

# Effect of Molecular Size on the Correlated Dynamics of Low-Mass Molecule and Local Chain Motion in Antiplasticized Polycarbonate

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We have investigated the relation between the polymer and low-mass molecule (LM) dynamics in antiplasticized polycarbonate (PC). Antiplasticization results in enhancement of the Young's modulus of polymeric materials by adding LMs. Comparison of the dynamic mechanical properties and dielectric relaxation behavior suggests that the LMs are immobile below room temperature ( $\sim 25$  °C) and mobile above room temperature. The LM dynamics shows a similar trend to the local chain motion of PC, indicating the dynamical relation between the two components. Additionally, we investigated the effect of the LM size on antiplasticization and the local chain motion of PC by using alkyl cyano-biphenyl with various carbon numbers and 4-pentyl-4'-cyanoterphenyl. The LM size does not affect the degree of modulus enhancement of PC at the room temperature. However, mechanical relaxation of the local chain motion of PC shows wider temperature dependence for shorter LM size. The activation energy of molecular motion decreases with decreasing LM size, indicating that restriction of the local chain motion of PC and the LMs becomes weaker for smaller LM size.

**Key Words:** Antiplasticization / Polycarbonate / Molecular dynamics / Dielectric relaxation / Mechanical relaxation

## 1. INTRODUCTION

Bisphenol A type Polycarbonate (PC) has attracted attention as an inorganic glass substitute because of transparency, crush-proof, formability and light weight<sup>1-4)</sup>. However, since the mechanical properties of PC, such as Young's modulus and surface hardness are lower than those of inorganic glass, many improvement methods of the mechanical properties for PC have been reported<sup>5-10)</sup>.

Antiplasticization is defined to be "improvement of Young's modulus" for glassy polymers such as PC by adding a small amount of low-mass molecules (LMs), which are called "antiplasticizers"<sup>11, 12)</sup>. Generally, addition of LMs enhances the chain mobility of the polymer owing to an increase of the free volume fraction<sup>13, 14)</sup>. However, antiplasticizers increases Young's modulus of some polymers, such as PC<sup>11, 12, 15, 16)</sup>, polystyrene<sup>17)</sup>, poly(vinyl chloride)<sup>11, 12)</sup>, polyamide<sup>18)</sup>, and PMMA<sup>12, 19, 20)</sup>, owing to restriction of the polymer chain motion without strong interactions such as hydrogen bonding. In antiplasticized PC systems, the addition of LMs

reduces the free volume and suppresses the local dynamics of PC, which is related to the secondary relaxation around  $-100$  °C<sup>20)</sup>. The restriction of the local chain motion of PC enhances Young's modulus at the room temperature. Antiplasticization has been investigated by various techniques, such as positron annihilation lifetime spectroscopy<sup>13, 17, 18)</sup>, proton spin-lattice relaxation of NMR<sup>21-24)</sup>, pressure-volume-temperature diagram<sup>19)</sup>, and thermo-mechanical analysis<sup>15)</sup>.

In general, LMs with high mobility act as plasticizers for glassy polymers, and thus decrease Young's modulus. Therefore, it can be considered that LMs in antiplasticized PC have lower mobility than in plasticized systems. Ngai *et al.*<sup>21, 22)</sup> investigated the dynamics of LMs in PC by deuterium NMR. The experimental data showed that addition of LMs increases the activation energy and broadness of the relaxation time distribution and delays the relaxation time of the local chain motion for the antiplasticized PC. On the basis of the coupling model, which explains effects of intermolecular coupling on the uncoupled relaxation rate of an intramolecular motion, Ngai *et al.* suggested that LMs affect the secondary relaxation of PC, which is attributed to the phenylene motion<sup>22)</sup>.

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Inglefield and co-workers<sup>24)</sup> discussed the size of the mobile domains in antiplasticized PC containing LMs. They used the proton spin diffusion technique to evaluate the size of the mobile domains in the polymer by distinguishing spatial regions based on the mobility differences. The results showed the presence of both fast and slow decay components. Size of the mobile domain consisted of the fast component was about 12 Å from 339 to 369 K, which corresponds to approximately 11 repeat units of the polymer and two diluent molecules.

In previous studies, although dynamic domains containing polymer and LMs were considered for evaluation of the size or relaxation time, the dynamics of the LMs was not discussed independently of the polymer dynamics. To understand the mechanism of antiplasticization, the dynamics of the LMs in antiplasticized PC need to be understood.

Because dielectric relaxation (DR) measurements can detect rotational relaxation of electric dipoles under an alternating electric field, the rotational dynamics of small amounts of polar molecules can be evaluated<sup>25, 26)</sup>. Additionally, DR measurements cover wide ranges of applied frequency and temperature with high sensitivity. Therefore, DR measurements are suitable for evaluating the LM dynamics in antiplasticized PC. Urakawa *et al.*<sup>27-32)</sup> investigated the component dynamics in polystyrene (PS) containing polar LMs by DR measurements and dynamic mechanical analysis (DMA). In these studies, the two component dynamics of PS and the LMs were independently evaluated and the timescale and temperature dependence of the component relaxation times were discussed.

In this study, we performed DMA and DR measurements to investigate the dynamics of PC and LMs in PC/LM systems, respectively. In our approach, the DMA and DR data in a wide temperature range are compared to discuss the correlation of component dynamics in the antiplasticized PC. Although the rotational motion of polar LMs is evaluated by DR, the local chain motion of PC is also observed because the polymer has polar groups<sup>33-37)</sup>. To evaluate the LM dynamics, we used two types of LMs, a polar molecule with a large electric dipole and a non-polar molecule, and compared the dynamics of PC and the LMs (rotational motion). In particular, a cyano group was introduced to the LMs to enhance the intensity of DR for the LM component. In addition, the effect of the molecular size on antiplasticization of PC is discussed from the DR and DMA data by using LMs with various sizes.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

PC (bisphenol A type, Fig. 1) was used as the matrix polymer. The number-average and weight-average molecular weights are  $1.9 \times 10^4$  and  $9.7 \times 10^4$ , respectively. The chemical structures of the LMs used in this study are shown in Fig. 1: *p*-terphenyl (*p*-tPh), alkyl cyano-biphenyl (*n*CB,  $n = 0, 1, \text{ and } 3$ , where  $n$  is the number of carbon atoms in the normal alkyl group of the LM) and 4-pentyl-4'-cyanoterphenyl (5CT). *p*-tPh was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and the other LMs were purchased from Wako Pure Chemicals (Tokyo, Japan). All the materials were used without further purification. Values of dipole moment ( $\mu$ ) and molecular size for the LMs are listed in Table I.

Blend samples of PC and the LMs were prepared by a 7 cc twin-screw extruder (Haake Minilab, Thermo Fisher Scientific Inc., MA, USA) at 240 °C ( $T_g + 100$  °C) for 3 min with a screw rotation speed of 50 rpm. The mixing condition was determined from three following reasons. (1) In the absence of oxygen, PC undergoes limited thermal degradation below 250 °C<sup>38)</sup>. (2) During the mixing, the torque level was too high at higher rotation speed than 50 rpm. (3) The torque level became almost a constant at 3 min, indicating that the blend samples were mixed well. After being kept in a vacuum oven at 80 °C for 4 h to prevent the bubble formation, the mixed samples were compressed into sheets with thicknesses of 100 and 300  $\mu\text{m}$  at 240 °C for 3 min under 20 MPa by a compression-molding machine (Gonno Hydraulic Press Manufacturing Co., Japan). The condition was chosen in

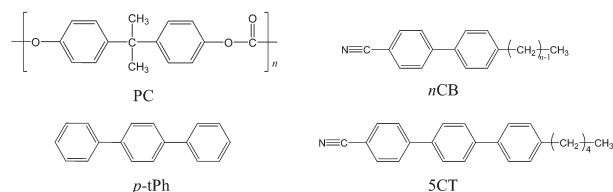


Fig. 1 Chemical structures of PC and LMs (antiplasticizers).

Table I Dipole moment ( $\mu$ ) and sizes of PC and LMs.

code	$\mu$ (Debye) <sup>a)</sup>	Total average length <sup>b)</sup> (Å)	Rigid part length <sup>b)</sup> (Å)
PC (repeating unit)	0.06	—	—
<i>p</i> -tPh	0	13.5	13.5
0CB	4.58	10.7	10.7
1CB	5.46	11.5	11.5
3CB	5.43	12.2	11.5
5CT	5.55	16.7	15.4

a) Calculated by a semi-empirical method (PM6) with Gaussian 09W software (1 Debye =  $3.33564 \times 10^{-30}$  Cm).

b) Reported by Urakawa *et al.*<sup>27)</sup>

order to relax the chain orientation generated by the compression stress. After the compression, the samples were quenched and kept at 25 °C for 3 min because the cooling time influences crystallization and local motion of PC<sup>39, 40</sup>. In this study, the content of LMs was fixed at the same weight concentration, 5 wt%.

## 2.2 Measurements

Storage and loss moduli ( $E'$  and  $E''$ , respectively) were determined by using DMA with an oscillatory tensile rheometer (DMS6100, Seiko Instruments Inc., Japan) at a heating rate of 2 °C min<sup>-1</sup>. Frequency ( $f$ ) and temperature ( $T$ ) ranges were 5 to 100 Hz and -150 to 180 °C, respectively.

Dielectric permittivity and loss ( $\epsilon'$  and  $\epsilon''$ , respectively) were measured by using DR with an LCR meter (E4980AL, Precision LCR meter, Keysight Technologies, CA, USA) at a heating rate of 2 °C min<sup>-1</sup>. The  $f$  and  $T$  ranges were 20 Hz to 1 MHz and -150 to 180 °C, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Effects of the cyano group in the LM on the dynamic mechanical properties of PC

To investigate the effect of the cyano group (polar group) in the LM on antiplasticization of PC, the DMA data of PC/*p*-tPh and PC/3CB blends were compared. Here, the length of 3CB (12.2 Å) is close to that of *p*-tPh (13.5 Å). The temperature dependence of  $E'$  and  $E''$  at  $f = 10$  Hz for PC, PC/*p*-tPh, and PC/3CB is shown in Fig. 2. As shown in Fig. 2(a), the additions of *p*-tPh and 3CB enhance the  $E'$  values from -50 to 100 °C to the same degree. In Fig. 2(b), three relaxation processes are observed as a peak or shoulder in the  $E''$  data: (1) the primary relaxation process ( $\alpha$  relaxation), which is related to the glass transition, appears in the highest temperature region for each system, (2) the secondary process ( $\beta$  relaxation), which mainly appears as a shoulder peak around 80 °C, except for pure PC, and (3) the tertiary relaxation process ( $\gamma$  relaxation) at -100 °C. As previously reported by Miyagawa *et al.*<sup>15</sup>, the appearance of  $\beta$  relaxation for PC/*p*-tPh in Fig. 2 (b) is correlated with reduction of the  $\gamma$  relaxation peak owing to restriction of the local chain motion of PC by antiplasticization. For PC blends, reduction of the  $\gamma$  peak enhances the  $E'$  value at 25 °C. Additionally, for PC/3CB, the temperature dependence of  $E'$  and  $E''$  is quite similar to that of PC/*p*-tPh, meaning that 3CB exhibits the same degree of antiplasticization as *p*-tPh. Considering that 3CB and *p*-tPh have similar lengths, we can conclude that the effect of the cyano group on antiplasticization is negligible.

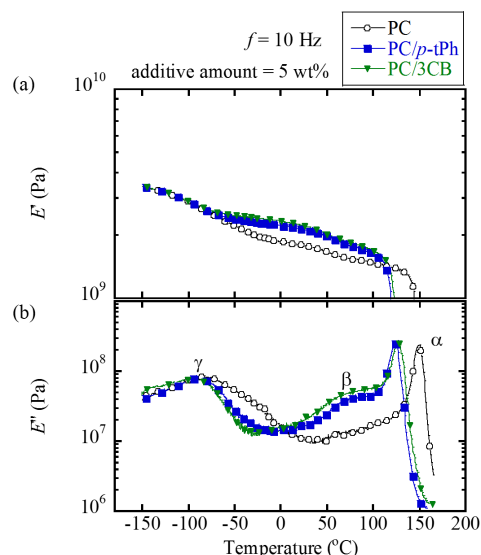


Fig. 2 Temperature dependence of (a)  $E'$  and (b)  $E''$  for PC, PC/*p*-tPh, and PC/3CB. The added amount of the LMs is 5 wt% for the blends.

### 3.2 Correlation between the dynamics of PC and the LMs

To evaluate the dynamics of the LMs in PC, the DR data for the three systems were compared. The complex dielectric permittivity  $\epsilon^* (= \epsilon' - i\epsilon'')$  was measured as a function of  $T$  and angular frequency  $\omega (= 2\pi f)$  for three systems. An intensity of DR measurement is given by dielectric intensity  $\Delta\epsilon$ , which is the difference between  $\epsilon(0)$  and  $\epsilon_\infty$  ( $\epsilon'$  at low ( $\omega = 0$ ) and high frequency ( $\omega = \infty$ )). According to Onsager theory<sup>41</sup>,  $\Delta\epsilon$  for a dilute molecule in a continuous matrix can be calculated from the electric dipole moment  $\mu$  and the volume fraction  $\phi$ . Here, the  $\mu$  values for the repeating units of PC and 3CB are 0.06 and 5.43 Debye, respectively, which were calculated by the PM6 semi-empirical method using Gaussian 09W software (HULINKS, Inc., Japan). The value of  $\phi$  for 3CB is assumed to be the same with the volume fraction ( $= 0.05$ ). From these values,  $\Delta\epsilon = 1.3$  for 3CB, which is much larger than  $\Delta\epsilon = 0.0023$  for PC. Therefore, the molecular motion of 3CB can be detected by DR measurements. In contrast,  $\Delta\epsilon$  of *p*-tPh can be ignored because  $\mu = 0$ .

The temperature dependence of the dielectric loss  $\epsilon''$  for PC, PC/*p*-tPh, and PC/3CB is shown in Fig. 3(b). As mentioned above, because  $\Delta\epsilon$  of *p*-tPh is zero, the temperature dependence of  $\epsilon''$  for PC/*p*-tPh originates from the chain dynamics of PC. Comparing the two PC blends, the peak intensity of  $\epsilon''$  at around 80 °C (the  $\beta$  relaxation region) for PC/3CB is much larger than that for PC/*p*-tPh owing to the contribution of the 3CB dynamics. Conversely, in the  $\gamma$  relaxation region (lower temperature region than the  $\beta$  relaxation region),  $\epsilon''$  for PC/3CB is smaller than those for PC/*p*-tPh and bulk PC. If 3CB motion is restricted in the  $\gamma$  relaxation

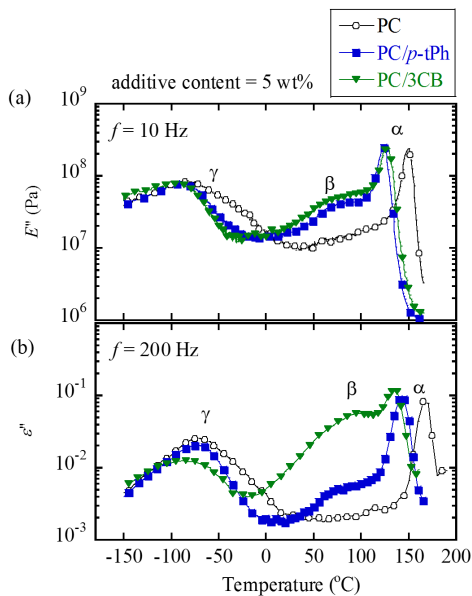


Fig. 3 Temperature dependence of (a)  $E''$  and (b)  $\varepsilon''$  for PC, PC/*p*-tPh, and PC/3CB.

region,  $\varepsilon''$  for the PC/3CB blend should be similar to that for PC/*p*-tPh, as well as the DMA ( $E''$ ) data in Fig. 3(a). Although the detailed mechanism is still unclear, the lower  $\varepsilon''$  for PC/3CB compared with PC/*p*-tPh might be because of the anti-parallel alignment of the cyano group of 3CB to the carbonyl group of PC.

The DMA and DR results indicate that both the LMs (*p*-tPh and 3CB) and PC are immobile in the low temperature range ( $\gamma$  region) and become mobile in the high temperature range ( $\beta$  region).

### 3.3 Effects of the LM size on the PC dynamics

To investigate the effect of the molecular size of the LM on the mechanical properties of PC, the DMA data of bulk PC and four PC/LM blends were compared. The temperature dependence of  $E'$  and  $E''$  at  $f = 10$  Hz for PC, PC/0CB, PC/1CB, PC/3CB, and PC/5CT is shown in Fig. 4. Comparing the three PC/*n*CB systems, the shapes of the  $\beta$  relaxation peak for PC/1CB and PC/3CB are almost the same and narrower than that of PC/0CB. In contrast, the  $\gamma$  relaxation peak does not change. Compared with the data of PC/*n*CB,  $\beta$  relaxation of PC/5CT is smaller and merges into  $\alpha$  relaxation. Furthermore, for PC/5CT, suppression of the  $\gamma$  relaxation peak is smaller than for PC/*n*CB. The  $E'$  values at 25 °C for PC and the PC/LM blends are shown in Fig. 5. The  $E'$  value for PC/5CT is obviously lower than those for the PC/*n*CB blends. This result indicates an existence of a threshold size between 11.5 Å (3CB) and 15.4 Å (5CT) for enhancement of Young's modulus for PC, as explained below. The  $E'$  values are consistent with suppression of the  $\gamma$  peak because PC/*n*CB showed larg-

er reduction of the peak than PC/5CT.

Liu *et al.*<sup>24)</sup> evaluated the size of the mobile domains in antiplasticized PC. They reported that the domain size is approximately 11–12 Å using trioctyl phosphate as the antiplasticizer LM. 5CT (15.4 Å) is larger than the domain size, while the *n*CB molecules (10.7–11.5 Å) are smaller. Because 5CT cannot fit into the mobile domain, antiplasticization is weaker than for the PC/*n*CB systems. Additionally, although the weight concentration for the LMs was the same (5 wt%), the mol concentration of 5CT (0.015 mol/g) is lower than *n*CB (0.023–0.028 mol/g) due to the difference in molecular weights. Therefore, the lower mol concentration of 5CT has also the potential to originate the low degree of improvement in  $E'$  represented in Fig. 5. However, there is no data to discuss the effect of mol concentration on the antiplasticization. In order to understand the detailed mechanism of antiplasticization, further investigations for the molecular size and the mol concentration are necessary.

The temperature dependence of  $\varepsilon''$  for PC, PC/0CB, PC/1CB, PC/3CB, and PC/5CT is shown in Fig. 6.  $\beta$

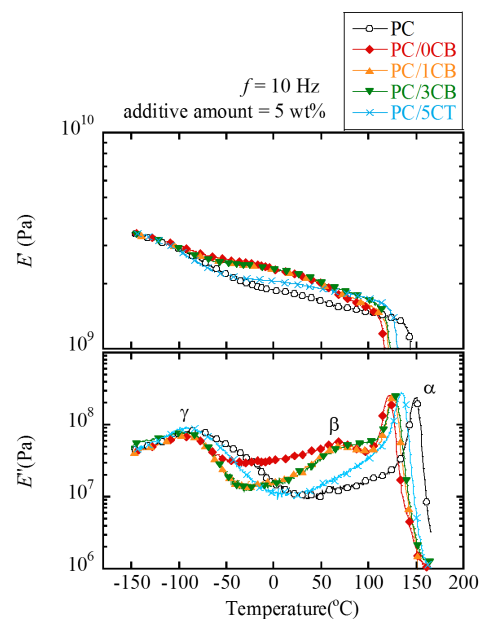


Fig. 4 Temperature dependence of  $\varepsilon''$  for PC, PC/0CB, PC/1CB, PC/3CB, and PC/5CT.

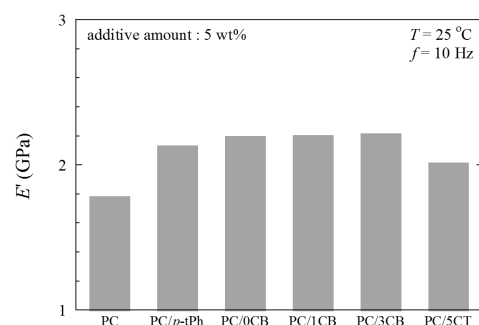


Fig. 5  $E'$  at 25 °C for PC and the PC/LM blends.

relaxation shifts to higher temperature as the LM size increases. In their study of the LM dynamics in PS, Urakawa *et al.*<sup>27, 28)</sup> concluded that  $\beta$  relaxation depends on the size of the rigid part of the LM in the PS/*n*CB system. In this study, the shape and peak temperature of  $\beta$  relaxation depend on the LM size, although the sizes of the rigid parts of *n*CB are the same. This result for PC/*n*CB is different from that for PS/*n*CB. PC is ductile while PS is brittle. The differences in the mechanical properties are associated with the local chain dynamics of the polymers in the glassy state. As shown in Fig. 6, PC exhibits local chain motion as  $\gamma$  relaxation at  $-100$  °C. In contrast, PS shows local chain motion at  $50$  °C, which is close to the glass transition temperature ( $T_g$ ) ( $\sim 100$  °C)<sup>42)</sup>. The temperature for local chain motion affects the mechanical properties of polymeric materials in the glassy state<sup>43, 44)</sup>. Therefore, the effect of *n*CB on the dynamics of PC is different from the PS system.

To discuss the dynamic heterogeneity in PC/*n*CB, the relaxation time distribution for the  $\beta$  mode was analyzed by using the Cole–Cole type function<sup>45)</sup>:

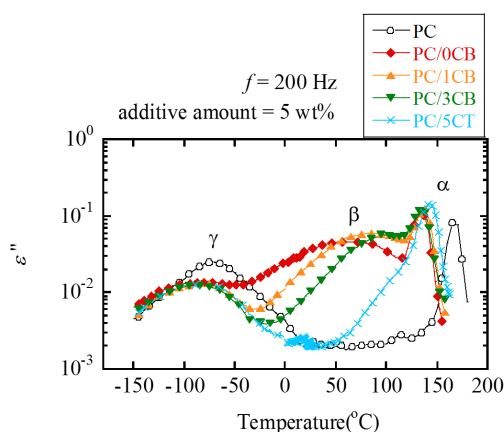


Fig. 6 Temperature dependence of  $\varepsilon''$  for PC, PC/0CB, PC/1CB, PC/3CB, and PC/5CT.

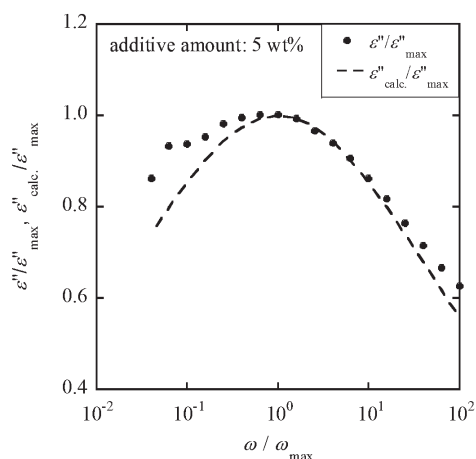


Fig. 7 An example of  $\beta$  relaxation fitting data in  $\varepsilon''$  for PC/3CB. The dash line overlaid on  $\varepsilon''$  curve is fitted results with Eq. (1). The vertical and horizontal axes are normalized by  $\varepsilon''_{\max}$  and  $\omega_{\max}$  for DR peak, respectively.

$$\varepsilon^* = \frac{\Delta\varepsilon}{1 + (i\omega\tau)^{1-\alpha}} \quad (1)$$

where  $\alpha$  is a fitting parameter representing the broadness of relaxation and  $\tau$  ( $= 1/\omega_{\max}$ ) is the relaxation time. A larger  $\alpha$  value means a broader relaxation time distribution. An example of the  $\beta$  relaxation fitting data for  $\varepsilon''$  of PC/3CB is shown in Fig. 7. The  $\alpha$  values for PC/0CB, PC/1CB and PC/3CB are 0.72, 0.67, and 0.66, respectively. Therefore, a smaller LM makes  $\beta$  relaxation broader, suggesting that the molecular dynamics of small LMs becomes heterogeneous in PC.

### 3.4 Activation energies for $\beta$ and $\gamma$ relaxation of the PC and LM dynamics

To investigate the dynamics of PC and the LMs appearing as  $\beta$  and  $\gamma$  relaxation in the DR measurements, the activation energies ( $E_a$ ) of the  $\beta$  and  $\gamma$  relaxation modes were estimated for bulk PC and the PC/*n*CB and PC/5CT blends. The Arrhenius plots of  $\gamma$  and  $\beta$  relaxation of PC and the PC/*n*CB and PC/5CT blends are shown in Figs. 8 and 9. The  $E_a$  values can be estimated from the slopes of the curves.

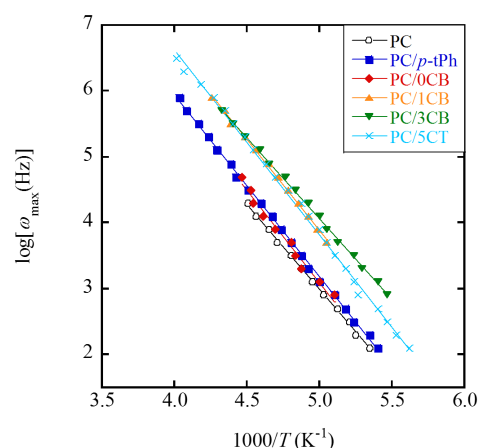


Fig. 8 Arrhenius plots of angular frequency versus  $\gamma$  relaxation temperature for PC and the PC/LM blends.

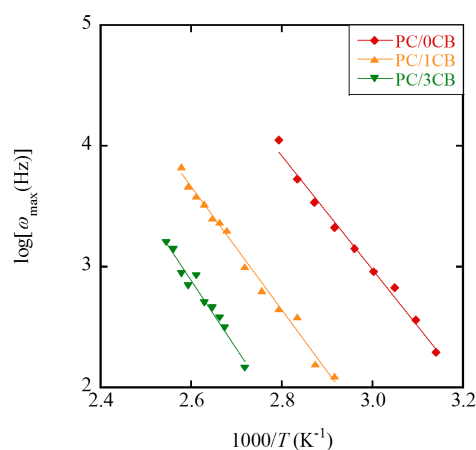


Fig. 9 Arrhenius plots of angular frequency versus  $\beta$  relaxation temperature for the PC/*n*CB blends.

The  $E_a$  values are given in Table I. To compare two results of DMA and DR, the  $E_a$  values of  $\gamma$  relaxation mode in DMA were also estimated although the Arrhenius plots are not indicated here. The  $E_a$  values in the two measurements are almost the same. This result is reasonable because the  $\gamma$  relaxation region in DR reflects only the local dynamics of PC as well as that in DMA, as mentioned in previous Sections 3.2 and 3.3. Although  $E_a$  of the PC/3CB blend is slightly lower than those of the others, the effect of the LM size on  $E_a$  of  $\gamma$  relaxation is negligible. It is predicted that  $E_a$  of  $\gamma$  relaxation increases with addition of LMs, because the local motion of PC is suppressed by antiplasticization. However, the obtained results are not consistent with the prediction. The inconsistency will be explained in the following paragraph.

According to previous studies, the local motion of PC for  $\gamma$  relaxation is the sum of two (or three) types of PC chain motion. The local motion at lower than  $-70$  °C is derived from  $\pi$ -flip motion of phenylene groups and the local motion at higher than  $-70$  °C is derived from rotational fluctuation of the carbonate and phenylene groups<sup>36, 46</sup>. From the DMA results in Figs. 2 and 4,  $\gamma$  relaxation is reduced in the higher temperature region by addition of LMs. This indicates that LMs suppress the local chain motion of PC in the higher temperature region of  $\gamma$  relaxation and do not affect the lower temperature region. Because the  $E_a$  values of  $\gamma$  relaxation for the PC/ $n$ CB and PC/5CT blends reflect the lower temperature region, there are no significant differences in the  $E_a$  values in Table II.

The  $E_a$  values of  $\beta$  relaxation estimated from Fig. 9 are given in Table II. The  $E_a$  value increases with increasing LM size. The increase of  $E_a$  indicates that the dynamics of larger molecules becomes more strongly restricted. By comparing the DMA and DR results, the  $\beta$  peak temperatures of  $E''$  and  $\epsilon''$  are similar at various frequencies, suggesting that  $\beta$  motion of PC (carbonyl and phenylene rotational fluctuation<sup>42, 46</sup>) and LM rotational motion are cooperative. Because of the cooperative motion, a larger molecular size results in a larger cooperative domain. Because a larger cooperative domain is more strongly restricted, the  $E_a$  value increases. In Section

3.3, we suggested that 5CT is larger than the mobile domain size (11-12 Å). However, as suggested by the  $E_a$  values, the mobile domain size in antiplasticized PC might be dependent on the LM size. For further discussion, it is necessary to investigate the mobile domain size.

## 4. CONCLUSION

We have investigated the component dynamics in antiplasticized PC containing LMs by DMA and DR measurements. Mechanical relaxation in DMA reflects the various types of dynamics of PC. The DMA data indicate that the local chain motion of antiplasticized PC is suppressed around  $-100$  °C ( $\gamma$  relaxation) and activated around  $80$  °C ( $\beta$  relaxation). DR is associated with the rotational motion of the polar LMs. The DR results suggest that rotational motion of the LMs does not occur at the  $\gamma$  relaxation temperature but it does occur at the  $\beta$  relaxation temperature. The LM dynamics show a similar trend to the local motion of antiplasticized PC, meaning that there is a dynamical correlation between PC and the LMs.

The effects of the LM size on antiplasticization and the local chain motion of PC were also investigated by using  $n$ CB ( $n = 0, 1, \text{ and } 3$ ) and 5CT as LMs. We found that the LM size does not affect the degree of modulus enhancement at  $25$  °C, except for 5CT. In contrast, mechanical relaxation in DMA for PC containing smaller LMs shows a wider relaxation time distribution in  $\beta$  relaxation. DR in the  $\beta$  relaxation region shows the same trend as mechanical relaxation, meaning that the dynamics of LM is strongly correlated with the PC dynamics. The activation energy for the PC/ $n$ CB system was estimated from the relaxation times at various frequencies in the DR data. The activation energy of  $\beta$  relaxation increases with increasing LM size, suggesting that the dynamics of larger LMs becomes more strongly restricted. Larger LM size might generate larger cooperative domains in PC. Because larger cooperative domains are more tightly restricted, the activation energy increases.

Table II  $E_a$  values of  $\beta$  and  $\gamma$  relaxation for PC and the PC/LM blends.

	$E_a$ (kJ/mol) ( $\gamma$ relaxation in DMA)	$E_a$ (kJ/mol) ( $\gamma$ relaxation in DR)	$E_a$ (kJ/mol) ( $\beta$ relaxation in DR)
PC	42.8 ± 4.5	49.3 ± 1.4	—
PC/0CB	54.7 ± 3.3	53.8 ± 5.1	71.6 ± 1.5
PC/1CB	69.3 ± 16.1	52.4 ± 1.6	83.7 ± 4.2
PC/3CB	45.3 ± 3.8	47.0 ± 1.1	132.4 ± 4.7
PC/5CT	59.9 ± 11.0	53.7 ± 0.7	—

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