JOURNAL OF MATERIALS SCIENCE **34** (1999) 337–347

Preparation, characterization, and optical properties of disulfide-comprising oligo[2,5-bis(thiomethyl)-1,4-dithiane] and its poly[S-alkylcarbamate]

TSUYOSHI OKUBO*, SHIGEO KOHMOTO, MAKOTO YAMAMOTO
Graduate School of Science and Technology, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan

TAKAYUKI NAKAHIRA
Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan
E-mail: tokubo@rdc.hoya.co.jp

Novel poly[S-alkylcarbamate]s were prepared by polyaddition of oligo [2,5-bis(thiomethyl)-1,4-dithiane] (oligo[BMMD]) with isocyanate for optical polymers having high refractive indices (n_D) and Abbe's numbers (ν_D). Oxidation of 2,5-bis(mercaptomethyl)-1,4-dithiane (BMMD) with ferric chloride or methylsulfoxide gave oligo[BMMD] in a mixture of *n*-mers (typically $n = 1$–6) by disulfide-forming propagation. The use of the former oxidant giving mainly BMMD dimer appeared to be preferable for the subsequent preparation of transparent poly[S-alkylcarbamate]. With 1,3-bis(isocyanatomethyl)cyclohexane, 1,6-diisocyanatohexane, or 1,3,5-tris(isocyanatomethyl)cyclohexane, $n_D : \nu_D$ values of poly[S-alkylcarbamate]s ranging from 1.609:38.0 to 1.659:35.6 were comparable to those of flint glasses. Copoly[S-alkylcarbamate]s were prepared using 2-mercaptoethylsulfide or 2-mercaptoethylether for modification of n_D and ν_D. Contribution of the disulfide bond and the 1,4-dithiane ring in oligo[BMMD] to increase n_D is discussed in terms of molar refraction. Suppressed UV absorption of the polymer, which caused high ν_D, was attributed to the *trans-gauche-trans* conformation around the disulfide bond. This work shows that oligo[BMMD] serves as a useful material for the preparation of polymers having high n_D and high ν_D and that poly[S-alkylcarbamate]s thus obtained are promising optical materials. *© 1999 Kluwer Academic Publishers*

1. Introduction

Organic polymer materials have been widely used for optical applications as substitutes for inorganic glasses, while taking advantage of their relative ease of processing, better impact resistance, and lightness [1, 2]. In practice, polymethylmethacrylate, CR-39, and polycarbonates have been used as conventional optical polymer materials [3]. Optical materials are usually characterized by such properties as transparency, refractive index (n_D), and Abbe's number (ν_D). The latter describes optical dispersion 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 sodium D line (589.3 nm), the hydrogen F (486.1 nm) and C (656.3 nm) lines, respectively [1]. The n_D and ν_D of polymers and inorganic glasses are generally related: the higher the n_D the lower the ν_D, and vice versa [1, 4]. When a polymer and an inorganic glass of almost the same ν_D are compared, the former usually has a lower n_D than the latter [4, 5]. This has prevented the use of many polymers for critical optical applications and preference has been given to high n_D inorganic glasses [1, 2, 4]. This work aims at the synthesis of a polymer possessing n_D and ν_D that are comparable to or higher than those of inorganic glasses.

Organic-based polymers with an improved n_D have appeared in the literature, but some of their ν_D values actually degraded or were simply not discussed [2, 6–15]. Polyelectrolytes that are composed of specific organic polymer chains and inorganic moieties showed remarkably high n_D and ν_D values due to the presence of the heavier latter components [16]. Polymers incorporating such structures as aromatic groups [17], halogenated aromatic groups [18], and

---

[*] *Present address*: Advanced Technology Laboratory, R&D Center, Hoya Corporation, 3-3-1 Musashino, Akishima-shi, Tokyo 196, Japan.

alicyclic condensed rings [19] only showed moderate n_D and ν_D. Sulfur-containing polymers having such groups as sulfides [20], S-alkyl esters [21], and S-alkylcarbamates [22] successfully improved n_D and ν_D. For the preparation of the latter polymers, which recently emerged as one of the most useful optical polymers, many thiols such as pentaerythritoltetrakis(mercaptopropionate) [23], 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane [24] or 2,5-bis(mercaptomethyl)-1,4-dithiane (BMMD) [25] were synthesized and applied. In a molecular design of a high n_D polymer, the Lorentz–Lorenz equation predicts that the n_D of a polymer should increase with increasing sulfur content in a reduced molar volume [26]. A disulfide–comprising polymer is easily designed based on this prediction, and, in fact, such polymers were synthesized for optical uses [27–30]. However, ν_D values of these polymers were rather degraded. This is possibly caused by the incorporation of the disulfide having characteristic UV absorption at 240–300 nm with molar absorption coefficient (ε) ranging 100–600 [31, 32]. We could not currently find a study on the relation between the structure and the ν_D in the disulfide-comprising polymers. The problem is therefore to elucidate the structure of such polymers so as to obtain a polymer having both high n_D and high ν_D. Bi-functional BMMD, which proved to be a useful material for the preparation of poly[S-alkylcarbamate] having high n_D and high ν_D [25, 33], is expected to give soluble linear oligo[BMMD], whose chains propagated with disulfide formation by oxidation at the mercapto groups. The resulting oligo[BMMD] is also expected to give a disulfide-comprising poly[S-alkylcarbamate] by polyaddition of their terminal mercapto groups with isocyanates. Based on this idea, we investigated the optimal preparation condition of oligo[BMMD] to obtain an optically applicable poly[S-alkylcarbamate]. In addition, this paper describes the characterization, $n_D : \nu_D$ of oligo[BMMD] and poly[S-alkylcarbamate] and discusses the ν_D of the poly[S-alkylcarbamete] obtained with regard to the UV absorption and the conformation around the disulfide bond.

2. Experimental

2.1. Measurement

^{1}H-NMR (nuclear magnetic resonance) (270 MHz) and ^{13}C-NMR (67.8 MHz) spectra were recorded on a JEOL EX-270 in $CDCl_3$ or $(CD_3)_2SO$ solutions using tetramethylsilane as an internal reference. The amount of the mercapto group in a oligo[BMMD] (A_{SH}) was determined from a signal ratio in the ^{1}H-NMR spectrum of a mixture of oligo[BMMD] and 1,1,2,2-tetrachloroethane (TCE) by the following equation: A_{SH} (mol) $= 1.2 \times 10^{-2} \times (W_{oligo[BMMD]} \times W_{TCE} / W'_{oligo[BMMD]}) \times (I_{oligo[BMMD]}/I_{TCE})$, where $W_{oligo[BMMD]}$ and W_{TCE} are the weight (g) of oligo[BMMD] and that of TCE, respectively, $I_{oligo[BMMD]}$ and I_{TCE} are the signal intensities of the mercapto group of the oligo[BMMD] and that of the methylene group of TCE, respectively, and $W'_{oligo[BMMD]}$ is the weight (g) of the oligo[BMMD] used in the NMR measurement. IR spectra were recorded on a NICOLET 20 SXB. Raman spectra were recorded on a JASCO NR-1000 Laser Raman spectrophotometer with an Ar-ion laser (514.5 nm). Gas chromatographmass spectra were recorded on a JEOL JMS-DX303 (column: 2% silicone SE-30, Chromosorb W, 1 m-length, He flow rate: 40 ml min^{-1}, injection temperature: 280 °C, column temperature: 70–280 °C (16 °C min^{-1})) at an ionization energy of 70 eV. The molecular weight distributions were observed by gel permeation chromatography (GPC) on a TOSOH GPC system (column: TSKgel G2000HXL for the oligo[BMMD] or G4000HXL for the polymers, detector: UV at 254 nm, eluent: tetrahydrofuran (1 ml min^{-1}). Average molecular weights of polymers were determined on the basis of a standard polystyrene calibration. The thermomechanical property was analyzed using a RHEOLOGRAPH SOLID (Toyoseiki Co., Ltd.) at a heating rate of 2 °C min^{-1} and a frequency of 10 Hz. Refractive index (n_D) and Abbe's number (ν_D) were measured on an ATAGO Abbe refractometer 3T. Ultraviolet visible light spectra were recorded on a HITACHI UV-330 spectrophotometer. An ether (for BMMD) or a dioxane (for oligo [BMMD]) solution, or a polished polymer disk of 50 μm thickness were employed for UV measurements.

2.2. Materials

1,3-bis(isocyanatomethyl)cyclohexane (BIC) and 1,3,5-tris(isocyanatomethyl)cyclohexane (TIC) were purchased from Takeda Chemical Industries, Ltd and 1,3-bis(isocyanatomethyl)benzene (BIB) from Tokyo Kasei Kogyo Co. Ltd and were used without further purification. 1,6-diisocyanatohexane (DIH) was purchased from Aldrich Chemical Company, Inc. and distilled under reduced pressure (92 °C at 2 mm Hg) prior to use. All other reagents, including 2-mercaptoethylsufide (MES) and 2-mercaptoethylether (MEE), were used without purification. All the solvents were distilled prior to use.

2.3. 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, and the mixture was stirred continuously for 24 h 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 vacuo* 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 subjected to vacuum distillation (bp = 121.5 °C at 0.02 mm Hg) to give colorless BMMD (7.76 g, 52.0% yield 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): 670, 731, 863, 895, 923, 1028, 1153, 1215, 1232, 1260, 1313, 1410, 2545, 2906 cm^{-1}. Raman shift (neat): 252, 316, 355, 383, 631, 702, 726, 790, 916, 1265, 1407, 2553 cm^{-1}. Analysis Calculated 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%.

2.4. Preparation of oligo [BMMD]

To a vigorously stirred solution of BMMD (92.83 g, 0.437 mol) in methyl alcohol (438 ml), a solution of ferric chloride hexahydrate (118.13 g, 0.437 mol) in methyl alcohol (305 ml) was added rapidly at room temperature, and then the reaction mixture was stirred for 10 min to 8 h at that temperature. Oil separated was extracted with chloroform (400 ml). The extract was washed with water (400 ml) six times and dried over anhydrous magnesium sulfate. The chloroform was removed at a reduced pressure, and the residue was dried at 150 °C for 1 h *in vacuo* to give colorless and viscous oligo[BMMD] weighing more than 90% of the BMMD used. The following data are for oligo[BMMD] obtained by 8 h reaction. ^{1}H-NMR in $CDCl_3$: δ1.61–1.68 (m, 1H), δ2.88–3.31 (m, 10H). ^{13}C-NMR in $CDCl_3$: δ28.5, δ31.2, δ37.9, δ38.4, δ42.3. IR (neat): 907, 1152, 1209, 1229, 1259, 1311, 1408, 2546, 2902 cm^{-1}. Raman shift (neat): 323, 361, 387, 505, 550, 637, 716, 792, 1266, 1403 cm^{-1}.

A solution of BMMD (22.93 g, 0.108 mol) in DMSO (33.74 g, 0.432 mol) also gave oligo[BMMD] by heating at 80 °C with stirring under Ar for 0.5–4.0 h. After preparation in the same manner as in the case of Fe^{3+} catalytic oxidation, oligo[BMMD]s weighing at least 20 g were obtained. Their spectral data were almost the same as those of the oligo[BMMD]s obtained from Fe^{3+} catalytic oxidation.

2.5. Co-oligomerization of BMMD with MES or MEE

To a vigorously stirred solution of BMMD (19.17 g, 90.2 mmol) and MES (3.30 g, 22.6 mmol) in ethyl alcohol (56 ml), a solution of ferric chloride hexahydrate (15.24 g, 56.4 mmol) in ethyl alcohol (50 ml) was added rapidly at room temperature, and then the reaction mixture was stirred for 1.5 h at that temperature. It was prepared in the same manner as in the case of oligo[BMMD] preparation to give oligo[BMMD-*co*-MES] (7.24 g). ^{1}H-NMR in $CDCl_3$: δ1.57–1.67 (t, 13H), δ1.70–1.81 (m, 1H), δ2.71–2.86 (m, 18H), δ2.86–3.28 (m, 100H). ^{13}C-NMR in $CDCl_3$: δ24.8, δ28.2, δ31.0, δ36.1, δ38.3, δ42.0. Raman shift (neat): 361, 385, 505, 548, 638, 687, 744, 1273, 1405 cm^{-1}.

Oligo[BMMD-*co*-MEE] was prepared under similar reaction conditions using MEE (3.12 g, 22.6 mmol) instead of MES. ^{1}H-NMR in $CDCl_3$: δ1.56–1.68 (m, 8H), δ2.82–3.33 (m, 100H), δ3.75 (t, 9H). ^{13}C-NMR in $CDCl_3$: δ31.2, δ38.4, δ38.6, δ41.8, δ42.3, δ69.1. Raman shift (neat): 318, 359, 384, 499, 545, 632, 713, 788, 1261, 1397 cm^{-1}.

2.6. Fractionation of oligo[BMMD]

Oligo[BMMD] prepared from the Fe^{3+} catalytic oxidation of BMMD for 30 min was fractionated by GPC (column: G2000H, mobile phase: $CHCl_3$ (6 ml min^{-1}), sample concentration: 10 mg ml^{-1}, detector: UV 254 nm), and the last three fractions were collected separately. The last fraction gave the GC-MS (EI) data indicating that it is the monomer (BMMD): m/z (relative peak intensity) 212 (45.3 $[M]^+$), 178 (20.6), 165 (8.6), 145 (7.8), 131 (70.7), 119 (15.2), 105 (30.7), 91 (14.4), 73 (100), 59 (20.9). ^{1}H-NMR showed signals of the same chemical shifts and intensities as those of pure BMMD. The second fraction from the last was the dimer; GC-MS (EI): m/z (relative peak intensity) 211 (62.8 $[M/2]^+$), 177 (21.7), 165 (13.6), 145 (10.1), 131 (85.6), 105 (29.8), 73 (100). ^{1}H-NMR in $CDCl_3$: δ1.58 (t, 1H), δ2.80–3.27 (m, 10H). The third fraction from the last was the trimer; GC-MS (EI); m/z (relative peak intensity) 209 (100 $[(M/3)–2]^+$), 164 (18.2), 149 (53.9), 138 (22.6), 105 (25.2), 85 (28.2), 73 (63.6). ^{1}H-NMR in $CDCl_3$: δ1.61 (t, 1H), δ2.71–3.46 (m, 15H).

2.7. Polyaddition of oligo[BMMD] and isocyanates

A homogeneous mixture of oligo[BMMD] (4.00 g, 20.2 mmol of thiol group) prepared from the Fe^{3+} catalytic oxidation of BMMD for 30 min, BIC (1.96 g, 20.2 mmol of isocyanate group), and di-n-butyl tin dilaurate (3.4 mg, 11.0 μmol) was poured into a glass ampoule, and degassed under vacuum. The ampoule was filled with argon, sealed, and heated gradually from room temperature to 120 °C in 21 h to give poly[oligo(BMMD)-BIC]. ^{1}H-NMR in $(CD_3)_2SO$: δ0.37–1.85 (m, 10H), δ2.84–3.44 (m, 22H), δ8.19 (bs, 2H). ^{13}C-NMR in $(CD_3)_2SO$: δ20.1, δ24.9, δ28.8, δ30.8, δ32.8, δ34.6, δ37.4, δ41.5, δ44.8, δ165.3. IR (KBr pellet): 1197, 1397, 1502, 1655, 2910, 3305 cm^{-1}. Raman shift (bulk): 368, 390, 480, 507, 557, 626, 641, 686, 720, 794, 1143, 1213, 1271, 1409, 1441, 1673 cm^{-1}. Similarly, other poly[S-alkylcarbamate]s were prepared using BIB, DIH, or TIC instead of BIC. Oligo[BMMD-*co*-MES (or MEE)], instead of oligo[BMMD], was also used in the preparation of copoly[S-alkylcarbamate]s of TIC. Codithiol such as MES or MEE was copolymerized into poly[S-alkylcarbamate] of TIC by adding it to the monomer mixture so that the total amount of mercapto groups (oligo[BMMD]+codithiol) should be equimolar to the isocyanate groups used.

Poly[oligo(BMMD)-BIB]; ^{1}H-NMR in (CD$_3$)$_2$SO: δ2.86–3.71 (m, 18H), δ4.30 (d, 4H), δ7.08–7.37 (m, 4H), δ8.76 (bs, 2H). ^{13}C-NMR in (CD$_3$)$_2$SO: δ30.7, δ32.7, δ37.6, δ41.4, δ44.0, δ125.9, δ128.3, δ139.0, δ165.2. IR (KBr pellet): 1191, 1404, 1490, 1658, 2255 (remaining NCO), 2902, 3027, 3299 cm^{-1}. Raman shift (bulk): 364, 387, 504, 553, 623, 637, 743, 997, 1200, 1239, 1403, 1605 cm^{-1}.

Poly[oligo(BMMD)-HDI]; ^{1}H-NMR in (CD$_3$)$_2$SO: δ1.18–1.50 (m, 8H), δ2.87–3.33 (m, 22H), δ8.17 (bs, 2H). ^{13}C-NMR in (CD$_3$)$_2$SO: δ25.8, δ28.9, δ30.7, δ32.6, δ37.5, δ41.1, δ41.4, δ164.6. IR (KBr pellet): 1205, 1404, 1503, 1651, 2855, 2929, 3315 cm^{-1}. Raman shift (bulk): 361, 385, 472, 507, 551, 620, 638, 686, 720, 744, 1202, 1269, 1305, 1402, 1432, 1641 cm^{-1}.

Poly[oligo(BMMD)-TIC]; IR (KBr pellet): 1196, 1407, 1505, 1659, 2257 (remaining NCO), 2911, 3317 cm^{-1}. Raman shift (bulk): 363, 387, 475, 502, 550, 620, 635, 716, 1131, 1202, 1264, 1403, 1438, 1658 cm^{-1}.

Copoly[oligo(BMMD-*co*-MES)-TIC]; IR (KBr pellet): 1196, 1407, 1502, 1660, 2260 (remaining NCO), 2913, 3303 cm^{-1}. Raman shift (bulk): 364, 388, 472, 507, 554, 637, 714, 746, 1142, 1203, 1266, 1403, 1439, 1658 cm^{-1}. Copoly[oligo(BMMD-*co*-MEE)-TIC]; IR (KBr pellet): 1199, 1407, 1504, 1660, 2260 (remaining NCO), 2913, 3310 cm^{-1}. Raman shift (bulk): 364, 385, 477, 502, 551, 620, 637, 716, 1139, 1202, 1261, 1400, 1432, 1665 cm^{-1}. Copoly[oligo(BMMD)-MES-TIC]; IR (KBr pellet): 1196, 1408, 1505, 1659, 2260 (remaining NCO), 2914, 3308 cm^{-1}. Raman shift (bulk): 363, 387, 472, 505, 551, 637, 752, 1134, 1205, 1267, 1403, 1436, 1645 cm^{-1}.

Copoly[oligo(BMMD)-MEE-TIC]; IR (KBr pellet): 1099, 1198, 1407, 1504, 1659, 2260 (remaining NCO), 2914, 3311 cm^{-1}. Raman shift (bulk): 363, 387, 472, 502, 550, 620, 634, 716, 1128, 1202, 1264, 1397, 1433, 1640 cm^{-1}.

3. Results and discussion

3.1. Preparation and characterization of oligo[BMMD]

BMMD, which has been prepared previously [25], was oxidized at its thiol to oligomerize by disulfide formation (Fig. 1). A mild oxidant, ferric chloride or DMSO, was employed to prevent an undesired oxidation of the sulfur atoms on the 1,4-dithiane ring or of the disulfide bond formed. IR spectrum of the oligo[BMMD] was similar to that of BMMB (Fig. 2). No apparent signals assignable to sulfoxides or sulfones were observed. ^{1}H-NMR of the oligo[BMMD] was also similar to that of BMMD except that the ratio of signals for thiols to those for the other protons decreased (Fig. 2). This indicates that BMMD oligomerized with dehydrogenation of its thiols. Formation of disulfide bonds was exclusively determined by signals at 505 cm^{-1} and 500 cm^{-1} in the Raman spectrum of oligo[BMMD]. These spectral data, together with ^{13}C-NMR, support the structural formula of oligo[BMMD] shown in Fig. 1. The GPC chart (Fig. 3) of oligo[BMMD] prepared by Fe^{3+} catalytic oxidation of BMMD for 30 min shows five fractions. Mass and ^{1}H-NMR spectra of the last three

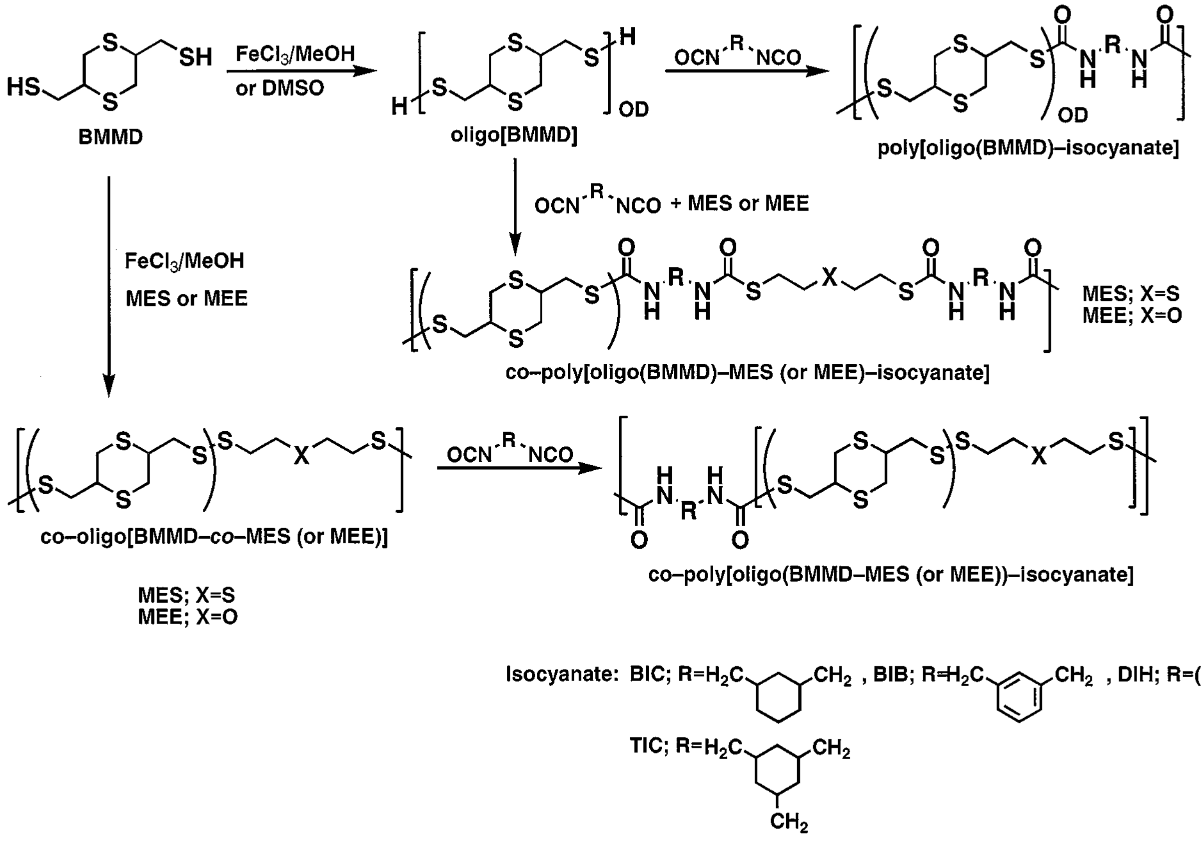

Figure 1 Preparation of oligo[BMMD] and its poly[S-alkylcarbamate]s and their codithiol modifications.

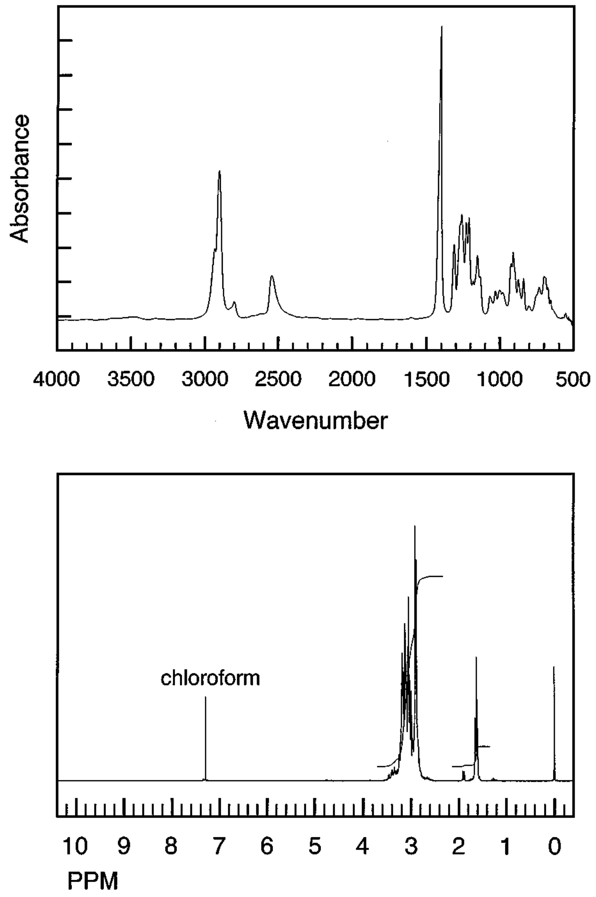

Figure 2 IR (top) and ^{1}H-NMR (bottom) spectra of oligo[BMMD]. The sample was obtained by Fe^{3+} catalytic oxidation of BMMD for 8 h.

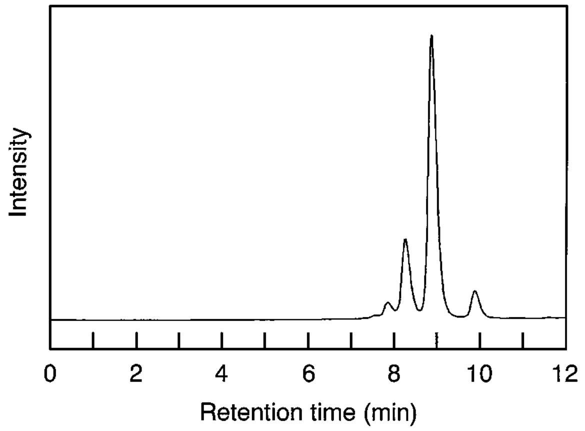

Figure 3 Gel permeation chromatogram of oligo[BMMD]. The sample was obtained by Fe^{3+} catalytic oxidation of BMMD for 30 min.

TABLE I The distribution of oligomers in oligo[BMMD] prepared in different oxidation conditions

Time (h)	Content* (%)				
	Monomer	Dimer	Trimer	Tetramer	>Pentamer
Fe^{3+} catalytic oxidation (molar ratio of Fe^{3+}/BMMD = 1.0)					
0.1	39.4	48.4	10.3	1.9	—
0.5	6.8	68.4	20.1	4.3	0.4
2.0	4.9	62.0	24.2	6.9	2.0
4.0	3.6	58.6	26.5	8.5	2.8
8.0	3.2	50.2	28.1	12.2	6.3
DMSO oxidation (molar ratio of DMSO/BMMD = 4.0)					
0.5	23.5	50.3	18.6	5.5	2.1
1.0	12.8	41.5	25.1	11.3	9.3
1.5	8.9	35.8	27.2	14.9	13.2
2.0	6.5	29.9	26.4	17.7	19.5
4.0	4.5	23.1	24.7	17.9	29.8
DMSO oxidation (molar ratio of DMSO/BMMD = 1.0)					
0.5	30.4	38.4	22.8	6.6	1.8
1.0	21.9	31.1	26.3	13.2	7.5
1.5	16.5	26.1	26.2	16.4	14.8
2.0	12.1	24.7	26.4	17.7	19.1
4.0	6.9	25.5	27.4	18.8	21.4

* The content is the percentage of the peak area of the fraction assigned to the oligomer.

fractionation products revealed that they are monomer (BMMD), dimer, and trimer in the order of decreasing retention time. The other two fractions appear to be tetra- and pentamers, in that order. In both oxidation systems the amount of an oligomer with a higher oligomerization degree (OD) increases with increasing oxidation time (Table I).

In the Fe^{3+} catalytic oxidation BMMD rapidly gives the dimer, however, the content of oligomers with OD > 4 did not increase at the same rate. Such behavior was not observed in the DMSO oxidation. The dimer was insoluble in methyl alcohol, and its oxidation rate in the Fe^{3+} system was slower than that in the DMSO oxidation due to precipitation. DMSO oxidized the dimer or the soluble oligomers further as oxidation time increased, but when the oxidation time exceeded 4 h, the oligo[BMMD] turned opaque due to inclusion of high-OD oligomers (the OD was estimated to be more than eight from GPC analysis). To minimize the content of high-OD oligomers, the amount of DMSO used was reduced (molar ratio of DMSO/BMMD = 1.0 in Table I), which, however, did not affect the distributions of the oligomers significantly, and the oxidation time was still limited within 4 h for transparent oligo[BMMD] production. Moreover, the conversion decreased with decreasing molar ratio. The Fe^{3+} catalytic oxidation is more suitable for preparation of oligo[BMMD], because the opaque oligo[BMMD] obtained by DMSO oxidation could not afford transparent poly[S-alkylcarbamate] applicable to optics by subsequent polyaddition with isocyanates.

3.2. n_D and ν_D of oligo[BMMD]

Fig. 4 shows the changes of n_D and ν_D of oligo[BMMD] with oxidation time. In the Fe^{3+} catalytic oxidation the n_D increased significantly within 0.5 h, and then gradually reached 1.68. In the DMSO oxidation the n_D also increased with oxidation time, but its change was not so large. With both oxidants, ν_D decreased and n_D increased with increasing oxidation time. The maximum n_D value for the DMSO oxidation products is expected to exceed 1.68 from the curve, which, however, was prevented by the formation of turbid oligo[BMMD] discussed above, and n_D of transparent oligo[BMMD] was limited to around 1.68 in both oxidation conditions.

The n_D and ν_D of oligo[BMMD] depend on the conversion of BMMD, but they drastically change when the conversion reaches around 100 % (Fig. 5).

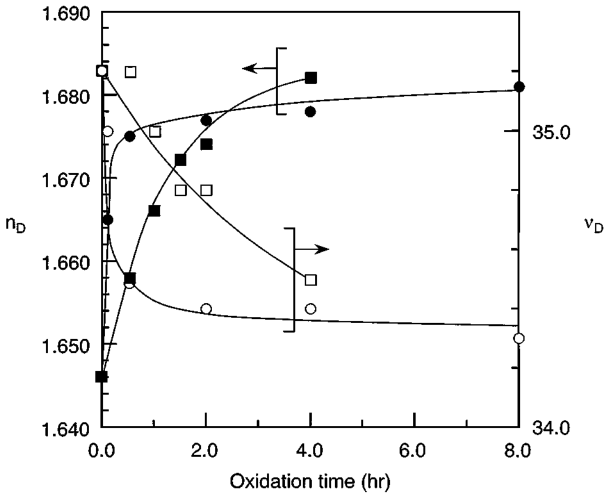

Figure 4 The dependence of n_D and ν_D of oligo[BMMD] on oxidation time. ●, ○ Fe^{3+} catalytic oxidation (molar ratio of Fe^{3+}/BMMD = 1.0). ■, □ DMSO oxidation (molar ratio of DMSO/BMMD = 4.0).

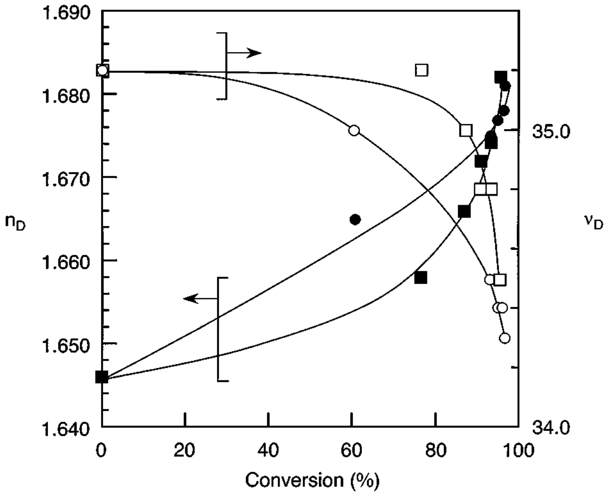

Figure 5 The dependence of n_D and ν_D of oligo[BMMD] on conversion. ●, ○ Fe^{3+} catalytic oxidation (molar ratio of Fe^{3+}/BMMD = 1.0). ■, □ DMSO oxidation (molar ratio of DMSO/BMMD = 4.0).

These relations indicate that the contribution of each oligomer to incrase the n_D and to decrease the ν_D of oligo[BMMD] is not equal. The formation of high-OD oligomers apparently causes these significant changes.

3.3. Co-oligomerization of BMMD with MES and MEE

Oligo[BMMD] was modified by co-oligomerization with MES or MEE codithiol. The codithiol molar fraction in feed was 20 mol %, and that incorporated determined from the signal intensities of ^{1}H-NMR was 18.4 mol % for MES and 19.5 mol % for MEE. The codithiols were found to be incorporated in the co-oligomer quantitatively within 30 min from the complete disappearance of their spot on thin layer chromatography. It is noteworthy that the co-oligomerization formed opaque products in shorter oxidation periods than that employing only BMMD even when ferric chloride was used. The co-oligomers obtained in the oxidation period just before they began to become turbid had n_D:ν_D of 1.674:34.5 (MES) and 1.669:34.6 (MEE). These values were comparable to those of the oligo[BMMD] obtained in the early oxidation stage (Fig. 4).

3.4. Preparation and characterization of poly[S-alkylcarbamate]s

Poly[S-alkylcarbamate]s were prepared from the oligo[BMMD]s and co-oligomers possessing mercapto groups at their terminals by polyaddition with isocyanates such as BIC, BIB, DIH, and TIC (Fig. 1). Fig. 6 shows the IR and ^{1}H-NMR spectra of the poly[S-alkylcarbamate] obtained from BIC and the oligo[BMMD] prepared by the Fe^{3+} catalytic oxidation for 8 h. The negligible signal at 2255 cm^{-1} in the IR spectra shows almost quantitative polyaddition. From the ratio of signal intensities at δ2.84–3.44 (22H) and δ0.37–1.85 (10H) in the ^{1}H-NMR, the average OD of oligo[BMMD] used was calculated to be 1.8. This value was consistent with that (1.9) calculated from the terminal mercapto groups given in the ^{1}H-NMR of the oligo[BMMD] used. This agreement meant that every oligomer in the oligo[BMMD] reacted equally with BIC. The poly[S-alkylcarbamate] of BIC completely dissolved in chloroform, but those of BIB and DIH showed poor solubility in common organic solvents including dimethyl sulfoxide, dimethyl formamide, hexamethyl phosphoric acid, tetrahydrofuran, hexafluoro *i*-propyl alcohol. It was expected that

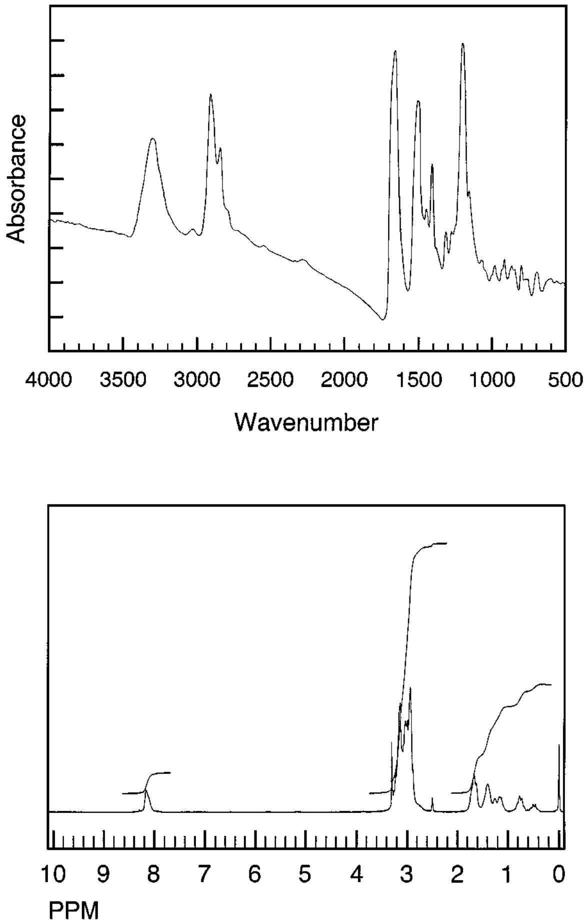

Figure 6 IR (top) and ^{1}H-NMR (bottom) spectra of poly[oligo-(BMMD)-BIC]. The averaged OD of oligo[BMMD] used is 1.9.

TIC gave cross-linked poly[S-alkylcarbamate]s due to its three functionalities, and this is confirmed from the facts that the poly[S-alkylcarbamate]s of TIC showed no solubility to these solvents but swelling only with chloroform, tetrahydrofuran and hexafluoro *i*-propyl alcohol. The $(CD_3)_2SO$ soluble parts of the poly[S-alkylcarbamate]s of BIB and DIH were employed for the NMR measurements, and only the IR spectrum was used for the characterization of the poly[S-alkylcarbamate] of TIC. The IR spectra of the poly[S-alkylcarbamate]s of BIB and TIC showed strong signals assigned to the remaining isocyanate group, whose intensities indicate poor polyaddition yields, in contrast to the case of BIC. The poly[S-alkylcarbamate] of TIC, giving the highest n_D among those of the other isocyanates, was modified structurally by incorporation of MES or MEE via two different procedures: polyaddition of the co–oligomer and TIC, and co-polyaddition of the mixture of the codithiol, oligo[BMMD] and TIC. These modified poly[S-alkylcarbamate]s were expected to have different structures around the disulfide bond, but could not be distinguished by the IR spectra. From these spectroscopic data, we conclude that the poly[S-alkylcarbamate]s were consistent with the structural formula shown in Fig. 1.

Fig. 7 shows the GPC charts of the poly[S-alkylcarbamate] and those of oligo[BMMD]s used for the polymer preparation. From the GPC curves, difference of oligomer distributions in oligo[BMMD] did not affect the molecular weight distribution and the average molecular weights of both poly[S-alkylcarbamate]s. This fact supports the above discussion about the similar reactivity of different OD oligomers. Usually, the refractive index of polymers depend on the molecular weight at low degrees of polymerization. However, in the poly[S-alkylcarbamate]s with molecular weight more than 10 000, their refractive indices approach limiting value [34]. These poly[S-alkylcarbamate]s proved to have sufficient molecular weights for the discussion of their inherent optical properties.

Fig. 8 shows temperature dependencies of elastic constant and tangent δ observed in thermomechanical analysis of the poly[S-alkylcarbamate] obtained from TIC and the oligo[BMMD] prepared by the Fe^{3+} catalytic oxidation for 8 h. The polymer has the elastic constant in the order of 10^9 Pa at room temperature, and the elasticity is maintained up to 120 °C. The glass transition temperature of the polymer defined

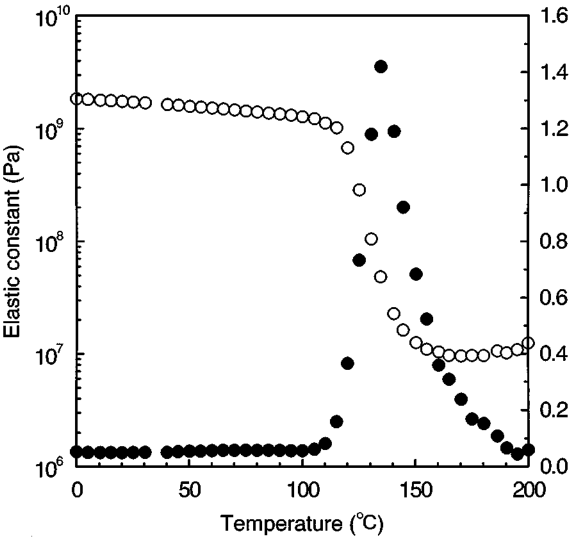

Figure 8 Temperature dependencies of elastic constant (○) and tangent δ (●) observed in the thermomechanical analysis of poly[oligo(BMMD)-TIC].

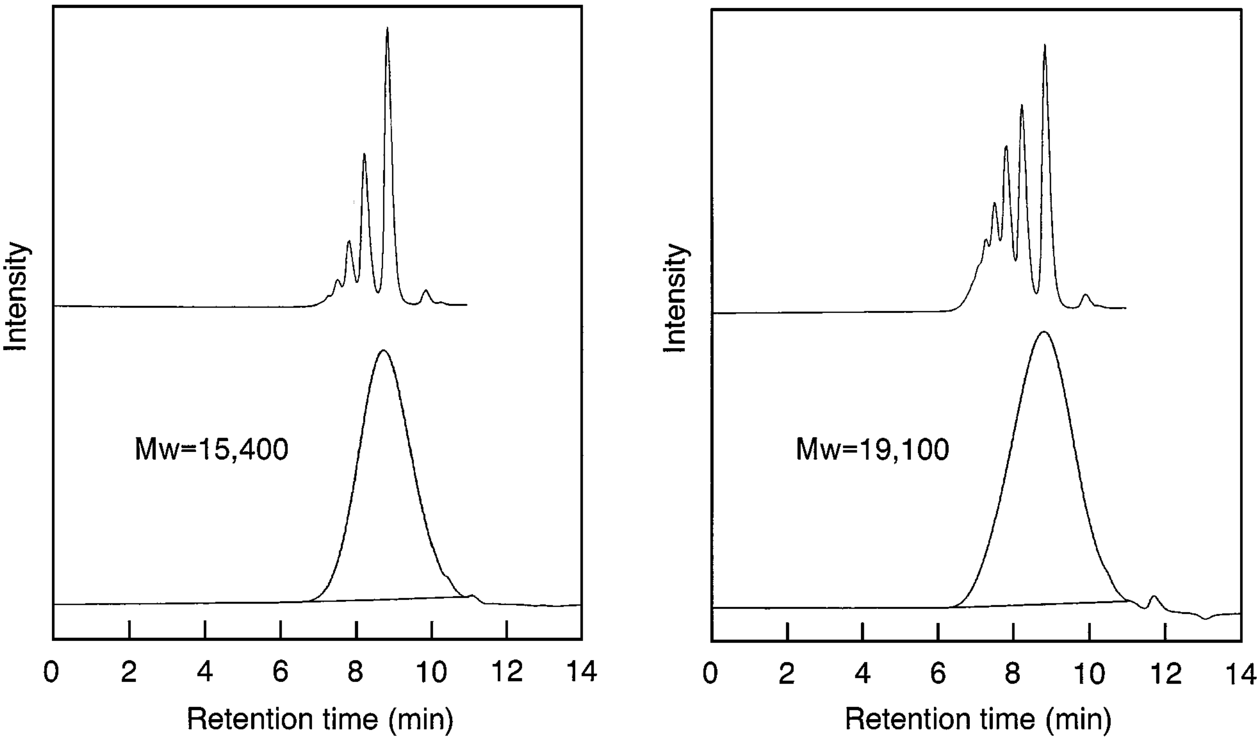

Figure 7 Gel permeation chromatograms of oligo[BMMD] (top) and its poly[oligo(BMMD)-BIC] (bottom).

TABLE II The n_D:ν_D of poly[S-alkylcarbamate]s prepared from oligo[BMMD]s with different n_D:ν_D

Isocyanates (n_D:ν_D)	n_D:ν_D of oligo[BMMD]	n_D:ν_D of poly[S-alkylcarbamate]s
BIC (1.484:52.1)	1.665:35.0	1.630:38.3
”	1.681:34.3	1.645:37.0
BIB (1.541:33.7)	1.665:35.0	1.668:32.8
”	1.681:34.3	1.677:32.5
DIH (1.452:50.7)	1.665:35.0	1.632:38.2
”	1.681:34.3	1.646:36.9
TIC (1.500:51.4)	1.665:35.0	1.646:36.6
”	1.681:34.3	1.659:35.6

by the temperature showing the maximum of the tangent δ is 134.7 °C. As evidenced by these thermomechanical properties, the poly[S-alkylcarbamate] is hard and glassy amorphous polymer. The amorphous nature contributes transparency of the poly[S-alkylcarbamate] showing light transmittance of 89% at 550 nm. Similarly, the other poly[S-alkylcarbamate]s obtained are all hard and transparent.

3.5. n_D and ν_D of the poly[S-alkylcarbamate]s

Table II gives n_D and ν_D of the poly[S-alkylcarbamate]s prepared from oligo[BMMD]s with different n_D and ν_D values. It is obvious that the oligo[BMMD] with higher n_D always gave the poly[S-alkylcarbamate]s with higher n_D, when the same isocyanate was used. BIB, having the highest n_D among the isocyanates used, gave the poly[S-alkylcarbamate]s with the highest n_D. These results indicate that the n_D of poly[S-alkylcarbamate] increases with increasing n_D of the oligo[BMMD] and that of the isocyanate. The incorporation of the benzene ring into the poly[S-alkylcarbamate]s by using BIB effectively increases n_D, while it significantly degrades ν_D due to a large molar dispersion of the benzene ring [35]. TIC gave the poly[S-alkylcarbamate] having a high n_D, second to that of BIB, but it gave a higher ν_D. Use of 1.5-fold mole of oligo[BMMD] for stoichiometric polyaddition with TIC, which possesses three isocyanate functionalities, is more advantageous for the preparation of high-n_D poly[S-alkylcarbamate]s than their preparation using BIC or DIH. In Fig. 9, the n_D and the ν_D of TIC-based poly[S-alkylcarbamate]s were plotted against those of oligo[BMMD]s used for their preparation. The n_D of the poly[S-alkylcarbamate] increases proportionally with that of oligo[BMMD], but the ν_D of the poly[S-alkylcarbamate] decreases drastically below 34.4 with slight change of ν_D of the oligo[BMMD]. Similar observations regarding n_D and ν_D have been reported for copolymers of benzylmethacrylate and 1,2-dimethacryloxyethane [36]. In this case, the sequences from the former unit contribute to decrease the ν_D, as their content increases, due to the benzene ring. Based on this consideration, our results indicate that the oligo[BMMD] containing a small amount of the high-OD oligomer causes the significant decrease of ν_D of the poly[S-alkylcarbamate] obtained.

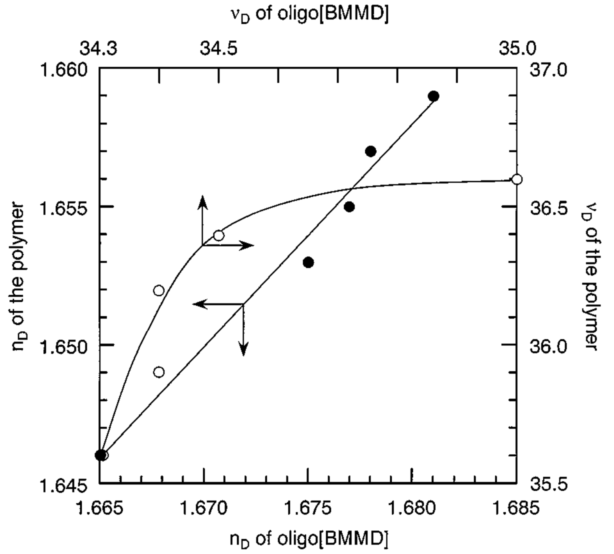

Figure 9 Dependence of n_D and ν_D of poly[oligo(BMMD)-TIC] on those of oligo[BMMD] used.

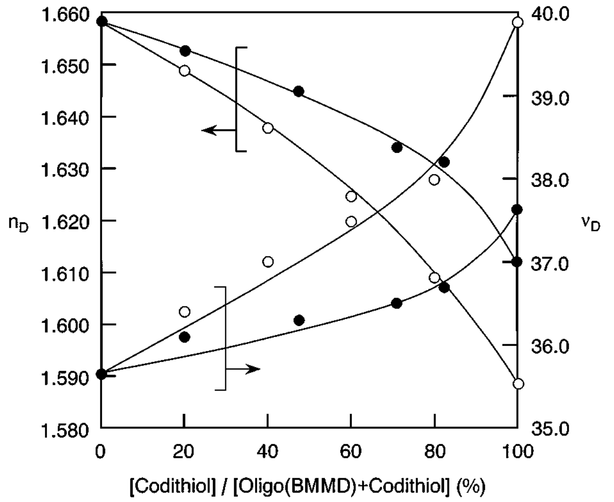

Figure 10 Changes of n_D and ν_D of copoly[oligo(BMMD)-codithiol-TIC] with the molar fraction of the codithiol in feed. Codithiols are MES (●) and MEE (○).

This is similar to the preceding discussion on ν_D of the oligo[BMMD]. Therefore, such oligo[BMMD]s should not be polymerized for the preparation of the poly[S-alkylcarbamate] with high ν_D. Consequently, polyaddition using the oligo[BMMD] prepared with a high conversion to the dimer or the dimer only should give poly[S-alkylcarbamate] with high n_D and high ν_D. The selective synthesis of the dimer is most desirable, but is not currently feasible. Fig. 10 shows the change of n_D and ν_D of copoly[oligo(BMMD)-codithiol-TIC] with the amount of codithiol in feed. In both cases, as the amount of the codithiol increased, the n_D decreased and the ν_D increased, which is attributed to the incorporation of the codithiol with lower n_D and higher ν_D than those of oligo[BMMD]. The n_D : ν_D of the poly[S-alkylcarbamate]s from the co-oligomers having approximately 20 mol % of MES and MEE were 1.654:36.0 and 1.651:36.2, respectively. These values were comparable to those of the copolymers obtained using 20 mol % of the respect codithiols (Fig. 10). The

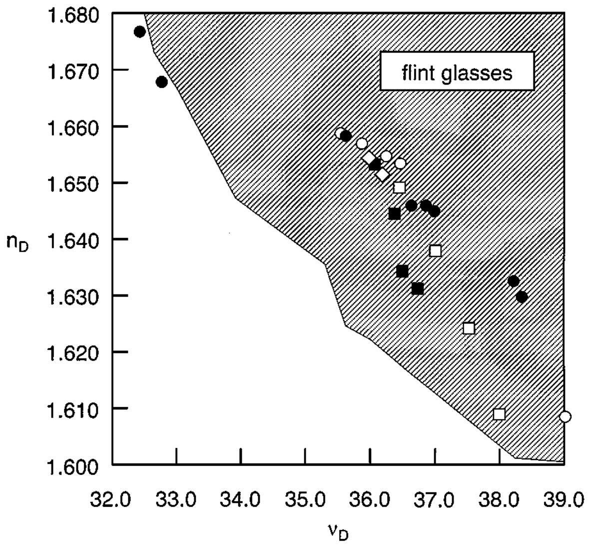

Figure 11 Refractive indices (n_D) and Abbe's numbers (ν_D) of the poly[S-alkylcarbamate]s. The region of flint glasses is also shown (shaded). ● poly[S-alkylcarbamate]s given in TABLE II, ○ poly-[oligo(BMMD)-TIC]s shown in Fig. 9, ■ copoly[oligo(BMMD)-MES-TIC]s shown in Fig. 10, □ copoly[oligo(BMMD-MEE-TIC]s shown in Fig. 10, ◇ copoly[oligo(BMMD-*co*-MES (or MEE))-TIC]s.

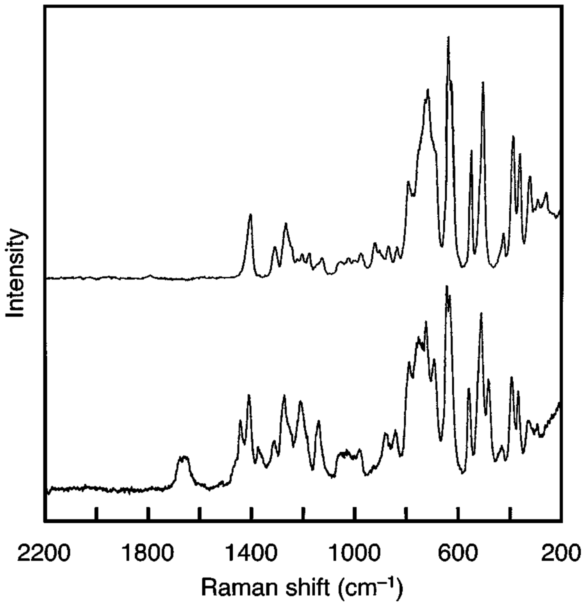

Figure 12 Raman spectra of oligo[BMMD] (top) and poly[oligo-(BMMD)-TIC] (bottom). The sample of oligo[BMMD] was the same as that of Fig. 2. The polymer was prepared using this oligo[BMMD].

structural change around the disulfide bond did not affect the optical properties of both copolymers.

The n_D versus ν_D diagram of the all poly[S-alkylcarbamate]s obtained in the present work is shown in Fig. 11. Obviously, the n_D and ν_D of most polymers intrude into the region of flint glasses [37]. The oligo[BMMD] contributes to increase not only n_D but also ν_D. Consequently, we propose that these poly[S-alkylcarbamate]s with high n_D and high ν_D can be used as promising optical materials. The n_D and the ν_D of the polymer obtained using BIB, however, were not comparable to those of the other polymers or of flint glasses, although it had higher n_D than the other polymers. The poor optical properties are attributable to low ν_D, because its n_D is consistent with that estimated from the Lorentz–Lorenz equation [26]. The incorporation of the benzene ring caused this degradation, as discussed below.

3.6. Relationship between the ν_D and the structure of poly[S-alkylcarbamate]

The Raman spectra of the oligo[BMMD] and poly[oligo(BMMD)-TIC] show signals about 505 and 550 cm^{-1}, which are assignable to the S–S stretching (Fig. 12). All the other co-oligomers and poly[S-alkylcarbamate]s also show both signals within a deviation of 7 cm^{-1}. In a C_1-C_2-S_1-S_2-C_3-C_4 system, where the conformation of C_2-S_1-S_2-C_3 is fixed in *gauche*, the signal around 505 cm^{-1} and that around 550 cm^{-1} indicates the presence of a *gauche* (C_1-C_2-S_1-S_2)–*gauche* (C_2-S_1-S_2-C_3)–*gauche* (S_1–S_2–C_3–C_4) (GGG) conformation and that of a *trans* (C_1-C_2-S_1-S_2)–*gauche* (C_2-S_1-S_2-C_3)–*trans* (S_1-S_2-C_3-C_4) (TGT) conformation, respectively [38]. Thus, oligo[BMMD] and its poly[S–alkylcarbamate] consist of both GGG and TGT conformers for the C*-C-S-S-C-C* linkage, in which C* is the carbon at the 2- or 5-position in the 1,4-dithiane ring. The lack of the signal at about 525 cm^{-1} indicates the absence of other conformers such as GGT [38]. As is exemplified by the UV spectrum of alkyl disulfide, *t*-butyldisulfide in the TGT conformation hardly absorbs UV light, while the other in the GGG or the GGT conformation show characteristic UV absorption [31, 32]. Optical dispersion, which normally decreases ν_D, is caused by electronic transitions at UV frequencies [39]. Accordingly, the GGG conformer or other UV absorbing groups in poly[S-alkylcarbamate] contributes to degrade the ν_D of the polymer, while the TGT conformer does not do so. The UV spectrum of oligo[BMMD] (Fig. 13) is similar to that of non-disulfide-containing BMMD in that the molar absorption coefficient measured is relatively low. Nevertheless, it shows slight absorption between 250–300 nm which is attributed to the GGG conformer and its content is thought to be small. In the UV spectra of poly[oligo(BMMD)-TIC] and poly[oligo(BMMD)-BIC], no apparent absorption band was observed between 260–300 nm (Fig. 14). In this region, the slight increase in optical density with

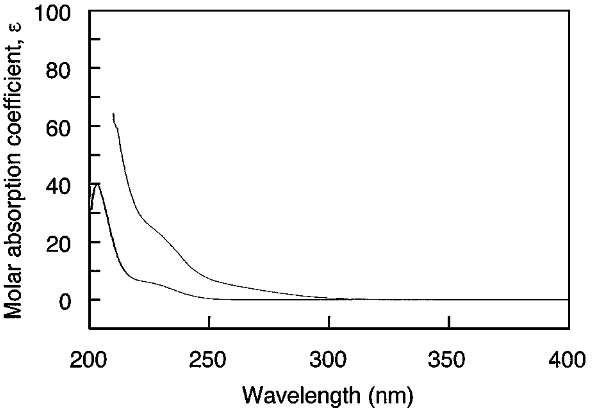

Figure 13 UV spectra of oligo[BMMD] (top) and BMMD (bottom). The sample of oligo[BMMD] was the same as that of Fig. 2.

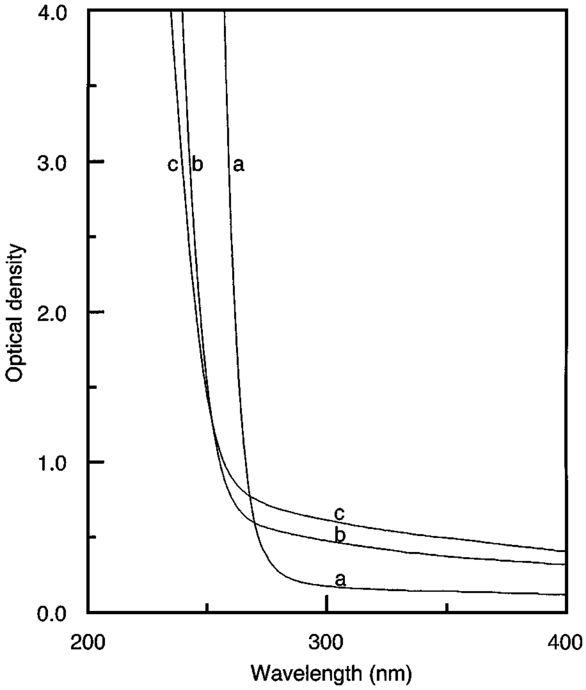

Figure 14 UV spectra of poly[S-alkylcarbamate]s prepared with BIB (a), TIC (b), and BIC (c).

decreasing wavelength is due to scattering loss of UV light on the polymer surface. The spectra suggest that the GGG conformers hardly contribute to UV absorption of the poly[S-alkylcarbamate] and that it may be due to the contribution of the TGT conformer that their ν_D values are comparable to those of flint glasses having nearly the same n_D values as those of the polymers. The same discussion may be applicable to most of the other poly[S-alkylcarbamate]s. Poly[oligo(BMMD)-BIB] significantly absorbs UV light below 280 nm (Fig. 14). The wavelength at the end of the absorption for the polymer is longer than that for poly[oligo(BMMD)-TIC] or poly[oligo(BMMD)-BIC]. Benzene shows the UV absorption at 255 nm with ε of 219, [40] and its resonance effects may cause the UV absorption and the ν_D degradation of poly[oligo(BMMD)-BIB].

4. Conclusions

In order to obtain an optical polymer material with high n_D and high ν_D, poly[S-alkylcarbamate]s were designed and prepared from the disulfide-comprising oligo[BMMD] and the isocyanates. The BMMD oligomers were successfully prepared by the Fe^{3+} catalytic oxidation or DMSO oxidation of BMMD. The former condition tends to give the dimer-rich oligo[BMMD], which was suitable to give poly[S-alkylcarbamate]s having good transparency, high n_D, and high ν_D. Among the isocyanates used, TIC gave poly[S-alkylcarbamate]s having comparably high n_D and high ν_D due to its triisocyanates functionalities. Codithiols such as MES and MEE were applied to modify the optical properties of the poly[S-alkylcarbamate] by polyaddition of the isocyanate and co-oligo[BMMD-codithiol], or by that of the isocyanate and a mixture of oligo[BMMD] and the codithiol. Compared with other conventional optical polymers, most of the poly[S-alkylcarbamate]s, including these codithiol modified polymers, had relatively high n_D and high ν_D, and these values were comparable to those of flint glasses. The poor optical properties of poly[oligo(BMMD)-BIB] were attributed to degradation in ν_D. The high n_D observed was attributed to the increased molar refraction caused not only by the presence of the 1,4-dithian ring [25, 33] but also by that of the disulfide bond that introduces high sulfur content in the polymer.

The effects of the disulfide bond and other group in the poly[S-alkylcarbamate]s on the ν_D value were discussed in terms of UV absorption. From their Raman spectra, oligo[BMMD] and its poly[S-alkylcarbamate]s prove to have both GGG and TGT conformers in the C-C-S-S-C-C linkage. The former shows characteristic UV absorption, whereas the latter does not. The representative UV spectra of poly[oligo(BMMD)-BIC] and poly[oligo(BMMD)-TIC] show that the TGT conformer in the poly[S-alkylcarbamate]s contributes to suppress the UV absorption beyond 260 nm. As a result, n_D and ν_D values comparable to those of flint glasses are observed for the poly[S-alkylcarbamate]s. The contribution of the TGT conformer should be applicable to all the oligo[BMMD]-based poly[S-alkylcarbamate]s. The degradation of ν_D of poly[oligo(BMMD)-BIB] is an exceptional case due to its significant UV absorption, which ends at 280 nm. This absorption is attributed to the benzene ring introduced by BIB.

We thus conclude that oligo[BMMD], particularly its dimer, serves as a useful material for the preparation of polymer having high n_D and high ν_D and that the polymers obtained are promising optical materials.

References

1. H. DISLICH, *Angew. Chem. Int. Ed. Engl.* **18** (1979) 49.
2. M. A. OLSHAVSKY and H. R. ALLCOCK, *Macromolecules* **28** (1995) 6188.
3. J. M. YOUNG, *Opt. World* **18** (1989) 10.
4. C. HOFMANN, *Feingerätetechnik* **39** (1990) 124.
5. H. DISLICH and A. JACOBSEN, *Angew. Chem. Int. Ed. Engl.* **12** (1973) 439.
6. 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** (1991) 521.
7. R. A. GAUDIANA and R. A. MINNS, *J. Macromol. Sci.-Chem.* **A28** (1991) 831.
8. B. WANG, G. L. WILKES, J. C. HEDRICK, S. C. LIPTAK and J. E. McGRATH, *Macromolecules* **24** (1991) 3449.
9. B. WANG, G. L. WILKES, C. D. SMITH and J. E. McGRATH, *Polym. Commun.* **32** (1991) 400.
10. M. WEIBEL, W. CASERI, U. W. SUTER, H. KIESS and E. WEHRLI, *Polym. Adv. Technol.* **2** (1991) 75.
11. S. S. HARDAKER, S. MOGHAZY, C. Y. CHA and R. J. SAMUELS, *J. Polym. Sci. B, Polym. Phys.* **31** (1993) 1951.
12. R. A. GAUDIANA, R. A. MINNS and H. G. ROGERS, US Patent 5 132 430 (1992).
13. R. A. MINNS and R. A. GAUDIANA, *J. Macromol. Sci.-Pure Appl. Chem.* **A 29** (1992) 19.
14. L. ZIMMERMANN, M. WEIBEL, W. CASERI and U. W. SUTER, *J. Mater. Res.* **8** (1993) 1742.

15. T. NAGATA, K. OKAZAKI and T. MIURA, European Patent 351 073 A2 (1990).
16. H.-U. SIMMROCK, A. MATHY, L. DOMINGUEZ, W. H. MEYER and G. WEGNER, *Angew. Chem. Int. Ed. Engl. Adv. Mater.* **28** (1989) 1122.
17. N. AMAYA, K. ANAN, Y. MURATA, T. MOGAMI, Y. SANO, H. IKEBE and R. SEITA, US Patent 4 948 854 (1990).
18. M TABATA, N. KUSHIBIKI and Y. YOSHINAGA, US Patent 5 082 358 (1992).
19. K. ISHIKAWA, Y. HAYAKAWA and Y. YOSHIDA, Japanese Patent 60 124 607 A2 (1985).
20. S. TABATA, W. YAN, K. YOKOTA, N. KUSHIBIKI, Y. KUWAE and N. KANEKO, *Polymer Preprints, Japan* **36** (1987) 1163.
21. S. KOBAYASHI, K. KAWAUCHI, M. IMAI and K. FUJII, Japanese Patent 09 124 592 A2 (1997).
22. T. NAGATA, K. OKAZAKI, N. KAJIMOTO, T. MIURA, Y. KANEMURA and K. SASAGAWA, European Patent 329 386 A2 (1989).
23. Y. KANEMURA, M. IMAI, K. SASAGAWA, N. KAJIMOTO and T. NAGATA, US Patent 4 775 733 (1988).
24. Y. KANEMURA, K. SASAGAWA, M. IMAI and T. SUZUKI, US Patent 5 087 758 (1992).
25. T. OKUBO and R. OKADA, in Proceedings of the Polyurethanes World Congress 1993, Canada, October 1993 (The SPI/ISOPA, Canada, 1993) p. 527.
26. N. TANIO and Y. KOIKE, *Jpn. J. Appl. Phys*. **36** (1997) 743.
27. K. OKAZAKI, Y. KANEMURA and T. NAGATA, European Patent 665 219 A1 (1995).
28. Y. KANEMURA, K. SASAGAWA and S. KOBAYASHI, European Patent 528 590 A1 (1993).
29. H. NAGO, H. KAZAMA and S. MATSUOKA, Japan Patent 05 051 412 A2 (1993).
30. S. KOBAYASHI, K. SASAGAWA and Y. KANEMURA, Japan Patent 05 320 301 A2 (1993).
31. A. ROSENTAL and G. OSTER, *J. Am. Chem. Soc.* **83** (1961) 4445.
32. C. C. PRICE and S. OAE, in “Sulfur Bonding” (Ronald Press, New York, 1962) pp. 44–46.
33. T. OKUBO and A. J. IKUSHIMA, in “Frontiers of Polymers and Advanced Materials,” edited by P. N. Prasad (Plenum, New York, 1994) p. 187.
34. L. BOHN, in “Polymer Handbook,” 2nd edition, edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1975) p. III-241.
35. N. TANIO, *Kobunshi Kako* **46** (1997) 18.
36. T. MATSUDA, Y. FUNAE, M. YOSHIDA, T. YAMAMOTO and T. TAKAYA, *J. Appl. Polym. Sci.* **65** (1997) 2247.
37. F.-T. LENTES, in “The Properties of Optical Glasses,” edited by H. Bach and N. Neuroth (Springer, Berlin, 1995) p. 32–57.
38. H. SUGETA, A. GO and T. MIYAZAWA, *Bull. Chem. Soc. Jpn.* **46** (1973) 3407.
39. D. MARCUSE, in “Light Transmission Optics, 2nd Edn.,” (Robert E. Krieger, Florida, 1989) p. 482–485.
40. R. M. SILVERSTEIN, G. C. BASSLER and T. C. MORRILL, in “Spectrometric Identification of Organic Compounds, 4th Edn.,” (Wiley, New York, 1981) p. 327.

Received 30 November 1997
and accepted 14 August 1998