Rheological Properties of Liquid Crystalline Copolyesters

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Synopsis

Copolyesters were synthesized by modifying poly(ethylene terephthalate) (PET) with *p*-acetoxybenzoic acid (PAB) and hydroquinone diacetate/tetrasubstituted (tetramethyl, tetrachloro, and tetabromo) terephthalic acid (HQTS). It was found that the copolyesters containing 33 mol % or higher concentrations of (PAB + HQTS) form mesomorphic liquid crystalline structures. Rheological properties of copolyesters formed of PET, modified with PAB and hydroquinone diacetate/tetramethyl terephthalic acid (HQTM), were measured using a cone-and-plate rheometer. It was found that the copolyesters in the mesomorphic state exhibit yield values at a low shear rate (or at a low shear stress), and negative values of first normal stress difference were observed for certain compositions of (PAB + HQTM), over the range of shear rates (or shear stresses) tested.

INTRODUCTION

Liquid crystals may be divided into two subgroups, thermotropic liquid crystals formed by heat and lyotropic liquid crystals formed by mixing.[1,2] More recently, one finds in the literature such terms as mesomorphs, mesoforms, mesomorphic states, and anisotropic liquids.[3] The kinds of molecules which form liquid crystals generally possess certain common molecular features. The structural characteristics that determine the type of mesomorphism exhibited by various molecules has been reviewed.[4]

Poly(ethylene terephthalate) (PET) has long been used in producing fibers and films. More recently, PET has been introduced into the market as an injection-moldable thermoplastic. Some attempts have been made at modifying PET, for instance, by introducing a third component either to reduce the degree of crystallinity, thereby achieving enhanced dyeability, or to increase chain stiffness, thereby increasing the heat deflection temperature. Addition of halogen or phosphorus compounds to PET has been attempted to improve flame retardancy.

Hamb[5] has shown a novel method for modifying PET with bisphenols. His method of synthesis involves modification of polyesters using preformed polyester with diacids and diacetates, resulting in a high molecular weight copolyester, in contrast to the use of the reaction of acids and glycol esters giving low molecular weight products.

It was Jackson and Kuhfuss[6] who first utilized Hamb's method of synthesis for the modification of PET with *p*-hydroxybenzoic acid (PHB). They determined the range of compositions that yield the turbid melts which are characteristic of liquid crystalline behavior, and found that copolyesters containing 40 mol % or higher concentrations of *p*-hydroxybenzoic acid exhibit liquid

crystalline structure. Later, McFarlane et al.[7] looked into the synthesis of various copolyesters exhibiting crystalline behavior. For instance, they obtained liquid crystalline copolyesters by modifying PET with p-acetoxybenzoic acid (PAB), p-hydroquinone diacetate and terephthalic acid (HQTA).

It was reported that the effect of monosubstitution on the hydroquinone component with either chlorine or methyl substitution changes the turbid melt composition range.[8] For example, turbid melts were observed with 15 mol % or higher concentrations of hydroquinone diacetate/terephthalic acid (HQTA), but with 40 mol % or higher concentrations of monosubstituted hydroquinone diacetate and terephthalic acid.

Very recently, we have attempted to modify PET with p-acetoxybenzoic acid (PAB) and hydroquinone diacetate/tetrasubstituted (tetramethyl, tetrachloro, and tetrabromo) terephthalic acid (HQTS) in order to investigate the effect of steric interactions in the copolymer structure on the formation of liquid crystalline mesophases, thermal properties, flame retardancy, and rheological behavior. In this paper we shall report the rather unusual rheological behavior of copolyesters formed of PET, modified with p-acetoxybenzoic acid (PAB) and hydroquinone diacetate/tetramethylterephthalic acid (HQTM).

BACKGROUND

High-modulus/high-strength fibers composed of aromatic polyamides have recently been introduced.[9-18] DuPont's Kevlar,[12] for instance, appears to be based on structures of the poly(p-benzamide) (PBA) or the poly(p-phenylene terephthalamide) (PPTA) type. Syntheses of these materials, and other similar polymers, have been discussed in recent literature.[19-26] Because of the high melting temperature of these polymers, indicative of a high degree of chain rigidity, fibers are spun using solution spinning techniques. What is of particular interest to us in discussing the spinning of these polymers lies in the fact that they form anisotropic solutions (i.e., liquid crystalline solutions) in such solvents as sulfuric acid and/or dialkylamide–salt mixtures.[19-22] The use of anisotropic spin dopes is believed to be a key factor in achieving the unusually high modulus and tensile strength of Kevlar.[12,19]

According to Morgan,[20] the requirements for the formation of liquid crystalline solutions are an appropriate polymer structure, the molecular weight to exceed a minimum value, and a solvent capable of dissolving the polymer beyond the critical concentration value. The formation of an anisotropic phase can be detected by measuring, for instance, the occurrence of depolarization with optical microscopy. Liquid crystalline solutions (e.g., solutions of PBA) are turbid in appearance and optically birefringent in an unstrained state; i.e., they depolarize plane-polarized light.

The formation of liquid crystalline solutions may be construed as the occurrence of a transition to a nematic phase. It has been reported[10,12,19,27-30] that the viscosity increases at first with concentration when only the isotropic solution exists. Then, at a critical concentration, a liquid crystalline phase begins to form and the viscosity decreases rapidly with increased concentration. When only the anisotropic phase is present, the viscosity increases again with concentration.

In the past, some investigators have reported on the rheological properties

of anisotropic solutions.[27-33] Papkov et al.[29] reported on the rather interesting rheological behavior of PBA solutions, showing that, at low shear stress, the viscosity of isotropic solutions (say, 3% PBA) shows Newtonian behavior, which is as expected. However, as the concentration of the solutions is increased, the anisotropic solutions show Newtonian behavior over a certain range of low shear stresses, but exhibit a yield phenomenon at much lower values of shear stress. On the other hand, as the shear stress is increased somewhat, all solutions (isotropic and anisotropic) give rise to shear-thinning non-Newtonian behavior.

Another interesting rheological behavior of anisotropic solutions may be seen in the temperature dependence of viscosity. According to Papkov et al.,[29] the zero-shear viscosity of poly(p-benzamide) (PBA) solutions decreases with increasing temperature up to about 40°C, but, beginning at 40°C, the viscosity increases with increasing temperature. They attributed this unusual phenomenon to the disintegration of the ordered liquid crystalline structure as the temperature is increased.

It has also been known for some time that the mesophase transformation takes place in graphitizable organic materials during carbonization at temperatures between 350°C and 550°C. It is in this transformation that the large lamellar molecules, formed by the reactions of thermal cracking and aromatic polymerization, are aligned parallel to form an optically *anisotropic* liquid crystal, known as the carbonaceous mesophase.[34-38] The carbonaceous mesophase is not a single material, but rather a particular class of liquid crystalline materials whose structure and properties are in turn determined by the chemical reactions of organic pyrolysis as well as the structure of the starting material (e.g., petroleum coke, coal–tar pitch).

When ordinary commercial pitches, for instance, are heated for a prolonged time at temperatures above 400°C, either at constant temperature or with gradually increasing temperature, small spheres appear, forming a liquid crystalline mesophase with nematic order. The mesophase forms small liquid crystals which grow in size, coalesce into larger spheres, and eventually into extended anisotropic regions. Being strongly anisotropic in their optical properties, the morphology of mesophase spherules can be detected by using the light optical microscope with reflected light.

Because of the experimental difficulties involved with high temperature, information on the rheology of mesophase pitches is scarce.[39,40] Barr et al.[39] report the apparent viscosity of three different pitches as a function of temperature, showing that the viscosity of the isotropic pitch goes through a minimum at temperatures between about 350°C and 400°C, whereas the viscosity of mesophase pitches shows two minima and a maximum at certain temperatures. The viscosity begins to increase rapidly at about 450°C, and it is believed to be irreversible as the pitch begins to convert into coke.

EXPERIMENTAL

Liquid crystalline copolyesters were synthesized by means of a procedure similar to that described in the literature,[6,7] namely by modifying polyethyleneterephthate (PET) with p-acetoxybenzoic acid (PAB), and hydroquinone di-

acetate/tetrasubstituted terephthalic acid (HQTS):

PET   PAB

HQTS
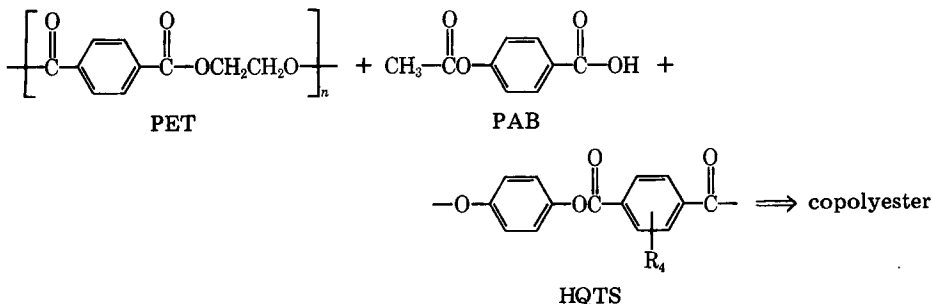
in which R represents CH_3 for tetramethyl substitution, Cl for tetrachloro substitution, and Br for tetrabromo substitution. The PET used in synthesis was obtained from the Celanese Corp., and had an inherent viscosity of 0.71.

The following procedure describes the preparation of a typical liquid crystalline copolyester derived, for instance, from PET, PAB, and hydroquinone diacetate/tetramethylterephthalic acid (HQTM).

To a single-neck 100-mL round-bottomed flask, which was fitted with a nitrogen inlet and condensate take-off, was charged with the following components:

poly(ethylene terephthalate):   10.00 g (0.052 mol)
p-acetoxybenzoic acid: 6.20 g (0.0345 mol)
hydroquinone diacetate: 6.84 g (0.0345 mol)
tetramethylterephthalic acid: 7.66 g (0.0345 mol)

The condensate take-off was connected by ground glass fittings to a receiver cooled by dry ice and with provision for applying vacuum. After the flask was purged with nitrogen, it was immersed into a thermostatically controlled sand bath at 150°C and the temperature was then raised to 270°C during a 30-min period. A clear, low-viscosity melt was obtained with acetic acid evolution when the temperature reached 260–270°C. After about 20 min, the temperature was then raised to 290°C and pressure reduced to 0.2 mm Hg and polymerization continued for 2.5 h. After cooling the flask, the polymer was dissolved in hot phenol/tetrachloroethane (60/40 by weight) and precipitated in methanol. The precipitated polymer was washed repeatedly with hot methanol and dried under vacuum at 60°C for 72 h.

Copolyesters with at least 33 mol % of (PAB + HQTS) gave turbid melts, and the precipitated polymers were tan in color. The melts were clear when less than 33 mol % of (PAB + HQTS) was used.

Dilute solution's viscosities were determined using an Ubbelohde Viscometer at 30°C with a polymer concentration of 0.5 g/100 mL. The relative viscosities (η_r) obtained were converted to inherent viscosities (IV) by the standard relation: IV = (ln η_r)/C, in which C denotes polymer concentration.

The inherent viscosities of copolyesters obtained by modification of PET with p-acetoxybenzoic acid and hydroquinone diacetate/tetrasubstituted (tetramethyl, tetrachloro, and tetrabromo) terephthalic acids are shown in Table I. Cast films, prepared in trifluoroacetic acid, of copolyesters containing PET and 18 mol % of (PAB + HQTS) are transparent. At and above 33 mol % of (PAB + HQTS), the copolyester films are opaque, which is an indication of liquid

TABLE I
Composition and Inherent Viscosity (IV) of Copolyesters Synthesized

PET (mol %)	(PAB + HQTS) (mol %)	Inherent viscosity (IV)			Film appearance[b]
		$R = CH_3$[a]	$R = Cl$[a]	$R = Br$[a]	
81.82	18.13	0.50	0.48	0.43	clear
66.67	33.33	0.54	0.45	0.52	opaque
53.85	46.15	0.56	0.58	0.57	opaque
42.86	52.14	0.71	0.60	0.61	opaque
33.33	66.67	0.63	0.57	0.64	opaque
25.00	75.00	0.65	0.59	0.57	opaque
12.65	82.35	0.54	0.53	0.54	opaque
11.11	88.89	—	—	—	opaque
5.27	94.73	—	—	—	opaque

[a] HQTS:
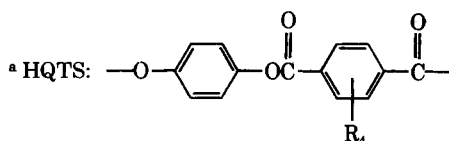
[b] Cast films in trifluoroacetic acid.

crystalline behavior. This is interesting because, for PET modified with p-acetoxybenzoic acid alone, liquid crystalline behavior (opacity in the cast films or turbidity in the melts) is reported to occur when the concentration of p-acetoxybenzoic acid is at least 40 mol %.[6] In our systems containing sterically hindered substituents, the steric hindrance does not seem to have prevented the formation of liquid crystalline structure in the copolyesters. Table II gives the glass transition temperature (T_g) and melting temperature (T_m) of copolyesters synthesized in our laboratory. Copolyester samples, which had been compression-molded in the form of disks, were dried in a vacuum oven before being subjected to rheological measurements.

Rheological properties of PET/(PAB + HQTM) copolyesters were measured in steady shearing flow, using a cone-and-plate rheometer (Weissenberg Rheogoniometer, Model R16). Evidence of the formation of the liquid crystalline state when cast films of copolyesters become opaque has also been reported by other investigators[6,7] who studied copolyester systems very similar to ours.

TABLE II
Glass Transition (T_g) and Melting Temperatures (T_m) of Copolyesters Synthesized

PET (mol %)	(PAB + HQTS) (mol %)	Tetramethyl		Tetrachlaro		Tetrabromo	
		T_g(°C)	T_m(°C)	T_g(°C)	T_m(°C)	T_g(°C)	T_m(°C)
81.82	18.18	69	210	70	226	71	219
66.67	33.33	76	188	77	202	75	185
53.85	46.15	79	170	80	174	74	189
42.86	52.14	74	—	81	—	78	—
33.33	66.67	76	—	80	—	83	—
25.00	75.00	83	—	95	—	79	—
12.65	82.35	85	—	85	—	90	—
11.11	88.90	94	—	80	—	80	—
5.27	94.73	98	—	83	—	93	—

RESULTS AND DISCUSSION

Figure 1 gives plots of viscosity (η) vs. shear rate ($\dot{\gamma}$) for copolyesters, PET/(PAB + HQTM), at 260°C. It is seen that PET homopolymer follows Newtonian behavior at shear rates up to 100 s^{-1}, but copolyesters, especially those containing 46 mol % of (PAB + HQTM) or greater, exhibit strong shear-thinning behavior. Figure 2 gives plots of η vs. mol % of (PAB + HQTM) for copolyesters, with shear rate as parameter. It is seen that, at low shear rates, η goes through a maximum and then a minimum, and at high shear rates η goes through a minimum as the concentration of (PAB + HQTM) is increased.

It is worth mentioning at this juncture that Papkov et al.[29] have shown how strongly the concentration required for phase separation depends on the zero-shear viscosity of poly(p-benzamide) (PBA) in dimethylacetamide–lithium-chloride (DMAC—LiCl), as given in Figure 3. It shows the effect of molecular weight on the degree to which the viscosity of a solution decreases with phase separation. It is seen that, on the isotropic portion of the curves, the viscosity increses very dramatically with concentration for the high molecular weight polymers.

Jackson and Kuhfuss[6] also reported shear-thinning behavior and seemingly unusual composition-dependent viscosity behavior similar to those shown, in Figures 1 and 2, for PET modified with p-hydroxybenzoic acid.

Figure 4 gives plots of viscosity (η) and shear stress (τ_w) for PET/(PAB + HQTM) copolyesters at 260°C. It is seen that pronounced yield values are observed in those copolyesters containing 33 mol % or higher concentrations of (PAB + HQTM). It should be recalled that copolyesters containing 33 mol % or higher concentrations of (PAB + HQTM) form liquid crystalline structures
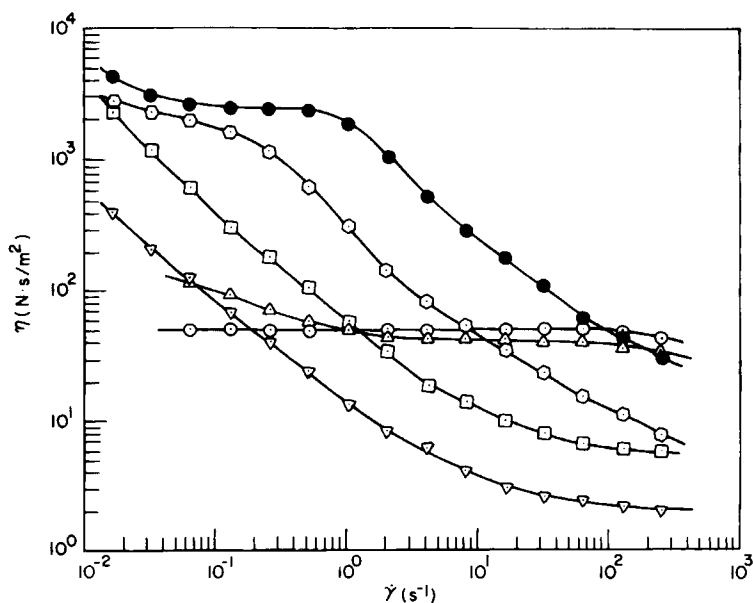

Fig. 1. Viscosity vs. shear rate for copolyesters of PET and (PAB + HQTM) at 260°C: (⊙) PET homopolymer; (△) PET/(PAB + HQTM) = 82/18 (molar ratio); (▣) PET/(PAB + HQTM) = 54/46; (▽) PET/(PAB + HQTM) = 43/57; (⊙) PET/(PAB + HQTM) = 33/67; (●) PET/(PAB + HQTM) = 25/75.
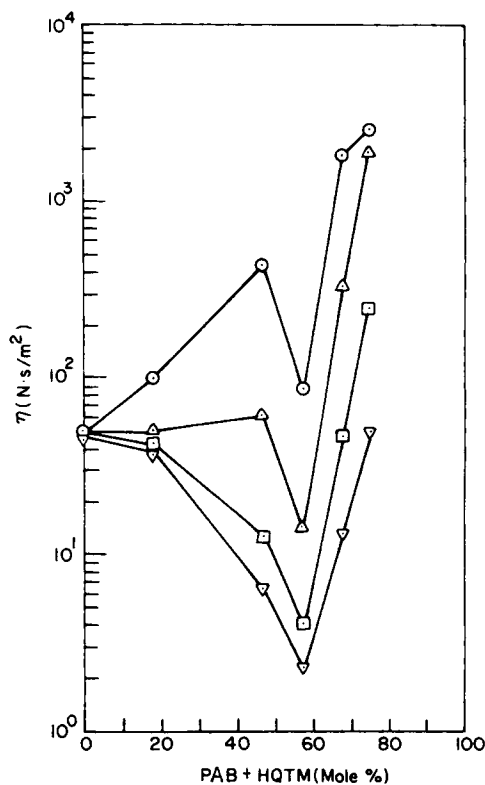
Fig. 2. Viscosity vs. concentration of (PAB + HQTM) in copolyesters (T = 260°C) at various shear rates (s^{-1}): (⊙) 0.1; (△) 1.0; (□) 10; (▽) 100.

(see Table I). It appears therefore that the yield stress observed in Figure 4 is associated with the liquid crystalline structure of the copolyesters. It is of interest to point out that concentrated suspensions (e.g., highly filled polymer melts) usually exhibit yield stresses. The phenomenon of yield behavior, observed above in polymeric mesophase melts, may be attributable to the presence of the crystalline phase in the isotropic, continuous phase.

It is of interest to note that the viscosity behavior of the melts of PET/(PAB + HQTM) copolyesters given in Figure 4 is very similar to that of the solutions of poly(p-benzamide) (PBA) in DMAC—LiCl, given in Figure 5, reported by Papkov et al.[29] The difference between the two systems, besides their chemical structures, lies in that the mesophase is formed in the former by the thermal effect (i.e., thermotropic liquid crystal) and in the latter by the solvent effect (i.e., lyotropic liquid crystal). It can be concluded therefore that the fundamental rheological behavior of polymeric liquids in the mesomorphic state is very similar, regardless of whether they are thermotropic or lyotropic liquid crystals.

Figure 6 gives plots of first normal stress difference ($\tau_{11} - \tau_{22}$) vs. shear rate ($\dot{\gamma}$) for copolyesters, PET/(PAB + HQTM), at 260°C. It is seen that, at certain concentrations of (PAB + HQTM) in copolyesters, negative values of $\tau_{11} - \tau_{22}$ are observed. Our rheological measurements were repeated several times to check the accuracy of the data, and the instrument was calibrated against isotropic polymeric liquids whose rheological properties had previously been de-
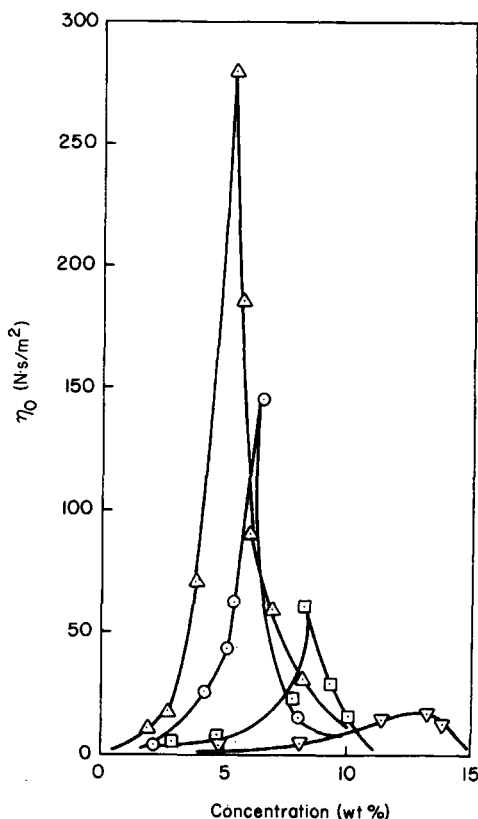
Fig. 3. Viscosity vs. concentration for a solution of poly(p-benzamide) (PBA) in dimethylacetamide–LiCl (DMAC—LiCl) for different weight-average molecular weights[29]: (▲) 69,000; (○) 23,800; (□) 16,000; (▽) unknown.

termined. It appears from Figures 4 and 6 that negative values of $\tau_{11} - \tau_{22}$ are associated with the phenomenon of yield behavior.

Earlier negative values of $\tau_{11} - \tau_{22}$ had also been reported by Kiss and Porter,[33] who used liquid crystalline polymeric solutions of poly(γ-benzyl-L-glutamate) (PBLG) and poly(ϵ-carbobenzyloxy-L-lysine) (PCBZL), subjected to steady shearing flow over a range of shear rates, 0.01–16,000 s^{-1}. It should be pointed out that, in their experiments with the PBLG and PCBZL solutions, the steady shear viscosity observed did not give rise to yield stress as the shear rate approaches zero. Kiss and Porter[33] observed negative normal stresses at shear rates as low as $1 \sim 10$ s^{-1}, which is well within the range in which rheological measurements are routinely made without consideration of possible secondary flow effects. They concluded that the phenomenon giving rise to negative normal stress is characteristic only of the liquid crystalline solutions tested.

More recently, Wissbrun[41] reported that, during the transient period upon startup of steady shearing flow, negative values of normal stress were observed for some liquid crystalline copolyesters (e.g., PET modified with 60 mol % of p-hydroxybenzoic acid, and several other copolyesters of undisclosed molecular structure prepared at the Cellanese Research Co.). He noted that such behavior has never been observed on their cone-and-plate rheometer with isotropic
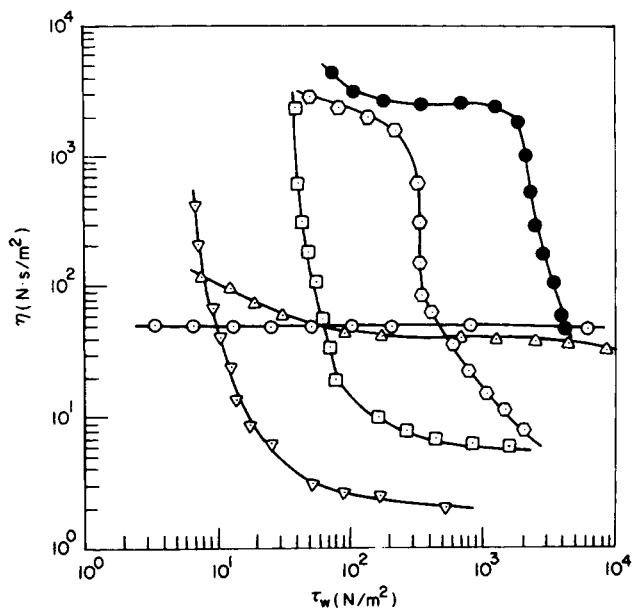
Fig. 4. Viscosity vs. shear stress for copolyesters of PET and (PAB + HQTM) at 260°C. Symbols are the same as in Figure 1.

polymers. Furthermore, he observed a yield stress with thermotropic polymers. According to Wissbrun, the normal stress behavior was quite sensitive to thermal and deformation histories, and the yield stress exhibited at low temperatures tended to disappear as the melt temperature was increased.

Figure 7 gives viscosity (η) and normal stress difference ($\tau_{11} - \tau_{22}$) versus shear stress (τ_w) for PET modified with 60 mol % and 80 mol %, respectively, of p-hydroxybenzoic acid. The copolyesters employed for the rheological measure-
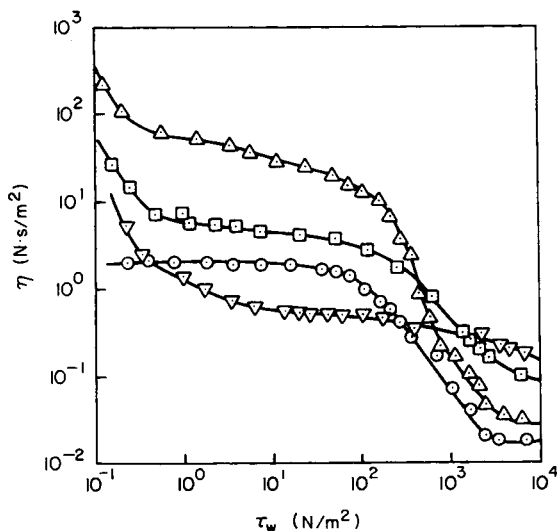

Fig. 5. Viscosity vs. shear stress for solutions of PBA in DMAC—LiCl, for different concentrations (wt %)[29]: (⊙) 3; (▲) 5; (□) 7; (▽) 9.5.
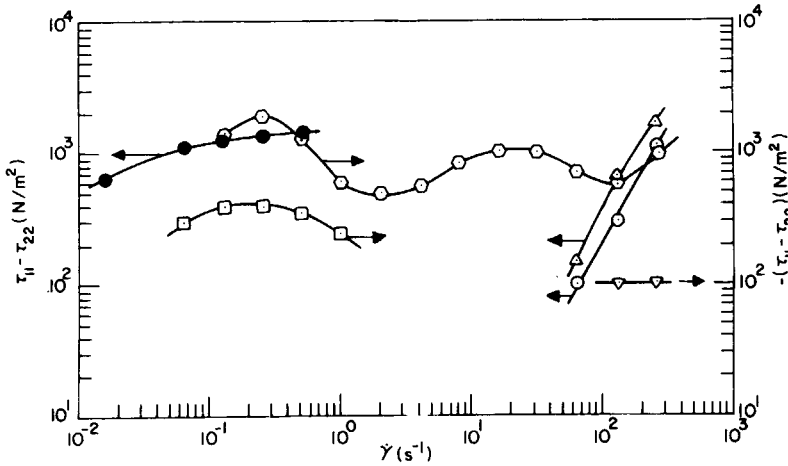
Fig. 6. First normal stress difference vs. shear stress for copolyesters of PET and (PAB + HQTM) at 260°C. Symbols are the same as in Figure 1.

ment were supplied to us by Dr. W. J. Jackson of Tennessee Eastman Co. It is seen that the Tennessee Eastman copolyesters exhibit shear-thinning behavior without apparent yield values and that the values of $\tau_{11} - \tau_{22}$ are positive over the shear stresses tested. It should be mentioned that the same cone-and-plate rheometer (Weissenberg Rheogoniometer, Model R16) was employed for generating the data given in Figures 1, 4, 6, and 7.
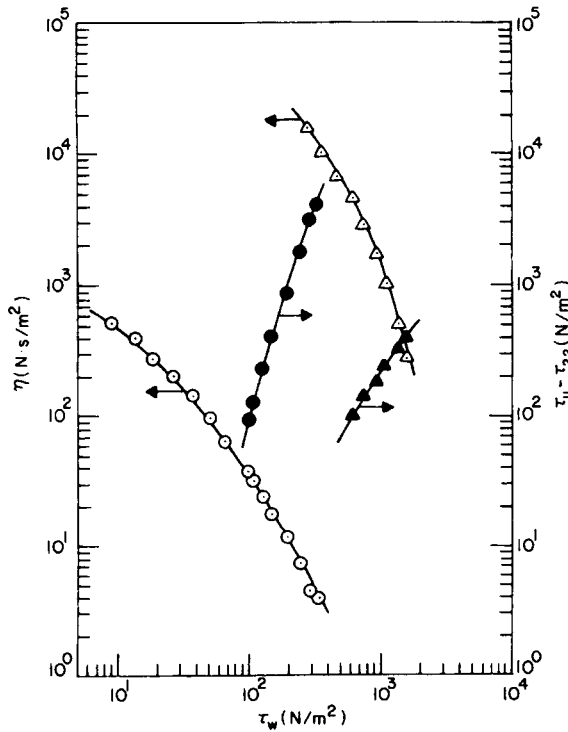

Fig. 7. Viscosity and first normal stress difference vs. shear stress for copolyesters of PET and p-hydroxybenzoic acid (PHB): (⊙, ●) 60 mol % of PHB at 260°C; (△, ▲) 80 mol % of PHB at 290°C.

We are certain that the negative values of $\tau_{11} - \tau_{22}$ given in Figure 6 have *not* resulted from an artifact. As much as we are puzzled by the seemingly unusual experimental evidence, we hope that continuing efforts by us and other investigators will soon unravel the physical origin of negative values of normal stress, experimentally observed with some polymeric liquids in the mesomorphic state.

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