

Polycondensation of Bis(cyanoacetate) and *a,10b*Dihydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarbaldehyde via Knoevenagel Reaction: Synthesis of Donor–Acceptor Polymers Containing Shoulder-to-Shoulder Main Chains

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ABSTRACT: Compound **5a,10b**-dihydrobenzofuro[2,3-**b**]benzofuran-2,9-dicarbaldehyde (**II**) was prepared by two-step reactions from *p*-cresol and glyoxal. The bis(cyanoacetate) monomers (**III**) were prepared in a high yield by reacting ethyl cyanoacetate with the appropriate diol in the presence of tetra-*n*-butyl titanate. The polymers from **II** and **III** were synthesized by Knoevenagel polycondensation that was first carried out in anhydrous THF and followed by a solid-state polycondensation, and main-chain polymers with good glass transition temperatures in high yield were obtained. The polymerization of **II** and **III** afforded polymers **IV**, which exhibited good solubility in most organic solvents. The structure of all the monomers and polymers were characterized by conventional spectroscopic methods. The synthesized polymers contain acceptor groups (cyanide and carbonyl) and a donor group (benzodihydrofuran) in their main chain. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 505–511, 2001

Key words: nonlinear optical polymers; main-chain polymers; shoulder-to-shoulder; donor–acceptor polymers

INTRODUCTION

In general, organic molecules bearing electron donor and acceptor groups separated by large conjugated frameworks have been shown to possess large values of second-order molecular hyperpolarizability.¹ In the other words, new nonlinear optics (NLO phores) continue to be discovered; the basic components remain the same: a strong donor moiety in conjugation with strong acceptor groups.²

Polymeric systems offer a potential for optical device production that includes high process flexibility, higher transparency, and large second-order susceptibilities.² For NLO application, three types of organic polymers have been developed with guest–host polymers, side-chain polymers, and main-chain polymers.^{2,3} The more promising system is that the chromophore is a part of the polymer's main chain. There are several reasons: First, a bulk material with aligned polymer chains should have excellent temporal stability. Second, there is no need for supporting backbone or crosslinking functionalities. Third, the theory has been well established. A theoretical discus-

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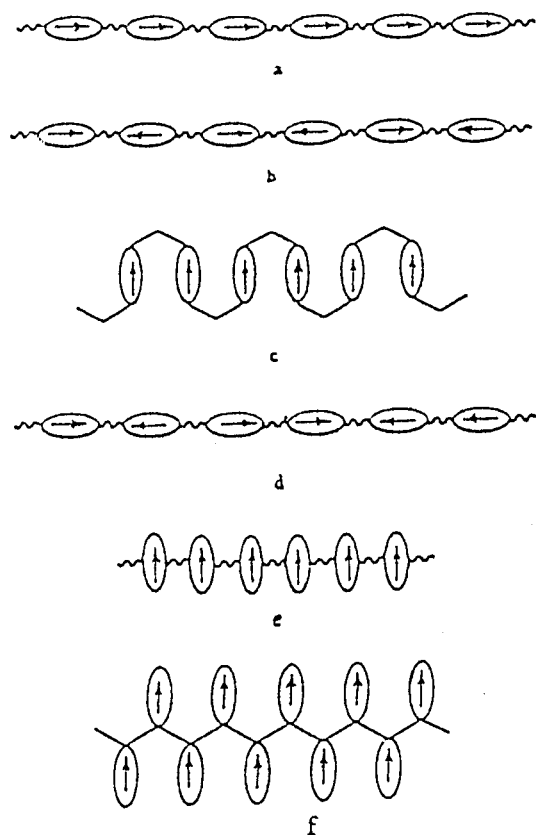


Figure 1 Chromophore arrangements in a main-chain polymer: (a) head-to-head; (b) head-to-tail; (c) tail-to-tail; (d) accordion; (e) random; (f) shoulder-to-shoulder.

sion on main-chain NLO phore enhancement was given by Willand and Williams.⁴ The main-chain polymers are classified head-to-head, head-to-tail, tail-to-tail, accordion, random, shoulder-to-shoulder, and slipped shoulder-to-shoulder (Fig. 1).^{3–20}

In the shoulder-to-shoulder arrangement, the dipole alignment should be easier to achieve by applying an electric field than in a structure where the dipole moments are pointing along the polymer main chain. Main-chain polymers in which the chromophores are arranged as shoulder-to-shoulder were reported first by Wade and coworkers.⁶ In this work, dihydrofuran derivatives as donor and bis(cyanoacetate) as acceptor parts were selected. The polymers of *5a,10b*-dihydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarbaldehyde (**II**) and bis(cyanoacetate) monomers (**III**) were prepared by Knoevenagel polycondensation.⁶ In the resulting polymers, dipoles lie parallel to each other shoulder-to-shoulder. The shoulder-to-shoulder arrangement of NLO chromophores^{21,22} introduce a main-chain polymer with large off-diagonal tensor components.

EXPERIMENTAL

Materials

All manipulations of the compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under argon and nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ¹H-NMR spectra were obtained on Bruker 300 and 80 MHz spectrometers; FTIR spectra were performed with a Shimadzu-8010 M; and mass spectra were carried out on a Hewlett-Packard mass spectrometer Model 5890. ¹H-NMR chemical shifts are reported in δ (ppm) versus TMS in CDCl₃. Ethyl cyanoacetate (98% purity), 1,6-hexanediol, 1,4-butandiol, *p*-cresol, glyoxal (40% aqueous solution), and titanium tetrachloride were purchased from Aldrich (U.K.). Thermal analysis of the copolymers was performed using a DSC, STA 625. GPC data were collected on a Maxima 820 employing a size-exclusion column ($10^3 \times 10^4 \times 10^5 \times 10^6$ Å). Molecular weight data are referenced relative to polystyrene standards.

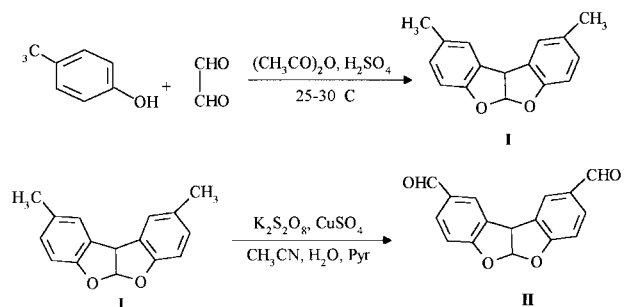
5a,10b-Dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran, **I**

A mixture of *p*-cresol (0.10 mol) and glyoxal (0.05 mol, 40% aqueous solution) was dissolved in glacial acetic acid (100 mL). Concentrated sulfuric acid (20 mL) was added drop by drop with stirring, and the temperature of the reaction mixture was kept between 25 and 30°C. During the addition of sulfuric acid (25–30 min), the acetal began to precipitate from the solution. Then, the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water (500 mL), and the product was removed by filtration and washed with abundant water and dried at 100°C. The crude product recrystallized from ethanol gave 6.3 g (53%) of acetal **I**; mp 194–195°C.

¹H-NMR (CDCl₃): δ 4.89 (d, 1H, 10b), 6.6–7.0 (m, 7H, aromatic protons and 5b) and 2.1 (s, 6H, 2CH₃). FTIR (KBr), ν (cm⁻¹): 2994.0, 1612.7, 1497.0, and 1000.0. MS: *m/z*, 238 (M, 100%), 195 (39.4%), and 165 (18.1%).

5a,10b-Dihydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarbaldehyde, **II**

A solution of compound **I** (1 g, 4.2 mol) in acetonitrile (60 mL) was added to the solution of potassium peroxydisulfate (6.8 g, 25 mmol) in 20



Scheme 1

mL of water and copper sulfate (0.62 g, 2.5 mmol). To the resulting solution, pyridine (2 mL, 25 mmol) was added and stirred at 65–70°C for 3 h and then extracted with ether. The solvent was removed and the dialdehyde compound (**II**) was separated by a 5% NaOH solution; yield 0.68 g, (60%).

$^1\text{H-NMR}$ (CDCl_3): δ 9.7 (s, 2H, CHO), 6.7–8.0 (m, 7H, aromatic protons and 5b) and 5.0 (d, 1H, 5b). FTIR, $\nu(\text{cm}^{-1})$: 3000.0, 2892.0, 2797.0, 1693.8, 1616.6, 1493.1, 980.0, and 617.3. MS: m/z , 266 (M^+), 237, 209, 181, 152, 132, 104, 76, 63, and 39.

Tetra-*n*-butyl Titanate

A mixture of anhydrous *n*-butanol (0.4 mol) and anhydrous triethylamine (0.4 mol) was dissolved

in anhydrous dichloromethane (100 mL). To the resulting solution, titanium tetrachloride (0.1 mol), which was previously dissolved in anhydrous dichloromethane (40 mL) was added drop by drop and stirred at 0–10°C. During the addition of titanium tetrachloride in anhydrous dichloromethane, triethylammonium chloride began to precipitate from the solution. The precipitate was removed by filtration, and a crude solution of tetra-*n*-butyl titanate was distilled under reduced pressure to give a high-boiling-point yellow liquid (bp 160–163°C/3 mmHg).

Bis(cyanoacetate), IIIa

A Schlenk flask was charged with cyanoacetate (10.0 g, 88.4 mmol), 1,6-hexanediol (5.22 g, 44.2 mmol), and tetra-*n*-butyl titanate (0.45 g, 0.3 mL, 1.5 mol %). The mixture was heated in an oil bath at 100°C for 12 h under a slow stream of nitrogen to purge the ethanol from the reaction vessel. The mixture was allowed to cool and filtered through a pad (4 × 7 cm) of deactivated alumina. The alumina was washed with chloroform (150 mL) and the solvents were removed from the filtrate under reduced pressure. The crude products were recrystallized from hot hexane and ethylacetate (1/1, v/v). The white crystalline compound was collected and dried under reduced pressure to afford 10.0 g (90%) of $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_6\text{O}_2\text{CCH}_2$ (**IIIa**); mp 69–70°C;

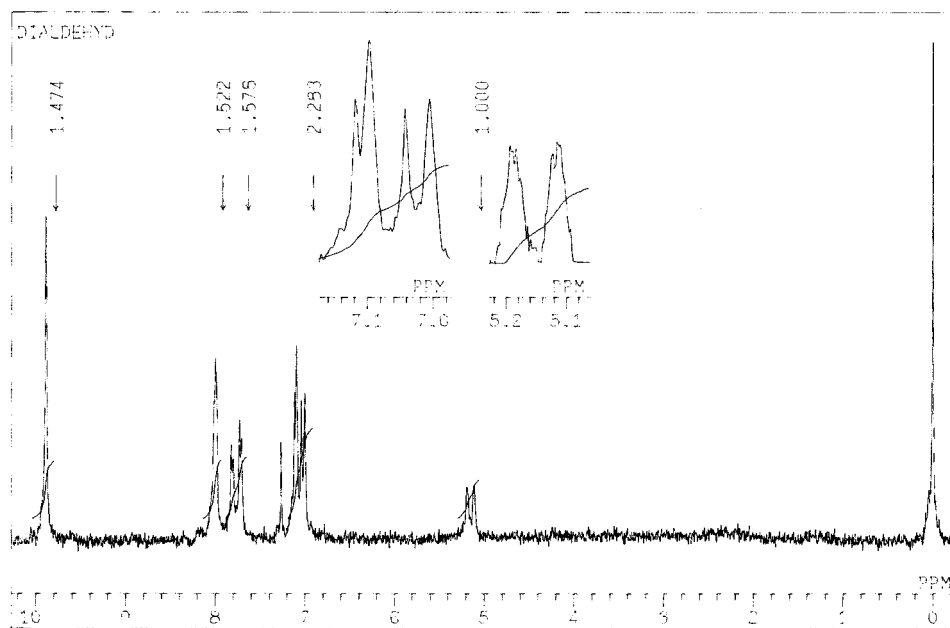
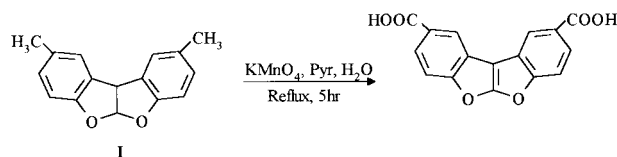


Figure 2 $^1\text{H-NMR}$ spectrum of **5a,10b**-dihydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarbaldehyde (**II**) in CDCl_3 .



Scheme 2

$^1\text{H-NMR}$ (CDCl_3): δ 4.23–4.25 (t, 4H, $2\text{CH}_2\text{O}$), 3.45 (s, 4H, $2\text{CH}_2\text{CN}$), 1.6 (m, 4H, 2CH_2), and 1.3 (m, 4H, 2CH_2). FTIR (KBr), $\nu(\text{cm}^{-1})$: 2945.6, 2277.5, 1742.2, 940.0, 739.4, and 585.1. MS: m/z , 99, 84, 83, 68, 42, 41, 40, and 39.

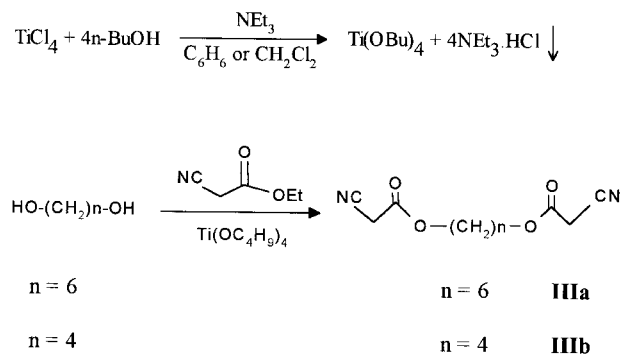
Bis(cyanoacetate), IIIb

The same reaction conditions were conducted except for 1,6-hexanediol to give $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_4\text{O}_2\text{CCH}_2\text{CN}$ (**IIIb**); yield (88%); mp 43–44°C.

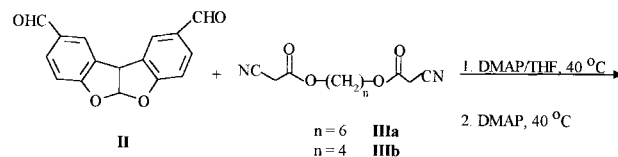
$^1\text{H-NMR}$ (CDCl_3): δ 4.3 (m, 4H, $2\text{CH}_2\text{O}$), 3.4 (s, 4H, $2\text{CH}_2\text{CN}$), and 1.7 (m, 4H, 2CH_2). FTIR (KBr), $\nu(\text{cm}^{-1})$: 2984.2, 2266.8, 1749.9, 1202.3, and 939.9. MS: m/z , 99, 82, 71, 68, 55, 40, and 39.0.

Preparation of Polymers IVa and IVb with Polycondensation Reaction

To a solution of 5*a*,10*b*-dihydrobenzofuro[2,3-*b*]benzofuran-2,9-dicarbaldehyde (**II**) (1 g, 3.7 mmol) and bis(cyanoacetate), **IIIa** and **IIIb** (3.7 mmol) in anhydrous THF (50 mL) was added to 4-(dimethylamino)pyridine (DMAP; 1.35 g, 11.1 mmol) and stirred at 40°C for 1 h; then, the solvent was removed by an argon purge. Polycondensation was carried out at 40°C for 4 h under anhydrous argon. The yellow viscous solid was cooled to room temperature and dissolved in chloroform. The polymer product was purified by reprecipitation into a mixture solution of hexane



Scheme 3



Scheme 4

and ethylacetate (60/40, v/v) to give (89%) yellow powder polymers **IVa** and **IVb**.

IVa: $^1\text{H-NMR}$ (CDCl_3): δ 6.8–8.1 (m, 7H, aromatic protons and 5a), 6.3–6.5 (br, 2H, vinyl protons), 4.9–5.2 (d, 1H, 10b), 4.0–4.4 (d, 4H, 2OCH_2), and 1–3.5 (m, 8H, 4CH_2); FTIR (KBr), $\nu(\text{cm}^{-1})$: 3045.0, 2932.2, 2215.4, 1720.3, 1585.1, 1493.8, 1327.6, 1242.1, 1196.2, 1088.5, 976.0, 822.5, and 760.4; $T_g = 86^\circ\text{C}$.

IVb: $^1\text{H-NMR}$ (CDCl_3): δ 6.4–8.4 (m, 9H, aromatic protons, 5a and vinyl protons), 4.9–5.2 (d, 1H, 10b), 4–4.4 (br, 4H, 2OCH_2), and 1–3.5 (m, 4H, 2CH_2). FTIR (KBr), $\nu(\text{cm}^{-1})$: 3045.0, 2942.5, 2222.0, 1724.1, 1585.1, 1493.8, 1447.0, 1327.6, 1242.1, 1196.2, 1084.4, 1030.5, 976.4, 945.0, 822.7, and 760.1. $T_g = 125^\circ\text{C}$.

RESULTS AND DISCUSSION

Monomers

The reaction of phenols and glyoxal is a known reaction leading to benzofuro[2,3-*b*]benzofuran-type molecules, which was discussed fully by Coxworth²³ and this reaction was used to prepare a thermally stable kind of polymers by Maravigna.²⁴ Further complimentary reactions on the product of *p*-cresol and glyoxal were reported to yield benzofuro[2,3-*b*]benzofuran-2,9-dicarboxylic

Table I Comparison of IR Bonds [$\nu(\text{cm}^{-1})$] for Carbonyl and Cyanide Groups in **III** and **IV**

$\nu(\text{cm}^{-1})$	IIIa	IVa	IIIb	IVb
Carbonyl	1742.22	1720.00	1749.94	1724.00
Cyanide	2277.49	2215.00	2266.77	2222.00

INSTRUMENT	SMPL ID : n=6	DATE RUN: Jul/31/1986
Polymer Laboratories	RUN ID : DR 5712241	GAS 1 :
	SIZE : 3.850 MG	GAS 2 :
	RAIR : 10	DATE : 29.7.77

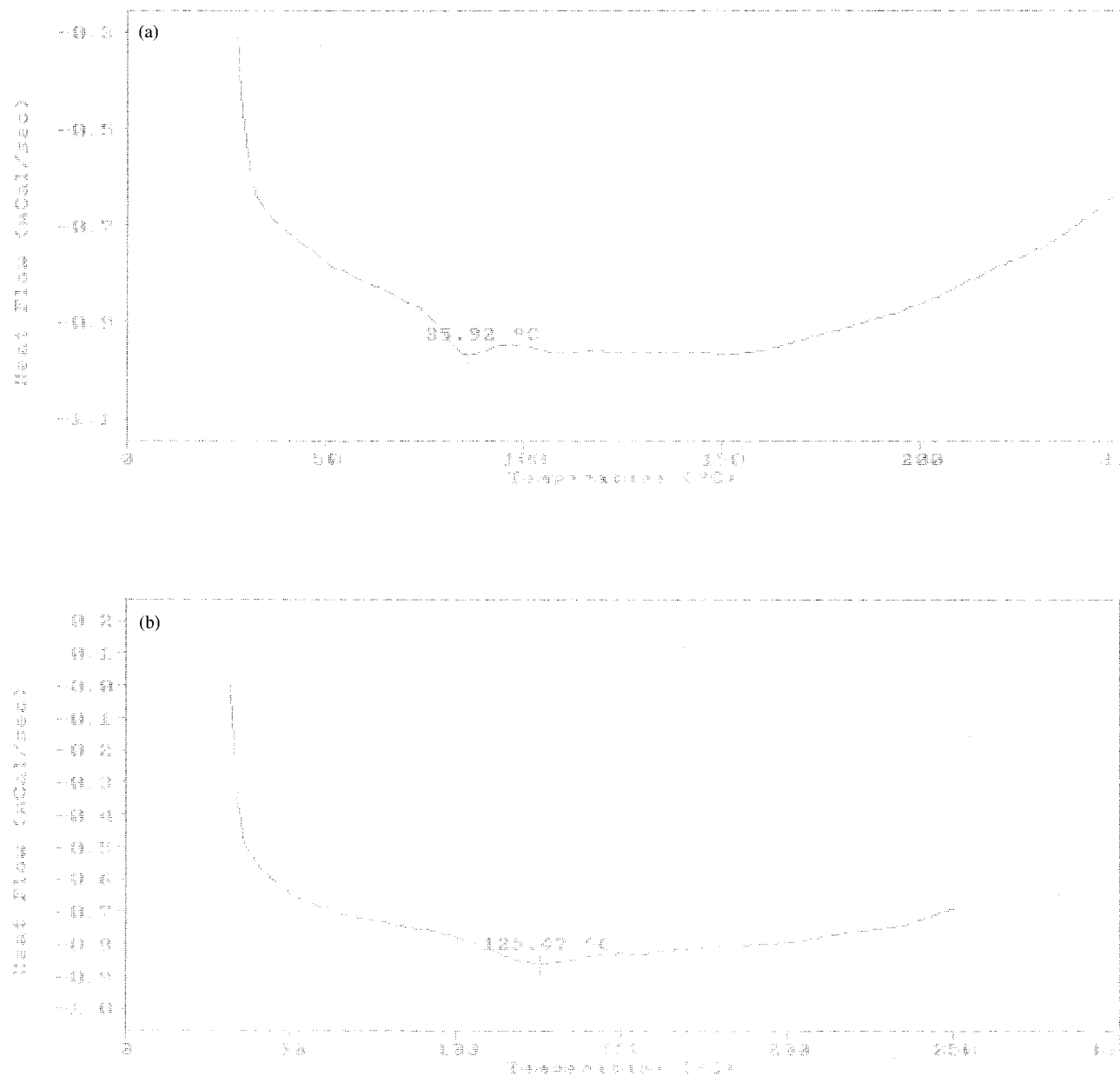


Figure 3 DSC of polymers (a) IVa and (b) IVb.

acid.²⁵ In this work, a dialdehyde molecule with the benzofuro[2,3-*b*]benzofuran structure was synthesized to introduce a Knoevenagel polycondensation reaction. Dialdehyde compound **II** was prepared in two steps from *p*-cresol and glyoxal: The first step involves the reaction of *p*-cresol and aqueous glyoxal which produced 5*a*,10*b*-dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran (**I**).²³ The second step was the oxidation of methyl groups to

aldehyde groups on (**I**) using copper sulfate and peroxydisulfate (Scheme 1).²⁵ The dialdehyde compound was characterized by conventional spectroscopic methods such as FTIR, ¹H-NMR, and mass spectroscopy. The ¹H-NMR spectrum of **II** is shown in Figure 2. However, many oxidation procedures²⁶ with various reagents, such as activated MnO₂, SeO₂, KMnO₄/crown ether, and BaMnO₄, on (**I**) failed to produce a dialdehyde

Table II Molecular Weight and Glass Transition Temperature of Polymers **IVa** and **IVb**

Polymer	M_w	M_n	Polydispersity	T_g (°C)
IVa	4068	3310	1.22	86
IVb	3501	2694	1.29	125

compound with a full aromatic structure. The number of applicable oxidation procedures was limited because of the sensitivity of (**I**) to an acidic condition. Oxidation of **I** with KMnO_4 /pyridine which results in a diacid with a full aromatic structure was previously reported (Scheme 2). Bis(cyanoacetate)–**IIIa** and **IIIb** were prepared in a high yield from the reaction of corresponding diols and ethyl cyanoacetate in the presence of tetra-*n*-butyl titanate.¹⁵ Tetra-*n*-butyl titanate was synthesized separately by the reaction of titanium tetrachloride and *n*-butanol in the presence of triethylamine (Scheme 3).²⁸

Polymers

Polymers **IVa** and **IVb** were prepared by Knoevenagel polycondensation of **II** with **IIIa** and **IIIb**, respectively.⁶ As shown in Scheme 4, the polymers contain highly dipolar repeating units and are the family of main-chain and shoulder-to-shoulder-type polymers. FTIR bands for carbonyl and cyanide groups in bis(cyanoacetate) (**IIIa** and **IIIb**) and the polymers (**IVa** and **IVb**) are summarized in Table I. Comparison of the absorbed bands between the polymers and their corresponding monomers in their IR spectra indicated that a high degree of electron delocalization occurred from donor toward acceptor groups (Table I). The weight-average and number-average molecular weight and polydispersity index of the polymers **IVa** and **IVb** were measured in THF by gel permeation chromatography (GPC) using polystyrene as a standard. The T_g for the polymers obtained from differential scanning calorimetric (DSC) analysis studies (Fig. 3) and the results are shown in Table II. The solubility behavior of the polymers showed that they are completely soluble in common organic solvents such as CHCl_3 , THF, EtOAc, and DMF.

CONCLUSIONS

Polymers **IVa** and **IVb** showed a good glass transition temperature with $T_{ga} = 86^\circ\text{C}$ and $T_{gb} =$

125°C , respectively, and a good solubility in most organic solvents. The synthesized polymers containing highly dipolar repeating units such as acyanide and carbonyl as acceptor groups and benzodihydrofuran as the donor group are main-chain and shoulder-to-shoulder-type polymers which will have third-order NLO properties. In this work, we presented the synthesis of the monomers **II**, **IIIa**, and **IIIb** with high yield. Because of the sensitivity of compound **I** as a precursor to the acidic conditions, the synthesis of the dialdehyde compound (**II**) is a delicate work. The application of many oxidation procedures with various oxidants failed to produce a dialdehyde compound and usually resulted in the formation of diacid groups with a full aromatic structure. The structure of the obtained monomers and polymers were characterized and the data of the NLO properties will be reported later.

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