

Synthesis and Free Radical Polymerization of *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl Acrylate

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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 Polyacrylonitrile has high concentrations of nitrile dipoles, but the helical 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 resulting in high piezoelectric activity.⁴ 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.⁵ We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,⁵⁻⁸ 1,1,2-tricyano-2-carbomethoxycyclopropane,^{9,10} 1,2-dicyano-1,2-dicarbomethoxycyclopropane units.¹¹ 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 acrylate 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. Ethylene group was introduced as a spacer to increase flexibility of the polymer chain.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich Chem. Co. and purified by either distillation or recrystallization before use. 2-Iodoethanol was used after distillation. *p*-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. γ -Butyrolactone was dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. Acryloyl chloride was distilled and used immediately. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pres-

sure. Bromomalononitrile was prepared according to the literature procedure¹² and recrystallized twice from chloroform.

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ¹H 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. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

***p*-(2-Vinyloxyethoxy)benzaldehyde 1.** 4-Hydroxybenzaldehyde (12.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60 °C for 72 hr under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 50 mL of acetone. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product **1**. Compound **1** was crystallized in the refrigerator (6 °C). Bp: 72-74 °C (0.2 mmHg). ¹H NMR (acetone-*d*₆) δ 9.89 (s, 1H, -CHO), 7.63-7.99 (m, 2H, aromatic), 6.87-7.28 (m, 2H, aromatic), 6.32-6.73 (q, 1H, =CH-), 4.18-4.48 (m, 2H, CH₂=), 3.70-4.17 (m, 4H, -O-CH₂-CH₂-O-). IR (neat) 3119, 3068 (m, =C-H), 2940, 2878, 2833 (m, C-H), 1684 (vs, C=O), 1603, 1579 (vs, C=C) cm⁻¹.

Methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate 2. Piperidine (0.17 g, 2.0 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)bnzaldehyde **1** (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of *n*-butanol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 1 hr at 0 °C and 10 hr at room temperature. After cooling in an ice bath, the product was filtered and washed successively with cold *n*-butanol (30 mL), water (50 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.90 g (72% yield) of **2**. Mp: 95-97 °C. ¹H NMR (acetone-*d*₆) δ 7.84-8.25 (3H, m), 6.93-7.29 (2H, m), 6.32-6.75 (1H, q), 4.25-4.50 (2H, m), 3.87-4.24 (4H, m), 3.88 (3H, s). IR (KBr) 3103, 3016, 2957, 2930 (C-H), 2220 (CN), 1726 (C=O), 1618, 1588 (C=C) cm⁻¹. Anal. Calcd for C₁₅H₁₅NO₄: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.49; N, 5.18.

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 hr 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. ¹H NMR (CDCl₃) δ 3.92 (s, 3H, CO₂CH₃), 3.99-4.05 (d, 2H, -CH₂-OH), 4.16-4.20 (q, 2H, -O-CH₂-), 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 C₁₃H₁₃NO₄: C, 63.15; H, 5.30; N, 5.66. Found: C, 64.28; H, 5.38; N, 5.58.

Methyl *p*-(2-Acryloyloxyethoxy)benzylidenecyanoacetate **4.** 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 1 N-HCl, once with 50 mL of H₂O, 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 **4**. Mp: 59-61 °C. ¹H NMR (CDCl₃) δ 3.92 (s, 3H, CO₂CH₃), 4.29-4.33 (m, 2H, -O-CH₂-), 4.53-4.57 (m, 2H, -CH₂-OCO-), 5.86-5.91 (2d, 1H, vinylic), 6.12-6.21 (q, 1H, vinylic), 6.43-6.50 (2d, 1H, vinylic), 6.99-7.04 (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 C₁₆H₁₅NO₅: C, 63.78; H, 5.01; N, 4.65. Found: C, 63.86; H, 5.12; N, 4.58.

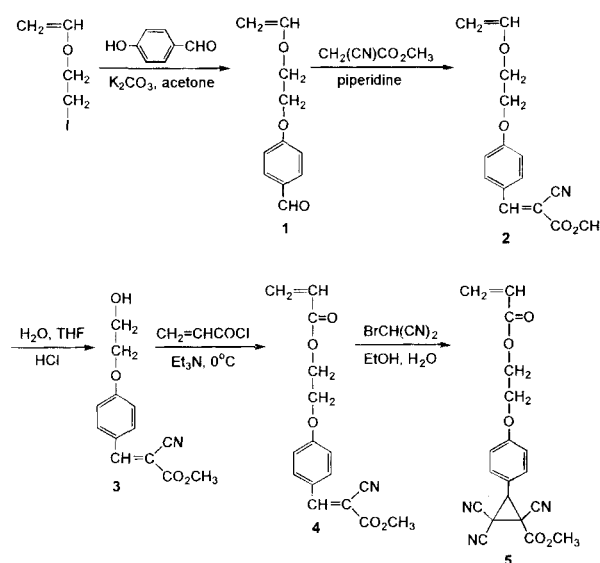
***p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate **5**.** Methyl *p*-(2-acryloyloxyethoxy)benzylidenecyanoacetate (1.81 g, 0.006 mol) and bromomalononitrile (1.30 g, 0.009 mol) were dissolved in 30 mL of 85% aqueous ethanol with stirring at 0 °C. After stirring for 6 hr at 0 °C, 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 1.53 g (70% yield) of **5**. Mp: 146-148 °C. ¹H NMR (CDCl₃) δ 3.98 (s, 1H, cyclopropyl), 4.06 (s, 3H, CO₂CH₃), 4.17-4.26 (t, 2H, -O-CH₂-), 4.46-4.55 (t, 2H, -CH₂-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 C₁₉H₁₅N₃O₅: C, 62.46; H, 4.14; N, 11.50. Found: C, 62.54; H, 4.08; N, 11.58.

Radical polymerization of monomer **5.** A representative radical polymerization procedure was as follows: In a polymerization tube were placed 0.73 g (2.0 mmol) of **5**, 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 hr the polymerization tube was opened and the polymer was poured into 300 mL of methanol. The precipitated polymer was collected and dried under vacuum to give 0.55 g (75% yield) of polymer **6**: η_{inh} =0.23 dL/g (c, 0.5 g/dL in acetone at 25 °C). ¹H NMR (acetone-*d*₆) δ 1.48-2.05 (br, 3H, -CH₂-CH-), 3.84-3.90 (br, 1H, cyclopropyl), 3.94-4.08 (br, 3H, CO₂CH₃), 4.12-4.28 (br, 2H, -O-CH₂-), 4.29-4.52 (br, 2H, -CH₂-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 (C₁₉H₁₅N₃O₅)_n: C, 62.46; H, 4.14; N, 11.50. Found: C, 62.58; H, 4.24; N, 11.42.

Results and Discussion

Synthesis of monomer **5.** *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**.¹³ Compound **2** was hydrolyzed to give acetaldehyde and compound **3**. Methyl *p*-(2-acryloyloxyethoxy)benzylidenecyanoacetate **4** was prepared by the well-known Schotten-Baumann method. *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate **5** was prepared by the reaction of bromomalononi-



Scheme 1

trile with methyl *p*-(2-acryloyloxyethoxy)benzylidenecyanoacetate **4**, according to a variation of the Wideqvist reaction.¹⁴ In 85% aqueous ethanol solution at room temperature, monomer **5** was obtained in moderate yields. The chemical structure of the compounds was confirmed by proton-NMR, IR spectra, and elemental analysis. The signal at 3.84-3.90 ppm of the ¹H NMR spectrum assigned to the cyclopropyl proton indicates the formation of cyclopropane ring.

Radical polymerization of monomer 5. *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate **5** was polymerized by AIBN to obtain the polymer **6**. Polymerization reactions were carried out in solution at 65 °C. The polymerization results are summarized in Table 1. Chemical structures of polymer **6** were determined by proton-NMR, IR spectra, and elemental analyses. ¹H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. Monomer **5** was quite reactive toward free radical initiator and polymerized readily. The free radical initiator did not attack the cyclopropane ring during polymerization. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities. We now have well defined polymer **6**

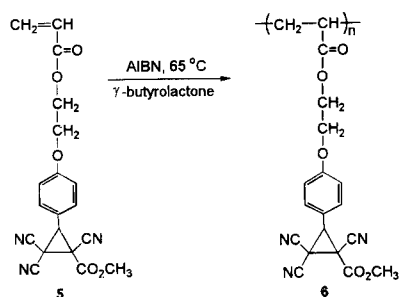
and investigate their properties.

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 0.20-0.25 dL/g. The thermal behavior of the polymer **6** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (*T*_g). The resulting polymer 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 two rings in the pendant group. The *T*_g of polymer from DSC thermograms were around 120-150 °C, and these *T*_g values are higher than those for poly(methyl acrylate) (10 °C) and for poly(methyl methacrylate) (105 °C). Piezoelectric activities of the polymer films such as transverse piezoelectric coefficients (*d*₁₃) and the hydrostatic piezoelectric coefficient (*d*_h) are under study and the full account of the work will be reported later.

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Scheme 2

Table 1. Free Radical Polymerization of **5**^a with AIBN in γ -Butyrolactone at 65 °C

Monomer	Monomer/ Solvent (mol/ L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)	η_{inh}^b (dL/g)
5	1.00	0.6	12	75	0.23
5	0.67	1.0	24	80	0.22
5	1.00	1.0	24	84	0.25

^a**5** = *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenoxyethyl acrylate. ^bInherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 °C.