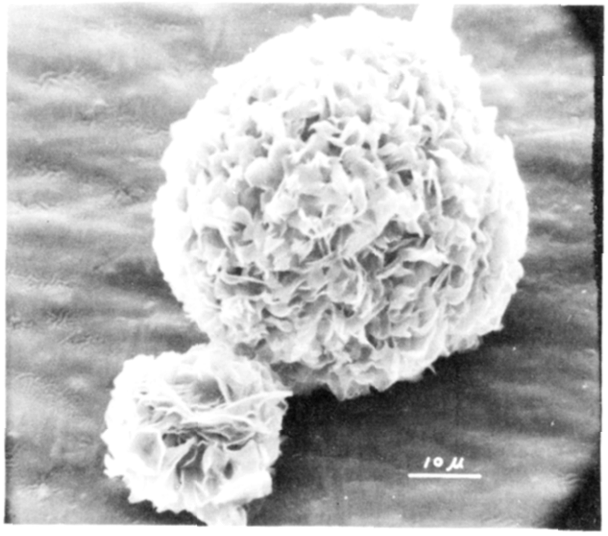

Figure 11. Scanning electron micrograph of TPI with $M_v = 5.9 \times 10^5$ crystallized from 1% amyl acetate solution at 20 °C for 3 h, treated in suspension with OsO_4, and coated with Au/Pd.

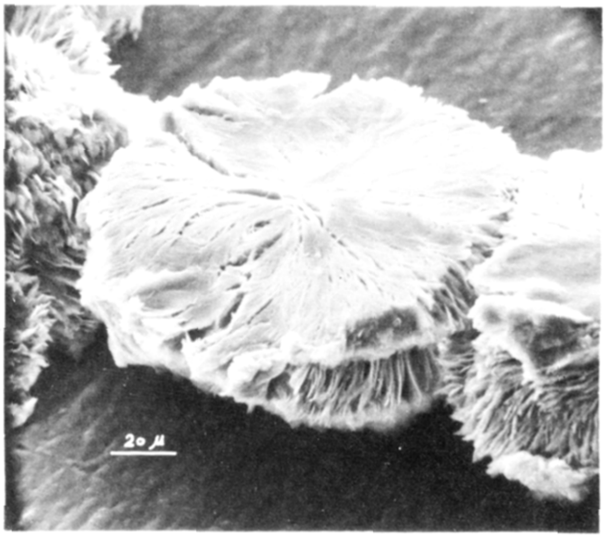

Figure 12. Scanning electron micrograph of unfractionated TPI crystallized from 1% amyl acetate at 30 °C for 4 days, treated in suspension with OsO_4, and coated with Au/Pd.

found at lower molecular weight. After 24-h crystallization curved overgrown lamellas (30–40%) are also evident. The spherulites are evident in optical micrographs taken both before and after OsO_4 treatment without drying. When subjected to ultrasonic vibration, the spherulites show little change.

When a crystallization temperature of 10 °C is used, single (overgrown) curved lamellas and lamellar stacks with a small number of layers (<10) and few, if any, interconnections or branchings are the morphologies found after 24 h for all three of the fractions used. At a crystallization temperature of 0 °C (24 h) single curved lamellas, similar to those obtained at 10 °C, are found.

Direct crystallization of unfractionated TPI was carried out at 30 °C for 4 days. Crystallization appeared to occur mainly but not exclusively at the glass surfaces and gave a number of structures with a cylindrical morphology, as shown in Figure 12. Crystallization by the precooling method of the $M_v = 2.6 \times 10^5$ fraction (T_d = 90–95 °C $\rightarrow$ T_p = 0 °C $\rightarrow$ T_r = 31.7 °C $\rightarrow$ T_c = 30 °C) gave complex lamellar stacks. One such object is seen in Figure 13; a higher magnification micrograph of part of it is given in Figure 14.

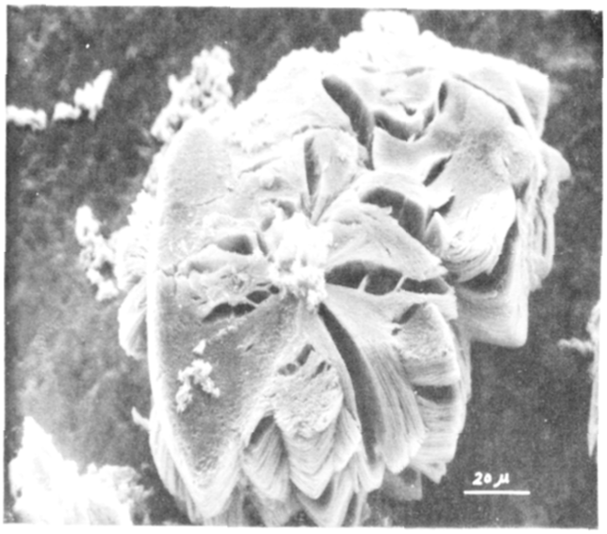

Figure 13. Scanning electron micrograph of TPI with $M_v = 2.6 \times 10^5$ crystallized from 1% amyl acetate at 30 °C for 4 days, treated in suspension with OsO_4, and coated with Au/Pd.

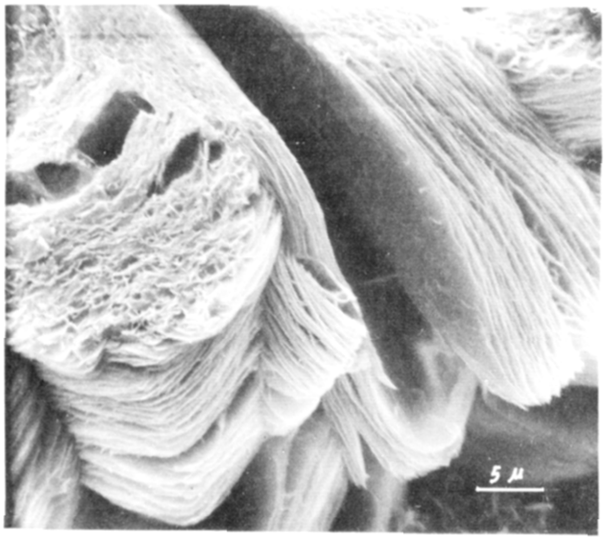

Figure 14. Same as Figure 13, but a higher magnification.

Discussion

In the present study, it is found that at a moderate crystallization temperature (20 °C) the morphology of *trans*-1,4-polyisoprene directly crystallized from 1% amyl acetate solution changes with molecular weight (M_v) in the $(1.4\text{–}5.9) \times 10^5$ range and with crystallization time. The change with molecular weight is from stacks of overgrown lamellas that are curved and interpenetrating to spherically shaped structures containing twisted and curved lamellar ribbons. The large structures observed at short times for the two fractions with the lower molecular weights apparently start as lamellar stacks and become large due to the presence of relatively few nuclei. These could possibly grow from nuclei previously formed and not destroyed by the thermal treatment; however, if this were the case similar structures would be expected at lower crystallization temperatures and these are not found. Another possibility is that preferential nucleation of the high molecular weight portion of all three fractions occurs at early time at 20 °C, leading to the large structures. From earlier studies[5,6] it is known that the dominant crystal form present at 20 °C is α. At temperatures where the β-form predominates, 10 and 0 °C, curved single lamellas and simple stacks of lamellas are found in the present work. An optical microscopy investigation of the morphology of *trans*-1,4-

polyisoprene from gutta percha using three fractions with molecular weights (M_w) of 3.6×10^4, 1.6×10^5, and 3.3×10^5 and direct crystallization temperatures of −15, 0, +5, +10, +15, +20–21, and +32 °C was carried out earlier in these laboratories.[5] The lamellar interpenetration and the high degree of curvature clearly in evidence by scanning electron microscopy of TPI sheaves obtained at 20 °C and treated in suspension with OsO_4 were not apparent in the earlier work due possibly to the lower contrast and magnification as well as to possible motion of the structures in the suspension liquid. Definite morphological differences in the two works do appear for crystallizations at 10 and 0 °C since in the previous study lamellar stacks, spherulites, and aggregates of curved lamellas were evident for TPI with $M_w = 1.6 \times 10^5$ and 3.3×10^5. These differences could be due to small differences in thermal history or the polymer structure, since the trans content differs by about 1%.[5] Previously, spherulites of α-TPI, similar in overall shape to those appearing at 20 °C in the current work, were obtained from dibutyl ether at 0 °C ($M_w = 3.3 \times 10^5$).

The layers of the structures crystallized at 20 °C are thicker than a single lamella and therefore are overgrown, presumably by screw dislocation growth, as is also found by using transmission electron microscopy for single TPI lamellas grown by the seeding technique at the same temperature.[4] Interpenetration and branching have been observed in melt-crystallized samples of polyethylene[7,8] and are believed to occur at screw dislocations.[9] In the present work, interpenetrations not only occur at or near the center of the solution-grown TPI lamellar stacks, accounting for the large curvature of the layers on one side, but also take place more or less randomly along the length of them. The interpenetration and branching act in opposition to one another. Interpenetration keeps adjacent layers together and roughly parallel. Branching causes the stack to thicken at the growing ends and leads to curvature there. When growth is prevented in one direction, such as would occur for structures growing against the container wall, interpenetration could take place more readily. This apparently occurs, particularly at lower concentrations (0.1%). The tendency for the lamellar stacks and the larger rounded objects associated with them to fracture sideways across the center portion when subjected to ultrasonic vibration suggests that this region is under stress, is highly defective, or both. The high curvature of the inner lamellas observable in these structures would be expected to lead to high stresses at the center.

The spherulitic structures found for TPI with $M_v = 5.9 \times 10^5$ at a crystallization temperature of 20 °C appear to be less tightly packed due to branching and twisting and are made up of ribbons smaller in width than for the structures found for lower molecular weight material. The resistance of these spherulitic structures to ultrasonic vibration suggests that due to the differences in construction the center portion is less defective than that of the lamellar stacks.

For the samples crystallized from amyl acetate at 30 °C in this work two types of structures appear; larger, flatter ones apparently grow at the glass surfaces while smaller, more highly curved ones crystallize from solution.

The lamellas that make up the various structures discussed above contain a sizable noncrystalline component present as chain folds, interlamellar traverses, noncrystallizing chain ends, and defects within the lamella itself. The curvature in dished (cup-shaped) TPI lamellas has been discussed previously[5] in terms of fold domain buckling.[10] The noncrystalline component at the lamellar surfaces can be investigated for TPI by chemical addition reactions such as epoxidation and hydrochlorination carried out in suspension. Some preliminary investigations of this type on overgrown single lamellas[4,5,11] and on sheaves[5] using epoxidation have been reported. More complete studies employing carbon-13 NMR to quantitatively characterize in solution the block copolymers that result[11] from reactions with TPI structures, including those prepared in this study, are in progress; the results of those investigations will be reported in later papers.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Support was also provided by the PSC–CUNY Research Award Program of the City University of New York. We are grateful to H. D. Keith for a valuable discussion.

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