

# Melt Viscosity and Flow Birefringence of Polycarbonate

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## SYNOPSIS

Melt viscosity and flow birefringence of bisphenol A-type polycarbonate were measured and analyzed by the application of rubber-like photoelastic theory. The melt viscosity in the Newtonian flow region increased with the molecular weight to the power of 3.4. In polycarbonate, the shear stress of the Newtonian flow region was to  $10^6$  dyn/cm<sup>2</sup>, whereas in PMMA it was at most  $3 \times 10^5$  dyn/cm<sup>2</sup>.

The flow birefringence  $\Delta n$  has a linear relation with shear stress  $S$ , that is  $\Delta n = 5.7 \times 10^{-10} S$ . The principal polarization difference of flow unit  $\alpha_1 - \alpha_2$  was  $1.62 \times 10^{-23}$  cm<sup>3</sup>, which was obtained by the application of the rubber-like elastic theory. In PMMA, it was  $3.9 \times 10^{-25}$  cm<sup>3</sup>; about 1/40 of that was polycarbonate. The anisotropy of polarizability of the flow unit of polycarbonate was also about 40 times larger than that of PMMA. So the anisotropy reflected the large flow birefringence of the polycarbonate.

## INTRODUCTION

Polycarbonate is an amorphous polymer and has not only a high optical transparency, but also good thermal stability, so it is used for optical parts, such as optical lenses and, recently, optical disk substrate. However, polycarbonate has the disadvantage of having a large birefringence, which causes noise and signal error. So in polycarbonate it is necessary to investigate the appropriate fabrication conditions for minimizing the large birefringence.

As for the birefringence produced in optical parts, two main causes are considered; one is the orientation of the longchain molecule; another is the intramolecular distortion in polymer processing in the melt. Since the former cause is known to be larger by two or three orders than the latter,<sup>1</sup> and can not be diminished by means of the thermal annealing, it is necessary to investigate the molecular orientation.

In polycarbonate, birefringent behavior due to molecular distortion is well known, however, the behavior due to molecular orientation has not been analyzed in detail. Therefore, we studied the flow birefringent behavior for the commonly used bisphenol A-type polycarbonate samples.

## EXPERIMENTAL

### Materials

The characteristics of the polycarbonate samples used are listed in Table I. Molecular weights were measured by Gel Permeation Chromatography, with THF as the diluent.

### Structural Characterization

Structural characterization was carried out by use of IR and proton NMR. Every sample had the characteristic IR absorption, 5.62 ( $\nu C = O$ ), 8.1 ( $\nu C = O$ ), 8.35 ( $\nu C = O$ ), and 8.65 ( $\nu C = O$ )  $\mu m$  originating from the carbonate group.<sup>2</sup>

The proton NMR spectrum of polycarbonate is shown in Figure 1. Two types of hydrogen, corresponding to methyl groups and aromatic groups, could be assigned. The ratio of these peaks show that these samples are bisphenol A-type polycarbonate.

### Viscoelasticity

The viscoelastic properties were measured with a Rheovibron DDV-II-EA, made by Orientec Co., Ltd.<sup>3</sup> The frequency was 110 Hz and the heating rate was 1°C/min. The result is shown in Figure 2. Every sample had the same glass transition tem-

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**Table I** Samples of Polycarbonate

Sample No.	1	2	3
$\bar{M}_w$ ( $10^4$ )	3.6	3.1	2.9
$E'$ ( $10^{10}$ dyn/cm <sup>2</sup> ) 25°C	2.21	2.21	2.25
$T_g$ (°C)	152	155	152
$\eta$ ( $10^3$ Poise) 300°C	1.8	1.0	0.7
$\bar{M}_w/\bar{M}_n$	3.0	2.8	3.0

perature,  $T_g$ , at 152°C and gamma absorption at -76°C associated with the motion of the monomer unit as a whole. These results are almost the same as those previously reported in the literature.<sup>4</sup>

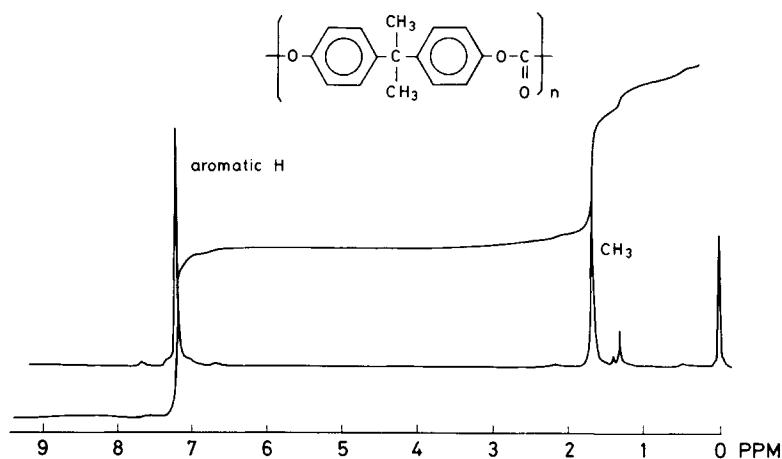
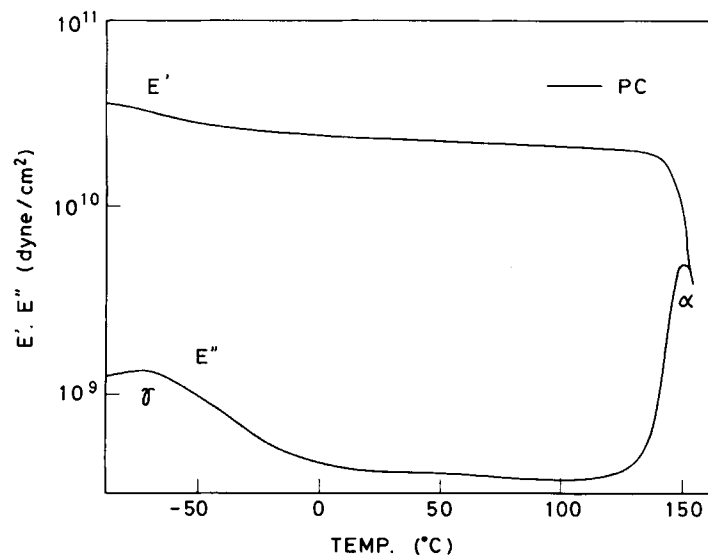
The magnitude of absorption in polycarbonate was small around room temperature and the dy-

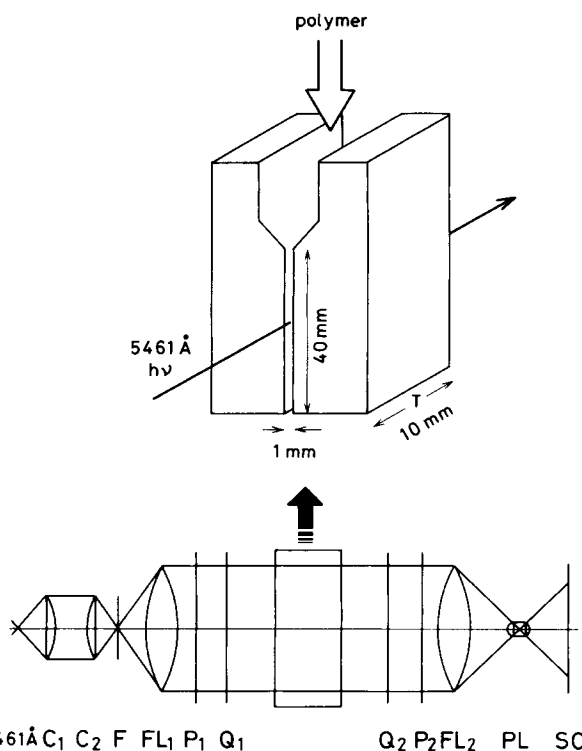
namic viscoelastic modulus was nearly constant at  $2.2 \times 10^{10}$  dyn/cm<sup>2</sup> from 10–120°C.

### Melt Viscosity and Flow Birefringence

The flow properties were measured using a capillary rheometer, made by Iwamoto Seiki Co., Ltd.<sup>5</sup> The diameter of the capillary was 1 mm and the length was 10 mm,  $L/D = 10$ . Bagley's correction was not carried out because no pressure drop at the entrance of the capillary was observed.

The block diagram of the flow birefringence measurement system is shown in Figure 3. The slit was connected to the bottom of the capillary rheometer. Monochromatic light, with wavelength 546.1 nm, was supplied from a mercury light source. By in-

**Figure 1** N.M.R. spectrum of polycarbonate.**Figure 2** Viscoelastic property of polycarbonate.



5461Å C<sub>1</sub> C<sub>2</sub> F FL<sub>1</sub> P<sub>1</sub> Q<sub>1</sub> Q<sub>2</sub> P<sub>2</sub> FL<sub>2</sub> PL SC  
**Figure 3** Block diagram of flow birefringence measurement.

serting a  $\frac{1}{4}$  wavelength plate ( $Q_1, Q_2$ ), the linear polarized light ( $P_1, P_2$ ) was changed to circularly polarized light. The circularly polarized light was then passed through a 1 cm path glass cell containing the molten polycarbonate. The resultant image was projected onto a screen and was photographed.

## RESULTS AND DISCUSSION

### Melt Viscosity

#### Flow Curve

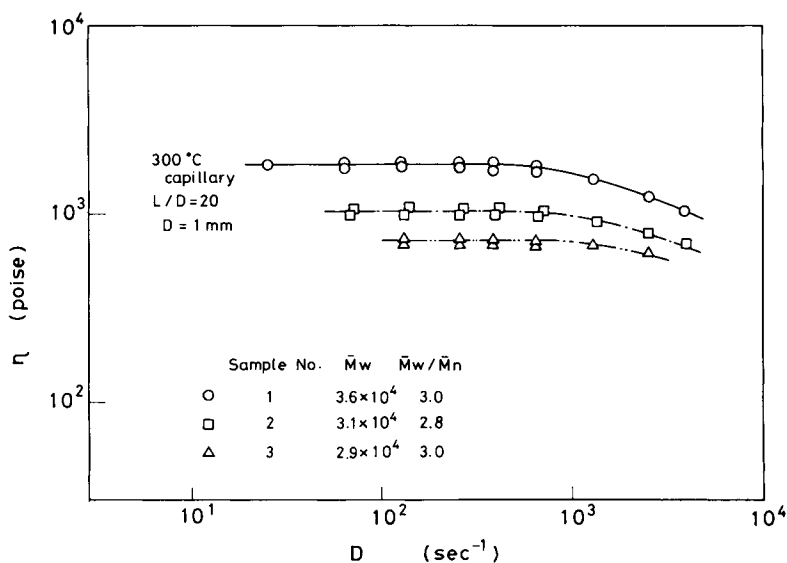
The flow curves at 300°C for PC samples with various molecular weights are shown in Figure 4. For any sample, the Newtonian flow changes to the non-Newtonian flow at a shear rate of around  $10^3 \text{ sec}^{-1}$ .

In Figure 5, the effect of temperature on the melt viscosity for the sample of molecular weight  $3.1 \times 10^4$  is shown. The temperature varied from 210 to 340°C. As the temperature increased, the melt viscosity lowered and the Newtonian flow region extended further to the higher shear rates.

A straight line through the points on each curve, which mark the change from Newtonian to non-Newtonian flow, produces a line with a slope of -45 degrees. This line corresponds to a shear stress of  $S = 10^6 \text{ dyn/cm}^2$ . The same measurement was done for PMMA<sup>5</sup> ( $\bar{M}_w = 7.3 \times 10^4, \bar{M}_w/\bar{M}_n = 1.7$ ). The result for PMMA at 222°C is also shown in Figure 5. For this sample, non-Newtonian flow was observed at a lower shear stress,  $S = 3 \times 10^5 \text{ dyn/cm}^2$ .

#### Non-Newtonian Flow of Polycarbonate and PMMA

In the previous section, the non-Newtonian flow region of polycarbonate was observed to occur in the higher shear rate region. PMMA has a polar group with a large dipole moment of 1.41 D in the side



**Figure 4** Flow behavior of polycarbonate with various molecular weights.

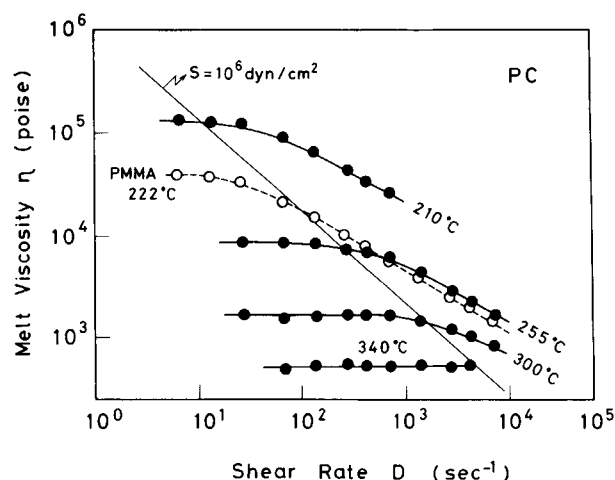


Figure 5 Flow curves of polycarbonate and PMMA.

chain,<sup>6</sup> and large inter- and intramolecular chain interactions. Therefore, the deformation of these bondings by shear force is directly reflected in the decrease of viscosity. That is, the large molecular interaction in PMMA causes non-Newtonian flow at lower shear rates to be produced. In contrast, polycarbonate has a polar group whose dipole moment is  $0.87 D$  in the main chain and has weaker molecular interaction, which is considered to be mainly an intramolecular interaction.

The melt viscosity of polycarbonate in the non-Newtonian flow region decreases linearly with the shear rate  $D$ , whose slope, that is, flow index, was  $-0.68$  at any temperature, as is shown in Figure 5. This value is near to the reported value of PMMA,

$-0.63$ .<sup>5</sup> The die swell in polycarbonate was observed at  $3 \times 10^6$  dyn/cm<sup>2</sup>, whereas in PMMA it was at  $1 \times 10^6$  dyn/cm<sup>2</sup>. Consequently both the die swell and non-Newtonian flow of polycarbonate were observed at a shear rate three times higher than those in PMMA. The difference of these is also explained by the difference in the strength and type of molecular interactions as described above.

## Flow Birefringence

### Flow Birefringence Measurement

An example of flow birefringence photographs is shown in Figure 6. As the shear rate increased, the fringe order was also observed to increase.

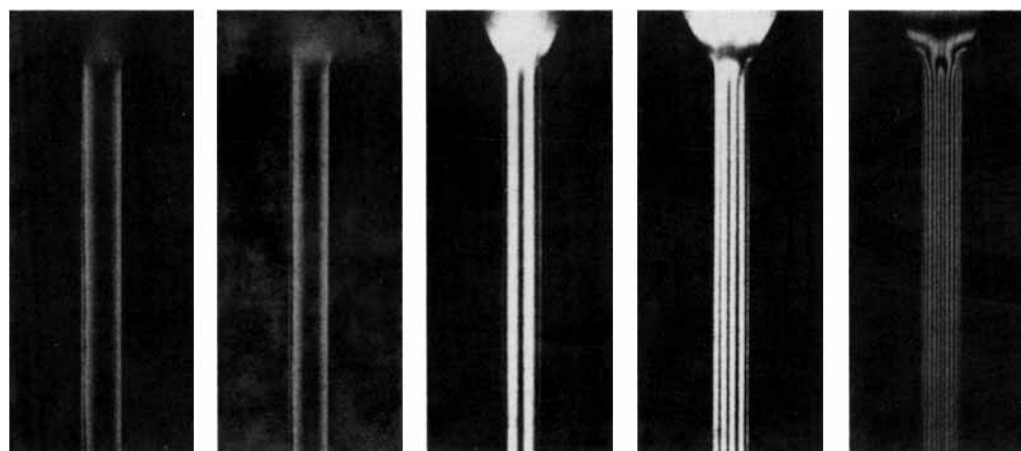
The flow birefringence  $\Delta n$  could be calculated by the following equation.

$$\Delta n = \lambda N / T \quad (1)$$

Here,  $\lambda$  is the wavelength of the light source, 546.1 nm, and  $T$  is the optical path length, 10 mm.  $N$  is the fringe order. The shear rate  $D$  was calculated assuming that the slit had parallel flat surfaces. The relationship between  $\Delta n$  and  $D$  is shown in Figure 7. The value of  $\Delta n$  changes largely depending upon the molecular weight and temperature.

The relationship between  $\Delta n$  and  $S$  is shown in Figure 8. The relation was almost linear and independent of both molecular weight and temperature. This relation is expressed as follows.

$$\Delta n = 5.7 \times 10^{-10} S \quad (2)$$



Shear Rate  $D=62.8\text{sec}^{-1}$      $94.2\text{sec}^{-1}$      $157\text{sec}^{-1}$      $314\text{sec}^{-1}$      $628\text{sec}^{-1}$

Figure 6 Shear rate dependence of fringe order of molten polycarbonate at 300°C.

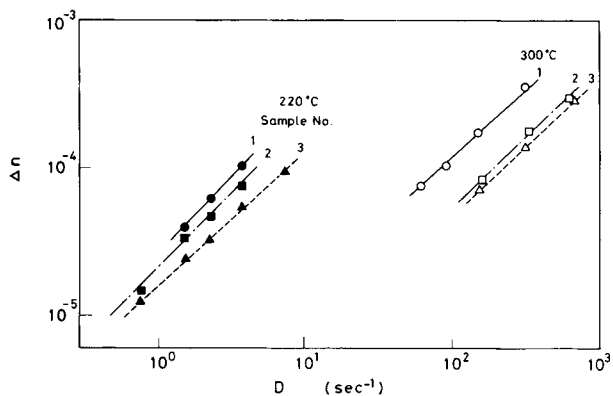


Figure 7 Shear rate dependence of birefringence of polycarbonate.

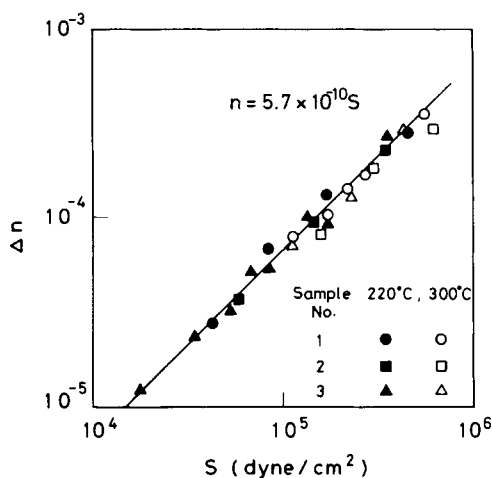


Figure 8 Shear stress dependence of birefringence of polycarbonate.

This means that the  $\Delta n$  produced by flow is determined mainly by the shear stress  $S$ .

**Application of Rubber-Like Photoelastic Theory**

From the photoelastic theory,

$$S = \frac{1}{2}(\sigma_1 - \sigma_2) \sin 2\phi \tag{3}$$

$$\Delta n = C(\sigma_1 - \sigma_2) \tag{4}$$

Here,  $\sigma_1 - \sigma_2$  is the first normal stress difference,  $C$  is the stress optical coefficient, and  $\phi$  is the extinction angle. From these equations we can obtain the relationship:

$$\Delta n = 2CS / \sin 2\phi \tag{5}$$

In order to evaluate the extinction angle, the isoclinic line without a  $\frac{1}{4}$  wave length plate was observed. An example of the result is shown in Figure 9. From this figure, the extinction angle was 45 degrees. The same results were obtained under various measuring conditions. Equation (5) thus becomes.

$$\Delta n = 2CS \tag{6}$$

By use of this equation, stress optical coefficient  $C$  can be calculated. The calculated values are shown in Table II. Schrijver and Werumeus Buning<sup>7</sup> measured the flow birefringence of polycarbonate from the interference between the injected and reflected laser light. They obtained a value for the stress op-

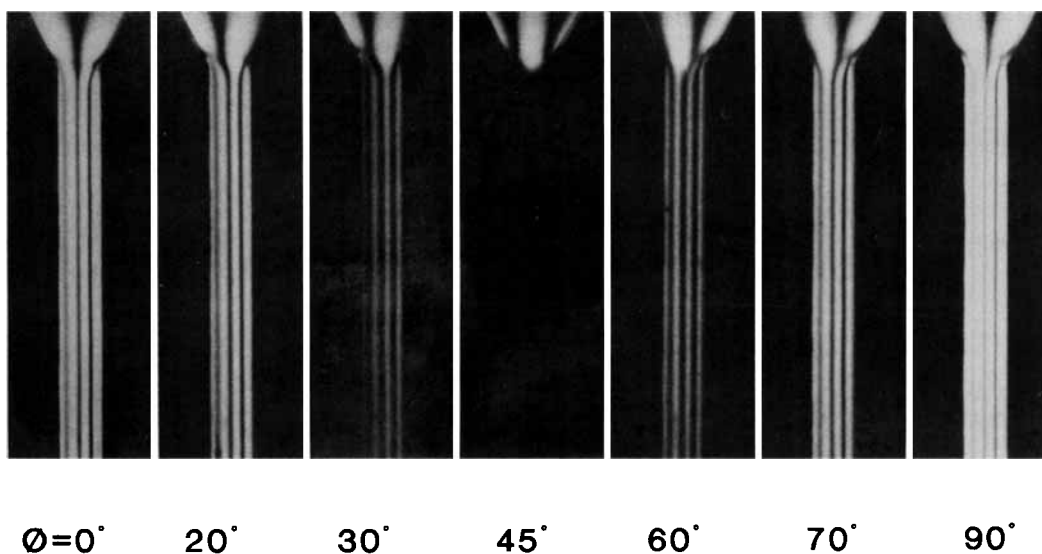


Figure 9 Extinction angle of molten polycarbonate at  $D = 62.8 \text{ sec}^{-1}$ ,  $260^\circ\text{C}$ .

**Table II Principal Polarizability Difference of Polycarbonate**

Temp. (°C)	$C$ (cm <sup>2</sup> /dyn)	$CT$ (cm <sup>2</sup> K/dyn)	$\alpha_1 - \alpha_2$ (cm <sup>3</sup> )
220	$4.1 \times 10^{-10}$	$2.0 \times 10^{-7}$	
260	3.9	2.1	$1.62 \times 10^{-23}$
280	3.8	2.1	
300	3.5	2.0	

tical coefficient  $C$  of  $3 \times 10^{-10}$  cm<sup>2</sup>/dyn at 255°C. This is nearly equal to our results.

In Table II, the  $CT$  values are also shown for various temperatures. They were almost constant at  $2.0 \times 10^{-7}$  cm<sup>2</sup>K/dyn. By applying rubber-like photoelastic theory, the principal polarizability difference of flow unit  $\alpha_1 - \alpha_2$  could be obtained,

$$C = \frac{2\pi}{45kT} \cdot \frac{(n_0^2 + 2)^2}{n_0} (\alpha_1 - \alpha_2) \quad (7)$$

Here,  $n_0$  is the refractive index and  $k$  is the Boltzman constant. In polycarbonate,  $\alpha_1 - \alpha_2$  was equal to  $1.62 \times 10^{-23}$  cm<sup>3</sup>.

#### Comparison between Polycarbonate and PMMA

We made the same measurement for PMMA, which is known as a low birefringent material, by use of the same material previously reported.<sup>5</sup> The results are shown in Table III. The value of  $C$  of PMMA was  $-1.0 \times 10^{-11}$  cm<sup>2</sup>/dyn at 220°C. Retting<sup>8</sup> also measured the  $C$  at 140°C as  $-1.11 \times 10^{-11}$  cm<sup>2</sup>/dyn. These values were almost the same, independent of the temperature.

Using of eq. (7),  $\alpha_1 - \alpha_2$  of PMMA was calculated to be  $3.9 \times 10^{-25}$  cm<sup>3</sup>. The principal polarization difference of polycarbonate proved to be 40 times larger than that of PMMA.

The anisotropy of the polarizability of the monomer unit of these two polymers has already been studied. Dettenmaire and Fischer<sup>9</sup> obtained, using the light scattering method, values of  $5.6 \times 10^{-24}$

for polycarbonate, and  $1.4 \times 10^{-25}$  cm<sup>3</sup> for PMMA. Erman et al.<sup>10</sup> measured the anisotropy of polycarbonate using depolarized Rayleigh scattering and electrical birefringence, and found it to be  $5.2 \times 10^{-24}$  cm<sup>3</sup>. This value is almost equal to Dettenmaire's one.

These results showed that the anisotropy of the polarizability of the monomer unit of polycarbonate was also about 40 times larger than that of PMMA. Therefore the large flow birefringence of polycarbonate is mainly due to the anisotropy of the polarizability of the monomer unit itself.

The reason that the polycarbonate has a large birefringence in flow is that the polycarbonate has two benzene rings in each monomer unit. The benzene ring has a large anisotropy of polarizability,<sup>11</sup>  $5.96 \times 10^{-24}$  cm<sup>3</sup>. The in plane polarizability is larger than that of the polarizability perpendicular to the plane.

#### CONCLUSION

Melt viscosity and flow birefringence of the bisphenol A-type polycarbonate were measured and analyzed from the point of molecular orientation, and were discussed in relation to PMMA.

The melt viscosity in the Newtonian flow region increased according to the 3.4th power of the molecular weight. Newtonian flow was observed for shear stresses below  $10^6$  dyn/cm<sup>2</sup>, whereas, in PMMA, the non-Newtonian region started at  $3 \times 10^5$  dyn/cm<sup>2</sup>. The reason for such a difference in these materials was explained in terms of the weak main chain polar-group in polycarbonate, giving rise to weaker intermolecular interaction than that which occurs in PMMA.

The flow birefringence,  $\Delta n$ , in the Newtonian flow region has a linear relation with shear stress  $S$ . In polycarbonate, the relation was obtained as  $\Delta n = 5.7 \times 10^{-10} S$ . The rubber-like elastic theory was applied to the flow birefringence and the principal polarization difference of flow unit,  $\alpha_1 - \alpha_2$ , was obtained as  $1.62 \times 10^{-23}$  cm<sup>3</sup>. In PMMA, the difference was  $3.9 \times 10^{-25}$  cm<sup>3</sup>, about 1/40 of that in polycarbonate.

**Table III Comparison between Polycarbonate and PMMA**

Sample	Temp. (°C)	$C$ (cm <sup>2</sup> /dyn)	$\alpha_1 - \alpha_2$ (cm <sup>3</sup> )	$(\delta_0^2)^{1/2}$ (cm <sup>3</sup> )
PC	220	$4.1 \times 10^{-10}$	$1.62 \times 10^{-23}$	$5.6 \times 10^{-24}$
PMMA	220	$0.1 \times 10^{-10}$	$3.93 \times 10^{-25}$	$1.4 \times 10^{-25}$

The anisotropy of polarizability of the monomer unit in polycarbonate was also about 40 times larger than that in PMMA. Therefore the large flow birefringence of polycarbonate was mainly due to the anisotropy of the polarizability of the monomer unit itself.

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