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Physical and Dynamic Mechanical Properties of Ultradrawn Polypropylene Films

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ABSTRACT: Dynamic mechanical measurements were made on gel films of high molecular weight polypropylene prepared by gelation/crystallization from 1% (w/v) decalin solutions. The measurements were performed at different frequencies in the temperature range from −160 °C to the melting point of the sample. The dry gel films were uniaxially drawn at 150 °C to various draw ratios (λ) between 6.5 and 48. The morphology and orientation of the samples were characterized by density, differential scanning calorimetry, infrared dichroism, wide-angle X-ray diffraction, small-angle light scattering, scanning electron microscopy, and dynamic storage modulus. WAXS studies showed that very high degrees of orientation were achieved at the higher draw ratios. SEM of highly drawn specimens revealed that the initially random texture of crystallites transforms into fibrous form with the fiber axis parallel to the draw direction. DSC and density measurements show that the melting point and crystallinity increase with λ, reaching a maximum at $\lambda = 30$. The complex elastic modulus (E^*) increased with increasing λ and leveled off beyond $\lambda = 40$. In the dynamic mechanical measurements the γ peak was either weak or absent in both the loss tangent (tan δ) and loss modulus curves. At a given frequency, the β-relaxation intensity decreased and shifted to lower temperatures with increasing λ. Activation energies (ΔH) of the β dispersion process were obtained from an Arrhenius-type plot of log frequency versus the reciprocal temperature of the β-dispersion maximum. The values of ΔH ranged from 59 to 119 kcal/mol. In the crystalline α-relaxation region a sharp rise in tan δ was observed and the α-peak position shifts to higher temperature with increasing λ. The activation energy for this process is about 53 kcal/mol. On the basis of the dynamic mechanical measurements the origins of the various relaxation processes are discussed.

Introduction

The mechanical relaxation processes of polypropylene have been relatively less studied in comparison with numerous studies of polyethylene.[1] Isochronal dynamic mechanical properties of polypropylene over a wide temperature range were first investigated by Flocke.[2] These measurements were conducted with a torsion pendulum instrument operating at approximately 1 Hz. Three relaxation peaks, identified as α, β, and γ in descending order of temperature, were observed. The intermediate β peak around 0 °C was found to be very intense and was identified with the glass transition temperature. Passaglia and Martin attributed this peak to the atactic fraction of the polymer.[3] From dynamic X-ray and dynamic birefringence studies on melt-crystallized polypropylene, Kawai et al. concluded that the β-mechanical relaxation is an interlamellar grain boundary phenomenon.[4,5] The lowest temperature γ-relaxation in the vicinity of −100 °C is weak or absent and has been attributed to the local motions in the amorphous fraction of the polymer.[6,7] McCrum attributed the highest temperature α-relaxation to the crystalline morphology of polypropylene.[8] On the basis of dynamic X-ray diffraction studies of melt-crystallized spherulitic material, Kawai et al.[5] have recently suggested that the α process in polypropylene is of intralamellar origin, involving lamellar tilting in the polar zone of the spherulites.

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Most investigators, although differing in their detailed interpretation, have concluded that the α-relaxation arises from the crystalline regions of the polymer. On the other hand several conflicting interpretations have been given concerning the origin and molecular nature of the β- and γ-mechanical relaxations.

The complex nature of the mechanical relaxations in semicrystalline polymers is inherent mainly in the structural heterogeneity of the specimens. For example, when a spherulitic semicrystalline polymer is deformed, unlike amorphous polymers, the microscopical strain will differ locally for a given macroscopic strain of the specimen. The deformation mechanism of the lamellae at the equatorial zone of a given spherulite may be different from that at the polar zone.[5] Therefore, it seems desirable to use specimens of less structural complexity to further elucidate these relaxation mechanisms. In this regard, gelation-crystallized samples of ultrahigh molecular weight polypropylene are ideal model systems. Dry gel films of this polymer, obtained through gelation/crystallization show remarkable drawability,[9-11] and the highly drawn samples show fibrous extended chain structures that are highly anisotropic with minimum structural heterogeneity. The amorphous fraction at high draw ratios is not detectable and may be simply considered as defects in the crystalline regions. Dynamic mechanical measurements on anisotropic polypropylene samples are very limited.[12-14] A probable reason is that melt-crystallized polypropylene may rarely be drawn to high draw ratios. Furthermore, the mechanical or morphological anisotropies of these samples are not remarkable compared to the drawn gelation-crystallized specimens (e.g., compare draw ratios of 6.5[12] and 4.47[13] with over 47 for the present investigation).

In the present paper, we report on the morphology and dynamic mechanical properties of highly drawn polypropylene specimens. The mechanical relaxation processes will be compared with those obtained for melt-crystallized samples and discussed in relation to existing models of relaxations in semicrystalline polymers.

Experimental Section

The isotactic polypropylene (PP) used was Profax 786223 resin from Hercules Inc. The nominal intrinsic viscosity was 16.8 dL/g which corresponds to a molecular weight of approximately 3×10^6 according to the viscosity-molecular weight relation of Kinsinger and Hughes.[15] The solvent was decalin (Fischer Scientific Company); it was used without further purification. Irganox-1076 (Ciba-Geigy Company) was added as antioxidant (0.5% w/w on polymer).

Dry gel films were produced by a method similar to that of Cannon.[9] The mixture of polymer, solvent, and antioxidant (containing 1% w/v of polymer) was degassed for 1 h under vacuum. The solution was prepared by refluxing under nitrogen with vigorous stirring at close to the solvent boiling temperature (185–190 °C) for 40–45 min. The hot solution was transferred to an open beaker thermostated at 90 °C. The clear solution was manually stirred with a stainless steel spatula until the onset of gelation, as detected by a sudden increase in solution viscosity. At this point stirring was stopped, the heater was turned off, and the solution was allowed to slowly cool to room temperature. Within a few hours the solution turned turbid and the gel thickened and shrank while expelling some solvent by syneresis. Most of the expelled solvent was pipetted out. Finally the gel was pressed between filter papers on a laboratory press at 300 psi for half an hour. At this stage a clear film of ca. 0.5–1 mm thickness was obtained. The remaining solvent was allowed to evaporate in an air current at room temperature for several weeks. Rectangular strips with dimensions of about 3 × 0.5 cm were cut from the film and drawn at a cross-head speed of 2.0 cm/min at 150 °C on an Instron tensile testing machine (Model 1123) fitted with a hot air oven. The draw ratios (λ), determined from the separation of the midpoints of ink marks initially placed at 2-mm intervals on the samples, ranged up to 47.5.

In passing it may be noted that the as-received sample contained atactic and stereoblock material. The removal of these impurities prior to gelation/crystallization results in films that are very brittle and unsuitable for drawing. Thus the impurities presumably exert a plasticizing effect and facilitate the drawing process.

Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) patterns were recorded with a flat film camera, using Ni-filtered Cu Kα radiation produced by a Philips X-ray generator operating at 40 kV and 25 mA.

Freshly fractured and laterally fibrillated surfaces, lightly sputtered with gold, were examined in an International Scientific Instruments scanning electron microscope (Model ISC-SX30) operating at 15 kV.

Infrared dichroic ratios were measured on a Fourier transform infrared spectrometer (Nicolet-6000). A gold wire grid polarizer (Perkin-Elmer) was used to measure the absorption in the direction parallel to the fiber axis ($A_\parallel$) and perpendicular to the fiber axis ($A_\perp$). From the measured absorptions the dichroic ratio was obtained as $D = A_\parallel/A_\perp$.[16] The orientation function of the crystalline and amorphous regions was obtained from the Hermans orientation function which is related to the dichroic ratio by the equation[16]

$$f = \frac{(D - 1)(D_0 + 2)}{(D + 2)(D_0 - 1)}$$

where D_0, the dichroic ratio of an ideally oriented sample, is given by $D_0 = 2 \cot^2 \Phi$ and Φ is the transition moment angle between the helix axis and the infrared transition moment. For polypropylene the 1220-cm^{-1} band is due to absorption by the crystalline phase, while the band at 2725 cm^{-1} is due to absorption by the amorphous phase.[17] The transition moment angle $\Phi = 90°$ for both the crystalline and amorphous bands.[17]

Small-angle light scattering (SALS) patterns were recorded by using a 15-mW He–Ne gas laser as a light source. Both cross (H_v) and parallel (V_v) polarized scattering patterns were recorded.

Density measurements were made by the floatation method, using carbon tetrachloride and *p*-xylene as a mixed-solvent pair. Prior to the measurements, the samples were ultrasonified in one solvent to remove tiny air bubbles adhering to the film surface.

The melting endotherms were obtained on a Perkin-Elmer DSC-2C differential scanning calorimeter at a scan speed of 10 °C/min. Nitrogen was used as a purging gas. Indium was used to calibrate the instrument. Typical sample weights ranged from 1 to 5 mg.

Dynamic mechanical measurements were performed on a Rheovibron DDV-IIc mechanical spectrometer (Toyo Baldwin Co., Japan) at 3.5, 11, and 110 Hz in the temperature range from −160 °C to the softening point of the samples. The values of tan δ, complex modulus (E^*), storage modulus (E'), and loss modulus (E'') were obtained.

Results and Discussion

Characterization of Morphology and Orientation.

As shown previously by Cannon[9] the WAXD patterns, with the X-ray beam either parallel or perpendicular to the film surface, show isotropic diffraction rings for the undrawn PP films, indicating random orientation of the crystallites. The SAXS patterns shown an isotropic ring corresponding to a long spacing of about 100 Å, while the SALS pattern shows only a broad halo. The absence of four-leaf clover patterns in SALS indicates that these gel films do not have a spherulitic morphology. These observations suggest that the undrawn gelation-crystallized sample is composed of randomly arranged folded-chain lamellae. A SEM micrograph of a freshly fractured surface of such a film is shown in Figure 1a. No distinct lamellar texture is discernible, and it is clearly evident that it does not show any spherulitic morphology. A SEM micrograph of a fibrillated film of a drawn sample (λ = 47.5) is shown in Figure 1b. It reveals that the originally random textures have been transformed into a highly oriented fiber structure. The

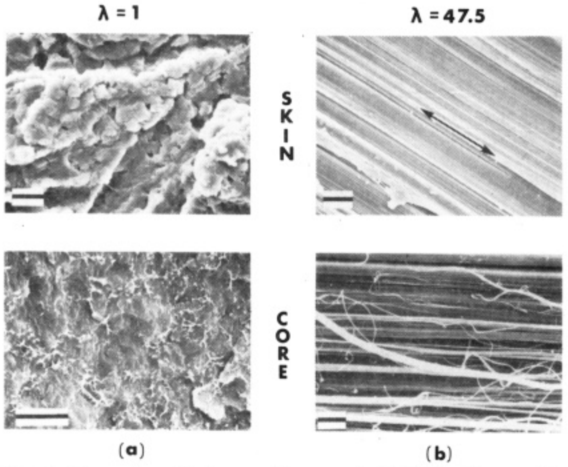
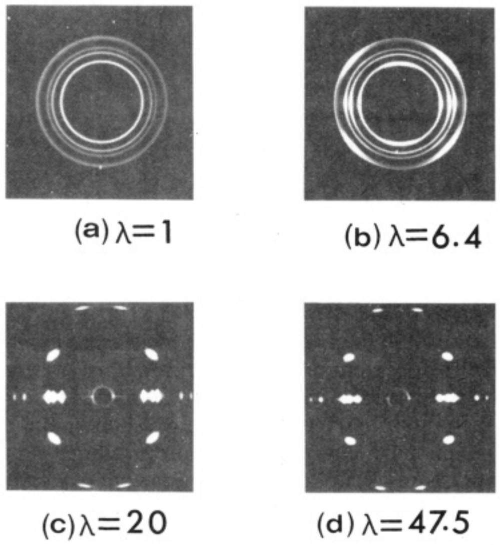


Figure 1. Scanning electron micrographs (SEM) of an undrawn (λ = 1) and a highly drawn (λ = 47.5) PP film. (Bar line represents 10 μm.)


(a) λ=1 (b) λ=6.4

(c) λ=20 (d) λ=47.5

Figure 2. Wide-angle X-ray diffraction (WAXD) patterns of PP gel films at various draw ratios (λ).

fibers are oriented in the draw direction (indicated with an arrow in the figure). In Figure 2, the WAXD patterns, with the X-ray beam perpendicular to the film surface, are shown for films of various λ's. The initially isotropic Debye rings for the undrawn sample (λ = 1) transform into arcs with increasing draw ratio, and furthermore, for highly drawn samples the arcs transform into points in a fiber pattern where the crystal *c* axis orientation along the draw direction is almost complete.

In the DSC experiments a single sharp melting endotherm was obtained for all samples. The peak melting point shifted to higher temperatures with increasing λ (Figure 3) reaching a maximum at λ ~ 30. The heat of fusion also increased with increasing λ due to an increase in crystallinity of the drawn samples. The percent crystallinity, based on a heat of fusion of 33 cal/g for perfectly crystalline PP samples,[18] versus λ is shown in Figure 4. The crystallinities based on densities are also shown in this figure for comparison. The change in crystallinity with λ is very similar in both cases. Initially, at low draw ratios the crystallinity increases rapidly in an almost linear fashion and it reaches a maximum value of about 96% at λ = 30 and then decreases slightly at higher values of λ.

The room temperature dynamic storage modulus (E') at various values of λ is shown in Figure 5. First, it is noted that the values are remarkably high compared to those obtained from melt-crystallized PP where the values range from 1.0 to 1.5 GPa.[13,14] Therefore, it is evident that gelation/crystallization followed by hot drawing produces PP films of remarkable stiffness. Second, the increase in E' with increasing λ follows a similar pattern to that shown in Figures 3 and 4 for the melting point and percent crystallinity, respectively, i.e., E' increases linearly initially and then levels off at higher draw ratios. Similar behavior was reported by Kanamoto et al. for moduli of coextruded polyethylene at different λ.[19]

The amorphous and crystalline orientation functions (f_a and f_c, respectively) were obtained by using the dichroic ratios corresponding to the amorphous and crystalline bands at 2725 and 1220 cm^{-1}. The results as a function of draw ratio are shown in Figure 6. It is observed that f_c increases rapidly at low λ and eventually reaches a lim-

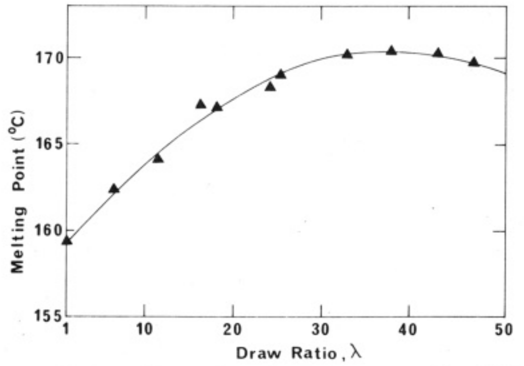


Figure 3. Peak melting point of gelation-crystallized PP films as a function of draw ratio (λ).

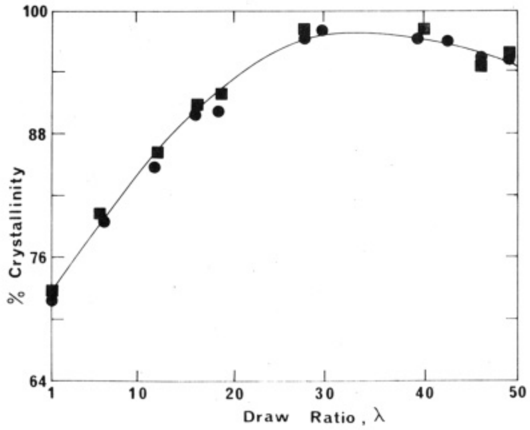


Figure 4. Percent crystallinity as calculated from DSC and density measurements of PP gel films as a function of draw ratio (λ): DSC, circles; density, squares.

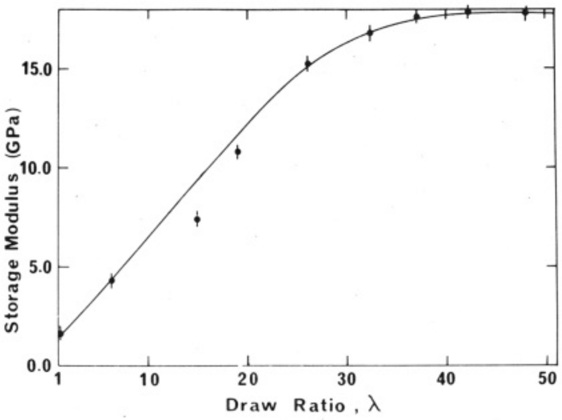


Figure 5. Dynamic storage modulus (E') at 110 Hz for PP films as a function of draw ratio (λ).

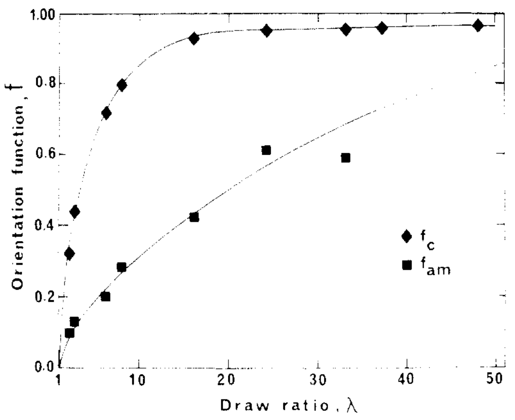


Figure 6. Infrared crystalline and amorphous orientation functions, f_c and f_a, for PP films at various draw ratios (f_c from the 1220-cm^{-1} band; f_a from the 2725-cm^{-1} band).

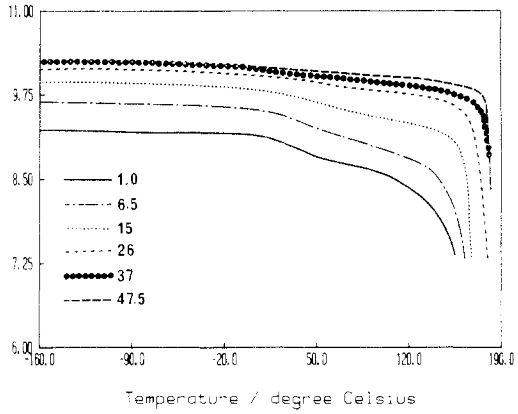


Figure 7. Dynamic storage modulus (E') at 110 Hz as a function of temperature for gelation-crystalline PP films of various draw ratios (λ).

iting value at $\lambda \simeq 20$. The amorphous orientation function (f_a) increases continuously with increasing λ, though at a much slower rate compared to the initial change in f_c. At high λ's the amorphous IR band (2725 cm^{-1}) disappears and no dichroism is detected. It is thought that for specimens of higher λ's having a high degree of crystallinity and crystal orientation the amorphous chains may not be distinguished from crystal defects. In a separate study of orientation by the method of infrared reflection spectroscopy (IRS) using samples prepared in the present study, Mirabella has also shown that the total crystalline orientation function reaches a limiting maximum value ($f_c \approx 1.0$) at around $\lambda = 26$.[20] Mirabella's measurements corroborate our results of WAXD, DSC, density, IR, and modulus measurements.

From the discussion so far it is seen that the change in any property of the PP films with increasing draw ratio levels off for λ values greater than 26–30. Thus it may be said that for the present samples and experimental conditions the optimum properties are already realized for samples with $\lambda \approx 30$, which is much lower than the maximum attainable draw ratio ($\lambda_{max} \sim 48$). This phenomenon can probably be explained by assuming that draw ratios greater than $\lambda \approx 30$ are obtained at the expense of chain slippage and rupture of taut tie molecules.[21]

Dynamic Mechanical Properties. In Figure 7, the storage modulus, E', at 110 Hz is plotted against temperature for samples of different λ. For the undrawn sample ($\lambda = 1$) the loss in E' over the temperature range from −160 to 130 °C is less than half a decade. For comparison, it may be noted that a melt-crystallized sample would have lost about two decades in E' over the same temperature range.[13] As λ increases, the loss in E' becomes even less significant. The sudden drop in E' between 120 and 190 °C corresponds to the premelting and α-transition regions. As expected, the onset of the drop in E' shifts to higher temperatures with increasing λ as a result of the increase in crystallinity. The process of gelation/crystallization therefore allows the highly drawn PP films to retain their stiffness over a wider temperature range.

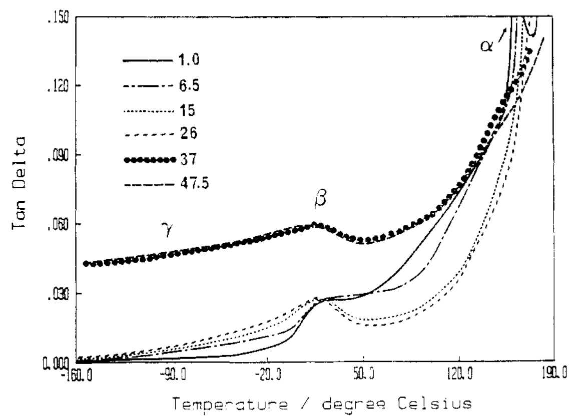


Figure 8. Loss tangent (tan δ) at 110 Hz as a function of temperature for gelation-crystallized PP films of various draw ratios (λ). (For clarity the curves for $\lambda = 37$ and 47.5 have been shifted upward by tan $\delta = 0.04$.)

Table I
Temperature of the β-Relaxation Maximum at 110 Hz for PP Samples at Various Draw Ratios (λ)

λ	temp, °C	λ	temp, °C
1.0	26.6	26	12.5
6.4	19.0	37	9.20
15	15.0	48	8.93

Figure 8 shows the loss tangent (tan δ) measured at 110 Hz as a function of temperature for samples at various draw ratios. For clarity the curves for $\lambda = 37$ and 47.5 have been shifted upward by 0.04 units on the tan δ scale. Three main relaxation regions, labeled α, β, and γ, are identified in the figure. It is seen that the γ-relaxation is not discernible. It is, however, evident in the loss modulus (E'') versus temperature curves, especially for the highly drawn specimens (Figure 11). As indicated earlier, the literature shows that this phenomenon is always very small in polypropylene; thus the behavior of the present samples is not unusual.

Continuing with the discussion of Figure 8, the β-relaxation peak is clearly discernible. The peak intensity decreases and the peak position shifts to lower temperature with increasing λ. Since the latter effect is not readily visible in the figure, it is documented in Table I. As shown earlier, drawing enhances the orientation of both crystalline and amorphous regions along the draw direction. The gel film is transformed into highly oriented extended-chain fibers. In addition, the tie molecules become taut[21] and thus the amorphous regions essentially transform into "pseudocrystalline" form and can probably only experience cooperative relaxations with the crystalline core. Thus, it is not surprising that the peak intensity diminishes at very high draw ratios. The shift of the β peak to lower temperature with increasing λ is probably associated with the relaxation of the residual strains of the oriented chains in the amorphous phase.[22]

The classical view of the β-relaxation process in polypropylene is that it has its origin in the glass transition temperature. However, it has recently been suggested that this process in fact originates in the interlamellar zones.[5] In this connection it is noteworthy that gelation-crystal-

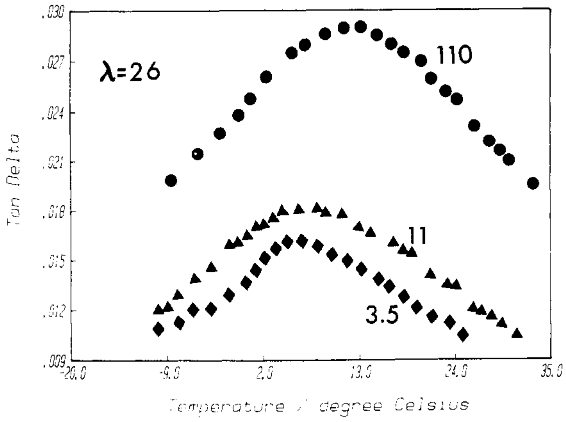


Figure 9. Loss tangent (tan δ) in the β-relaxation region as a function of temperature at various frequencies for PP films of λ = 26. (Frequencies are denoted on the respective curves.)

Table II
Activation Energies (ΔH) for the β-Relaxation Process of PP Samples at Various Draw Ratios (λ)

λ	ΔH, kcal/mol	λ	ΔH, kcal/mol
1.0	97	26	91
6.4	81	37	59
15	119	48	71

lized specimens from which the atactic fraction had been previously removed by solvent extraction did not show a β peak. This corroborates an earlier finding by Passaglia and Martin[3] and supports the view that the β-relaxation process in polypropylene is attributable to the glass transition.

The activation energies (ΔH) for the β process of all samples have been calculated from the Arrhenius plots of log ν versus reciprocal absolute temperature, corresponding to the relaxation maximum at a given frequency, ν. An example of the shift in the relaxation maximum with frequency is shown in Figure 9 for λ = 26. The Arrhenius plots are shown in Figure 10. The corresponding activation energies are listed in Table II where examination of the ΔH values reveals that they range from 59 to 119 kcal/mol, but no clear pattern of ΔH variation with draw ratio can be found. The average of the ΔH values for this process is 87 kcal/mol, which is not inconsistent with the values reported for melt-crystallized samples which range from 38 to 76 kcal/mol.[5,14,23]

Finally, the crystalline α-relaxation in PP is discussed. For all specimens, in the temperature region corresponding to this relaxation process, tan δ rises very sharply, indicating that the mechanism involves a single process. This is also clearly seen in the loss modulus (E'') curves in Figure 11 where only a single peak is observed. Kawai et al. have recently suggested, based on dynamic X-ray studies of crystal orientation dispersions in spherulitic PP, that the α process is an intralamellar phenomenon which involves lamellar reorientations such as tilting.[5] The average activation energy (ΔH) estimated by these authors for this relaxation process is 47.4 kcal/mol. In the present work, the activation energy of the α process for all PP specimens ranges from 48 to 70 kcal/mol; the average value being about 53 kcal/mol. This is comparable to the value reported by Kawai et al.[5] This suggests that the α process has the same origin in both melt-crystallized samples and those used in the present investigation. The mechanism of lamellar reorientation through detwisting and/or tilting, as proposed by Kawai et al., can explain the α relaxation in the undrawn PP films (λ = 1) composed of randomly oriented lamellae and the films of low draw ratios in which partial lamellar-type texture remains. On the other hand, for the highly drawn specimens the initial lamellar morphology is transformed into fibrous extended-chain crystals oriented along the draw direction (which is also the direction of the dynamic strain). Therefore, for these specimens crystal reorientation relaxation cannot take place. Hence it is suggested that for these highly oriented specimens, the α process involves only intracrystalline chain motions.

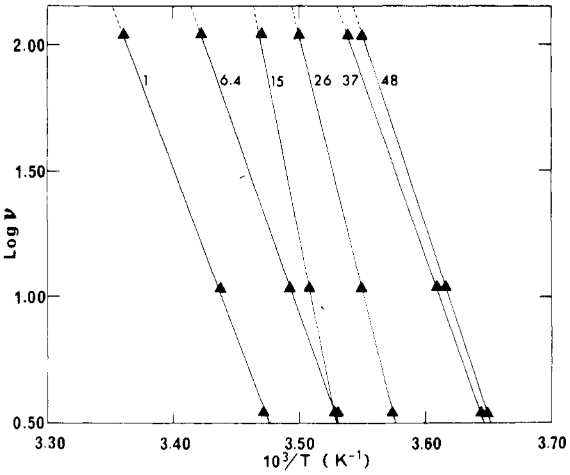


Figure 10. Plots of log frequency versus reciprocal absolute temperature for the β-relaxation in PP films of various draw ratios. (The draw ratios are identified on the figure.)

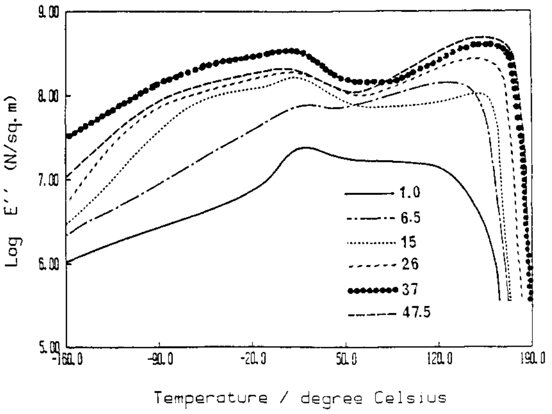


Figure 11. Loss modulus (E'') at 110 Hz as a function of temperature for PP films of various draw ratios (λ).

Further examination of the α relaxation from Figure 11 reveals that the peak maximum shifts to higher temperatures with increasing λ. This suggests that the intracrystalline relaxation dispersions (e.g., intralamellar reorientation at low λ and chain motions at high λ) must occur with increasing difficulty as λ increases.

Concluding Remarks

The principal findings and conclusions are as follows: (1) As has been shown previously,[9-11] ultrahigh molecular weight PP films produced by gelation/crystallization from dilute solution exhibit remarkably high drawability as compared to melt-crystallized material. The drawing process causes an initial rapid increase in crystallinity and orientation and these properties reach a plateau at $\lambda \approx 30$. The morphological examination by SEM and WAXD revealed that the highly drawn samples have a fibrous texture with the chain axis almost perfectly oriented in the draw direction.

(2) Highly drawn films have remarkable stiffness which is retained over a much wider temperature range compared to melt-crystallized specimens. The characteristic of

stiffness retention improves with increasing λ.

(3) The dynamic mechanical relaxation spectra of these films revealed that the low-temperature γ peak is very weak or absent.

(4) The β-relaxation peak diminishes in intensity and the peak position shifts to lower temperature with increasing draw ratio. Drawing increases the crystallinity of the specimens and thus causes a reduction of the interlamellar content which leads to a decreased peak intensity. It is proposed that the shift to lower temperature is associated with the relaxation of the stretching-induced residual strains of molecules located in the intercrystalline regions. The activation energy for the β-relaxation process for these solution-crystallized specimens is comparable to that of conventional melt-crystallized samples. This is due to physical constraints, such as increased orientation and tautness of tie molecules, imposed on the sample due to drawing.

(5) The α relaxation involves a single mechanism as evident from a sharp rise in tan δ with temperature and the presence of a single peak in the loss modulus (E'') curves. The average activation energy (53 kcal/mol) for this process is comparable to the values obtained for melt-crystallized PP. It is suggested that, although for undrawn and lightly drawn PP films lamellar reorientation may take place, for the highly drawn PP films the α process involves intracrystalline chain motions only.

Registry No. Polypropylene, 9003-07-0.

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Motional Behavior and Correlation Times of Nitroxide Spin Probes in Polymers above and below the Glass Transition

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ABSTRACT: The reorientational motions of nitroxide spin probes have been investigated in several polymers above and below the glass transition temperature, T_g. Three amine-cured epoxy resins having different cross-link densities and the thermoplastics bisphenol A polycarbonate and poly(dimethylphenylene oxide) were studied. At sub-T_g temperatures from 100 to 300 K the reorientational correlation times were the same for two small spherical probes and one large cylindrical probe in all the epoxy systems. Below T_g the activation energies for the nitroxide correlation times were typically ~11 kJ/mol, whereas above T_g the corresponding value was 24 kJ/mol after a correction for temperature-dependent changes in free volume. This result is explained in terms of differences in amplitudes of the motions (i.e., whether the motions involve restricted or unrestricted rotational diffusion) and differences in the coupling of the probe motions to the matrix motions below and above T_g.

Introduction

It is well-known that the mechanical, thermal, and transport properties of polymers change markedly in the region of the glass transition temperature, T_g. Such properties include the elastic moduli, the hardness, and the thermal expansion coefficients, as well as the translational diffusion coefficients for small molecules. These changes in polymer properties are related to the nature of the molecular motions above and below T_g.[1,2] For example, above T_g, where the motions of a polymer segment are rapid and correlated with the motions of surrounding segments, the polymer responds mechanically as a viscous liquid or a viscoelastic solid. On the other hand, below T_g, where the segmental motions are more localized and less cooperative,[1,3] the polymer exhibits the properties of a rigid glassy solid. At still lower temperatures, below the sub-T_g β transition, where even these noncooperative motions cease to be active at any significant rate, polymers tend to be even more brittle.

To understand this relationship between the macroscopic properties and the polymeric motions in more detail, we are exploring the dependence of molecular motion on temperature and fractional free-volume content[1,4] in polymers. In this paper we describe the results of some electron paramagnetic resonance (EPR) experiments which involve the measurement of another molecular parameter both below and above T_g, namely, the motional correlation time, τ_c, for the reorientational motions of small para-

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