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ORIGINAL ARTICLE

Birefringent properties of poly(phosphonate)s and poly(thiophosphonate)s derived from various bisphenols

Ryoyu Hifumi[1,2] · **Ikuyoshi Tomita**[1]

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Abstract

The birefringent properties of poly(phosphonate)s and poly(thiophosphonate)s possessing various bisphenol structures were investigated. The C_R values (orientational birefringence) of the poly(phosphonate)s and the poly(thiophosphonate)s range from -0.3×10^{-9} to $+1.3 \times 10^{-9}$ Pa^{-1} and from -0.6×10^{-9} to $+0.8 \times 10^{-9}$ Pa^{-1}, respectively, which are lower than those of the corresponding bisphenol A-based polymers. The C_D values (photoelastic birefringence), which range from $+4.0 \times 10^{-11}$ to $+4.9 \times 10^{-11}$ Pa^{-1}, are also lower than those of the corresponding bisphenol A-based polymers.

Introduction

Low birefringent polymers are very important functional materials for high-performance optical devices. For example, low birefringent properties are essential to maintain the polarization state of the transmitted light for some flat-panel display films and to achieve fine focusing for plastic lens modules.

Among the several types of birefringence in polymers, orientational birefringence and photoelastic birefringence are important for the optical fields. Orientational birefringence is observed when polymers with optically anisotropic repeating units are oriented and can be expressed as follows [1]:

$$\Delta n = C_R \sigma \tag{1}$$

where Δn, C_R, and σ are the birefringence, the stress-optical coefficient for the rubbery state, and the stress, respectively. Photoelastic birefringence is observed when glassy polymers are subjected to stress and can be expressed as follows [1]:

$$\Delta n = C_D \sigma \tag{2}$$

where C_D is known as the photoelastic coefficient. The coefficients (C_R and C_D) are useful to quantitatively compare birefringence among a wide variety of polymers.

A number of low birefringent polymers have been developed. For example, polymers composed of aliphatic building blocks such as poly(cycloolefin)s and their copolymers have C_R values ranging from 0.1×10^{-9} to 2.0×10^{-9} Pa^{-1} and have C_D values ranging from 0.4×10^{-11} to 3.3×10^{-11} Pa^{-1} [2–4], which are remarkably lower than those of conventional engineering plastics, such as a 2,2-bis(4-hydroxyphenyl)propane (bisphenol A)-based poly(carbonate) ($C_R = +5.6 \times 10^{-9}$ Pa^{-1} and $C_D = +8.9 \times 10^{-11}$ Pa^{-1}) [5]. It has also been reported that both the orientational birefringence and photoelastic birefringence of polymers can be canceled by the terpolymerization of three kinds of methacrylates with positive–positive, positive–negative, and negative–negative orientational and photoelastic birefringence [6]. Although conventional engineering plastics generally exhibit high birefringence, as mentioned above, the introduction of aromatic structures at a direction perpendicular to the main chain has successfully realized low birefringent polymers. For example, poly(carbonate)s possessing phenyl substituents perpendicularly oriented to the main chain direction and poly(ester)s possessing 9,9-diarylfluorene moieties have been reported as achieving low C_R values in the range from 0.6×10^{-9} to 2.3×10^{-9} Pa^{-1} and from 0.3×10^{-9} to 1.8×10^{-9} Pa^{-1}, respectively [7–9].

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✉ Ikuyoshi Tomita
tomita@echem.titech.ac.jp

[1] Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Nagatsuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502, Japan

[2] JSR Corporation, Kawajiri-cho 100, Yokkaichi, Mie 510-8552, Japan

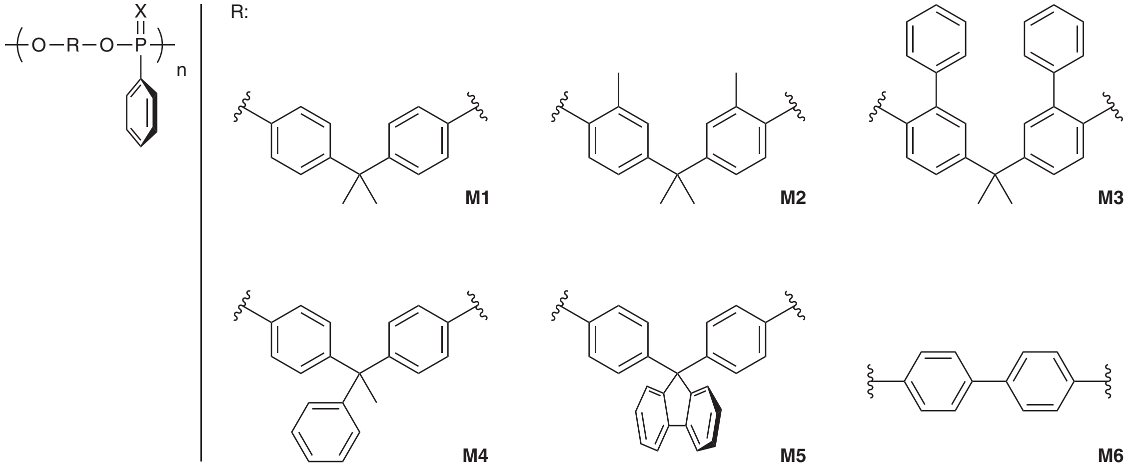

Fig. 1 Structures of poly(phosphonate)s (X = O) and poly(thiophosphonate)s (X = S)

We have recently reported the low birefringent properties of the bisphenol A-based poly(phosphonate) and poly(thiophosphonate) [5]. Their C_R and C_D values ranged from $+1.2 \times 10^{-9}$ to $+1.5 \times 10^{-9}\,\mathrm{Pa}^{-1}$ and from $+5.7 \times 10^{-11}$ to $+6.1 \times 10^{-11}\,\mathrm{Pa}^{-1}$, respectively, which are lower than those of the conventional bisphenol A-based polymers having carbonate, ester, and ether linkers in the main chains.

In addition to the bisphenol A-based poly((thio)phosphonate)s, poly((thio)phosphonate)s possessing various bisphenol structures have been synthesized, and the highly refractive nature of some of these polymers has been described independently by Shobha et al., Macdonald et al., and us [10–12]. These results indicate that poly((thio)phosphonate)s may serve as novel plastic lens materials. Although low birefringent properties are required for plastic lens materials, as mentioned above, those properties of poly((thio)phosphonate)s have scarcely been studied except in our previous paper [5]. In this paper, we wish to describe the orientational birefringence and the photoelastic birefringence (C_R and C_D values, respectively) of poly((thio)phosphonate)s possessing various bisphenol structures.

Experimental procedures

The syntheses of **P1O**, **P1S**, **P2S**, and **P4S** have been described in our previous paper, and **P2O–P5O** and **P5S** were likewise synthesized (Fig. 1 and Table 1) [12]. A 4,4′-biphenol-based poly(phosphonate) (**P6O**) was synthesized according to the procedure reported by Shobha et al. [10]. All the polymers were fully characterized by ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) spectroscopy (see the Supplementary Information).

The orientational birefringence and photoelastic birefringence (C_R and C_D values, respectively) of the polymers were evaluated according to the method reported by Osaki and coworkers [13].

Results and discussion

The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers (**P1O–P6O**, **P1S**, **P2S**, **P4S**, and **P5S**) were estimated by size-exclusion chromatography (SEC) and are in the range of 8,500–53,300 and 46,500–150,100, respectively, which are high enough to obtain freestanding films (Table 1).

The thermal properties of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC). From the TGA measurements, the polymers (**P1O–P6O**, **P1S**, **P2S**, **P4S**, and **P5S**) exhibit excellent thermal stabilities: their 5% weight loss temperatures were found to be greater than 420 °C (Fig. S19). The glass transition temperatures of the polymers (**P1O–P6O**, **P1S**, **P2S**, **P4S**, and **P5S**) are in the range of 107–173 °C, which are suitable for the injection-molding process (Fig. S20).

The orientational birefringence (C_R values) of the polymers was evaluated based on Eq. (1). The linear relationships between the birefringence (Δn) and the stretching stress (σ) were observed (Fig. S23), and the C_R values of the polymers were determined from the slopes. The C_R values of the poly(phosphonate)s (**P2O–P4O**) and the poly(thiophosphonate)s (**P2S** and **P4S**) range from $+0.4 \times 10^{-9}$ to $+1.3 \times 10^{-9}\,\mathrm{Pa}^{-1}$ and from $+0.6 \times 10^{-9}$ to $+0.8 \times 10^{-9}\,\mathrm{Pa}^{-1}$, respectively (Table 1 and Fig. 2), which are lower than those of the corresponding bisphenol A-based polymers (**P1O** and **P1S**, respectively). These results are most likely due to the presence of substituents perpendicularly oriented to the main chain direction, and similar trends have been observed in a series of poly(carbonate)s having **M1–M4** units, as reported

Table 1 Molecular weights and birefringent properties of poly(phosphonate)s (**P1O**–**P6O**) and poly(thiophosphonate)s (**P1S**, **P2S**, **P4S**, and **P5S**)

Polymer	R	X	M_n [a]	M_w [a]	C_R (10^{-9} Pa^{-1})	C_D (10^{-11} Pa^{-1})
P1O	**M1**	**O**	29300	57500	$+1.5$[b]	$+6.1$[b]
P1S	**M1**	**S**	18500	57200	$+1.2$[b]	$+5.7$[b]
P2O	**M2**	**O**	46900	104600	$+1.3$	$+4.9$
P2S	**M2**	**S**	26100	150100	$+0.8$	$+4.7$
P3O	**M3**	**O**	53300	146800	$+0.4$	$+4.6$
P4O	**M4**	**O**	11500	56400	$+0.7$	$+4.6$
P4S	**M4**	**S**	16500	84600	$+0.6$	$+4.6$
P5O	**M1/M5**[c]	**O**	9900	73100	-0.3	$+4.5$
P5S	**M1/M5**[c]	**S**	9800	60000	-0.6	$+4.0$
P6O	**M6**	**O**	8500[d]	46500[d]	$+7.2$	$+14.0$

[a] Measured by SEC (calibrated with polystyrene standards in $CHCl_3$)

[b] These values have been reported in our previous paper [5]

[c] **M1**:**M5** = 1:1 molar ratio

[d] Measured by SEC (calibrated with polystyrene standards in 1-methyl-2-pyrrolidone)

by Shirouzu et al. (Fig. 2) [7]. In addition, the polymers possessing the fluorene moieties (**P5O** and **P5S**) exhibit low C_R values of -0.3×10^{-9} Pa^{-1} and -0.6×10^{-9} Pa^{-1}, respectively. As expected from the highly anisotropic main chain structure caused by the 4,4′-biphenol moieties, **P6O** exhibits a C_R value of $+7.2 \times 10^{-9}$ Pa^{-1}, which is the highest among the values of the polymers examined here. However, it can be noted that **P6O** exhibits a relatively low C_R value with respect to that of the corresponding poly(ether sulfone)s (Fig. S24).

The photoelastic birefringence (C_D values) of the polymers was likewise evaluated based on Eq. (2). The linear relationships between the birefringence (Δn) and the tensile stress (σ) were observed (Fig. S25), and the C_D values of the polymers were determined from the slopes. The C_D values of the poly(phosphonate)s (**P2O**–**P5O**) and the poly(thiophosphonate)s (**P2S**, **P4S**, and **P5S**) range from $+4.5 \times 10^{-11}$ to $+4.9 \times 10^{-11}$ Pa^{-1} and from $+4.0 \times 10^{-11}$ to $+4.7 \times 10^{-11}$ Pa^{-1}, respectively (Table 1 and Fig. 3), which are lower than those of the corresponding bisphenol A-based polymers (**P1O** and **P1S**, respectively). On the other hand, **P6O** exhibits the highest C_D value of $+14.0 \times 10^{-11}$ Pa^{-1}. It has been reported that the C_D value decreases with decreasing C_R value [14, 15], and similar trends were observed in the case of the polymers examined here (Figs. 2 and 3).

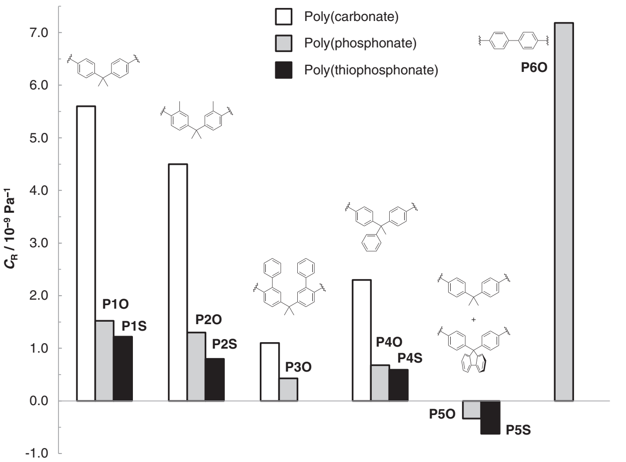

Fig. 2 Comparison of C_R values of poly(carbonate)s, poly(phosphonate)s (**P1O**–**P6O**), and poly(thiophosphonate)s (**P1S**, **P2S**, **P4S**, and **P5S**). The values for poly(carbonate)s having **M1** and **M2**–**M4** units are taken from our previous paper (i.e., ref. [5]) and ref. [7], respectively

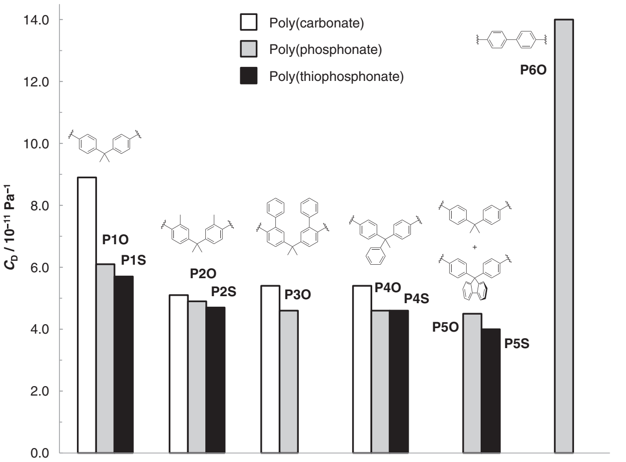

Fig. 3 Comparison of C_D values of poly(carbonate)s, poly(phosphonate)s (**P1O**–**P6O**), and poly(thiophosphonate)s (**P1S**, **P2S**, **P4S**, and **P5S**). The values for poly(carbonate)s having **M1** and **M2**–**M4** units are taken from our previous paper (i.e., ref. [5]) and ref. [14], respectively

Conclusions

The birefringent properties of poly(phosphonate)s and poly(thiophosphonate)s possessing various bisphenol structures were investigated. The C_R values (orientational birefringence) of the poly(phosphonate)s (except for the 4,4′-biphenol-containing sample) and the poly(thiophosphonate)s range from -0.3×10^{-9} to $+1.3 \times 10^{-9}$ Pa^{-1} and from -0.6×10^{-9} to $+0.8 \times 10^{-9}$ Pa^{-1}, respectively, which are lower than those of the corresponding bisphenol A-based polymers. The C_D values (photoelastic birefringence), which range from $+4.0 \times 10^{-11}$ to $+4.9 \times 10^{-11}$ Pa^{-1}, are also lower than those of the corresponding bisphenol A-based polymers. These results indicate that poly(phosphonate)s and poly(thiophosphonate)s are attractive candidates for optical applications that require low birefringent properties.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing financial interest.

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