



Synthesis and high refractive index properties of poly(thiophosphonate)s

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Introduction

Phosphorous-containing polymers are one of the most important classes of materials, and they have been widely studied in both scientific and industrial fields for the past few decades [1, 2]. These polymers are used in various applications, including polymeric flame-retardant additives, biomedical materials, polymer coatings, fuel cell membranes and optical materials, because of the unique properties originating from the presence of phosphorus atoms.

Among the various types of phosphorus-containing polymers, considerable attention has been paid to poly(phosphonate) derivatives, which can be regarded as phosphorus analogues of poly(carbonate)s. Poly(phosphonate) derivatives can be classified according to the substituent of the phosphorus atom (X), such as poly(phosphonate)s ($X = O$), poly(thiophosphonate)s ($X = S$), and poly(sele-nophosphonate)s ($X = Se$) (Fig. 1). They have high flexibility in terms of molecular design of both the main chain (R) and the pendant group (Z), through which various functional groups can be easily introduced into their repeating units.

Of these polymers, poly(phosphonate)s ($X = O$) have been the most widely studied and are easily synthesized by conventional polycondensation methods, such as solution [3, 4], interfacial or phase-transfer catalyzed [5–7], and melt

[8, 9] polymerizations. In addition, Nishikubo and co-workers have synthesized poly(phosphonate)s with pendant chloromethyl groups by the polyaddition of bis(epoxide)s with phosphonic dichlorides [10]. Wurm and co-workers have recently reported new synthetic approaches, such as organocatalyzed ring-opening [11], ring-opening metathesis and acyclic diene metathesis polymerizations [12].

Poly(phosphonate)s are mainly applied as halogen-free flame retardant additives because phosphonate groups can act as a char promoter and a radical trapping agent during the combustion of polymers [1, 2, 8, 13]. For example, poly(phosphonate)-based flame-retardants with a very high limiting oxygen index (LOI) above 50 are commercialized under the name Nofia® (FRX Polymers Inc.) [13, 14].

In addition, there are a few reports on the optical properties of poly(phosphonate)s. McGrath and co-workers have reported the synthesis of a high-molecular-weight 2,2-bis(4-hydroxyphenyl)propane (bisphenol A)-based poly(phosphonate) (**P1**) with a refractive index of 1.60, which is higher than that of the corresponding poly(carbonate) (**PC**) [4]. They have also synthesized a 4,4'-biphenol-based poly(phosphonate) with a refractive index of 1.64. Shaver and co-workers have recently reported the refractive indices of poly(phosphonate)s with various structures [15], finding that a 9,9-bis(4-hydroxyphenyl)fluorene-based poly(phosphonate) provided the highest refractive index of 1.66. In addition, they have described that these polymers have Abbe numbers that are relatively high for this class of materials, i.e., in the range of 22–31.

Since chalcogen atom-containing polymers are expected to exhibit unique behaviors, such as high refractive indices, heavy-atom effects and specific ligation with soft metals [16], poly(phosphonate) derivatives possessing heavier chalcogen atoms ($X = S$, Se , etc.) are likewise potentially interesting functional materials. Wang and co-workers developed two kinds of oligomeric poly(thiophosphonate)s ($X = S$) that exhibited excellent flame-retardant properties [17, 18]. Gray and co-workers have synthesized various types of poly(phosphonate)s ($X = O$, S , Se) with bithienyl substituents on

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the phosphorus atoms and reported their nonlinear absorbance behavior, which increased in the order of O < S < Se [19]. However, the applications of these polymers to high-refractive-index materials have scarcely been studied.

In this paper, we report novel high-refractive-index materials consisting of poly(thiophosphonate)s ($X = S$), which were synthesized by the polycondensation of phenylthiophosphonic dichloride with various bisphenols. These polymers proved to achieve high refractive indices of 1.626–1.687 owing to the highly polarizable sulfur and phosphorous atoms in their backbones. Their thermal properties and UV-vis absorption behavior are also described.

Experimental procedures

A typical synthetic procedure for the poly(thiophosphonate)s is as follows: A mixture containing bisphenol, 2-phenylphenol (which was added to adjust the molecular weight to an appropriate range when the molecular weights became too high) and sodium hydride in dry tetrahydrofuran (THF) was stirred at 60 °C for 0.5 h under argon. After cooling to 0 °C, a dry THF solution of phenylthiophosphonic dichloride was added dropwise to the reaction mixture over 1 h. The reaction mixture was warmed to 60 °C and stirred for 2.5 h. After the reaction, acetic acid and deionized water were added, and the mixture was extracted with CHCl₃. The organic layer was washed three times with deionized water, and the solvent was evaporated under reduced pressure. The residue was poured into acetone, and the obtained solid was washed three times with acetone. The solid was dissolved in CHCl₃, and the resulting solution was precipitated into hexane or methanol to obtain poly(thiophosphonate) as a fibrous white solid. The obtained polymer was dried in a vacuum oven at 90–120 °C for 13 h.

Detailed experimental procedures and nuclear magnetic resonance (NMR) spectra are shown in the Supplementary Information.

The polymer films for optical measurements were prepared according to the following procedure: A dichloromethane (50 ml) solution of the polymer (2.5 g) was cast onto a Petri dish (15 cm diameter) and dried under ambient conditions for 14 h. The obtained freestanding film was dried under vacuum at a temperature lower than its T_g by 20 °C for 24 h. The thicknesses of the obtained films were in the range of 80–130 μm.

Results and discussion

When the conditions reported for the synthesis of poly(phosphonate)s were followed (i.e., polymerization using triethylamine and 1-methylimidazole as a base and a

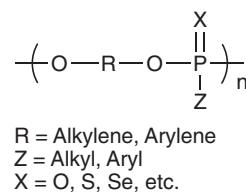


Fig. 1 Structures of poly(phosphonate) derivatives

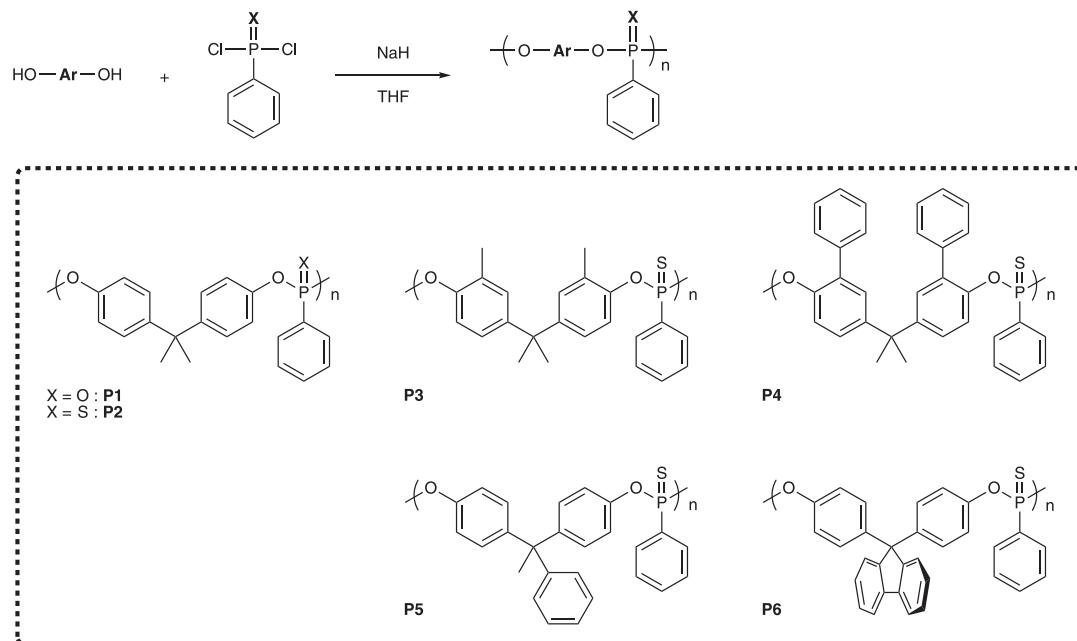
catalyst, respectively) [4], poly(thiophosphonate)s with high molecular weights could not be obtained. In our attempts, the use of sodium hydride as a base proved to result in poly(thiophosphonate)s with high molecular weights (Scheme 1). For example, a bisphenol A-based poly(thiophosphonate) (**P2**) with a number-average molecular weight (M_n) of 18,500 and a weight-average molecular weight (M_w) of 57,200 was obtained (Table 1). The structure of **P2** was fully characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy (Supplementary Information). The peaks observed in the ¹H and ¹³C NMR spectra were consistent with the peaks expected from the structure of **P2**. In the ³¹P NMR spectrum, a typical peak corresponding to the phosphorus atom in the thiophosphonate moieties was clearly observed at 82.7 ppm. Poly(thiophosphonate)s derived from various bisphenols (**P3–P6**) and a bisphenol A-based poly(phosphonate) (**P1**) were also synthesized by the same method. In the cases of **P1** and **P3–P5**, high-molecular-weight polymers were successfully obtained, whereas the molecular weight of **P6** did not increase sufficiently, probably due to the low solubility of 9,9-bis(4-hydroxyphenyl)fluorene (Table 1). All these polymers were also characterized by NMR spectroscopy (Supplementary Information).

The thermal properties of **PC** and **P1–P6** were investigated by the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques (Table 1; for detailed profiles, see the Supplementary Information).

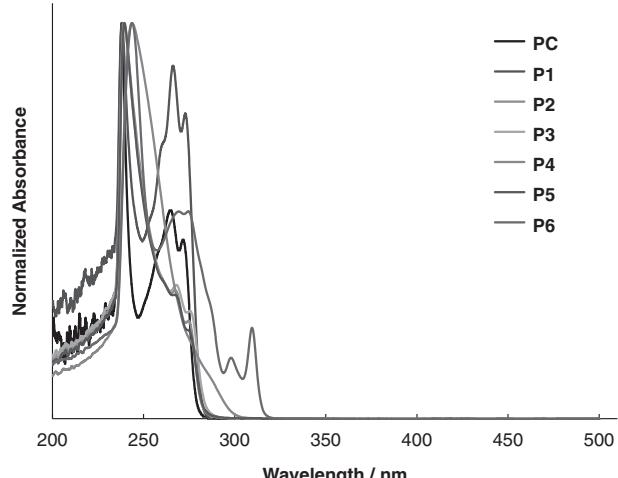
In the TGA measurements, the 5% weight-loss temperatures (T_{d5}) of **P2–P6** were observed to be greater than 420 °C under nitrogen (Figure S20), which are sufficient for practical applications.

Regarding the glass transition temperatures (T_g) of the polymers derived from the same bisphenol monomer (**PC**, **P1**, and **P2**), the poly(thiophosphonate) (**P2**) exhibits a slightly higher T_g than the corresponding poly(phosphonate) (**P1**) but a lower T_g than the corresponding poly(carbonate) (**PC**). Within the series of poly(thiophosphonate)s (**P2–P6**), their T_g values, which ranged from 117 to 204 °C, were found to be dependent on the structures of their bisphenol moieties.

The UV-vis absorption spectra of **PC** and **P1–P6** in CHCl₃ solution are shown in Fig. 2. The absorption behaviors of **P2–P3** and **P5** are very similar, and their absorption edges are comparable to those of **PC** and **P1**. On the other hand, **P4** and **P6** absorb longer-wavelength light than **P2–**

**Scheme 1** Synthesis of **P1–P6****Table 1** Molecular weights, thermal and optical properties of **PC** and **P1–P6**

Polymer	M_n^a	M_w^a	T_{d5} (°C) ^b	T_g (°C) ^b	n_D^c	ν_D^d
PC	—	—	471	150	1.587	29.3
P1	29,300	57,500	484	107 ^e	1.611 ^f	28.8
P2	18,500	57,200	446	120	1.636	26.9
P3	26,100	150,100	429	117	1.626	27.5
P4	9,300	47,200	452	136	1.658	23.3
P5	16,500	84,600	449	151	1.652	25.4
P6	3,700 ^g	10,600 ^g	453	204	1.687	21.3

^a Measured by a GPC calibrated with polystyrene standards in CHCl₃^b Measured under nitrogen^c The refractive index at 589 nm^d The Abbe number^e In reference [4], the T_g value of **P1** was reported to be 115 °C^f In reference [4], the refractive index of **P1** was reported to be 1.60^g Measured by a GPC calibrated with polystyrene standards in 1-methyl-2-pyrrolidone**Fig. 2** UV-vis absorption spectra of **PC** and **P1–P6** in CHCl₃ solution (1.0 × 10⁻⁴ mol/L)

P3 and **P5** because they are composed of biphenyl groups or fluorene moieties in their backbones. Notably, **P4** and **P6** have no absorption above 350 nm, and all the polymers exhibit high transparency in the visible light region.

The refractive indices of **PC** and **P1–P6** and their wavelength dependence are shown in Fig. 3 and Table 1. The refractive indices at 589 nm (n_D) were estimated by Eq. 1 (the three-term Cauchy equation) using the refractive

indices measured at 408, 633, and 828 nm: [20]

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

where n is the refractive index, λ is the wavelength, and A – C are constants.

The n_D values of **PC** and **P1** are 1.587 and 1.611, respectively, and these values are in good agreement with the values previously reported [4]. Among the polymers having the same bisphenol moieties (**PC**, **P1**, and **P2**), the poly(thiophosphonate) (**P2**) exhibits the highest n_D value

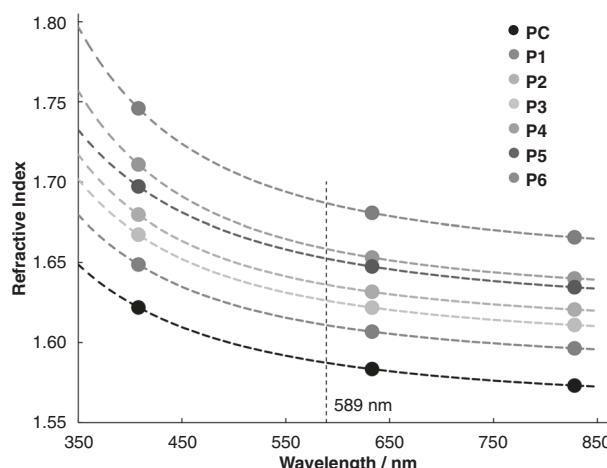


Fig. 3 The refractive indices of **PC** and **P1–P6** and their wavelength dependence. Closed circles represent measured values. Dashed lines are calculated according to Eq. 1.

(1.636). This result is most likely due to the thiophosphonate moieties being more polarizable than the carbonate and phosphonate moieties. The n_D values of **P2–P6** are in the range of 1.626–1.687 and are dependent on the structures of the bisphenol moieties. The n_D value of **P6** is the highest among the poly(phosphonate) derivatives reported [15] due to the high content of aromatic units derived from the fluorene moieties (Figure S22).

The Abbe numbers (ν_D) were estimated by Eq. 2: [15]

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \quad (2)$$

where ν_D is the Abbe number and n_D , n_F , and n_C are the refractive indices at 589, 486, and 656 nm, respectively, which were calculated by Eq. 1. In general, the Abbe number decreases as a function of the refractive indices. Similar trends were observed in the cases of **P2–P6**, which have Abbe numbers ranging from 21.3 to 27.5 (Table 1). These values were found to be slightly higher than those of conventional polymers with a similar range of the refractive indices (Figure S23), which might be useful for the precise design of chromatic aberration compensating lens materials.

Conclusions

We have developed novel high-refractive-index materials consisting of poly(thiophosphonate)s, which were synthesized by the polycondensation of phenylthiophosphonic dichloride with various bisphenols. These polymers exhibit excellent thermal stability ($T_{d5} > 420^\circ\text{C}$), moderate to high glass transition temperatures (117–204 °C) and high transparency in the visible light region. Furthermore, they achieve high refractive indices of 1.626–1.687 owing to the highly polarizable sulfur and phosphorous atoms in their

backbones and relatively high Abbe numbers of 21.3–27.5. These results indicate that poly(thiophosphonate)s are promising candidates as novel high-refractive-index materials. Further studies on the optical properties of poly(thiophosphonate)s are in progress.

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Compliance with ethical standards

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

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