Synthesis, Characterization, and Optical Properties of Polymers Comprising 1,4-Dithiane-2,5-Bis(thiomethyl) Group

TSUYOSHI OKUBO,[1,2] SHIGEO KOHMOTO,[1] MAKOTO YAMAMOTO[1]

[1] Graduate School of Science and Technology, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan

[2] R&D Center, HOYA Corporation, 3-3-1 Musashino, Akishima-shi, Tokyo 196, Japan

ABSTRACT: To obtain an optical polymer with a high refractive index (n_D) and Abbe's number (ν_D), a series of 1,4-dithiane-2,5-bis(thiomethyl)(DBT) group-bearing poly(S-alkylcarbamate) and polyvinylsulfide were synthesized by the polyaddition of 2,5-bis(mercaptomethyl)-1,4-dithiane (BMMD) with diisocyanates and by the addition polymerization of 2,5-bis(2-thia-3-butenyl)-1,4-dithiane (TBD) in bulk, respectively. Their $n_D : \nu_D$ values, ranging from 1.598 : 38.2 to 1.678 : 34.8, are comparable to those of flint glass. Some of the polymers having a high transparency and glass transition temperature were suggested to be useful as optical polymers. The DBT group contribution to the increase of the n_D value of the obtained polymer was explained in terms of the ϕ value defined by the ratio of molar refraction to molar volume and was concluded to be of primary importance because the value for the DBT group (0.38) was greater than that for the residual group making up the polymer structure. This group's contribution in preventing the degradation of the ν_D of the polymers was also discussed based on the UV spectrum of BMMD, which only showed a suppressed absorption band. BMMD and TBD are useful monomers for preparing an optical polymer with high n_D and ν_D values. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1791–1799, 1998

Key words: 1,4-dithiane; poly(S-alkylcarbamate); polyvinylsulfide; refractive index; Abbe's number

INTRODUCTION

In optical tools such as lenses, prisms, and filters, polymer materials have replaced conventional inorganic glass materials, and in practice, poly(methyl methacrylate), CR-39, and polycarbonates have been used.[1] The advantage of using polymers lies in their relative ease of processing, better impact resistance, and lightness compared to their inorganic glass counterparts.[2] Optical materials are usually characterized by the main properties of transparency, refractive index (n_D), and Abbe's number (ν_D). The Abbe's number, which describes optical dispersion, is given by $\nu_D = (n_D - 1)/(n_F - n_C)$, where n_D, n_F, and n_C are the refractive indices of the material at the wavelengths of the D, F, and C lines of the sodium spectrum, respectively.[2] The refractive index and Abbe's number of polymers and inorganic glasses generally relate to each other: The higher the refractive index, the lower the Abbe's number and vice versa.[3] The n_D of an organic polymer is relatively lower than that of an inorganic glass when these materials having almost the same ν_D are

compared.[3] This has prevented the use of many polymers for critical optical applications because preference has been given to high refractive index inorganic glasses.[2,4] Organic-based polymers with an improved refractive index have appeared in a considerable amount of literature, but their Abbe's numbers actually degraded or were simply not discussed at all.[5–14] This work aimed at a synthesis of a polymer that possesses a refractive index and an Abbe's number that are as high as those of inorganic glasses.

To obtain polymers with those high values, polymers incorporating such characteristic structures as an aromatic group,[15–17] a halogenated aromatic group,[16–20] and an alicyclic condensed ring[21] were synthesized, but their n_D and ν_D values were improved moderately. Polyelectrolytes that are composed of specific organic polymer chains and inorganic moieties showed remarkably high n_D and ν_D values due to the latter components.[22] Based on molar refraction and molar dispersion, sulfur-containing polymers would have higher n_D and ν_D values. For instance, polymers possessing sulfide,[23] S-alkyl ester,[24] and S-alkylcarbamate[25,26] showed comparably high n_D and ν_D values. It is well known that the latter polymers are easily obtained by the polyaddition of polythiol and polyisocyanate and that the polymers from pentaerythritoltetrakis(mercaptopropionate) and 1,3-bis(isocyanatomethyl)benzene or from 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane and bis(isocyanatomethyl)bicyclo[2.2.1]heptane show $n_D : \nu_D$ values of 1.59 : 36.0 or 1.620 : 41.0, respectively.[25,26]

These reports indicated that the introduction of the alicyclic sulfide moiety into a polymer chain may improve the n_D and ν_D values of the polymer. Based on this indication, we prepared the following two types of 1,4-dithiane-2,5-bis(thiomethyl) (DBT)-group-containing polymers; one of them is a polyaddition product using 2,5-bis(mercaptomethyl)-1,4-dithiane (BMMD) and a diisocyanate, and the other one is an addition polymerization product using 2,5-bis(2-thia-3-butenyl)-1,4-dithiane (TBD). In addition to the polymer synthesis, their characterization and optical properties are discussed.

EXPERIMENTAL

General

^{1}H-NMR (270 MHz) and ^{13}C-NMR (67.8 MHz) spectra were recorded on a JEOL EX-270 in CDCl$_3$ (for monomers) and (CD$_3$)$_2$SO (for polymers) solutions using tetramethylsilane as the internal reference. IR spectra were recorded on a Nicolet 20 SXB. The molecular weight distributions of polymers were observed by gel permeation chromatography performed on a Tosoh GPC system (column: TSKgel G6000HXL and G4000HXL; detector: UV at 254 nm; eluent: tetrahydrofuran [1 mL/min]). Molecular weights were determined on the basis of a standard polystyrene calibration. The intrinsic viscosities of poly(S-alkylcarbamate)s were measured at 25°C in methyl sulfoxide (DMSO) with a Ubbelohde-type viscometer. Thermomechanical analysis was performed using a Rheolograph Solid (Toyoseiki Co.) at a heating rate of 2°C/min and a frequency of 10 Hz. Glass transition temperature (T_g) was defined by the temperature at the maximum tan δ of the analysis. The refractive index (n_D) and Abbe's number (ν_D) were measured using an Abbe refractometer 3T (ATAGO Co.) and a specimen ($15 \times 8 \times 5$ mm) with a polished surface. Differential scanning calorimetry (DSC) was performed in air with a DSC-3110 instrument (MAC Science Co.) using an Al$_2$O$_3$ reference at a heating rate of 10 K/min. Visible light transmittance ($T\%$) was measured with a UV-330 spectrophotometer (Hitachi) using a sample with a thickness of 1 mm. Molar refraction and molar volume of the DBT, phenyl, and bromophenyl groups referred to in the following discussion were estimated by a Synthia module running on an Insight II (version 4.0.0) program (Molecular Simulations Inc.).

Materials

Preparation of BMMD

To a mixture of allyldisulfide (10.3 g, 70.2 mmol), calcium carbonate (0.14 g), and dichloromethane (170 mL), sulfuryl chloride (9.5 g, 70.2 mmol) was added dropwise in 45 min at −30°C; then, the mixture was stirred continuously for 24 h at the same temperature. The reaction mixture was filtered, and the solvent was evaporated from the filtrate to give 15.4 g of crude 2,5-dichloromethyl-1,4-dithiane (DCMD). The mixture of crude DCMD and thiourea (10.8 g, 0.142 mol) in ethanol (47 mL) was refluxed for 1 h, then cooled to room temperature. The resulting precipitate was filtered and dried in a vacuum to give 22.0 g of the isothiuronium salt of DCMD (TSDCMD). To the dispersion of the TSDCMD in 63 mL of water, a solution of sodium hydroxide (5.81 g, 0.145 mol)

in 31 mL of water was added dropwise at 90°C; then, the reaction mixture was stirred for 1 h at the same temperature. It was cooled to room temperature and acidified by adding 6N HCl(aq) until its pH value dropped to 2–3. The separated oil was extracted with benzene, and the extract was washed with water and dried over anhydrous magnesium sulfate. The benzene was removed at a reduced pressure and the residue was purified by vacuum distillation (bp = 121.5°C at 0.02 mmHg) to give colorless BMMD (7.76 g, yield = 52.0% from allyldisulfide). Its n_D and ν_D values were 1.646 and 35.2, respectively.

^{1}H-NMR in CDCl$_3$: δ1.62 (t, 1H), δ2.88–3.14 (m, 5H). ^{13}C-NMR in CDCl$_3$: δ28.4, δ31.2, δ42.2. IR (neat): 2905 (C—H), 2545 (C—SH), 1410 (—CH$_2$—) cm^{-1}.

ANAL: Calcd for C$_6$H$_{12}$S$_4$ (212.40): C, 33.93%; H, 5.69%; S, 60.38%. Found: C, 33.75%; H, 5.75%; S, 59.99%.

Diisocyanates

1,6-Diisocyanatohexane (DIHE, $n_D : \nu_D$ = 1.452 : 50.7) was purchased from Aldrich Chemical Co., (Milwaukee) and distilled under reduced pressure (92°C at 2 mmHg) prior to use. 1,3-Bis(isocyanatomethyl)cyclohexane (BIC, $n_D : \nu_D$ = 1.484 : 52.1) and 1,3-bis(isocyanatomethyl)benzene (BIB, $n_D : \nu_D$ = 1.541 : 33.7) were purchased from Takeda Chemical Industries (Osaka) and Tokyo Kasei Kogyo Co., (Tokyo) respectively, and were used without further purification. All other diisocyanates used in this experiment were prepared from the corresponding acylazide via a Curtius rearrangement.[27] 1,n-Diisocyanatoalkane [boiling point in °C/mmHg (lit.); $n_D : \nu_D$]: 1,3-diisocyanatopropane [76/15 (30–85/14–16)[28]; 1.449 : 50.5], 1,4-diisocyanatobutane [99/10 (94–98/10)[28]; 1.450 : 50.6], 1,5-diisocyanatopentane [103/4 (105/4)[29]; 1.451 : 51.4], 1,7-diisocyanatoheptane [104/1 (105–106/1.5)[30]; 1.452 : 50.6], 1,8-diisocyanatooctane [149/10 (152–154/11)[31]; 1.453 : 50.6], 1,9-diisocyanatononane [134/0.5 (134/0.6)[29]; 1.455 : 51.4], and 1,10-diisocyanatodecane [136/0.3 (132/0.2)[29]; 1.455 : 50.7].

Polyaddition of BMMD and Diisocyanates

A homogeneous mixture of an appropriate amount of BMMD, an equimolar diisocyanate to the BMMD, and 0.1 mol % of di-n-butyltindilaurate to the BMMD as a catalyst was poured into a glass

ampule and degassed in a vacuum. The ampule was filled with argon, sealed, and heated gradually from room temperature to 120°C within 21 h. The poly(S-alkylcarbamate)s thus obtained were all solid and hard.

Preparation and Polymerization of TBD

A mixture of an ethanol solution of sodium ethoxide [prepared from sodium (32.75 g, 1.42 g atom) and 1000 mL of ethanol] and BMMD (151.25 g, 0.711 mol) was stirred for 30 min at room temperature. The mixture of the resulting sodium salt of BMMD and vinylbromide (182.71 g, 1.71 mol) was allowed to stand at 80°C for 24 h in a sealed reaction vessel. Most of the ethanol in the reaction mixture evaporated, and the benzene solution of the residue was washed with 2% NaOH(aq) and brine, then dried over anhydrous magnesium sulfate. After the benzene was removed from the solution, the residue was distilled in a vacuum (bp = 134–136°C/0.025 mmHg) to give a colorless TBD (96.07 g, yield = 51.0%). Its n_D and ν_D values were 1.627 and 33.8, respectively.

^{1}H-NMR in CDCl$_3$: δ2.9–3.2 (m, 10H), δ5.19 (d, 2H, J = 16.5 Hz), δ5.26 (d, 2H, J = 9.9 Hz), δ6.33 (dd, 2H, J_1 = 16.7 Hz, J_2 = 10.0 Hz). ^{13}C-NMR in CDCl$_3$: δ31.3, δ35.3, δ38.3, δ112.4, δ131.4. IR (neat): 3082, 2902, 1584, 1409, 954, 866, 590 cm^{-1}.

ANAL: Calcd for C$_{10}$H$_{16}$S$_4$ (264.48): C, 45.40%; H, 6.07%; S, 48.53%. Found: C, 45.19%; H, 6.01%; S, 48.64%.

A degassed homogeneous mixture of an appropriate amount of TBD and 0.1 mol % of 2,2′-azobis(2,4-dimethylvaleronitrile)(V65) as an initiator was heated in a sealed ampule filled with argon from room temperature to 120°C within 21 h to give a transparent hard polymer.

IR (KBr pellet): 2897, 1584, 1409, 1310, 1250, 1206, 1159, 951, 871, 698 cm^{-1}.

RESULTS AND DISCUSSION

Preparation of BMMD-based Poly(S-alkylcarbamate)s and Poly(TBD)

Scheme 1 shows the preparation of novel BMMD, TBD, and their polymers. DCMD **2** was prepared
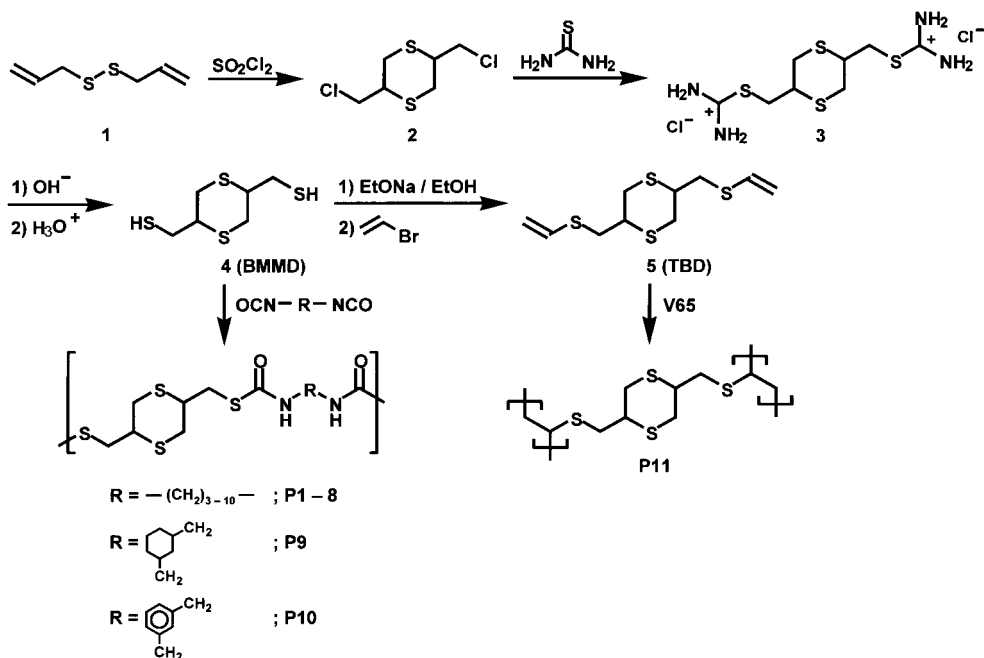
**Scheme 1**   Synthesis of polymers comprising DBT group.

according to Thaler and Butler[32] with a modification of the reaction temperature. This reaction gave DCMD and undesired polymeric byproducts, and based on the GPC analysis, the yield of the former appears to be maximized at a lowered temperature [temperature/yield (area %): $-9°C/78.6\%, -20°C/84.5\%, -30°C/92\%$]. Crude **2** was subjected to the next reaction without purification because only pure **3** precipitated, and its hydrolyzed product was almost pure **4** (BMMD). The S_N2 reaction of its sodium thiolate with vinylbromide, which is specific to thiolate anion,[33] gave **5** (TBD) in a moderate yield due to its consecutive conversion to an unidentified polymeric product. The refractive index and Abbe's number of BMMD or TBD are relatively large compared with those of common organic compounds. Moreover, BMMD and TBD are useful to prepare bulk polymers composing the characteristic DBT group. The former gave poly(S-alkylcarbamate)s by polyaddition with isocyanates, and the latter gave poly(TBD) by radical addition polymerization of vinylsulfide.

Characterization of the Poly(S-alkylcarbamate)s and Poly(TBD)

The ^{1}H-NMR (Fig. 1) and IR (Fig. 2) spectra of unpurified P-1 are typical of poly(S-alkylcarbamate)s. The complete disappearance of the signal corresponding to isocyanate ($2150–2050$ cm^{-1})

indicates the quantitative polyaddition of BMMD and diisocyanates. These spectra and those of the other poly(S-alkylcarbamate)s are consistent with the structural formula shown in Scheme 1.

Figure 3 shows the IR spectra of TBD and P-11, where characteristic signals observed at 1584 and 1409 cm^{-1} were assigned to those of vinylsulfide[34] and the methylene group, respectively. The
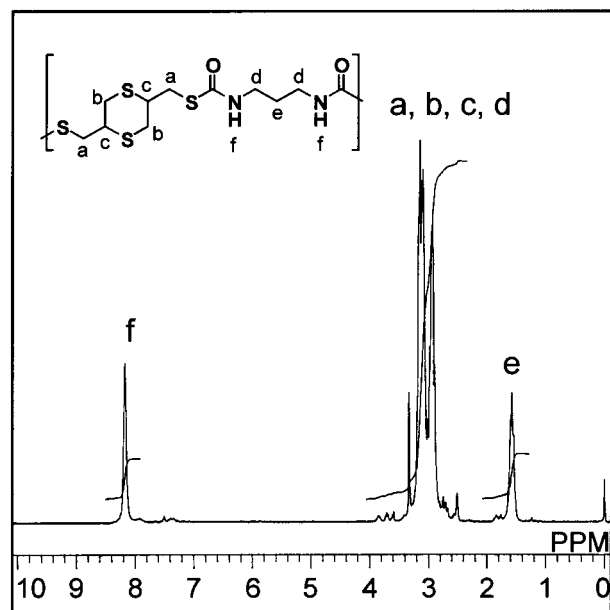
Figure 1 ^{1}H-NMR spectrum of P-1.

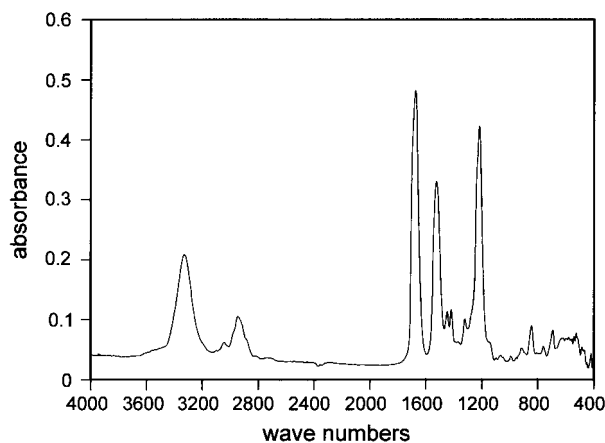**Figure 2** IR spectrum of P-1.

weaker intensity of the signal at 1584 cm^{-1} of P-11 than that of TBD indicated that the TBD polymerized at vinylsulfide as shown in Scheme 1. This mechanism was supported with the radical addition polymerization of vinylsulfide monomers studied by Otsu and Inoue[35] and Gollmer et al.[36] The conversion yield (Y) of the vinylsulfide group, which is considered to be the polymerization yield, was determined by the following eq. (1) and was 61.9% under the polymerization conditions given in the Experimental section:
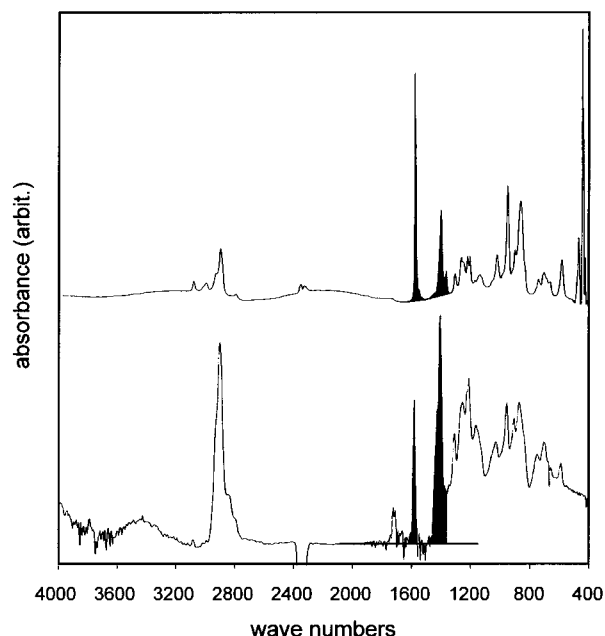

Figure 3 IR spectra of (top) TBD and (bottom) P-11. The shadowed signals at 1584 and 1409 cm^{-1} are assigned to vinylsulfide and the methylene group, respectively.

Table I Molecular Weight (M_n, M_w), Intrinsic Viscosity ([η]), and Specific Gravity (SG) of the Polymers Obtained

Polymer	M_n	M_w	[η] (dL/g)	SG
P-1	5430	13,000	0.20	1.38
P-2	34,900	65,600	0.28	1.37
P-3	63,100	174,500	0.23	1.34
P-4	19,300[a]	70,200[a]	0.73[b]	1.32
P-5	46,500	122,000	0.27	1.30
P-6	19,200[a]	41,900[a]	0.28[b]	1.28
P-7	37,300[a]	209,000[a]	0.24[b]	1.25
P-8	44,300	180,000	0.20	—
P-9	13,600	29,200	0.31	1.31
P-10	32,100	170,000	0.11	1.38
P-11	—	—	—	1.36

[a,b] Only the (a) THF and (b) DMSO soluble parts were used.

$$Y = (A_m^p A_v^m - A_v^p A_m^m)/(A_m^p A_v^m + A_v^p A_m^m) \quad (1)$$

where A_v^m and A_m^m are the absorbencies of signals at 1584 and 1409 cm^{-1} for TBD, respectively, and A_v^p and A_m^p are those at 1584 and 1409 cm^{-1} for P-11, respectively. From this conversion yield, propagation in TBD polymerization was considered to be limited by the steric hindrance of bulky 1,4-dithiane rings and a closely crosslinked structure, which formed as propagation proceeded. Table I gives the molecular weight, intrinsic viscosity, and specific gravity of the polymers obtained in this work. P-4, P-6, and P-7 were not completely dissolved in common organic solvents such as tetrahydrofuran (THF), DMSO, dimethylformamide, and hexafluoroisopropanol due to the presence of small dispersive particles. Their THF- and DMSO-soluble parts obtained by filtration through a 1 μm pore were used to measure the molecular weight and intrinsic viscosity, respectively. The amount of these particles were negligible, and their removal proved not to affect these characters significantly since these values of P-4, P-6, and P-7 were comparable with those of the other polymers. P-11 also did not dissolve in common organic solvents. This insolubility of P-11 might be caused by a crosslinked structure due to TBD's bifunctionalities. Therefore, further characterization through NMR spectrometry and solution properties could not be attempted.

T_g and Optical Properties of the Poly(S-alkylcarbamate)s and Poly(TBD)

Table II summarizes the T_g and optical properties of the polymers obtained in this work. The T_g of

Table II T_g **and Optical Properties of the Polymers Obtained**

Polymer	T_g (°C)	T (%) (450–900 nm)	n_D	ν_D
P-1	105.3	88–96	1.646	35.6
P-2	105.3	87–95	1.637	37.1
P-3	99.4	76–89	1.628	37.3
P-4	94.1	Opaque	—	—
P-5	87.1	76–87	1.613	37.5
P-6	80.4	Opaque	—	—
P-7	78.9	66–81	1.598	38.2
P-8	76.3	Opaque	—	—
P-9	130.0	90–98	1.620	38.5
P-10	122.4	92–84	1.661	32.0
P-11	—	86–94	1.678	34.8

the poly(S-alkylcarbamate) of P-1–8 decreases as the number of the methylene units of the used diisocyanate increases. P-9 had the highest T_g among the poly(S-alkylcarbamate)s due to incorporation of an alicyclic ring, and P-11 did not show its T_g below 200°C in the thermomechanical analysis. The thermomechanical property of a higher T_g is advantageous for the application of a polymer material in optical tools because it hardly deforms even at elevated temperatures.

From the visible light transmittance, these polymers are colorless and optically clear except P-4, P-6, and P-8, which are opaque. This turbidity was explained in terms of their crystallinity, which was evidenced by the melting point shown in their DSC charts (Fig. 4). It is well known that the melting point of linear aliphatic polyurethane changes periodically as the number of the methylene units between the two carbamate bonds increases.[37] A similar periodical change in crystallinity was observed for P-4–8.

It is notable that the n_D of the diisocyanate does not affect that of the poly(S-alkylcarbamate) systematically. The n_D of P-1 is higher than that of P-9, although the n_D of the diisocyanate used for the former is lower than that used for the latter. The n_D of P-10 was the highest among those of the poly(S-alkylcarbamate)s, and that of P-11, which were prepared without diisocyanate, exceeded it.

The refractive index of a material can be estimated by the following eqs. (2) and (3), which are derived from the Lorentz–Lorenz equation, where $[R]$ and V are the molar refraction and the molar volume, respectively.[38] When these equations are applied to polymers, the values of $[R]$ and V are regarded as those of the repeating unit of the polymer[38]:
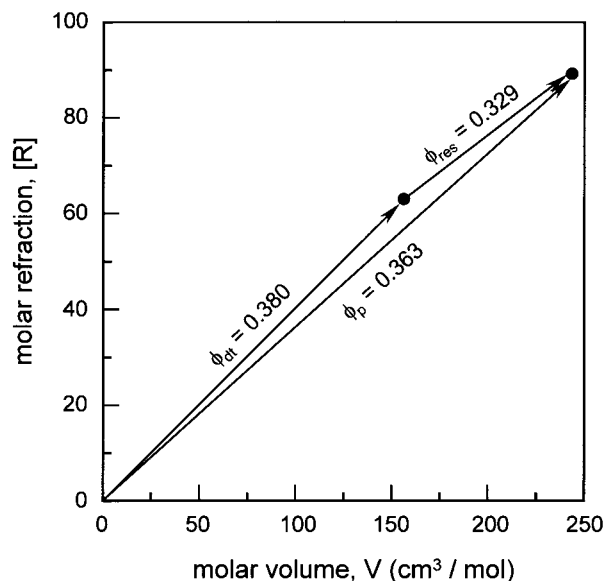
$$\phi = [R]/V \qquad (2)$$

$$n_D = [(2\phi + 1)/(1 - \phi)]^{1/2} \qquad (3)$$

It is obvious that the n_D is increased with increasing $[R]$ or with decreasing V. According to the group additive method, the ϕ of a polymer (ϕ_p) can be split into ϕ components attributed to the groups, which build up the polymer structure, in the $[R]$ versus V coordinate.[39] For example, if P-1 is considered to be composed of DBT and residual groups, then ϕ_p is expressed by the ϕ component of the former group (ϕ_{dt}) and that of the latter (ϕ_{res}) as shown in Figure 5. In this expression, $[R]$, V, and the resultant ϕ for the polymer ($[R]_p$, V_p, and ϕ_p, respectively) are calculated from observed specific gravity (1.38) and n_D (1.646) to be 89, 245.1 cm³/mol, and 0.363, respectively. According to Ohtsuka,[39] those for the DBT group ($[R]_{dt}$, V_{dt}, and ϕ_{dt}, respectively) are estimated to be 61.7, 162.1 cm³/mol, and 0.380, respectively. The slope of the line through points $(V_p, [R]_p)$ and $(V_{dt}, [R]_{dt})$ consequently corresponds to the $\phi_{res}([R]_p - [R]_{dt}/V_p - V_{dt})$ being 0.329. Table III gives the $[R]$, V, and ϕ for the polymer obtained in this work with the ϕ_{res} evaluated in the same manner as in the case of P-1. Every polymer shows the relation of $\phi_{dt} > \phi_{res}$. This means that incorporation of a DBT group in a polymer causes its n_D to be increased, while a residual group, rather, contributes to its decrease. The nearly identical ϕ_{res} value of P-11 as ϕ_{dt} indicates that the residual group of P-11 does not cause the polymer n_D to
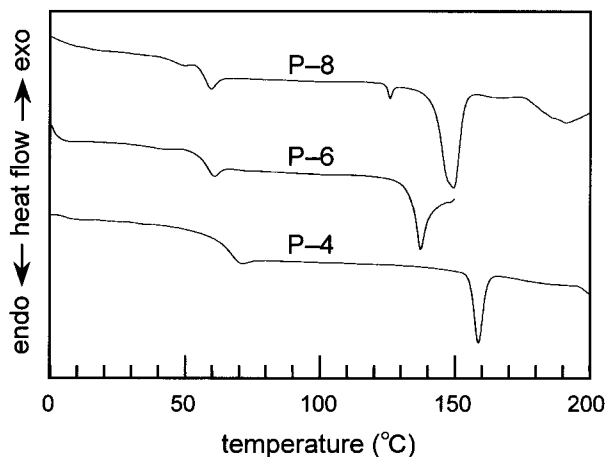
Figure 4 DSC curves of P-8, P-6, and P-4.

Figure 5 Plots of $[R]_{dt}$ versus V_{dt} and $[R]_p$ versus V_p, and relations among ϕ_{dt}, ϕ_p, and ϕ_{res}.

Table III   Calculation of $[R]_p$, V_p, and ϕ_p and Evaluation of ϕ_{res} for the Polymers Obtained

Polymer	$[R]_p$	V_p	ϕ_p	ϕ_{res}
P-1	89.0	245.1	0.363	0.329
P-2	92.3	257.1	0.359	0.322
P-3	97.1	273.4	0.355	0.318
P-4	—	—	—	—
P-5	105.5	303.3	0.348	0.310
P-6	—	—	—	—
P-7	115.2	337.8	0.341	0.304
P-8	—	—	—	—
P-9	114.7	310.0	0.370	0.358
P-10	107.2	290.1	0.370	0.356
P-11	147.7	391.9	0.377	0.374

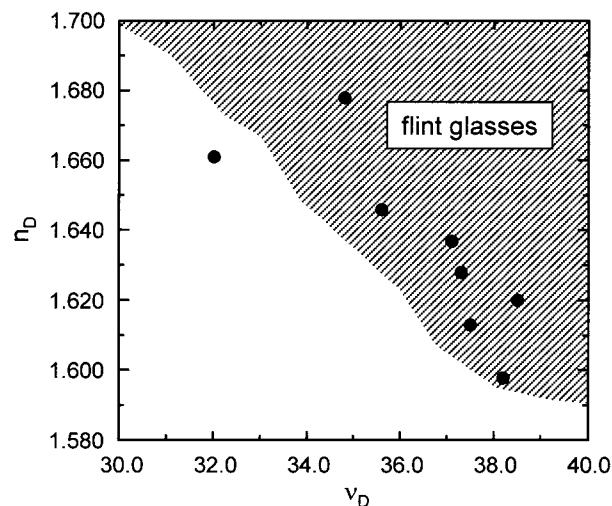decrease as much as does that of the poly(S-alkylcarbamate).

The value of ϕ_{dt} is comparable to the value of ϕ for the phenyl or bromophenyl group* that has been often incorporated into conventional optical polymers with high n_D due to its 61% content of sulfur atoms which have a relatively high atomic refraction. In the n_D versus ν_D diagram (Fig. 6), obviously, the refractive indices and Abbe's numbers of most polymers obtained in this work intrude into the region of those for inorganic optical glasses.[40] The DBT group contributes to increase not only n_D but also ν_D. P-10 shows the highest n_D among the poly(S-alkylcarbamate)s with degrading ν_D. The n_D of P-10 seems to be increased with the incorporation of both phenyl and DBT groups; however, the former group contributes to decreasing ν_D much more than the latter or the aliphatic groups incorporated into P-1–9. Dispersion, which normally decreases ν_D, is caused by electronic transitions at UV frequencies, one of the resonance effects.[41] The fact that benzene has an absorption band ($\lambda_{max} = 255$ nm, $\varepsilon_{max} = 219$)[42] can explain the decrease of ν_D of P-10, which includes a phenyl group and would have a similar absorption band. The DBT group has a structure that is characterized by the separation of every sulfur atom with at least two carbon atoms. We

could molecularly design an alicyclic group having a higher sulfur content than the DBT group by introducing disulfide or 1,3,5-trithiane. The n_D of a polymer possessing such an alicyclic group would increase; however, the ν_D of it would decrease due to the characteristic UV absorption assigned to disulfide or 1,3,5-trithiane.[43–45] As evidenced by the suppressed UV absorption spectrum of BMMD shown in Figure 7, the DBT group is properly designed to have an increased ϕ value without showing any strong UV absorption. Consequently, we propose that a polymer consisting of DBT and other non-UV light-absorbable groups can be used as a promising optical material with a high n_D and a high ν_D.

---

* The ϕ ($=[R]/V$) value estimated for the H—C—Ph and Br$_2$Ph—C(CH$_3$)$_2$—PhBr$_2$ are 0.353 ($=28.6/81.1$) and 0.384 ($=104.0/271.1$), respectively.

Figure 6 Refractive index (n_D) and Abbe's number (ν_D) of (dotted) the polymers obtained and (shadowed region) flint glasses.
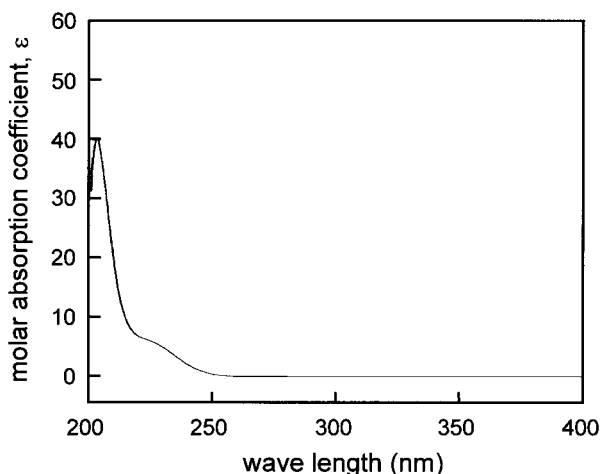
Figure 7   UV spectrum of BMMD.

CONCLUSIONS

Two different types of polymers comprising DBT groups were molecularly designed and synthesized to prepare an optically applicable polymer material with a high n_D and a high ν_D. They were obtained through the polyaddition and addition polymerization of BMMD and TBD, respectively. Compared with other conventional optical polymers, most of the polymers obtained in this work had relatively high n_D and ν_D values, which are almost the same as those of flint glasses. Their other properties, such as high transparency and high T_g, are advantageous for optical material. The ϕ value ($[R]/V$) is an index to evaluate the contribution of the DBT group and the residual group to the n_D of the polymers. The ϕ_{dt} is higher than that of phenyl or halogenated alkyl groups, which have often been incorporated into conventional, high-n_D polymers. The contribution of this group to a polymer does not cause degradation of its ν_D as the phenyl group does, which is believed to be due to the suppressed UV absorption spectrum of BMMD. Considering these advantages of the DBT group, we propose that the group, which has a possibly increased ϕ_{dt} with suppressed UV absorption, is a very useful building block for high n_D and ν_D polymers and that the polymers obtained using BMMD, TBD, and other non-UV-absorbable compounds appear to be promising for optical applications.

REFERENCES

1. J. M. Young, *Opt. World,* **18**(124), 10 (1989).
2. H. Dislich, *Angew. Chem. Int. Ed. Engl.,* **18,** 49 (1979).
3. C. Hofmann, *Feingerätetechnik (Berl.),* **39,** 124 (1990).
4. H. Dislich and A. Jacobsen, *Angew. Chem. Int. Ed. Engl.,* **12,** 439 (1973).
5. B. Wang, A. Gungor, A. B. Brennan, D. E. Rodrigues, J. E. McGrath, and G. L. Wilkes, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.,* **32,** 521 (1991).
6. R. A. Gaudiana and R. A. Minns, *J. Macromol. Sci.-Chem. A,* **28,** 831 (1991).
7. B. Wang, G. L. Wilkes, J. C. Hedrick, S. C. Liptak, and J. E. McGrath, *Macromolecules,* **24,** 3449 (1991).
8. B. Wang, G. L. Wilkes, C. D. Smith, and J. E. McGrath, *Polym. Commun.,* **32,** 400 (1991).
9. M. Weibel, W. Caseri, U. W. Suter, H. Kiess, and E. Wehrli, *Polym. Adv. Technol.,* **2,** 75 (1991).
10. S. S. Hardaker, S. Moghazy, C. Y. Cha, and R. J. Samuels, *J. Polym. Sci. Part B Polym. Phys.,* **31,** 1951 (1993).
11. R. A. Gaudiana, R. A. Minns, and H. G. Rogers, U.S. Pat. 5,132,430 (1992).
12. R. A. Minns and R. A. Gaudiana, *J. Mater. Sci.-Pure Appl. Chem. A,* **29,** 19 (1992).
13. L. Zimmermann, M. Weibel, W. Caseri, and U. W. Suter, *J. Mater. Res.,* **8,** 1742 (1993).
14. M. A. Olshavsky and H. R. Allcock, *Macromolecules,* **28,** 6188 (1995).
15. M. S. Misura and E. J. Sare, EP. Pat. 224,123 A2 (1987).
16. N. Amaya, K. Anan, Y. Murata, T. Mogami, Y. Sano, H. Ikebe, and R. Seita, U.S. Pat. 4,948,854 (1990).
17. K. Maeda, M. Yoshida, M. Funaki, and Y. Shirota, Jpn. Pat. 60,092,313 A2 (1985).
18. M. Tabata, N. Kushibiki, and Y. Yoshinaga, U.S. Pat. 5,082,358 (1992).
19. J. Kawashima and T. Mogami, Jpn. Pat. 61,245,101 A2 (1986).
20. K. Uchida, A. Nagata, and A. Iyoda, Jpn. Pat. 60,173,006 A2 (1985).
21. K. Ishikawa, Y. Hayakawa, and Y. Yoshida, Jpn. Pat. 60,124,607 A2 (1985).
22. H.-U. Simmrock, A. Mathy, L. Dominguez, W. H. Meyer, and G. Wegner, *Angew. Chem. Int. Ed. Engl. Adv. Mater.,* **28,** 1122 (1989).
23. S. Tabata, W. Yan, K. Yokota, N. Kushibiki, Y. Kuwae, and N. Kaneko, *Polym. Prepr. Jpn.,* **36,** 1163 (1987).
24. T. Matsuda, Y. Funae, M. Yoshida, T. Yamamoto, and N. Takatani, Jpn. Pat. 1,207,307 A2 (1989).
25. Y. Kanemura, M. Imai, K. Sasagawa, N. Kajimoto, and T. Nagata, U.S. Pat. 4,775,733 (1988).
26. Y. Kanemura, K. Sasagawa, M. Imai, and T. Suzuki, U.S. Pat. 5,087,758 (1992).
27. C. F. H. Allen and A. Bell, in *Organic Syntheses,*

Collective Vol. 3, E. C. Horning, Ed., Wiley, New York, 1955, p. 846.

28. A. A. R. Sayigh, N. Haven, and H. Ulrich, U.S. Pat. 3,410,887 (1968).

29. A. A. R. Sayigh, Brit. Pat. 1,086,782 (1967).

30. T. Leslak and K. Seyda, *J. Prakt. Chem.,* **321,** 161 (1979).

31. D. Emmons, U.S. Pat. 3,989,752 (1976).

32. W. A. Thaler and P. E. Butler, *J. Org. Chem.,* **34,** 3389 (1969).

33. N. W. Cusa and H. McCombie, *J. Chem. Soc.,* 767 (1937).

34. H. Ringsdorf and C. G. Overberger, *J. Polym. Sci.,* **61**(171), S11 (1962).

35. T. Otsu and H. Inoue, *J. Makromol. Sci.-Chem. A,* **4,** 35 (1970).

36. K. D. Von Gollmer, F. H. Müller, and H. Ringsdorf, *Makromol. Chem.,* **92,** 122 (1966).

37. D. W. Van Krevelen, in *Properties of Polymers,* 3rd ed., Elsevier, New York, 1990, Part II, Chap. 6, pp. 151–166.

38. Y. Ohtsuka, *Kobunshi High Polym. Jpn.,* **27,** 90 (1978).

39. Y. Ohtsuka, *Kobunshi High Polym. Jpn.,* **33,** 266 (1984).

40. F.-T. Lentes, in *The Properties of Optical Glasses,* H. Bach, and N. Neuroth, Eds., Springer, Berlin, 1995, Chap. 2, pp. 32–57.

41. D. Marcuse, in *Light Transmission Optics,* 2nd ed., Robert E. Krieger, FL, 1989, Chap. 12.2, pp. 482–485.

42. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, in *Spectrometric Identification of Organic Compounds,* 4th ed., Wiley, New York, 1981, Chap. 6-IV, p. 327.

43. A. Rosental and G. Oster, *J. Am. Chem. Soc.,* **83,** 4445 (1961).

44. C. C. Price and S. Oae, in *Sulfur Bonding,* Ronald Press, New York, 1962, Chap. 2, pp. 44–46.

45. S. Oae, in *Organic Sulfur Compounds, Synthetic Reaction, Ed.,* Kagakudojin, Kyoto, 1982, Chap. 3, p. 5, and Chap. 4, pp. 89–90.