1786 *Macromolecules* **2003,** *36,* 1786−1792

Synthesis of New Photoresponsive Polymers Containing Trifluoromethyl-Substituted Norbornadiene Moieties

Takabumi Nagai* and Miwa Shimada

Daikin Environmental Laboratory, Ltd., 3 banchi, Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan

Yoshitomo Ono and Tadatomi Nishikubo

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Received September 3, 2002; Revised Manuscript Received January 6, 2003

ABSTRACT: Polymers containing trifluoromethyl (CF_3)-substituted donor−acceptor NBD moieties in the side chain or in the main chain were synthesized by substitution or addition of a CF_3−NBD−carboxylic acid derivative or by polycondensation of a CF_3−NBD−dicarboxylic acid derivative. The photoisomerization of the NBD moieties in these polymers proceeded very smoothly to give the corresponding QC moieties. Furthermore, the NBD moieties exhibited efficient fatigue resistance.

Introduction

Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system,[1] since photoenergy can be stored as strain energy (about 20 kcal/mol) in a QC molecule. Recently, this photochemical reaction has also been investigated as an optical waveguide utilizing photoinduced refractive index changes[2a−d] or as a photochromic system potentially applicable to data storage.[2e]

Taking these unique characteristics of NBD into account, Nishikubo et al. have investigated the synthesis and photochemical reaction of various photoresponsive polymers containing NBD moieties in the side chain[3−6] or in the main chain.[7,8] However, the photoreactivity and fatigue resistance of these polymers were insufficient for practical use as advanced materials. To improve the photoreactivity of these polymers, they recently synthesized polyesters containing donor−acceptor (D−A) NBD moieties and found these polyesters had high photoreactivity and good durability for repeated cycles of interconversion.[9] On the other hand, Nagai et al. reported the synthesis of CF_3-substituted D−A−NBD derivatives. These compounds had large absorption in a visible region and photoisomerized to give the corresponding QC derivatives efficiently. Furthermore, they exhibited efficient fatigue resistance.[10] Therefore, we now report the synthesis of new photoresponsive polymers containing CF_3-substituted D−A−NBD moieties, the photochemical reaction of the resulting polymers, and the durability of the NBD moieties in the polymers.[11]

Experimental Section

Materials. Poly(glycidyl methacrylate) (PGMA),[5a] poly(2-chloroethoxy vinyl ether) (PEVE),[12] and 2-(benzofuran-2-yl)-4,4-dimethyl-2-cyclopentenone[10] were prepared according to reported methods. 1,6-Hexanediol and *trans*-1,4-diaminocyclohexane were recrystallized from hexane. Poly(chloromethylstyrene) (3−/4− = 3/2, $M_w = 55\,000$, PCMS), dimethylaminopropylethylcardodiimide hydrochloride (WSCD), (dimethylamino)pyridine (DMAP), diphenylphosphoryl azide (DPPA), hafnium chloride−THF complex, 3-nitrobenzeneboronic acid, tetrabutylammonium bromide (TBAB), and hexafluoro-2-butyne (HFB) were used without further purification.

Apparatus. Melting points were determined with a Yanaco MP-500D hot-stage microscope and are not corrected. Infrared spectra were obtained on a Perkin-Elmer 1600 FT-IR either neat or in KBr pellets. Absorption was expressed as reciprocal centimeters (cm^{-1}). ^1H NMR were recorded at 200 MHz on a Varian Gemini-200 instrument and indicated in parts per million (ppm) downfield from tetramethylsilane as the internal standard (δ). ^{19}F NMR spectra were measured at 188 MHz on a Varian Gemini-200 instrument and indicated in parts per million (ppm) upfield from CCl_3F as the internal standard. Low- and high-resolution mass spectral analyses were performed under 70 eV electron-impact (EI) conditions on a Kratos CONCEPT-1H double-focusing magnetic sector spectrometer. Elemental analyses were made at Toray Research Center, Inc., Tokyo.

Ultraviolet (UV) spectra were recorded on a Hitachi model U-3500 and model UV-2500PC. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Shimadzu model LC-10 equipped with a refractive index detector using Shodex GPC KD 804 column (eluent: DMF solution at flow rate of 1.0 mL/min, calibrated using narrow molecular weight polystyrene as standards).

Synthesis of 2-(Benzofuran-2-yl)-7,7-dimethyl-3-(5-carboxythiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (NBD−Carboxylic Acid 1). 3-(Benzofuran-2-yl)-4,4-dimethyl-1-(thiophene-2-yl)-2-cyclopentenol (5). A solution of 2-(benzofuran-2-yl)-4,4-dimethyl-2-cyclopentenone (**4**, 13.26 g, 59 mmol) in THF (30 mL) was added dropwise at −78 °C to a THF solution of lithium reagent obtained from thiophene (5.7 mL) with *n*-BuLi (1.52 M, 46.7 mL). The mixture was stirred for 30 min at this temperature, then poured into ice−water, and extracted with ether. The ether layer was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 5:1) to give **5** (16.68 g, 91%) as a colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.22 (s, 3H), 1.32 (s, 3H), 2.33−2.49 (m, 2H), 2.73 (s, 1H), 6.37 (s, 1H), 6.52 (s, 1H), 6.90−6.92 (m, 2H), 7.09−7.28 (m, 3H), 7.36−7.45 (m, 2H). IR (KBr, cm^{-1}): 3457, 2958, 1723, 1451, 1257, 751, 701. MS *m/z* 310 (M^+). HRMS calcd for $C_{19}H_{18}O_2S$ 310.103; found 310.102.

2-(Benzofuran-2-yl)-3-(thiophene-2-yl)-5,5-dimethylcyclopentadiene (6). A solution of **2** (16.68 g, 53.7 mmol) and *p*-TsOH·H_2O (0.93 g, 5.4 mmol) in toluene (400 mL) was refluxed for 30 min. The mixture was poured into10% NaOH solution and extracted with ether. The ether layer was washed

---

* To whom all correspondence should be addressed.

10.1021/ma0214207 CCC: $25.00

with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 100:1) to give **6** (12.31 g, 78%) as a slightly yellow viscous oil. ^1H NMR ($CDCl_3$): δ 1.34 (s, 6H), 6.38 (s, 1H), 6.41 (d, $J = 2.6$ Hz, 1H), 6.83 (d, $J = 2.6$ Hz, 1H), 6.99−7.07 (m, 2H), 7.12−7.30 (m, 3H), 7.42−7.49 (m, 2H). IR (KBr, cm^{-1}): 2961, 1450, 1256, 750, 699. MS *m/z* 292 (M^+). HRMS calcd for $C_{19}H_{16}OS$ 292.092; found 292.092.

2-(Benzofuran-2-yl)-3-(5-ethoxycarbonylthiophene-2-yl)-5,5-dimethylcyclopentadiene (7). Ethyl chloroformate (4 mL, 42.1 mmol) was added dropwise at −78 °C to a THF solution of lithium reagent obtained from **6** (12.31 g, 42.1 mmol) with *n*-BuLi (1.52 M, 36 mL, 54.7 mmol). The mixture was stirred for 30 min at this temperature, then poured into ice−water, and extracted with ether. The ether layer was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 20:1) to give **7** (12.78 g, 83%) as a yellow viscous oil. ^1H NMR ($CDCl_3$): δ 1.35 (s, 6H), 1.39 (t, $J = 7.1$ Hz, 3H), 4.37 (q, $J = 7.1$ Hz, 2H), 6.40 (s, 1H), 6.50 (d, $J = 2.7$ Hz, 1H), 6.84 (d, $J = 2.7$ Hz, 1H), 6.97 (d, $J = 3.8$ Hz, 1H), 7.14−7.32 (m, 2H), 7.73 (d, $J = 3.8$ Hz, 1H). IR (KBr, cm^{-1}): 1702, 1450, 1288, 1256, 1098. MS *m/z* 364 (M^+). HRMS calcd for $C_{22}H_{20}O_3S$ 364.113; found 364.113.

2-(Benzofuran-2-yl)-7,7-dimethyl-3-(5-ethoxycarbonylthiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (8). **7** (12.78 g, 35 mmol) was placed in a stainless steel tube with toluene (95 mL). To this tube, hexafluoro-2-butyne (HFB, 5.67 g, 35 mmol) was introduced by a vacuum line. The mixture was stirred at 80 °C for 15 h in the tube. After the tube was cooled in an ice bath, it was opened and the mixture was extracted with ether. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 20:1) to give **8** (17.73 g, 96%) as yellow needles; mp 99.2−99.7 °C. ^1H NMR ($CDCl_3$): δ 1.29 (s, 3H), 1.31 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H), 3.94 (m, 2H), 4.39 (q, $J = 7.1$ Hz, 2H), 6.95 (bs, 1H), 7.20−7.40 (m, 2H), 7.46−7.64 (m, 3H), 7.79 (d, $J = 4.1$ Hz, 2H). ^{19}F NMR ($CDCl_3$): δ −61.23 (q, 3F, $J = 6.7$ Hz), −61.26 (q, 3F, $J = 6.7$ Hz). IR (KBr, cm^{-1}): 1703, 1452, 1299, 1272, 1179, 1145, 1102. Anal. Calcd for $C_{26}H_{20}F_6O_3S$: C, 59.31; H, 3.83. Found: C, 59.39; H, 3.82.

2-(Benzofuran-2-yl)-7,7-dimethyl-3-(5-carboxythiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (1). A 1 N NaOH solution (120 mL) was added to a THF (120 mL) solution of **5** (17.4 g, 33 mmol) and stirred at 50 °C for 48 h. After the mixture was acidified, it was extracted with ether. The ether layer was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was recrystallized with EtOAc to give **1** (15.79 g, 96%) as yellow needles; mp 162.4−163.0 °C. ^1H NMR ($CDCl_3$): δ 1.30 (s, 3H), 1.32 (s, 3H), 3.96 (s, 2H), 6.97 (s, 1H), 7.20−7.40 (m, 2H), 7.50−7.65 (m, 3H), 7.90 (d, $J = 4.1$ Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −60.98 to −61.55 (m). IR (KBr, cm^{-1}): 3379, 2989, 1679, 1395, 1348, 1294, 1213, 1156, 1134. Anal. Calcd for $C_{24}H_{16}F_6O_3S$: C, 57.83; H, 3.24. Found: C, 57.58; H, 3.30.

2-(Benzofuran-2-yl)-7,7-dimethyl-3-(thiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (16). **16** was synthesized in a similar way from **6** with HFB in 91% yield as yellow viscous. ^1H NMR ($CDCl_3$): δ 1.30 (s, 6H), 3.93 (s, 2H), 6.89 (s, 1H), 7.07−7.18 (m, 1H), 7.18−7.40 (m, 2H), 7.42−7.62 (m, 4H). ^{19}F NMR ($CDCl_3$): δ −60.98 (q, 3F, $J = 8.9$ Hz), −61.34 (q, 3F, $J = 8.9$ Hz). IR (KBr, cm^{-1}): 1450, 1346, 1296, 1177, 1135. MS *m/z* 454 (M^+). HRMS calcd for $C_{23}H_{16}F_6OS$ 454.083; found 454.082.

Synthesis of 2,3-Bis(5-carboxythiophene-2-yl)-7,7-dimethyl-5,6-bis(trifluoromethyl)-2,5-norbornadiene (NBD−Carboxylic Acid 2). **4,4-Bimethyl-1-(thiophene-2-yl)-2-cyclopentanone-1-ol (9).** A solution of **3** (18.0 g, 143 mmol) in THF (150 mL) was added dropwise at −78 °C to a THF (350 mL) solution of lithium reagent obtained from thiophene (25 mL, 314 mmol) with *n*-BuLi (1.54 M, 203 mL, 314 mmol). The mixture was stirred for 1 h at this temperature. After normal workup, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 5:1) to give **9** (24.6 g, 82%) as a colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.13 (s, 3H), 1.21 (s, 3H), 2.31−2.57 (m, 4H), 3.02 (s, 1H), 6.93−7.00 (m, 2H), 7.27−7.34 (m, 1H). IR (KBr, cm^{-1}): 3435, 2957, 1746, 1370, 1240, 1066, 996, 704. MS *m/z* 210 (M^+). HRMS calcd for $C_{11}H_{14}O_2S$ 210.071; found 210.071.

4,4-Dimethyl-2-(thiophene-2-yl)-2-cyclopentene (10). A solution of **9** (24.6 g, 117 mmol) and *p*-TsOH·H_2O (2.1 g, 12 mmol) in toluene (700 mL) was refluxed for 20 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 10:1) to give **10** (20.15 g, 91%) as a colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.30 (s, 6H), 2.46 (s, 2H), 7.03−7.08 (m, 1H), 7.29−7.33 (m, 1H), 7.49 (s, 1H), 7.62−64 (m, 1H). IR (KBr, cm^{-1}): 2959, 1694, 1409, 1249, 836, 731, 713. MS *m/z* 192 (M^+). HRMS calcd for $C_{11}H_{12}OS$ 192.061; found 192.060.

4,4-Dimethyl-1,2-bis(thiophene-2-yl)-2-cyclopentenol (11). A solution of **10** (20.15 g, 105 mmol) in THF (150 mL) was added dropwise at −78 °C to a THF (200 mL) solution of lithium reagent obtained from thiophene (12.6 mL, 157 mmol) with *n*-BuLi (1.54 M, 102 mL, 157 mmol). The mixture was stirred for 1.5 h at this temperature. After normal workup, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 10:1) to give **11** (25.18 g, 87%) as a colorless viscous oil. ^1H NMR ($CDCl_3$): δ 1.19 (s, 3H), 1.28 (s, 3H), 2.40 (d, $J = 4.2$ Hz, 2H), 2.54 (s, 1H), 6.13 (s, 1H), 6.84−6.94 (m, 4H), 7.10−7.16 (m, 1H), 7.19−7.25 (m, 1H). IR (KBr, cm^{-1}): 3448, 2956, 1440, 1361, 1230, 1036, 832, 697. MS *m/z* 276 (M^+). HRMS calcd for $C_{15}H_{16}OS_2$ 276.064; found 276.063.

5,5-Dimethyl-2,3-bis(thiophene-2-yl)-cyclopentadiene (12). A solution of **11** (25.18 g, 91 mmol) and *p*-TsOH·H_2O (1.6 g, 9.1 mmol) in toluene (600 mL) was refluxed for 20 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 100:1) to give **12** (18.7 g, 79%) as a slightly yellow viscous oil. ^1H NMR ($CDCl_3$): δ 1.30 (s, 6H), 6.40 (s, 2H), 6.78−6.81 (m, 2H), 6.92−6.97 (m, 2H), 7.17−7.21 (m, 2H). IR (KBr, cm^{-1}): 2961, 1462, 1430, 1233, 825, 695. MS *m/z* 258 (M^+). HRMS calcd for $C_{15}H_{14}S_2$ 258.054; found 258.053.

7,7-Dimethyl-2,3-bis(thiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (13). **13** was synthesized in a similar way from **12** (18.7 g, 72 mmol) with HFB (11.7 g, 72 mmol) in 99% yield (30.13 g) as yellow needles; mp 80.0−80.8 °C. ^1H NMR ($CDCl_3$): δ 1.27 (s, 3H), 1.35 (s, 3H), 3.75 (s, 2H), 7.02−7.33 (m, 6H). ^{19}F NMR ($CDCl_3$): δ −61.40 (s). IR (KBr, cm^{-1}): 1670, 1295, 1178, 1133, 700. Anal. Calcd for $C_{19}H_{14}F_6S_2$: C, 54.28; H, 3.36. Found: C, 54.42; H, 3.36.

7,7-Dimethyl-2,3-bis(5-ethoxycarbonylthiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (14). Ethyl chloroformate (12.1 mL, 127 mmol) was added dropwise at −78 °C to a THF solution of lithium reagent obtained from 13 (25.39 g, 60 mmol) with *n*-BuLi (1.54 M, 86.3 mL, 133 mmol). The mixture was stirred for 40 min at this temperature. After normal workup, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 10:1) to give **14** (16.68 g, 49%) as yellow needles; mp 84.0−84.8 °C. ^1H NMR ($CDCl_3$): δ 1.29 (s, 3H), 1.34 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 6H), 3.78 (s, 2H), 4.35 (q, $J = 7.1$ Hz, 4H), 7.20 (d, $J = 4.0$ Hz, 2H), 7.72 (d, $J = 4.0$ Hz, 2H). ^{19}F NMR ($CDCl_3$): δ-61.54 (s). IR (KBr, cm^{-1}): 1708, 1454, 1297, 1252, 1172, 1135, 1096. Anal. Calcd for $C_{25}H_{22}F_6O_4S_2$: C, 53.19; H, 3.93. Found: C, 53.41; H, 4.02.

7,7-Bimethyl-2,3-bis(5-carboxythiophene-2-yl)-5,6-bis(trifluoromethyl)-2,5-norbornadiene (2). A 1 N NaOH solution (200 mL) was added to a THF (200 mL) solution of **14** (15.66 g, 27.7 mmol) and stirred at room temperature for 60 h. After normal workup, the product was recrystallized with hexane−ether to give **2** (11.39 g, 80%) as yellow needles; mp 246 °C (decomposition). ^1H NMR (CD_3OD): δ 1.30 (s, 3H), 1.37 (s, 3H), 4.00 (s, 2H), 7.31 (d, $J = 3.9$ Hz, 2H), 7.72 (d, $J = 3.9$ Hz, 2H). ^{19}F NMR (CD_3OD): δ −60.78 (s). IR (KBr, cm^{-1}): 2996, 1676, 1522, 1456, 1300, 1182, 1117. Anal. Calcd for $C_{21}H_{14}F_6O_4S_2$: C, 49.61; H, 2.78. Found: C, 49.90; H, 3.06.

Bis(4-nitrophenyl) Ester of 2 (15). A mixture of **2** (238.0 mg, 0.47 mmol), 4-nitrophenol (130.3 mg, 0.94 mmol), dimethylaminopropylethylcardodiimide hydrochloride (WSCD, 180.0 mg, 0.94 mmol), and (dimethylamino)pyridine (DMAP, 12 mg) in CH_2Cl_2 was stirred for 15 h at room temperature. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane−EtOAc, 3:1) to give **15** (220 mg, 60%) as yellow needles; mp 205.1−206.0 °C. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 3H), 1.40 (s, 3H), 3.86 (s, 2H), 7.33 (d, J = 4.0 Hz, 2H), 7.42 (d, J = 9.2 Hz, 4H), 7.96 (d, J = 4.0 Hz, 2H), 8.33 (d, J = 9.2 Hz, 4H). ^{19}F NMR ($CDCl_3$): δ −61.54 (s). IR (KBr, cm^{-1}): 1732, 1529, 1350, 1298, 1232, 1205, 1064. Anal. Calcd for $C_{33}H_{20}F_6N_2O_8S_2$: C, 52.80; H, 2.69; N, 3.37. Found: C, 52.90; H, 2.84; N, 3.61.

Synthesis of NBD Polymers. Synthesis of P-1. A mixture of PCMS (305 mg, 2.0 mmol), potassium salt of **1** (1.072 g, 2.0 mmol), and TBAB (64.5 mg, 0.2 mmol) in DMF (14 mL) was stirred at 60 °C for 72 h, and then the reaction mixture was poured into water. The polymer obtained was reprecipitated from $CHCl_3$ into methanol and dried in vacuo at 70 °C. The yield of polymer was 80%. The DF was 100 mol %, estimated by the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$): δ 0.98−1.80 (m, 9H), 3.73−3.90 (m, 2H), 4.80−5.30 (m, 2H), 6.10−6.62 (m, 2H), 6.70−7.25 (m, 5H), 7.25−7.57 (m, 3H), 7.57−7.80 (m, 1H). IR (KBr, cm^{-1}): 1713, 1453, 1296, 1268, 1179, 1136.

Synthesis of P-2. A mixture of PCVE (91 mg, 0.85 mmol), **1** (426 mg, 0.85 mmol), K_2CO_3 (373 mg, 2.7 mmol), and TBAB (276 mg, 0.85 mmol) was stirred in DMF (9 mL) at 80 °C for 72 h, and then the reaction mixture was poured into water. The polymer obtained was reprecipitated from THF into methanol and dried in vacuo at 70 °C. The yield of polymer was 401 mg (82%). The DF was 91 mol %, estimated by the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$): δ 0.95−2.05 (m, 9H), 3.40−3.95 (m, 4H), 4.20−4.55 (m, 2H), 6.77−6.98 (m, 1H), 6.98−7.33 (m, 2H), 7.33−7.63 (m, 3H), 7.63−7.70 (m, 1H). IR (KBr, cm^{-1}): 1712, 1453, 1296, 1268, 1178, 1136.

Synthesis of P-3. A mixture of PGMA (28 mg, 0.2 mmol), **1** (100 mg, 0.2 mmol), and TBAB (6.4 mg, 0.02 mmol) were stirred in a mixture of DMF (1 mL) and 2-propanol (0.05 mL) at 80 °C for 72 h, and then the reaction mixture was poured into water. The polymer obtained was reprecipitated from THF into *n*-hexane and dried in vacuo at 70 °C. The yield of polymer was 82%. The DF was 100 mol %, estimated by the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$): δ 0.70−2.20 (m, 11H), 3.00−3.30 (m, 1H), 3.50−4.80 (m, 7H), 6.73−6.95 (m, 1H), 6.97−7.35 (m, 2H), 7.35−7.63 (m, 3H), 7.65−7.85 (m, 1H). IR (KBr, cm^{-1}): 3436, 1715, 1453, 1296, 1263, 1179, 1136.

Synthesis of P-4 from Polycondensation of 15 with 1,4-Diaminocyclohexane. A mixture of **15** (32 mg, 0.04 mmol) and 1,4-diaminocyclohexane (4.7 mg, 0.04 mmol) was stirred in DMF (1.5 mL) at room temperature for 110 h, and then the reaction mixture was poured into water. The polymer obtained was reprecipitated from THF into H_2O and dried in vacuo at 70 °C. The yield of polymer was 19.6 mg (81%). The number-average molecular weight of polymer determined from GPC was 17 800. ^{1}H NMR (DMF-d_6): δ 1.30 (s, 3H), 1.38 (s, 3H), 1.35−1.68 (m, 4H), 1.86−2.14 (m, 4H), 3.55−4.00 (m, 2H), 4.15 (s, 2H), 7.32−7.48 (m, 2H), 7.82−7.96 (m, 2H), 8.40−8.60 (m, 2H). IR (KBr, cm^{-1}): 3307, 1630, 1540, 1455, 1296, 1178, 1138.

Synthesis of P-4 from Polycondensation of 2 with 1,4-Diaminocyclohexane using DPPA as Condensation Reagent. A mixture of **2** (44.8 mg, 0.09 mmol), 1,4-diaminocyclohexane (10.1 mg, 0.09 mmol), DPPA (48.3 mg, 0.18 mmol), and triethylamine (35.6 mg, 0.35 mmol) was stirred in DMF (1 mL) at room temperature for 48 h, and then the reaction mixture was poured into water. The polymer obtained was reprecipitated from DMF into H_2O and dried in vacuo at 70 °C. The yield of polymer was 45.8 mg (88%). The number-average molecular weight of polymer determined from GPC was 42 700.

Synthesis of P-4 from Polycondensation of 2 with 1,4-Diaminocyclohexane Using 3-Nitrobenzeneboronic Acid. In the presence of 3-nitrobenzeneboronic acid (1.5 mg, 0.009 mmol), a mixed solution of **2** (46.4 mg, 0.09 mmol) and 1,6-hexanediol (10.4 mg, 0.09 mmol) in *o*-xylene (3 mL) was refluxed for 48 h with removal of water (4 Å molecular sieves). The reaction products were not soluble in DMF.

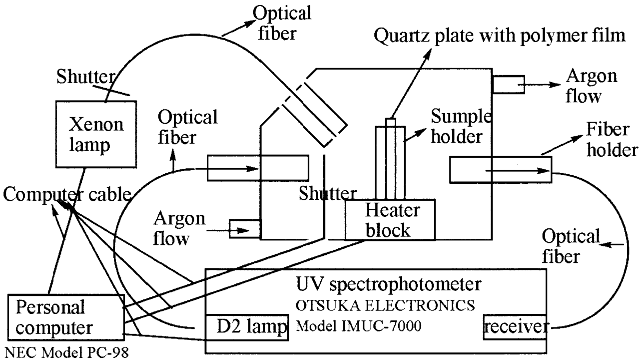


Figure 1. Apparatus for the examination of durability of NBD polymer. The spectrophotometer, heater, and shutter were controlled automatically by personal computer.

Synthesis of P-5 from Polycondensation of 2 with 1,6-Hexanediol Using $HfCl_4(THF)_2$. In the presence of $HfCl_4(THF)_2$ (11 mg, 0.005 mmol), a mixed solution of **2** (45.2 mg, 0.09 mmol) and 1,6-hexanediol (10.5 mg, 0.09 mmol) in *o*-xylene (1 mL) was refluxed for 48 h with removal of water (4 Å molecular sieves). The reaction mixture was poured into water, reprecipitated from THF into methanol, and dried in vacuo at 70 °C. The yield of polymer was 42.8 mg (82%). The number-average molecular weight of the polymer determined from GPC was 39 300. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 3H), 1.34 (s, 3H), 1.30−1.65 (m, 4H), 1.65−1.92 (m, 4H), 3.78 (s, 2H), 4.17−4.42 (m, 4H), 7.15−7.25 (m, 2H), 7.65−7.75 (m, 2H). IR (KBr, cm^{-1}): 1718, 1458, 1297, 1244, 1178, 1137.

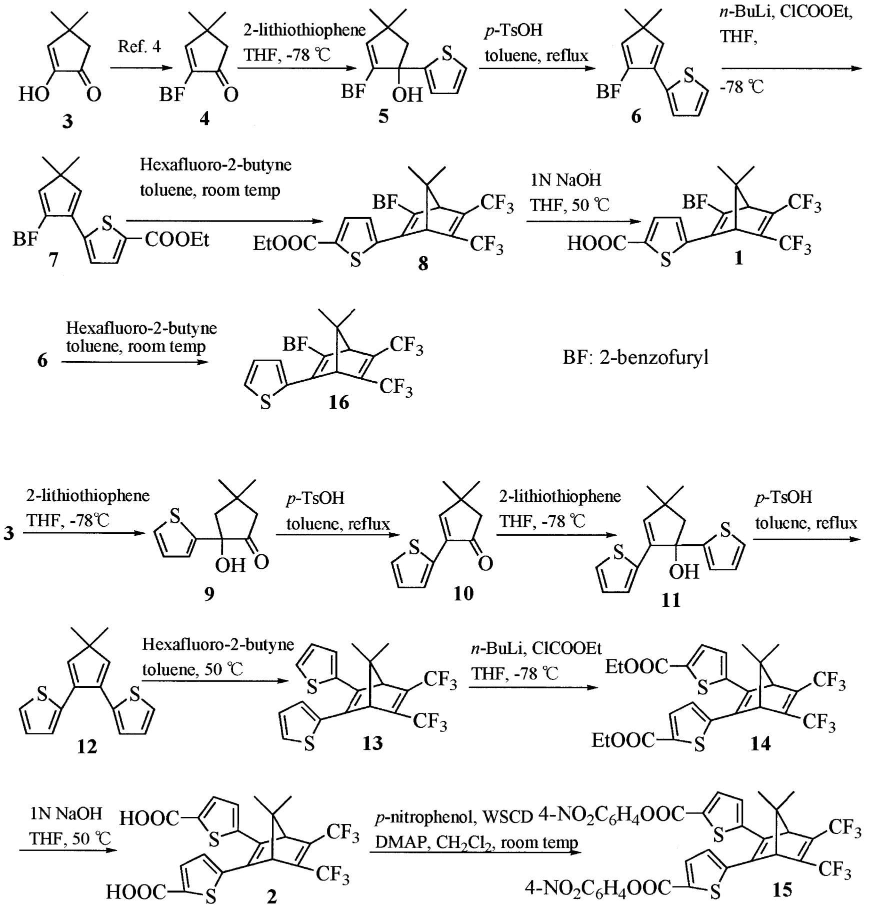
Synthesis of P-5 from Polycondensation of 2 with 1,6-Hexanediol Using WSCD as Condensation Reagent. A mixed solution of **2** (31.0 mg, 0.06 mmol), 1,6-hexanediol (7.2 mg, 0.06 mmol), DMAP (1.8 mg, 0.015 mmol), and WSCD (28.1 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) was stirred for 48 h at room temperature. The reaction mixture was poured into deuterated HCl. Then the polymer was washed with water, reprecipitated from THF into methanol, and dried in vacuo at 70 °C. The yield of polymer was 31.7 mg (88%). The number-average molecular weight of the polymer determined from GPC was 18 300.

Typical Procedure for the Photoisomerization of NBD Moieties in the Polymers in Solution. A quartz cell was charged with a solution of a NBD polymer in THF (5×10^{-5} mol/L), and then the solution was irradiated with a 500 W xenon lamp (Ushio Electric Co., UXL-500D-O) with a thermal-ray cut filter (Hoya; HA50), in which the energy of the incident light (1.8−2.0 mW/cm^2 (313 nm)) was monitored by an electric photon counter (ORC model UV-M30). The conversion and the photoisomerization rates from NBD moieties to QC moieties were calculated by the disappearance of the maximum absorption of the NBD moieties, as measured by a UV spectrophotometer.

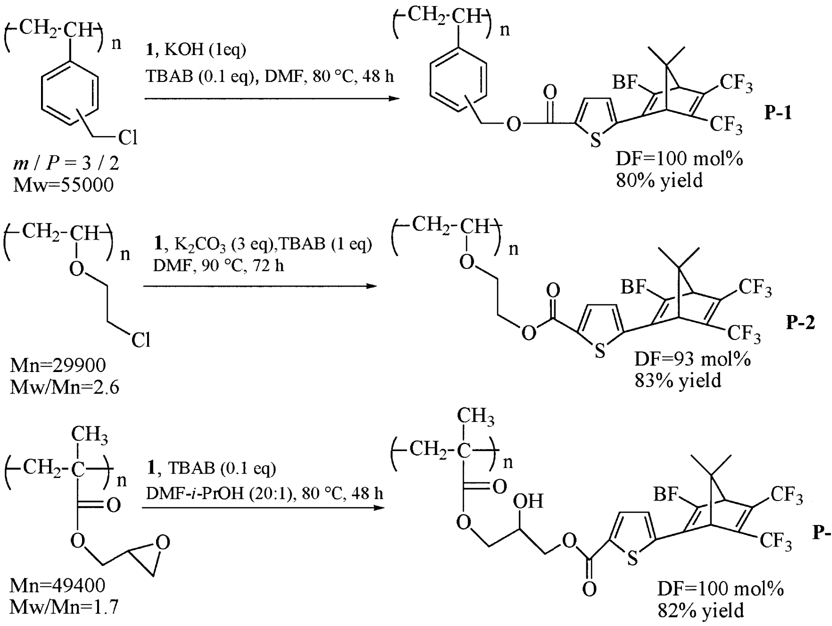
Examination of the Durability of the NBD Moieties in the Polymer. Preparation of Polymer Film. A solution of polymer (7.4 mg) in chloroform (1 mL) was degassed by three consecutive freeze−pump−thaw cycles and cast on a quartz plate. Then, the quartz plate-cast polymer was dried in vacuo at 80 °C for 15 h. Furthermore, a solution of PMMA in chloroform was cast on the film and dried in the same way as above.

Examination of the Durability. The experiment was performed under an argon atmosphere by the apparatus automatically, as shown in Figure 1. Initially, the polymer film was irradiated with a 500 W xenon lamp until the absorbance of the maximum absorption of the NBD moieties disappeared. Then, the irradiated film was heated on a hot plate until the absorbance of the NBD moieties was reversed (irradiated for 2 min and then heated at 80 °C for 20 min). The durability was evaluated from the differences in the absorbance values between the NBD moieties and the QC moieties at maximum absorption of the NBD moieties on the first and *n*th cycles of reactions.

Scheme 1. Synthesis of NBD Derivatives 1, 2, and 15



Scheme 2



Results and Discussion

Synthesis of Polymers Containing Trifluoromethyl-Substituted Donor−Acceptor NBD Moieties. NBD−carboxylic acid **1**, NBD−dicarboxylic acid **2**, and bis(4-nitrophenyl) esters of **2** (**15**) were synthesized from cyclopentanedione derivative **3** according to the reaction sequences shown in Scheme 1. This NBD synthesis strategy involves the facile introduction of a variety of substitutions into the 2,3-positions, the charge transfer (C−T) donor site, of the NBD framework. NBD−carboxylic acid **1** was synthesized from the Diels−Alder reaction of hexafluoro-2-butyne with cyclopentadiene derivative **7** containing an ethoxycarbonyl group at the 5-position of the thiophene ring, followed by hydrolysis using aqueous sodium hydroxide. The ethoxycarbonyl group was introduced to the thiophene ring of **6** by the

Scheme 3

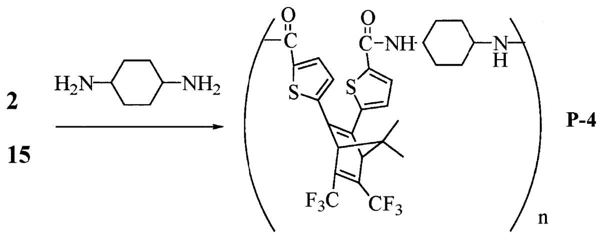


Table 1. Synthesis of Polyamide Containing CF_3−NBD Moieties

reagents and conditions	yield (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b
15, DMF, rt, 4 days	81	1.78	1.96
2, DPPA,[a] Et_3N, DMF, rt, 2 days	88	4.27	5.77
2, 3-$NO_2C_6H_4B(OH)_2$ (0.1 equiv), *o*-xylene, reflux, 2 days	gel		

[a] Diphenylphosphoryl azide. [b] Estimated by GPC based on polystyrene standards (eluent: DMF).

Scheme 4

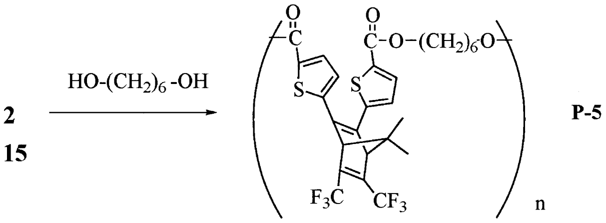


Table 2. Synthesis of Polyester Containing CF_3−NBD Moieties

reagents and conditions	yield (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c
2, $HfCl_4 \cdot THF_2$ (0.2 equiv), *o*-xylene, reflux, 2 days	82	3.93	2.33
2, WSCD,[a] DMAP,[b] CH_2Cl_2, rt, 2 days	88	1.83	2.32
15, DMF, rt, 7 days	no reaction		

[a] Dimethylaminopropylethylcarbodiimide hydrochloride. [b] (Dimethylamino)pyridine. [c] Estimated by GPC based on polystyrene standards (eluent: DMF).

reaction of ethyl chloroformate with a lithium reagent prepared from **6**. NBD−dicarboxylic acid **2** was synthesized from NBD derivative **13** containing two thienyl groups at the 2,3-positions of the NBD framework by the introduction of a carboxyl group in the same way as **1**. Bis(4-nitrophenyl) ester **15** was obtained from **2** by esterification with 4-nitrophenol using carbodiimide derivatives as condensation reagent. The structure of the resulting NBD derivatives was confirmed by elemental analysis, MS, IR, and NMR spectra.

Polymers containing CF_3−NBD moieties in the side chain were synthesized according to Scheme 2. The substitution reaction of potassium salt of **1** with PCMS[3] proceeded using TBAB as PTC catalyst in DMF at 80 °C for 48 h to give **P-1** in 80% yield. The substitution reaction of potassium salt of **1** with poly(2-chloroethyl vinyl ether)[4] also proceeded using TBAB in DMF at 90 °C for 72 h to give **P-2** in 83% yield. The addition reaction of **1** with poly(glycidyl methacrylate)[5] proceeded using TBAB in DMF−2-propanol (20:1) at 80 °C for 48 h to give **P-3** in 82% yields. The polymers obtained by the above reaction conditions did not contain any gel products. It was estimated from the ^1H NMR spectral data of the reaction mixture of **P-1**, **P-2**, and **P-3** that 100, 93, and 100% NBD carboxylic acid, respectively, were added to the pendant group in the polymers. The ^1H NMR spectrum of **P-1** showed a signal of the CH_2 protons of the benzyl ester at 4.75−5.40 ppm, although no signal of the CH_2 protons of the benzyl chloride at 4.10−4.55 ppm was detected. The ^1H NMR spectrum of **P-2** showed a signal of the aromatic protons of the thiophene ring at 7.43 and 7.66 ppm, although traces of the signal of the aromatic protons of the thiophene ring of **1** were found at 7.57 and 7.82 ppm. No traces of signals of the CH_2 protons of the glycidyl group at 2.65 and 2.85 ppm were detected in the ^1H NMR spectrum of **P-3**. Furthermore, the CH protons (5.00−5.50 ppm) from α cleavage of the epoxy ring were not detected. It seems that β cleavage of the epoxy ring proceeded selectively under the reaction conditions. These results show that CF_3−NBD moieties could be readily introduced in the side chain of many polymers.

Next, we synthesized polymers containing CF_3−NBD moieties in the main chain as shown in Schemes 3 and 4 and in Tables 1 and 2. Polyamide **P-4** was synthesized by polycondensation of the bis(4-nitrophenyl) ester **15**, obtained from NBD−dicarboxlic acid **2**, with *trans*-1,4-diaminocyclohexane as diamine.[8,13] The yield and the M_n of **P-4** were 82% and 17 800, respectively. This polyamide was also synthesized from **2** with diamine using DPPA as condensation reagent; the yield and the M_n were 88% and 42 900, respectively. On the other hand, gel products were produced when polycondensation was carried out using 3-nitrobenzeneboronic acid as the Lewis acid catalyst. These results suggest that the procedure using a condensation reagent was suitable for the synthesis of **P-4**. The polycondensation of **2** with 1,6-hexanediol as diol was carried out using hafnium chloride as the Lewis acid catalyst[14] to give polyester **P-5** with a small amount of gel products. The yield and the M_n of **P-5** were 82% and 39 300, respectively. This polyester was also synthesized from **2** with diol using WSCD as condensation reagent; the yield and the M_n were 88% and 18 300, respectively.

On the other hand, polycondensation of **15** with diol did not proceed, although polycondensation of **15** with diamine proceeded smoothly, because the nucleophilicity of diamine to **15** was higher than that of diol. These results suggest that the procedure using a Lewis acid catalyst was suitable for the synthesis of **P-5**. IR and NMR spectra confirmed the structure of the new polymers.

Photoisomerization of NBD Polymers. As shown in Table 3 and Figure 2, these polymers had a large absorption band in the visible region and the absorption edge reached 500 nm, because they had a charge-transfer absorption band ascribed to charge-transfer interaction between the donor olefin and acceptor olefin parts of the molecule. As shown in Table 3, the CF_3−NBD moieties in the polymer had a longer wavelength absorption band than the parent CF_3−NBD derivatives, **16** and **13**, which had no carbonyl group in the aryl group. This means that carbonyl seems to act mainly by extending the conjugation of the aryl group and that its electron-withdrawing effect does not compensate for its conjugative effect.

The photoisomerization of the NBD moieties in the polymer in THF solution (5×10^{-5} mol/L) was carried out by irradiation with a 500 W xenon lamp. Changes in the UV spectra of **P-1** and **P-5** in THF solution are shown in Figure 2. The maximum absorption of the NBD moieties decreased very rapidly, and the NBD

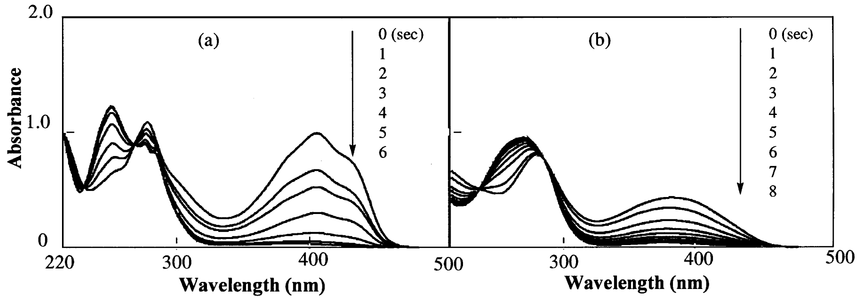


Figure 2. Change of UV spectra of NBD polymers in the THF solution upon irradiation with a Xe lamp (1.80−2.00 mW/cm^2 at 310 nm): (a) **P-1**; (b) **P-5**.

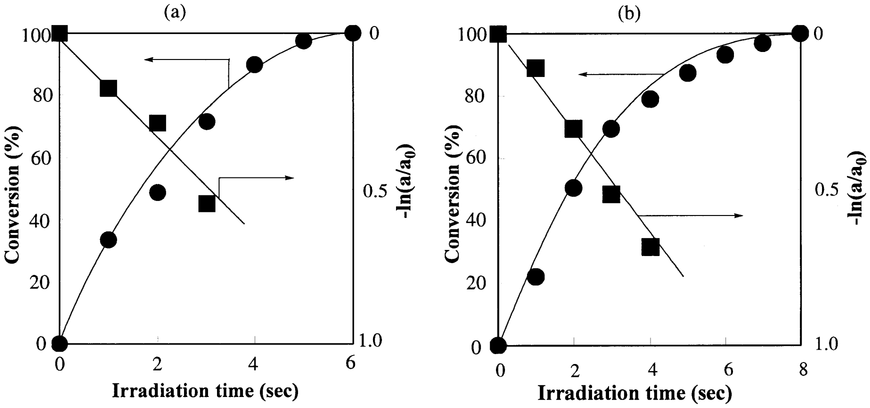


Figure 3. Photoisomerization of NBD moieties of NBD polymers in THF solution upon irradiation with a xenon lamp (1.80−2.00 mW/cm^2 at 310 nm): (a) **P-1**; (b) **P-5**.

Table 3. Absorption Spectral Data of Polymers Containing CF$_3$−NBD Moieties in THF

compound	λ_{max} (nm)^a	λ_{edge} (nm)^{a,b}	λ_{iso} (nm)^a
16	273, 389	480	
P-1	282, 407	505	271
P-2	282, 407	505	271
P-3	282, 407	505	271
13	364	470	
P-4	288, 379	503	288
P-5	285, 385	505	285

[a] 5 × 10^{-5} mol dm^{-3} solution in THF. [b] $\epsilon = 10$.

Table 4. First-Order Rate Constants of Photoisomerization of NBD Polymers[a]

polymer	k_{obsd} (s^{-1}) in THF solution^b	polymer	k_{obsd} (s^{-1}) in THF solution^b
P-1	0.65	**P-4**	*c*
P-2	0.63	**P-5**	0.64
P-3	0.83		

[a] Irradiated by 500 W Xe lamp. [b] 5 × 10^{-5} mol/L. [c] **P-4** solved in THF not completely.

moieties isomerized quantitatively to the corresponding QC moieties after 6 and 8 s of irradiation, respectively. In addition, isosbestic points at 235 and 272 nm in **P-1** or 241 and 288 nm in **P-5** were observed. These results mean that the photoisomerization of the NBD moieties in these polymers to the QC moieties occurred selectively without any side reactions.

As shown in Figure 3, the NBD moieties in these polymers in THF solution isomerized very fast, and the observed rate of the photoisomerization of the NBD moieties obeyed first-order kinetics. As shown in Table 4, the photoisomerization rate of **P-3** was slightly higher than that of **P-1** and **P-2**. These results suggest that the photoisomerization rate of the NBD moieties was affected by the structure of the main chain of the polymers. It has been reported that the photoisomerization rate of NBD derivatives was affected by the polarity of the solvent and was higher in a more polar solvent.[15] Furthermore, it has also been reported that the photoisomerization rate of the NBD moieties in a polymer was affected by the structure of the polymer chain.[4c] Photoisomerization of the NBD moieties in **P-3** proceeded more effectively, because **P-3** contains a hydroxy group which gives the NBD moieties a polar environment and, further, has flexibility which allowed the NBD moieties to take suitable conformations for photoisomerization. Furthermore, the photoisomerization rate of the NBD moieties in **P-5** was almost the same as that of the NBD moieties in **P-1** and **P-2**, although **P-5** contained the NBD moieties in the main chain and the structure of the NBD moieties was not the same as that of **P-1** and **P-2**. It seems that the photoisomerization rate of the NBD moieties in these polymers (**P-1**, **P-2**, and **P-5**) was the same irrespective of the structure of NBD molecules in this irradiation condition, since these two NBD moieties have a large absorption band in the visible region and the wavelength of the absorption edge of these NBD moieties was almost the same, although the reactivity of the photoisomerization of these NBD moieties was affected by the structure of NBD moieties.

Examination of the Durability of the NBD Moieties in the Polymer. We also examined the durability of the CF$_3$−NBD moieties in the polymer for repeated cycles of interconversion. Recently, Nagai et al. reported that CF$_3$−NBD derivatives had efficient fatigue resistance.[10] As shown in Figure 4, the CF$_3$−NBD moieties in **P-3** possessed good fatigue resistance, and the degradation of the NBD moieties was 55% after 1000 cycles. It is apparent that the NBD polymers containing CF$_3$−D−A NBD moieties are more durable than other NBD polymers as the introduction of the CF$_3$ groups

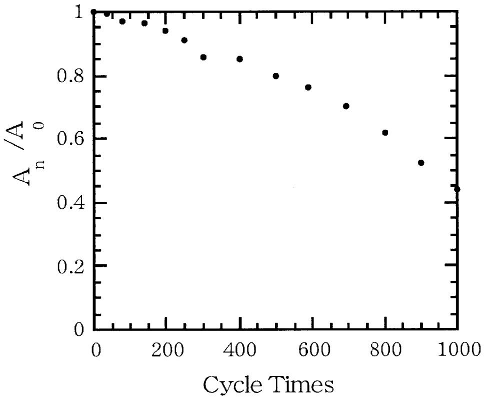


Figure 4. Durability of **P-3**.

and the donor substituents into the NBD framework suppresses the formation of byproducts caused by the polymerization of the NBD and QC moieties, since the large steric effect of the CF_3 groups and the donor substituents shield the $C{=}C$ bond of NBD moieties and the strained QC moieties which contained the cyclopropane and cyclobutane rings. It has been reported that the CF_3 group was rigid and spherical and showed as large a steric effect as that of the *sec*-butyl group.[16] Furthermore, the physical and chemical stability of the CF_3 groups possibly gives the NBD and QC moieties durability. It is known that fluorine imparts to molecules increased oxidative and thermal stability because the $C-F$ bond is stronger than the $C-H$, $C-C$, or $C-N$ bond.

However, these data show that the durability of the CF_3−NBD moieties in the polymer was slightly lower than that of the CF_3−NBD derivatives that were examined in PMMA solid film doped with NBD (5 wt %).[10] It was reported that the durability of fulgide derivatives decreased in PMMA solid film, which was highly doped with fulgide derivatives in comparison with that in a dilute solution.[17] It seems that a side reaction that produced polymerization of the NBD and QC molecules occurred readily in polymer film highly doped with NBD. Therefore, the monomer might show better durability than the CF_3−NBD moieties in the polymer that contained NBD moieties in high concentration.

Conclusion

From all these results, the following conclusions can be drawn. (1) Polymers containing CF_3−NBD moieties in the side chain or in the main chain were synthesized by substitution or addition of CF_3−NBD−carboxylic acid derivative or by polycondensation of CF_3−NBD−dicarboxylic acid derivative, respectively. (2) These polymers had a large absorption band in the visible region, and NBD moieties in these polymers isomerized very fast. (3) The CF_3−NBD moieties in these polymers showed efficient resistivity to repeated cycles of interconversion.

Acknowledgment. This work was partly supported by High-Tech Research Project from the Ministry of Education, Science, Sports and Culture, which is gratefully acknowledged.

References and Notes

(1) Hautala, R. R.; Little, J.; Sweet, E. *Sol. Energy* **1977**, *19*, 503. (b) King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 385. (c) Hautala, R. R.; King, R. B.; Kutal, C. *Solar Energy*; Hamana: Clifton, NJ, 1979; p 333.

(2) Nishikubo, T.; Shimokawa, T.; Sahara, A. *Macromolecules* **1989**, *22*, 8. (b) Morino, S.; Watanabe, T.; Magaya, Y.; Horie, K. *J. Photopolym. Sci. Technol.* **1994**, *7*, 121. (c) Kinoshita, K.; Horie, K.; Morino, S.; Nishikudo, T. *Appl. Phys. Lett.* **1997**, *70*, 2940. (d) Takahashi, S.; Samata, K.; Mura, H.; Machida, S.; Horie, K. *Appl. Phys. Lett.* **2001**, *78*, 1. (e) Kato, Y.; Muta, H.; Takahashi, S.; Horie, K.; Nagai, T. *Polym. J.* **2001**, *33*, 868. (f) Miki, S.; Asako, Y.; Yoshida, Z. *Chem. Lett.* **1987**, 195.

(3) Nishikubo, T.; Sahara, A.; Shimokawa, T. *Polym. J.* **1987**, *19*, 991. (b) Nishikubo, T.; Shimokawa, T.; Sahara, A. *Macromolecules* **1989**, *22*, 8. (c) Nishikubo, T.; Hijikata, C.; Iizawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 671. (d) Iizawa, T.; Hijikata, C.; Nishikubo, T. *Macromolecules* **1992**, *25*, 21. (e) Nishikubo, T.; Kameyama, A.; Kishi, K.; Hijikata, C. *React. Polym.* **1994**, *24*, 65. (f) Nishikubo, T.; Kameyama, A.; Kishi, K.; Mochizuki, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2765.

(4) Kameyama, A.; Watanabe, S.; Kobayashi, E.; Nishikubo, T. *Macromolecules* **1992**, *25*, 2307. (b) Hijikata, C.; Nishikubo, T. *Polym. J.* **1990**, *22*, 551. (c) Nishikubo, T.; Kameyama, A.; Kishi, K.; Kawashima, T.; Fujiwara, T.; Hijikata, C. *Macromolecules* **1992**, *25*, 4469.

(5) Nishikubo, T.; Kawashima, T.; Watanabe, S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1659. (b) Kishi, K.; Kameyama, A.; Nishikubo, T. *Kobunshi Ronbunshu* **1993**, *50*, 137. (c) Nishimura, I.; Kameyama, A.; Sakurai, T.; Nishikubo, T. *Macromolecules* **1996**, *29*, 3818.

(6) Iizawa, T.; Sueyoshi, T.; Hijikata, C.; Nishikubo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 3091.

(7) Takamura, S.; Kameyama, A.; Nishikubo, T. *Kobunshi Ronbunshu* **1995**, *52*, 684. (b) Tsubata, A.; Kameyama, A.; Nishikubo, T. *Kobunshi Ronbunshu* **1996**, *53*, 5307. (c) Tsubata, A.; Kameyama, A.; Nakamura, S.; Nishikubo, T. *Kobunshi Ronbunshu* **1997**, *54*, 37. (d) Tsubata, A.; Uchiyama, T.; Kameyama, A.; Nakamura, S.; Nishikubo, T. *Macromolecules* **1997**, *30*, 5649. (e) Ikeda, A.; Tsubata, A.; Kameyama, A.; Nishikubo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 917.

(8) Nishikubo, T.; Kameyama, A.; Kishi, K.; Nakajima, T. *Polym. J.* **1992**, *24*, 1165. (b) Nishikubo, T.; Kameyama, A.; Kishi, K.; Nakajima, T. *Macromolecules* **1994**, *27*, 1087. (c) Takamura, S.; Kameyama, A.; Nishikubo, T. *Kobunshi Ronbunshu* **1995**, *52*, 415.

(9) Kawashima, N.; Kameyama, A.; Nishikubo, T.; Nagai, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1764. (b) Konno, Y.; Kameyama, A.; Nishikubo, T.; Nagai, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2683. (c) Ikeda, A.; Kameyama, A.; Nakamura, S.; Nishikubo, T.; Nagai, T. *Macromolecules* **2001**, *34*, 2728.

(10) Nagai, T.; Takahashi, I.; Shimada, M. *Chem. Lett.* **1999**, 897. (b) Nagai, T.; Fujii, K.; Takahashi, I.; Shimada, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1673.

(11) The preparation of the polymers containing CF_3-substituted D−A−NBD moieties was reported as a communication. Nagai, T.; Shimada, M.; Nishikubo, T. *Chem. Lett.* **2001**, 1308.

(12) Coombers, J. D.; Eley, D. D. *J. Chem. Soc.* **1957**, 3700.

(13) Kamogawa, H.; Gochou, S.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2306.

(14) Ishihara, K.; Ohara, S.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4196. (b) Ishihara, K.; Ohara, S.; Yamamoto, H. *Macromolecules* **2000**, *33*, 3511.

(15) Ishihara, K.; Ohara, S.; Yamamoto, H. *Sience* **2000**, *290*, 1140.

(16) Maafi, M.; Aaron, J.-J.; Lion, C. *Chem. Lett.* **1994**, 1865.

(17) Nagai, T.; Nishioka, G.; Koyama, M.; Ando, A.; Miki, T.; Kumadaki, I. *Chem. Pharm. Bull.* **1992**, *40*, 593. (b) Nagai, T.; Nishioka, G.; Koyama, M.; Ando, A.; Miki, T.; Kumadaki, I. *J. Fluorine Chem.* **1992**, *57*, 229.

(18) Suzuki, H.; Tomoda, A.; Ishizuka, M.; Kaneko, A.; Furui, M.; Mastushima, R. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3968.

MA0214207