

Study of shear-induced Stabilization of the Nematic Phase in a Side Group-containing Poly (aryl ether ketone) Copolymer

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Introduction

Polarized optical microscopes (POM) are commonly used to identify liquid crystalline textures. However, it is often found problematic to employ this technique in investigating the mesophase transition of polymeric materials due to their higher viscosities. Rheological measurements at this juncture could provide us with valuable information about the mesophase transition of liquid crystalline polymers^[1]. Accordingly, there have been some rheological investigations reported on thermotropic liquid crystalline polymers (TLCPs) due to the high sensitivity of their rheological response to the morphological variation of the polymers^[2-5].

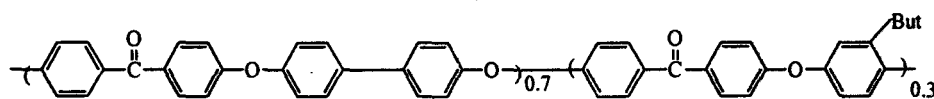
It has been shown that the polymers in mesophase exhibit an unusual feature, namely, the higher viscosity in the isotropic state than in the nematic state in spite of the higher temperature in the isotropic state. Obviously, this behavior does not obey the Arrhenius relationship^[6]. Phase transitions were verified by examining the variation tendencies of the rheological parameters such as viscosity and modulus^[7].

Newly developed thermotropic liquid crystalline poly(aryl ether ketone)s are of interest for both fundamental research and practical application because they exhibit not only a nematic but also a more ordered smectic phase^[8]. It has been demonstrated that the polymers in nematic state show much lower melt viscosities than the isotropic polymers with similar structures. The preparation of thermotropic liquid crystalline poly (aryl ether ketone)s has shown promise in improving the processibility of normal poly (aryl ether ketone)s^[9]. Many investigations have been reported on the relationship between their phase behavior and structures by using differential scanning calorimetry (DSC), wide angle X-ray diffraction, POM as well as transmission electron microscope (TEM)^[10-12]. However, a little work on their rheological behavior was reported^[13]. The present paper covers the rheological behavior of a thermotropic liquid crystalline poly (aryl ether ketone) and describes a shear-induced stabilization of the nematic phase.

Experimental

Material Preparation

The thermotropic liquid crystalline poly (aryl ether ketone) copolymer was prepared by reacting mesogenic 4,4'-biphenol, crystal-disrupting comonomer tert-butylhydroquinone with 1,4-difluorobenzophenone in tetramethylene sulfone in the presence of anhydrous potassium carbonate. The copolymer, referred to as DB3, with 30% of biphenol molar moiety was employed in the present work. The copolymers with other biphenol moieties showed more ordered smectic phase, which made the rheological properties complicated and they will be reported in a separate paper. The details of the synthesis of the copolymer were described in a literature ^[14] and also in a previous paper of ours ^[11]. It has a ¹⁹F NMR-based number average molecular weight of 7000 and its structural formula is shown as:



Instrument

The thermal transitions of DB3 were measured on a Perkin Elmer DSC-7 differential scanning calorimeter. The DSC scan showed that the thermal transitions of DB3 were a nominal melting transition at 325 °C and an isotropization transition around 395 °C. DB3 was thermally stable with a decomposition temperature above 500 °C in nitrogen at a 5% weight loss, as determined by means of a thermogravimetric analyzer (Perkin Elmer TGA7).

The rheological measurements were conducted on an rheometrics rheometer. The polymer samples were subject to steady shear flow.

Results and Discussion

Polymer DB3 has a relatively broad mesophase temperature region of 70 °C and an accessible clearing point. This unique feature as well as the excellent thermal stability with decomposition temperature much higher than its isotropization temperature enables us to perform rheological measurements in the temperature region covering the isotropization transition. In contrast many commercially available thermotropic liquid crystalline polyesters have inaccessible isotropic transition temperatures because they decompose before reaching their clearing temperatures.

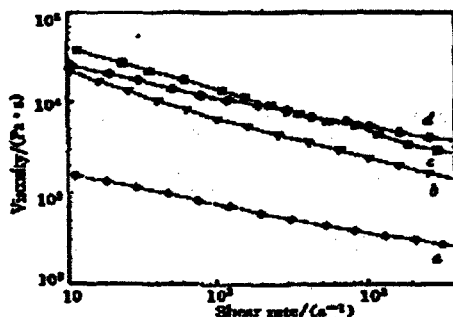


Fig. 1 Shear rate dependence of the viscosity of DB3 at different temperatures. a. 350 °C; b. 390 °C; c. 400 °C; d. 410 °C.

Figure 1 shows the flow plots of DB3 at different temperatures and different shear rates. The temperatures were chosen to cover the nematic phase, the transition region as well as the isotropic phase based on the DSC results. One can find from Figure 1 that the shear rate dependences of the viscosity at different temperatures are quite similar, indicating no obvious phase transition occurring with increasing temperature. However, it is evident that polymer DB3 displayed a viscosity more than one order of magnitude lower in the nematic region than in the temperature regions reaching the clearing point or above it. It is interesting to note that the viscosity plots at 400°C and 410°C crossed over with each other, with a viscosity at 400°C slightly higher or lower, depending on the shear rates. The above abnormal viscosity order compared to normal polymer melts could be attributed to the formation of biphasic below the clearing temperature. Before the sample became fully isotropic, nematic and isotropic phases already coexisted. In other words, some molecules with relatively lower molecular weights became isotropic and entered the nematic phase. There has been experimental evidence showing that the polymers with low molecular weights have lower clearing points. The interesting viscosity variation was reported for another TLCP^[15].

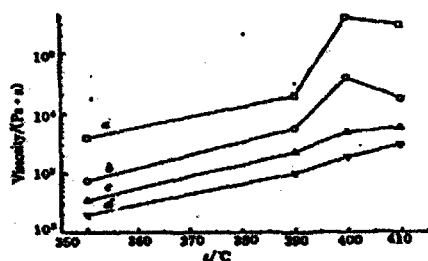


Fig. 2 Temperature dependence of the viscosity of DB3 at different shear rates. a. 10 s^{-1} ; b. 10^2 s^{-1} ; c. 10^3 s^{-1} ; d. $4 \times 10^3 \text{ s}^{-1}$.

Figure 2 displays the temperature dependence of viscosity at different shear rates based on the viscosity data in Figure 1. The results at shear rates of 10 s^{-1} , 10^2 s^{-1} , 10^3 s^{-1} and $4 \times 10^3\text{ s}^{-1}$ were plotted. Generally, the viscosity increases with increasing temperature. However, at the comparatively lower shear rates of 10 s^{-1} and 10^2 s^{-1} , the viscosities showed a maximum at 400°C , above which the shear viscosity decreased. It means that the viscosity may obey the Arrhenius relationship at temperatures above 400°C . Usually, the viscosity increases with increasing temperature in biphasic region. Here, the broad biphasic temperature interval indicate a relatively wide molecular weight distribution of the sample as the result of solution condensation in the sample preparation. The temperature at which the maximum viscosity appears is believed to be the transition temperature from nematic to isotropic, which agrees with the isotropization temperature from the DSC scan within experimental uncertainties.

At a higher shear rate of 10^3 s^{-1} , the viscosity maximum was found to appear at a much higher temperature as there was a viscosity plateau from 400°C to 410°C . At a shear rate of $4 \times 10^3\text{ s}^{-1}$, the viscosity continually increased with increasing temperature and no viscosity maximum was observed in the temperature range investigated. It means that viscosity maximum would presumably exist at an even higher temperature. That the temperature at which the viscosity maximum appears shifts to higher ones with increasing shear rate reveals a shear-induced mesophase stabilization of this thermotropic liquid crystalline polymer. That is, the nematic phase was maintained in a broader temperature region, which reflected the molecular orientation of liquid crystalline polymer under the applied shear flow. In fact, the similar complex shear rate dependence of viscosity for an all-aromatic thermotropic polyester with a helical chain conformation was reported^[16].

The above observation was believed to be the first steady rheological investigation on thermotropic liquid crystalline poly (aryl ether ketone) and to be of importance to the process of this material.

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帶有側基的聚芳醚酮共聚物中向列相的剪切诱导稳定性的研究