Macromolecules **2008**, *41*, 6165−6168 **6165**

Poly(thioether sulfone) with High Refractive Index and High Abbe's Number

Rie Okutsu, Yasuo Suzuki, Sinji Ando, and Mitsuru Ueda*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received April 9, 2008; Revised Manuscript Received June 20, 2008

ABSTRACT: A new thermoplastic, poly(thioether sulfone) (PES), with the highest refractive index and high Abbe's number among thermoplastics has been developed by the simultaneous introduction of sulfide, sulfone, and alicyclic units in the polymer chains. The PES with a high molecular weight was prepared by the Michael polyaddition of 2,5-disulfanyl-1,4-dithiane with divinyl sulfone. The flexible, tough, transparent, and amorphous PES film was obtained and showed a good thermal stability with 5% weight loss temperature of 275 °C in nitrogen and the glass transition temperature of 152 °C. The PES exhibited the highest refractive index of 1.686 and the Abbe's number of 48.6 among thermoplastics.

Introduction

Thermosets and thermoplastics with high refractive indices (n_D) and high Abbe's numbers (ν_D) are attracting significant interest because of their application as optical materials such as lenses, prisms, and waveguides that is made possible by their light weight, impact resistance, processability, and dying ability as compared to inorganic glasses.[1,2] The former such as resins from episulfides,[3] polythiols,[4] and polyisocyanates[5] have been developed for consumer use such as eyeglasses that are manufactured by cast molding. On the other hand, the latter such as poly(methyl methacrylate), polycarbonate, and cycloolefin polymers[6] are used in camera, pick-up, and projector lenses where injection molding is applied. Thermosets exhibiting both high n_D and high ν_D have been reported in patents as described above[3−5] and in papers such as those that describe the synthesis of optical polymers by the radical polymerization of 2,5-bis(2-thia-3-butenyl)-1,4-dithiane and the polyaddition of oligo[2,5-bis(thiomethyl)-1,4-dithiane] and di- or triisocyanates[7] and episulfide-type copolymers.[8] However, thermoplastics with high n_D and high ν_D have so far not been the subject of detailed investigation. Therefore, the development of high n_D thermoplastics with high ν_D values is a challenging topic.

According to the Lorentz−Lorentz equation, the introduction of substituents with high molar refractions and low molar volumes can efficiently increase the refractive indices of polymers.[9] It has been well established that sulfur atoms are effective in increasing refractive indices because of their high atomic refraction. Hence, sulfur-containing polymers such as poly(methacrylate)s[10] and poly(thiocarbonate)s[11] have been reported. However, the refractive indices of those polymers were ~1.60, which is not a very high value. In addition, the Abbe's number (ν_D), which is a key measure for refractive index dispersion, is also an important parameter for optical materials used in the visible region. The Abbe's number is given by the following equation

$$\nu_D = (n_D - 1)/(n_F - n_C) \qquad (1)$$

where n_D, n_F, and n_C are the refractive indices of the material at the wavelengths of the sodium D (589.3 nm), hydrogen F (486.1 nm), and hydrogen C (656.3 nm) lines, respectively.[12] There is a general relationship between the n_D and ν_D values for conventional optical polymers; that is, highly refractive materials generally exhibit small Abbe's numbers.[13] It is quite necessary to redesign the molecular structures of conventional polymers so as to fit the requirements for high n_D and high ν_D.

In a preceding paper,[14] we have synthesized a series of sulfur-containing poly(meth)acrylates by the radical polymerization of monomers consisting of cyclic dithiocarbonate, norbornene, and (meth)acrylate units. Among them, poly{2-{*exo*-3,5-dithiatricyclo[5.5.1.0^{2,6}]dectyl-4-one-8-sulfanyl}ethyl thiomethacrylate} exhibited the high n_D of 1.640 and the high ν_D of 42.1. To further increase the n_D and ν_D of thermoplastics is the next task.

In order to reduce the refractive index dispersion, we focused on an alicyclic group, which is also known to have a refractive index higher than that of an aliphatic moiety,[15,16] and a sulfonyl ($-SO_2-$) group, which is expected to endow polymers with high transparency and a low refractive index dispersion due to its very low molecular dispersion. On the basis of these considerations, we designed a novel polymer that contained sulfur, sulfonyl, and alicyclic units containing polymer. In this paper, we report here the synthesis and properties of a novel poly(thioether sulfone) with a high n_D of 1.686 at 589 nm and a large ν_D of 48.6. As described below, the combination of these n_D and ν_D values is extraordinarily high among the existing optical polymers.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium and distilled before use under nitrogen. All the other reagents and solvents were used without further purification.

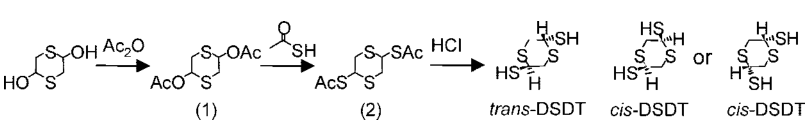
Monomer Synthesis. *Synthesis of 2,5-Diacetoxyl-1,4-dithiane (**1**).* To a solution of 2,5-dihydroxy-1,4-dithiane (10.4 g, 68.4 mmol) in dry pyridine (22 mL) cooled at 0 °C, acetic anhydride (15.4 g, 149.4 mmol) was added dropwise over 1 h using a dropping funnel under a nitrogen atmosphere. During the solution stirred for 1 h, the white solid began to precipitate. The mixture was poured into water. The precipitate was filtered and dried under reduced pressure. Recrystallization from methanol gave a white crystal (9.9 g, 61% yield); mp 161 °C. IR (KBr, cm^{-1}): ν = 2966, 2935 (alkyl C−H), 1739 (ester C=O), 1431 (alkyl C−H), 1369 (acetyl C−H), 725 (alkyl C−H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.18 (t, 2H; $-CH_3$), 2.81 (dd, 2H; CHO−CH_2−S), 3.69 (dd, 2H; CHO−CH_2−S), 5.83 (t, 2H; O−CH(CH_2)−S). ^{13}C NMR (300 MHz, $CDCl_3$ δ): 21.1 ($-CH_3$), 29.0 (S−CH_2−CHS), 66.1

---

* To whom correspondence should be addressed: Tel +81-3-57342127; Fax +81-3-57342127; e-mail ueda.m.ad@m.titech.ac.jp.

10.1021/ma800797p CCC: $40.75

Scheme 1. Synthesis of DSDT



(S−*CH*−O), 169.7 (C=O). Anal. Calcd for $C_8H_{12}O_4S_2$: C, 40.66; H, 5.12. Found: C, 40.75; H, 5.04.

*Synthesis of 2,5-Dithioacetoxyl-1,4-dithiane (**2**).* To a solution of **1** (8.32 g, 35.2 mmol) and thioacetic acid (6.43 g, 84.5 mmol) in dry methylene chloride cooled at 0 °C, boron trifluoride ether complex (0.19 mL) was added dropwise under a nitrogen atmosphere. The reaction mixture was stirred for 2 h at 0 °C and for 5 h at room temperature and quenched with 20 wt % K_2CO_3(aq). The organic layer was washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was recrystallized from methanol and gave a white crystal (6.29 g, 67% yield); mp 123 °C. IR (KBr, cm^{-1}): ν = 2958, 2904 (alkyl C−H), 1693 (thioester C=O), 1353 (acetyl C−H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.38 (s, 6H; −CH_3) 2.94 (dd, 1H; S−*CH_2*−CHS) 3.12 (dd, 1H; S−*CH_2*−CHS) 3.34 (dd, 1H; S−*CH_2*−CHS) 3.63 (dd, 1H; S−*CH_2*−CHS) 4.87 (m, 2H; S−*CH_2*−S). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ = 30.4 (−CH_3, *cis*) 30.5 (−CH_3, *trans*) 33.6 (CH−*CH_2*−S, *trans*) 35.6 (CH−*CH_2*−S, *cis*) 41.9 (S−*CH*−S, *trans*) 42.6 (S−*CH*−S, *cis*) 192.8 (C=O, *cis*) 193.4 (C=O, *trans*). Anal. Calcd for $C_8H_{12}O_2S_4$: C, 35.8; H, 4.51. Found: C, 35.79; H 4.34.

Synthesis of 2,5-Disulfanyl-1,4-dithiane (DSDT). A solution of **2** (13.5 g, 50.3 mmol) in HCl/methanol solution (3 wt %, 32.0 mL) and chloroform (81.0 mL) was heated at 60 °C for 15 h. Then, the solution was cooled to room temperature, concentrated to ca. 20 mL, and cooled to −40 °C to obtain the white precipitate of *trans*-DSDT. The *trans* isomer was filtrated and washed with water several times (3.0 g, 32% yield). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The obtained yellow oil was distilled under reduced pressure (0.12 Torr, 180 °C) to yield the mixture of *trans*- and *cis*-DSDT (0.75 g, 8% yield); mp 122 °C (*trans* isomer), 52 °C (*trans* and *cis* mixture). IR (KBr, cm^{-1}): ν = 2934, 2897 (alkyl C−H), 2499 (thiol S−H). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.26 (d, 2H; −SH *trans*), 2.72 (d, 2H; −SH *cis*), 3.14 (dd, 2H; S−*CH_2*−CH *trans*), 3.14 (dd, 2H; S−*CH_2*−CH *cis*), 3.27 (dd, 2H; S−*CH_2*−CH *trans*), 3.41 (dd, 2H; S−*CH_2*−CH *cis*), 4.10 (td, 2H; *CH*−SH *trans*), 4.20 (td, 2H; S−*CH*−SH *cis*). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ = 38.8 (S−*CH_2*−CH) 42.4 (S−*CH*−SH). Anal. Calcd for $C_4H_8S_4$: C, 26.06; H, 4.37. Found: C, 25.95; H, 4.09.

Polymer Synthesis (PES). To a solution of the mixture of *trans*- and *cis*-DSDT (0.163 g, 0.88 mmol) and divinyl sulfone (DS) (0.104 g, 0.88 mmol) in chloroform (2.9 mL) was added triethylamine (0.1 mL). The solution was stirred for 3 h at room temperature. The precipitated polymer was filtered, washed with chloroform, and dried at 60 °C in vacuo overnight. IR (KBr, cm^{-1}): ν = 2962, 2908 (alkyl C−H), 1404 (alkyl C−H), 1319 (sulfone −SO_2−), 1134 (sulfone −SO_2−). ^{1}H NMR (300 MHz, DMSO-d_6, 100 °C, ppm): δ = 3.08 (m, 6H, CH_2−*CH_2*−S, CHS−*CH_2*−S) 3.48 (m, 6H, SO_2−CH_2, CHS−*CH_2*−S), 4.38 (dd, 2H, S−*CH*−S). Anal. Calcd for $C_8H_{14}O_2S_5$: C, 31.76; H, 4.66. Found: C, 31.84; H, 4.42.

Measurements. The FT-IR spectra were obtained on a Horiba FT-720 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX300S spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent and trimethylsilane as the reference. Number- and weight-average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) on a JASCO PU-2080 Plus with two polystyrene gel columns (TSK GELS GMH$_{HR}$-M) DMF containing 0.01 M LiBr was used as a solvent at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. Preparative high-pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry LC-908 equipped with two consecutive gel columns, JAIGELs 1H and 2H, detected with refractive index and ultraviolet at 254 nm using chloroform as an eluent with a flow rate of 3.8 mL min^{-1}. The UV−vis transmittance spectra were recorded on a JASCO V-560 UV/vis spectrometer in the range 250−800 nm. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. The refractive indices of polymer films were measured at the wavelengths of 486, 589, and 656 nm by changing monochromatic filters with an Abbe refractometer (Atago, DR-M4). A halogen lamp with high brightness was used as a white light source.

Results and Discussion

Monomer Synthesis. As a monomer having a high sulfur content (40 wt %) with an alicyclic ring structure, 2,5-disulfanyl-1,4-dithiane (DSDT) was selected, and it was prepared via three steps from 2,5-dihydroxy-1,4-dithiane as shown in Scheme 1.[17] The DSDT was obtained as the *trans* isomer and the mixture of *trans* and *cis* isomers. The structure of the DSDT was characterized on the basis of elemental analysis as well as FT-IR and ^{1}H NMR spectroscopies. The IR spectra of monomers showed a characteristic absorption at 2499 cm^{-1} which is assignable to the mercapto group. Figure 1 shows the ^{1}H NMR spectra of the *trans* and the mixture of *trans* and *cis* isomers. The ^{1}H NMR spectrum of the *trans* isomers is shown in Figure 1a; the inset indicates the assignment of each resonance. All peaks agreed with the assignment to the expected structure of *trans* DSDT. Figure 1b shows doublet signals at 2.26 and 2.72 ppm assignable to the mercapto groups of the *trans* and *cis* isomers, respectively. Using these signals, the ratio of *trans* and *cis* isomers in the mixture was estimated to be 3:1.

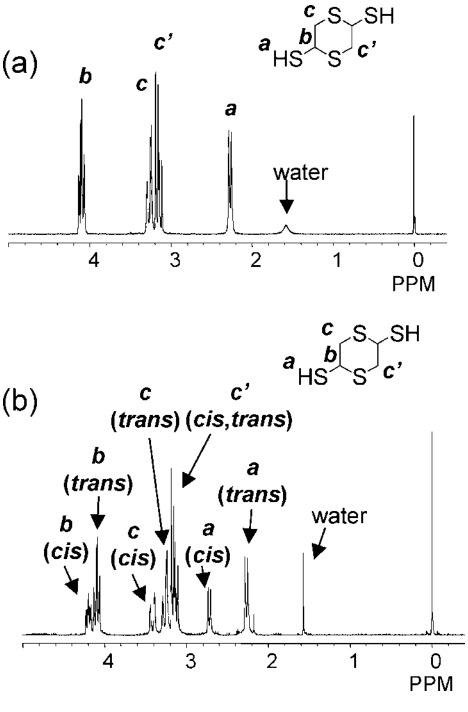
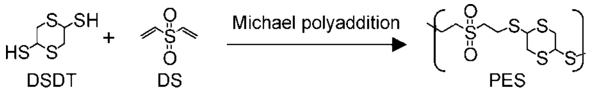


Figure 1. ^{1}H NMR spectra of (a) *trans*-DSDT and (b) the mixture of *trans*- and *cis*-DSDT in DMSO-d_6.

Scheme 2. Michael Polyaddition of DSDT with DS



Michael Polyaddition. Divinyl sulfone (DS) having a sulfonyl group was chosen as a counter monomer. The Michael polyaddition is a useful method to prepare polymers with high molecular weights from dithiols and divinyl sulfone. The polymerization of DSDT and DS was carried out at room temperature for 3 h in the presence of a catalytic amount of triethylamine as a basic catalyst in chloroform (Scheme 2). The polymerization using the *trans*-DSDT proceeded with the precipitation of the corresponding poly(ether sulfone) (PES) and yielded a polymer with a low molecular weight polymer. In contrast, the polymerization of the mixture of *trans*- and *cis*-DSDT with DS proceeded in the homogeneous state and provided PES with the number- and weight-average molecular weights (M_n, M_w) of 15 000 and 23 000, respectively. The polymer thus obtained was a white solid and soluble in chloroform, cyclohexanone, DMF, 1-methyl-2-pyrrolidinone, and heated γ-butylolactone. A tough and flexible film was readily obtained by casting a cyclohexanone solution of the polymer onto a fused silica substrate followed by drying in vacuo.

The structure of PES was characterized by FT-IR and ^{1}H NMR spectroscopies. The IR spectrum of the polymer demonstrated characteristic sulfonyl stretchings at 1134 and 1319 cm^{-1}. No absorption due to the mercapto group of DSDT was observed at 2499 cm^{-1}. Figure 2 shows the ^{1}H NMR spectrum of PES with the assignment of the observed resonance. The signals of monomers at 2.26 and 2.72 ppm assignable to the mercapto groups and those at 6.23 and 6.88 ppm to the vinyl group are not observed, and the signal of the methylene protons next to the sulfonyl group is clearly observed at 3.48 ppm. Furthermore, the atomic composition of the polymer was confirmed by elemental analysis.

Thermal Properties. The thermal properties of PES were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). As shown in Figure 3, the PE exhibits a 5% weight loss temperature at 271 °C in the air and 275 °C in nitrogen. A glass transition temperature (T_g) determined by DSC measurement is 152 °C (Figure 4). The rigid alicyclic structure and the bulky sulfonyl unit in the main chain may contribute to the relatively high T_g value.

Optical Properties. The UV−visible (UV−vis) absorption spectra of a DMF solution of PES and a film of PES (thickness: 17 μm) are shown in Figure 5. Both the solution and the film exhibit very high transparency (>99%) in the visible region (wavelengths: 400−800 nm). The absence of aromatic rings in the molecular structure and the introduction of sulfonyl group are important factors for the high transparency. The sulfonyl group is expected to lower the energy level of the highest occupied molecular orbital (HOMO) and increase the energy band gap between HOMO and the lowest unoccupied molecular orbital (LUMO); hence, the absorption edge is shifted to a shorter wavelength.

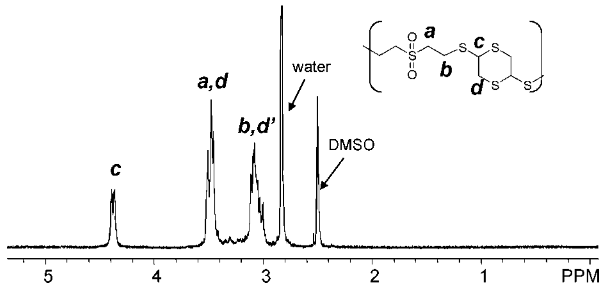


Figure 2. ^{1}H NMR spectra in DMSO-d_6. of PES.

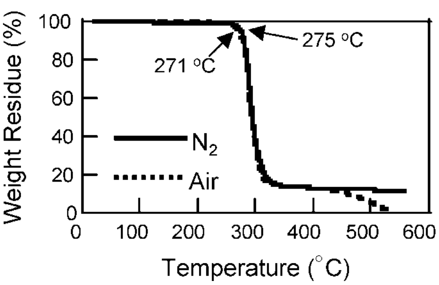


Figure 3. TG traces of PES, measured at a heating rate of 10 °C/min under nitrogen and air.

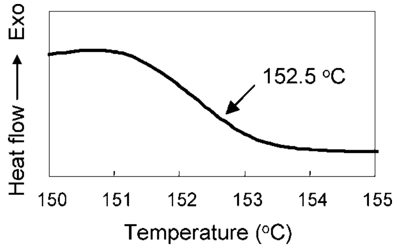


Figure 4. DSC trace of PES, measured at a heating rate of 10 °C/min under nitrogen.

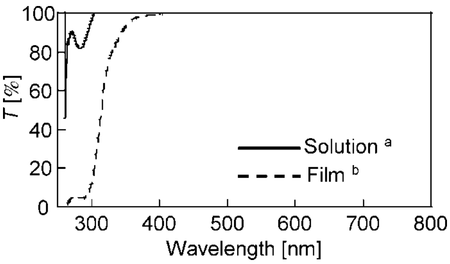


Figure 5. UV−vis transmittance spectra of PES: a, 1.0 mol L^{-1} DMF solution; b, 17 μm thick polymer film formed on a fused silica substrate.

Table 1. Measured Refractive Index (n) and Abbe's Number (ν_D) of PES

d^a (μm)	$n_D{}^b$	$n_F{}^c$	$n_C{}^d$	$\nu_D{}^e$	$n_\infty{}^f$	D^f
230	1.6859	1.6961	1.6820	48.6	1.6647	7413

[a] Sample film thickness. [b] Measured at 589 nm. [c] Measured at 486 nm. [d] Measured at 656 nm. [e] Calculated using eq 1. [f] Estimated from the curve fitting using the simplified Cauchy's formula.

The refractive indices of the polymer film observed at 486, 589, and 656 nm are listed in Table 1. The wavelength dispersion of refractive indices (n_λ) thus obtained is plotted in Figure 6 with a fitted curve using the simplified Cauchy's equation[18]

$$n_\lambda = n_\infty + D/\lambda^2 \tag{2}$$

The coefficients of n_∞, D, and ν_D are also presented in Table 1. The highest values of n_D and ν_D among thermoplastics having optical applications are 1.686 and 48.6, respectively, whereas the (n_D, ν_D) values for PMMA, polystyrene, and polycarbonate are (1.491, 57), (1.590, 30), and (1.581, 29), respectively. Figure 7 shows the relationship between the refractive indices (n_D) and the Abbe's numbers for the reported optical polymers; the dotted line is, what we call, "the limiting line". Conventional optical polymers do not go beyond this line as indicated by × symbols.

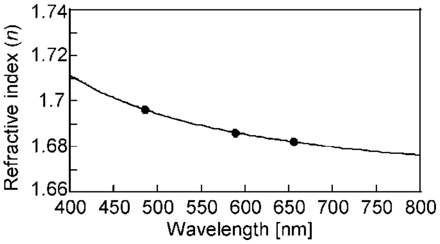


Figure 6. Wavelength dispersion of the experimental refractive indices of PES. The dispersion is fitted by the simplified Cauchy's formula.

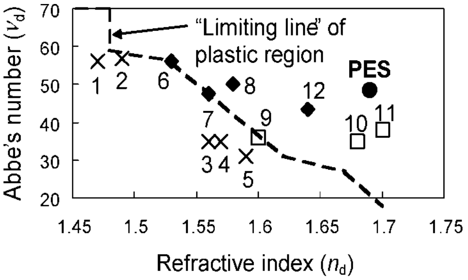


Figure 7. Plastic region in the $n_D-\nu_D$ diagram: (—) the empirical limiting line of the region of transparent plastics; (×) conventional thermoplastic optical polymers 1−5, where 1 = poly(4-methylpentene), 2 = poly(methyl methacrylate), 3 = poly(styrene-*co*-methyl methacrylate), 4 = poly(acrylonitrile-*co*-styrene), 5 = polycarbonate; (◆) thermoplastics with high n_D and high ν_D 6−8 and 12, where 6 = ZEONEX,[6] 7, 8 = poly(sulfur-containing alicyclic methacrylate),[10] and 12 = poly{2-{*exo*-3,5-dithiatricyclo[5.5.1.$0^{2,6}$]dectyl-4-one-8-sulfanyl}ethyl thiomethacrylate};[14] (●) PES; (□) thermosets with high n_D and high ν_D 10−13; 9 = MR-6,[19] 10 = dithiane-based polyurethane,[20] 11 = polymer from episulfides.[8]

Table 2. Molecular Refraction and Molecular Dispersion

molecules	R_D	ΔR	$R_D/\Delta R$
−S−	7.80	0.22	35.5
$-SO_2-$	9.76	0.09	103.9

Typical thermosets such as MR-6 (Mitsui Chemicals Co.) (1.60, 36) and dithiane-based cross-linking polyurethane (1.68, 34.8) are also plotted for comparison.[19,20] The (n_D, ν_D) points of the PES are located very far from those of the thermoplastic optical polymer and even beyond the region for the thermosets developed for high refractive indices and high Abbe's numbers. These facts clearly demonstrate that the (n_D, ν_D) values of PES are extraordinarily high.

The optical thermosets with high n_D that have been developed for eyeglasses generally contain a large number of sulfur atoms because the n_D of synthetic polymers significantly depend on the number of sulfide groups present due to the high molecular refraction of sulfur. On the other hand, the fundamental absorptions of optical polymers have to be blue-shifted in order to achieve a low dispersion of refractive indices with a high ν_D because the refractive indices of condensed matters significantly increase near the absorption edges.[21] However, a polymer with a high sulfur content generally exhibits a low ν_D due to the absorptions in the UV and visible regions. As described above, the introduction of the $-SO_2-$ group effectively displaces the absorption edge to the shorter wavelengths, which leads to an increase in ν_D, though $-SO_2-$ is not effective in increasing the n_D. However, the simultaneous introduction of plural −S− linkages would compensate for and increase the n_D without reducing the ν_D.

Furthermore, the relation between n_D and ν_D is shown in the equation

$$\nu_D = 6n_D/\{(n_D+2)(n_D+1)\}[R]/[\Delta R] \qquad (3)$$

where [R] and [ΔR] show the molecular refraction and molecular dispersion, constants peculiar to each molecule, respectively. From this equation, it can be concluded that the higher the n_D, the lower is the ν_D. On the other hand, a large value of [R]/[ΔR] can increase the ν_D. The values of [R], [ΔR], and [R]/[ΔR] for sulfide and sulfone groups are summarized in Table 2. Note that the sulfonyl group shows a much lower dispersion with a slightly higher molecular refraction compared to the sulfide group. Despite the high molecular refraction, the large volume of $-SO_2-$ generally decreases the n_D. However, the compact ring structure of dithiane would compensate for the bulkiness of $-SO_2-$. Hence, the combination of a $-SO_2-$ and plural −S− groups is very effective in increasing both the n_D and ν_D values at same time. As evidenced in the case of PES, the potential of the molecular design concept is clearly demonstrated in Figure 7.

Conclusions

In summary, we have developed a new thermoplastic with the highest n_D of 1.686 and ν_D of 48.6 by a simultaneous introduction of sulfide, sulfone, and alicyclic units in the polymer chains. The film-forming polymer was easily prepared by the Michael polyaddition of DSDT with DS. The PES thermoplastic that has well-balanced optical properties is a promising candidate for advanced optical applications.

References and Notes

(1) Gao, C.; Yang, B.; Shen, J. *J. Appl. Polym. Sci.* **2000**, *75*, 1474–1479.
(2) Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. *J. Appl. Polym. Sci.* **2000**, *76*, 50–53.
(3) Morishiri, H.; Kobayashi, S. Jpn. Kokai Tokkyo Koho JP 2005325274, **2005** [*Chem. Abstr.* **2005**, *143*, 478988t].
(4) Morishiri, H.; Kobayashi, S. Jpn. Kokai Tokkyo Koho JP 2006131724, **2006** [*Chem. Abstr.* **2006**, *144*, 489903h].
(5) Okada, R.; Ohkubo, T.; Kosaka, M. Eur. Pat. Appl. EP 530757, **1993** [*Chem. Abstr.* **1993**, *119*, 97514g].
(6) Kohara, T. *Macromol. Symp.* **1996**, *101*, 571–579.
(7) Okubo, T.; Kohmoto, S.; Yamamoto, M. *J. Mater. Sci.* **1999**, *34*, 337–347.
(8) Lü, C.; Cui, Z.; Wang, Y.; Yang, B.; Shen, J. *J. Appl. Polym. Sci.* **2003**, *89*, 2426–2430.
(9) Helmut, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 49–59.
(10) Matsuda, T.; Funae, Y.; Yamamoto, T.; Takaya, T. *J. Appl. Polym. Sci.* **2000**, *76*, 45–49.
(11) Hikosaka, T.; Tamura, H.; Morishita, H. Jpn. Kokai Tokkyo Koho JP 2005029608, **2005** [*Chem. Abstr.* **2005**, *142*, 157410g].
(12) Okubo, T.; Kohmoto, S.; Yamamoto, M. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 1819–1834.
(13) Yang, C.-J.; Jenekhe, S. A. *Chem. Mater.* **1995**, *7*, 1276–1285.
(14) Okutsu, R.; Ando, S.; Ueda, M. *Chem. Mater.* **2008**, 20.
(15) Uozu, Y.; Hirota, N.; Horie, K. *Macromol. Mater. Eng.* **2004**, *289*, 56–62.
(16) Takashima, Y.; Nasuno, I.; Shibata, M. Jpn. Kokai Tokkyo Koho JP 2005035968, **2005** *[Chem. Abstr.* **2005**, *142*, 198492d].
(17) Wang, M.; Honma, M.; Takamatsu, T. Jpn. Kokai Tokkyo Koho JP 2005029499, **2005** *[Chem. Abstr.* **2005**, *142*, 177304d].
(18) Li, J.; Wu, S. *J. Appl. Phys.* **2004**, *95*, 896–901.
(19) Kawauchi, K.; Sasagawa, K.; Kobayashi, S. Jpn. Kokai Tokkyo Koho JP 07165859, **1995** [*Chem. Abstr.* **1995**, *123*, 342702z].
(20) Okubo, T.; Kohmoto, S.; Yamamoto, M. *J. Appl. Polym. Sci.* **1998**, *68*, 1791–1799.
(21) Fox, M. In *Optical Properties of Solids*; Oxford University Press: New York, 2001.

MA800797P