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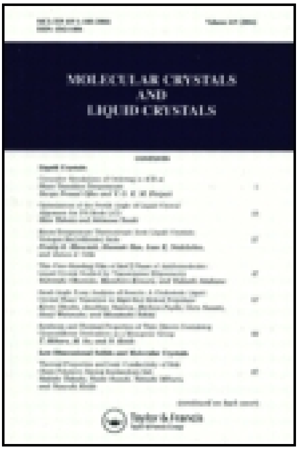

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RHEOLOGY OF A LYOTROPIC POLYMER LIQUID CRYSTAL OF RODLIKE POLYMERS AND MAIN-CHAIN THERMOTROPIC LIQUID-CRYSTALLINE POLYMERS

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Abstract Dynamic viscoelastic properties of main-chain thermotropic liquid crystalline copolymers random copolyesters (PHB/PET) at different temperatures have been investigated. The form of the viscoelastic functions depends on both temperature and the composition ratio of copolymers. It was cleared that in certain temperature region, the viscoelastic behaviors for random copolyesters with optimum composition ratio were quite similar to those for a lyotropic polymer liquid crystals of PBG.

INTRODUCTION

Liquid crystal is one of states, which exhibits both fluidity in liquid and optical anisotropy in solid. The flow curve of most liquid crystals in the bulk has been able to be characterized by three region flow curve[1] schematically shown by a solid curve in Figure 1 ; Region I (shear thinning region) where viscosity decreases with increasing shear rate at lower shear rate, Region II (Newtonian region) where viscosity does not depend on shear rate, and Region III (shear thinning region) where viscosity decreases again with increasing shear rate at higher shear rate. For example, thermotropic liquid crystals of low molecular weight molecules[2,3] and lyotropic polymer

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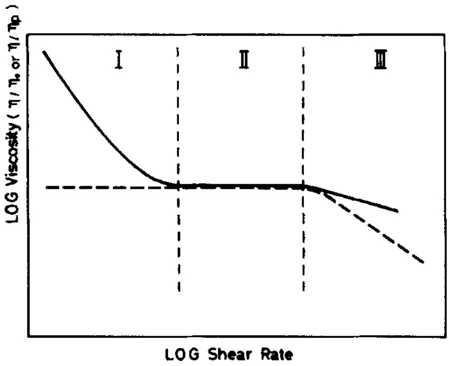

FIGURE 1. Schematic representation of the shear rate dependence of viscosity for liquid crystalline polymers.
Solid line : for liquid crystalline phase
Broken line : for isotropic phase

liquid crystals[4,5] of rodlike polymers gave the three region flow curves, though the feature of a curve in Region I is affected by the thermal, shear history experienced by a sample, and somewhat wall effects. The data for low molecular weight liquid crystals reported by Porter and Johnson[6,7], Fisher and Fredrickson[8] show Region I and II. Measurements of wider shear rate range show Region III, even for low molecular weight liquid crystals[9]. Since these materials described above are considered to be composed of single liquid crystalline phases, it seems that the three region flow curve can be considered to be seen generally for liquid crystals in the bulk, regardless of the molecular dimension, i.e. low molecular weight molecules or macromolecules. As for main-chain thermotropic liquid crystalline copolyesters at their liquid crystalline temperature, however, patterns of flow curves reported so far[10-12] sometimes were not three region pattern like a solid curve in Figure 1. They were lacking in region II

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even if the copolymer has the most suitable composition for the formation of liquid crystalline phase. Moreover, there are some differences among results obtained for samples with the same composition[10-13].

One of possible reasons why lacking in Region II might be the lower degree of randomness in copolymers, resulting in a copolymer containing blockpolymer parts. Many factors may be also responsible for the latter in complicated manners. They include thermal degradation and oxidation of a sample and the change in the degree of randomness on the steady rheological measurements. Taking above consideration into account, dynamic viscoelastic measurements (which may be carried out in shorter time) have been carefully performed on the copolyesters with complete randomness ascertained by NMR studies and the results obtained have been compared with those of a lyotropic nematic polymer liquid crystals of rodlike polymers. Here, we use the term "Polymer Liquid Crystals", only when the polymer is wholly liquid crystalline state.

RHEOLOGICAL PROPERTIES OF A LYOTROPIC NEMATIC POLYMER LIQUID CRYSTAL

In the polymer liquid crystalline systems of rodlike molecules, each molecule plays the same role as that of small molecules of liquid crystals and their textures are also quite similar to those observed in small molecular weight liquid crystals, though there remains a problem of distribution in the length of rods. Therefore, among available systems, the polymer liquid crystals of rodlike molecules can be considered to be one of polymer liquid crystals most analogous to low molecular weight liquid

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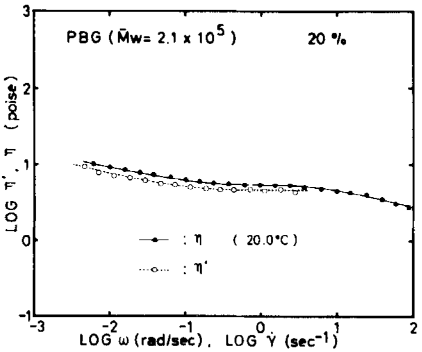

FIGURE 2. Comparison between steady-flow viscosity and dynamic viscosity for an anisotropic solution of PBG.

crystals. Preceding to the results on dynamic measurements for copolyesters, viscoelastic properties[14] of nematic polymer liquid crystals of rodlike molecules done by ourselves will be briefly introduced. In Figure 2 the dependence of steady-flow viscosity η (poise) on shear rate $\dot{\gamma}$ (sec^{-1}) and dynamic viscosity η' on angular frequency ω are shown with logarithmic scales.

The sample is a 20 wt% solution of PBG (an equimolar mixture of L and D enantiomers of poly-γ-benzyl-glutamate) in *m*-cresol. The concentration is above B-point and the solution is in nematic phase at room temperature. As shown in the Figure, dynamic viscosity and steady-flow viscosity have almost the same feature against angular frequency and shear rate, respectively. The results may suggest that the dynamic viscosity would be comparable to steady-flow viscosity, on condition that $\dot{\gamma} = \omega$ as reported by Kiss and Porter before[4]. Cox-Merz experimental law[15] seems to hold qualitatively for these systems.

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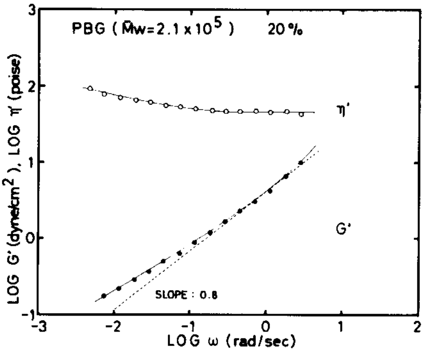

FIGURE 3. Angular frequency dependence of dynamic modulus G' and dynamic viscosity η' for an anisotropic solution of PBG.

Figure 3 shows the dependence of dynamic modulus G' and dynamic viscosity η'on ω. η' curve is composed of Region I and Region II in Figure 1 over the angular frequency range studied. On the other hand, the tendency of decreasing G' curve becomes weak with decreasing angular frequency and it seems that G' might become less dependent of ω at lower angular frequency, in contrast with conventional polymers and isotropic solutions of rodlike polymers for which G' are proportional to ω^2 in the flow region.

RHEOLOGICAL PROPERTIES OF MAIN-CHAIN THERMOTROPIC NEMATIC LIQUID CRYSTALLINE COPOLYESTERS

Samples used are copolymers of polyethylenetelephthalate (containing a flexible part) and *p*-oxybenzoate with molar ratios of the units being 60/40 and 40/60 (UT-4 and UT-6 respectively, hereafter). Both copolymers, UT-4 and UT-6, being of almost ideal randomness, was ascertained by 400-

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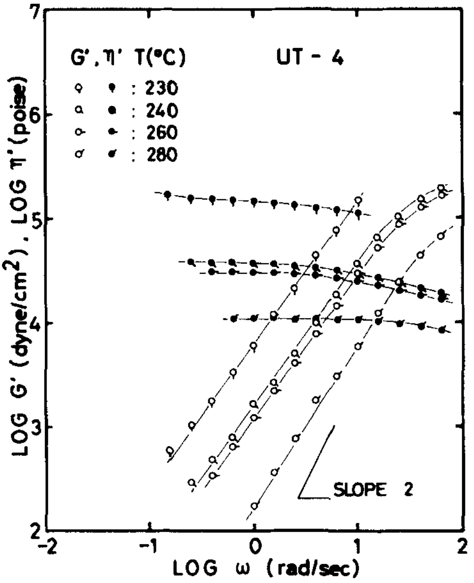

FIGURE 4. Angular frequency dependence of dynamic modulus G' and dynamic viscosity η' at different temperatures for UT-4.

MHz proton NMR spectrum studies.

Viscoelastic measurements have been performed on the samples described above with a cone and plate type rheometer at different temperatures (230°C-290°C) and dynamic modulus G' (dyne/cm^2) and dynamic viscosity η' (poise) were determined as a function of angular frequency ω (rad/sec). The environmental chamber was filled with dry nitrogen during experiments and sample pellets after drying were directly installed between cone and plate, followed by immediate measurements to avoid thermal degradation of a sample.

In Figure 4 the results of dynamic viscoelastic

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measurements at various temperatures obtained for UT-4 are presented with the same way in Figure 3. The contour of η' curve at 280°C is similar to that of broken line in Figure 1 and G' is almost proportional to ω^2. These viscoelastic behaviors imply that the system at 280°C is in nearly isotropic state, which is also supported by the microscopic observation between crossed polars. η' curve moves upwards with decreasing temperature. η' curves at 260°C and 240°C have the same feature as that at 280°C and Region II disappears at 230°C, that is, dynamic viscosity decreases monotonously with increasing angular frequency. The slope of G' curve below 260°C is smaller than that at 280°C. The smaller slope may be concerned with the emergence of anisotropic phase. Surely, anisotropic phase was confirmed by microscopic observation between crossed polars below 260 °C. Though Region I which will be characteristic of liquid crystals, was not seen at 260°C and 240°C in the angular frequency range studied, measurements at lower angular frequency might reveal the existence of Region I.

Figure 5 shows dynamic modulus and dynamic viscosity as a function of angular frequency at different temperatures for UT-6 containing more rigid parts than UT-4. It is evident from this Figure that the phase transition process of the sample UT-6 can be pursued by the form of viscoelastic functions. The shape of η' curves at 260°C, 280°C and 290 °C quite resembles to that of a solid line in Figure 1. They are just the three region flow curves on the assumption that dynamic viscosity should be comparable to steady-flow viscosity described above(Figure 2). On the other hand, dynamic modulus decreases with decreasing angular frequency at these temperatures. The trend of

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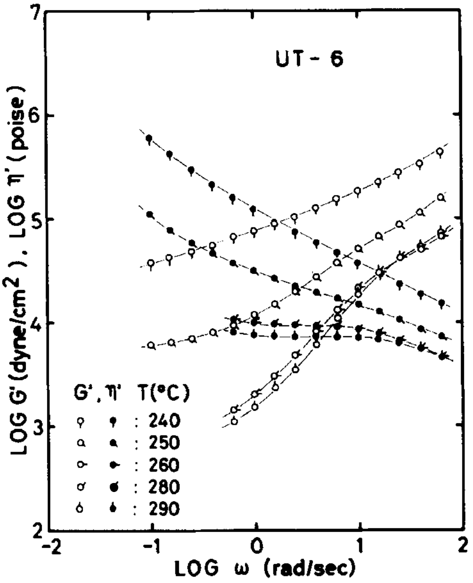

FIGURE 5. The same as in the Figure 4, for UT-6.

variation of G' with angular frequency is also reminiscent of PBG system shown in Figure 3. Comparing Figure 5 with Figure 3, it is clear that G' of UT-6 and PBG varies with ω in the same manner i.e. showing lower slope except for higher angular frequency region. At lower temperatures, η' curve does not have Region II and dynamic viscosity decreases monotonously with angular frequency, as observed in the case of UT-4 at 230°C. G' increases gradually with angular frequency and values of G' in itself is rather high as a whole over the angular frequency region investigated. These results obtained by viscoelastic measurements indicate that the state of the system should change from wholly liquid crystalline phase to an intermediate state (partially liquid crystalline state) which may be composed

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of both liquid crystals and crystallites. The observation of three region flow curve seems to be one of the evidence that a system is being wholly liquid crystalline state.

Viscoelastic properties may reflect the effects of difference in composition on liquid crystallinity. Though UT-6 contains larger amount of rigid parts than UT-4, η' in liquid crystalline temperature for UT-6 is lower than UT-4. These facts support the idea that there is the most suitable composition ratio of copolymers for the formation of liquid crystals and viscosity may take minimum at the composition[10]. According to the consideration, UT-4 at 240°C and 260°C might be in biphase. Moreover, the range of liquid crystalline temperature is wider for UT-6 than for UT-4, which indicates that UT-4 may not assume a wholly liquid crystalline phase, but an apparent liquid crystalline phase composed of both liquid crystalline phase and isotropic phase, because the composition ratio of UT-4 is less desirable for the formation of liquid crystalline state than that of UT-6 as mentioned above.

CONCLUSION

From viscoelastic measurements on main-chain thermotropic liquid crystalline polymers of random copolyesters under the conditions which are the most suitable for the formation of liquid crystalline state, the three region flow curve like the solid curve shown in Figure 1 is reduced and the form of viscoelastic functions obtained was similar to those of lyotropic nematic polymer liquid crystals of PBG. These results suggest that there is no fundamental difference in the rheological behaviors between lyotropic and thermotropic polymer liquid crystals so long as they are to be wholly polymer liquid crystalline state.

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