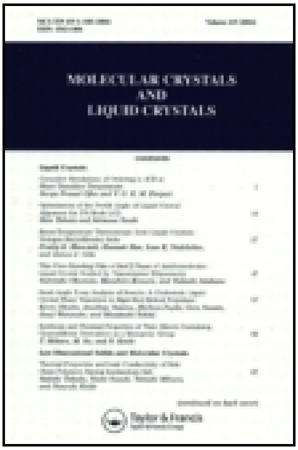

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RHEOLOGY AND PROPERTIES OF THERMOTROPIC LIQUID CRYSTALLINE POLY(BISPHENOL E ISOPHTHALATE-CO-NAPHTHALATE)

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Thermotropic liquid crystalline (LC) copolyesters of Bisphenol E isophthalate-co-naphthalate compositions, have been characterized by a range of rheological and other properties. All LC copolyesters contained the same nominal ratio of comonomers, but differed in molecular weight. Properties have been compared and contrasted to those of a non-liquid crystalline Bisphenol E isophthalate polyester. Interesting features exhibited by the LC copolyesters are a (1) minimum in viscosity as a function of temperature, (2) pronounced shear thinning, (3) the absence of a Newtonian viscosity plateau at low shear, (4) an order-of-magnitude lower viscosity for a LC copolyester compared to the conventional polyester of similar apparent molecular weight and (5) much lower (perhaps even negative) extrudate swell.

INTRODUCTION

A new family of aromatic polyesters - some of which are thermotropic liquid crystals (LC) - has been introduced in the patent literature by Monsanto Company[1-5]. These are

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*Present address: Bell Laboratories, Murray Hill, New Jersey polyesters of 1,2-bis-(4-hydroxy phenyl) ethane (called Bisphenol E and designated BPE) with one or more aromatic dicarboxylic acids. Within this family, thermotropic behavior is observed in the copolymer of BPE with a mixture of 80:20 isophthalic acid:2,6-naphthalene dicarboxylic acid, whereas isotropic behavior is observed in the homopolymer of BPE with isophthalic acid alone. Samples from these two members of the BPE family - some being thermotropic and another not (for comparison) - were obtained from Monsanto for this study. Our focus has been to compare the rheology of these polyesters using capillary rheometry. This is of interest because: 1.) little is known about the rheology of thermotropic LC polymers[6,7], 2.) previous studies of lyotropic and thermotropic LC polymers have revealed unusual rheology compared to conventional polymers, and 3.) understanding of LC polyester rheology may aid the optimization of processing conditions in production.

A review by Baird[6] in 1978 cited the single published investigation - that of Jackson and Kuhfuss[3] - on LC copolyesters, of poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHB). A review in 1981 by Wissbrun[7] also noted relatively few additional studies[4,8,9,10] - all of which again dealt with copolyesters of PET and PHB, but two which also included work on other rod-like thermotropic LC polyesters[4,10]. Interest in the rheology of rod-like thermotropic polymers is growing rapidly, as evidenced by recent papers[11-18].

There do not yet appear to be any reports in the literature concerning the effect of molecular weight on melt viscosity for thermotropic LC polymers. However, a number of studies have been made of the molecular weight dependence of solution viscosity for rod-like lyotropic polymers[7]. The point is that for rod-like polymers - at a constant temperature and constant mesogen concentration - viscosity may decrease with increasing molecular weight! Although this behavior has, as yet, been observed only with lyotropic polymers, it is likely that a similar decrease in viscosity with molecular weight could occur in the thermotropic liquid crystalline copolyesters studied here.

POLYMERS

All polyesters in this study were received from researchers at the Monsanto Company. LC copolyesters were kindly provided by Dr. Oliver Deex, Monsanto Co., St. Louis, Missouri. A non-liquid crystalline reference homopolyester was received from Dr. Morris Ort, Monsanto Co., Indian Orchard, Massachusetts. The polyesters were prepared from 1,2-bis(4-acetoxy phenyl) ethane (commonly called Bisophenol E diacetate; designated here as BPE diacetate) with one or more aromatic diacids. The compositions and polymerization conditions are covered by U.S. Patent 4,102,864[5]. A non-liquid crystalline homopolyester, which served as a reference for the LC copolyesters was synthesized from Bisphenol E diacetate and isophthalic acid (I) in a monomer mole ratio of 50:50 BPE:I (Fig. 1). This poly(Bisphenol E isophthalate) is referred to as BPE/I. It is semicrystalline with a melting point of 285-310°C. Its properties are similar to poly(butylene terephthalate)[5].

Six poly(Bisphenol E isophthalate-co-naphthalate) thermotropic LC copolyesters were available, all having the same relative composition, but differing in molecular weight (η_{inh}). These were prepared from Bisphenol E diacetate, isophthalic acid (I), and 2,6-naphthalene dicarboxylic acid (N) in a monomer mole ratio of 50:40:10 BPE:I:N, see Figures 1 and 2. This poly(Bisphenol E isophthalate-co-naphthalate) composition was designated BPE/I/N-20, where "N-20" refers to the 80:20 I:N ratio of the two diacids.

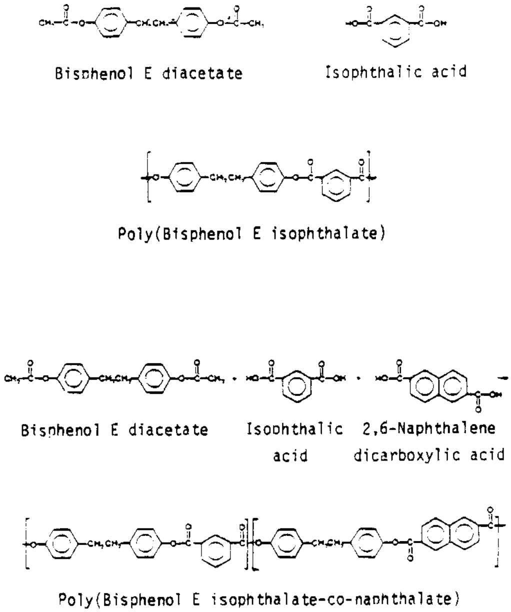

FIGURE 1 Reaction equations for BPE/I and BPE/I/N-20 polyesters

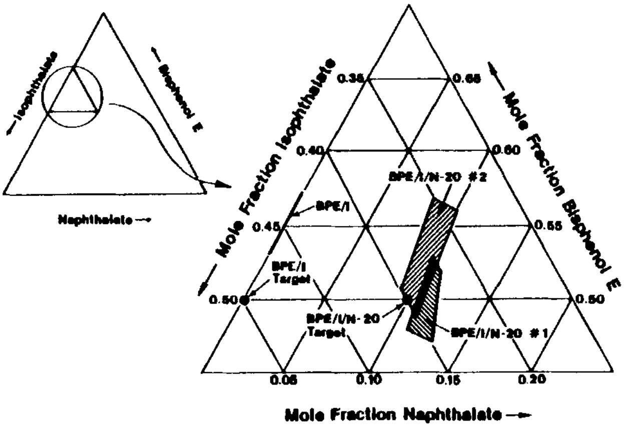

FIGURE 2 Three-component compositional diagram for BPE/N, BPE/I/N-20 #1, and BPE/I/N-20 #2 (based upon ^{1}H NMR analyses).

The BPE/I/N-20 composition exhibits a transition from a semicrystalline state to an anisotropic fluid at ~284°C. A transition to the isotropic state at higher temperatures is not readily observed, since pyrolysis intervenes. The exception has been a low molecular weight pre-polymer (η_{inh} ~0.38 dl/gm) in which a clearing temperature at ~380°C was observed. The BPE/I/N-20 mesophase is presumed to be nematic, based upon 1.) its appearance between cross-polarized lenses, 2.) the tendency to form fibrillar structures during extrusion or injection molding, and 3.) the similarity of its molecular structure to other nematic polymers[19]. The mesogen is the naphthyl moiety. The naphthyl rings, flanked by ester groups which are in turn attached to para-substituted phenyl rings, form rigid rod-like segments having sufficiently high aspect ratio to act as mesogens.

Polymerizations were accomplished by Monsanto using a two-step batch polycondensation procedure. The first step consisted of preparation of a low-molecular weight prepolymer (η_{inh} ~0.38 dl/gm) by reacting the monomers under vacuum to temperatures as high as ~260°C, with removal of acetic acid distillate. The second step involved granulation of the prepolymer and continued polymerization under higher vacuum to higher molecular weight (η_{inh} ~0.55-1.00 gm/ml) in the solid state - ie., above Tg but below Tm. Solid-state polymerization temperatures varied, but were typically in the range 260-280°C.

Inherent viscosities were determined using the mixed solvent of 60/40 wt % phenol/1,1,2,2-tetrachloroethane (Aquair, P.O. Box 7048, Charlotte, NC 28217). Determinations were made at 0.5 gm/100 ml using a size 150 Ubbelohde viscometer in a bath at 25°C. Difficulty in dissolving the polyesters, likely due to their crystallinity, required heating under reflux at 120°C for one to two hours. The inherent viscosities are reported in Table 1 along with other polyester characteristics.

TABLE 1 Characterization of Polyesters

	BPE/I	BPE/I/N-20 #1	BPE/I/N-20 #2
Physical appearance, as received	Amber translucent pellets	Off-white opaque powder	Tan opaque powder
η_{inh} dl/gm 0.5% in 60/40 phenol/1,1,2,2-tetrachloroethane	0.85	0.90	0.60
DSC transitions*			
1st heating:			
T_g onset, °C	214	111-120	111
T_m peak, °C	310	286	286, 310
ΔH, cal/gm polymer	17.0	5.3	5.3
2nd heating:			
T_g onset, °C	137	110	110
T_m peak, °C	288	284	250, 285, 293
ΔH, cal/gm polymer	~7.0	~4.0	~3.6
Temperature range for melt turbidity and stir opalescence, °C	None	~290 to > 400	~290 to > 400

*Heating and cooling rates extrapolated to 0°C/min.

The transitions in the polyesters were examined using a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a Thermal Analysis Data Station. The BPE/I/N-20 endotherms occurred at lower temperatures (~287°C) than in the as received BPE/I. These peaks have been labelled $T_{C \rightarrow N}$ (crystal-nematic transition temperature) since they correspond to the transition from a semicrystalline solid to an anisotropic LC melt. However, it is not clear from this data whether the molecular structure undergoing a change in enthalpy involves only the mesogenic units, or simply crystals of BPE/I sequences whose Tm has been lowered by the presence of the naphthalate groups - or some combination of both. It is likely that crystals of pure BPE/I are present in the BPE/I/N-20 copolyesters, since 90 mole % of their composition is BPE/I. The thermograms of the copolyesters showed only mesomorphic behavior to ~345°C. No other significant thermal transitions were noted until ~380-420°C, where irregular endothermic response indicated the onset of degradation. Figure 3 shows the evaluation of polyester stability in terms of inherent viscosity changes on extrusion.

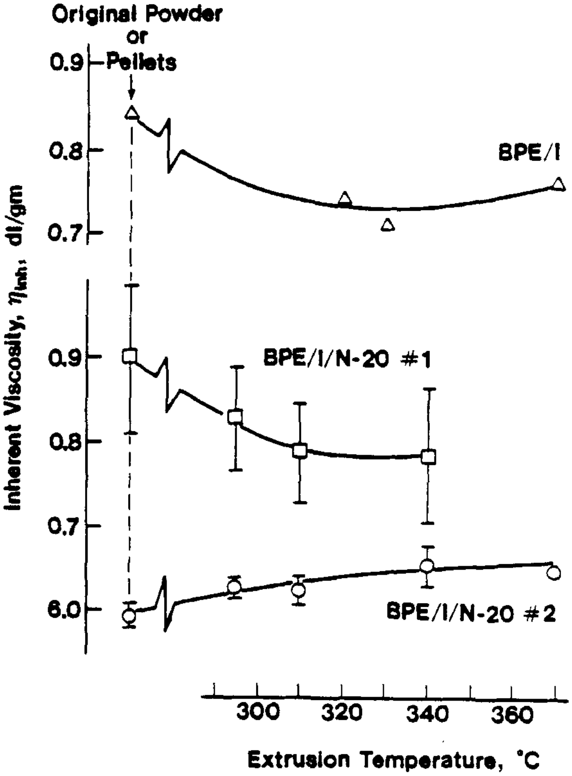

FIGURE 3 Inherent viscosities of rheometer extrudates as a function of extrusion temperature

The BPE/I/N-20 copolyesters all exhibited turbid LC melts and stir opalescence above ~290°C. These characteristics persisted to temperatures as high as 400°C, with the exception of the low-molecular weight copolymer (η_{inh} ~0.38

dl/gm), which showed an apparent clearing temperature at ~380°C, above which it was transparent. Even this clearing temperature was difficult to observe, since it coincided with rapid degradation, evidenced by bubbling. None of the higher molecular weight BPE/I/N-20 samples exhibited a clearing transition, with all degrading above ~370°C, manifested by yellowing and bubble formation. The BPE/I homopolyester melted at ~290-315°C to a transparent fluid, indicative of a true melt.

^{1}H Nuclear Magnetic Resonance

Of the techniques chosen to study copolymer composition, ^{1}H nuclear magnetic resonance (NMR) proved to be the most successful for quantitation. Polyester samples were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at concentrations of ~8% (wt.vol.). Due to the poor solubility of the highly crystalline as-received polyester powders and pellets, solutions were prepared from rheometer extrudates which were less crystalline.

A major question is whether the two principal BPE/I/N-20 copolyesters differed in composition? Within the uncertainty of the NMR measurements, they appear both to be close to the targeted 50:40:10 mole ratio of BPE:I:N. Sample #2, see Table 1 and Figure 2, may contain slightly less naphthalate and slightly more Bisphenol E than sample #1. A reduced naphthalate content in sample #2 would be consistent with its observed higher viscosity vs. sample #1. In addition, an elevated Bisphenol E content would explain the unexpectedly low inherent viscosity found for sample #2. That is, if the initial monomer fraction of BPE differed from 0.50, there would not have been an exact molar equivalence of acid and alcohol groups during polymerization, and the potential degree of polymerization would have been limited. Hence, it is feasible that the BPE/I/N-20 polyesters do differ slightly in composition, with sample #2 having less naphthalate and more Bisphenol E than sample #1. Analyses for the three polyesters are given in the compositional map in Figure 2.

Capillary Flow Studies

All bulk viscosity measurements were made using a Sieglaff-McKelvey Model R-64 capillary rheometer manufactured by the Tinius Olsen Testing Machine Company. The instrument was operated exclusively in the constant shear rate mode. Extrusions were conducted at a series of constant temperatures from 288-370°C. A number of capillary geometries and sizes were investigated with measurements generally made with two capillaries. One had a nominal L/D of 20/1 (25.4 mm length, L, X 1.296 mm diameter, D, with 180° entrance angle); the other had a nominal L/D of 15/1 (19.05 mm length X 1.290 mm diameter), both with a 180° entrance angle.

A 2000-lb. load cell was used for experiments with the BPE/I and BPE/I/N-20 #2 polymers. For the lower viscosity of the BPE/I/N-20 #1, a 200-lb. load cell was used. Both load cells were calibrated with dead weights, with data between cells agreeing well.

Copper-beryllium piston tips were used to prevent backflow in the rheometer during viscosity measurements. In the as-received condition, these tips contributed greater than 10 lb_f (44.5 Newtons) in frictional resistance against the barrel wall. Modifications were thus made by sanding the tips lightly with medium sandpaper, so that friction was reduced to only 0-2 lb_f (0-9 Newtons), as observed during travel of the piston-plus-tip through an empty barrel at the test temperature.

Polyesters in general are known to be sensitive to hydrolytic and oxidative degradation so that precautions were necessary to minimize exposure to moisture and oxygen. Prior to viscosity measurements, samples were dried in a vacuum oven at 110°C for 48 hours. After drying, the oven was opened with a nitrogen purge. Samples were transferred to the rheometer while hot; the barrel was purged with nitrogen during sample loading; the polyester stability under these conditions are shown in Figure 3.

After sample loading, the polymer was allowed to heat-soak for at least ten minutes prior to initiating viscosity measurements. The attainment of thermal equilibrium during testing was checked by the following procedure: shear stress was measured at a number of different shear rates, with the sequence of shear rates being randomized. Measurements were repeated at selected shear rates. Thermal equilibrium was considered to be reached if all shear stress-vs-shear rate data from a given run produced a constant curve.

Shear stress at the wall, τ_w (Pascals), and apparent shear rate at the wall γ_{app} (s^{-1}) were determined from conventional expressions. Corrections to the shear rate for a non-parabolic velocity profile were applied to the Rabinowitsch equation. Bagley corrections to the shear stress for entrance pressure losses were not, in general, applied. However, plots of ΔP vs capillary length-to-radius ratio were made for the two primary capillaries to estimate the magnitude of this correction, see Figure 4 for results on Sample #2. The pressure drop at various shear rates has been plotted vs L/R (= 2 L/D). Extrapolations have been made to zero pressure drop to show the effective capillary length contributed by entrance pressure losses. The vertical error bars represent the ranges of observed pressure drops.

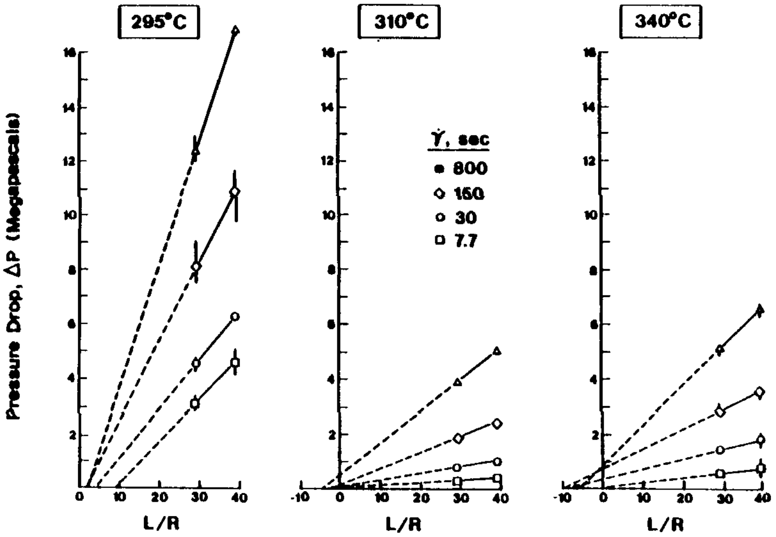

FIGURE 4 Bagley end correction plots for BPE/I/N-20 #2

RESULTS

The rheological data obtained for the three main polyesters - BPE/I, BPE/I/N-20 #1, and BPE/I/N-20 #2 - have been interpreted in several ways to emphasize different aspects of behavior.

In Figures 5-7 shear viscosities at fixed temperatures are plotted as a function of shear rate for the three polyesters. The dashed lines in Figure 6 and 7 highlight regions where viscosity, compared at constant shear rate, increases with temperature - an unusual feature for fluids.

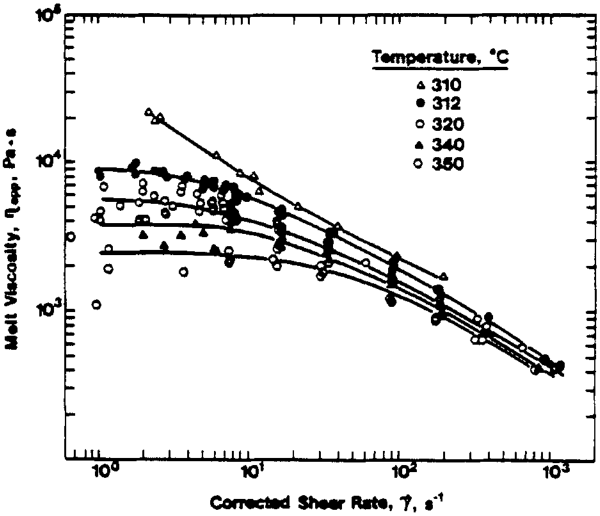

FIGURE 5 Melt viscosity vs corrected shear rate for BPE/I

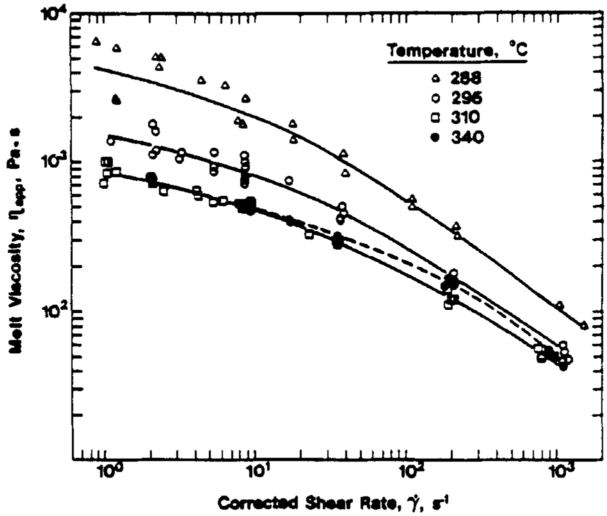

FIGURE 6 Melt viscosity vs corrected shear rate for BPE/I/N-20 #1

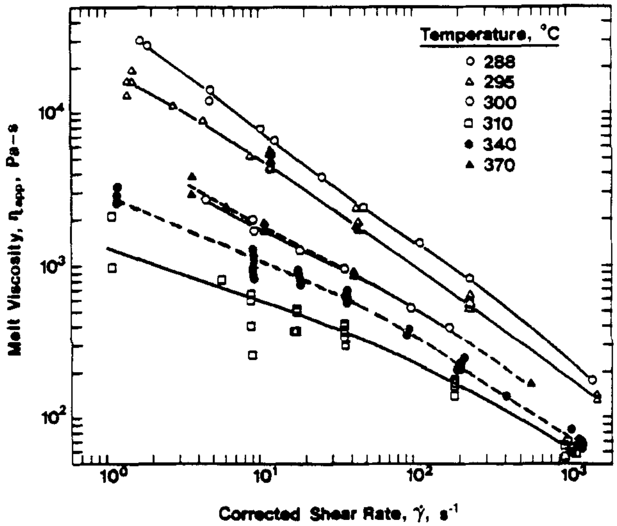

FIGURE 7 Melt viscosity vs corrected shear rate for BPE/I/N-20 #2

The temperature dependence of viscosity for the three polyesters in Arrhenius form is shown in Figures 8-10. The logarithm of viscosity at constant shear stress (as opposed to constant shear rate) is plotted vs the reciprocal of extrusion temperature, $1/T(K^{-1})$. Viscosities at a series stresses are shown in Figs. 8&9. In Figure 10 the three polyesters are compared at a constant shear stress of 20 kPa.

Poly(Bisphenol E isophthalate)

The BPE/I non-LC homopolyester exhibited conventional behavior for thermoplastic polymer melts, and consistent with the rheology of other BPE/I samples characterized by R.A. Mendelson at Monsanto[20]. Shear thinning is observed for the BPE/I at shear rates above ~10 s^{-1}, as manifested by reversible viscosities decreasing with increasing shear rate. Shear thinning is characteristic for polymers which exceed a critical entanglement molecular weight (M_c).

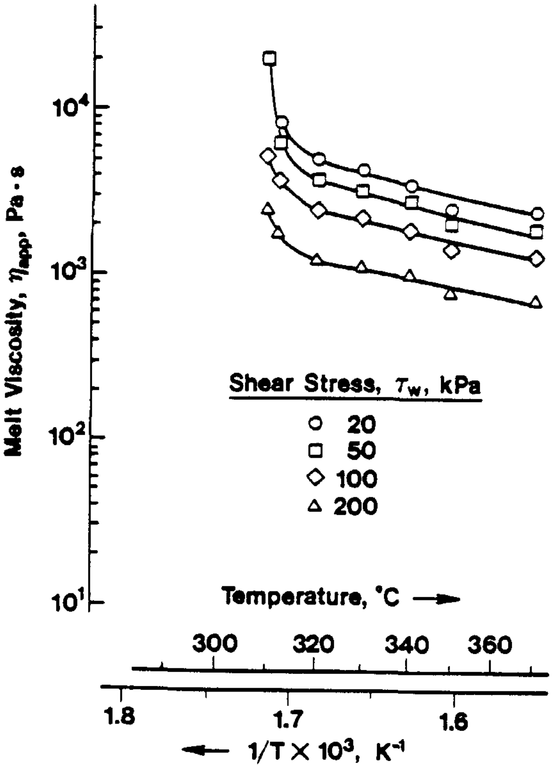

FIGURE 8 Temperature dependence of viscosity at constant shear stress for BPE/I

Mendelson's study suggests that M_c for BPE/I occurs near a viscosity - average molecular weight, $\bar{M}_v$, of ~30,000 which corresponds to an inherent viscosity η_{inh} ~0.60 dl/gm. Since the BPE/I studied here had η_{inh} ~0.85 dl/gm, it was expected to display shear thinning.

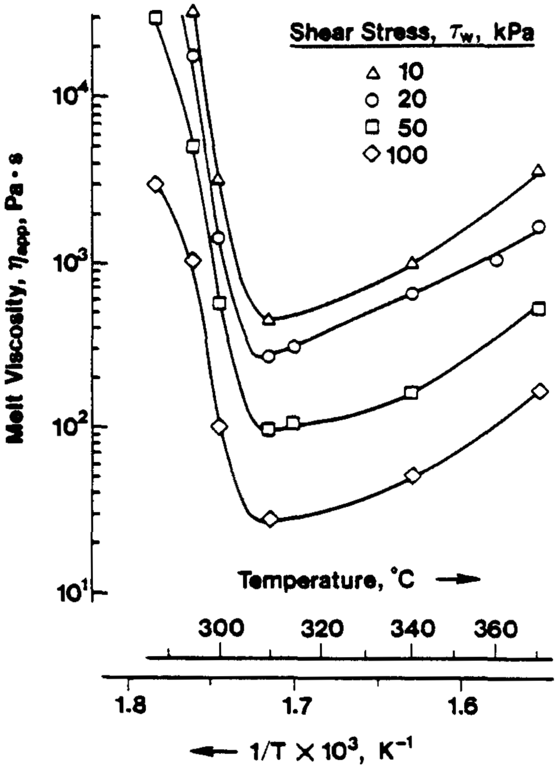

FIGURE 9 Temperature dependence of viscosity at constant shear stress for BPE/I/N-20 #2

At shear rates near ~1000 s^{-1} a power-law dependence is approached by the BPE/I, with a (dlog τ_w/dlog γ_{app}) near constant at ~0.4. This is greater than the ~0.3 predicted by Graessley[21] for a polymer having the most-probable molecular weight distribution (MWD) of 2.0. Since BPE/I is a condensation polymer it is expected to have this MWD. Possible reasons for the higher value of n include: 1) the power-law dependence has not been reached, or 2) the BPE/I has an MWD greater than 2. However, an n ≅ 0.4 appears reasonable and consistent with the n = 0.42 reported in empirical models by Mendelson[20].

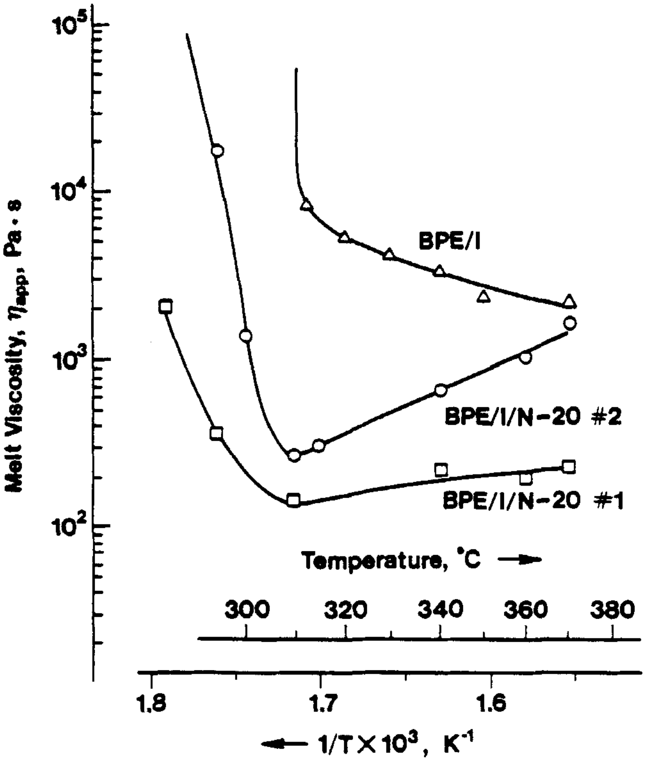

FIGURE 10 Comparison of the temperature dependence of viscosity for BPE/I, BPE/I/N-20 #1, and BPE/I/N-20 #2 at constant shear stress, τ_w = 20 kPa

The temperature dependence of viscosity for BPE/I shows a conventional monotonic decrease in viscosity with temperature. Above 320°C, the data fit an Arrhenius relationship:

$$\eta \text{ (const } \tau_w) = k \exp(E_a/RT)$$

The activation energy for viscous flow, E_a, found for BPE/I was 10 ± 2 Kcal/g mole. This is lower than the ~15 Kcal/g mole estimated by Mendelson. However, E_a was generated using temperatures as low as 316°C, which may have been too close to the melting point for BPE/I. Indeed, the one BPE/I curve which does not show Newtonian behavior at low shear rates is that at 310°C, which infers a yield and crystallinity.

Poly(Bisphenol E isophthalate-co-naphthalate) Sample #1. This copolyester exhibits a number of differences in rheology compared to the BPE/I. At the same temperatures and shear rates, BPE/I/N-20 #1 shows lower viscosities than BPE/I by more than an order of magnitude! The lower viscosities are due to liquid crystallinity. Analogous behavior has been observed with copolyesters of PET and p-hydroxybenzoic acid (PHB)[3,4].

An alternative explanation for the low melt viscosities of BPE/I/N-20 #1 is that it may be of lower molecular weight than the BPE/I. This possibility is not obvious from inherent viscosities: η_{inh} = 0.90 dl/gm for BPE/I/N-20 #1; η_{inh}= 0.85 dl/gm for BPE/I. The Mark-Houwink coefficients, which provide the relationship between inherent viscosity and molecular weight, have not been measured for BPE/I/N-20. However, the copolyester may have a higher Mark-Houwink exponent than the homopolymer. Thus, at similar inherent viscosities, the BPE/I/N-20 might have a lower molecular weight.

One argument against attributing the lower melt viscosity of BPE/I/N-20 #1 to a lower molecular weight is the extent of shear thinning. The steeper shear thinning of BPE/I/N-20 #1 likely results from its liquid crystallinity, as observed in other nematic polymers - both lyotropic and thermotropic. Another hypothesis suggests the formation of a boundary layer during capillary flow of anisotropic fluids. The boundary layer would have a lubricating effect, resulting in slip at the wall. A third possible reason is that rods orient differently than flexible chains. Any of these three mechanisms might explain the steeper shear thinning (lower power-law index) observed for BPE/I/N-20 #1 vs BPE/I.

BPE/I/N-20 #1 is also unusual in its dependence of viscosity upon temperature. Above 310°C, viscosity does not decrease with temperature, in fact, it increases slightly. The possibility that degradative cross-linking could be possible for the viscosity increase has been ruled out. The increase is consequently believed to result from LC character, and to correspond to a gradual transition from a nematic to an isotropic structure over a temperature range. The temperature where viscosity passes through a minimum for BPE/I/N-20 #1 (and #2) is ~310°C. This appears to correspond to the peak melting point for BPE/I homopolymer and suggests that residual unmelted crystallites of the BPE/I homopolymer are likely to be present in the BPE/I/N-20 on extrusion at < 310°C. Evidence for such high-melting crystallites has been observed in extrudates of BPE/I/N-20 #1 (and #2) collected at < 310°C. No residual crystallites are observed for samples extruded > 310°C.

Poly(Bisphenol E isophthalate-co-naphthalate) Sample #2. This copolyester exhibited rheology similar to that of BPE/I/N-20 #1. It also displayed interesting differences. Similarities to BPE/I/N-20 #1 included an increase in melt viscosity with temperature > ~310°C, the absence of Newtonian behavior, steeper shear-thinning than the BPE/I reference homopolymer, and lower viscosity than the BPE/I by roughly an order of magnitude. However, for the BPE/I/N-20 #2, the lower melt viscosity may be attributable simply to lower molecular weight. The inherent viscosity of BPE/I/N-

20 #2 is ~0.60 dl/gm, compared to ~0.85 dl/gm for the BPE/I. Mendelson's study of BPE/I rheology[20] predicts a 14-fold drop in Newtonian melt viscosity for a change in η_{inh} from 0.85 to 0.60 dl/gm, and this is roughly the difference observed between BPE/I and BPE/I/N-20 #2. Hence, the LC structure of BPE/I/N-20 #2 did not contribute to a reduction in melt viscosity versus BPE/I of the same inherent viscosity!

The BPE/I/N-20 #2 melt viscosity is greater than that of BPE/I/N-20 #1 - surprising, since BPE/I/N-20 #2 has an apparently lower molecular weight than BPE/I/N-20 #1 (η_{inh}= 0.60 dl/gm vs η_{inh} = 0.90 dl/gm, respectively). Conventional behavior dictates that, for polymers having the same composition, melt viscosity should increase with solution viscosity. This reversal of behavior between the two BPE/I/N-20 copolyesters is not yet understood. It is conceivable that this inverse dependence is a result of LC behavior. Studies of additional BPE/I/N-20 copolyesters indicated a possible maximum in melt viscosity with molecular weight. Such a maximum has also been noted for lyotropic LC solutions.

Extrudate Diameter

Low and even negative, extrudate expansion (die swell) has been observed in previous studies of rod-like LC polymers[9-13,17,18,22]. It has been suggested by R.S.P. that this may be a general characteristic of LC polymers[13].

Extrudate dimensions were determined for polymer strands which had been collected during the capillary flow studies. Dimensions were computed as the ratio of extrudate diameter to capillary diameter, D_e/D_o. Extrudate diameters were measured with a micrometer on solidified, unannealed extrudates. Diameter measurements were compared at a point 4 mm from the leading ends of the extrudates, to avoid error due to gravitational draw. The results are shown in Figure 11.

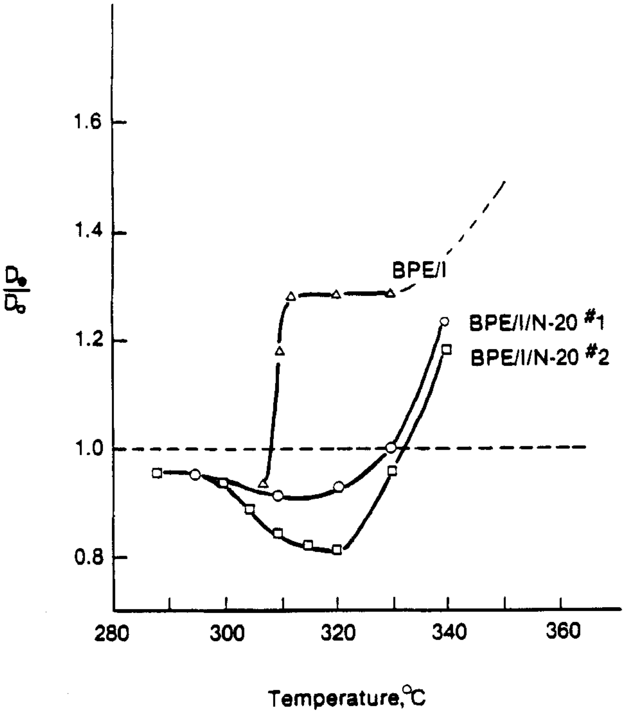

FIGURE 11 Comparison of extrudate swell for BPE/I, BPE/I/N-20 #1, and BPE/I/N-20 #2 as a function of extrusion temperature ($\dot{\gamma}$=30 s^{-1})

In general, the extrudate swell measured for the BPE/I/N-20 polymers was much lower than for the BPE/I reference polymer. In fact, below ~330°C swelling for the BPE/I/N-20 polymers appeared to be <u>negative</u> as measured by this technique. BPE/I/N-20 #2 exhibited a definite decrease and a <u>minimum</u> in extrudate swell between 300°C and 330°C.

Above 330°C the extrudate swell for the BPE/I/N-20 polymers increased and became positive. This increase in extrudate swell paralleled an increase in viscosity with temperature. It is possible that both phenomena are a result of a decrease in LC order with increasing temperature. However, at higher temperatures thermal degradation also occurs, accompanied by generation of bubbles in the extrudates that affect extrudate diameter, thus contributing to the observed increase in D_e/D_o.

For the BPE/I reference polymer, extrudate swell was positive over the main range studied. From 312 to 330°C swelling was essentially constant at $D_e/D_o \sim 1.28$. Above 330°C, the BPE/I polymer exhibited an increase in swelling with temperature similar to that observed for the BPE/I/N-20 polymers - again due, at least partially, to bubble formation.

Below 312°C, extrudate swell for BPE/I decreased - dropping to a "negative" value (D_e/D_o - ~0.93) at 307°C. This temperature was near the peak melting point for BPE/I, and corresponds to solid-state extrusion. Under these conditions, a yield stress was also found in the BPE/I polyester which could inhibit elastic recovery, and accounts for the negligible swell.

The BPE/I/N-20 polymers may display low extrudate swell because elastic recoil did not have time to occur before the extrudates crystallized. To test for residual elastic recovery, selected extrudates were annealed in silicone oil (Dow 210H) above their peak transition temperatures (T_m or $T_{c \rightarrow n}$) for varying lengths of time. Specifically, strands of BPE/I/N-20 #2 which had been extruded at 295, 310, and 340°C and 7.7 s^{-1} were annealed under the following conditions: 280°C for 20 min.; 290°C for 2 min.; 310°C for 2 min. Under these annealing conditions, no additional swelling was observed. Since these strands were among those having the least swell initially, and might have been expected to exhibit the greatest residual recovery.

The contraction of the extrudates is also due to decrease in volume (increase in density) during cooling, since measurements were made on solidified extrudates. By calculation, the "true" extrudate swell for the BPE/I/N-20 polyesters is probably 6-9% greater than the value measured on solidified strands. Thus, particularly for BPE/I/N-20 #2, the volume change upon cooling does not appear to completely account for the negative extrudate swell. The data suggest that either 1.) the polymers truly exhibit negative extrudate swell at the capillary exit under these conditions, or 2.) that the extrudates must undergo axial extension, rather than recoil, during their cooling (crystallization) process. Either of these possibilities represent a departure from conventional polymer behavior.

Other Properties

Orientation Studies. Generally, rod-like crystals can be oriented more easily than isotropic fluids. Greater orientation was shown by BPE/I/N-20 #1 than by BPE/I in extrudates produced under similar conditions. The extrudates were examined via wide-angle x-ray scattering (WAXS), and scanning electron microscopy (SEM). Greater orientation in the BPE/I/N-20 #1 was manifested by a greater tendency to form diffraction arcs (rather than rings) in WAXS, and by the exhibition of a fibrillar morphology via SEM. The x-ray evaluation of approximate crystallinity in two of the polyesters is given in Table 2.

TABLE 2 Results of X-Ray Crystallinity Measurements

Sample	Wt. Fraction Crystals, x_c, (crystal/polymer)
BPE/I pellets, as-receive	38
BPE/I rheometer extrudate	15
BPE/I/N-20 #1 powder, as-received	24
BPE/I/N-20 #1 rheometer extrudate	Not measured, due to anisotropic scattering

Tensile Modulus. The current high interest in LC polymers is largely due to their potential for forming high-strength, high-modulus fibers. The moduli of BPE/I/N-20 #1 and BPE/I were compared in terms of rheometer extrudates produced under identical conditions. Neither polymer displayed a high modulus. A similar result has been obtained on other thermotropic LC polyesters[23]. However, the BPE/I/N-20 #1 did exhibit a modulus *nearly twice* that of the BPE/I, and may have the potential for achieving high modulus under optimized processing conditions.

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