Reduced stress-optical coefficient of polycarbonate by antiplasticization

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Abstract

We have investigated the effect of antiplasticization on the stress-optical behavior of polycarbonate (PC) containing terphenyls (tPh) and di(2-ethylhexyl)adipate (DEHA). Addition of the three tPhs (*p*-, *o*-, and *m*-tPh) and DEHA at contents of 5–10 wt % increases the tensile storage modulus (E') of PC owing to the antiplasticization effect. In particular, *p*-tPh increases E' more than the other additives, suggesting that the rod-like shape matches the free volume of PC in the glassy state. The three tPh isomers improve the glassy birefringence of PC while DEHA does not change the glassy birefringence, which corresponds to the polarizability anisotropy. The stress-optical coefficient, a ratio of stress and birefringence, of PC decreases with increasing additive content in order of *p*-tPh >> *o*-tPh > *m*-tPh ≈ DEHA. This result is agreement with a restricted rotational motion of additive molecule in PC, which is observed in dynamic mechanical and birefringence data.

Keywords: additives; mechanical properties; optics; polycarbonates; modulus

1. Introduction

It is necessary to control the optical properties of polymers used for optical devices, such as liquid crystal displays (LCDs)[1] and pickup lens.[2] For example, it is desirable to reduce the birefringence generated by external forces in the glassy state for optical films because high birefringence causes low performance, such as color heterogeneity in LCDs. According to the stress-optical rule (SOR),[3,4] the birefringence Δn of glassy polymers is proportional to the tensile stress σ:

$$\Delta n = C_G \sigma \tag{1}$$

where C_{G} is the stress-optical coefficient (SOC) in glassy state, which is related to the polarizability anisotropy of the molecule. Dividing both sides by the tensile strain ε gives the following equation for the tensile mechanical and optical properties:

$$O = C_G E \tag{2}$$

where E is the tensile elastic modulus and O is the strain-optical coefficient, which is defined as the ratio of Δn to ε.

Aromatic polymers with strong polarizability anisotropy, such as polycarbonate (PC,

Fig. 1) and polyethylene terephthalate, exhibit high glassy birefringence because of their large SOC (C_G). In applications for optical devices, the value of C_G is used as an index parameter to compare the birefringence property of polymers because of the proportionality of birefringence and stress represented by eq 1. For example, birefringence of laminated films is generated by the difference in shrinkage stress between neighbor layers.

In general, polymer blending[5] and copolymerization[6] with other components that have the opposite sign of the birefringence are used to fabricate zero or low birefringent materials. Koike and co-workers synthesized zero birefringent polymers at glassy sate by blending acrylic polymer and anisotropic small molecule[5], and copolymerization of four acrylic monomers.[6] However, these methods are not applicable to reduce the birefringence of aromatic polymers, such as PC, because the positive birefringence is too large to compensate the negative value of the additive component. For PC, C_G (in the glassy state) is around 100×10^{-12} Pa^{-1}, which is one or two orders of magnitude larger than those of other synthetic polymers, such as poly(methyl methacrylate) (PMMA) and PS. The modification of chemical structure in a repeating unit of PC is more effective to reduce C_G, although the elastic modulus decreases.[7] Therefore, other technique based on the stress-optical relation should be considered to reduce C_G of PC.

In previous papers,[8,9] we reported that the tensile modulus of PC in the glassy state can be enhanced from 1.8 to 2.5 GPa by adding 5 wt % *p*-terphenyl (*p*-tPh, Fig. 1) without decreasing the optical transparency because of the good miscibility with the matrix polymer. The phenomenon is called antiplasticization. From thermal expansion data, we concluded that the improvement of the elastic modulus is associated with the restricted local motion of the PC chain caused by filling of the free volume by the *p*-tPh molecule. For the glass-to-rubber transition region, the additive molecule decreases the glass transition temperature (T_{g}).

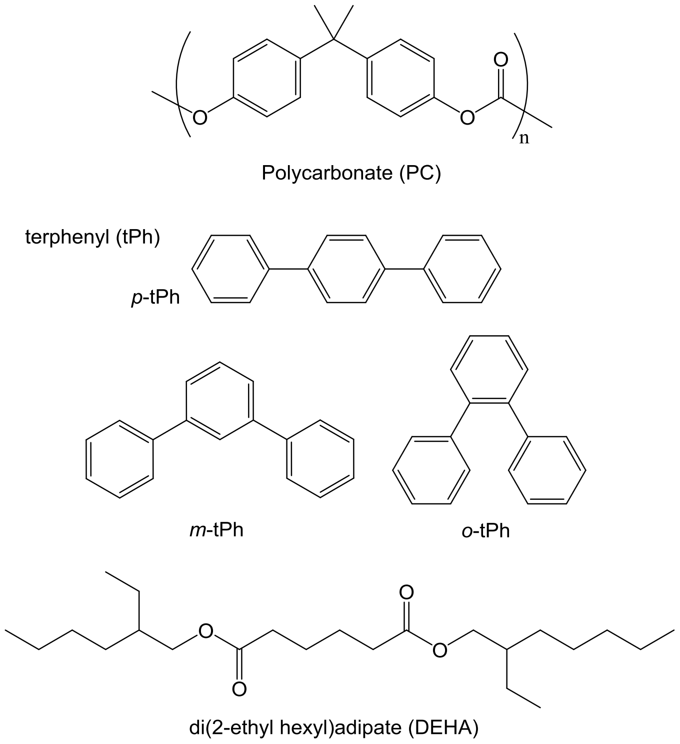

Figure 1. Chemical structures of PC, *p*-, *o*- and *m*-tPh, and DEHA.

Because C_{G} is inversely proportional to E as represented in eq 2, enhancement of the elastic modulus might decrease the optical value under a constant O. Therefore, it can be predicted that the antiplasticization phenomenon might reduce the optical anisotropy of polymers with large C_G. Based on this idea, in this study, the effect of additive molecules on C_G of PC was investigated. Additionally, the contribution of additive molecules to the glassy birefringence was investigated by mixing the tPh isomers (*p*-, *o*-, and *m*-tPh) and a low birefringent molecule with the matrix PC.

2. Experimental Section

2.1 Sample preparation

PC (bisphenol-A type, Fig. 1) was supplied by Teijin Ltd. (Tokyo, Japan). The weight- and number-average molecular weights (M_w and M_n) of PC determined by gel-permeation chromatography (GPC, HLC-8020 Tosoh, Japan) with a polystyrene standard are 9.7×10^4 and 1.9×10^4, respectively. The three tPh isomers (*p*-, *o*-, and *m*-tPh, Fig. 1) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan), and di(2-ethylhexyl)adipate (DEHA, Fig. 1) was supplied by New Japan Chemical Co., Ltd. (Japan). These additive molecules were used as antiplasticizers without further purification. The blend samples of PC and tPh were prepared using a 30 cc batch-type internal mixer (Labo-plastmil, Toyoseiki, Japan) at 240 °C for 3 min with a blade rotation speed of 30 rpm. After being kept in a vacuum oven at 80 °C for 4 h, the mixed samples were compressed into sheets with a thickness of 300 μm at 240 °C for 3 min under 10 MPa by a compression-molding machine (Table-type-test press SA-303-I-S, Tester Sangyo, Japan) and then cooled at 25 °C for 3 min.

2.2 Measurements

Dynamic mechanical analysis of the annealed and stretched films was performed to determine the tensile storage and loss moduli (E' and E'', respectively) at 10 Hz as a function of temperature from −150 to 180 °C at a heating rate of 2 °C min^{-1} using a tensile oscillatory rheometer (DVE-E4000, UBM, Japan).

Dynamic mechanical and optical analysis was performed to determine the C_G at 10 Hz from 25 to 150 °C using the DVE-E4000 tensile oscillatory rheometer equipped with an optical system, as reported by Inoue et al.[10] The wavelength (λ) for birefringence is 633 nm in this study. The birefringence and dynamic elastic modulus were recorded as a function of time by applying an oscillatory strain. The strain-optical coefficient (O) was evaluated at various temperatures by

$$O = \Delta n / \varepsilon \tag{3}$$

3. Results and Discussion

3.1 Dynamic mechanical properties of the PC/additive blends

Fig. 2 shows the temperature dependence of the storage and loss moduli (E' and E'') of PC and PC/additive (*p*-, *o*-, and *m*-tPh, and DEHA) blends with additive contents of 5 and 10 wt %. The α relaxation peak associated with the glass transition, where E' sharply decreases from 10^9 to 10^6 Pa, is observed for all of the blends and shifts to lower temperature with increasing additive content. At this point, the additives plasticize the matrix PC. The glass transition temperature T_g, which is defined as the peak temperature in E'', is plotted as a function of the additive content in Fig. 3. The reduction of T_g by *p*-tPh is smaller than that of the other additives. Because an attractive interaction between the components increases T_g of polymer blends,[11] the T_g difference in Fig. 3 indicates that *p*-tPh is more tightly confined in the PC matrix than *o*-tPh, *m*-tPh, and DEHA. This is reasonable because rod-shaped *p*-tPh has a smaller free volume than disk-shaped *o*-tPh and *m*-tPh.

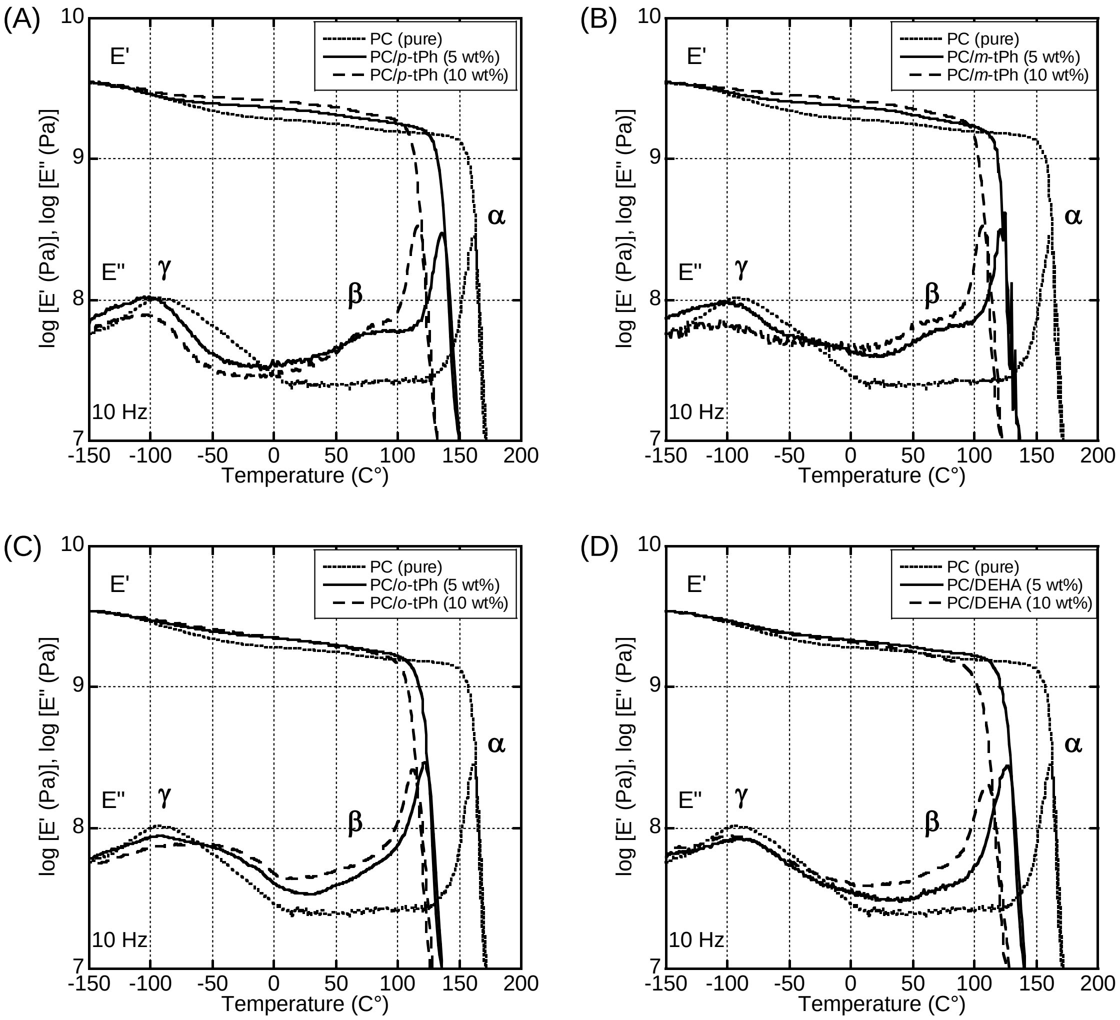

Figure 2. Temperature dependence of the storage and loss moduli (E' and E'') of the PC and PC/additive blends. (A) PC/*p*-tPh, (B) PC/*o*-tPh, (C) PC/*m*-tPh, and (D) PC/DEHA.

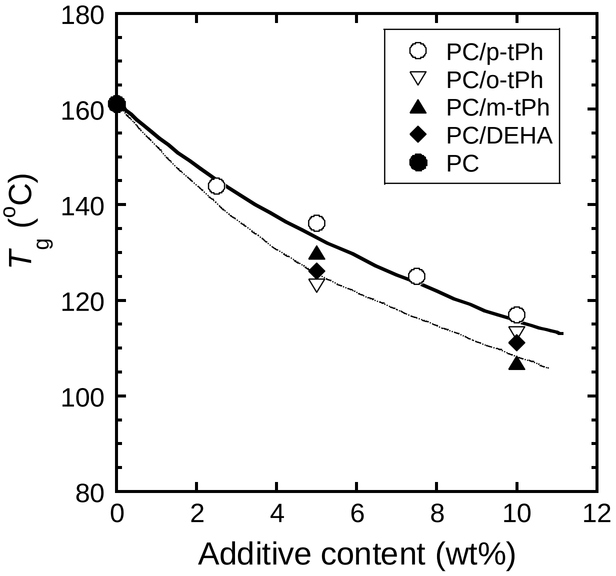

Figure 3. Glass transition temperature (T_g) of the PC/additive blends at various additive contents. Solid and broken lines are drawn for eye guides.

As shown in Fig. 2, the E' values of the blends from −50 to 50 °C are larger than those of bulk PC, meaning that all of the additives act as antiplasticizers for PC. The modulus enhancement originates from suppression of γ relaxation represented by E'' located at around −100 °C.[8] The *p*-tPh molecule fills the free volume of PC and suppresses local chain motion of PC represented by γ relaxation. For PC/*p*-tPh, the suppressed motion of PC is activated again above 50 °C, as shown by the shoulder peak in Fig. 2(A), which is called β relaxation. According to Belfiore et al.,[12] diluent molecules also exhibit cooperative motion with the local dynamics of PC in β relaxation.

Fig. 4 compares the additive effect on E' at 25 °C. The three tPh isomers (*p*-, *o*-, and *m*-tPh) equally increase E' of PC, while DEHA only slightly increases E'. This difference might originate from the chemical structures: tPh is composed of rigid phenyl groups, whereas DEHA has a flexible alkyl chain. As shown in Fig. 2, the γ relaxation peaks of the four blends are clearly different. The PC/tPh blends exhibit smaller γ peaks than bulk PC, indicating that the local motion of PC is restricted by addition of tPh. In contrast, the PC/DEHA blends show similar strength γ peaks to bulk PC, meaning that the local motion of PC is not suppressed owing to the flexibility of the DEHA molecule. Because the peak area of E'' is directly related to the decrease of E' with temperature, the increase of E' can be explained by the γ relaxation peak. The order of E' in Fig. 4 is almost in agreement with the order of γ peak suppression: *p*-tPh > *m*-tPh ≈ *o*-tPh >> DEHA.

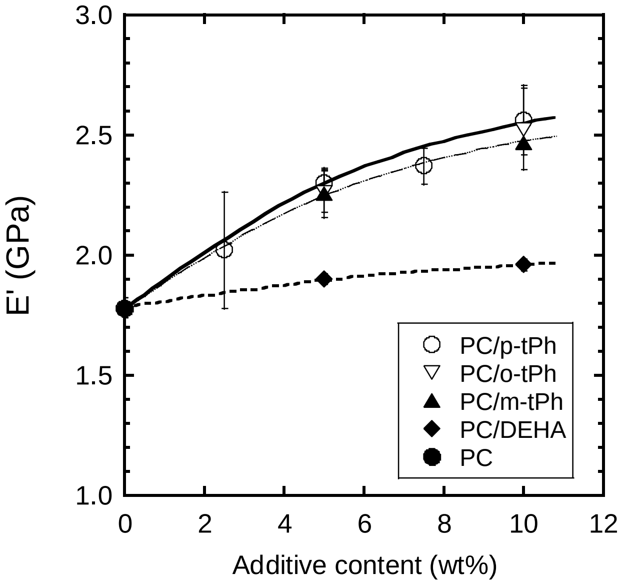

Figure 4. Storage modulus (E') of the PC/additive blends at 25 °C. The applied frequency is 10 Hz. Solid, dotted and broken lines are drawn for eye guides.

The reason why *p*-tPh improves the elastic modulus more than the other additives is related to filling of the free volume in the PC matrix. The molecular shape of *p*-tPh is rod-like whereas *m*-tPh and *o*-tPh are disk-like. In our previous reports for polystyrene (PS) blends,[13,14] the additive dynamics become more restricted by PS segmental motion when the additive size is closed to the Kuhn segment size of PS. The Kuhn segment size of PC calculated from literature data[15,16] is approximately 2.1 nm, which is longer than the longitudinal lengths of *p*-tPh (1.4 nm), *m*-tPh (1.2 nm), and *o*-tPh (0.81 nm). From the viewpoint of the size difference and molecular shape, rod-like *p*-tPh more tightly packs in the PC matrix than disk-like *m*-tPh and *o*-tPh, resulting in the improvement of the elastic modulus in Fig. 4.

3.2 Glassy birefringence of the PC/additive blends

Because the birefringence in the glassy state is proportional to the strain with small deformation, the strain-optical coefficient (eq 3) can be used to discuss the glassy birefringence of the PC/additive blends. Fig. 5 shows the dependence of the additive content on the real part of O^* (O') at 25 °C. For the PC/tPh blends, O' increases with increasing additive content. In contrast, for the PC/DEHA blend, O' is almost constant. In this study, since the imaginary part of O^* (= O'') is much smaller than O', the absolute value of O^* (= O) approximately equals to O'.

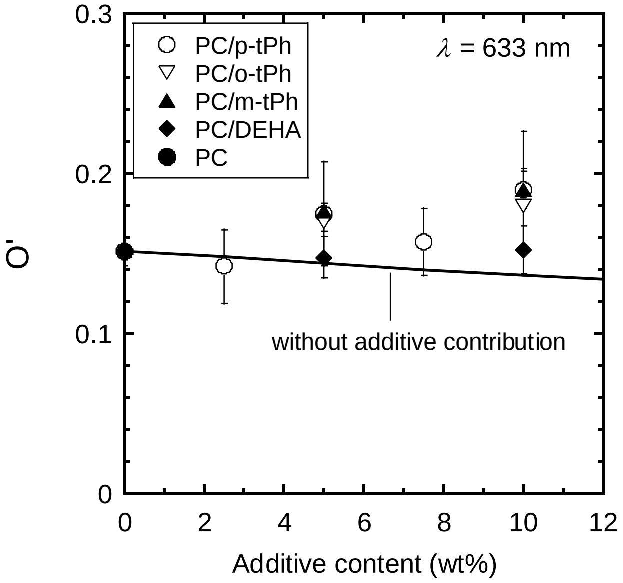

Figure 5. Real part of the complex strain-optical coefficient (O') of the PC/additive blends at 25 °C. The light wavelength is 633 nm and the applied frequency is 10 Hz. The solid line represents O' without additive contribution by using eq.5.

The glassy birefringence (Δn) of the PC/additive blends is the sum of two components:

$$\Delta n = \Delta n_{PC} + \Delta n_{add} \tag{4}$$

Dividing by the strain, the following equation for a strain-optical coefficient (O) is obtained:

$$O = O_{PC} + O_{add} \tag{5}$$

The glassy birefringence of vinyl polymers originates from the polarizability anisotropy of the repeating unit.[17] In particular, aromatic groups, such as biphenyl and naphthalene groups, increase the birefringence because of their large polarizability anisotropy. From the chemical structures shown in Fig. 1, the tPh molecule, which consists of three phenyl groups, has larger anisotropy than DEHA. Therefore, it is reasonable that the PC/tPh blends have higher O values than the PC/DEHA blend, as shown in Fig. 5. In addition, the increase of O with increasing tPh content can be explained by the lower number density of the phenyl group in PC than in tPh.

3.3 SOC of the PC/additive blends

Fig. 6 shows the SOC (C_G) of the PC blends at room temperature (25 °C) with various additive contents. All of the blends show suppression of C_G with increasing additive content. In particular, *p*-tPh has the greatest effect on reduction of C_G. As mentioned in sections 3.1 and 3.2, both E and O increase with increasing additive content, except for the PC/DEHA blend. As represented in eq 2, the changes of E and O must affect the C_G suppression. Although the simple additive rule is applicable for birefringence ($\propto O$) of PC blends as represented by eqs 4 and 5, it is inapplicable for stress ($\propto E$) because the glassy stress is affected by intermolecular and interaction between PC and additive molecule. Therefore, a theoretical equation for C_G using the additive concentration of PC blends cannot be introduced.

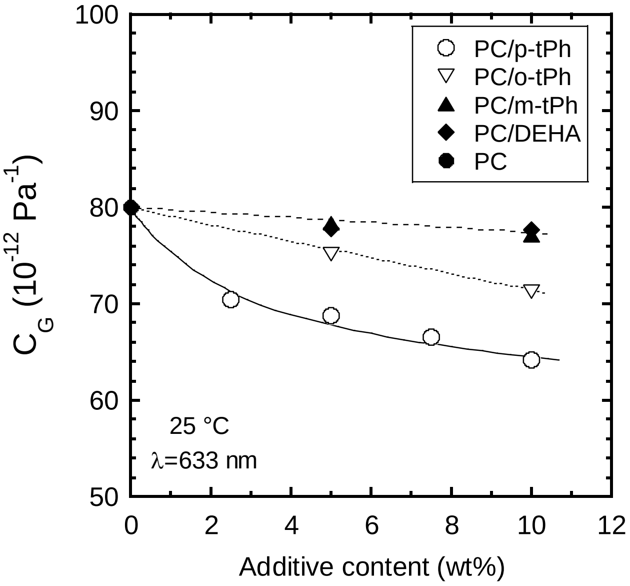

Figure 6. C_G of the PC/additive blends at 25 °C. The applied frequency is 10 Hz. The thick solid line shows C_G value in eq 6 without additive contribution. The three lines are drawn for eye guides.

In order to investigate the reduction of C_G for PC/additive blends as shown in Fig.6, the contribution of anti-plasticization to C_G is discussed. From the SOR in eq 3, the inverse proportionality between C_G and E is given as

$$C_G = \frac{O}{E} \tag{6}$$

Since E'' and O'' are much smaller than E' and O', respectively, $E \approx E'$ and $O \approx O'$. As already mentioned, the suppression of C_G for PC/tPh blends is dependent on the substitution position of tPh. Because O has the same value for the three PC/tPh blends, as shown in Fig. 5, the difference in C_G might originate from the elastic modulus (E). From eq 6, C_G is inversely proportional to E, that is, the smaller the C_G of PC/*p*-tPh, the higher the E, as shown in Fig. 4. Moreover, the PC/*m*-tPh blend has the same C_G as PC/DHEA even though the O value is different. These results suggest that C_G of the PC/additive blends is affected by enhancement of the elastic modulus (i.e., antiplasticization).

To investigate the antiplasticization effect, Fig. 7 shows plots of C_G against E for the PC blends. All of the blends show a decreasing trend of C_G with E, although the slope depends on the additive species. In particular, *p*-tPh decreases C_G more than the other additives. Therefore, modulus enhancement clearly contributes to reduction of C_G for all of the PC blends. By considering eq 6, the slope change is associated with the O value (i.e., the glassy birefringence). The dotted line in Fig. 7 was calculated with a constant value of O (~0.15 for bulk PC). The curves for all of the blends differ from the calculated curve, meaning that the additive molecules enhance the optical anisotropy. This result is in agreement with the previous results of O for the PC blends (Fig. 5).

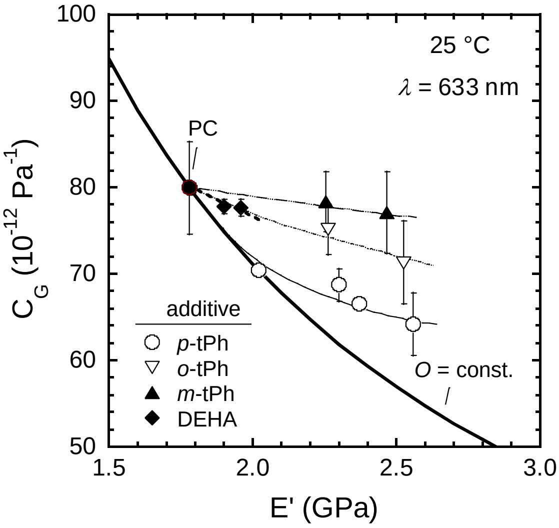

Figure 7. Relation between C_G and E' of the PC/additive blends at 25 °C. The thick line represents the value calculated with eq 6 with a constant value of O (0.15 for bulk PC). The other lines are drawn for eye guides.

The substitution position in tPh clearly affects the C_G value of the PC blends, as shown in Fig. 7. The order of C_G is *m*-tPh > *o*-tPh > *p*-tPh, which is consistent with that of *E* in Fig. 4. Therefore, it can be concluded that modulus enhancement is strongly related to the reduction of C_G. In addition, *p*-tPh more effectively improves the elastic modulus of PC than the other additives, because the local chain dynamics of PC are restricted. In the next section, the molecular dynamics of *p*-tPh and PC are discussed.

3.4 Dynamics of *p*-tPh in the PC matrix

The mobility of the additive molecules in glassy PC is important for the mechanical properties and optical anisotropy. As discussed in previous sections 3.1 and 3.2, the three isomers of tPh contribute to the birefringence to the same extent but the increase of the tensile modulus depends on the molecular structure.

Fig. 8 shows the temperature dependence of the complex modulus ($E^* = E' + iE''$) and strain-optical coefficient ($O^* = O' + iO''$) for PC/*p*-tPh blends with 0–10 wt % *p*-tPh. With addition of *p*-tPh, a β relaxation peak appears at 25–100 °C for E'', which is assigned to the restricted local motion of the PC chain. In contrast, O'' does not show any peaks in this temperature region, meaning that β relaxation is associated with the local chain motion with small polarizability anisotropy, such as the chain slip suggested by Inoue et al.[18] No peak in O'' also indicates that rotational motion of *p*-tPh, leading to large birefringence, does not occur in the β temperature range.

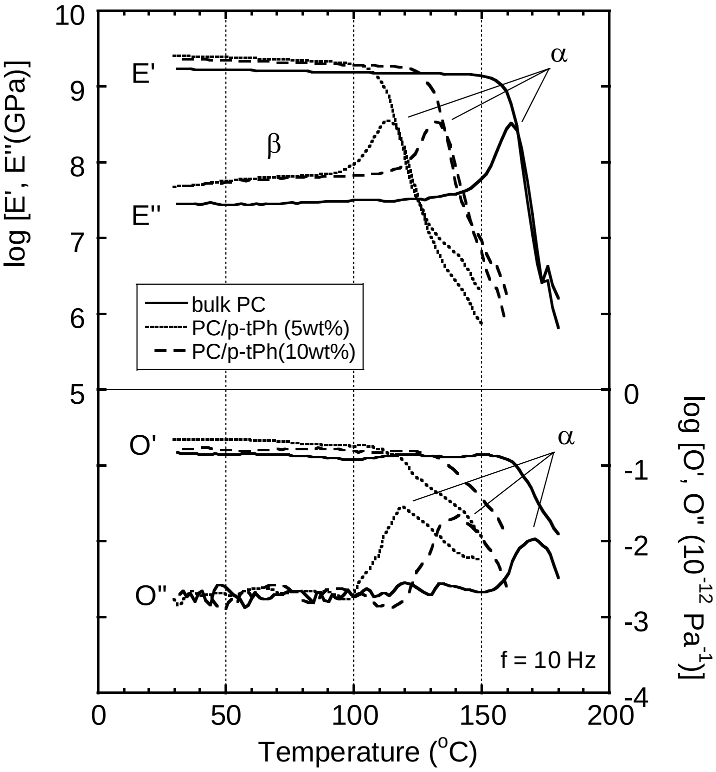

Figure 8. Comparison of the dynamic mechanical and optical properties of the PC/*p*-tPh blends.

As shown in Fig. 8, α relaxation peaks related to the glass transition are observed in both E'' and O'' for PC and the PC/*p*-tPh blends. With addition of *p*-tPh, the α peaks in E'' and O'' shift to lower temperature but the peak strength in O'' slightly increases. We previously reported that a small molecule exhibits a cooperative glass transition with a matrix polymer when the molecular size is consistent with the chain segment.[19] Because *p*-tPh has large polarizability anisotropy originating from the three phenyl groups, the increase of the O'' peak intensity suggests that *p*-tPh also contributes to the increase of the α peak with increasing *p*-tPh content. Therefore, *p*-tPh shows cooperative motion with the segmental motion (α relaxation) of the PC matrix. The restricted molecular dynamics of *p*-tPh in glassy PC might be related to the largest modulus enhancement and the lowest C_G of the additives considered.

4. Conclusion

In this study, we have investigated the effect of antiplasticization on the stress-optical behavior of PC by addition of small molecules, such as tPh isomers. Addition of the three tPh isomers (*p*-, *o*-, and *m*-tPh) and DEHA improves the tensile storage modulus (E) of PC at additive contents of 5–10 wt %, although the glass transition temperature decreases, as with general plasticizers. In particular, *p*-tPh has the greatest effect on E owing to the packing efficiency of the free volume of PC in the glassy state. The three tPh isomers improve the glassy birefringence of PC while DEHA has no effect. By comparing the chemical structures of tPh and DEHA, the results suggest that the increase of the birefringence in the glassy state is determined by the polarizability anisotropy of the additive molecule.

The stress-optical coefficient in glassy state (C_G) of PC decreases with increasing additive content. The decreasing trend is dependent on the additive structure. Rod-shaped *p*-tPh exhibits the minimum C_G while disk-shaped *o*- and *m*-tPh only make a small contribution to the C_G value. The order of C_G (*p*-tPh << *o*-tPh < *m*-tPh) corresponds to that of the tensile modulus (*p*-tPh > *o*-tPh > *m*-tPh) rather than the strain-optical coefficient (*p*-tPh ≈ *o*-tPh ≈ *m*-tPh). This can be explained by the SOR, which predicts an inversely proportional relation between E and C_G.

From dynamic mechanical and optical analysis, we investigated the dynamics of *p*-tPh in antiplasticized PC. The dynamic mechanical data show a β relaxation peak at 25–100 °C, which is assigned to local chain fluctuation of PC. In contrast, the dynamic birefringence shows no extra peak at the β relaxation temperature in the mechanical data, indicating that the additive molecules are less mobile in PC in the glassy state. This feature is associated with the reduced C_G at room temperature because tPh has larger birefringence than PC from their chemical structures.

Both enhancement of the tensile modulus and reduction of the optical anisotropy can be achieved for PC. Since the suppression of C_G is originated from improvement of elastic modulus, this finding is applicable to minimizing optical anisotropy for other polymers. This result is important for the design of low birefringent and tough polymer films for optical devices, such as LCDs.

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Figure captions

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