

## Thermotropic Liquid Crystals of Main-Chain Polyesters Having a Mesogenic 4,4'-Biphenyldicarboxylate Unit XI. Smectic Liquid Crystalline Glass

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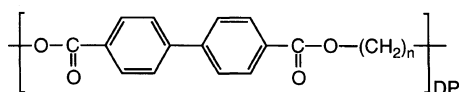
(Received January 7, 1998)

**ABSTRACT:** From examination of transition behavior in poly(pentamethylene 4,4'-biphenyl dicarboxylate) (BB-5) forming crystal,  $S_{CA}$  and isotropic phases, it was found that the liquid crystallization proceeds promptly and completely from the isotropic phase while the crystallization takes place partly even from the ordered smectic phase. The solid state of liquid crystal (LC) polymer is thus composed of crystal and smectic LC glass. Similarly as in the isotropic liquid glass of conventional polymers, the glass transition of the smectic LC glass is detected as an  $\alpha$ -relaxation which appears at around  $T_g = 50^\circ\text{C}$  by a dynamic mechanical method. The  $\alpha$ -relaxation shows considerable mechanical anisotropy such that the  $\tan \delta$  peak measured in a direction parallel to the layer is larger than that in a perpendicular direction. This anisotropy can be explained according to the structural characteristics of the smectic phase. Dynamic mechanical properties were also examined for a series of BB- $n$  polyesters with  $n$  of 5—12 and compared to those for poly(alkylene 2,6-naphthalene dicarboxylate)s (N- $n$ ) with the identical values of  $n$ . The smectic LC glass formed from BB- $n$  polyesters with  $n$  of 5—9 have the lower  $T_g$  than the isotropic liquid glass of N- $n$  polyesters with the corresponding  $n$ . Similar trend is observed in BB-6-co-N-6 copolymer system in which the  $S_A$  phase can be formed only from the copolymers with the N-6 compositions less than 60%. We thus concluded that the glass transition temperature of the smectic LC glass is lower than that of the isotropic liquid glass. The temperature of  $\gamma$ -relaxation due to the local motion of alkylene spacer is relatively higher in the smectic LC glass than that in the isotropic liquid glass. This may reflect the more stretched conformation of the flexible spacer in the smectic structures.

**KEY WORDS** Main-Chain Polymer / Polyester / Liquid Crystal / Smectic Liquid Crystalline Glass / Glass Transition / Mechanical Property /

The thermotropic liquid crystalline behavior of polymers with rigid mesogenic units interconnected through flexible spacers is well known from reports over the past two decades. The polymers are termed main-chain liquid crystalline (LC) polymers, which have generated much interest because of challenge of understanding such systems and their many industrial and commercial applications.

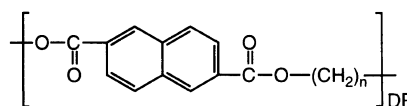
In this series of studies,<sup>1-9</sup> we have treated the following main-chain LC polyesters, poly(alkylene 4,4'-biphenyl dicarboxylate)s:



The polymers are designated as BB- $n$  ( $n$ ; carbon number of the methylene spacer). These BB- $n$  polyesters invariably form smectic mesophases when  $n$  varies from 3 to 9. In BB- $n$  with an even  $n$ , a  $S_A$  phase is formed with both axes of the polymer chain and biphenyl mesogen lying perpendicular to the layers. In contrast, the smectic structure of BB- $n$  with an odd  $n$  was identified as a  $S_{CA}$  phase, in which the tilt direction of the mesogenic group is the same in every second layer but opposite between neighboring layers.<sup>2,3,6,9</sup>

Despite detailed studies on liquid crystals, the structure and properties of solid films and fibers in BB- $n$  polyesters are relatively little known.<sup>7-13</sup> Assuming that the formation of a smectic phase takes place completely from the isotropic melt, BB- $n$  polyesters include the smectic LC glass instead of the isotropic liquid glass. Here, isotropic liquid glass and smectic LC glass are defined as the glassy states of isotropic liquid and smec-

tic liquid crystal, respectively. The smectic LC glass possesses long-range orientational and positional orders and so its properties are completely different from those of the isotropic liquid glass. This study clarifies the solid state morphology for the LC BB- $n$  ( $n = 5, 6, 7, 8, 9$ ) and shows the dynamic mechanical properties of the smectic LC glasses. The mechanical properties of the smectic LC glasses are compared with those of the isotropic liquid glasses observed in BB- $n$  with  $n$  of 10—12 and poly(alkylene 2,6-naphthalene dicarboxylate)s (N- $n$ ) with  $n = 5—12$ ,



which form no mesophase and solidify directly from isotropic liquid.

### EXPERIMENTAL

The polyesters were synthesized by melt transesterification of dimethyl 4,4'-biphenyl dicarboxylate and dimethyl-2,6-naphthalene dicarboxylate with  $n$ -alkane diols. Isopropyl titanate was used as catalyst. The inherent viscosities of the sample,  $\eta_{inh}$ , were measured at  $30^\circ\text{C}$  by using  $0.5\text{ g dL}^{-1}$  solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, and the polyesters with the inherent viscosities ranged from  $0.6$  to  $1.5\text{ dL g}^{-1}$  were used.

Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC II under a flow of dry nitrogen. Wide angle X-ray measurements were performed using a Rigaku-Denki RU-200 BH with Ni-filtered  $\text{Cu-K}_\alpha$  radiation. Dynamic mechanical mea-

measurements were carried out with a Seiko Instruments DMS 210 working in the tensile mode. The solid specimens were prepared by quenching the preceding phase (*i.e.*, the smectic phase for the LC polyesters and the isotropic phase for the non-LC polyesters). After the thermal treatments, the sample was cut out into a rectangular strip of 20 mm length, 2 mm wide and 0.2 mm thickness. The complex moduli and loss tangent were determined at frequencies of 0.01 to 20 Hz under a dry nitrogen atmosphere. The temperature was varied from  $-150^{\circ}\text{C}$  to  $250^{\circ}\text{C}$  at a rate of  $3^{\circ}\text{C min}^{-1}$ .

## RESULTS AND DISCUSSION

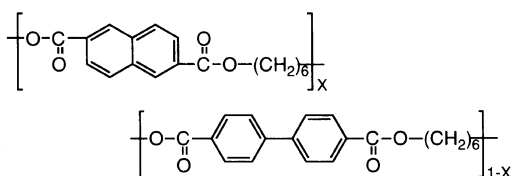
### Characterization of Polyesters

Two series of homopolyesters, BB-*n* and N-*n*, were prepared with the carbon numbers of the methylene spacer from 5 to 12 and their thermotropic behavior was analyzed from DSC thermograms.

BB-*n* polyesters with *n* of 5–9 exhibit the two transitions at  $T_m$  and  $T_i$  assigned to the crystal-LC phase transition and the isotropization of the LC phase, respectively. As mentioned in Introduction, the  $S_A$  and  $S_{CA}$  phases are formed from BB-6 and BB-8 and from BB-5, BB-7, and BB-9, respectively. BB-*n* with *n* of 10–12 form no mesophase, showing one peak of crystal melting on both the heating and cooling DSC thermograms.

N-*n* polyesters with even *n* show one peak of crystal melting while the odd-numbered N-*n* polyesters do not show any peak but a clear step in heat capacity associated with the glass transition. All the N-*n* polyesters with *n* of 5–12 thus form no mesophase and solidify directly from isotropic melt.

A series of BB-6-co-N-6 copolyesters having the molar ratios of BB-6 : N-6 = 75 : 25, 50 : 50, 40 : 60 and 25 : 75



were prepared. The transition temperatures from the cooling DSC data are plotted against the content of N-6 unit in Figure 1. Only the copolymers with N-6 contents less than 60% form a  $S_A$  phase and so solidify from the  $S_A$  phase, while the copolymers with the N-6 contents above 60% solidify directly from isotropic liquid state.

The inherent viscosities and thermodynamic data of the homopolymers and copolymers are listed in Table I.

### Representative Smectic LC Glass Prepared from BB-5 and Its Thermal and Mechanical Properties

Thermotropic LC polymers form isotropic liquid, LC, and crystal phases in order of decreasing temperature. In the liquid state, a polymer molecule is capable of assuming a large number of conformations due to the rotational freedom of individual chain atom about their connecting bonds. There is no significant correlation between the conformations assumed by the individual

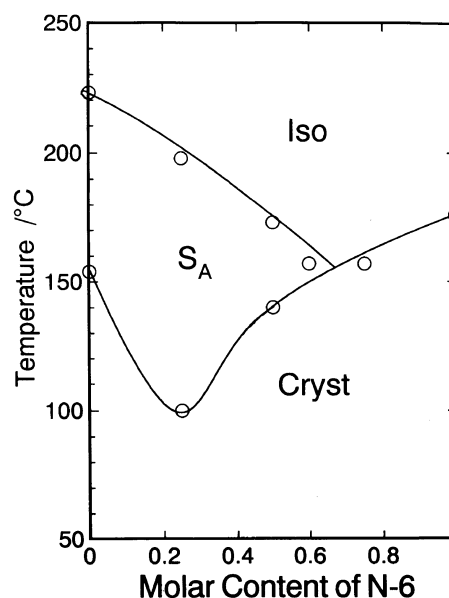


Figure 1. Transition temperatures and phase behavior of BB-6-co-N-6 copolyesters. Transition temperatures were determined from the cooling DSC curves measured at a rate of  $10^{\circ}\text{C min}^{-1}$ .

molecules so that the liquid state is characterized with random, haphazard arrangements of the polymer chain segments. In the LC phase, a long range orientational order requires polymer molecules to take some extended conformations. Starting from coiled, mutually interpenetrating macromolecules, these specified conformations in the LC phase seem to be hardly achieved instantaneously from purely kinetic reasons. We thus have a significant question as to whether the isotropic phase can be transformed to the LC phase completely or not in the polymeric system.

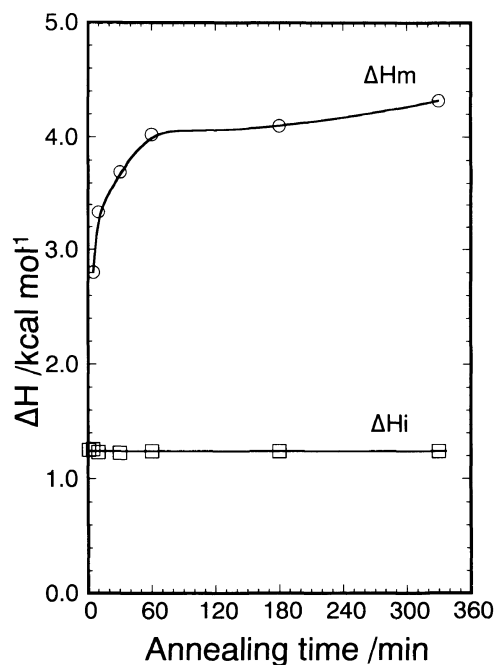
To examine this point, the isotropization enthalpy,  $\Delta H_i$ , was measured for the  $S_{CA}$  phase of BB-5 formed under an isothermal condition. On this measurement, BB-5 polyester was preheated for 5 min at isotropic temperature of  $230^{\circ}\text{C}$  to eliminate the effect of thermal history. The sample was then quenched to the  $S_{CA}$  phase of  $185^{\circ}\text{C}$ . After the isothermal formation of the  $S_{CA}$  phase at this temperature for a certain period, isotropization enthalpy,  $\Delta H_i$ , was measured at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . The crystallization behavior from the smectic phase was also examined with a similar procedure. After the sample was annealed at the  $S_{CA}$  temperature of  $185^{\circ}\text{C}$  for 30 min, it was quenched to the room temperature, heated up to  $140^{\circ}\text{C}$ , and maintained for a certain period for crystallization. The melting enthalpy of the crystal,  $\Delta H_m$ , was measured at a heating rate of  $10^{\circ}\text{C min}^{-1}$ .

In Figure 2,  $\Delta H_i$  and  $\Delta H_m$  thus determined are plotted against the time of the isothermal transformation, respectively.  $\Delta H_i$  is relatively constant independent on the transformation time which was varied from 1 to 330 min. This feature of the liquid crystallization is in contrast to that for the crystallization where  $\Delta H_m$  decreases significantly with a decrease of the crystallization time. Thus, it is likely that the perfect transformation of the isotropic phase to smectic phase takes place in a short period even in the polymeric system. This is reasonable since in the smectic phase the molecules

**Table I.** Characterization of polyesters

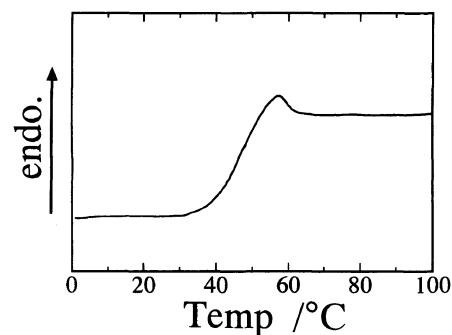
Sample	$\eta_{inh}/dL g^{-1}$	Calorimetric data <sup>a</sup>						
		Transition temperatures					Transition enthalpy <sup>b</sup>	
		Heating process			Cooling process			
		$T_g/^\circ C$	$T_m/^\circ C$	$T_i/^\circ C$	$T_m/^\circ C$	$T_i/^\circ C$	$\Delta H_m/kcal mol^{-1}$	$\Delta H_i/kcal mol^{-1}$
BB-5	0.91	43	173	212	86	196	0.60	1.27
BB-6	1.33	40	210	240	154	223	1.66	2.19
BB-7	0.77	35	165		97	139	2.52	3.10
BB-8	1.00	34	195		160	180	1.84	2.23
BB-9	0.65	37	154		111	115	3.11 <sup>c</sup>	
BB-10	0.64	40	171		152		3.97	
BB-11	0.73	36	149		107		2.89	
BB-12	0.70	35	161		138		4.41	
N-5	0.60	39						
N-6	0.62	55	213		175		3.50	
N-7	0.95	36						
N-8	0.69	46	181		141		3.32	
N-9	0.75	37						
N-10	0.77	37	144		106		3.57	
N-11	0.95	35						
N-12	0.74	32	139		102		3.67	
BB-6-co-N-6								
75:25	1.27	36	184	216	100	198	0.88	1.87
50:50	0.63	38	178	187	140	173	0.73	1.76
40:60	0.66	42	185		157 <sup>c</sup>		2.75 <sup>c</sup>	
25:75	1.53	61	190		157		1.85	

<sup>a</sup> Based on DSC data measured at a rate of  $10^\circ C min^{-1}$ . <sup>b</sup> Based on cooling DSC data. <sup>c</sup> Significant overlapping of the two peaks due to the isotropic to smectic and smectic to crystal transition.



**Figure 2.** Variation in isotropization enthalpy,  $\Delta H_i$  (rectangles), and the crystal melting enthalpy,  $\Delta H_m$  (circles), for BB-5 with the isothermal formation time.  $\Delta H_i$  (or  $\Delta H_m$ ) was measured for the sample which was quenched from the isotropic (or  $S_{CA}$ ) phase and held at  $185^\circ C$  (or at  $140^\circ C$ ) during a certain period for isothermal formation of the  $S_{CA}$  (or crystal) phase.

are mobile and can be packed without significant defects although some deformation might be included with respect to the orientation of  $n$ - and  $c$ -directors. The



**Figure 3.** DSC thermograms showing the glass transition of  $S_{CA}$  LC phase in BB-5.

crystallization does not proceed completely in a short period even if it takes place from the ordered  $S_{CA}$  phase. This may be due to the fact that the structural order of the  $S_{CA}$  phase is fairly less than that of the crystal. Such a characteristic transformation results in the interesting solid morphology in which no isotropic liquid glassy phase is included. In other words, the solid of LC polymers is composed of two phases, LC glass and crystal while the solid of the conventional polymers is composed of isotropic liquid glass and crystal.

Because of a very late crystallization, it is possible to prepare the BB-5 solid composed only of the glassy smectic phase by quenching the smectic phase to the room temperature. This can be clearly recognized from the X-ray photograph as shown later in Figure 6, where the pattern characteristic of the mesophase is still observed. DSC thermogram of this sample shows the typical

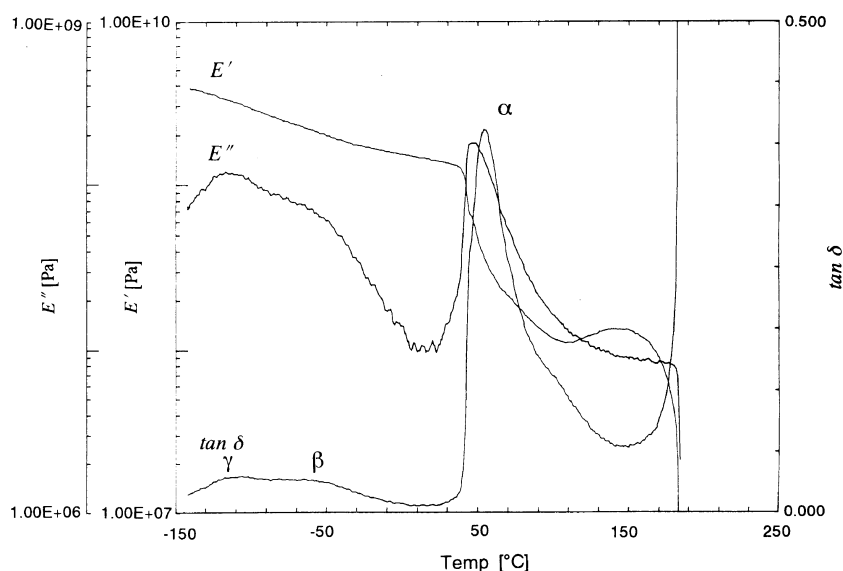


Figure 4. Storage modulus, loss modulus, and loss tangent as a function of temperature at 10 Hz for BB-5 specimen quenched from smectic melt.

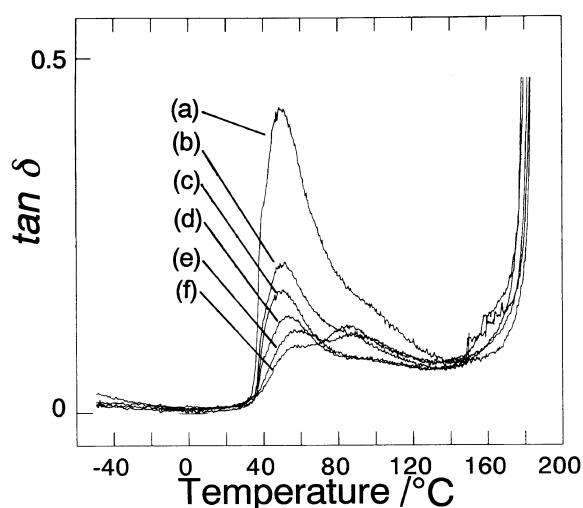


Figure 5. Loss tangent as a function of temperature at 10 Hz for BB-5 samples with different degrees of crystallinity. The crystallinity was controlled by annealing the specimen at 140°C for a certain period of (a) 0 min (as quenched from  $S_{CA}$ ), (b) 1 min, (c) 5 min, (d) 10 min, (e) 30 min, and (f) 60 min (refer to Figure 2).

jump of the heat capacity at around 45°C (see Figure 3) and dynamic mechanical analysis (DMA) shows the relaxations characteristic to the glass transition as stated in details below.

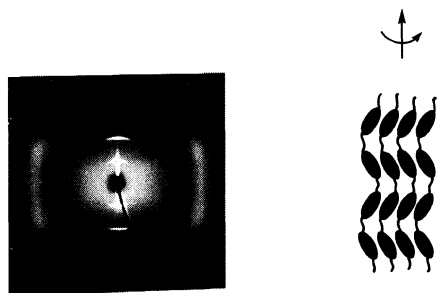
Figure 4 shows the temperature dependence of the storage tensile modulus ( $E'$ ), the loss modulus ( $E''$ ) and the mechanical loss tangent ( $\tan \delta$ ) for a glassy smectic film of BB-5. Data were obtained with a forced oscillation at a frequency of 10 Hz. Three relaxations can be detected at around 50, -60, and -120°C, and designated here as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -processes, respectively. Since the temperature of  $\alpha$ -relaxation corresponds to the glass transition temperature ( $T_g$ ) detected by DSC,  $\alpha$ -relaxation can be connected to the glass transition and attributed to the segmental motion of molecules. The  $\beta$ -process can be connected with the motion of the aromatic part including the ester group.<sup>11-13,15</sup> The  $\gamma$ -process is attributed to local rotation of methylene group commonly observed for polymers containing methylene sequences.<sup>14,16</sup> These mechanical relaxations

are similar to those observed in the isotropic liquid glass of the conventional polymers. The activation energies estimated from the frequency dependence of the relaxation temperature are 75, 35, and 10 kcal mol<sup>-1</sup> for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxations, respectively.

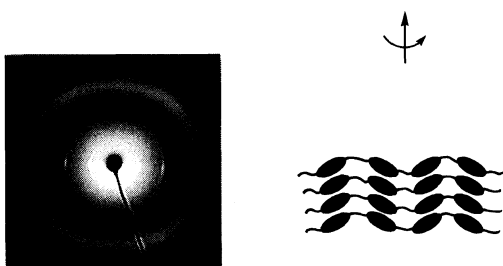
The dependence of the strength of  $\alpha$ -relaxation on the degree of crystallinity was examined as shown in Figure 5. The BB-5 sample was quenched from the  $S_{CA}$  phase and annealed at 140°C for a certain period for controlled enhancement of the crystallinity (refer to Figure 2). Since the sample became brittle as the crystallization proceeded more and more,  $\beta$ - and  $\gamma$ -transitions could not be measured. Increasing crystallinity results in decrease of the loss signal, indicating that the  $\alpha$ -process is attributed to a smectic LC glass.

The use of oriented specimens is a further step to understand molecular relaxation. Two smectic LC glassy fibers of BB-5 with different orientation were produced by the two methods of spinning. Fiber A was prepared by drawing the isotropic melt at a high rate of about 1 m s<sup>-1</sup>. The X-ray pattern of fiber A shows that the polymer chains lie parallel to the axis and hence that the smectic layers arrange perpendicular to the fiber axis as found in part (a) of Figure 6. Drawing the smectic melt at a low rate of about 1 cm s<sup>-1</sup> produced fiber B in which the smectic layers lie parallel to the fiber axis, *i.e.*, the polymer chains lie perpendicular to the axis (see part (b) of Figure 6). The orientation of fiber B is unusual, but can be explained by a chain folded lamellar structure such that the lamellae lie preferentially in a direction parallel to the elongation flow.<sup>7-9</sup> The results of DMA obtained for the two oriented fibers of A and B are shown in Figure 7, where only  $\tan \delta$  is presented because the small cross section of the fibers prevents to determine the accurate value of Young's modulus from being obtained. Considerable mechanical anisotropy with  $\tan \delta$  of fiber B larger than that of fiber A can be seen for the  $\alpha$ -relaxation while the intensities of  $\beta$  and  $\gamma$  relaxations are similar. The ratio of  $\tan \delta$  peak height is around 3. This anisotropy is simply explained according to the layered characteristics of the smectic structure as following. In the  $S_{CA}$  phase, the mesogenic

## (a) Fiber A



## (b) Fiber B



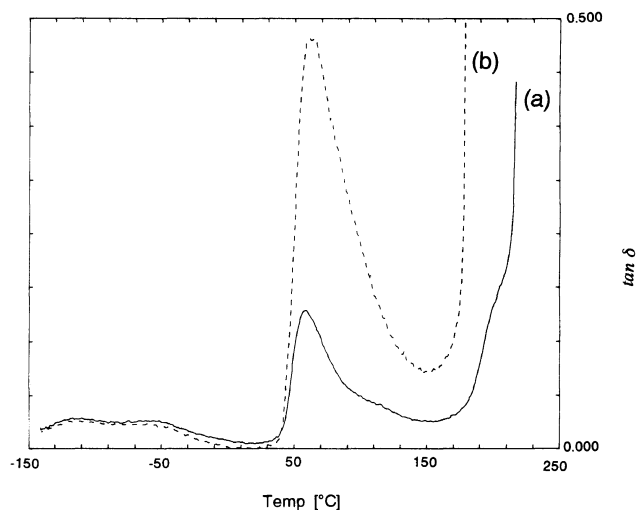
**Figure 6.** X-Ray photographs for (a) fiber A drawn from the isotropic melt of BB-5 at a rate of around  $1 \text{ m s}^{-1}$  and (b) fiber B drawn from the smectic melt of BB-5 at a rate of  $1 \text{ cm s}^{-1}$ . The fiber axis is in the vertical direction. The molecular arrangements deduced from the X-ray patterns are also illustrated.

groups lie with one-dimensional positional order along the polymer chain axes and so form the layers. Along each layer, their centers of gravity have no positional order, *i.e.* the mesogens are laterally packed with liquid-like nature. Hence, the motion of the chain in the direction perpendicular to the layer is restricted while relatively free motion is allowed in the parallel direction.

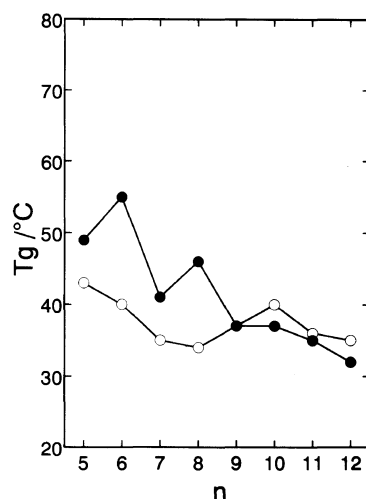
Anisotropy in mechanical properties is also observed with respect to the terminal flow behavior in the fibers. As seen in Figure 7, the temperature at which the terminal flow takes place and so that  $\tan \delta$  diverges to infinity, corresponds to  $T_i$  ( $210^\circ\text{C}$ ) for fiber A while it corresponds to  $T_m$  ( $170^\circ\text{C}$ ) for fiber B. This can be also explained in terms of the structural features of smectic phase as mentioned above.

#### Dependence of Glass Transition Temperature on Carbon Number

It is interesting to examine how  $T_g$  of the LC glass depends on the carbon number of flexible spacer. With respect to this, we first refer to  $T_g$  of the isotropic liquid glass observed in the N- $n$  polyesters with  $n = 5$ – $12$ . These polyesters form no mesophase so that crystallization takes place directly from the isotropic melt like in the conventional polymers.  $T_g$  temperatures as determined by DSC are plotted against  $n$  by closed circles in Figure 8. Figure 9 shows the typical viscoelastic properties observed in N-6. As observed in BB-5, three  $\alpha$ ,  $\beta$ , and  $\gamma$ -relaxations can be observed. The temperatures of these relaxations are plotted against  $n$  by closed marks in



**Figure 7.** Temperature dependence of loss tangent measured at 10 Hz for the two different BB-5 fibers; (a) solid curve for fiber A and (b) dashed curve for fiber B (refer to Figure 6).

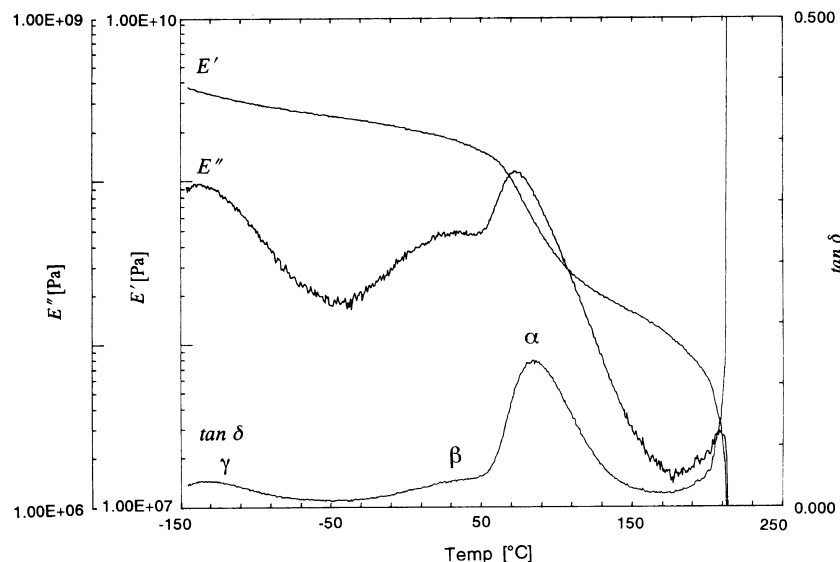


**Figure 8.** Variation in DSC glass transition temperatures in BB- $n$  (open circles) and N- $n$  (closed circles) polyesters with  $n$ .

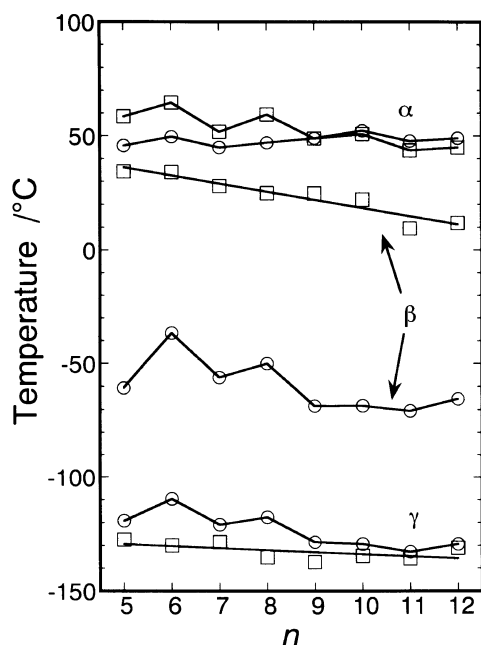
Figure 10. Here, it should be noted that the  $\beta$ -relaxation temperature was determined with a significant error because of the overlapping with  $\alpha$ -relaxation.  $T_g$  and  $T_\alpha$  showing the odd-even oscillation decrease steadily with an increase of  $n$ .  $T_\beta$  also decreases with  $n$  although  $T_\gamma$  is relatively constant at around  $-130^\circ\text{C}$ .

$T_g$  in BB- $n$  determined by DSC are plotted against  $n$  by open circles in Figure 8. The mechanical  $\alpha$ ,  $\beta$ , and  $\gamma$ -relaxation temperatures are given by open marks in Figure 10. It must be noted that the BB- $n$  polyesters show an unusual variation of  $T_g$  and  $T_\alpha$  on  $n$ . The LC BB- $n$  polyesters with  $n$  of 5–8 forming the smectic phase show the lower  $T_g$  and  $T_\alpha$  than the non-LC BB- $n$  with  $n$  of 10–12 despite the higher chain stiffness. This variation is contradictory to that observed in N- $n$  polyesters, in which  $T_g$  decreases steadily with increase of chain flexibility.<sup>16</sup> Since  $T_g$  and  $T_\alpha$  are almost same between non-LC BB- $n$  and N- $n$  with  $n$  of 10–12, this anomalous variation can be understood if the smectic LC glass shows the lower  $T_g$  and  $T_\alpha$  than the isotropic liquid glass.

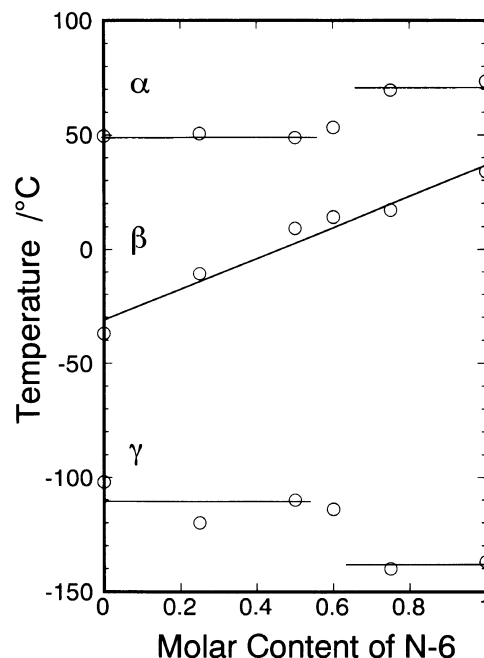
Let us now expand the observation to the copolymers



**Figure 9.** Temperature dependence of storage modulus, loss modulus, and loss tangent for N-6 specimen quenched from isotropic melt. Frequency was 10 Hz.



**Figure 10.** Variation in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxation temperatures for BB- $n$  (circles) and N- $n$  (rectangles) polyesters with  $n$ . The temperatures were determined from the peak of loss modulus,  $E''$ , measured at 10 Hz.



**Figure 11.** Variation in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxation temperatures of BB-6-co-N-6 copolyesters with the molar content of N-6. Temperatures were determined from the peak of loss modulus,  $E''$ , measured at 10 Hz.

of BB-6-co-N-6. As observed in the homopolymers of BB- $n$  and N- $n$ , the copolymers show up three  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxations. The relaxation temperatures,  $T_\alpha$ ,  $T_\beta$ , and  $T_\gamma$  are plotted against the molar content of N-6 units in Figure 11. The glass transition temperatures in a copolymer system is related to its composition as described in many cases successfully and simply with the 'Fox-Flory' equation where the glass transition temperature is represented with a continuous function of the volume fractions. In this series of copolymers,  $T_\alpha$  remains almost constant around 50°C up to a N-6 content of 60%. For higher N-6 content,  $T_\alpha$  rises discontinuously to 70°C. On comparing this feature with the phase behavior of Figure 1, one can find that the lower  $T_\alpha$  is observed for the copolymers forming the  $S_A$  phase.

The overall results thus lead to the conclusion that a

LC glass shows a lower transition temperature than the isotropic liquid glass. Similar conclusion has been deduced in the aromatic copolyesters forming nematic liquid crystal by Zachmann *et al.*<sup>17,18</sup> Lower  $T_g$  of LC glass is explainable, as reported by Zachmann *et al.*,<sup>17</sup> if the change of the volume on the isotropic-smectic transition at  $T_i$  is smaller than the volume difference between the smectic LC and isotropic liquid glasses. Such a situation can be expected since the free volume necessary to promote the restricted motion in the smectic LC glass is considerably smaller than the one which allows segmental motion in the isotropic liquid glass.

### Local Motion of Polyesters Associated with $\beta$ - and $\gamma$ -Relaxations

With respect to the  $\beta$ -relaxation, we find that  $T_\beta$  of N- $n$  is fairly higher than that of BB- $n$  (see Figure 10). This means that the rotational motion of the naphthalene moiety is more restricted than that of biphenyl moiety.  $T_\beta$  decreases with increase of  $n$  in both the BB- $n$  and N- $n$  polymers although  $T_\beta$  of the smectic LC BB- $n$  with  $n$  of 5 to 9 shows some odd-even oscillation. In the BB-6-co-N-6 copolymers, as seen in Figure 11,  $T_\beta$  increases continuously with molar content of N-6 unit, suggesting that the  $\beta$ -relaxation is not closely associated with the structure of the glassy state.

$T_\gamma$  of LC BB- $n$  polymers with  $n$  of 5—9, showing some odd-even oscillation, is relatively higher than that in non-LC N- $n$  polymers with identical  $n$  (see Figure 10). Higher  $T_\gamma$  of the LC glass can be also observed in the copolymer system as found in Figure 11.  $T_\gamma$  is around  $-110^\circ\text{C}$  for the LC copolymers while  $-140^\circ\text{C}$  for the non-LC copolymers. This may be caused by the extended conformation of polymethylene units in the smectic structures.

### CONCLUSIONS

The transformation behavior from isotropic liquid to smectic phase was examined for the BB-5 polyester. The transformation proceeds promptly and completely even in the polymeric LC while the crystallization occurred partly even from the smectic phase. The solid state of LC polymer is thus composed of crystal and smectic LC glass. The glass transition of the smectic LC glass was detected as a jump of heat capacity by the DSC and the related segmental motion was observed as an  $\alpha$ -relaxation by the dynamic mechanical method. The  $\alpha$ -relaxation of the BB-5 polyester showed considerable mechanical anisotropy.  $\tan\delta$  of  $\alpha$ -relaxation measured in the direction parallel to the layer was larger than that in the perpendicular direction. Structural characteristics of the smectic phase can explain this anisotropy.

Dynamic mechanical properties of BB- $n$  polyesters with  $n$  of 5—12 were studied and compared with those for N- $n$  polyesters with the corresponding  $n$ . The smectic

LC glass prepared from BB- $n$  polyesters with  $n$  of 5—9 had relatively lower  $T_\alpha$  than the isotropic liquid glass of polyesters of BB- $n$  with  $n$  of 10—12 and N- $n$  polyesters with the identical  $n$ . The same was found for BB-6-co-N-6 copolymers which form a  $S_A$  phase depending on the composition. We thus conclude that the glass transition temperature of the smectic LC glass is lower than that of the isotropic liquid glass.

The temperature of  $\gamma$ -relaxation due to the local motion of alkylene spacer is relatively higher for the smectic LC glass than that for the isotropic liquid glass. This may be due to more stretched conformation of the flexible spacer in the smectic LC glass.

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