pressure, the critical entanglement molecular weight is about 30,000.[19] In Figure 3 the measured α_0 values were for the range M_w = 7500–74000. However, for M_w = 267,000 (log M_w = 5.43), which corresponds to an average of about eight entanglements per molecule, $10^3\alpha_0$ = 4.4 bar^{-1} at 165°, completely out of line with the trend of α_0 values in Figure 3. If this single datum is correct, it has important implications regarding the dynamics of chain entanglement–disentanglement in viscous flow. Presumably, also, processes involving only short segments of the polymer chains (*i.e.*, volume or dielectric relaxation) should not be complicated by entanglements, and α_0 for such processes should show a monotonic change with molecular weight, as does T_g, for example.[7]

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Dynamic Mechanical Properties of Transcrystalline Regions in Two Polyamides

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ABSTRACT: The influence of a surface transcrystalline region on the viscoelastic properties of nylon 6 and nylon 6-6 films was investigated. For thin films, an upper limit of *E* appears to exist when the thickness of the transcrystalline region equals the thickness of the entire film. The modulus of the transcrystalline region is higher than that of the bulk phase.

This work is a continuation of the study investigating the correlation between morphology and the physical characteristics of crystalline polymers. The earlier paper by Kwei, *et al.*,[1] reported on two polyolefins—high density polyethylene and isotactic polypropylene. The results established that oriented lamellae existed near the surfaces, and the viscoelastic properties of these polymer films are influenced by the relative amount of oriented surface region to the bulk phase.

The oriented surface structure which can be produced in crystalline polymers has been observed by many previous investigators.[2–6] It has also been noted that this phenomenon is highly dependent upon thermal history.[1–6] The application of proper cooling techniques during crystallization from the melt can induce the development of lamellae from nuclei to propagate normal to the polymer film surface. The result is an overall columnar surface alignment of spherulite sectors or transcrystalline region that has been observed in polyamides,[2,3] polyurethanes,[2] and polyolefins.[1,4–6] The purpose of this study is to describe an evaluation of the mechanical properties of the oriented surface regions of two polyamides—nylon 6 and nylon 6-6.

Experimental Section

Materials. Unmodified nylon 6 and nylon 6-6 were used. The nylon 6, Du Pont Zytel Type 211, was used from a newly opened air-tight container. The nylon 6-6, Du Pont Zytel Type 101, was oven dried for 4 days at 60° before compression molding.

Film Preparation. Polymer films were prepared by compression molding between two sheets of copper which had been oxidized in an oven for 7 min at 350°. The weak cohesive properties of the resulting copper oxide facilitated the removal of the polymer film from the copper substrate. Any residual copper oxide which adhered to the surface of the film was easily removed by a dilute solution of hydrochloric acid. This method of film preparation was useful for avoiding possible film distortion during the peeling process.

A second method for preparing compression-molded polymer films was also used. It was found that molding between two sheets of 0.003-in. thick, hard aluminum also gave easy release characteristics. Inspection showed that peeling of the aluminum substrate from the polymer film had little or no damaging effect on the morphology pattern of the film. Because of the relative ease with which compression molded films could be prepared, this method was ultimately used throughout the remainder of the program.

Thermal History. Nylon 6 was compression molded by keeping it in the melt state at 250° for 2 min. The film-substrate assembly was removed, while hot, from the press and cooled in air to room temperature. Nylon 6-6 was treated in the same manner except the melt temperature was at 300° prior to crystallization. All film specimens were tested immediately after preconditioning for a minimum of 16 hr at 23° and 50% relative humidity.

Dynamic Modulus. The dynamic Young's modulus *E* was measured by the use of the Vibron dynamic viscoelastometer, Model DDV-II, of Toyo Measuring Instrument Co. The description of the instrument was given by Takayanagi.[7] In the present study, all the experiments were carried out at 23° and a frequency of 110 Hz.

Results

Figure 1 is a photomicrograph of a transverse microtome section cut from a 7-mil thick nylon 6 film. The thickness of each oriented surface is estimated to be 1.2 mils. The combined surface thickness constitutes roughly 33% of the total film thickness. Films used in this study were prepared with the transcrystalline zone thickness relatively constant regardless of the film thickness.

The dynamic Young's modulus (*E*) of both polyamides was found to decrease with increasing thickness (*t*), as shown in Figure 2. A projected extension of the curves in Figure 2

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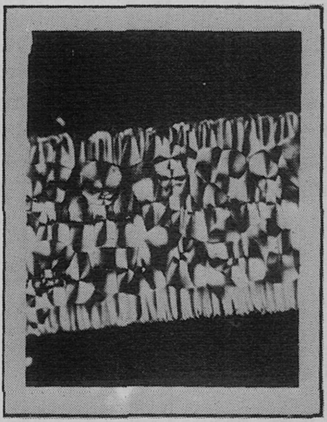

Figure 1. Cross-polarized photomicrograph showing the transcrystalline surface regions bordering the bulk polymer phase in polyamide film. The specimen used was a transverse microtome section cut from a 7-mil thick film. Magnification is 312×.

indicates that both the nylon materials would reach an asymptotic lower limiting value at about 23 mils thickness. By extrapolation then, the lower E values expected would be 1.1×10^{10} dyn/cm^2 for nylon 6 and 1.35×10^{10} dyn/cm^2 for nylon 6-6.

It is also apparent that decreases in the film thickness are complemented by increases in the E value. The rate of increase becomes progressively greater as the film thickness (t) is reduced. At a film thickness of 3 mils or less for nylon 6 and 2.5 mils or less for nylon 6-6, the magnitude of E remains relatively constant. The limiting value of E is 2.60×10^{10} dyn/cm^2 for nylon 6 and 2.92×10^{10} dyn/cm^2 for nylon 6-6. Upon reaching these upper E value limits, it is considered that the transcrystalline region may constitute the entire polymer film thickness.

Discussion

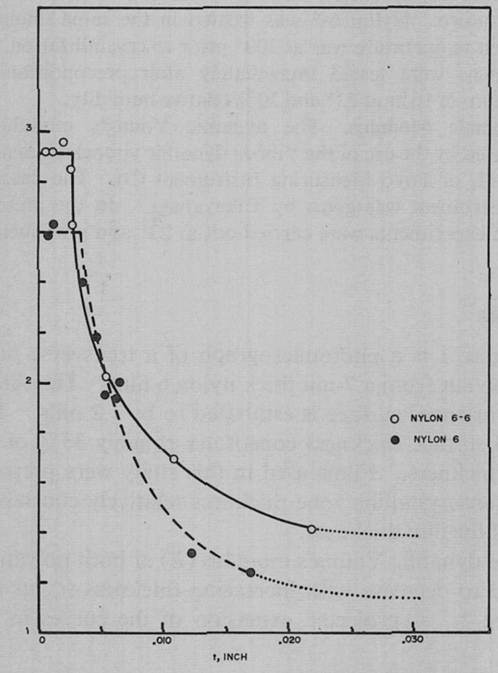

Figure 2. Graphic presentation showing the dependence of modulus E on the thickness of polyamide films.

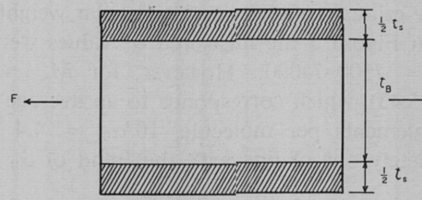

Figure 3. A "parallel" combination of the surface and the bulk regions.

Kwei, *et al.*, proposed a model to explain the contribution of oriented surface regions to the dynamic properties of crystalline polymer films (Figure 3). The model depicts a polymer film of thickness t with two oriented surface regions of modulus E_s, each having a thickness of $^1/_2t_s$. The remaining bulk phase has a modulus E_B and thickness t_B which is equal to $(t - t_s)$. According to the model, the contribution of the surface regions to the properties of the polymer would become proportionately less as t increased, and the modulus E of the sample would approach a limiting value equal to that of the bulk phase E_B. When t is very small, the film consists entirely of the oriented surface structure and the modulus of the polymer film is equal to E_s. At intermediate values of t, the contribution of the intrinsic properties of both phases is governed by the ratio t_s/t_B or $t_s/(t - t_s)$ and therefore varies with t. The mechanical response of a parallel combination of the surface and bulk phases of a film with respect to the direction of oscillatory stress was reduced to the simplified equation

$$E = E_B + t_s(E_s - E_B)t^{-1} \qquad (1)$$

According to eq 1, a plot of E *vs.* t^{-1} should result in a straight line with a slope of $t_s(E_s - E_B)$ and an intercept E_B on the ordinate. This is shown in Figure 4.

From the intercepts, the lower limits of E obtained are 1.12×10^{10} dyn/cm^2 for nylon 6 and 1.33×10^{10} dyn/cm^2 for nylon 6-6. This is in very close agreement with the estimated values from Figure 2. From the slope of the linear plot $t_s(E_s - E_B)$, since E_s is equal to a limiting value at

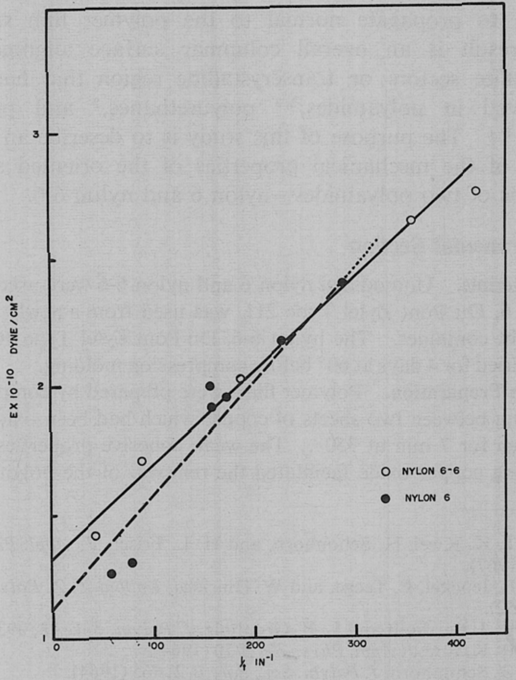

Figure 4. Plot of E according to eq 1.

small t in Figure 2, a calculated value for t_s can be obtained. For nylon 6, t_s is 3.03 mils and for nylon 6-6, t_s is 2.27 mils. This again is in good agreement with the values taken from Figure 2 and that estimated from the photomicrograph in Figure 1.

Conclusion

The dynamic Young's moduli of molded films of two polyamides, nylon 6 and nylon 6-6, decrease with increasing thickness. The modulus of the transcrystalline region in each polymer is higher than that of the bulk phase. Both polyamides appear to reach an asymptotic lower limiting value of E in films 23 mils or thicker. An upper limiting value of E is reached at 2.60×10^{10} dyn/cm^2 for 3-mil thick nylon 6 films and 2.92×10^{10} dyn/cm^2 for 2.5-mil thick nylon 6-6 films. The mechanical response of a combination of the surface and bulk regions can be described quantitatively by a "parallel" model.

Rheological Properties of Anionic Polystyrenes. III. Characterization and Rheological Properties of Four-Branch Polystyrenes

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ABSTRACT: The viscoelastic properties of four-branch polystyrene were measured in the molten state by means of a concentric cylinder-type rheometer over wide ranges of frequency and temperature. The star polymer samples were prepared by coupling narrow-distribution polystyryl anion with $SiCl_4$ and were characterized in terms of molecular weight, molecular weight distribution, and coupling ratio. From the frequency dependence of the storage shear modulus G' and the loss modulus G'', the characteristic parameters in the terminal and rubbery zones were evaluated, and their dependences on molecular weight were compared with those for narrow-distribution linear polystyrene. The zero-shear viscosity η_0 and the elasticity coefficient A_G for the star polymer are generally lower than those for the linear polymer having the same molecular weight. The steady-state compliance J_e^0, on the other hand, is about one decade higher. The entanglement compliance J_{eN}^0 of the star polymer is somewhat higher than that of the linear polymer at lower molecular weights, but approaches the latter at higher molecular weights. The average molecular weight between entanglement loci M_e varies similarly with molecular weight. The effects of molecular weight distribution and branching on the G' *vs.* frequency curve and relaxation spectrum are compared for three typical samples having almost the same molecular weights.

In our previous papers, the viscoelastic properties in the rubbery and flow or terminal zones of anionic polystyrene[1,2] and poly(methyl methacrylate)[3–5] were measured over wide ranges of frequency and temperature, and the results were compared with the predictions of the current molecular theories for viscoelasticity. These studies provided much new information on the effects of molecular weight and its distribution on the rheological properties of amorphous polymers.

The effect of branching on the viscoelastic properties is another important but unsolved problem in polymer science, and is difficult to separate from that of molecular weight distribution. Although many papers on the effect of branching have hitherto been published, in most of these papers either the type, number, or length of the branches has not been well characterized,[6–10] or only viscous properties have been measured for well-characterized samples.[11,12] In order to clarify the effect of branching, branched polymers that are well characterized with respect to type, number, and length of branches as well as molecular weight distribution should be employed as samples. Furthermore, it is highly important to measure not only the viscous but also the elastic properties of these samples over wide ranges of time scale and temperature, because such materials are typical viscoelastic materials and their behavior thus depends strongly upon time scale and temperature. The only study which satisfies such conditions is that by Fujimoto, *et al.*[13] These investigators employed comb-shaped polystyrenes having very narrow distributions of molecular weight, which showed viscoelastic properties quite different from those of the corresponding linear polymers. As is well known, however, there are other types of branched polymers than the comb shaped, such as star shaped and randomly branched polymers.

The present paper deals with the viscoelastic properties of four-branch star polystyrenes of differing molecular weights, comparing the results with those for the corresponding linear polystyrenes of narrow distribution, as reported in the previous papers.[1,2]

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