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Ultrahigh Modulus Liquid Crystalline Polyesters. p-Hydroxybenzoic Acid Copolyesters

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ABSTRACT: Filaments of two samples of poly(ethylene terephthalate-*co*-*p*-oxybenzoate) containing 30 ($T_2/30$) and 60 ($T_2/60$) mol % *p*-oxybenzoate were obtained by melt spinning at temperatures between 225 and 285 °C. As-spun filaments with varying degrees of orientation were obtained by altering the take-up velocity at constant outflow velocity. The as-spun filaments were further subjected to mechanical and thermal treatments. Determination of mechanical properties, wide-angle X-ray scattering, differential scanning calorimetry, and electrohydrodynamic instabilities was carried out. $T_2/30$, which exhibited extensive poly(ethylene terephthalate) crystallinity and melted into an amorphous phase, yielded a maximum elastic modulus on the order of 3 GPa. $T_2/60$ exhibited crystallinity due to short sequences of *p*-hydroxybenzoic acid residues which persisted up to about 240 °C. Electrohydrodynamic instabilities were observed for $T_2/60$ only above 265 °C, at which temperature clear-cut evidence of a fluid nematic mesophase was exhibited. The elastic modulus of $T_2/60$ spun at 225 and 245 °C, when some small degree of crystallinity likely persisted, reached ca. 32 GPa. Considerably lower moduli were observed by spinning $T_2/60$ above 260 °C. It is suggested that orientation and ultrahigh modulus in the present system are obtained by virtue of a superimposition of a small degree of crystallinity to the mesophase.

Introduction

Rigid-chain molecules such as poly(*p*-benzamide) (PBA) have been shown to yield fibers endowed with superior mechanical properties when spun from anisotropic solutions.[1-5] The directors of liquid crystalline domains tend to align along the flow direction, giving rise to a high degree of orientation of macromolecules along the fiber axis and hence to high modulus and strength.

High orientation and superior mechanical properties may also be obtained by solid-state[6,7] or solution processing[8,9] of flexible polymers such as polyethylene (PE) which do not form mesophases. In this case, opening or preventing chain folds is a major mechanism involved. Behavior intermediate between rigid and flexible molecules is exhibited by semirigid polymers such as the polyterephthalamide of *p*-aminobenzhydrazide (X-500), which may form mesophases only in a flowing solution.[10,11] The rheological and processing characteristics of the above systems (PBA, PE, and X-500) have been the subject of considerable investigation.

Still a different situation is exhibited by thermotropic polyesters having a semirigid conformation and forming nematic mesophases at rest and in the absence of a solvent. Some of these systems may develop superior mechanical properties,[12,13] often following a postpolymerization in the solid state.[14] A considerable number of thermotropic systems has been reported,[12-18] and interest in this class of polymers is due to their simple processing and relatively high melting temperatures. Although a few reports on their rheological behavior have appeared,[19,20] less reported has been the study of conditions leading to high modulus. A recent study[18] describes the development of structure and orientation during melt spinning of a cholesteric cellulose derivative. In analogy to the case of lyotropic systems discussed above, it is generally believed that the partial order of the mesophase is responsible for the superior mechanical properties that result from melt processing. This paper deals in detail with the spinning of a well-known nematic copolyester[12,13] formed by transesterification of poly(ethylene terephthalate) (PET) with *p*-acetoxybenzoic acid (HBA). Our emphasis is on the elastic modulus and the conditions under which it can be maximized. The general considerations of structure and orientation are only preliminarily explored. It will be shown that although the mesophase will generally play an important role, high modulus is obtained also by virtue of mechanisms that were believed to be relevant only for flexible, nonmesogenic polymers.

Experimental Section

Materials. Two samples of poly(ethylene terephthalate-co-*p*-oxybenzoate) containing 30 and 60 mol % *p*-oxybenzoate were

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kindly supplied by the Tennessee Eastman Co. and used as such. These copolymers are referred to as $T_2/30$ and $T_2/60$, respectively. The inherent viscosity was 0.5 dL/g for $T_2/30$ and 0.66 dL/g for $T_2/60$. These polymers are believed to be similar to those described in papers by Tennessee Eastman investigators[12,13] and are the same samples used for the characterization of electrohydrodynamic instabilities by Krigbaum et al.[21]

Fiber Preparation. Spinning was performed with a small-scale melt-spinning unit designed and constructed in the School of Textiles, University of Bradford (Dr. E. Dyson). The piston-type extruder operated at constant velocity, with a die having a 2-mm diameter.

The extrusion rate V_0, was ~10 cm/min and the output flow rate, Q, was ~0.30 cm^3/min. About 3-4 g of polymer was used for each extrusion. The extrusion temperature was 245 and 275 °C for $T_2/30$ and varied betwen 225 and 285 °C for $T_2/60$. The filament was extruded in air at room temperature and collected on a 6-cm-diameter bobbin placed at a distance of ~1.5 m from the extruder die. The take-up velocity, V_f, was varied between 10 and 300 m/min. Correspondingly, the V_f/V_0 ratio (cross-sectional area attenuation) varied between 100 and 3000.

Fibers as obtained above (as-spun fibers) were subjected to additional annealing or drawing treatments. Annealing was performed in a vacuum oven at 170°C for 17 h for $T_2/60$ and at 100 °C for 0.5 h for $T_2/30$. It was not necessary to clamp $T_2/60$ fibers during annealing since, rather remarkably, no shrinkage was exhibited. Drawing was performed at 40 °C for $T_2/30$ using the Instron machine, with an initial elongation rate of 0.33 min^{-1}. Maximum draw ratio (draw length L divided by as-spun length L_0) obtainable was ~1.5. No drawing could be performed for $T_2/60$, which was too brittle and invariably broke. Samples were stored at room temperature and ambient humidity.

Mechanical Properties. Young's modulus, E, strength, σ_b, and elongation to break, ϵ_b, were determined from stress-strain data obtained with an Instron machine Model 1115 at an elongation rate of 0.33 min^{-1}. Measurements were performed at room temperature on single filaments, about 3 cm long, and averaging over at least five individual determinations (maximum variation on E was ~10%). Cross-sectional area was determined with a microscope and was constant along each filament. Tensile tester compliance problems[6] were not considered because we have not observed extremely large ultrahigh moduli (the relative assessment of spinning conditions on mechanical data was of greater interest than high accuracy on absolute values). Storage modulus, E', loss modulus, E'', and tan δ were determined with a Rheovibron DDVII C. The frequency was 11 Hz and the heating rate 1.5 °C/min.

X-ray Diffraction. Wide-angle X-ray patterns were obtained for fibers or virgin samples at room temperature using an Astbury flat camera with Cu Kα radiation (40 kV, 30 mA) filtered through a Ni film. Film-to-sample distance as 4 cm, and exposure time was about 1.5 h.

Differential Scanning Calorimetry. DSC scans were obtained with a Perkin-Elmer DSC-2 apparatus using a heating rate of 20 °C/min and about 10 mg of polymer. The polymer was either a virgin sample or an as-spun fiber. Various annealing temperatures and times were employed. Annealing was performed under vacuum.

Microscopy. Samples were observed under a Reichert Zetopan polarizing microscope equipped with a hot stage. Electrohydrodynamic instabilities were observed by applying a dc field of 6.4 and 8 V, following the technique described by Krigbaum et al.[21]

Viscosity. Inherent viscosities were measured with a suspended level Ubbelhode viscometer having flow time for the solvent (a 60/40 (v/v) mixture of phenol and tetrachloroethane) greater than 100 s. Measurements were performed at 25 °C with 0.5 g/100 mL polymer.

Results

The variation of the as-spun modulus with the V_f/V_0 ratio for $T_2/60$ is illustrated in Figure 1. Data were obtained for different extrusion temperatures. The modulus increases with V_f/V_0 ratio but decreases with increasing extrusion temperature. The highest modulus obtained, ~32 GPa, is well within the ultrahigh modulus range[3] (it corresponds to about 250 g/denier). These data can be compared with those reported in Figure 2 for as-spun and for drawn $T_2/30$. Even for drawn fibers, the modulus of $T_2/30$ is much smaller than for $T_2/60$. It is to be noted that $T_2/30$ could not be spun at 225 °C due to solidification. Spinning at higher temperatures caused only a small reduction of the modulus of $T_2/30$. The effect of annealing on the modulus of $T_2/60$ and $T_2/30$ is illustrated in Figure 3. The modulus is increased by annealing, but $T_2/60$

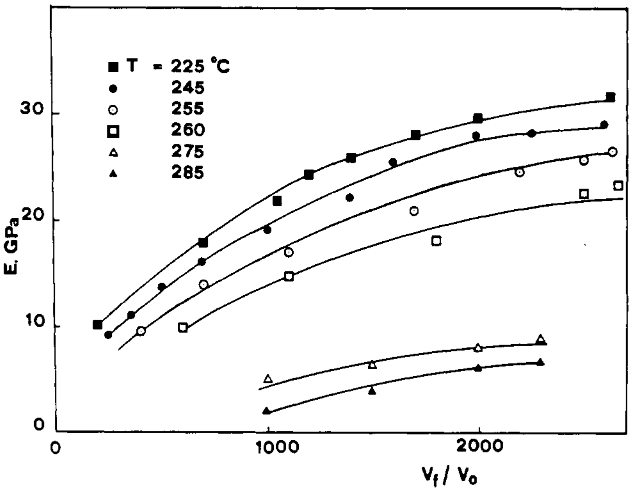

Figure 1. Elastic modulus for as-spun $T_2/60$ vs. the V_f/V_0 ratio. Extrusion temperatures are indicated.

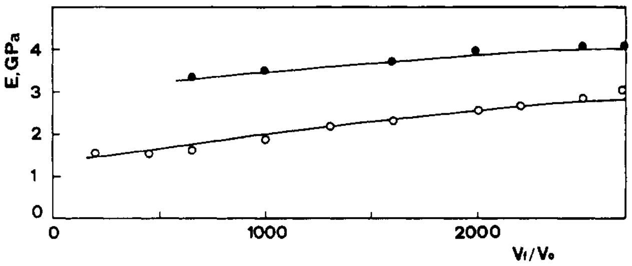

Figure 2. Elastic modulus for as-spun (○) and for drawn (●) $T_2/30$ fibers vs. the V_f/V_0 ratio. Extrusion temperature is 245 °C. Draw ratio is ~1.5.

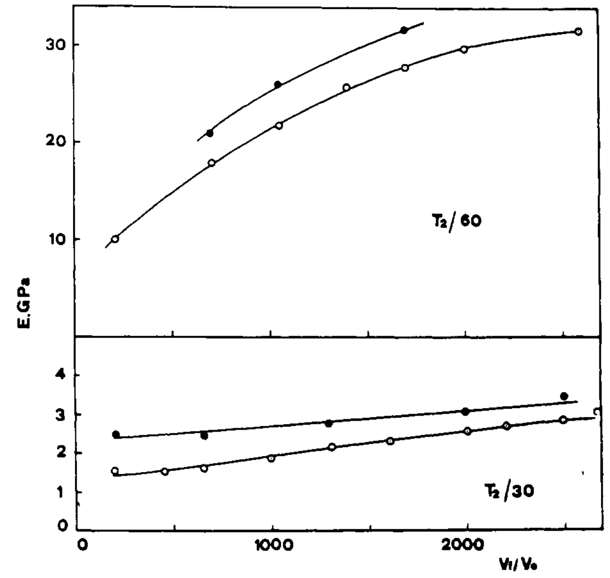

Figure 3. Elastic modulus for as-spun (○) and for annealed (●) fibers of $T_2/60$ and $T_2/30$ vs. the V_f/V_0 ratio. Extrusion temperature is 245 °C for $T_2/30$ and 225 °C for $T_2/60$. Annealing temperature and annealing time were 170 °C and 17 h for $T_2/60$ and 100 °C an 0.5 h for $T_2/30$.

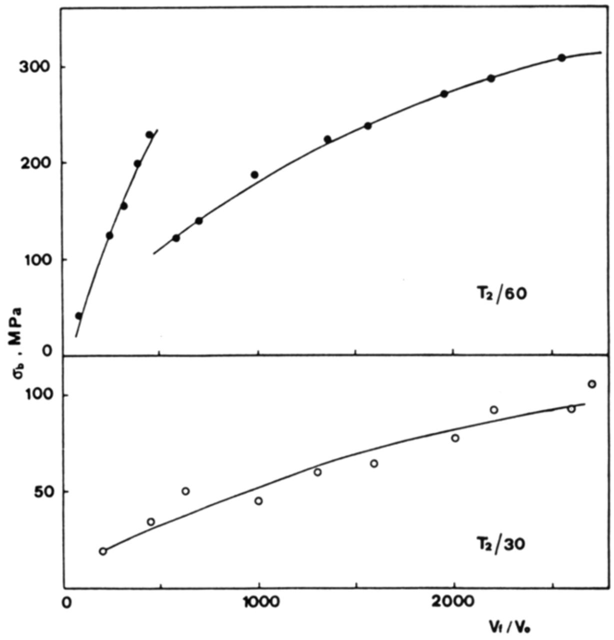

Figure 4. Variation of strength for as-spun $T_2/60$ and $T_2/30$ with the V_f/V_0 ratio. Extrusion temperature is 245 °C.

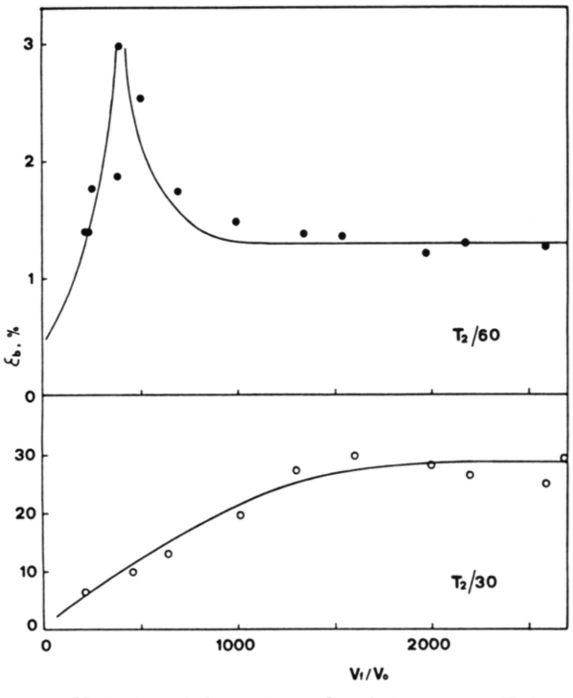

Figure 5. Variation of elongation to break for as-spun $T_2/60$ and $T_2/30$ with the V_f/V_0 ratio. Extrusion temperature is 245 °C.

always exhibits better properties than $T_2/30$.

Strength and elongation to break for as-spun $T_2/60$ and $T_2/30$ are compared in Figures 4 and 5. The strength of $T_2/60$, although considerably larger than for $T_2/30$, is not in the ultrahigh strength range. The relatively low molecular weight is probably responsible for the low strength. The elongation to break of $T_2/60$ is sharply below that of $T_2/30$. We note, for $T_2/60$, a discontinuity on the ϵ_b vs. V_f/V_0 dependence (noticeable also in the σ_b vs. V_f/V_0 plot), which is typical of amorphous, oriented polymers.[22] Tennessee Eastman investigators[12,13] have reported tensile and flexural properties for the same polymers. The values of modulus and strength they report for $T_2/60$ are smaller than our tensile data. They showed that flexural properties improve when the specimen thickness decreases. Thus it appears that working with thin fibers allows an improvement of orientation and mechanical properties.

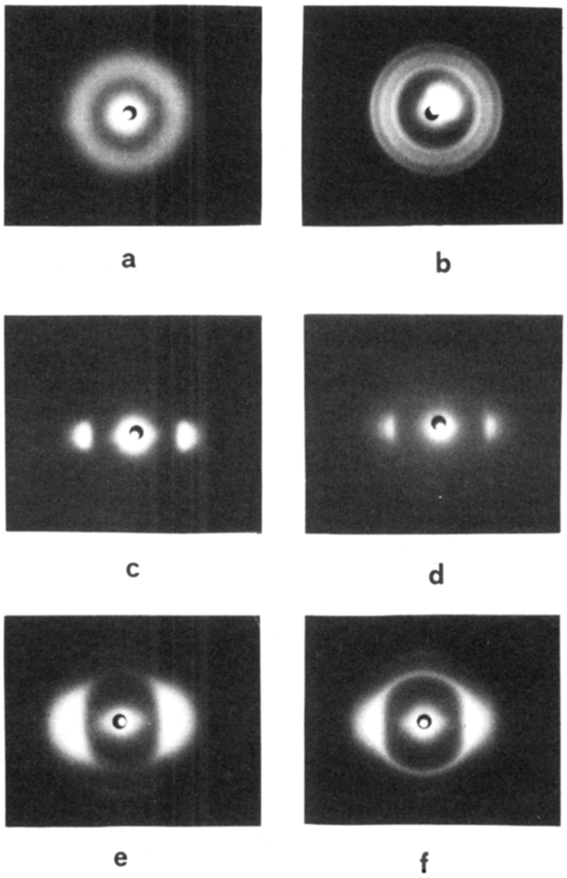

Figure 6. Wide-angle X-ray patterns for $T_2/60$ and $T_2/30$: (a) $T_2/30$ as-spun at 245 °C, $V_f/V_0 = 400$; (b) $T_2/30$ spun at 245 °C and annealed for 0.5 h at 100 °C, $V_f/V_0 = 400$; (c) $T_2/60$ as-spun at 245 °C, $V_f/V_0 = 2500$; (d) $T_2/60$ spun at 275 °C and annealed for 70 h at 240 °C, $V_f/V_0 = 2500$; (e) $T_2/60$ virgin; (f) $T_2/60$ cycled between 245, 285, 200, and 245 °C (see Discussion).

Figure 6 illustrates various X-ray patterns for the two copolymers. $T_2/30$, particularly when annealed, revealed extensive crystallization and poor orientation. The strongest reflections, observed at 5.0, 3.91, and 3.43 Å, correspond closely to those we observed for a pure PET sample (5.10, 3.83, and 3.43 Å). The latter was extensively annealed following spinning.[23] As-spun (or virgin) $T_2/60$ revealed only a faint, oriented crystallinity, which developed rather clearly upon annealing. The spacings observed are at 4.48, 4.24, and 3.73 Å, very close to those observed[20] for pure poly(p-hydroxybenzoic acid). The latter conclusion is in line with that reached by Wissbrun for a similar $T_2/60$ polymer.[20]

DSC data for $T_2/30$, Figure 7, are similar to those discussed by Lader and Krigbaum[24] and are indicative of the melting of PET sequences. DSC data for virgin (or as-spun) $T_2/60$ were featureless. Annealed $T_2/60$ exhibited, however, an endotherm at ~230–250 °C, depending upon annealing conditions. In line with a suggestion by Wissbrun,[20] we attribute this endotherm to the fusion of short sequences of HBA.

Examination of virgin $T_2/60$ under the polarizing microscope revealed a softening between ~220 and 240 °C (noticeable by applying a small pressure over the cover slip) but no evidence of a mesophase until about 265 °C. Fluidity, high birefringence, color, and motion of microdomains due to thermal instability all appeared suddenly between 265 and 270 °C. Upon further increase of temperature up to 300 °C the latter features became more

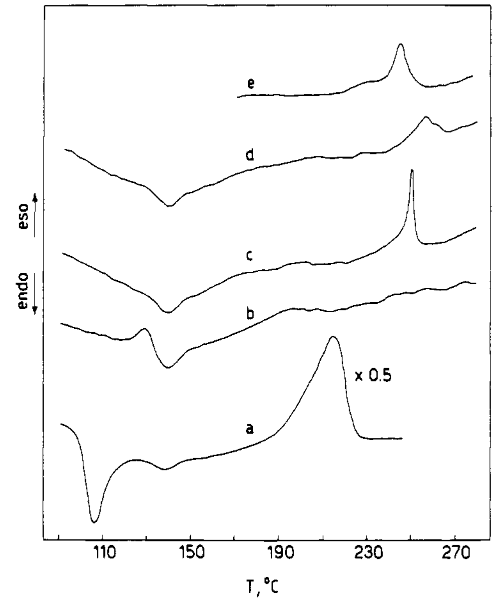

Figure 7. DSC thermograms for virgin $T_2/30$ (a), virgin $T_2/60$ (b), $T_2/60$ annealed for 5 days at 230 °C (c), $T_2/60$ annealed for 70 h at 240 °C (d), and $T_2/60$ as-spun at 245 °C and annealed for 70 h at 230 °C (e).

conspicuous, while isotropic regions appeared. Upon cooling, color and high birefringence remained evident even at 200 °C, while fluidity and motion were already inhibited. Evidently, HBA crystallinity reduces the fluidity of the system. Past the melting temperature of HBA sequences, the mesophase can fully develop. Upon cooling, the topology of the mesophase is preserved to lower temperatures until the supercooled HBA recrystallization inhibits fluidity. The electric field produced no Williams domains[21] below 265 °C, even after 24 h following the application of the field. Williams domains, similar to those described by Krigbaum et al.,[21] appeared in a few hours between 265 and 270 °C, and the formation time decreased between 270 and 280 °C. None of the above effects were evident with $T_2/30$.

Some results of dynamic mechanical measurements are illustrated in Figure 8. Due to the brittleness of $T_2/60$ only a restricted temperature range could be explored. The maximum of E'' at ~70 °C is indicative of a glass transition. In the case of as-spun $T_2/30$, the decrease of E' at T_g is followed by an increase until a maximum is reached at ~120 °C. This behavior is typical of amorphous PET[25] and is due to a rapid crystallization past T_g. In fact, annealed $T_2/30$ did not exhibit the latter maximum, and its larger E' value and broader transition are indicative of a greater degree of crystallinity (cf. also patterns a and b of Figure 6).

Finally, inherent viscosity data obtained for as-spun and annealed samples indicated that some chain degradation had occurred as a result of the mechanical or thermal treatments. For instance, the value of the inherent viscosity measured for the original $T_2/60$ sample (0.66 dL/g) decreased to 0.54 dL/g for the same polymer as-spun at 275 °C.

Discussion

At first glance the above results would indicate a behavior to be expected on the basis of published results[12,13,21,24] on the same copolymers investigated here. $T_2/30$ exhibits features typical of a conventional crystalline polymer such as PET (cf., in particular, the dynamic mechanical data). There is no evidence of a mesophase, of high orientation, and of ultrahigh modulus and strength.

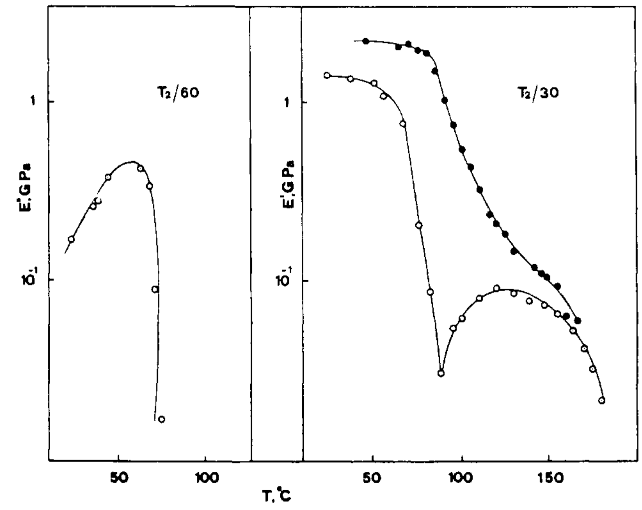

Figure 8. Left: Loss modulus vs. temperature for $T_2/60$ as-spun at 245 °C. Right: Storage modulus vs. temperature for $T_2/30$ as spun at 245 °C (○) and spun at 245 °C and annealed 0.5 h at 100 °C (●).

On the other hand, $T_2/60$ shows no PET crystallization (even upon extensive annealing) but ample evidence of a mesophase, of high orientation, and ultrahigh modulus.

A closer inspection of the results reveals, however, some unexpected features. In fact, Figure 1 shows that the highest $T_2/60$ modulus was obtained by spinning at 225 °C. The modulus decreased between 225 and 285 °C, with a sharper decrease above 260 °C. However, according to the microscopic and electric field observations on a *virgin* sample, a clear-cut mesophase only appeared at about 265 °C. Thus there is an indication that the highest modulus was achieved when $T_2/60$ as spun below the melting temperature of HBA sequences.

In order to establish the nature of the phase prevailing below 260 °C, we consider the X-ray data, which reveal that a small amount of HBA crystallinity can occur for $T_2/60$. Short sequences of HBA should be most prone to enter a mesophase (above their melting temperature) since the compound $CH_3COO\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}COOC_2H_5$ was reported to be nematogenic (T_{CN} = 142, T_{NI} = 282 °C).[26] Once these sections are involved in a crystallite, the rigidity of the remaining chain may be below that required for a stable mesophase.[27] However, the flow field will stabilize both the mesophase[11] and the crystallites. The DSC data indicate that the largest part of this crystallinity melts below 250 °C. The exact assessment of the amount of crystallinity and of its melting temperature for $T_2/60$ *during* the spinning process is, however, problematic and would require extensive and sophisticated investigation. In fact the above-quoted X-ray data were obtained at room temperature, and the DSC evidence refers to annealed samples.

The present results could be interpreted by assuming that a very small degree of HBA crystallinity was present during the extrusion at the lower temperatures, while only during the extrusion performed above 260 °C the polymer was in true fluid mesophase. The relatively lower modulus observed at the highest temperatures may thus reflect the melting of short HBA sequences as well as a partial disorientation of the mesophase. This interpretation finds support in the results of Wissbrun,[20] who noticed that thermal history effects may be rather important, as indicated by drastic effects on the melt viscosity of $T_2/60$. He found that the viscosity measured at 210 °C strongly decreased when the measurement was repeated after the sample was held for a few minutes at 240 °C. The decrease was much more pronounced when the sample was held at 300 °C, with a corresponding alteration of the shape of the flow curve measured at 210 °C, which changed from solid-like to a typical viscoelastic one. Wissbrun found no evidence of degradation, and the results were attributed to melting (around 240 °C) of HBA sequences. Thermal history effects in thermotropic polyesters have also been reported and discussed by Cogswell.[28]

According to the above interpretation, an important contribution to the ultrahigh modulus obtained by spinning at the lower temperatures would arise from small crystallites of HBA sequences. A minute amount of HBA crystallites may have existed even before the melt began to flow or may have developed as a more labile entity along the flow field. Reinforcing contacts of this type may render more efficient the orientation of chain segments that are not in a crystalline state. Similar mechanisms have been invoked by some of the present authors to explain the orientation of amorphous nylon 6, which is more efficient when salt bridges (i.e., LiBr) are present.[29] Physical entanglements between flexible PE chains have also been suggested to be responsible for the high orientation of the polymer during the gel spinning process.[9] Chain entanglement has also been suggested to be important for the development of a flow-induced mesophase for semirigid polymers.[11] It is also well-known that high modulus and orientation are obtained by solid-state extrusion at temperatures below T_m for polyethylene.[7]

However, in view of the occurrence of some chemical degradation, the above interpretation must be taken with considerable reservation. From the data of Jackson and Kuhfuss,[12] we note that a decrease of inherent viscosity from 0.62 to 0.50 dL/g caused a reduction of ~30% of the flexural modulus of $T_2/60$. Our as-spun $T_2/60$ at 275 °C exhibits a similar decrease of viscosity (from 0.66 to 0.54 dL/g). However, the modulus at 225 °C is several times larger than that observed at 275 °C. Thus degradation may not be the sole cause of the observed effects.

The modulus obtained above 260 °C for $T_2/60$, although considerably smaller than at 225 °C, is still greater than that obtained for amorphous $T_2/30$. Thus the mesophase clearly helps in achieving greater orientation. The fact that the improvement is not as great as one could have expected from the results for the lyotropic systems[1-3] may be attributed to the semirigid nature of $T_2/60$, to some disorientations of the mesophase, and probably to a too low molecular weight.

We note that Jackson and Kuhfuss[12] reported flexural modulus for injection-molded $T_2/60$ which increased from 210 to 250 °C and then decreased upon further heating to 260 and 280 °C. While the latter decrease is in line with our data, the former increase is not. A possible explanation of this discrepancy is a greater orientation of the fibers than of the injection-molded samples, which is particularly effective at the lower processing temperatures.

To seek additional support for the suggestion that crystallization of HBA sequences affects the properties of $T_2/60$ spun at 245 °C, we investigated the effect of thermal history by spinning at 245 °C a sample that had first been brought to 285 °C. The heating and cooling cycle between 245 and 285 °C was performed in the extruder and lasted about 15 min. The modulus, measured at $V_f/V_0 = 2500$, was found to be ~19 GPa, which is considerably below the value, ~29 GPa (cf. Figure 1), measured for a virgin sample spun directly at 245 °C. We were, however, unable to verify that redevelopment of HBA crystallinity caused a reincrease of the modulus. In fact, following the extrusion of the 19-GPa fiber, we lowered the temperature of the extruder to 200 °C and then returned slowly to 245 °C. This new cycle lasted about 1 h (the sample contained in the extruder was always the same sample that had been previously exposed to 285 °C and partly extruded at 245 °C). An attempt to extrude again at 245 °C revealed an extremely large increase (about 2 orders of magnitude) of extruding pressure. The inherent viscosity of the sample removed from the extruder was found to be 0.43 dL/g, considerably below the value (0.66 dL/g) of the virgin sample. The type and degree of crystallinity were not considerably affected (compare patterns e and f of Figure 6). In spite of the large extruding pressure, we were able to spin a new fiber at 245 °C, but its modulus was only ~10 GPa.

The assessment of the fundamental factors controlling mesophase formation and spinnability was particularly complicated due to crystallization and to the random copolymeric nature of the present system. In subsequent work it will be of interest to analyze the behavior of mesogenic homopolyesters such as those composed of rigid units separated by flexible spacers.[15-18]

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Mechanism for Long-Chain Branching in the Thermal Degradation of Linear High-Density Polyethylene

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ABSTRACT: A mechanism for long-chain branching in the thermal degradation of a linear high-density polyethylene (LHDPE) has been discussed on the basis of the changes in the contents of *trans*-vinylene groups and long-chain branches (LCB) in the polymer residues, especially the average number of LCB per molecule (L). From the *trans*-vinylene/LCB content ratios, the probability of the recombination termination reaction between primary and secondary macroradicals seems to be 2–5 times that of the disproportionation reaction. The above-mentioned ratio was about 0.3 at all temperatures, but the value of L increased with a decrease in temperature. The value of L at 350 °C suggests the formation of a branched polymer having one LCB per molecule. Moreover, these facts suggest the formation of branched polymers having several long branches and of cross-linked polymers at temperatures below 350 °C. It is thought that the branches are formed by recombination via intermolecular chain transfer of two radicals occurring by initiation in a cage and lead to molecular weight increases. Furthermore, if either of the radicals diffuses outside the cage, the usual propagations (depolymerization and intra- and intermolecular radical transfers) and terminations take place, leading to the formation of volatiles and a decrease in molecular weight. Thus both the molecular weight increase and the degradation reactions are considered to be dependent on the rate of diffusion, in relation to the viscosity of the media, of the two radicals outside the cage.

The mechanism of thermal degradation of polymers is an interesting subject not only from the standpoint of fundamentals of a polymer reaction but also with respect to understanding heat-resisting characteristics, polymer processes such as extrusion or injection molding, and the effective utilization of plastic wastes. Recently, the thermal degradation of polymers has been also widely reinvestigated to synthesize new compounds, including polymers, oligomers, and monomers,[1] and is very interesting from the standpoint of unit reactions in the synthetic chemistry.

The mechanisms of thermal degradation of polyethylene (PE) have been so far discussed as typical random scission type reactions from changes in their intrinsic viscosity and the chemical structures of the thermally degraded polymer or by observing changes in the volatilization and the compositions of the volatiles. In the initial stage of the reaction, a large decrease in the intrinsic viscosity of the thermally degraded polymer occurs. This phenomenon has been interpreted to be caused by the scission of the weak link in the polymer chain[2,3] or by a random intermolecular chain transfer of macroradicals followed by β scission.[4] Moreover, it has been interpreted from various experimental studies[5-7] that a small quantity of volatiles is formed by intramolecular chain transfer (back-biting) of macroradicals followed by β scission. Recently, however, a molecular weight increase reaction as well as the above-mentioned molecular weight decrease reaction has been reported. Witt et al.[8] and Tanaka et al.[9] have suggested by studying the melt viscosity of high-density polyethylene (HDPE) at about 200 °C that molecular weight increases when long-chain branches (LCB) are formed. Holmström et al.[10] carried out the heat treatment of low-density polyethylene (LDPE) and HDPE at temperatures between 284 and 355 °C under nitrogen containing 0.0005–0.16% oxygen. They observed both a molecular weight increase and formation of LCB on the basis of their studies of gel permeation chromatography (GPC) and intrinsic viscosities of the degraded PE. These facts are extremely important for the proposal of a detailed reaction mechanism, and the formation of a branched polymer having a controlled average number of LCB is expected.

We have established a quantitative method for determining the number of double bonds (terminal vinyl, *trans*-vinylene, and vinylidene groups), terminal methyl groups, and LCB by ^{1}H and ^{13}C NMR spectroscopies, taking into account the currently available information related to the structural changes in the thermally degraded polymer.[11] In this paper, a mechanism for the formation of LCB in the thermal degradation of a linear high-density polyethylene (LHDPE) is discussed on the basis of quantitative results of the contents of these functional groups, especially the average number of LCB per molecule (L) in the thermally degraded polymer.

Experimental Section

Material. The LHDPE sample used was a Phillips-type PE, which is free of branching and contains one terminal vinyl group per molecule.[11] The molecular weights were as follows: $M_w = 15.0 \times 10^4$ (by light scattering); $M_n = 1.4 \times 10^4$ (by osmometry). These data have been furnished by the supplier of the LHDPE sample.

Apparatus. Details of the apparatus used and the procedures used for this experiment have been described in a previous report.[11] One gram of sample was degraded under a pressure of 4 mmHg and flowing nitrogen (99.999% purity), which was reported to contain 0.0007% oxygen by volume. After the reaction,

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