Effect of monomer composition on the rheological properties of poly(p-oxybenzoate-co-ethylene terephthalate)s

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Summary
    Effect of monomer composition on the dynamic viscoelastic properties and the steady flow properties of thermotropic liquid crystalline poly(p-oxybenzoate-co-ethylene terephthalate)s in the fluid state have been investigated as compared with the isotropic melt of the copolyester including 28 mol% p-oxybenzoate unit (POB). The liquid crystalline copolyesters show the rheological transition temperature, which increases with increasing the content of POB unit. Above the transition temperature, all the thermotropic copolyesters exhibit much higher compliance and much more shear-thinning behavior of the apparent viscosity than the isotropic melt of the non-liquid crystalline copolyester.

Introduction
    The authors have investigated the rheological properties of thermotropic liquid crystalline poly(p-oxybenzoate-co-ethylene terephthalate) of 60/40 mol ratio with respect to thermal history dependence (1,2), flow history dependence (3), dynamic viscoelastic properties (1), and steady flow properties (2). The principal conclusions are as follows.
    The copolyester shows the rheological transition based on the fusion of a minute amount of crystallites. The rheological properties below the transition temperature are markedly dependent on the thermal history, which can be explained in terms of formation of the crystallites and the supercooling effect. Above the transition temperature, the rheological properties are independent of thermal history, and are thermorheologically simple. It has been suggested that the characteristics of the rheological properties in the liquid crystalline state above the transition temperature are high compliance and marked shear-thinning of apparent viscosity.
    The present research has been carried out in order to confirm the above suggestion by using the copolyesters which are composed of different monomer ratio.

Experimental part
    The well-known poly(p-oxybenzoate-co-ethylene terephthalate)s which had been synthesized by Jackson et al. (4) from p-hydroxybenzoic acid (PHB) and poly(ethylene terephthalate) with the PHB content of 28, 50, 60, 70, and 80 mol% were used. These copolyesters are referred to as PHB28, PHB50, PHB60, PHB70, and PHB80, respectively. It has been verified that thermotropic liquid crystallinity and the copolyester containing 28 mol% PHB does not form a liquid crystalline phase. The weight-average

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molecular weight of PHB60 was 14000 (5). The inherent viscosity
was 0.56 dL/g for PHB28, 0.54 dL/g for PHB50, 0.68 dL/g for
PHB60, 0.78 dL/g for PHB70 using a mixed solvent of phenol/p-
chlorophenol/1,1,2,2-tetrachloroethane (25/40/35 by weight) at a
concentration of 0.1 g/dL and 25 °C. The copolyester of PHB80
was insoluble in the solvent, and showed a melt flow rate of 5.7
g/10 min at 325 °C under the condition defined by ASTM D-1238.
     Rheological measurements except for temperature sweep were
performed using a cone-plate of 50 mm in diameter and a cone
angle of 0.04 rad. Dynamic measurements were carried out by
imposing a small strain amplitude of 5 % to maintain the linear
response. Temperature sweep measurements were carried out using
parallel plates of 50 mm in diameter at a heating and cooling
rate of approximately 1 °C/min.

Results and discussion
Temperature dependence of dynamic properties
     It has been shown by the authors that the temperature de-
pendence curves of dynamic viscoelastic properties of PHB60 show
a well-defined transition based on the melting of a minute amount
of crystallites, i. e. a crystal-nematic transition (1).
     Results of temperature dependence curves of dynamic viscoe-
lastic properties are shown in Figs. 1 and 2 for PHB50 and PHB70,
respectively. The heating measurement for PHB50 was carried out
from 200 °C after 170 °C for 10 min, this having been proceeded
by 300 °C for 5 min. The storage modulus (G') and the dynamic
loss modulus (G") sharply decrease crossing each other at about
220 °C, and gradually decrease above 240 °C with increasing tem-
perature. The cooling measurement was done from 270 °C. The G'
and G" gradually increase with decreasing temperature. Conse-
quently, the G' and G" curves in cooling process give values
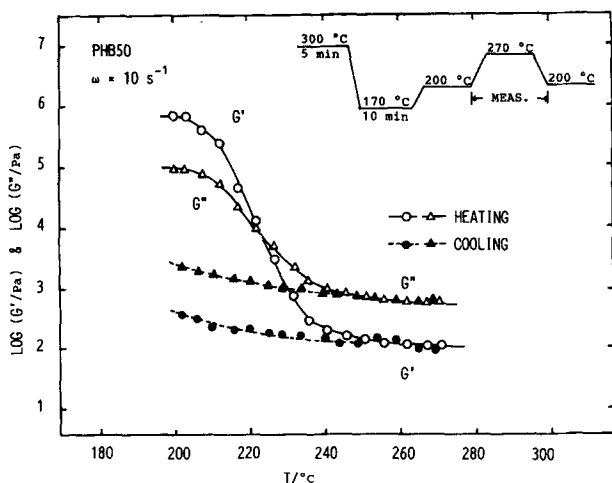smaller than those in heating process below 240 °C, although the

Fig. 1. Temperature dependence of the dynamic viscoelastic
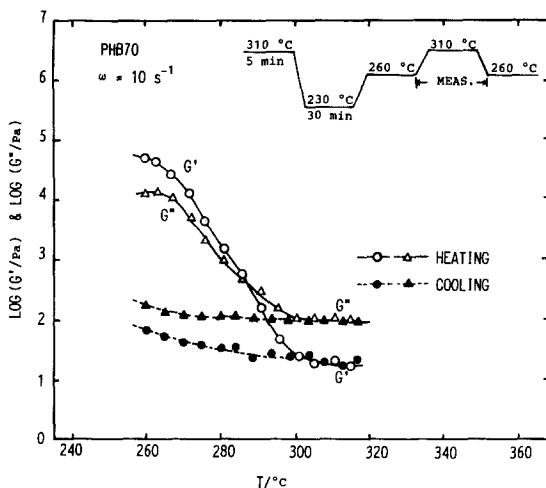properties of PHB50 at 10 s^{-1}. Open marks; in heating, closed
marks; in cooling.

Fig. 2. Temperature dependence of the dynamic viscoelastic properties of PHB70 at 10 s^{-1}. Open marks; in heating, closed marks; in cooling.

both curves nearly agree with each other above 240 °C.

The heating measurement for PHB70 was carried out from 260 °C to 310 °C after holding at 230 °C for 30 min, which was proceeded by 310 °C for 5 min. The cooling measurement was carried out after the heating measurement from 310 °C to 260 °C as shown in Fig. 2. The G' and G" sharply decrease, crossing each other with inflection points at around 285 °C in heating, while in cooling they gradually increase, giving a result much different from that obtained in heating below 300 °C.

The behavior of temperature dependence curves of G' and G" for PHB50 and PHB70 can be explained by the melting of a small amount of crystallites (crystal-nematic transition) and very slow crystallization of the crystallites, similar to PHB60 (1). The copolyester of PHB80 in the heating and cooling curves of dynamic properties showed much difference below 320 °C. It can be concluded that the crystal-nematic or melting transition temperatures of PHB50, PHB70, and PHB80 are 240, 300, and 320 °C, respectively.

Melting temperarure vs. monomer composition

In Fig. 3, the melting temperature determined for the copolyesters in a previous section is plotted against PHB content along with the melting point for poly (ethylene terephthalate) and PHB28 (4,6). It is clearly shown that the copolymerization results in the depression of the melting temperature. This behavior is consistent with result of almost random sequence for the copolyester chain, analyzed by NMR (4,7-8). The rheological measurement shows higher values of the melting transition than the DSC measurements (4,6,9-10). This is partly caused by a difference in where the melting transition was measured, i. e. the ending position for the rheological measurements and the top of an endotherm peak for usual DSC. Furthermore, there have been large differences in the scores of temperatures reported for the melting transition measured by DSC, probably because the endo-
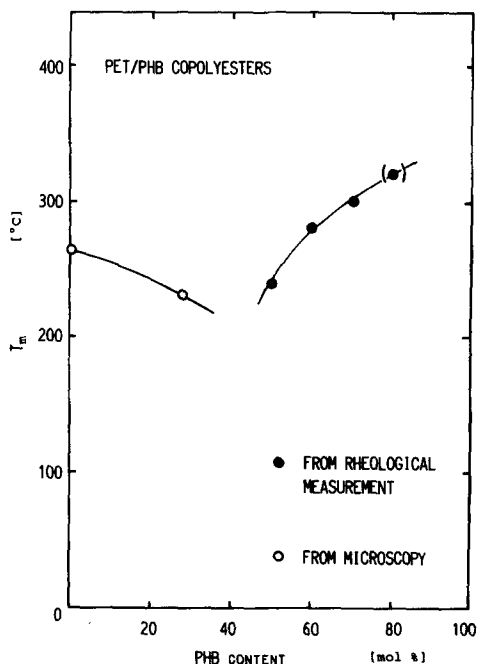
Fig. 3. The plot of melting temperature (T_m) against the content of p-hydroxybenzoic acid (PHB). Open marks; from microscopic observation equipped with a hot stage, closed marks; from rheological transition.
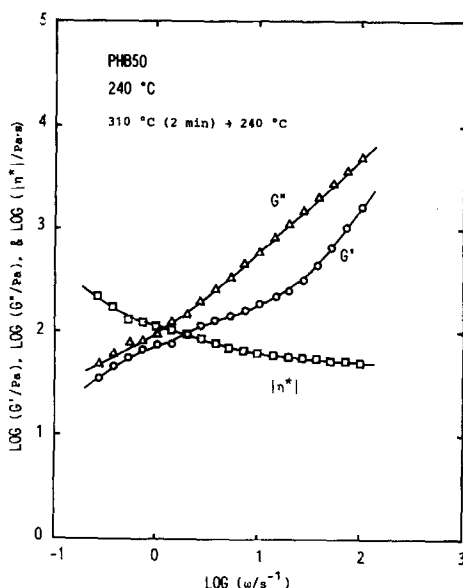
Fig. 4. Frequency dependence of the dynamic viscoelastic properties of PHB50 at 240°C. The sample was holded at 310°C for 2 min prior to the measurement.

therm is weak and broad. On the contrary, the melting transition can be determined clearly from the temperature dispersion curves of the rheological properties.

Dynamic viscoelastic properties
    The frequency dependence of dynamic viscoelastic properties was measured for PHB50 and PHB70 at 240 and 300 °C, respectively, as shown in Figs. 4 and 5. The copolyester of PHB50 shows the behavior similar to PHB60 (1,2), while the behavior of PHB70 is quite different from that of PHB60. For example, the copolyester of PHB50 shows the shear-thinning behavior of absolute value of complex viscosity ($|\eta^*|$) with a narrow plateau region at about 2×10 s^{-1}, while PHB70 shows Newtonian viscosity up to 10 s^{-1}. Generally, the frequency dependence of $|\eta^*|$ cannot be directly related to the composition, because it is affected by many variables such as molecular weight and temperature. It has been pointed out by the authors (2) that the compliance vs. shear stress plot is not affected by the temperature measured. The authors (2) have suggested that thermotropic liquid crystalline polymer melts exhibit compliance ten times as high as isotropic polymer melts when compared at the same shear stress, based on the fact that the dynamic compliance (J') is independent of molecular weight for PHB60 compared at the same value of $|G^*|$
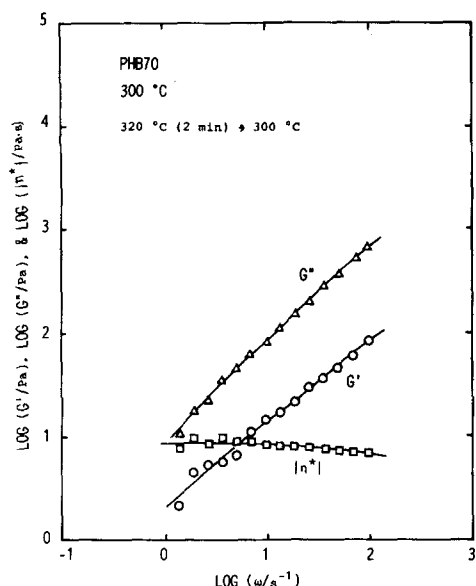
Fig. 5. Frequency dependence of the dynamic viscoelastic properties of PHB70 at 300 °C. The sample was holded at 320°C for 2 min prior to the measurement.
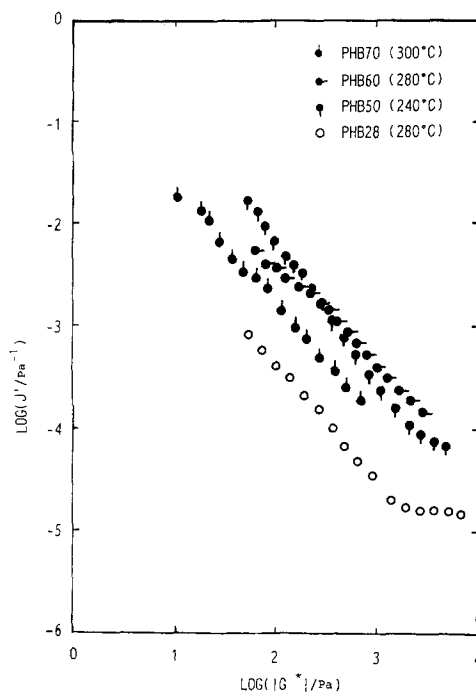

Fig. 6. The plot of storage compliance against absolute value of complex shear modulus for the thermotropic copolyesters of PHB50, PHB60, and PHB70 in the liquid crystalline state as compared with the isotropic melt of PHB28.

(11). Figure 6 shows the plot of J' against $|G^*|$ for PHB50 and PHB70 along with PHB60 and the isotropic melt of PHB28. Both PHB50 and PHB70 exhibit higher compliance than PHB28 as observed for PHB60.

Steady flow properties

Results of the shear rate dependence of shear stress (σ), first normal stress difference (N_1), and apparent viscosity (η) for PHB50 and PHB70 are shown in Figs. 7 and 8, respectively. The apparent viscosity exhibits marked shear-thinning in the both copolyesters. This behavior is not consistent with the frequency dependence of $|\eta^*|$ shown in the previous section. It is clear that the Cox-Merz rule (12) does not hold for the thermotropic liquid crystalline copolyesters.

Figure 9 shows plots of steady shear compliance (J_s) against shear stress (σ) for PHB50 and PHB70 along with PHB60 and the isotropic melt of PHB28. All copolyesters of PHB50, PHB60, and PHB70 in the liquid crystalline states indicate one order of magnitude higher compliance than the isotropic PHB28 melt. The value of J_s seems to increase with increasing the content of a rigid unit of p-hydroxybenzoic acid, which is in contrast to the result of dynamic compliance in a previous section.
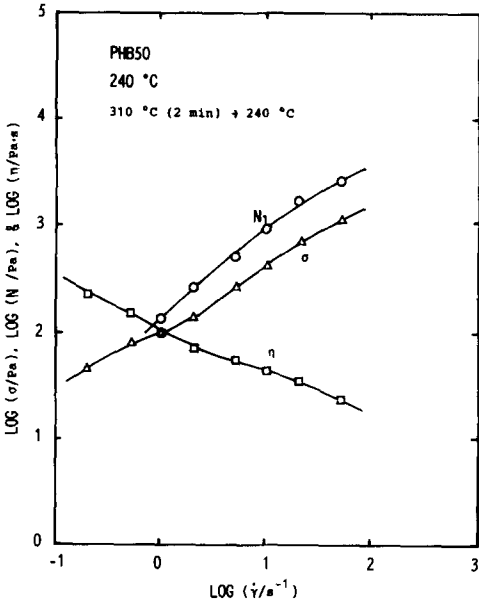
Fig. 7. Shear rate dependence of the shear stress, the first normal stress difference, and the apparent viscosity of PHB50 at 240 °C.
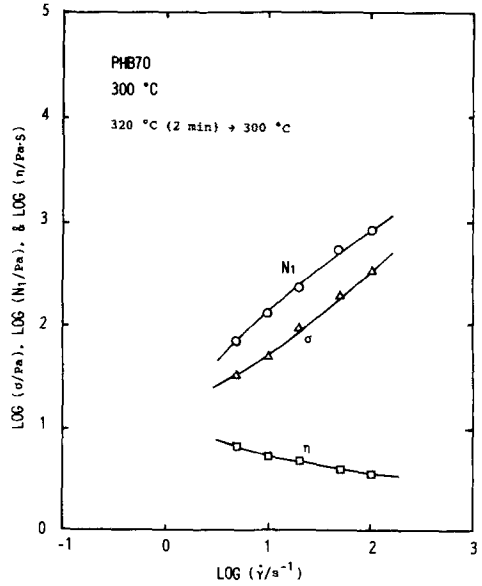
Fig. 8. Shear rate dependence of th shear stress, the first normal stress difference, and the apparent viscosity of PHB70 at 300°C.
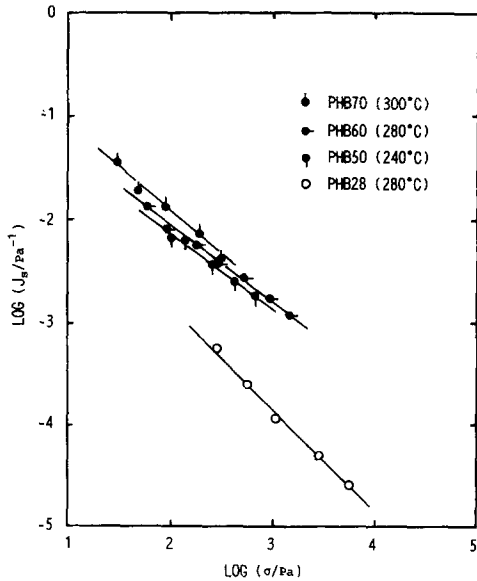

Fig. 9. The plot of steady shear compliance against shear stress for the thermotropic liquid crystalline copolyesters of PHB50, PHB60, and PHB70 as compared with the isotropic melt of PHB28.

Conclusions

The temperature dependence curves of dynamic viscoelastic properties of PHB50, PHB70, and PHB80 in heating and cooling have clearly indicated the rheological transition temperature caused by the melting of a minute amount of crystallites, as already observed for PHB60 (1).

The monomer composition dependence of the melting temperature is qualitatively consistent with the result of random sequence distribution indicated by NMR, for the backbone of the copolyesters.

Some characteristics of viscoelastic properties in the liquid crystalline states of the copolyesters have been confirmed as follows.

(a) The Cox-Merz rule does not hold for the "as-received" sample.
(b) The dynamic and steady shear compliances are much higher than those of isotropic melts.
(c) The apparent viscosity in steady shear flow exhibits marked shear-thinning behavior from low shear rates.

The high compliance and the marked shear-thinning behavior imply that relaxation times of the thermotropic liquid crystalline copolyesters are very long.

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