Synthesis of Novel Polyurethanes Containing Tricyanocyclopropyl Group as a Piezoelectric Chromophore and Their Properties

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1-(2',2',3'-Tricyano-3-carbomethoxycyclopropyl)-3,4-di-(2'-hydroxyethoxy)benzene (**4**) was prepared by the reaction of bromomalononitrile with methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**). Diol **4** was condensed with tolylene-2,4-diisocyanate, 3,3'-dimethoxy-4,4'-biphenylenediisocyanate, and 1,6-hexamethylenediisocyanate to yield polyurethanes **5**, **6**, and **7** containing tricyanocyclopropane functionalities in the pendant group. The resulting polymers **5-7** were soluble in common organic solvents and the inherent viscosities were in the range of 0.25-0.30 dL/g. Polyurethanes **5-7** showed a thermal stability up to 300 °C in TGA thermograms. Solution-cast films showed T_g values in the range of 100-125 °C and piezoelectric coeffcients (d_{31}) of the poled polymer films were 1.3-2.0 pC/N, which are acceptable for piezoelectric device applications.

Keywords : 1-(2',2',3'-Tricyano-3'-carbomethoxycyclopropyl)-3,4-di-(2'-hydroxyethoxy)benzene, Polyurethane, Piezoelectric effect.

Introduction

Functional polymers of 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.[2,3] Polyacrylonitrile has high concentrations of nitrile dipoles, but the helical structure of the polymer chains causes the radiating dipoles to cancel each other, and it does not show piezoelectric effect.[4] In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation resulting in high piezoelectric activity.[5] A potentially piezoelectric polymer must contain a large concentration of dipoles and be able to withstand high voltages without breakdown. These polymers have to be film-forming and mechanically very strong. We have recently proposed that three- and four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments and these polymers are potential piezoelectric materials.[6] We have previously prepared a series of polymers containing tetracyanocyclopropane,[8,9] tricyanocyclopropane,[10-13] dicyanocyclopropane units.[14] These polymers showed a thermal stability up to 300 °C with a T_g of 120-150 °C, and the piezoelectric coeffcients (d_{31}) of the poled films were 1.5-1.6 pC/N, which are acceptable for piezoelectric applications.[13] In the developments of piezoelectric polymers for device applications, stabilization of electrically induced dipole alignment is important considrations. Two approaches to minimize the randomization have been proposed. One is to use cross-linking method and the other is to use a high T_g polymers. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increased rigidity prevents the relaxation of oriented dipoles. In this work we prepared novel polyurethanes containing tricyanocyclopropane ring, which may act as an effective piezoelectric-chromophore in the side chain. We selected trisubstituted cyclopropyl group as a piezoelectric chromophore because it is easy to synthesize and have a large dipole moment. Besides, polyurethane matrix forms extensive hydrogen bond between urethane linkage and increased rigidity prevents the relaxation of oriented dipoles. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and piezoelectric activity. We now report the results of the initial phase of the work.

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Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich Chem. Co. and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled under vacuum. Sodium iodide was dried for 4 h at 100 °C under vacuum. 3,4-Dihydroxybenzaldehyde was used as received from Aldrich. 1-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. Tolylene-2,4-diisocyanate (TDI) and 1,6-hexamethylenediisocyanate (HDI) were purified by distillation under reduced pressure. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate was recrystallized from ethyl acetate. Piperidine was dried with calcium hydride and fractionally distilled. *N*,*N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Bromomalononitrile was prepared according to the literature procedure[15] and recrystallized twice from chloro-

form. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.[16]

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM 360L NMR (60 MHz) and Varian 300 MHz 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 under 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, 6 kV 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 1-butanol yielded 25.0 g (90% yield) of pure product **1**. Mp 56-57 °C. ^{1}H NMR ($CDCl_3$) 4.04-4.36 δ (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 1-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 1-butanol (60 mL), water (20 mL), and cold 1-butanol (15 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 6.18 g (86% yield) of **2**. Mp=86-87 °C. ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H, -CO_2CH_3), 4.02-4.38 (m, 12H, 2 CH2=, 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'-hydroxyethoxy)benzene (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 polyurethanes 5-7. A representative polymerization procedure (the case of **5**) was as follows: Tolylene-2,4-diisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 3.60 g of diol **4** (0.01 mol) in 40 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 DMSO 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} = 0.23 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, -OCH_3, -O-CH_2-CH_2-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. Polymer **7**: η_{inh} = 0.22 dL/g (c, 0.5 g/dL in acetone at 25 °C). ^{1}H NMR (DMSO-d_6) δ 1.12-1.41 (m, 8H, -$(CH_2)_4$-), 2.83-2.98 (m, 4H, 2 -NH-CH_2-), 3.64-4.29 (m, 12H, -OCH_3, 2 -O-CH_2-CH_2-O-, cyclopropyl), 5.67-5.75 (m, 2H, 2 N-H), 7.05-7.78 (m, 3H, aromatic). IR (KBr) 3340 (m, N-H), 2934, 2860 (m, C-H), 2270 (m, CN), 1735, 1710 (s, C=O), 1651 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{26}H_{29}N_5O_8)_n$: C, 57.88; H, 5.42; N, 12.98. Found: C, 57.78; H, 5.49; N, 12.88.

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 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate **2**.[17] Compound **2** was hydrolyzed to yield acetaldehyde and methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate **3**. 1-(2',2',3'-Tricyano-3'-carbomethoxycyclopropyl)-3,4-di-(2'-hydroxyethoxy) benzene (**4**) was prepared by the reactions of bromomalononitrile with compound **3**, according to a variation of the Wideqvist reaction.[18] 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 polymers 5-7. Polyurethanes **5-7** were prepared by polyaddition between a diol **4** and tolylene-2,4-diisocyanate (TDI), 3,3'-dimethoxy-4,4'-biphenylenediisocyanate, and 1,6-hexamethylenediisocyanate (HDI) in a DMF solvent. The polymerization results are summarized in Table 1. 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 well consistent with the proposed polymer structures. The signal at 8.48-9.03 ppm assigned to the aromatic amine proton in the ^{1}H NMR spectra of polymers **5** and **6** indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak around 1703 cm^{-1} indicating the presence of urethane bond. We now have well defined polyurethanes (**5-7**) and investigate their properties.

Table 1. Polymerization of **4**[a] with TDI[b], DMBPI[c], and HDI[d] in DMF at 80 °C

Monomer	Monomer/ Solvent (mol/L)	Diol **4** to Diisocynate (mol%)	Time (h)	Yield (%)	η_{inh}[e] (dL/g)
4, TDI	0.50	1.0	6	80	0.25
4, TDI	0.80	1.0	10	83	0.29
4, DMBPI	0.50	1.0	6	78	0.23
4, DMBPI	0.80	1.0	10	82	0.27
4, HDI	0.50	1.0	6	75	0.24
4, HDI	0.80	1.0	10	77	0.26

[a]**4**=1-(2',2',3'-Tricyano-3'-carbomethoxycyclopropyl)-3,4-di-(2'-hydroxyethoxy)benzene. [b]TDI=Tolylene-2,4-diisocyanate. [c]DMBPI=3,3'-Dimethoxy-4,4'-biphenylenediisocyanate. [d]HDI=1,6-Hexamethylenediisocyanate. [e]Inherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 °C.

Properties of polymers. The polymers 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 **5-7** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. The resulting polymers showed a thermal stability up to 300 °C, and shows a double phase degradation pattern in their TGA thermograms, probably due to the presence of multiple rings. Polymer films cast from solvent were clear and brittle, and T_g values from DSC thermograms were around 100-125 °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 1.3-2.0 pC/N. These values are similar to those of poly(1-bicyclobutanecarbonitrile),[5] but are smaller than those of the copolymer of vinylidene cyanide and vinyl acetate.[3]

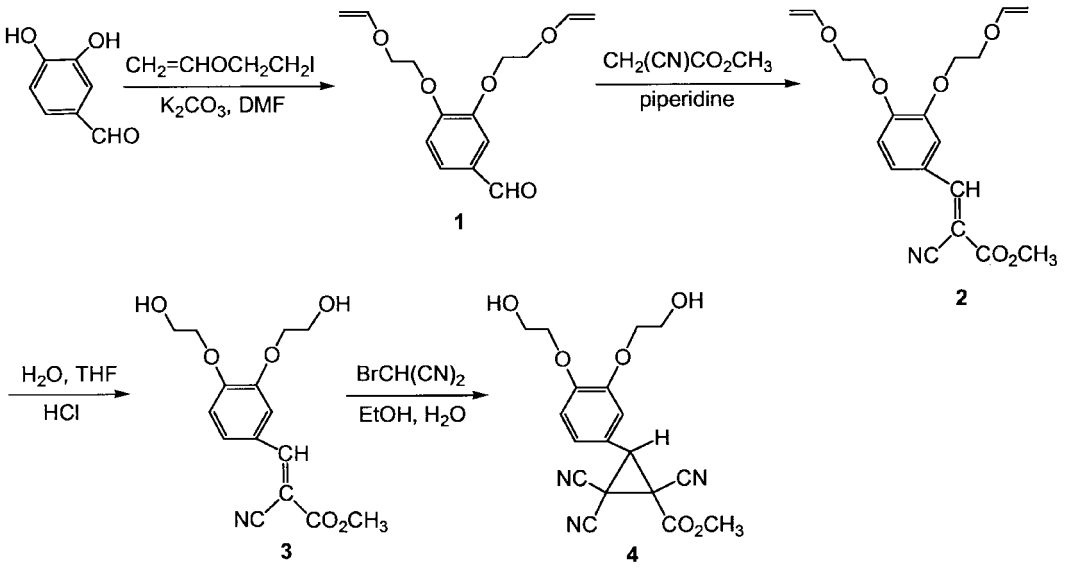
Conclusions

We prepared novel polyurethanes **5-7** having tricyanocyclopropane functionality as a NLO-chromophore in the

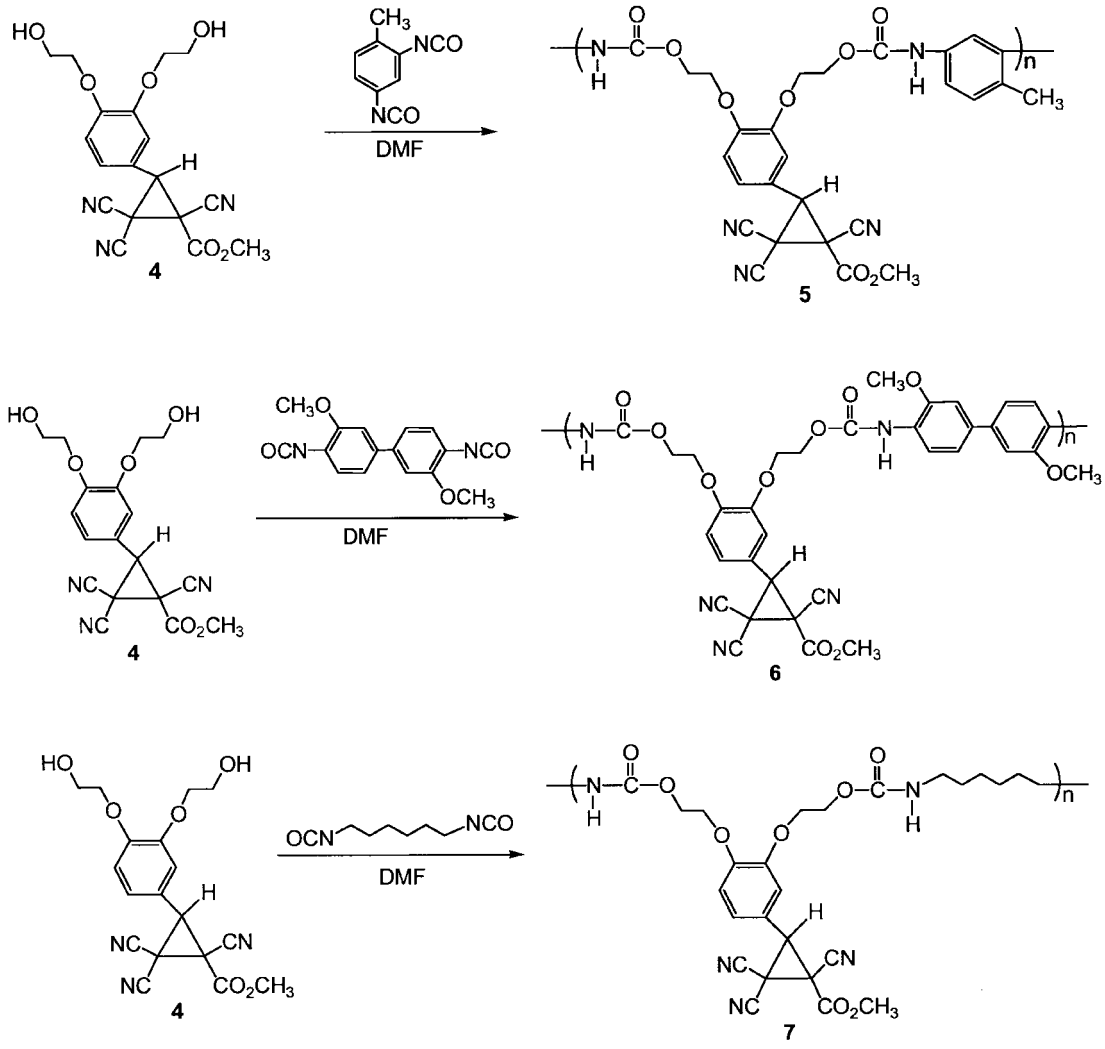
Table 2. Thermal Properties of Polymers **5-7**

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
7	-	268	351	438	10.7	1.3

[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.



Scheme 1



Scheme 2

pendant group. The resulting polymers were soluble in common organic solvents such as acetone and DMF. Polymers **5-7** showed a thermal stability up to 300 °C with a T_g of 100-125 °C. The transverse piezoelectric coeffcients (d_{31}) of the corona poled polymer films were in the range 1.3-2.0 pC/N, which is acceptable for piezoelectric device applications. We are now exploring further the polymerization of other multicyanocyclopropane systems and the full account of the work will be reported later.

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