Isomer Effect on Liquid Crystallinity of Semi-aliphatic Polybenzoxazoles and Improved Thermal Conductivity by Magnetic Orientation

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1. Introduction

Recently, heat release from semiconductor chips is becoming a very crucial problem. So far, much effort has been made for development of electrically insulating heat-releasing materials. Most of common polymeric materials as the matrix resins (binders) are thermally less conductive with thermal conductivity λ = 0.1–0.2 $Wm^{-1}K^{-1}$. Therefore, resins dispersing inorganic particles (typically, Al_2O_3 with a high λ of 30 $Wm^{-1}K^{-1}$) at considerably high contents (>> 50 wt%) are often used for this purpose, although the increment in thermal conductivity is not so drastic even at considerably high additive contents. The excessively introduced additives also often cause serious problems such as a significant decrease in resin flexibility, particle-dropping, and an apparent decrease in practical surface areas as arising from an increase in local surface roughness. Much more effective strategy is to enhance the thermal conductivity of the matrix resins themselves as continuous phases.

It is known that highly uniaxially oriented polymeric fibers such as polyethylene, polyesters, polyimides, polybenzoxazoles (PBOs) exhibit much higher thermal conductivity along their fiber direction than non-oriented resins. In particular, commercially available PBO fiber (Zylon) is far superior to other fibers although it is not clear that the result is primarily attributed to whether its backbone (chemical) structure or its fiber crystal structure (or degree of orientation). But unfortunately, it is difficult to form a high quality of thin films from the PBO fiber alone without any binders.

However, the PBO system, which is derived from 2,4-diaminoresorcinol with terephthalic acid, is quite insoluble in common organic solvents owing to its too stiff backbone structure. On the other hand, we have successfully developed some colorless PBO systems possessing high T_g's, excellent

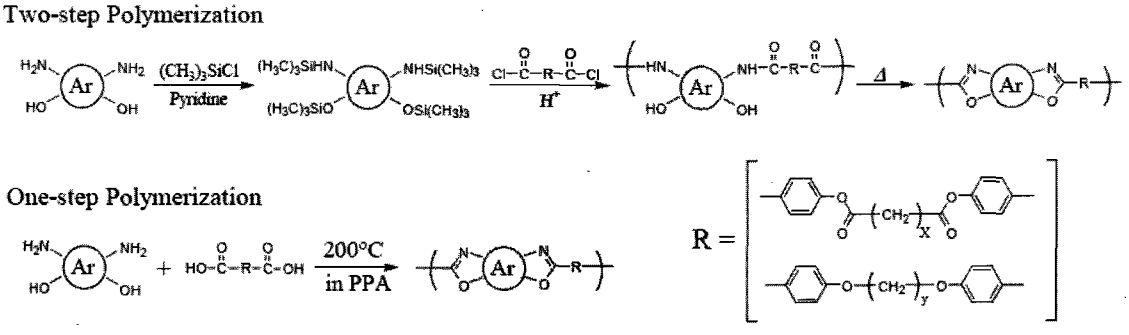

Fig.1 Polymerization schemes of semi-aliphatic PBOs.

solubility, thermoplasticity, and good film toughness at the same time [**1,2**]. Our previous work was extended to the present approach, although the coloration of PBO films is beyond as yet the present target properties. We report here thermotropic liquid-crystalline PBO systems soluble in common organic solvents and an attempt of improvement of thermal conductivity along the film thickness (Z) direction by a magnetic orientation technique [**3**]. This idea is based on the assumption that the benzoxazole (BO) structural units themselves in the PBO fiber mentioned above (chemical factor) may also play an important role to the high thermal conductivity in addition to its crystal structure (physical factor).

If PBOs possessed thermotropic liquid crystallinity, the polymer chains in the domains can be oriented along a magnetic field on the basis of the presence of the anisotropic magnetic susceptibility ($\Delta\chi = \chi_{//} - \chi_{\perp}$) inherent to the polymeric materials. When an elliptical shape of a diamagnetic material (such as the present samples) with a $\Delta\chi$ and a volume (V) was placed under a magnetic field of a magnetic flux density (B), the free energy change (ΔG) is expressed by equation (1):

$$\Delta G = -(1/2)\mu_0^{-1}V\chi_{\perp}B^2 - (1/2)\mu_0^{-1}V \mid \Delta\chi \mid B^2\cos^2\theta \qquad (1)$$

where μ_0 is permeability in vacuum and θ is the angle between the magnetic filed and the orientational axis. If the second term in equation (1) was higher than thermal energy for randomization, magnetic orientation takes place, namely, under the following condition:

$$(1/2)\mu_0^{-1}V \mid \Delta\chi \mid B^2\cos^2\theta > kT \qquad (2)$$

Thus, the primary factors for magnetic orientation are the domain size (V), $\Delta\chi$, and B. This is the reason why better thermotropic liquid crystallinity and lower melt viscosities are required for magnetic orientation of the present PBO systems.

2. Experimental

Some PBO systems containing flexible long alkylene units in the main chains were prepared by two synthetic pathways as shown in **Fig.1**: (1) the two-step processes, that is, polymerization of PBO precursors [polyhydroxyamides (PHAs)] from tetra-silylated bis(o-aminophenol)s with dicarboxylic acid dichlorides in NMP at room temperature in the presence of LiCl, precipitation/desilylation, and thermal cyclo-dehydration of the PHAs at 280–300°C for 1 h in vacuum, and (2) the one-step polycondensation from bis(o-aminophenol)s with dicarboxylic acids in polyphosphoric acid (PPA) at elevated temperatures in a nitrogen atmosphere. In this work, we used isomeric bis(o-aminophenol)s which provide rigid structural units; bis(4-hydroxy-3-amino)biphenyl (*m*-HAB) and bis(3-hydroxy-4-amino) biphenyl (*p*-HAB). Two types of flexible dicarboxylic acids with ester and ether linkages (**Fig.1**) were

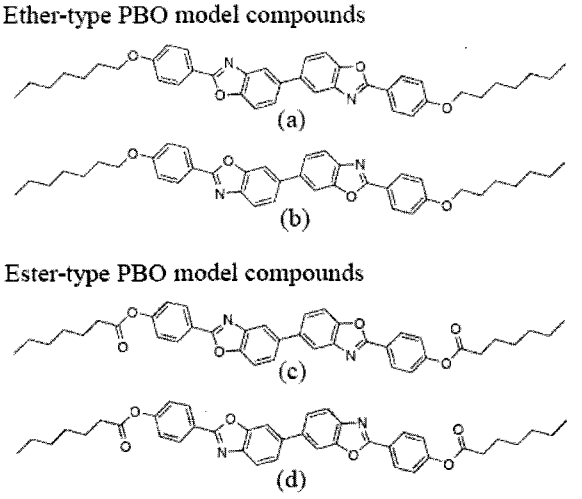

Fig.2 Structures of PBO model compounds.

used for comparison.

In order to investigate inherent thermotropic liquid crystallinity of our semi-aliphatic PBO systems, low-molecular weight PBO model compounds (**Fig.2**) composed of bisbenzoxazole mesogenic units and flexible C_7 alkyl chains were also synthesized and purified by repeated recrystallization from suitable solvents.

Optically anisotropic textures for the semi-aliphatic PBO films and the model compounds were observed on an optical polarizing microscope system (POM, Olympus BX51) equipped with a temperature-controlled hot stage (Mettler Toledo, FP82HT hot stage and FP 90 central processor) and a digital camera (Nikon Coolpix 950) at a heating rate of 2 or 5 K/min. Differential scanning calorimetry (DSC) were carried out in the heating and the cooling processes in a nitrogen atmosphere to detect some thermal transitions on Bruker-AXS DSC3100. Heat capacities (C_P) of PBO films were also measured on the same instrument.

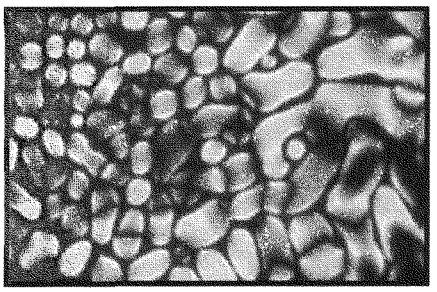

Fig.3 POM photograph of model (a) at 220°C in the cooling process (× 500).

The densities (ρ) of PBO films were measured at 30 °C by a density gradient column system (Shibayama Scientific Co, type A) composed of density-predetermined glass bead floats and 20 steps of xylene–CCl_4 layers with different compositions on the basis of a perfect linear plot (calibration curve) between the float densities and the graduations of the column.

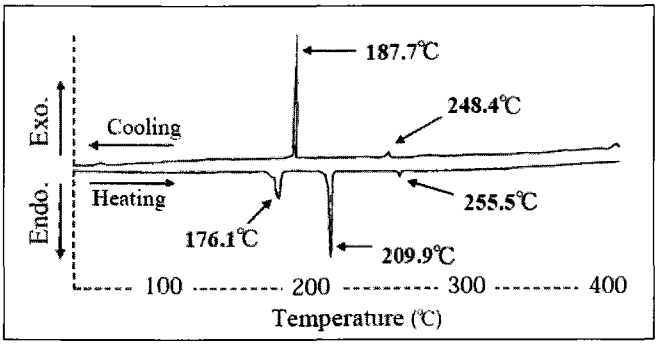

Fig.4 DSC thermograms of model (a) in the heating and the cooling processes.

The storage modulus (E') and the loss energy (E'') of PBO films were measured by the dynamic mechanical analysis (DMA) as a function of temperature to determine T_g from a peak temperature of the E'' curve by using the same TMA instrument at a heating rate of 5 K/min in a nitrogen atmosphere with a sinusoidal load frequency of 0.1 Hz.

Thermal stability of PBO films was evaluated from the 5 % weight loss temperatures (T_d^5) by thermogravimetric analysis (TGA) on Bruker-AXS, TGA2000 as performed at a heating rate of 10 K/min in nitrogen and air atmosphere.

The tensile modulus (E), tensile strength (σ_b), and elongation at break (a_b) of PBO specimens (3 mm wide and 30 mm long, typically 20 μm thick, sample numbers > 15) were measured using a mechanical testing machine [Toyo Boldwin (A & D at present), Tensilon UTM-II] at a cross head speed of 8 mm/min.

Thermal diffusivity (D_T) of PBO films were measured on a thermal diffusivity measurement system based on the temperature wave analysis (ai-Phase Co., ai-Phase Mobile 1u). Thermal

conductivity (λ) of the PBO films was calculated from the relation: $\lambda = D_T \rho C_P$

Results and Discussion

3.1 Liquid crystallinity of PBO model compounds

A significant isomer effect on thermotropic liquid crystallinity was observed in comparison between *m*-HAB- and *p*-HAB-based model compounds in spite of almost the same structural shapes of them. The *m*-HAB-based model compounds [ether type (a) and ester type (c) in **Fig.2**] showed optically anisotropic textures, whereas the *p*-HAB-based counterparts [ether type (b) and ester type (d)] did not, although the reason is not clear as yet. A similar trend for the liquid crystallinity was also observed in the corresponding PBO systems. Therefore, in this work, the *m*-HAB-based semi-aliphatic PBOs were focused as the target materials. A typical liquid crystal (LC) texture of the ether-type model compound (a) was observed at 220°C in the cooling process as shown in **Fig.3**. **Fig.4** displays the DSC thermograms of model (a), indicating that the LC phase can be stably formed in a relatively wide temperature range between a clearing temperature (T_c) at 248°C and a freezing point at 188°C in the cooling process. On the other hand, ester-type model compound (c) showed an optically anisotropic texture (**Fig.5**) in a much narrower temperature range between a T_c at 254°C and a freezing point at 240°C in the cooling process. The much more stable LC phase formation of model (a) is probably due to a higher flexibility at the ether-linked aliphatic units in (a), which contributes to a decrease in the melting (LC transition) temperature by an entropy effect. Thus, the present model compound approach suggests that ether-linked *m*-HAB-based PBOs are more advantageous than the ester-linked PBOs for the current purpose.

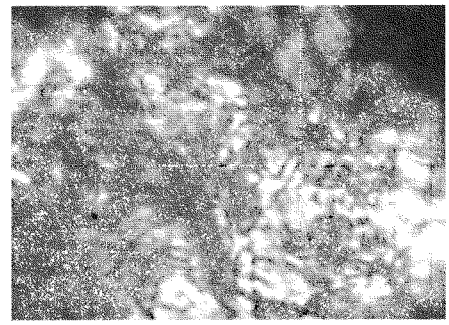

Fig.5 POM photograph of model (c) at 250°C in the cooling process (× 500).

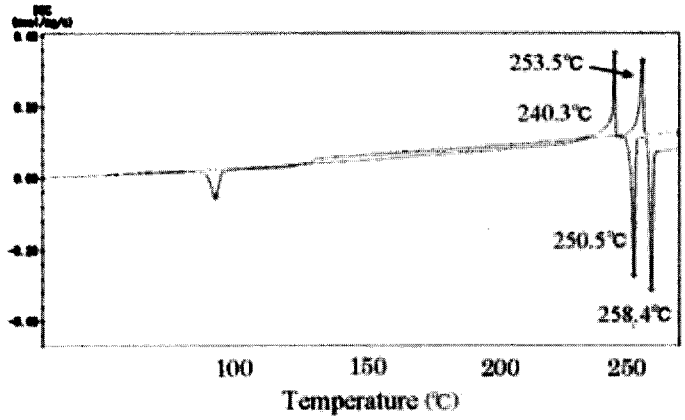

Fig.6 DSC thermograms of model (c) in the heating and the cooling processes.

3.2 Polymerization of semi-aliphatic PBOs

Our previous work revealed that the one-step (one-pot) polymerization in PPA at elevated temperatures is much more suitable for maintaining original good solubility of the formed PBOs than the two-step method [**1,2**]. But unfortunately, the one-pot PBO polymerization in strongly acidic hot PPA is not applicable to the current ester-linked systems which undergo hydrolytic decomposition. However, even in the ether-linked systems, the one-pot polymerization did not practically proceed

probably owing to some hydrolytic decomposition of the ether-linked dicarboxylic acid monomers in hot PPA. Accordingly, the two-step method was adopted in this work.

Different alkyl chain lengths of dicarboxylic acids were synthesized to investigate the effect on liquid crystallinity: C_6 (x =4) , C_9 (x = 7), and C_{10} (x = 8) for the ester type and C_9 (y = 9), and C_{10} (y = 10) for the ether type. The results of PHA polymerization are listed in **Table 1**.

Table 1 Reduced viscosities of PHAs and qualitative film properties of PBOs.

System	η_{red} (PHA) (dL/g)	Melt-flowability on POM	Thermotropic LC formation	Film toughness
C_6-ester	2.53	×	×	○
C_9-ester	0.54	△	△	△
C_{10}-ester	0.97	◎	○	△
C_9-ether	0.58	×	×	○
C_{10}-ether	1.38	×	×	◎

Sufficiently high molecular weights of PHAs were obtained with the reduced viscosities ranging 0.54–2.53 dL/g. The large difference of the resultant η_{red} values is probably due to slightly different purities of the dicarboxylic acid dichlorides used for the PHA polymerization. The PHA films were thermally cyclodehydrated at 280–300°C for 1 h in vacuum to ensure complete transformation to the corresponding PBOs without any undesirable thermal decomposition. All the obtained PBO films possessed film-formability.

3.3 PBO film properties and effect of magnetic orientation on thermal conductivity

The ether-type PBO films tend to provide much higher film toughness (elongation at break, ε_b) than the ester-type counterparts probably owing to better chain entanglement arising from more flexible ether linkages. In contrast to the results of the model compound approach, the ester-type PBOs showed higher thermotropic liquid crystallinity, which is closely related to their higher melt-flowability, than the ether-type counterparts, although the reason is not clear. The film properties of C_{10}-PBOs are summarized in **Table 2**.

Table 2 Film properties of *m*-HAB-based ester- and ether-linked PBO systems (C_{10}).

	Solubility in NMP	T_g (°C)	T_g^5 in N_2 (°C)	E (GPa)	σ_b (GPa)	ε_b (%)	λ (before) ($W\,m^{-1}K^{-1}$)	λ (after) ($W\,m^{-1}K^{-1}$)
C_{10}-ester	○	149	360	2.30	0.055	6.5	0.36	1.8
C_{10}-ether	○	110	450	3.12	0.128	86.2	0.27	0.38

The ester-type PBO (C_{10}) displayed an optically anisotropic phase between 214 and 340°C in the heating process on POM. The typical texture is shown in **Fig.7**, whereas the ether-type counterpart (C_{10}) possessed practically no thermotropic liquid crystallinity probably owing to its too high melt

viscosity. In order to improve the poor melt-flowability of the ether-type PBOs, we attempted two approaches: molecular weight control by using an adequate amount of a mono-functional end-capper and the incorporation of methoxy substituents into the dicarboxylic acid monomers. However, these approaches were less effective for reducing the melt viscosities of the ether-type PBOs.

Fig.7 POM photograph of the PBO film at 275°C (×500).

Thus, only the *m*-HAB-based ester-linked PBO system (C_{10}) survived as the candidate for the present purpose. The promising PBO film was inserted in a super-conducting magnet equipped with a temperature-controlled heating block as shown in **Figs.8** and **9** and kept at 230°C for 10 min in a nitrogen atmosphere under a considerably strong continuous magnetic field of 10 T along the sample thickness (Z) direction. The ester-type PBO sample (C_{10}) in the LC state was slowly cooled down to room temperature under the constant magnetic field. This procedure caused a drastic increase in thermal conductivity in the thickness direction from 0.36 $W m^{-1}K^{-1}$ without the magnetic treatment to 1.8 $W m^{-1}K^{-1}$ as listed in Table 2, which is about ten times higher than that of a commercially available polyimide film (Kapton-H, λ = 0.17 $Wm^{-1}K^{-1}$). This pronounced effect is attributed to the PBO chain alignment to the thickness direction, in accordance with the SEM observation of the cross section of the PBO film. On the other hand, the magnetic treatment effect was much smaller for the ether-type counterpart probably owing to its poor thermotropic liquid crystallinity.

Fig.8 Super-conducting magnet.

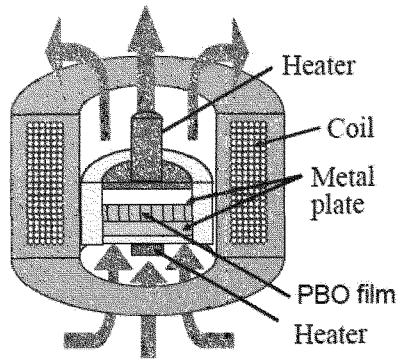

Fig.9 Schematic structure of magnet.

4. Conclusions

The model compound approach revealed that the use of *p*-HAB completely erases the thermotropic liquid crystallinity and that the ether type is much more advantageous for LC formation than the ester type. However, the relevant PBOs showed quite opposite results. After all, only the *m*-HAB-based ester-linked PBO system (C_{10}) survived for the present purpose among various semi-aliphatic PBO systems examined in this work. The ester-type PBO (C_{10}) achieved a very high Z-direction thermal conductivity of 1.8 $Wm^{-1}K^{-1}$ by magnetic orientation (10 T) at the LC state.

References

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