Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Optical Polymer Having a High Refractive Index and High Abbe Number Prepared by Radical Polymerization Using 2,5-BiS(2-Thia-3-Butenyl)-1,4-Dithiane

Tsuyoshi Okubo[a]; Shigeo Kohmoto[a]; Makoto Yamamoto[a]
[a] Graduate School of Science and Technology, Chiba University, Chiba, Japan

To cite this Article Okubo, Tsuyoshi , Kohmoto, Shigeo and Yamamoto, Makoto(1998) 'Optical Polymer Having a High Refractive Index and High Abbe Number Prepared by Radical Polymerization Using 2,5-BiS(2-Thia-3-Butenyl)-1,4-Dithiane', Journal of Macromolecular Science, Part A, 35: 11, 1819 — 1834

To link to this Article: DOI: 10.1080/10601329808000555

URL: http://dx.doi.org/10.1080/10601329808000555

J.M.S.—PURE APPL. CHEM., A35(11), pp. 1819–1834 (1998)

OPTICAL POLYMER HAVING A HIGH REFRACTIVE INDEX AND HIGH ABBE NUMBER PREPARED BY RADICAL POLYMERIZATION USING 2,5-BIS(2-THIA-3-BUTENYL)-1,4-DITHIANE

Tsuyoshi Okubo,*† Shigeo Kohmoto, and Makoto Yamamoto
Graduate School of Science and Technology
Chiba University
1-33 Yayoi-cho
Inage-ku, Chiba 263, Japan

ABSTRACT

Novel poly(vinylsulfide)s were prepared by addition polymerization using 2,5-bis(2-thia-3-butenyl)-1,4-dithiane (TBD) with a radical initiator for an optical polymer having a high refractive index (n_D) and Abbe number (ν). Homopolymerization of TBD (72.9% conversion) and copolymerization with acrylonitrile or acrylates having nonpolar groups (50.4-81.3% conversion according to the comonomers used) in a limited composition range yielded hard and transparent polymers suitable for application in optics. The methacrylates used yielded no polymeric product as a result of the copolymerization. The obtained polymers had T_g, n_D and ν ranging between 41.0-124.0°C, 1.678-1.546 and 34.1-43.8, respectively, except that poly(TBD) did not exhibit T_g below 200°C, and it had the highest n_D. Most of the polymers have higher n_D and ν than those of other conventional optical polymers and moreover, their values are comparable to those of flint glasses. The copolymerizability of TBD and the group contribution to n_D and ν are discussed based on the *Q-e* scheme and on the Lorentz-Lorenz equation, respectively. This work shows that TBD serves as a useful material for the preparation of polymers having high n_D and ν along with a T_g of more than 100°C, and that the polymers thus obtained are promising optical materials.

---

† Present address: Advanced Technology Laboratory, R&D Center, Hoya Corporation, 3–3–1 Musashino, Akishima–shi, Tokyo 196–8510, Japan

www.dekker.com

INTRODUCTION

Materials used for optics are usually characterized in terms of transparency, refractive index (n_D) and Abbe number (ν), which describes the optical dispersion given by ν=(n_D – 1)/(nF – nC), where n_D, n_F and n_C are the refractive indices of the material at the wavelengths of the sodium D line (589.3nm), the hydrogen F (486.1nm) and C (656.3nm) lines, respectively [1, 2]. Polymers and inorganic glasses have a general correlation with respect to n_D and n such that the higher the n_D, the lower the ν, and vice versa [1, 3]. When a polymer and an inorganic glass, both of which have almost the same ν, are compared, the former usually has a lower n_D than the latter. [2-4] In recent studies of optical materials for geometrical optics, photonics and optical communications, various organic–based polymers having high n_D were prepared as alternatives to the inorganic glasses, however, their ν values were unclear or significantly decreased. [5-9] Particularly, a polymer having low ν below 30, as exemplified by a π–conjugated polymer, [6-8, 10] is not suitable for use in geometrical optics, however high its n_D is, because a low ν value indicates a substantial change in the refractive index over the visible spectrum. [2] Surprisingly, little information is available on polymers having both high n_D and high ν. Therefore, this work aims at the preparation of such a polymer for an optical material useful over a wide bandwidth.

Sulfur–containing polymers are presumed to have high n_D from the Lorentz–Lorenz equation [6, 11] due to high atomic refraction of sulfur and are expected to be promising for optical use. [12-14] For instance, poly(S–alkylcarbamate)s prepared by polyaddition between 2,5–bis(mercaptomethyl)–1,4–dithiane (BMMD) and isocyanates showed higher n_D and ν values than those of common optical polymers due to the incorporation of 1,4–dithiane ring and S–alkylcarbamate bond. [13, 14] It has been established that alkylvinylsulfide (RVS) polymerizes via addition polymerization or cyclopolymerization with a radical initiator, [15-21] and this polymerization is one of the preparative methods suitable for sulfur–containing polymers. Numerous studies regarding poly(RVS) have been devoted to polymerization kinetics, synthesis and properties, [15-23] but little attention is currently focused on its preparation and properties for optical polymers. To explore the potential optical properties of 1,4–dithiane comprising polymers not having a conjugated system, 2,5–bis(2–thia–3–butenyl)–1,4–dithiane (TBD) is the one of most useful monomers for their preparation.

This article deals with the synthesis and radical polymerization of TBD and the polymers prepared are described in terms of optical properties including transparency, n_D and n together with their thermomechanical properties. In addition, the contribution of the1,4-dithiane-2,5-bis(thiomethyl) (DBT) group to n_D and ν is discussed.

EXPERIMENTAL

General

^{1}H-NMR (270MHz) and ^{13}C-NMR (67.8MHz) spectra were recorded on a JEOL EX-270 in CDCl3 solutions using tetramethylsilane as an internal reference. IR spectra were recorded on a NICOLET 20 SXB. The nD and n were measured on an ATAGO Abbe refractometer 3T at 25°C. The thermomechanical property was analyzed using a RHEOLOGRAPH SOLID (Toyoseiki Co., Ltd.) at a heating rate of 2°C/min and a frequency of 10Hz. The UV spectrum was recorded on a UV-330 spectrophotometer (Hitachi, Ltd.). Molar refraction and molar volume referred to in the following discussion were estimated using a Synthia module running on an *Insight II* (version 4. 0. 0) program (Molecular Simulations Inc.).

Materials

The following commercially available comonomers were used: 2-hydroxyethyl methacrylate (HEMA), N,N-dimethylacrylamide (DMAA), N-vinyl-2-pyrrolidone (NVP), acrylic acid (AA), vinyl acetate (VA), acrylonitrile (AN), acrylate and methacrylate of cyclohexyl- (CHA and CHMA), isobornyl- (IBA and IBMA), methyl- (MA and MMA), 1,3-propanediyl- (PDA and PDMA), 1,6-hexanediyl- (HDA and HDMA) and 1,9-nonanediyl- (NDA and NDMA) esters, 1,8-diacryloxy-3,6-dioxaoctane (3EGA) and 1,26-diacryloxy-3,6,9,12,15,18,21,24-octaoxahexacosane (9EGA). They were passed through an inhibitor remover column (Aldrich Chemical Co., Inc.) to prepare monomers free of hydroquinone monomethyl ether. The first twelve comonomers were further purified by vacuum distillation. Polymerization initiator, 2,2'-azobis(2,4-dimethyl-valeronitrile) (ADVN) purchased, was used without further purification. All solvents were distilled prior to use.

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 minutes at -30°C, and the mixture was stirred continuously for 24 hours at that temperature. The reaction mixture was filtered, and the solvent was evaporated 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 ethyl alcohol (47 ml) was refluxed for an hour, 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 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, and the reaction mixture was stirred for an hour at that temperature. It was then 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 distilled in a vacuum (b.p. =121.5°C at 0.02 mmHg) to give colorless BMMD (7.76 g, 52.0% yield from allyldisulfide). Its nD and n values were 1.646 and 35.2, respectively. ^{1}H-NMR in $CDCl_3$: δ 1.62 (t, 2H), δ 2.88-3.14 (m, 10H). ^{13}C-NMR in $CDCl_3$: δ 28.4, δ 31.2, δ 42.2. IR (neat): 670, 731, 863, 895, 923, 1028, 1153, 1215, 1232, 1260, 1313, 1410, 2545, 2906 cm$_{-1}$. Anal. Calcd. for $C_6H_{12}S_4$ (212.40): C, 33.93%; H, 5.69%; S, 60.38%. Found: C, 33.75%; H, 5.75%; S, 59.99%.

Preparation of TBD

A mixture of sodium ethoxide, which was 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 minutes at room temperature. The mixture of the resulting sodium thiolate of BMMD and vinylbromide (182.71 g, 1.71 mol) was allowed to stand at 80°C for 24 hours in a sealed reaction vessel. After removal of most of the ethanol in the reaction mixture by vacuum evaporation, a benzene solution of the residue was washed with 2%–NaOH(aq.) and brine and then dried over anhydrous magnesium sulfate. After removal of benzene from the solution, the residue was distilled in a vacuum (b.p=134-136°C at 0.025 mmHg) to give colorless TBD (96.07 g, yield=51.0%). Its n_D and v values were 1.627 and 33.8, respectively. ^{1}H–NMR in $CDCl_3$: δ2.9-3.2 (m, 10H), δ5.19 (δ, 2H, J=16.5Hz), δ5.26 (d, 2H, J=9.9Hz), δ6.33 (dd, 2H, J_1=16.7Hz, J_2=10.0Hz). ^{13}C–NMR in $CDCl_3$: δ31.3, δ35.3, δ38.3, δ112.4, δ131.4. IR (neat): 3082, 2902, 1584, 1409, 954, 866, 698, 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%.

Homopolymerization and Copolymerization of TBD

A degassed homogeneous mixture of TBD and ADVN (1% to the weight of TBD) was heated in a sealed ampoule filled with argon from room temperature

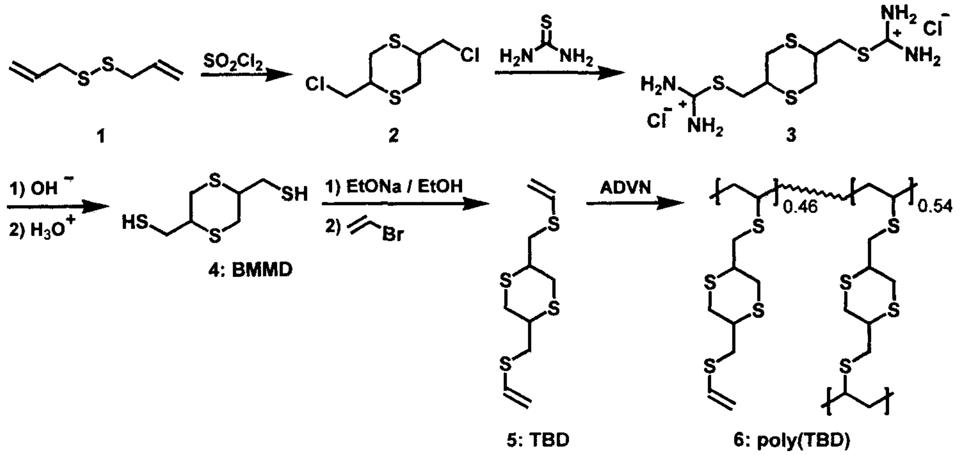


Figure 1. Preparation and Homopolymerization of TBD.

to 120°C within 21 hours to yield a transparent hard poly(TBD). IR (KBr pellet): 2897, 1584, 1409, 1310, 1250, 1206, 1159, 951, 871, 698 cm^{-1}. A similar procedure was applied to the mixtures of TBD and the comonomer, whose composition was increased by 10 mol%. The amount of ADVN added was 1% to the weight of the mixture.

RESULTS AND DISCUSSION

Preparation and Characterization of poly(TBD)

Figure 1 shows the preparation and polymerization of TBD. According to Thaler and Butler **2** was prepared, [24] but the reaction temperature was modified to –30°C to reduce polymeric by–product. Crude **2** was subjected to the next reaction without purification since only pure **3** precipitated, and its hydrolyzed product was almost pure **4** (BMMD). A S_N2 reaction of sodium thiolate of **4** with vinylbromide yielded 5 (TBD) in a moderate yield due to its consecutive conversion to an unidentified polymeric by–product. [25] The n_D and ν of TBD were relatively large compared with those of common organic compounds. TBD polymerized in bulk with a radical initiator such as ADVN to give a hard and transparent 6 (poly(TBD)). Figure 2 shows the IR spectra of TBD and its homopolymer, where characteristic signals observed at 1584 cm^{-1} and 698 cm^{-1} are assigned to those of vinylsulfide [21] and the methylene adjacent to sulfur atom, [26], respectively. The intensity of

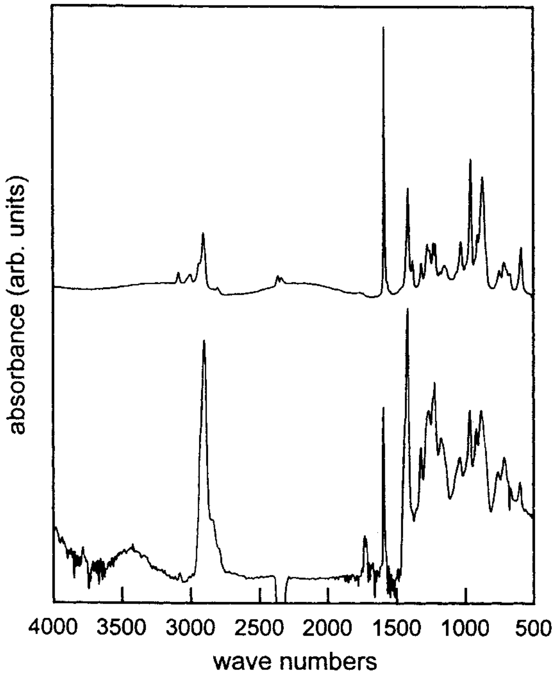


Figure 2. IR Spectra of TBD (Top) and poly(TBD) (Bottom).

the signal at 1584 cm^{-1} of poly(TBD) is weaker than that of TBD, indicating that the TBD polymerized at vinylsulfide as shown in Figure 1. [23] This mechanism is supported by a number of studies relating to the radical addition polymerization of vinylsulfide monomers. [15-20] Conversion of the vinylsulfide group determined by the following equation (Equation 1) was 72.9% under the polymerization conditions given in the experimental section:

$$\text{Conversion (\%)} = \{1 - (A_v{}^p A_m{}^m / A_m{}^p A_v{}^m)\} \times 100, \qquad (1)$$

where $A_v{}^m$ and $A_m{}^m$ are the absorbencies of signals at 1584 cm^{-1} and 698 cm^{-1} for TBD, respectively, and $A_v{}^p$ and $A_m{}^p$ are those at 1584 cm^{-1} and 698 cm^{-1} for poly(TBD), respectively. From poor polymerizability of bulky RVS reported, [17, 19] propagation of growing TBD radical is considered to be limited by certain steric hindrance of bulky 1,4-dithiane rings in a closely crosslinked structure formed. Free TBD remaining in poly(TBD) was determined to be 4.7 wt% by Soxhlet extraction

TABLE 1. Comonomer and its Composition Yielding a Transparent or Hard Copolymer

comonomers	comonomer in feed (mol%)	
	transparent	hard
HEMA, DMAA, NVP, AA	— (turbid)	10~40
AN	20~50	10~50
CHA, IBA	20~70	10~70
MA	10~40	10~90
PDA, HDA, NDA	50	10~90
3EGA	10~50	10~90
9EGA	20	10~50

The copolymerization with VA yielded turbid and gummy products, and with the methacrylates including CHMA, IBMA, MMA, PDMA, HDMA and NDMA yielded heterogeneous viscous oils over all the composition ranges used.

with acetone. From this result, it can be estimated that 95.3% of TBD polymerized and about 54% of TBD crosslinked as shown in Figure 1.

Copolymerization of TBD

The vinyl monomers given in the experimental section were copolymerized with TBD under the same condition as in the case of the homopolymerization of TBD. Table 1 lists the comonomers giving hard copolymers, and separately summarizes their composition ratios in monomer mixtures yielding transparent or hard copolymers. When the hard copolymer was not obtained, the products were gummy and most of TBD used remained. The copolymerization with VA yielded turbid and gummy products. With the methacrylates except HEMA no copolymers,

TABLE 2. Conversion of the Polymerization using TBD and the Properties of the Polymer Obtained

Polymer	monomers in feed (mol%)		conversion (%)	T_g (°C)	n_D	ν
P–1	TBD	(100)	72.9	—	1.678	34.8
P–2	TBD/AN	(80/20)	81.3	106.0	1.663	34.1
P–3	"	(50/50)	80.6	63.1	1.647	35.9
P–4	TBD/CHA	(80/20)	61.4	85.2	1.651	36.3
P–5	"	(50/50)	60.7	76.1	1.606	40.0
P–6	"	(30/70)	68.1	81.3	1.579	43.8
P–7	TBD/IBA	(80/20)	52.2	99.6	1.633	35.2
P–8	"	(50/50)	51.8	105.3	1.589	38.9
P–9	"	(30/70)	50.4	124.0	1.546	39.0
P–10	TBD/MA	(90/10)	79.0	96.0	1.669	35.4
P–11	"	(70/30)	79.9	98.1	1.655	35.3
P–12	"	(60/40)	78.6	81.3	1.635	36.9
P–13	TBD/PDA	(50/50)	66.7	98.1	1.605	40.1
P–14	TBD/HDA	(50/50)	64.3	95.0	1.590	41.3
P–15	TBD/NDA	(50/50)	50.4	87.1	1.577	41.0
P–16	TBD/3EGA	(90/10)	69.8	68.1	1.658	36.1
P–17	"	(70/30)	61.8	64.6	1.625	37.9
P–18	"	(50/50)	64.7	62.5	1.585	42.4
P–19	TBD/9EGA	(80/20)	63.4	41.0	1.596	39.8

not even gummy products, could be isolated, but the only products obtained were heterogeneous viscous oils, indicating formation of insoluble oligomers or polymers in very low conversion. The comonomers which yielded optically applicable copolymers from the given composition were AN and the acrylates. Many RVSs, ranging in their Q and e values of 0.3-0.5 and –1.1-1.7, respectively were reported to yield copolymers by radical addition polymerization with reactive conjugate vinyl monomers having various e values. [16, 18-21] According to the Alfrey and Price's Q–e scheme, TBD should copolymerize with the methacrylates, particularly with MMA (Q=0.74 and e=0.40). [27] These reported copolymerizabilities, however, were derived from kinetic studies of the copolymerization within approximately 10% conversion and are different from the observations in this study in that they were determined regardless of the feature of the resultant copolymers which is important for optical polymer preparation. It is considerable that the solubility of the growing radicals in the monomer mixture dominates their propagation rate and the features of the polymer, and currently, observed copolymerizabilities, which limited the type of comonomers, are interpreted in terms of the low solubility together with steric hindrance previously discussed.

The conversions were determined according to Equation 1, where instead of $A_m{}^m$ and $A_m{}^p$, the absorbencies of the signals assigned to the carbonyl or cyano group in the IR spectra of the monomer mixtures and the copolymers were used, respectively (Table 2). The amount of free TBD in the copolymers ranged from 2.5 to 6.8 wt%. Based on the ratio of crosslinking TBD estimated for them as discussed in the homopolymerization, the IBA or NDA copolymer is expected to be loosely crosslinked, but the copolymerization was sterically hindered by its bulky ester residue, resulting in the decreased conversion. The conversion of the copolymerization with MA or AN was higher than that with IBA or NDA. This indicates that in contrast to the copolymerization with bulky monomers, monomers of small molecule can copolymerize with TBD easily even in a closely crosslinked polymer network. Due to a flexible side chain, the copolymers of 3EGA and 9EGA have relatively low T_gs, which indicate that their matrices in propagation stage allow the monomers to diffuse more easily for the copolymerization than in those of poly(TBD) or the other copolymers. As a result of this diffusivity, their conversion increased.

Thermomechanical– and Optical Properties of poly(TBD) and TBD–based Copolymers

Table 2 gives the glass transition temperature (T_g), n_D and ν of the polymers obtained in this work. T_g was defined by the temperature at the maximum tangent δ of the thermomechanical analysis. The analysis revealed obvious T_g for all copolymers, whereas poly(TBD) did not show it below 200°C. Matrix motion of the polymer sequence incorporated by the polymerization of comonomers is attributed to their T_g. Comparison of the T_g of copolymers prepared using different comonomers reveals that their values depend on molar composition in feed and the rigidity of the side chain originating from the comonomer used. T_g increases with both or decreases with a small or flexible side chain, even when the molar composition increases. This relation follows the results of Hidalgo and Mijangos, [28] and indicates that, according to their interpretation, free monomers remaining in the copolymer hardly affect the T_g. The thermomechanical property with a higher T_g is advantageous for the application of a polymer material in optical tools because it barely deforms, even at elevated temperatures. Poly(MMA) is one of the best polymers for optical uses and is applied widely for fibers, lenses and filters. While its T_g (100°C) is a criterion for optical usefulness, [29] it is considered from the point of view of thermomechanical property that poly(TBD) and some TBD–based copolymers have suitable T_g for these applications.

The n_D values of the copolymers are lower than that of poly(TBD) due to the copolymerization of monomers whose homopolymers have lower n_D than that of poly(TBD) and have a linear correlation with the weight ratio of TBD in feed except those of IBA. As evidenced from these results, n_Ds of poly(TBD) and most TBD–based copolymers reach almost theoretical values determined from the monomer composition in their preparation, where the conversion varies from 60.7 to 81.3. [30] The n_Ds of IBA copolymers deviate to lower than those estimated from the linear relation due to the low conversion around 50%. It is expected that most copolymers having the same n_D value should have the same n value and vice versa. The n_D values of P–8 and P–14 are nearly equal, however, these copolymer show different n values, and when the copolymers having almost the same δ values are compared, a significant difference in n_D can be found between P–8 and P–9, P–14 and P–15 or P–7 and P–11. These unexpected results can be attributed to n degradation of P–79 or P–15. In their preparation, the conversion is around 50%. The absorption peak at 238nm (ε = 8704) in the UV spectrum of TBD (Figure 3) is identical to that of methylvinylsulfide and is assigned to vinylsulfide groups [16, 18]. Residual vinylsulfide groups in P–79 and P–15 obviously cause the UV absorption of these copolymers, resulting in the decrease of ν due to electronic transitions [31].

The n_D of a polymer can be estimated by the following equations (Equations 2 and 3), which are derived from the Lorentz-Lorenz equation, where

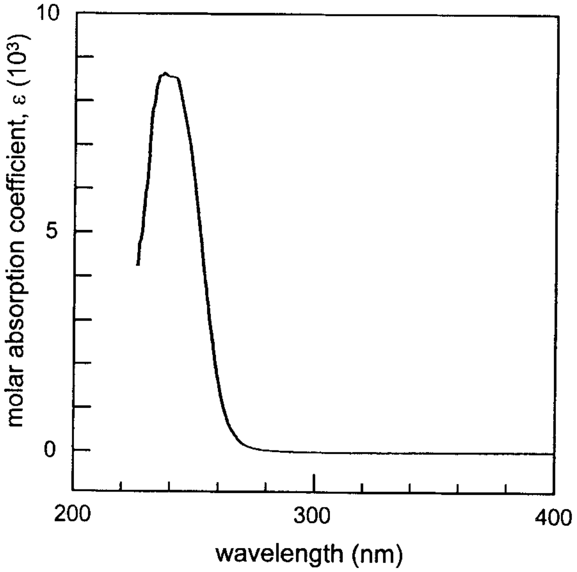


Figure 3. UV Spectrum of TBD (1,4–Dioxane Solution).

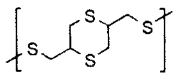
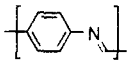
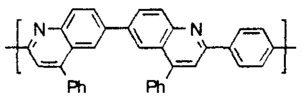
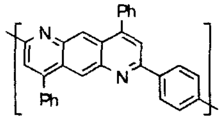
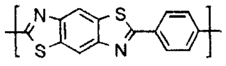
[R] and V are the molar refraction and the molar volume of the repeating unit, respectively [11].

$$\phi = [R]/V \qquad (2)$$

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

It is obvious that n_D depends on ϕ, but it is difficult to increase molar refraction in a reduced molar volume. Table 3 gives the structure of the repeating unit and ϕ of poly(DBT), whose repeating unit corresponds to the side chain of poly(TBD), along with those of p–conjugated polymers having high n_D. The ϕ of the π–conjugated polymers are calculated based on the n_D derived from the three-term Sellmeire equation, [6] and that of poly(DBT) is calculated from [R] and V [11]. The ϕ value of poly(DBT) proves to be comparable to those of polyquinoline and polyanthrazoline and is not significantly different from those of other π–conjugated polymers. This is due to the increased [R] of the DBT group having 61% content of sulfur in a simple structure, where electron delocalization is unlikely since all the sulfur atoms are separated from one another by at least two carbon atoms. As exemplified by poly(TBD) and most of the TBD–based copolymer, n of

TABLE 3. The ϕ Values of poly(DBT) and π–Conjugated Polymers

repeating unit	ϕ
	0.380 ([R] = 61.7 and V = 162.1)
	0.500
	0.407
	0.454
	0.472

poly(DBT) is expected to be considerably higher than those of π–conjugated polymers, which tend to show large optical dispersion [6, 8, 10]. To confirm the optical properties of poly(DBT), its synthesis was attempted by oxidation of BMMD, which polymerizes by the disulfide bond formed, but unfortunately the only polymeric product was crystalline white powder.

The n_D versus n diagram of all the polymers obtained in the present work is shown in Figure 4. Nevertheless exceptional results were observed for P–7, P–8, P–9 and P–15 due to degradation of their δ, obviously, the n_D and ϕ of most polymers intrude into those region of flint glasses [32]. As was confirmed by this finding and the ϕ–value–evaluation, the DBT group contributes to increase not only n_D, but also δ of these polymers. Consequently, an optical polymer having high n_D and high δ along with high T_g can be prepared more facilely from TBD than from conventional optical polymers or known monomers.

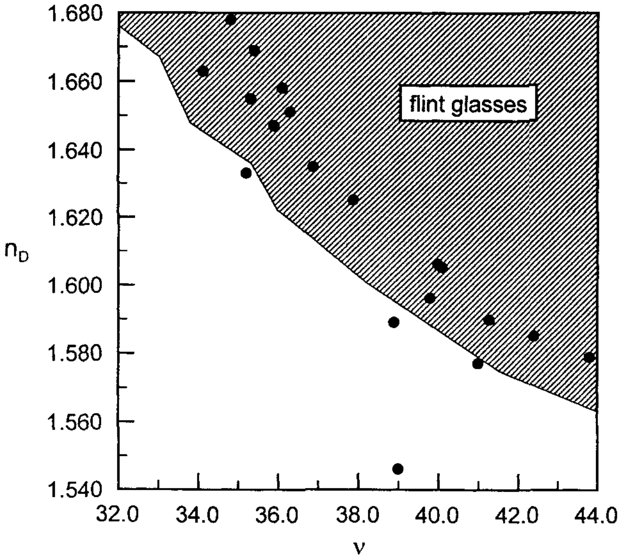


Figure 4. Refractive Indices (n_D) and Abbe Numbers (v) of poly(TBD) and the TBD–Based Copolymers. The Region for Flint Glasses is also Shown (Shadow).

CONCLUSION

In order to obtain an optical polymer material with high n_D and high δ, TBD–based polymers were prepared. Both in the homo– and copolymerization of TBD with ADVN hard and transparent polymers were given in 72.9% conversion for poly(TBD) and 50.4-81.3% conversion for the copolymers according to the comonomers used. The conversion should be more than 60% so that the residual vinylsulfide groups in the polymers obtained may not cause degradation of the optical properties. In the present work, suitable comonomers for the copolymerization proved to be AN and acrylates having nonpolar groups. However, their use in rich compositions or the use of other comonomers did not result in copolymers with sufficient properties for the application to optical materials. These copolymerizabilities could not be discussed systematically in terms of the *Q–e* scheme but are simply interpreted as that the growing radical having low solubility in the monomer composition no longer propagates in the bulk polymerization.

The obtained polymers characteristically possess the DBT group and their T_g, n_D and v values ranged between 41.0-124.0°C, 1.678-1.546 and 34.1-43.8, respectively. The DBT group contribution to increase n_D proves to be similar to that of polyquinoline or polyanthrazoline, a π–conjugated polymer having relatively high n_D, from the ϕ–value–evaluation based on the Lorentz-Lorenz equation. These ν values reveals that the DBT group does not cause significant degradation of ν unlike the π–conjugated polymers. Poly(TBD) and most of the TBD–based copolymers have higher n_D and n than those of other conventional optical polymers, and moreover, these values are comparable to those of flint glasses.

We conclude that TBD serves as a useful material for the preparation of polymers having high n_D and high n along with T_g of more than 100°C, and that the polymers obtained using TBD are promising optical materials.

REFERENCES

[1] H. Dislich, *Angew. Chem. Int. Ed. Engl., 18,* 49 (1979).

[2] M. Olshavsky and H. R. Allcock, *Macromolecules, 30,* 4179 (1997).

[3] C. Hofmann, *Feingerätetechnik, Berlin, 39*, 124 (1990).

[4] H. Dislich and A. Jacobsen, *Angew. Chem. Int. Ed. Engl., 12*, 439 (1973).

[5] T. Doi, A. Akimoto, A. Matsumoto, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed., 34*, 367 (1996); M. A. Olshavsky and H. R. Allcock, *Macromolecules, 28*, 6188 (1995); S. S. Hardaker, S. Moghazy, C. Y. Cha, and R. J. Samuels, *J. Polym. Sci., Polym. Phys. Ed., 31*, 1951 (1993); L. Zimmermann, M. Weibel, W. Caseri, and U. W. Suter, *J. Mater. Res., 8*, 1742 (1993); R. A. Minns and R. A. Gaudiana, *J. Mater. Sci.–Pure Appl. Chem., A29,* 19 (1992); 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); R. A. Gaudiana and R. A. Minns, *J. Macromol. Sci. Chem., A28*, 831 (1991); B. Wang, G. L. Wilkes, J. C. Hedrick, S. C. Liptak, and J. E. McGrath, *Macromolecules, 24,* 3449 (1991); B. Wang, G. L. Wilkes, C. D. Smith, and J. E. McGrath, *Polym. Commun., 32,* 400 (1991); M. Weibel, W. Caseri, U. W. Suter, H. Kiess, and E. Wehrli, *Polym. Adv. Technol., 2*, 75 (1991); H-U. Simmrock, A. Mathy, L. Dominguez, W. H. Meyer, and G. Wegner, *Angew. Chem. Int. Ed. Engl. Adv. Mater., 28*, 1122 (1989).

[6] C.–Jen Yang and S. A. Jenekhe, Chem. Mater., 7, 1276 (1995).

[7] A. K. Agrawal and S. A. Jenekhe, Chem. Mater., 4, 95 (1992).

[8] J. A. Osaheni and S. A. Jenekhe, *Chem. Mater.*, *7*, 672 (1995); C.–Jen Yang and S. A. Jenekhe, *Chem. Mater.*, *6,* 196 (1994); W. –Chang Chen, S. A. Jenekhe, J. S. Meth, and H. Vanherzeele, *J. Polym. Sci., Polym. Phys. Ed.*, *32*, 195 (1994).

[9] T. Matsuda, Y. Fanae, M. Yoshida, T. Yamamoto, and T. Takaya, *J. Appl. Polym. Sci.*, *65*, 2247 (1997); L. L. Beecroft and C. K. Ober, *J. Macromol. Sci.–Pure Appl. Chem.*, *A34*, 573 (1997).

[10] T. Fukuda, T. Kanbara, T. Yamamoto, S. Nakao, K. Ishikawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, *35*, 761 (1996).

[11] N. Tanio and Y. Koike, *Jpn. J. Appl. Phys.*, *36*, 743 (1997).

[12] S. Tabata, W. Yan, K. Yokota, N. Kushibiki, Y. Kuwae, and N. Kaneko, *Polym. Prepr. Jpn.*, *36*, 1163 (1987).

[13] T. Okubo and A. J. Ikushima, in *Frontiers of Polymers and Advanced Materials*, P. N. Prasad, Ed., Plenum, New York, 1994, p. 187.

[14] T. Okubo and R. Okada, *Proceedings of the Polyurethanes World Congress 1993,* The SPI/ISOPA, Canada, October 1993, p. 527.

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

[16] T. Otsu and H. Inoue, *J. Macromol. Sci.–Chem.*, *A4*, 35 (1970).

[17] H. Kawa, S. N. Partovi, B. J. Ziegler, and R. J. Lagow, *J. Polym. Sci., Polym. Lett. Ed.*, *28*, 297 (1990).

[18] W. Tagaki, T. Tada, R. Nomura, and S. Oae, *Bull. Chem. Soc. Jpn.*, *41*, 1696 (1968).

[19] T. Otsu, K. Tsuda, T. Fukumizu, and H. Inoue, *Nihon Kagaku Zasshi, 89*, 892 (1968).

[20] E. A. Mash, H.–Gert Korth, and S. M. DeMoss, *Tetrahedron, 53*, 15297 (1997); S. V. Amosova, L. I. Antsiferova, L. P. Shaulina, I. P. Golentovskaya, V. V. Nosyreva, O. V. Akhramovich, O. T. Kim–Pi–i, A. V. Tarasov, and Yu. A. Moskvichev, *Russ. J. Appl. Chem.*, *69*, 1156 (1996); S. Iwatsuki, M. Kubo, M. Wakita, Y. Matsui, and H. Kanoh, *Macromolecules, 24*, 5009 (1991); T. Otsu and H. Onishi, *Chemistry, 31*, 76 (1976); T. Otsu and H. Inoue, *Makromol. Chem.*, *128,* 31 (1969).

[21] H. Ringsdorf and C. G. Overberger, *J. Polym. Sci.*, *61*, S11 (1962).

[22] C. Mijangos and D. López, *Macromolecules, 28,* 1364 (1995); E. Saiz, C. Mijangos, E. Riande, and D. López, *Macromolecules, 27*, 5716 (1994); S. V. Amosova, L. I. Antsiferova, O. V. Akhramovich, V. V. Nosyreva, A.

V. Tarasov, Y. A. Moskvichev, I. P. Golentovskaya, and L. P. Shaulina, *Chem. Sustainable Dev.*, *2*, 385 (1994).

[23] S. V. Amosova, L. I. Antsiferova, V. I. Gostevskaya, and G. M. Gavrilova, *Chem. Sustainable Dev.*, *4*, 9 (1996).

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

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

[26] H. Sugeta, A. Go, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, *46*, 3407 (1973).

[27] H. Yasuda and V. Stannett, in *Polymer Handbook*, 2nd edition, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, III-392.

[28] M. Hidalgo and C. Mijangos, *J. Polym. Sci., Polym. Chem. Ed.*, *33*, 2941 (1995); C. Mijangos and M. Hidalgo, *Polymer*, *35*, 348 (1994).

[29] H. Kawai, *Jpn. J. Optics*, *24*, 69 (1995).

[30] L. Bohn, in *Polymer Handbook*, 2nd edition, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, III-241.

[31] D. Marcuse, in *Light Transmission Optics*, 2nd edition, Robert E. Krieger, Florida, 1989, pp. 482-485.

[32] F. -T. Lentes, in *The Properties of Optical Glasses,* H. Bach and N. Neurothedited, Eds., Springer, Berlin, 1995, pp. 32-57.

Received February 28, 1998
Revision received May 20, 1998