Reliability of intrinsic birefringence estimated via the modified stress-optical rule

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Intrinsic birefringence, a material constant for the orientational birefringence of polymers, has been measured by many researchers using a variety of methods. However, there is some disagreement among researchers regarding the reported values for the same polymer. This disagreement may be due to the complexity of conventional methods such as infrared dichroism and X-ray scattering methods to determine the degree of orientation. In addition, highly oriented polymers are often utilized, and the local structure of repeating units, including a side chain conformation, may be unnaturally changed owing to the high degree of orientation of the main chain. Alternatively, a new method using the modified stress-optical rule (MSOR) has been proposed for the measurement of intrinsic birefringence. In this article, the published data regarding the intrinsic birefringence for various polymers are assessed and the reliability of intrinsic birefringence estimated via MSOR is discussed.

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INTRODUCTION

Several polymeric materials have been widely used for optical devices, including optical discs, optical fibers and lenses. These particular materials are used because 'optical resins,' that is, polymeric materials for optical use, have features such as being light in weight, highly shock resistant and easy to process in comparison with inorganic glasses that are typical and traditional optical materials. However, optical resins have certain disadvantages, such as a lower heat resistance and a narrow range of refractive indices. In addition, polymeric materials are more birefringent under deformation than inorganic glasses. Birefringence induced by chain orientation is called 'orientational birefringence'. One material constant used to characterize the orientational birefringence is the intrinsic birefringence, Δn_0 , that represents the virtual birefringence of perfectly oriented chains. Δn_0 can be related to the anisotropy of the polarizability of repeating units of the chain, $\Delta \alpha$, through the Lorentz–Lorenz equation.

$$\Delta n_0 = \frac{2}{9} \pi \frac{\left(\overline{n^2} + 2\right)^2}{\overline{n}} \frac{\rho N_{\rm A}}{M_0} \Delta \alpha \tag{1}$$

Here, \overline{n} , ρ and $N_{\rm A}$ are the average refractive index, density and Avogadro's number, respectively. M_0 is the molar mass of the repeating units. Because \overline{n} and ρ do not vary much within polymer species, the intrinsic birefringence is determined mainly by $\Delta \alpha/M_0$. The value of $\Delta \alpha$ may be calculated by the valence-optical scheme,¹⁻⁶ and therefore Δn_0 can be theoretically estimated from the molecular structure of repeating unit. In modern chemistry, $\Delta \alpha$ may be calculated by computational chemistry using software such as MOPAC.⁷ For the case of uniaxially oriented polymers, the orientational birefringence, Δn , can be described with Δn_0 and the orientational degree, *f*.

$$\Delta n = \Delta n_0 f \tag{2}$$

$$f = \frac{3\langle \cos^2\theta \rangle - 1}{2} \tag{3}$$

Here, θ is the angle between the main chain direction of the polymers and the direction of uniaxial orientation; $\langle \rangle$ represents the statistical average.

A fundamental experimental method to determine Δn_0 is the use of Equation (2) with the measurements of Δn and f for the uniaxially oriented samples, produced by stretching of polymers above the glass transition temperature. For measuring f, infrared dichroism or X-ray scattering have been utilized in most cases. However, measuring f with these methods is somewhat complicated and time consuming; moreover, this may result in large experimental uncertainty. In addition, highly oriented polymers are often used for these measurements and the orientation of side groups of repeating units may be unnaturally changed by the high content of the trans conformation of the main chain. In any case, the reported values of Δn_0 sometimes vary with the researcher. Table 1 shows the typical Δn_0 values found in textbooks for some representative polymers^{8,9} (see Appendix for abbreviations of polymers). For example, the reported Δn_0 value for bisphenol A polycarbonate varies with the range of 0.1-0.2. The large uncertainty suggests that the variation of Δn_0 values is not simply related to the statistical experimental error but rather to the systematic error related to the methods.

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Table 1 Intrinsic birefringence of representative polymers obtained from the literature

Sample	Ref A ²⁸	Ref B ²⁹	Ref C ³⁰	Ref D ³¹	Calculated ⁷
PS	-0.1	-0.1			-0.035
PMMA	-0.004	-0.001			-0.008
PVC	0.01	0.0027		0.0102	-0.008
PP	0.04		0.04-0.06	0.035	0.0016
PE	0.052	0.044	0.12	0.058	0.005
PA6	0.083		0.08-0.1	0.06	
PC	0.106	0.202	0.182		0.0475
PET	0.22	0.105	0.220.29		0.0745
PPE	0.21				0.0565
PEEK	0.34				
PVA			0.0443	0.0433	
PA610			0.065		
Celu			0.055	0.086	
P2VN					-0.059
PLLA					0.02
PEN					0.118

Abbreviations: Celu, cellulose; PA6, polyamide 6; PA610, polyamide 6-10; PC, bisphenol A polycarbonate; PE, polyethylene; PEEK, polyethretherketone; PEN, poly(ethylene naphthalate); PET, poly(ethylene terephthalate); PLLA, poly(L-lactic acid); PMMA, poly(methyl methacrylate); PP, atactic polypropylene; PPE, poly(phenyl ether); PS, polysters; PVA, poly(vinyl alcohol); PVC, poly(vinyl chloride); P2VN, poly(2-vinylnaphthalate).

Another material constant for the orientational birefringence is the stress-optical coefficient, $C_{\rm R}$. This coefficient is defined with the stress-optical rule (SOR) for polymer melt.¹⁰ The SOR states that the principal axes of the refractive index tensor and the stress tensor agree with each other and that the proportionality holds between the deviatoric parts of the refractive index and stress tensors. The proportionality coefficient, $C_{\rm R}$, can be related to the optical anisotropy of the segments, $\Delta \beta$.¹¹

$$C_{\rm R} = \frac{2\pi}{45k_{\rm B}T} \frac{\left(\overline{n}^2 + 2\right)^2}{\overline{n}} \Delta\beta \tag{4}$$

Here, $k_{\rm B}$ is the Boltzmann constant. The optical segment size, $n_{\rm s}$, can be defined as follows:⁶

$$\Delta\beta \sim n_s \Delta\alpha \tag{5}$$

The optical segment size, $n_{\rm s}$, is determined by the chain statistics. For the first approximation, the number of repeating units per Kuhn segment, $n_{\rm K}$, can be used alternatively for $n_{\rm s}$.¹² The $n_{\rm K}$ values for various polymers have been determined. We can therefore estimate a value for $\Delta \alpha$ from the $C_{\rm R}$ data, and then Δn_0 can be calculated using Equation (1). Because measuring stress is convenient, this method has been widely used. In addition, a simple evaluation method of $C_{\rm R}$ has been proposed.¹³ However, theoretical considerations have revealed that the short-range ordering of chains because of the nematic interaction (NI) increases the $C_{\rm R}$ values for bulk systems.^{14–16} Although the strong NI effect has been realized for polyethylene (PE), evaluation of the NI effect for other polymers is very limited. For the case of bulk polystyrene, the NI effect is believed to give an ~ 30% larger $C_{\rm R}$ value.

One problem of the estimation based on $C_{\rm R}$ measurements is that the orientational degree, f, is estimated from the *stress* that is sensitive to the intermolecular interaction such as the NI effect. An alternative method to estimate Δn_0 is using *the modified stress-optical rule* (MSOR) that is based on the simultaneous measurement of Young's modulus and the strain-optical coefficient.⁸ In this method, f in the glassy state is estimated by using the pseudo-affine deformation model. In other words, *f* is estimated from the macroscopic *strain*. The simple relation between *f* and strain holds only in the glassy state because *f* relaxes with time by molecular motions over longer time periods. To be more specific, the strain-induced birefringence in the glassy state has two origins: the orientational birefringence and the glassy birefringence. The details of the glassy birefringence are explained in the next section. To remove the glassy contribution, MSOR is applied with the simultaneously measured complex Young's modulus and the strain-optical coefficient. The merit of this method is its high applicability to various polymers, even those for which $n_{\rm K}$ data are not available. In this study, we compared Δn_0 data determined by various methods to identify the most reliable Δn_0 values. We note that all the data, including the results obtained via MSOR, were collected from published studies.

PRINCIPLE

Estimation of the intrinsic birefringence through the MSOR

Because the details of MSOR have been described elsewhere,^{8,17} we explain it only briefly here. For the case of the tensile deformation of rubbery materials, SOR holds well between their birefringence and the tensile stress. SOR is well established for various polymeric materials.¹⁰ SOR states that the molecular origin of birefringence and stress is the orientation of the segments.¹¹ SOR is now a basic concept in various molecular theories to calculate the stress from the chain conformations. On the other hand, in the glassy state at low temperatures, the glassy response contributes to both the birefringence and the stress, in addition to the orientation of the segments. Consequently, the relationship between the birefringence and stress is rather complicated in the glassy state, and therefore MSOR becomes necessary. The MSOR for oscillatory tensile deformation can be written as follows:⁸

$$E^*(\omega) = E_R^*(\omega) + E_G^*(\omega) \tag{6}$$

$$O^{*}(\omega) = O_{R}^{*}(\omega) + O_{G}^{*}(\omega) = C_{R}E_{R}^{*}(\omega) + C_{G}E_{G}^{*}(\omega)$$
(7)

Here, E^* is the complex Young's modulus and O^* is the complex strain-optical coefficient that is the complex ratio of oscillatory birefringence to oscillatory strain. ω is the angular frequency. The subscripts R and G represent the rubbery and the glassy components, respectively. MSOR states that the molecular origin of birefringence is the sum of the rubbery component and the glassy component.^{8,17} Regarding the two proportionality coefficients, $C_{\rm R}$ can be determined experimentally from the limiting values of $O'(\omega)/E'(\omega)$ (= $O''(\omega)/$ $E''(\omega)$) at $\omega \to 0$, and $C_{\rm G}$ can be determined from $O''(\omega)/E''(\omega)$ at $\omega \to \infty$. The component functions $E_{\rm R}^{\,*}(\omega)$ and $E_{\rm G}^{\,*}(\omega)$ are estimated by solving the simultaneous Equations (6) and (7). By applying the frequency-temperature superposition principle, the composite curve of $E_{\rm R}^{*}(\omega)$ and $E_{\rm G}^{*}(\omega)$ can be constructed. Details of the separation procedure and examples of $E_{\rm R}^{*}(\omega)$ and $E_{G}^{*}(\omega)$ are described elsewhere.^{8,9} MSOR has been verified for more than 10 polymers.¹⁸ The separation into the rubbery and the glassy components makes it easier to interpret the viscoelastic properties of amorphous polymers around the glass-to-rubber transition zone. For example, Plazek¹⁹ reported that timetemperature superposition does not hold around the glass-to-rubber transition zone, and this can be attributed to a different temperature dependence of the $E_{\rm R}^{*}(\omega)$ and $E_{\rm G}^{*}(\omega)$.^{8,20}

The glassy component function is very similar to the complex modulus of oligomers.²¹ At high temperatures or at low frequencies, the glassy component is relaxed $(E_{G}'(\omega), E_{G}''(\omega) \rightarrow 0)$ and Equations (6) and (7) are reduced to the ordinary SOR, $O^{*}(\omega) = C_{R}E_{R}^{*}(\omega) = C_{R}E^{*}(\omega)$. Therefore, the rubbery component originates from the orientation of the segments. On the other hand, the molecular origin of the glassy component is assigned to the rotational orientation of repeating units about the main chain axis.¹⁷ The glassy component has strong nonlinearity and shows a large deformation yield.²² The birefringence of a highly stretched sample is mainly caused by the rubbery component. However, at small strains, the strain-induced birefringence includes both the contributions. In the glassy state, the limiting value of $C_{R}E_{R}'(\infty)$ at high frequencies $(\omega \rightarrow \infty)$ represents the birefringence induced by chain orientation without any relaxation. The value of $E_{R}'(\infty)$ is obtained from

Table 2 Stress-optical coefficient, characteristic modulus and Δn_0 via the MSOR method

Polymer	<i>C</i> _R /10 ⁻¹² <i>Pa</i> ⁻¹	E _R '/MPa	Δn_0	$C_{\rm G}/10^{-12} Pa^{-1}$	E _G ′/MPa	<i>C</i> _d / <i>10⁻¹² Pa</i> ^{-1a}	T _r ∕°C
PS ⁸	- 5000	12	-0.1	32	2500	8	116
α-PMS ⁹	- 3400	16	-0.091	20	2300	-3.7	180
PP ¹⁷	1230	20	0.041	-14.4	2000	-2.7	2
hvPB ¹⁷	790	20	0.026	-9.5	1500	1	-27
vPB ¹⁷	200	30	0.01	13.5	1500	17.2	-10
P4MS ³²	-6500	10.2	-0.11	49	1820	12.5	120
PtBS ³²	- 5000	7.4	-0.062	32	1380	5.7	
PVBPh ¹⁷	-6900	7.9	-0.091	130	1100	80	180
PIP ³³	2000	35	0.117	-10.7	2700	14	-52
APO ³⁴	1720	13.4	0.038	-13	1130	7.3	165
PC ⁹	4700	26	0.203	35	1500	111	164
PCAP ³⁵	3300	21	0.116	27	1350	74	188
PES ³⁶	4300	26	0.186	40	1900	98	230
PEI ³⁶	8500	24	0.34	35	1700	153	222
PSF ³⁶	4900	27	0.221	33	1800	105	189
UP ³⁷	6800	27	0.306	38	1120	202	156
UPAP ³⁸	2800	25	0.117	45	910	120	234
PArl ³⁷	900	53	0.0795	31	1150	72	177
PPE	5000	20	0.17				
PEN ³⁹	12 400	16	0.34	63		270	135
PET ⁴⁰	3800	26	0.165				

Abbreviations: APO, amorphous; hvPB, hydrogenated vinyl-polybutadiene; PArl, polyarylate from 2,2'-dicarboxybiphenyl and 2,2-bis(4-hydroxyphenyl) propane (bisphenol A); PC, bisphenol A polycarbonate; PCAP, bisphenol AP polycarbonate; PEI, poly(ether imide); PEN, poly(ethylene naphthalate); PES, poly(ether sulfone); PET, poly(ethylene terephthalate); PIP, polyisoprene; P4MS, poly(4-methyl styrene); α -PMS, poly(α -methyl styrene); α -PMS, poly(α -methyl styrene); PP, atactic polypropylene; PEF, poly(beneyl ether); PS, polystyrene; PSF, polysulfone; PIBS, poly(4-*tert*-butyl styrene); PVBPh, poly (vinylbiphenyl); UP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A); UPAP, polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl) and 2,3-bis(4-hydroxyphenyl) and 3,3-bis (4-hydroxyphenyl) and 3,3-bis (4-hydroxyphenyl) and 3,3-bis (4-

the frequency dispersion of the composite curve of $E_{\rm R}^{*}(\omega)$. Assuming the pseudo-affine deformation, the orientation degree, *f*, of repeating units can be estimated from the tensile strain, *e*.

$$f = \frac{3}{5} \varepsilon \tag{8}$$

Considering Equation (2), we can estimate the intrinsic birefringence as

$$\Delta n_0 = \frac{5}{3} O_{\rm R}'(\infty) = \frac{5}{3} C_{\rm R} E_{\rm R}'(\infty)$$
(9)

Thus, the intrinsic birefringence can be estimated from C_R and $E_R'(\infty)$ data. We note this method is immune from the NI effect. The NI effect gives a larger C_R value but a smaller $E_R'(\infty)$ value, resulting in the NI effect being canceled out for $C_R E_R'(\infty)$. In other words, a relatively weak coupling effect through the NI does not affect the orientation of repeating units in the glassy state. The NI effect is significant only in the rubbery zone. A detailed discussion of the NI effect has been described elsewhere.¹²

Evaluation of the intrinsic birefringence from the stress-optical coefficient

For a very few polymers, MSOR does not hold and therefore the separation into $E_{\rm R}'(\omega)$ and $E_{\rm G}'(\omega)$ cannot be performed.²³ One of the reasons for this is the existence of the sub-relaxation around the glass transition zone. For such a case, we obtained Δn_0 values by a different method. From Equations (1), (4), and (5), we can derive the following equation.

$$\Delta n_0 = \frac{5}{3} C_{\rm R} \, \frac{3\rho RT}{M_{\rm K}} \tag{10}$$

This equation enables us to calculate Δn_0 values from the $C_{\rm R}$ and $M_{\rm K}$ data.¹² The Δn_0 values thus determined are summarized in Table 3. The NI effect can affect Δn_0 values in this method.

On the other hand, $E_{\rm R}'(\infty)$ can be generally related to the Rouse segment size, $M_{\rm S}{}^8$

$$E_{\rm R}'(\infty) = \frac{3\rho RT}{M_{\rm S}} \tag{11}$$

Note that the Δn_0 values obtained via the SOR (Equation (10)) and MSOR methods (Equation (9)) agree for Equation (11) when $M_{\rm K} = M_{\rm S}$. In other words, the difference between the MSOR and the SOR methods can be attributed to the difference between $M_{\rm K}$ and $M_{\rm S}$. A previous study showed that the Rouse segment size is almost the same as the Kuhn segment size, $M_{\rm K}$, for undiluted systems.¹⁸ This means that either the SOR or MSOR method gives similar values for Δn_0 , suggesting that the effect of NI is negligibly weak. On the other hand, the difference between the two segment sizes becomes significant in dilute solutions, where $M_{\rm S}$ becomes approximately 5 times larger than $M_{\rm K}$ owing to suppression of fast local dynamics.^{12,24–26}

RESULTS AND DISCUSSION

The intrinsic birefringence estimated via the MSOR method

Table 2 summarizes $C_{\rm R}$, $E_{\rm R}'(\infty)$, and Δn_0 values for various polymers that have already been reported in previous studies. The Δn_0 value obtained via the MSOR method for polystyrene is -0.1 and agrees with the experimental value, indicating the potential of the MSOR method. As described before, MSOR does not hold for some polymers because of sub-relaxation in the glassy state. For these polymers, the intrinsic birefringence is estimated from the SOR method using the Kuhn segment size and $C_{\rm R}$ data. These results are given in Table 3.

Figure 1 compares the intrinsic birefringence between our results and the reported values. In Table 2, the data for 21 polymers are listed, and the Δn_0 has been measured for only 9 polymers by conventional methods. For polymers having several experimental values, all the data points are plotted in Figure 1. As described in the Introduction, the large scatter of the Δn_0 data suggests that the origin of the variation is not simply related to the statistical experimental errors. Therefore, we

Table 3 Molar mass of the Kuhn segment, $M_{\rm K}$, and Δn_0 via the SOR method

Polymer	M _K /kg mol ⁻¹	<i>C</i> _R /10 ^{−12} <i>Pa</i> ^{−1}	Δn_0	T _r ∕°C
PS ^{8,41}	0.76	-5000	-0.11	116
P2VN ⁴²	1.39	-8300	-0.11	160
PP ^{17,41}	0.19	1230	6.59×10^{-2}	2
PET ⁴⁰	0.44	3800	0.18	100
PIB ^{41,43}	0.27	1400	8.76×10^{-2}	-45
PMMA ^{13,41}	0.64	50	1.42×10^{-3}	150
PE ^{10,41}	0.16	2100	0.22	150
PVC ^{10,41}	0.36	-500	-2.39×10^{-2}	22
PC ⁹	0.65	4700	0.16	164
PPE ⁴¹	0.23	5000	0.37	100

Abbreviations: PC, bisphenol A polycarbonate; PE, polyethylene; PET, poly(ethylene terephthalate); PIB, polyisobutylene; PMMA, poly(methyl methacrylate); PP, atactic polypropylene; PPE, poly(phenyl ether); PS, polystyrene; PVC, poly(vinyl chloride); P2VN, poly(2-vinylnaphthalene); SOR, stress-optical rule.



Figure 1 Comparison of Δn_0 via conventional methods and the modified stress-optical rule (MSOR) or stress-optical rule (SOR) method. See the text for details concerning the method determination. Black circles and red squares represent Δn_0 obtained via the MSOR and SOR methods, respectively. For polymers having several experimental values, the closest value to the data from the MSOR or SOR method is represented with filled marks and the others are represented with open marks. A full color version of this figure is available at *Polymer Journal* online.

did not calculate the average value. The elimination of the systematic errors originating from either the methods or the researchers because of the limited amount of data is a complicated issue, but here we found that some data points obtained via the conventional methods are close to the data obtained via the MSOR method. To illustrate this, the closest experimental value to the data obtained via the MSOR method in Figure 1 is represented by large filled marks. Figure 1 indicates a good agreement between our MSOR result and other selected experimental values.

For bisphenol A polycarbonate (PC),⁹ two groups of the reported value (~0.1 and ~0.2) exist. According to MSOR, the intrinsic birefringence of PC would be ~0.2. The intrinsic birefringence of polymers containing benzene rings in their main chain, such as PET (poly(ethylene terephthalate)) and PPE (poly(phenyl ether)), is consistently ~0.2.

The results of the SOR method using C_R data and Kuhn segment size, which is shown by red squares, also give reliable estimations. As explained in the theory, the NI effect gives a larger Δn_0 value. A careful



Figure 2 Comparison of Δn_0 by calculation and the modified stress-optical rule (MSOR) or stress-optical rule (SOR) method. See the text for details of the method determination. The blue line is an approximate straight line Δn_0 by each method. Black circles and red squares represent Δn_0 via the MSOR and SOR methods, respectively. A full color version of this figure is available at *Polymer Journal* online.

comparison of data from the SOR and MSOR methods reveals that this is true, except for PE, PC, and PPE. Note that polystyrene had negative Δn_0 and Δn_0 values estimated via the SOR method, located to the left side of those estimated by the MSOR method. A particularly large deviation was found for PE, and this can be attributed to the NI effect. The NI effect of PE was estimated to give approximately twice the values for Δn_0 .¹⁴ If we correct for the NI effect, Δn_0 obtained via the SOR method changes to ~0.11. The data point in Figure 1 is on the broken line by the horizontal shift. For the case of PPE, a large disagreement is observed. Because the value of $C_{\rm R}$ for PPE is comparable to that for PC or PET, the reported value of MK might include some experimental errors. For the case of PC, the SOR method provided a smaller value than MSOR method. The reason for this result is not clear at the present time. Strictly speaking, the relationship between n_s and n_K depends on details of chain statistics, and therefore the assumption, $n_s = n_K$ might be violated for PC. Further studies are needed for interpreting this irregular result.

For crystalline polymers such as PET, the Δn_0 value may be affected by the existence of crystals because in crystals, the local electric field is modified by regularly arranged neighboring chains. Rheo-optical measurements are normally performed with molten samples or quenched amorphous samples. The existence of crystals violates the SOR, hence making it detectable.²⁷

Comparison with simulations

As described above, $\Delta \alpha$ values can be estimated by computer simulations. The reported values of Δn_0 obtained via a computational method are summarized in Table 1. For polymers having side groups, $\Delta \alpha$ varies with the conformation of the side groups. In this calculation, $\Delta \alpha$ and the rotational energy of the side groups were calculated by Quantum Chemical calculation (density functional theory: B3LYP/6-31+G^{**} by Gaussian 03) for various conformations of the side groups, and then the statistical average was obtained following the Boltzmann distribution. In a previous study, a comparison was made with a set of experimental values.⁷ However, for some polymers, the agreement was not good. Here, we compare their calculated values with the Δn_0 value obtained via the MSOR method in Figure 2. The proportional relationship holds well between the experimental and calculated values. Again, a large difference for PE can be attributed to the NI effect.

A careful observation reveals that a systematic deviation between the experimental and simulated values is observed. Their relationships are described by Equation (12)

$$\Delta n_{0,\rm sim} = A \Delta n_{0,\rm exp} + B \tag{12}$$

Here, $\Delta n_{0,\text{sim}}$ and $\Delta n_{0,\text{exp}}$ are the Δn_0 values obtained via the simulation and the experimental methods, respectively. The values of A and B are constant and they are 0.28 and -0.075, respectively. We have not identified the origin of this systematic deviation, particularly why $A \neq 1$. Regarding the non-zero B parameter, we note that the Lorentz-Lorenz equation (Equation (1)) considers only the orientation of anisotropic repeating units. However, an anisotropic internal electrostatic field may be created by the surrounding anisotropic chains, and this can contribute to the birefringence. To consider such an effect, let us consider perfectly oriented chains. The free volume of polymeric materials is typically ~0.025 around the glass transition region, and its spatial distribution would also be anisotropic because the chain itself is rod-like and anisotropic. For such a system, we should consider the form birefringence of the free volume or chains. A very preliminary calculation predicts a form birefringence of ~ 0.01 . The non-ideal term that is not considered in the Lorentz-Lorenz equation is an important issue for future work.

CONCLUSION

We have discussed the reliability of intrinsic birefringence estimated via the MSOR and the SOR methods. The good agreement between our results and other experimental values has been established. On the other hand, a systematic deviation between the experimental values and the simulation values has been observed. An improvement of the simulation method is considered as an important issue for the precise prediction of intrinsic birefringence in addition to the consideration of the form birefringence of the chain.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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APPENDIX

Abbreviations Used for Polymer Identification

α -PMS	poly(α -methyl styrene)	PMMA	poly(methyl methacrylate)
APO	amorphous polyolefin, poly[1-ethyl-5-methyl-octahy-	P4MS	poly(4-methyl styrene)
	dro-4,7-methano-1H-indene-1 ² ,3-diyl]	PPE	poly(phenyl ether)
PP	atactic polypropylene	PS	polystyrene
hvPB	hydrogenated vinyl-polybutadiene	PSF	polysulfone
vPB	vinyl-polybutadiene	PVC	poly(vinyl chloride)
UP	polyarylate from tere- and isophthalic acids (mole ratio is	PE	polyethylene
	1:1) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A)	PA6	polyamide 6
UPAP	polyarylate from tere- and isophthalic acids (mole ratio	PA610	polyamide 6-10
	is 1:1) and 2,2,2-tris(4-hydroxyphenyl)phenylethane	PC	bisphenol A polycarbonate
	(bisphenol AP)	PEEK	polyetheretherketone
PtBS	poly(4- <i>tert</i> -butyl styrene)	PVA	poly(vinyl alcohol)
PCAP	bisphenol AP polycarbonate	Celu	cellulose
PEI	poly(ether imide)	P2VN	poly(2-vinylnaphthalene)
PES	poly(ether sulfone)	PLLA	poly(L-lactic acid)
PEN	poly(ethylene naphthalate)	P4MS	poly(4-methylstyrene)
PET	poly(ethylene terephthalate)	PVBPh	poly(vinylbiphenyl)
PES	poly(ethylene sulfone)	PArl	polyarylate from 2,2'-dicarboxybiphenyl and 2,2-bis
PIB	polyisobutylene		(4-hydroxyphenyl) propane (bisphenol A)
PIP	polyisoprene		

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