Viscoelasticity and Birefringence of Low Birefringent Polyesters

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ABSTRACT: Dynamic viscoelasticity and dynamic birefringence were investigated for a series of polyesters with various combinations of dimethyl decalin 2,6-carboxylate, DMHN and dimethyl terephthalate, DMT as acid component and 9,9-bis[4-(2-hydroxy-ethoxy)phenyl]fluorene, BPEF and ethylene glycol, EG as diol component. The lowering of the stress-optical coefficient was achieved by the displacement of phenylene (DMT) with a hydrogenated naphthylene ring (DMHN) in the main chain and by the introduction of BPFE in the place of EG. The former choice lowered the intrinsic birefringence but did not affect the chain flexibility. The latter enhanced the flexibility but did not affect the intrinsic birefringence. The systematic result clearly revealed the importance of two different factors, the anisotropy of structural units and the chain flexibility, in molecular designs for polymers with low stress-optical coefficient.

KEY WORDS Intrinsic Birefringence / Stress-Optical Coefficient / Polyester /

The birefringence of a polymeric material is often evaluated by measuring the remaining birefringence of a specimen prepared with the method similar to polymer processing, injection molding for example. This may be good for the evaluation of a particular material. On the other hand, it is not appropriate for comparing different species of polymers. The remaining birefringence depends on the rheological properties and thus varies much with processing conditions. For example, the result depends much on the molecular weight in addition to the properties characteristic of the chemical species, so that the evaluation must be performed for various molecular weights or else at various processing conditions.

Recently the authors have studied the dynamic birefringence, the birefringence under oscillatory deformation, and revealed the details of the relaxation process of the birefringence and its relation to the orientation of the structural unit.^{1–4} This method allowed us the comparison of birefringence of polymers of different species of any molecular weights. The origin of birefringence in various states, various temperatures for example, has been clarified for vinyl polymers through systematic studies.

The use of a low birefringent material is one of the ideas for removing the harmful effect of the birefringence in optical use of polymeric materials. Monomers of low anisotropy such as cyclic olefins lead to polymers with low birefringence.^{5,6} Low birefringence may also be achieved through mixing of materials with birefringence of opposite signs.⁷ Copolymerization of monomers with opposite anisotropies would improve the uniform mixing and still have the same effect for lowering of birefringence.⁸ The authors have been studying the possibility in polyesters with various combinations of components and have obtained a series of copolyesters with consider-

ably low birefringence.⁹ The purpose of the present study is to clarify the mechanism of lowering of the birefringence through detailed examination of the dynamic birefringence.

MATERIALS AND METHOD

Materials

The test materials were a series of copolyesters with various combinations of dimethyl decalin 2,6-carboxylate, DMHN and dimethyl terephthalate, DMT as acid component and 9,9-bis[4-(2-hydroxy-ethoxy)phenyl]fluorene, BPEF and ethylene glycol, EG as diol component. The preparation of the materials was published elsewhere.⁹ The structures of the components are shown in Figure 1. The compositions of the polymers used in the present study are shown in Table I together with the molecular weights, M_w , determined by GPC measurement and the glass transition temperature, T_g , determined by DSC measurement.

The DMHN was employed to represent a saturated cy-

Figure 1. The components of the samples.

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Table I. Composition, molecular weight, and glass transition temperature of samples

Polymer code	Acid/mol% ^a		Diol/mol% ^a		M_w ^b	T_g ^c
	DHMN	DMT	BREF	EG		
TF40	0	100	40	60	44000	125
TF70	0	100	70	30	41000	142
HNF20	100	0	20	80	88000	85
HNF40	100	0	40	60	39000	108
HNF70	100	0	70	30	49000	129
HN50F70	50	50	70	30	47000	135
HN40F70	40	60	70	30	47000	135
HN20F70	20	80	70	30	43000	139

^a Determined by NMR. ^b Determined by GPC calibrated with polystyrene standards. ^c Determined by DSC (heating rate = 10 K min⁻¹).

clic structure in the main chain and was expected to be a unit with low anisotropy compared to aromatic rings in the main chain. The BPEF was initially supposed to be a unit with negative birefringence (which turned out to be wrong in the present study) and expected to compensate the positive value due to other components.

Films with 0.3 mm thickness were made by melt press method at 200°C.

Measurements

Details of the apparatus and its operation for dynamic birefringence measurements were described elsewhere.¹⁰ The complex Young's modulus $E^*(\omega) = E'(\omega) + iE''(\omega)$ and the complex strain-optical ratio $O^*(\omega) = O'(\omega) + iO''(\omega)$ were measured with an elongational oscillatory rheometer (DVE III, Reorji Co. Ltd., Kyoto) equipped with an optical system. Here the strain-optical ratio is the ratio of the birefringence to the strain in oscillatory deformation; $O'(\omega)$ and $O''(\omega)$ respectively represent the in-phase and out-of-phase components of the birefringence just as $E'(\omega)$ and $E''(\omega)$ represent the in-phase and out-of-phase components of the stress. The range of frequency was from 1 to 130 Hz. The measurements were performed at several temperatures between $T_g + 20^\circ\text{C}$ and T_g .

Method of Analysis

The data were analyzed with the modified stress-optical rule (MSOR).¹⁰ This is to assume that $E^*(\omega)$ and $O^*(\omega)$ are written as follows.

$$E^*(\omega) = E_R^*(\omega) + E_G^*(\omega) \quad (1)$$

$$O^*(\omega) = C_R E_R^*(\omega) + C_G E_G^*(\omega) \quad (2)$$

The MSOR states that the complex modulus is composed of two components, $E_R^*(\omega)$ and $E_G^*(\omega)$, and the stress-optical ratio can also be related to two components. The subscripts R and G respectively represent the rubbery and the glassy component. The former is associated with longer relaxation times than the latter.

The coefficient, C_R , is the stress-optical coefficient determined in the terminal flow or rubbery zones. In the present study, the lowest frequency belonged to the boundary between the rubbery and the glass-to-rubber transition zones. The stress-optical coefficient could be derived as the ratio $O'(\omega)/E'(\omega)$ in this region accord-

ing to the results for various amorphous polymers.

The coefficient C_G is defined as the ratio $O''(\omega)/E''(\omega)$ in the glassy zone. The ratio remains constant over a wide frequency range for many polymers. This implies that the stress relaxation is due solely to the G component of stress and the R component of stress does not relax in the relevant time range. The ratio $O''(\omega)/E''(\omega)$ was constant in the glassy zone for the present systems and was taken as C_G .

The frequency dependence of the R component modulus, $E_R^*(\omega)$, is well described with the bead-spring model of Rouse and the molecular weight of the Rouse segment, M_s , is estimated from the high frequency limit of the modulus, $E_R'(\omega)$.

$$M_s = 3\rho RT/E_R'(\infty) \quad (3)$$

The M_s thus determined is approximately equal to the molecular weight of the Kuhn statistical segment determined from the dilute solution studies for many polymers.¹¹ The M_s can be a measure of the stiffness of the chain as compared to the assumed chain of free rotational bonds.

Some other characteristic parameters can be derived from the quantities obtained through the MSOR. The photo-elastic coefficient, $C_d = O'(\omega)/E'(\omega)$ at the limit of high frequency, is given by

$$C_d = C_G + C_R E_R'(\infty)/E'(\infty) \quad (4)$$

The intrinsic birefringence is given by¹²

$$\Delta n_0 = 5C_R E_R'(\infty)/3 \quad (5)$$

RESULTS

An Example of the Dynamic Data

The results of $E^*(\omega)$ and $O^*(\omega)$ for the sample TF 40 is given in Figure 2. The data were obtained for temperatures, 160–121°C and reduced to the reference temperature $T_r = 133^\circ\text{C}$ with the method of reduced variables.¹³ The master curves for $E'(\omega)$ and $E''(\omega)$ carry typical features of the complex modulus of amorphous polymers in the glass-to-rubber transition zone and the glassy zone. The $O'(\omega)$ and $O''(\omega)$ are always positive. The curves for $O'(\omega)$ and $O''(\omega)$ are similar to those for $E'(\omega)$ and $E''(\omega)$ in the following sense; $O'(\omega)$ is an increasing function of ω and levels off at high frequencies; $O''(\omega)$ exhibits one maximum.

For about one decade of the lowest frequencies the ratio $O'(\omega)/E'(\omega)$ remains approximately constant and $C_R = 1.8 \times 10^{-9} \text{ Pa}^{-1}$ is obtained. For two decades of high frequencies the ratio $O''(\omega)/E''(\omega)$ is approximately constant and $C_G = 5.9 \times 10^{-11} \text{ Pa}^{-1}$ is obtained.

The results for other samples were qualitatively the same as this example. The coefficients C_R and C_G were positive for all the samples tested. These are given in Table II. The results for other samples can be obtained on request.

Application of the Modified Stress-Optical Rule and the Characteristic Parameters

Figure 2. The complex Young's modulus and the complex strain-optical ratio for TF40.

Table II. Characteristic parameters for viscoelasticity and birefringence. $\text{Br} = 10^{-12} \text{ Pa}^{-1}$

Polymer code	C_R/Br	C_G/Br	C_d/Br	$E'_R(\infty)/\text{MPa}$	$E'_G(\infty)/\text{GPa}$	M_s	Δn_0
TF40	1800	59	98	37	1.6	340	0.11
TF70	1500	57	92	30	1.2	450	0.075
HNF20	750	9.5	27	25	1.0	470	0.031
HNF40	450	17	29	39	1.3	320	0.029
HNF70	323	21	34	55	1.2	240	0.030
HN50F70	750	34	55	35	1.2	390	0.043
HN40F70	930	42	65	31	1.1	430	0.047
HN20F70	980	45	69	31	1.1	430	0.050

The simultaneous eq 1 and 2 were solved for the component functions, $E'_R(\omega)$ and $E'_G(\omega)$, with the use of the data of $E^*(\omega)$ and $O^*(\omega)$ given in Figure 2 and the coefficients C_R and C_G determined by the procedure described above. The features of $E'_R(\omega)$ and $E'_G(\omega)$ shown in Figure 3 are qualitatively the same as those of many other amorphous polymers. The $E'_G(\omega)$, with one marked dispersion peak in the imaginary part corresponding to that of the glass-to-rubber transition, is similar to that of non-polymeric glass-forming materials. The $E'_R(\omega)$ shows a sign of rubbery plateau zone at low frequencies and a broad dispersion in the intermediate frequency region. The latter may be described with a bead-spring model of Rouse and Mooney. The molecular weight of the Rouse segment, M_s , is estimated as 340 with eq 3 and $E'_R(\infty) = 37 \text{ MPa}$.

Values of $E'_G(\infty)$, $E'_R(\infty)$, M_s , and Δn_0 are given in Table II for all the polymers. The $E'_G(\infty)$ is essentially equal to the instantaneous Young's modulus, $E'(\infty)$.

DISCUSSION

Effect of Varying Acid Compositions

For the samples TF70, HNF70, HN50F70, HN40F70, and HN20F70, the composition of the diol component is fixed at BPFE=70 mol% and EG=30 mol% and the composition of the acid component is varied. The variations of the characteristic parameters with the acid composition are shown in Figure 4.

The introduction of hydrogenated ring of DMHN in the main chain in the place of aromatic ring of DMT lowered all the parameters related to the birefringence: Δn_0 , C_R , and C_G . This is in accord with the similar effect

Figure 3. The component functions of the Young's modulus derived from the data of Figure 2.

attained for polyolefins with saturated rings in the main chain and probably indicates that the saturated ring in the main chain is regarded as a unit with small anisotropy. The molecular weight of the Rouse segment, M_s , remained almost constant except for the HNF70, for which the acid component was solely DMHN.

Effect of Varying Diol Compositions

For the samples HNF20, HNF40, and HNF70 (HNF series), the diol compositions are varied and the acid composition is fixed at DMHN=100 mol%. The characteristic parameters are shown in Figure 5. With varying fractions of BPEF, the intrinsic birefringence, Δn_0 , remained constant, the coefficient C_R decreased, and the coefficient C_G increased. This is in contrast with the case of varying amount of hydrogenated rings, for which all these quantities decreased with the increase of DMHN. The increase of C_G with increase of flat (or bulky) BPEF unit is in accord with previous works on various polymers. The different tendencies of Δn_0 and C_R may be accounted for by the variation of the chain flexibility as mentioned below.

The molecular weight of the Rouse segment, M_s , decreased with increasing BPEF and therefore the chain flexibility increased. Since the stress-optical coefficient, C_R , is a measure of optical anisotropy of the segments, it is proportional to M_s . On the other hand, Δn_0 is almost constant for varying BPEF fraction. BPEF has much larger molar volume than EG, and therefore substitution of EG with BPEF decreases concentration of DMHN. The almost constant Δn_0 value implies that anisotropy of DMHN, BPEF and EG is almost the same. Thus, the decrease of C_R with increasing BPEF is due to the increase of flexibility rather than to the decrease of the anisotropy of the structural unit.

For PET(TF0), TF40 and TF70 with DMT as acid (TF series), Δn_0 decreases with increasing BPEF (See Table II). This result contrasts with the case of DMHN=100 mol% in which Δn_0 was almost constant. Relatively large decrease of Δn_0 for TF series can be attributed to dilution of DMT, which is the most anisotropic unit. On the other hand, M_s increases with increasing BPEF for TF series. Direction of M_s variation with BPEF is opposite to HNF series. The increase of BPEF does not always enhance the flexibility. This is quite a reasonable result because flexibility is determined by the interaction between the consequent units in the chain.

Figure 4. DMHN fraction dependence of a) stress-optical coefficients and b) M_s and Δn_0 .

Two Measures of Birefringence, C_R and Δn_0

The remaining birefringence is associated with the birefringence at a certain level of stress in flow and stress relaxation in the processing and may be represented by the stress-optical coefficient, C_R . C_R characterizes anisotropy of segments, and therefore it depends on not only anisotropy of the structural units but also the size of segment. On the other hand, the intrinsic birefringence, Δn_0 , represents the birefringence for oriented materials, *e.g.*, for cross-linked polymers in elongation. The anisotropy of the structural unit apart from the chain flexibility may be represented by Δn_0 . For molecular design of polymers with low birefringence, with regard to the remaining birefringence, one has to take two factors in consideration; the anisotropy of the structural units and the chain flexibility. One known method for the former may be the use of saturated ring structure in the main chain. For the estimation of the chain flexibility, simple calculations such as that for the RIM model may be utilized.

CONCLUSION

Dynamic viscoelasticity and dynamic birefringence were investigated for a series of polyesters with various combinations of DMHN and DMT as acid component and BPEF and EG as diol component. The lowering of stress-optical coefficient was achieved by the displacement of phenylene (DMT) with a hydrogenated naphthylene ring (DMHN) in the main chain and by the introduction of BPFE. The former choice lowered the intrinsic birefringence but did not affect the chain flexibility. The latter enhanced the flexibility but did not affect

Figure 5. BPEF fraction dependence of a) stress-optical coefficients and b) M_s and Δn_0 .

the intrinsic birefringence. The systematic result clearly revealed the importance of two different factors in molecular designs for polymers with low stress-optical coefficient.

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