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Synthesis and characterization of poly(meth)acrylates containing tricyanocyclopropane ring for piezoelectric applications

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Summary

p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate (**5a**) and p-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate (**5b**) were prepared by the reactions of bromomalononitrile with methyl p-(2-acryloyloxyethoxy)benzylidene-cyanoacetate (**4a**) and methyl p-(2-methacryloyloxyethoxy)benzylidenecyanoacetate (**4b**), respectively. Monomers **5a** and **5b** were polymerized with free-radical initiators to obtain the polymers with multicyanocyclopropane functionalities in the pendant group. The resulting polymers **6a** and **6b** were soluble in acetone and the inherent viscosities were in the range of 0.20-0.25 dL/g. Solution-cast films 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.

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). 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 several cyano 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-tetra-cyanocyclopropane (5-6), 1,1,2-tricyano-2-carbomethoxycyclopropane (7). These polymers showed a thermal stability up to 300°C with a T_g of 120-150°C, which is acceptable for piezoelectric applications. In this work we prepared two poly(meth)acrylates containing tricyanocyclopropane ring, which is presumably effective piezoelectric-chromophore in the side chain. We selected trisubstituted cyclo

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propyl group as a piezoelectric-chromophore because it is easy to synthesize and have a large dipole moment. We attached ethylene group as a spacer to increase flexibility of the polymer chain. The present report describes the synthesis and radical polymerization of p-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate (**5a**) and p-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenoxyethyl methacrylate (**5b**). We characterized the resulting polymers and investigated their peizoelectric activities.

Experimental

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. p-Hydroxybenzaldehyde was crystallized from water containing small amount of sulfuric acid and dried under vacuum. Acryloyl chloride and methacryloyl chloride (Aldrich) were distilled and used immediately. Triethylamine was refluxed over potassium hydroxide and distilled. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. 1,2-Dichloroethane and acetonitrile were refluxed with calcium hydride and fractionally distilled. Benzene was purified by refluxing over sodium metal, distilled, and stored over 4A molecular sieves under nitrogen. γ-Butyrolactone was dried with anhydrous calcium sulfate and fractionally distilled. 1-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and stored at 5°C. 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 a procedure similar to that reported already (8) and purified by fractional distillation. Compounds **1** and **2** were prepared according to the literature procedure (9).

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 alignment of the piezoelectric-chromophore of the polymers was carried out by corona poling method. As the temperature was raised to 130°C, 6kV of corona voltage was applied and kept 130°C for 30 min. The piezoelectric coefficient (d_{31}) of the corona poled polymer film was mesured to demonstrate its piezoelectric activity. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Methyl p-(2-hydroxyethoxy)benzylidenecyanoacetate (**3**)

Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**2**) (7.10 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 5.52 g (86% yield) of **3**. Mp: 94-95°C. ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H, CO_2CH_3), 3.99-4.05 (d, 2H, $-CH_2-OH$), 4.16-4.20 (q, 2H, $-O-CH_2-$), 6.09-7.05 (d, 2H, aromatic), 7.98-8.04 (d, 2H, aromatic), 8.19 (s, 1H, -Ph-CH=). IR (KBr) 3489 (s, O-H), 3054 (w, =C-H), 2959 (m, C-H), 2231 (s, CN), 1728 (vs, C=O), 1587, 1560 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 64.28; H, 5.38; N, 5.58.

Methyl p-(2-acryloyloxyethoxy)benzylidenecyanoacetate (**4a**)

At 0°C under nitrogen, 1.81 g (0.02 mol) of freshly distilled acryloyl chloride in 15 mL of dry 1,2-dichloroethane was added dropwise to a solution of methyl p-(2-hydroxyethoxy)benzylidenecyanoacetate (**3**) (4.94 g, 0.02 mol), triethylamine (6.07 g, 0.06 mol), and 40 mL of 1,2-dichloroethane with stirring. The resulting solution was stirred for 72 hr at 0°C and 2 hr at room temperature. Triethylamine hydrochloride was filtered off and rinsed with 40 mL of 1,2-dichloroethane. Extractions were performed on the filtrate twice with 40 mL of 1N-HCl, once with 50 mL of H_2O, and twice with 40 mL of saturated sodium bicarbonate. The resulting organic layer was dried over anhydrous magnesium sulfate and filtered. The solution was concentrated by rotary evaporation, and the resulting liquid was placed in a refrigerator (-10°C) to crystallize. The obtained white crystals were collected and washed a few times with cold water to give 4.46 g (74% yield) of **4a**. Mp: 59-61°C. ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H, CO_2CH_3), 4.29-4.33 (m, 2H, -O-CH_2-), 4.53-4.57 (m, 2H, -CH_2-OCO-), 5.86-5.91 (2d, 1H, vinylic), 6.12-6.21 (q, 1H, vinylic), 6.43-6.50 (2d, 1H, vinylic), 6.99-704 (d, 2H, aromatic), 7.98-8.03 (d, 2H, aromatic), 8.19 (s, 1H, -Ph-CH=). IR (KBr) 3078 (w, =C-H), 2966 (m, C-H), 2222 (s, CN), 1724 (vs, C=O), 1591 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.01; N, 4.65. Found: C, 63.86; H, 5.12; N, 4.58.

Methyl p-(2-methacryloyloxyethoxy)benzylidenecyanoacetate (**4b**)

Compound **4b** was prepared from p-(2-hydroxyethoxy)benzylidenecyanoacetate (**3**) and methacryloyl chloride_according to the procedure of compound **4a**. Mp: 240°C (dec). ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H, -CH_3), 3.92 (s, 3H, CO_2CH_3), 4.29-4.33 (t, 2H, -Ph-O-CH_2-), 4.51-4.55 (t, 2H, -CH_2-OCO-), 5.61 (s, 1H, vinylic), 6.14 (s, 1H, vinylic)), 6.99-7.03 (d, 2H, aromatic), 7.98-8.03 (d, 2H, aromatic), 8.19 (s, 1H, -Ph-CH=). IR (KBr) 3072 (w, =C-H), 2955, 2850 (s, C-H), 2222 (s, CN), 1728 (vs, C=O), 1593 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.76; H, 5.43; N, 4.44. Found: C, 64.84; H, 5.56; N, 4.38.

p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phynoxyethyl acrylate (**5a**)

Methyl p-(2-acryloyloxyethoxy)benzylidenecyanoacetate (1.81 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 h 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 1.53 g (70% yield) of **5a**. Mp: 146-148°C. ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 1H, cyclopropyl), 4.06 (s, 3H, CO_2CH_3), 4.17-4.26 (t, 2H, -O-CH_2-), 4.46-4.55 (t, 2H, -CH_2-OCO-), 5.83-5.89 (2d, 1H, vinylic), 6.09-6.20 (q, 1H, vinylic), 6.38-6.48 (2d, 1H, vinylic), 6.97-7.04 (d, 2H, aromatic), 7.37-7.45 (d, 2H, aromatic). IR (KBr) 3053 (m, =C-H), 2961 (m, C-H), 2255 (m, CN), 1747, 1722 (vs, C=O), 1635,1612 (s, C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{15}N3O_5$: C, 62.46; H, 4.14; N, 11.50. Found: C, 62.54; H, 4.08; N, 11.58.

p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate (**5b**)

Compound **5b** was prepared from methyl p-(2-methacryloyloxyethoxy)benzylidenecyanoacetate (**4b**) and bromomalononitrile according to the procedure of compound **5a**. Mp: 90-91°C. ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H, -CH_3), 3.99 (s, 1H, cyclopropyl), 4.07 (s, 3H, CO_2CH_3), 4.23-4.27 (t, 2H, -O-CH_2-), 4.48-4.53 (t, 2H, -CH_2-OCO-), 5.60 (s, 1H vinylic), 6.14 (s, 1H, vinylic), 6.97-7.04 (d, 2H, aromatic), 7.38-7.45 (d, 2H, aromatic). IR (KBr) 3058 (m, =C-H), 2959 (m, C-H), 2255 (m, CN), 1755, 1732 (vs, C=O), 1611, 1591 (s, C=C) cm^{-1}. Anal. Calcd for $C_{20}H_{17}N_3O_5$: C, 63.32; H, 4.52; N, 11.07. Found: C, 63.42; H, 4.46; N, 11.18.

Free radical polymerization of compounds **5a** and **5b**.

A representative radical polymerization procedure (the case of **5a**) was as follows: In a polymerization tube were placed 0.73 g (2.0 mmol) of **5a**, 1.97 mg (0.012 mmol) of AIBN, and 2.0 mL of γ-butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65°C. After 12 h the polymerization tube was opened and the swelling polymer was poured into 300 mL of methanol. The precipitated polymer was collected and dried under vacum to give 0.55 g (75% yield) of polymer **6a**: η_{inh}=0.23 dL/g (c, 0.5 g/dL in acetone at 25°C). ^{1}H NMR (acetone-d_6) δ 1.48-2.05 (br, 3H, -CH_2-CH-), 3.84-3.90 (br, 1H, cyclopropyl), 3.94-4.08 (br, 3H, CO_2CH_3), 4.12-4.28 (br, 2H, -O-CH_2-), 4.29-4.52 (br, 2H, -CH_2-OCO-), 6.95-7.18 (br, 2H, aromatic), 7.55-7.73 (br, 2H, aromatic). IR (KBr) 2959 (m, C-H), 2253 (m, CN), 1751 (vs, C=O), 1611, 1590 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{19}H_{15}N_3O_5)_n$: C, 62.46; H, 4.14; N, 11.50. Found: C, 62.58; H, 4.24; N, 11.42. Polymer **6b**: η_{inh}=0.24 dL/g (c, 0.5 g/dL in acetone at 25°C). ^{1}H NMR (acetone-d_6) δ 0.98-1.21 (br, 3H, -CH_3-), 1.80-2.07 (br, 2H, -CH_2-), 3.94-4.03 (br, 3H, cyclopropyl), 4.12-4.43 (br, 4H, -OCH_2-CH_2O-), 4.18-4.24 (br, 3H, CO_2CH_3), 7.01-7.14 (br, 2H, aromatic), 7.58-7.72 (br, 2H, aromatic). IR (KBr) 2960 (m, C-H), 2250 (s, CN), 1745 (vs, C=O), 1606 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{20}H_{17}N_3O_5)_n$: C, 63.32; H, 4.52; N, 11.07. Found: C, 63.44; H, 4.43; N, 11.19.

Results and Discussion

Synthesis of monomers **5a** and **5b**

p-(2-Vinyloxyethoxy)benzaldehyde **1** was prepared from 2-iodoethyl vinyl ether and 4-hydroxybenzaldehyde, and reacted with methyl cyanoacetate via Knoevenagel condensation to give methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate **2** (10). Compound **2** was hydrolyzed to yield acetaldehyde and compound **3**. Methyl p-(2-acryloyloxyethoxy)benzylidenecyanoacetate **4a** and methyl *p*-(2-methacryloyloxyethoxy)benzylidenecyanoacetate **4b** were prepared by the well-known Schotten-Baumann method. *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate (**5a**) and *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate (**5b**) were prepared by the reactions of bromomalononitrile with methyl *p*-(2-acryloyloxyethoxy)benzylidenecyanoacetate (**4a**) and methyl *p*-(2-methacryloyloxyethoxy)benzylidenecyanoacetate (**4b**), respectively, according to a variation of the Wideqvist reaction (11). In 85% aqueous ethanol solution at room temperature, monomers **5a** and **5b** were obtained in moderate yields. The chemical structure of the compounds was confirmed by ^{1}H-NMR, IR spectra, and elemental analysis. The signal at 3.98-3.99 ppm in ^{1}H-NMR spectrum assigned to the cyclopropyl proton indicates the formation of cyclopropane ring.

Radical polymerization of monomers **5a** *and* **5b**

p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate (**5a**) and *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate (**5b**) were polymerized by AIBN to obtain the polymers **6a** and **6b**. Polymerization reactions were carried out in solution at 65°C. The polymerization results are summarized in Table 1. Structures of polymers were determined by ^{1}H-NMR and IR spectra. ^{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. Monomers **5a** and **5b** were quite reactive toward free radical initiator and polymerized readily. The free radical initiator did not attack the cyclopropane ring during polymerization. The signal at 3.84-4.03 ppm in ^{1}H-NMR spectrum assigned to the cyclopropyl proton indicates that the cyclopropane ring remained intact during free radical polymerization. We now have well defined polymers **6a** and **6b** and investigate their properties.

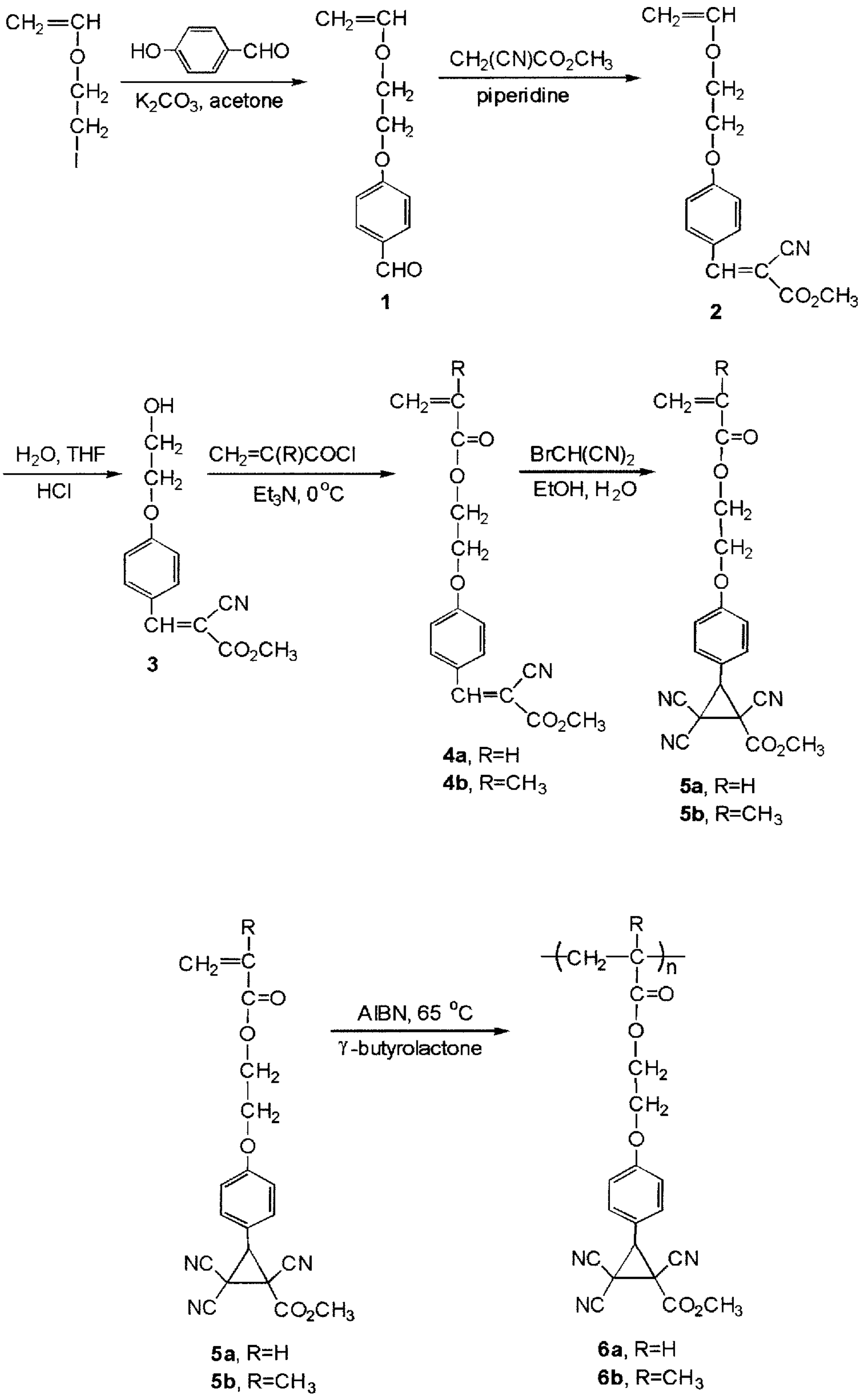

Table 1. Radical polymerizations of **5a**[a] and **5b**[b] by AIBN in γ-butyrolactone at 65°C

Monomer	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)	η_{inh}[c] (g/dL)
5a	1.00	0.6	12	75	0.23
5a	0.67	1.0	24	80	0.22
5b	1.00	0.6	12	82	0.24
5b	0.67	0.8	24	86	0.25

[a] **5a**=*p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate.
[b] **5b**= *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate.
[c] Inherent viscosity: Concentration of 0.5 g/dL in acetone.

Properties of polymers **6a** *and* **6b**

The polymers **6a** and **6b** 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 0.20-0.25 dL/g. The thermal behavior of the polymers **6a** and **6b** 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 130-150°C. These T_g values are higher than those for poly(methyl acrylate) (10°C) and for poly(methyl methacrylate) (105°C) due to the presence of polar pendant group. Piezoelectric coefficient of the poled polymer films were measured to demonstrate their piezoelectric activity. Preliminary results of the transverse piezoelectric coeffcients (d_{31}) of the poled films were 1.5-1.6 pC/N, which is acceptable for piezoelectric device applications.

Table 1. Thermal properties of polymers **6a** and **6b**

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 700 °C, %	d_{31} (pC/N)
		5%-loss	20%-loss	40%-loss		
6a	132	296	346	451	8.6	1.6
6b	149	297	349	459	10.5	1.5

[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.

Conclusion

We prepared *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate (**5a**) and *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phynoxyethyl methacrylate (**5b**). The cyclopropane-substituted acrylate and methacrylate **5a-b** were polymerized in solution by radical initiator to yield the polymers with multicyanocyclopropane functionality. The resulting polymers **6a-b** were soluble in common organic solvents such as acetone and DMSO. Polymers **6a-b** showed a thermal stability up to 300°C with a T_g of 130-150°C. The transverse piezoelectric coeffcients (d_{31}) of the poled films were 1.5-1.6 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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References

1. Hall Jr HK (1988) J Macromol Sci Chem A25: 729
2. Jo YS, Inoue Y, Chujo R, Saito K, Miyata S (1985) Macromolecules 18: 1850
3. Hall Jr HK, Chan RTH, Oku J, Hughes OR, Scheinbeim J, Newman B (1987) Polym Bull 17: 135
4. Hall Jr HK, Chan RTH, Oku J, Hughes OR, Scheinbeim J, Newman B, Henrici-Olive G, Olive S (1975) Adv Polym Sci 6: 421
5. Lee JY, Hall Jr HK (1990) Polym Bull 23: 471
6. Lee JY, Padias AB, Hall Jr HK (1991) Macromolecules 24: 17
7. Lee JY, Cho SO, Padias AB, Hall Jr HK (1991) Polym.Bull 27: 25
8. Hesse BC (1986) J Am Chem Soc 18: 723
9. Lee JY (1994) Polym Bull 33: 635
10. Corson BC, Stoughton RW (1928) J Am Chem Soc 50: 2825
11. Kim YC, Hart H (1969) J Chem Soc(C) 2409