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Synthesis and characterization of novel polyurethanes containing tricyanocyclopropane ring for piezoelectric applications

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Summary

1-(2',2',3'-Tricyano-3'-carbomethoxycyclopropyl)-3,4-di-2'-hydroxyethoxybenzene (**4**) was prepared by the reaction of bromomalononitrile with methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**). Diol **4** was condensed with 3,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocynate to yield polyurethanes **5** and **6** containing multicyanocyclopropane functionalities in the pendant group. The resulting polymers **5** and **6** were soluble in common organic solvents and the inherent viscosities were in the range of 0.25-0.30 dL/g. Polyurethanes **5** and **6** showed a thermal stability up to 300°C in TGA thermograms. Solution-cast films showed T_g values in the range of 100-130°C and piezoelectric coeffcients (d_{31}) of the poled polymer films were 1.8-2.0 pC/N, which are acceptable for piezoelectric device applications.

Introduction

Functional polymers with piezoelectric activity have long been the subject of curiosity and have caused recent interest (1). It is well-known that crystalline polymers such as poly(vinylidene) fluoride with a large dipole moment exhibit the piezoelectric effects. Amorphous polymers with a high concentration of dipole moments also show piezoelectric properties after poling, such as the copolymer of vinylidene cyanide and vinyl acetate (2). Poly(acrylonitrile) has high concentrations of nitrile dipoles, but the herical structure of the polymer chains causes the radiating dipoles to cancel each other (3). In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation and this polymer also show a piezoelectric activity (4). A potentially piezoelectric polymer must contain a large concentration of dipoles and also mechanically very strong. These polymers have to be film-forming and be able to withstand high voltages without breakdown. Hall and coworkers have proposed that three- and four-membered rings with multicyano substituents held rigidly in alignment will have large dipole moments (5) and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane (5-6) and 1,1,2-tricyano-2-carbomethoxycyclopropane (7-8). These polymers showed T_g values in the range of 130-150°C and piezoelectric coeffcients (d_{31}) of the poled films were 1.5-1.6 pC/N, which are acceptable for piezoelectric device applications. In the developments of piezoelectric polymers for device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization have been proposed. One is to use crosslinked systems and the other is to utilize a high T_g polymers. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. Physically crosslinked systems via hydrogen bonds have the advantages such as homogenity and good processibility relative to the chemically crosslinked systems, which suffer from significant optical loss and poor processibility. In this work we prepared two novel polyurethanes containing tricyanocyclopropane ring, which is presumably effective piezoelectric-chromophore in the side chain. We selected tricyano-substituted cyclopropyl group as a piezoelectric-chromophore because it is somewhat easy to synthesize and have a large dipole moment. We used polyurethane matrix because it forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. The present report describes the synthesis and properties of polyurethanes **5-6**. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and piezoelectric coeffcients (d_{31}) of the poled films. We now report the results of the initial phase of the work.

Experimental

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled under vacuum. Sodium iodide was dried for 4h at 100°C under vacuum. 3,4-Dihydroxybenzaldehyde was used as received. 1-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Piperidine was dried with calcium hydride and fractionally distilled. 2,4-Toluenediisocynate (TDI) was purified by distillation under reduced pressure. 3,3'-Dimentoxy-4,4'-biphenytenediisocynate was recrystallized from ethyl acetate. Bromomalononitrile was prepared according to a procedure similar to that reported already (9). 2-Iodoethyl vinyl ether was prepared according to the procedure previously described (10).

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H-NMR spectra were obtained on a Varian 300MHz NMR spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min up to 700°C was used for the thermal degradation study of polymers under nitrogen. The piezoelectric coefficient (d_{31}) of the corona poled polymer film was mesured to demonstrate its piezoelectric activity. The alignment of the polymer film was carried out by corona poling method. As the temperature was raised to 120°C, 6kV of corona voltage was applied and kept 120°C for 30 min. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

3,4-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**)

3,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from *n*-butanol yielded 25.0 g (90% yield) of pure product **1**. Mp=56-57°C. ^{1}H NMR ($CDC1_3$) δ 4.04-4.36 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.50-6.62 (q, 2H, 2 =CH-O-), 7.01-7.06 (d, 1H, aromatic), 7.45-7.52 (d, 2H, aromatic), 9.86 (s, 1H, -CHO). IR (KBr) 3099, 3080 (w, =C-H), 2952, 2872 (m, C-H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) cm-1.

Methyl 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**)

Piperidine (0.085 g, 1.0 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde **1** (5.57 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) in 140 mL of *n*-butanol with stirring at 0°C under nitrogen. After stirring for 4 h at 0°C, the reaction mixture was cooled to –10°C for crystallization. The product was filtered and washed successively with cold *n*-butanol (60 mL), water (20 mL), and cold *n*-butanol (15 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 6.18g (86% yield) of **2**. Mp=86-87°C. ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H, -$C0_2CH_3$), 4.02-4.38 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.48-6.60 (m, 2H, 2 =CH-O-), 6.95-7.02 (d, 1H, aromatic), 7.47-7.54 (m, 1H, aromatic), 7.75-7.79 (m, 1H, aromatic), 8.11-8.16 (m, 1H, aromatic). IR (KBr) 3113 (w, =C-H), 2954, 2934, 2876 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1638 (s, C=C), 1591, 1519 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.82.

Methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**)

Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl 3,4-di-(2-vinyloxyethoxy)benzylidenecyanoacetate (**2**) (9.34 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0°C. The mixture was stirred at 80°C for 8 h under nitrogen. The resulting solution was extracted with diethyl ether (80 mL) three times. The organic layer was washed successively with saturated sodium chloride, sodium hydrogen carbonate, and water, followed by drying with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.87 g (86% yield) of **3**. Mp: 120-122°C. ^{1}H NMR ($CDCl_3$) δ 2.80-2.88 (m, 2H, -OH), 3.86-3.88 (s, 3H, CO_2CH_3), 3.89-3.97 (m, 2H, -CH_2-OH), 4.14-4.27 (m, 2H, -O-CH_2-), 7.18-7.22 (m, H, aromatic), 7.68-7.73 (m, 1H, aromatic), 7.84-7.86 (m, 1H, aromatic), 8.22 (s, 1H, -Ph-CH=). IR (KBr) 3580, 3377 (s, O-H), 3103 (w, =C-H), 2934, 2876 (m, C-H), 2220 (m, CN), 1724 (vs, C=O), 1589 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.57; N, 4.56. Found: C, 58.74; H, 5.65; N, 4.68.

1-(2',2',3'-Tricyano-3'-carbomethoxycyclopropyl)-3,4-di-2'-hydroxyethoxybenzene (**4**)

Methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (1.84 g, 0.006 mol) and bromomalononitrile (1.30 g, 0.009 mol) were dissolved in 30 mL of 85% aqueous ethanol with stirring at 0°C. After stirring for 6 hr at 0°C, the product was filtered and rinsed once with 20 mL of 85% aqueous ethanol and twice with 20 mL of cold ethanol. The obtained white crystals were recrystallized from ethanol/acetone (90/10, vol./vol.) mixtures to give 1.55 g (72% yield) of **4**. Mp: 99-100°C. ^{1}H NMR (acetone-d_6) δ 2.04-2.07 (d, 2H, O-H), 3.83-3.89 (m, 2H, -O-CH_2-), 3.98 (s, 3H, CO_2CH_3), 4.08-4.16 (m, 2H, -CH_2-OCO-), 4.23 (s, 1H, cyclopropyl), 7.10-7.14 (d, 1H, aromatic), 7.27-7.31 (d, 1H, aromatic), 7.44 (s, 1H, aromatic). IR (KBr) 3381 (s, O-H), 2933, 2876 (m, C-

H), 2255 (m, CN), 1753, (vs, C=O) cm^{-1}. $C_{18}H_{17}N_3O_6$: C, 60.09; H, 1.55; N, 11.68. Found: C, 60.19; H, 1.64; N, 11.76.

Synthesis of polyurethane **5-6**

A representative polyaddition procedure (the case of **5**) was as follows: 3,4-Toluenediisocynate (1.74 g, 0.01 mol) was added slowly to a solution of 3.60 g of diol **4** (0.01 mol) in 50 ml of dry DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80°C. After heating 6 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and reprecipitated from acetone into methanol. Thus obtained polymer was dried under vacum to give 4.36 g (80% yield) of polymer **5**: η_{inh} = 0.25 dL/g (c, 0.5 g/dL in acetone at 25°C). ^{1}H NMR (acetone-d_6) δ 1.90-2.25 (m, 3H, $-CH_3$), 3.96 (s, 3H, CO_2CH_3), 3.64-4.53 (m, 9H, 2 $-O-CH_2-CH_2-O-$, cyclopropyl), 6.90-8.09 (m, 6H, aromatic), 8.48-8.67 (m, 2H, N-H). IR (KBr) 3373 (s, N-H), 2924 (m, C-H), 2254 (m, CN), 1748, 1703 (s, C=O) cm^{-1}. Anal. Calcd for $(C_{27}H_{23}N_5O_8)_n$: C, 59.45; H, 4.25; N, 12.84. Found: C, 59.56; H, 4.34; N, 12.95. Polymer **6**: η_{inh} = 0.28 dL/g (c 0.5 g/dL in acetone at 25°C). ^{1}H NMR (DMSO-d_6) δ 3.64-4.42 (m, 18H, -OCH3, -O-CH2-CH2-O-, cyclopropyl), 7.10-8.25 (m, 9H, aromatic), 8.58-9.03 (m, 2H, N-H). IR (KBr) 3392 (m, N-H), 2938 (w, C-H), 2253 (m, CN), 1746, 1702 (s, C=O), 1589 (s, C=C) cm-1. Anal. Calcd for $(C_{34}H_{29}N_5O_{10})_n$: C, 61.17; H, 4.38; N, 10.49. Found: C, 61.28; H, 4.45; N, 10.56.

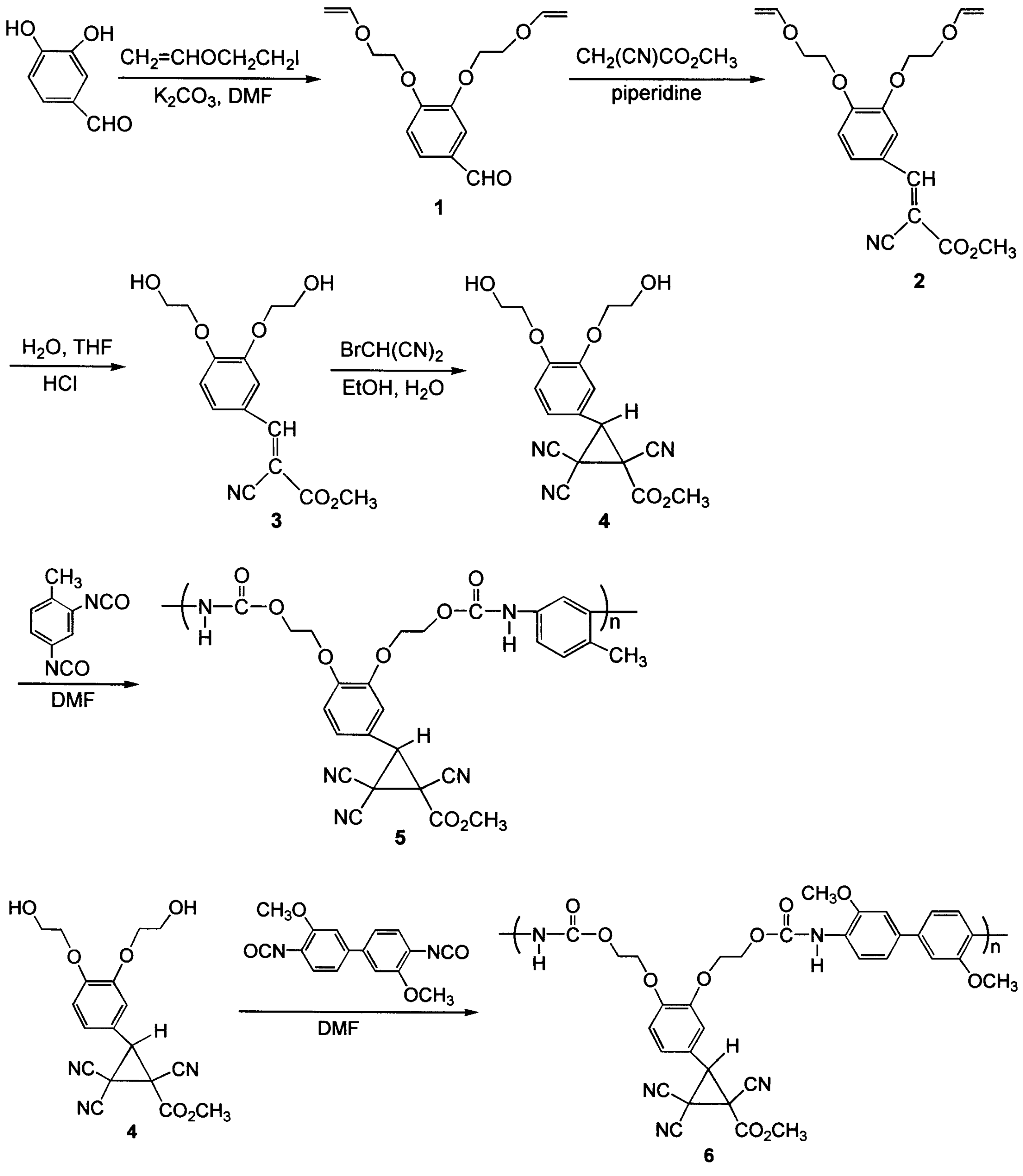
Results and Discussion

Synthesis of diol **4**

3,4-Di-(2'-vinyloxyethoxy)benzaldehyde **1** was prepared from 2-iodoethyl vinyl ether and 3,4-dihydroxybenzaldehyde, and reacted with methyl cyanoacetate via Knoevenagel condensation to give methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate **2** (11). Compound **2** was hydrolyzed to yield acetaldehyde and methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate **3**. 1-(2',2',3'-Tricyano-3'-carbomethoxy cyclopropyl)-3,4-di-2'-hydroxyethoxybenzene (**4**) was prepared by the reactions of bromomalononitrile with compound **3**, according to a variation of the Wideqvist reaction (12). In 85% aqueous ethanol solution at room temperature, compound **4** was obtained in moderate yields. The chemical structure of the compounds was confirmed by ^{1}H-NMR, IR spectra, and elemental analysis. The signal at 4.23 ppm in ^{1}H-NMR spectrum assigned to the cyclopropyl proton indicates the formation of cyclopropane ring.

Synthesis and characterization of polyurethanes **5-6**

Polyurethanes **5** and **6** were prepared by polyaddition between a diol **4** and 2,4-toluenediisocynate (TDI) and 3,3'-dimetoxy-4,4'-biphenylenediisocynate in a dry DMF solvent. The polymerization yield was 75-85%. The chemical structure of the compounds was identified by ^{1}H-NMR, IR spectra, and elemental analysis. ^{1}H-NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 8.5-9.0 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1703 cm^{-1} indicating the presence of urethane bond. We now have well defined polyurethanes (**5-6**) containing tricyanocyclopropane ring and investigate their properties.



Properties of polymers **5** *and* **6**

The polymers **5** and **6** were soluble in chloroform, acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosity, measured in acetone at 25°C was in the range of 0.25-0.30 dL/g. The thermal behavior of the polymers **5** and **6** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g) and the results are summarized in Table 2. The polymers shows a double phase degradation pattern in their TGA thermograms, probably due to the presence of two rings in the pendant group. The T_g values of polymers obtained from DSC thermograms were around 97-123°C. Piezoelectric coefficient of the corona poled polymer films were measured to demonstrate their piezoelectric activity. Preliminary results of the transverse piezoelectric coeffcients (d_{31}) of the poled films were 1.8-2.0

Table 1. Properties of polymers **5** and **6**

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 700 °C, %	d_{31} (pC/N)
		5%-loss	20%-loss	40%-loss		
5	97	292	346	445	7.6	1.8
6	123	297	358	459	9.5	2.0

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

pC/N, which is acceptable for piezoelectric device applications. We are now exploring further the polymerization of other cyanocyclopropane systems and the full account of the work will be reported later.

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