

RHEOLOGICAL PROPERTIES OF LIQUID CRYSTALLINE COPOLY (*p*-HYDROXYBENZOATE/BISPHENOL A TEREPHTHALATE)

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ABSTRACT

Various aspects of the rheological behaviour of liquid crystalline copolyesters, i.e., samples of copoly (*p*-hydroxybenzoate/bisphenol A terephthalate), were explored by using Instron capillary rheometer. The experimental results indicated that the apparent viscosity was affected significantly by shear rate, melt temperature and *p*-hydroxybenzoate unit content. The flow activation energies ΔE_f are in the range of 205.1 to 74.5 kJ/mol, depending on the shear rate of 10–1000 s⁻¹, at temperature 568–603K. These copolyesters exhibit a yield phenomenon in the shear flow, and the values of yield stress decrease with increasing temperature. It is quite unusual that the extrudate of the copolyester shows the smaller swelling ratio even than unity at the lower temperature and lower shear rates.

INTRODUCTION

In recent years, thermotropic liquid crystalline (LC) polyesters have received a great deal of attention^[1,2]. For these LC polyesters, the high degree of molecular order and high performance of solid materials are the direct result of molecular orientation generated during melt flow. Consequently, no further processing is required to produce plastics and fibers with desirable physical properties. It is well known that the rheological properties of LC polyesters are closely related with the choice of processing conditions. Although our fundamental understanding of their rheological behavior is still rather limited, yet among thermotropic copolyesters, those based on *p*-hydroxybenzoic acid (HBA) are especially attractive. Literatures relevant to the synthesis and characterization of copolyesters of HBA with polyethylene terephthalate, 2-hydroxyl-6-naphthoic acid, biphenol terephthalate and others have been reported. However, the study on the all aromatic copolyesters from *p*-acetoxybenzoic acid (PHBA), terephthalic acid (TPA)

and acetoxymbisphenol A (BPA) is not well documented. Because all monomers of this copoly (p-hydroxybenzoate/bisphenol A terephthalate), shortly called copoly (PHBA/BPA/TPA), are produced on large industrial scales, its synthesis and characterization^[3,4] will have special meaning for future applications. It is our purpose in this paper to explore various aspects of the rheological behavior of copoly (PHBA/BPA/TPA). In particular the influences of shear rate, temperature and chemical structure on rheological parameters such as shear viscosity η , flow-activation energy ΔE_η , yield stress τ_0 , swelling ratio B and structural viscosity index $\Delta\eta$ were discussed in detail.

EXPERIMENTAL

Preparation of copolyester samples

Three types of copoly (PHBA/BPA/TPA) samples were synthesized in our laboratories^[3,4]. The polycondensation for all the samples was carried out at 553—593K for 10.5h. The PHBA/BPA/TPA composition, intrinsic viscosity and transition temperatures of the copolyesters are listed in Table 1.

Rheological measurements

The rheological properties were measured by using Instron 3211 capillary rheometer at 568—603K. The length of the capillary was 50mm, its ratio of length to diameter $L/D=40$. The data were corrected by Rabinowitsh equation^[5] for evaluation of the real shear rate. The die swell was measured by using the techniques described by Jerman and Baird^[6].

Table 1 Monomer ratios, $[\eta]$ values and transition temperature of copoly (PHBA/BPA/TPA)

Samples No.	PHBA/BPA/TPA (mol ratio)	PHBA (mol %)	$[\eta]^a)$ (dl/g)	T_g (K)	T_m (K)	$T_d^b)$ (K)
1	1:2:2	20.0	0.603	453	558	701
2	1:1:1	33.3	0.560	450	553	703
3	2:1:1	50.0	0.522	461	573	698

a) Measured in p-chlorophenol at 45°C
b) The temperature at which a 5% weight loss occurred

RESULTS AND DISCUSSION

Liquid crystallinity

In certain conditions the polymers consisted of stiff chains can show liquid crystalline states. As an all aromatic copolymer, the backbone of polymeric chains in

copoly (PHBA/BPA/TPA) has enough stiffness to give liquid crystallinity. It was found that copolyesters, in which PHB mole amount is from 10—50%, displayed schlieren or threadlike nematic state at melt^[4]. After shearing the melt of the copolyesters, a row-like or banded structure with the striations perpendicular to the shearing direction was observed between crossed polarizers as shown in Fig. 1.

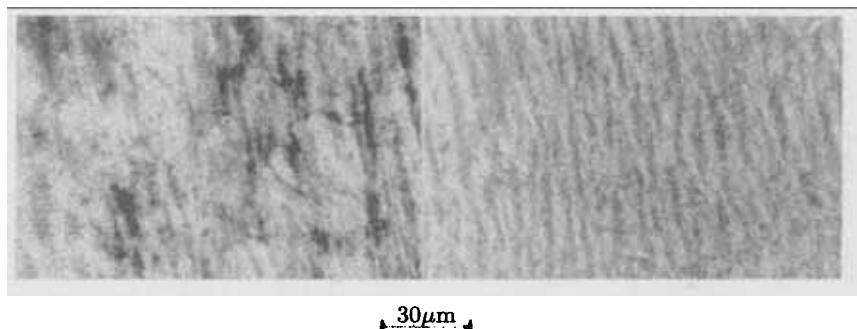


Fig. 1 Polarized photomicrograph of shearing-oriented melt for 33% HBA copolyester

Shear thinning

The apparent viscosities of copoly (PHBA/BPA/TPA) as a function of the shear rate and as a function of the chain composition at different temperatures were determined as shown in Fig. 2. The apparent viscosities are influenced strongly by the shear rate and melt temperature indicating obvious non-Newtonian behaviour of these copolyesters. Contrary to ordinary thermoplastic polyesters, the highly shear-thinning behaviour for the liquid crystalline copolyester melts was observed in the present experiment. In spite of the nonlinearity of some $\log \eta_a \sim \log \tau$ curves it could be suggested that the apparent viscosity of these copolyesters approximately follows the power law:

$$\eta_a = K \dot{\gamma}^{n-1}$$

where K is a constant and n is the power index showing the degree deviated from a Newtonian behaviour. The data of the power index n for the copolyester are listed in Table 2. If we compare this result with the data of polyethylene terephthalate, it can be concluded that the power index n for thermotropic liquid crystalline copolyester is almost comparable to that for the thermoplastic PET ($n = 0.7$ at 553K). It should be noted that, however, in the low $\dot{\gamma}$ range there is a plateau approaching the zero-shear viscosity for the latter and not for the former. This difference is connected with the yield phenomenon of the LC polyester which will be discussed in the latter section. In the microscopic viewpoint, it may be attributed to the orientation of rigid macromolecular chains of the copolyesters in mesomorphic state. During the

process of flow the oriented molecules slide smoothly over each other dissipating less energy than the random and entangled molecules. The other interesting aspect is the relationship between the flow property and the composition of copolyesters. It is clear that the higher the HBA unit content, the higher the shear thinning effect, i.e., the smaller the value of index n .

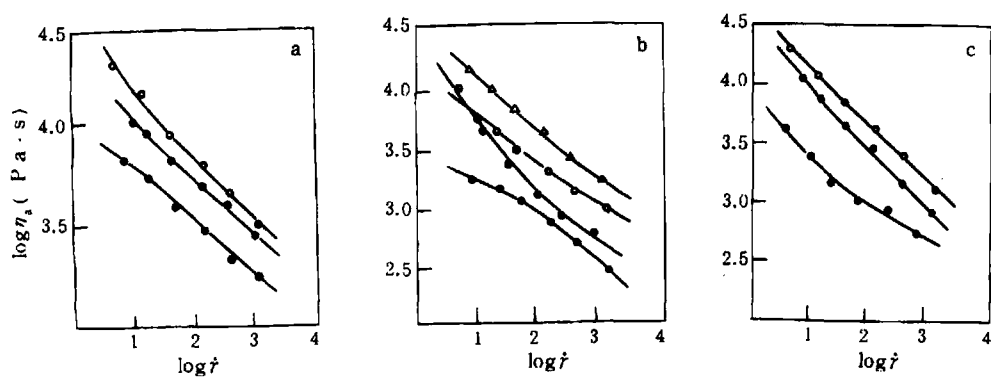


Fig. 2 Apparent melt viscosity η_a vs. shear rate $\dot{\gamma}$ for (a) 20% PHBA, (b) 33% PHBA, (c) 50% PHBA copolyesters as a function of temperature (Δ) 568K, ($\circ$) 578K, ($\bullet$) 593K, ($\bullet$) 603K

Table 2 The index n of the power law and the index (n') of Herschel-Bulkley equation for copoly (PHBA/BPA/TPA) at different temperatures (K)

Samples No.	Index n and index (n')		
	578K	593K	603K
1	0.67 (0.85)	0.72 (0.89)	0.74 (0.77)
2	0.65 (0.73)	0.46 (0.60)	0.67 (0.54)
3	0.54 (0.72)	0.48 (0.69)	0.63 (0.58)

Flow activation energy

Fig. 2 shows that the viscosity of the copolyester melts decreases with increasing temperature. To measure the sensitivity of viscosity to temperature, the flow activation energy ΔE_η is deduced by plotting $\log \eta_a$ against $1/T$ and using the Andrade equation:

$$\eta_a = A \exp(\Delta E_\eta / RT)$$

where A is a constant and R is the gas constant. The data are listed in Table 3. The data ΔE_η indicate that the flow activation energies are higher than those of some thermoplastic polyester melts (for PET, $\Delta E_\eta = 54$ to 84 kJ/mol). Moreover, the values of ΔE_η are rapidly decreasing when both of the shear rate $\dot{\gamma}$ and temperature are increasing. This can be explained also as a result of rigidity of molecular chains.

Macromolecules in the nematic state are readily oriented under the action of a shear stress and the orientation can increase the activation energy of the flowing process.

Table 3 Flow activation energies ΔE_η (kJ/mol) at constant shear rate $\dot{\gamma}$ (s⁻¹) for copoly (PHBA/BPA/TPA)

Samples No.	ΔE_η (kJ/mol)		
	10 (s ⁻¹)	100 (s ⁻¹)	1000 (s ⁻¹)
1	205.1	175.0	109.4
2	172.3	141.8	105.3
3	121.4	106.0	74.5

Yield stress

Generally speaking, the yield phenomenon characteristic for a solid is happened very often for polymeric fluids. The yield stresses τ_0 of LC copolyesters were calculated by means of Casson equation [8]:

$$\tau^{1/2} = \tau_0^{1/2} - K\dot{\gamma}^{1/2}$$

where K is a constant. The Casson plots of the experimental data are shown in Fig. 3. Obviously, with increasing temperature the yield stress decreases (see Fig. 4).

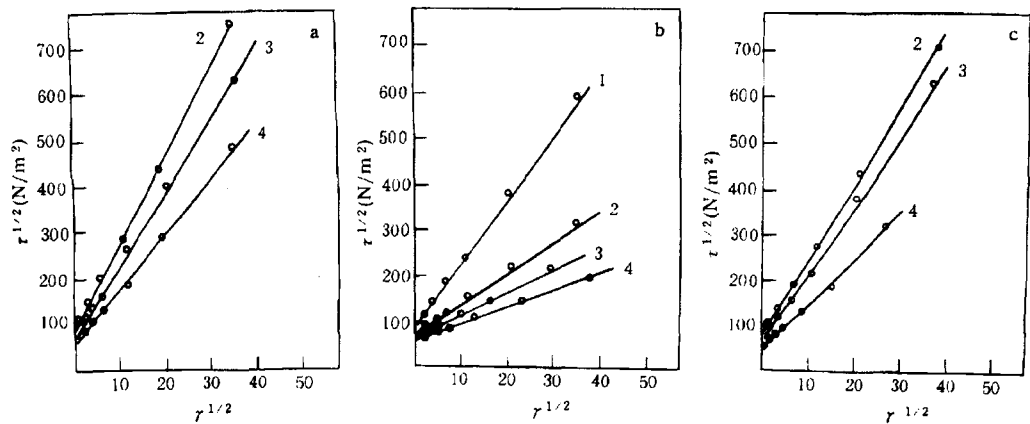


Fig. 3 Casson plots of $\tau_0^{1/2}$ vs. $\dot{\gamma}^{1/2}$ for (a) 20% PHBA, (b) 33% PHBA, (c) 50% PHBA copolyesters as a function of temperature (1) 569K; (2) 578K; (3) 593K; (4) 603K

Similar to the method of Fujiyama et al.[9], the flow behaviour for these LC copolyesters can also be expressed by Herschel-Bulkley[10] equation with an amazing precision:

$$\tau = \tau'_0 + K'\dot{\gamma}^{n'}$$

where K' is a constant and n' is a power index. Thus, the flow behaviour called

the nonlinear Bingham flow is a combination of a yield and a non-Newtonian flow and the extended form of Bingham flow showing a yield and a Netwonian flow. A comparison of two indexes n and n' is tabulated in Table 2.

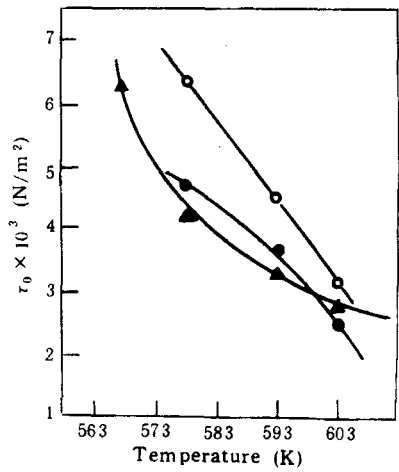


Fig. 4 Yield stress in shear flow as a function of temperature, (O) 20% PHBA (▲) 33% PHBA; (●) 50% PHBA

Die swell

The die swell is an interesting phenomenon from two points of view. First, it relates with the practical aspects of the plastics extrusion, man-made fiber spinning and so on. Secondly, as an expression of the fluid elasticity it is important to find the basic theoretical relationship between the die swell and the other parameters of polymer viscoelasticity. The quantitative parameter of die swell is defined as the swelling ratio:

$$B = D_f/D$$

where D_f is the maximum diameter of extrudate and D is the diameter of capillary tube. For a flow type of the elastic-recovery the main factor determining the swelling ratio is the ratio $(N_1/\tau)_w$ of the first normal stress difference to the shear stress at the tube wall. In fact, Tanner has given an analytic formula to calculate the resulting swelling ratio as in ref. [11]:

$$B = [1 + 1/8(N_1/\tau)_w^2]^{1/6}$$

Although the Tanner formula and its modified forms are supported quantitatively by a lot of experimental data for viscoelastic materials, it is not regarded as a suitable one for thermotropic LC polymers. The above formula can only give the lowest value B of unity. It is impossible to explain a value B less than unity based on this equation without modification. Representative data of die swell for all three

copolyesters at various temperatures are listed in Table 5. The swelling ratio B of the copolyesters is in the range of 0.96 to 1.32 at the shear rate of 10 to 10^3 s^{-1} at temperatures 568–603K. The values of B are lower than those of the ordinary thermoplastic resins (for PET, $B = 1.3$ –1.53). For copolyesters the swelling ratio B is extremely temperature-dependent. More interestingly, a negative swelling of the extrudate occurs at the relative low temperature and shear rate $\dot{\gamma}$ at which the flow just is possible. The lowest value of B is 0.96 at $\dot{\gamma} = 100 \text{ s}^{-1}$ and 578K for 50% HBA copolymer. The swelling ratio B less than unity is unusual, which has been observed in the case of Newtonian jet at high Reynolds number and also in polymeric liquid crystals of hydroxypropyl cellulose and polyesters. Jerman and Baird^[6] suggested that this phenomenon of negative swelling may be a general characteristic for polymeric liquid crystal. It is quite natural to relate the low value of extrudate swell with the slow process of disorientation of the stiff chains in LC polymers. On the other hand, it was^[6] suggested that the presence of yield stress inhibited the elastic recovery of extrudate of a liquid crystalline material. A similar phenomenon was observed in the extrusion of particle filled compounds^[12].

Table 4 Comparison of yield stresses τ_0 and $\tau'_0 \times 10^3 (\text{N/m}^2)$ determined by using Casson and Herschel-Bulkley methods

Sample No.	T (K)	Casson model	H-B model
1	578	6.35	6.25
	593	4.54	4.45
	603	3.06	3.10
2	568	6.25	6.30
	578	4.20	4.00
	593	3.42	3.52
	603	2.82	2.70
3	578	4.62	4.58
	593	3.69	3.65
	603	2.56	2.67

In order to explain the negative swelling quantitatively, all the present theories giving the higher swelling ratio B than unity were tried and found unsatisfactory. The above results lead us to believe there will be a necessity to build a new theoretical frame for the die swell of the liquid crystalline polymer in the future.

Structural viscosity index

The structural viscosity index $\Delta\eta$ indicates the degree of structurization of polymer melts, which is correlated with the spinnability of melts. Lower values of $\Delta\eta$

are indicative of better spinnability. The parameter $\Delta\eta$ can be defined from the following equation^[13]:

$$\Delta\eta = -(d \log \eta_a d\dot{\gamma}^{1/2}) \times 10^2$$

Table 5 Swelling ratio B of liquid crystalline melt for copoly (PHBA/BPA/TPA) ($L/D = 40$)

Sample No.	T (K)	B		
		$100s^{-1}$	$500s^{-1}$	$1000s^{-1}$
1	578	0.99	1.07	1.18
	603	1.15	1.22	1.32
2	568	1.01	1.08	1.20
	593	1.12	1.25	1.29
3	578	0.96	1.04	1.06
	603	1.16	1.20	1.23

Table 6 Structural viscosity index (SVI) of copoly (PHBA/BPA/TPA) melts

Sample No.	T (K)	SVI		
		$100s^{-1}$	$500s^{-1}$	$1000s^{-1}$
1	578	2.70	1.14	0.79
	603	2.18	0.93	0.64
2	578	3.03	1.26	0.87
	603	2.91	1.20	0.82
3	578	3.98	1.64	1.11
	603	3.11	1.28	0.87

the results are listed in Table 6. The experimental data indicate that a good spinnability of the copolyester melts can be attained at the high temperature and shear rate for the sample with the low content of PHBA unit.

Keywords:

Rheology; Copoly (p-hydroxybenzoate/bisphenol A terephthalate); Liquid crystalline polymer; Yield stress

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