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Interfacial effects on the viscosity and the morphology of a thermotropic liquid crystalline polymer

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SUMMARY

The apparent viscosity of nematic liquid crystal polyester measured by using capillary-tube viscometers showes a dependence on tube diameter and a yield stress in the low shear rate region called Region I. When the wall thickness measured by SEM is subtracted from the tube diameter, the viscosity becomes independent of tube diameter but still showes the Region I. This behavior may be caused by the molecular orientation at the wall of the capillary-tube.

INTRODUCTION

In recent years, many thermotropic liquid crystalline polymers have been synthesized(1). The interests on these polymers are accelerating because they have high strength and high modulus in fiber or plastic forms and they have a reasonable temperature range for melt processing. The melt of these polymers showes different aspects from flexible polymers such as unexpected temperature dependence of viscosity(2), apparatus geometry(3), thermal and shear history(3,4), and negative values of normal stress inducing no die swell(5).

It is well known that orientation of a nematic liquid crystal is affected by the nearness to the wall, the shear field, and the magnetic or electric fields. The apparent viscosity of liquid crystal obtained from Hagen-Poiseuille flow depends on the orientation of molecules at the wall(2). Fisher and Fredickson(6) showed that the viscosity of para-azoxyanisole was affected by the proximity to an interface that influence orientation. For the case of molecular orientation perpendicular to the wall, apparent viscosities were much dependent of capillary diameters. And they showed that the transient wall thickness made by molecular orientation decreased as the shear rate increased, i.e., 20 μm at nearly zero-shear rate, 7 μm at low shear rate (about 100 sec^{-1}) and 1 μm at high shear rate (about 10000 sec^{-1}). For a thermotropic liquid crystalline polymer, Wissbrun(3) reported that rheological properties were affected by the molecular orientation at the wall. Similar behavior was also observed by Yoon and Chung(7) for a lyotropic liquid crystalline polymer [poly(para-phenyleneterephthalamide)].

Accounting the anomalous flow curve of liquid crystal, Onogi and Asada(8) proposed that the flow curve of viscosity might be divided into three regions with shear rate, i.e., Region I of low shear rates, Region II of intermediate shear rates and Region III of hight shear rates. Region I and Region III showed shear thinning effects and Region II had a constant viscosity. In their proposal, the Region II and the Region III were valid

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in general, but the Region I had a little data for a thermotropic liquid crystalline polymer because of experimental difficulty such as a limited sensitivity of conventional instrument(3) like a Rheometrics Mechanical Spectrometer due to a low viscosity of liquid crystal melt. In order to overcome this difficulty at low shear rate, glass capillary-tube viscometers were used.

In this paper, the apparent viscosity of a thermotropic liquid crystalline polymer was measured by using capillary-tube viscometers with different diameters. In addition the cross-sectional morphology of a polymer rod was observed by fracturing perpendicularly to the flow direction. The transient wall thickness was obtained from SEM and the order of elastic constant was predicted from a theory(9).

EXPERIMENTAL

We synthesized a thermotropic polyester based on 4,4'dihydroxybiphenyl and azelaic acid following the method of Watanabe at al(10,11). This polymer was characterized by DSC (du Pont 910) and cross-polarizing microscope (Mettler FP-2). The polymer was crushed to fine powder and dried in vacuum oven for 24 hours at 120°C.

Intrinsic viscosities were determined at 35°C by using Cannon-Fenske type viscometer. Solvent was 60/40 mixture by weight of phenol and tetrachloroethane. Capillary-tube viscometers were made with glass. The detail set up of capillary-tube viscometers and measuring method were found in references (6) and (7). The driving force for flow was supplied by using high pressure nitrogen gas cylinder. Different shear rates were applied by changing outlet pressure of gas cylinder. Three capillary-tubes listed in Table I were used.

Entrance and exit effects could be ignored by increasing aspect ratios (L/D) of capillary-tubes. In order to calculate apparent viscosities, pressure gradient was obtained by reading the manometer on the nitrogen pressure line. The experimental apparatus immersed in a constant temperature bath filled with silicon oil. The temperature was controlled within the error of ±1°C. All the capillary-tubes were washed with distilled water and dried in vacuum oven at 100°C for 24 hours before experiment.

Fractured surfaces of polymer rods were observed by Scanning Electron Microscope (Hitachi model S-510). Polymer rod samples were made in the following way. After we read the pressure gradient and measured the flow rate of polymer melt driven by nitrogen gas pressure, the capillary-tube was taken out of the bath and quenched in cold water. The polymer rod sample was taken out of the broken capillary-tube glass. The polymer rods were very brittle at room temperature. The polymer rods were fractured perpendicularly to the direction of rod axis at room temperature and then coated with gold prior to examinations.

Table I Dimensions of Capillary-tube Viscometers

Tube No	Diameter (μm)	Length/Diameter
I	480	417
II	745	268
III	1255	159

RESULT AND DISCUSSION

When the polymer was examined by a cross-polarizing microscope, it showed typical threaded schlieren texture of nematic phase(10,11). From the DSC thermogram of the polyester, it exibited also a liquid crystal phase in the temperature range of 233°C-248°C. Therefore, experiments were performed at 242°C in the nematic phase range.

Inherent viscosities of samples were measured both before and after every main experiment in order to test the possibility of further polymerization and thermal degradation. The inherent viscosities of these samples are in the range of 0.503-0.562 (dl/g). In this range, the further polymerization and the thermal degradation were not detected(3). Before the main experiment we maintained the temperature at 242°C for an hour in order to make the same thermal history of the polymer in every reservoir.

The variation of apparent viscosity with shear rates and diameters for polyester used here are shown in Figure 1. The Hagen-Poiseuille equation is applied to calculate the apparent viscosity η_a:

$$\eta_a = \frac{PR/2L}{4Q/\pi R^3}$$

where R is the tube radius, P the pressure difference, Q the volumetric flow rate through the tube, and L the capillary-tube length. The quantities PR/2L and $4Q/\pi R^3$ are shear stress at the wall of the tube and effective shear rate, respectively. If the fluid is a homogeneous and simple fluid, η_a is a unique function of $4Q/\pi R^3$. As shown in Figure 1, all the curves show non-Newtonian behavior of a shear thinning type. The nematic phase of the polymer examined here is non-homogeneous fluid classified by Noll(12).

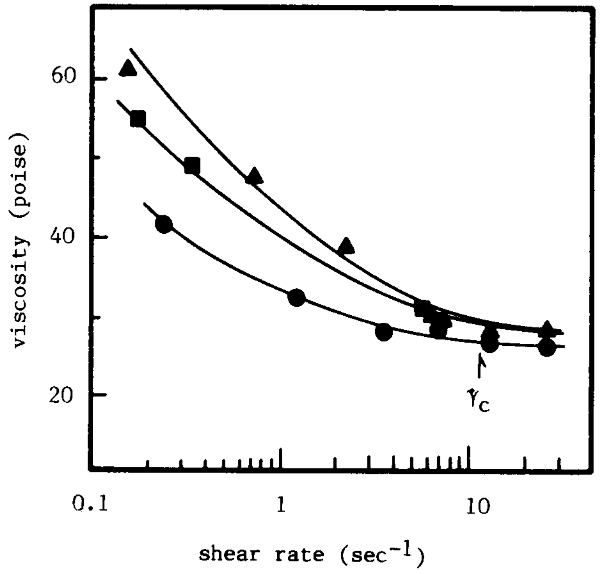


Figure 1. Comparision of flow curve of nematic polyester at 242° C with the tube diameter. (▲) 480 μm,(■) 745 μm, (●) 1255 μm

The shapes of flow curves in Figure 1 are similar to those of low molecular-weight liquid crystal(6), thermotropic and lyotropic liquid crystalline polymer(3,8) and filled polymer system(13), all of which have yield shear stresses. The flow curves are divided into shear thinning region (Region I) at low shear rate (below critical shear rate, $\dot{\gamma}_c$) and a plateau region (Region II) of nearly costant viscosity with shear rate (above critical shear rate). The existence of Region II is well understood. But below the critical shear rate, Region I with yield shear stress is very complex and least understood. Obviously, these flow curves show the yield stress like many other cases (2) when the shear rate approaches to zero.

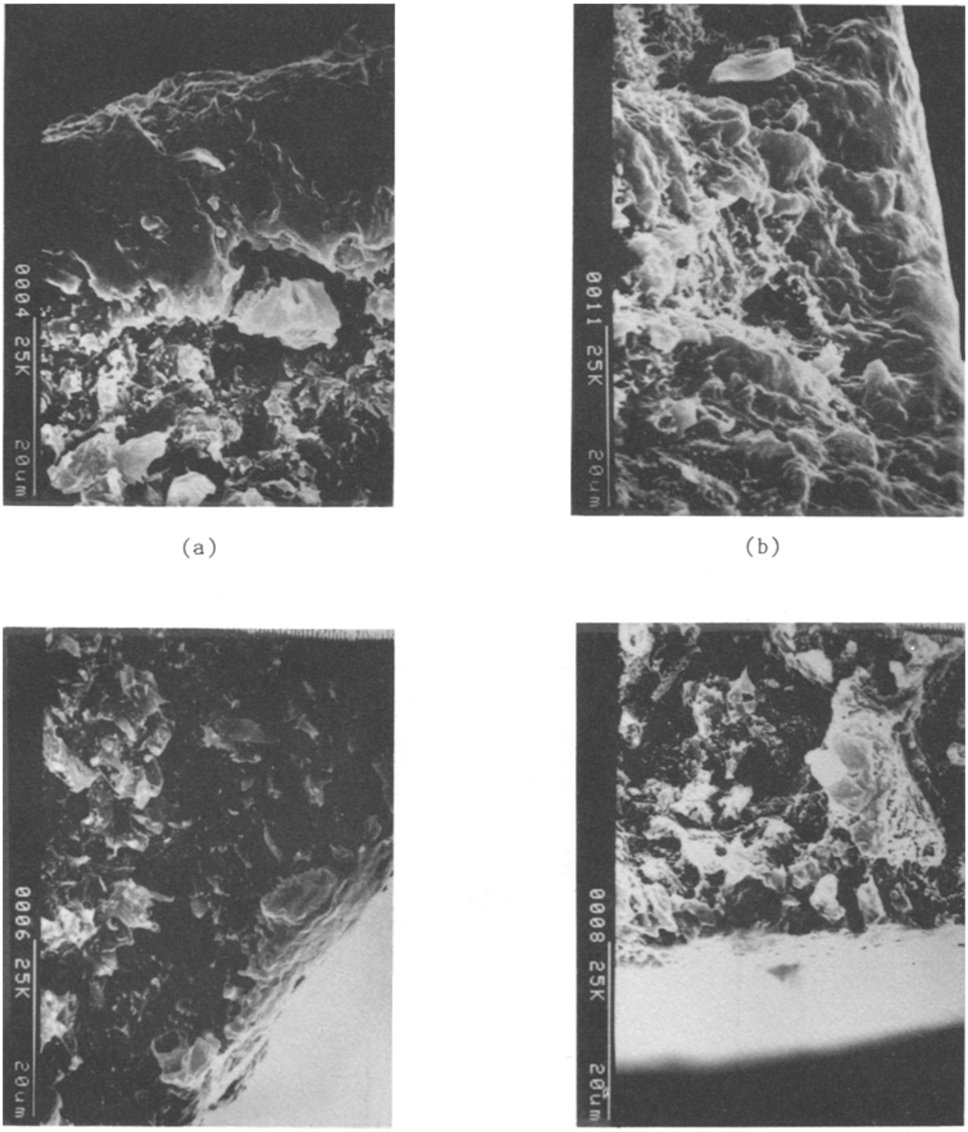
The effect of capillary-tube diameters on the apparent viscosities is significant as shown in Figure 1. This result may be due to the interfacial orientation of liquid crystal molecules at the wall, like the observation of Fisher and Fredrickson for a low molecular weight liquid crystal. Creagh and Kmetz(14) claimed that when the intermolecular forces within the liquid crystal were stronger than the forces across the interface, the solid wall did not get wet by the fluid and the elongated nematogenic molecules aligned in perpendicular to the surface to maximize their intermolecular interaction. The inner part of capillary-tubes was not wet when we obtained the polymer rod samples. Thus, the dependence of apparent viscosities on the capillary-tube diameters may be caused by perpendicular orientation of molecules at the interface.

Furthermore interfacial orientation of polymer molecules in Poiseuille flow was visualized by using SEM. A quenching technique was used to obtain the polymer rod out of capillary-tube during the flow of the melt. The structures of polymer orientations might be different for different positions along the radius due to the competition between the orientation of molecules at the boundary and in the shear field. Therefore we fractured the polymer rods carefully perpendicularly to the polymer rod axis.

The results are shown in Figure 2. The edge is the part near to the wall. All the scanning electron micrograps show that the morphology of the edge differs from that of the inner part; the shape of the edge shows a smooth form but the inner part exhibits a coarse shape. This observation assures the different structures by the molecular orientation. And it is considered that the thickness of smooth region is the transient wall thickness, which is formed by the molecular orientation perpendicular to the wall. The transient wall thickness, δ is calculated from the equation of $\delta \simeq (K/\eta\cdot\dot{\gamma})^{1/2}$ presented by de Gennes(9), where K a typical elastic constant, η an average viscosity of a fluid, and $\dot{\gamma}$ a shear rate. As shown in Figure 2, the thickness of smooth region decreases as the shear rate increases, which fits well the above theoretical equation.

Table II The Thickness of Smooth Region

$\eta_a\cdot\dot{\gamma}$(dyne/cm^2)	Thickness (μm)
11	20.0±3.0
38	11.0±2.0
111.4	7.0±2.0
211.6	5.0±1.0
688	2.5±0.5



(a) (b)

(c) (d)

Figure 2. Scanning electron micrographs of fractured surfaces of polymer rods obtained from tube III at various shear rate, (a) 0.256, (b) 1.154, (c) 7.29, (d) 25.62(sec^{-1})

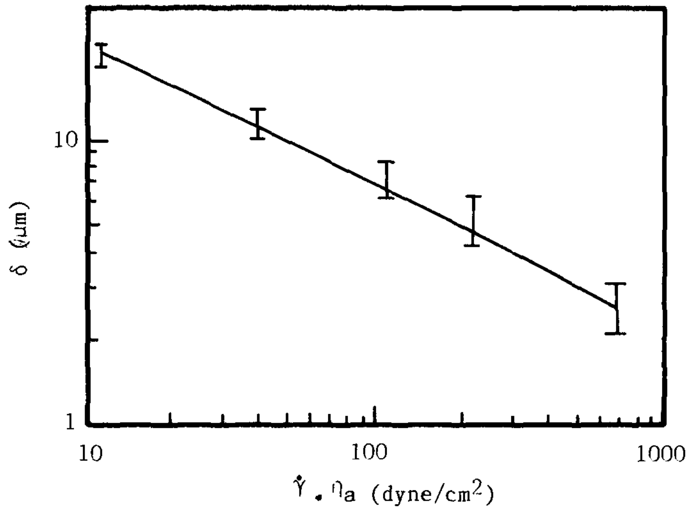


Figure 3. Variation of transient wall thickness against shear rate times apparent viscosity ($\dot{\gamma} \cdot \eta_a$)

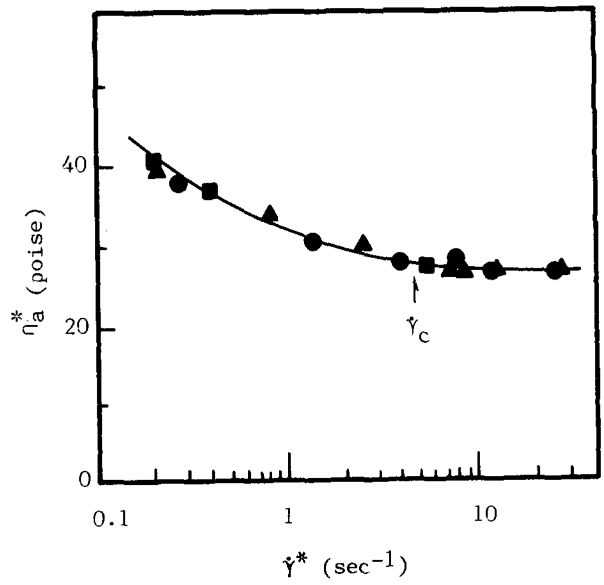


Figure 4. Comparision of virtual apparent viscosity behavior with the virtual effective tube diameter corrected from tube I (▲), tube II (■),tube III (●)

The thickness of smooth region vs. ($\eta_a \cdot \dot{\gamma}$) is plotted in Figure 3 and listed in Table II. Here it is assumed that the transient wall thickness only depends on the ($\eta_a \cdot \dot{\gamma}$) without regard to the tube diameter(6). As shown in Figure 3, the average value of slopes is about - 0.5. It has almost the same value with that predicted by de Gennes(9). The order of elastic constant calculated from the equation of de Gennes(9) is the order of 10^{-6} dynes. This is the same order for the small molecular liquid crystals(2,9) and the lyotropic liquid crystalline polymer [poly(benzylglutamate)](15). From these results, it is reasonable to say that the thickness of smooth region in Figure 2 is equal to the transient wall thickness.

We calculated the virtual effective diameters by subtracting the transient wall thickness in Table II from the tube diameters in Table I. From these virtual effective diameters, we could obtain a new shear stress τ^*, a shear rate $\dot{\gamma}^*$, and an apparent viscosity η_a^*. The plot of η_a^* vs. $\dot{\gamma}^*$ is shown in Figure 4. The new apparent viscosity η_a^* is independent of the capillary-tube diameters. From this result, it may confirm that the dependence of apparent viscosity on the tube diameters is caused by the transient wall thickness probably generated by the molecular orientation at the wall.

As compared with Figure 1, this new flow curve also shows Region I with yield shear stress but the slope of Region I decreases and the critical shear rate shifts to the lower shear rate. These results reveal that the explanation for the existence of Region I is complicated(2) and that the perpendicular orientation of polymer molecules at the wall may be one of the reasons for the occurrence of Region I.

The rheological property and the morphology are much affected by interfacial orientation of molecules for the thermotropic liquid crystalline polymer tested here. In addition the occurrence of Region I with yield stress can be partially explained by the interfacial orientation perpendicular to the wall but furthermore investigations must be made to clarify the existence of Region I.

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