

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

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Functional polymers with piezoelectric effect 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 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 A series of polymers containing tetracyanocyclopropane,^{5,8} tricyanocyclopropane,⁹⁻¹⁰ and dicyanocyclopropane units have been prepared.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. Recently we prepared polyacrylate and polymethacrylate containing *p*-(1,1,2-tricyano-2-carbomethoxycyclopropyl)phenoxyethyl group as a piezoelectric chromophore.¹²⁻¹⁵ These polymers could be formed as a film forming and showed a thermal stability up to 300 °C with a T_g of 130-150 °C. Piezoelectric coefficients (d_{31}) of the corona poled films were 1.5-1.6 pC/N, which are acceptable for piezoelectric device applications. This work is extended to the synthesis of another polyacrylate containing *p*-(1,1,2,2-tetracyanocyclopropyl)phenoxyethyl group. We selected tetracyanocyclopropyl group as a piezoelectric chromophore because it is somewhat easy to synthesize and have larger dipole moment than tricyanocyclopropyl group. Also we want to compare the piezoelectric activity of the resulting polymer with that of tricyanocyclopropyl derivative. We now report the results of the initial phase of the work.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich Chem. Co. and purified by either distillation or recrystallization before use. *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. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Acryloyl chloride was distilled and used immediately. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.¹³ Bromomalononitrile was prepared according to the literature procedure¹⁴ 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.** Compound 1 was prepared according to the literature procedure.¹²

***p*-(2-Vinyloxyethoxy)benzylidenemalononitrile 2.** Piperidine (0.26 g, 3.0 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde 1 (10.76 g, 56 mmol) and malononitrile (3.96 g, 60 mmol) in 100 mL of 1-butanol with stirring at 0 °C under nitrogen. After stirring for 1 h at 0 °C, the product was filtered and washed successively with cold 1-butanol (140 mL), water (60 mL), and cold 1-butanol (40 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 10.48 g (78% yield) of 2. Mp: 80-82 °C. ¹H NMR (acetone-*d*₆) δ 7.75-8.13 (m, 3H, aromatic & Ph-CH=), 6.83-7.28 (m, 2H, aromatic), 6.30-6.73

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(q, 1H, =CH-O-), 4.20-4.51 (m, 2H, CH₂=), 3.76-4.21 (m, 4H, -O-CH₂-CH₂-O-). IR (KBr) 3105, 3067, 2938, 2869 (C-H), 2230 (CN), 1628, 1603, 1579 (C=C) cm⁻¹. Anal. Calcd for C₁₄H₁₂N₂O₅: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.08; N, 11.58.

***p*-(2-Hydroxyethoxy)benzylidenemalononitrile 3.** Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl *p*-(2-vinyloxyethoxy)benzylidenemalononitrile (**2**) (6.24 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 4.57 g (82% yield) of **3**. Mp: 104-105 °C. ¹H NMR (CDCl₃) δ 3.86-3.97 (t, 2H, -CH₂-OH), 4.20-4.26 (t, 2H, -O-CH₂-), 7.06-7.22 (d, 2H, aromatic), 7.98-8.06 (d, 2H, aromatic), 8.16 (s, 1H, -Ph-CH=). IR (KBr) 3403 (s, O-H), 3026 (w, =C-H), 2941 (m, C-H), 2220 (s, CN), 1605, 1585, 1564 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₂H₁₀N₂O₃: C, 67.28; H, 4.71; N, 13.07. Found: C, 67.37; H, 4.68; N, 13.16.

***p*-(2-Acryloyloxyethoxy)benzylidenemalononitrile 4.** At 0 °C under nitrogen, 3.62 g (0.04 mol) of freshly distilled acryloyl chloride in 30 mL of dry 1,2-dichloroethane was added dropwise to a solution of methyl *p*-(2-hydroxyethoxy)benzylidenemalononitrile **3** (8.57 g, 0.04 mol), triethylamine (12.14 g, 0.12 mol), and 80 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 80 mL of 1,2-dichloroethane. Extractions were performed on the filtrate twice with 80 mL of 1 N HCl, once with 100 mL of H₂O, and twice with 80 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 7.73 g (72% yield) of **4**. Mp: 96-98 °C. ¹H NMR (CDCl₃) δ 4.28-4.35 (m, 2H, -O-CH₂-), 4.52-4.57 (m, 2H, -CH₂-OCO-), 5.86-5.91 (2d, 1H, vinylic), 6.11-6.21 (q, 1H, vinylic), 6.43-6.49 (2d, 1H, vinylic), 6.99-7.05 (d, 2H, aromatic), 7.66 (s, 1H, aromatic), 7.90 (s, 1H, aromatic), 7.93 (s, 1H, -Ph-CH=). IR (KBr) 3076 (w, =C-H), 2945, 2883 (m, C-H), 2225 (s, CN), 1712 (vs, C=O), 1639, 1605 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₅H₁₂N₂O₃: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.26; H, 4.62; N, 10.48.

***p*-(2,2,3-Tetracyanocyclopropyl)phenoxyethyl acrylate 5.** Methyl *p*-(2-acryloyloxyethoxy)benzylidenemalononitrile (3.22 g, 0.012 mol) and bromomalononitrile (2.60 g, 0.018 mol) were dissolved in 60 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 40 mL of 85% aqueous ethanol and twice with 40 mL of cold ethanol. The obtained

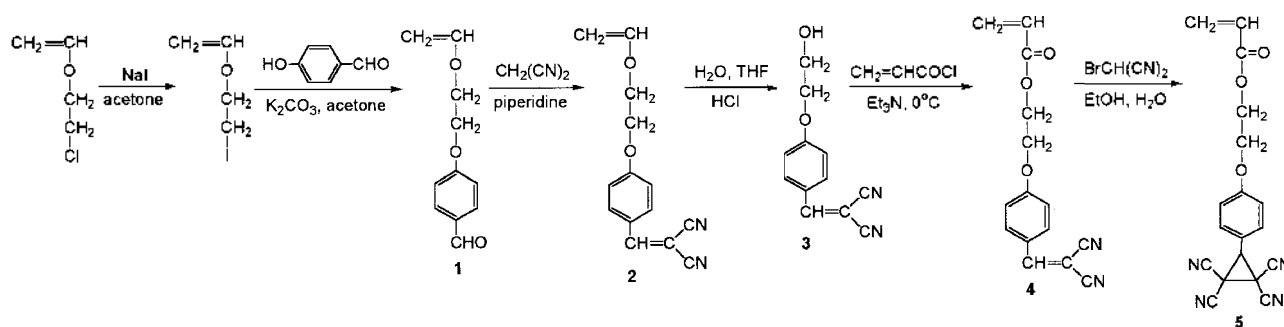
white crystals were recrystallized from ethanol/acetone (90/10, vol./vol.) mixtures to give 2.71 g (68% yield) of **5**. Mp: 146-148 °C. ¹H NMR (CDCl₃) δ 3.95 (s, 1H, cyclopropyl), 4.25-4.28 (t, 2H, -O-CH₂-), 4.52-4.55 (t, 2H, -CH₂-OCO-), 5.85-5.89 (2d, 1H, vinylic), 6.10-6.20 (q, 1H, vinylic), 6.42-6.48 (2d, 1H, vinylic), 7.05-7.08 (d, 2H, aromatic), 7.41-7.44 (d, 2H, aromatic). IR (KBr) 3048 (m, =C-H), 2957 (m, C-H), 2258 (m, CN), 1734 (vs, C=O), 1653, 1608 (s, C=C) cm⁻¹. Anal. Calcd for C₁₈H₁₂N₄O₃: C, 65.06; H, 3.64; N, 16.85. Found: C, 65.14; H, 3.58; N, 16.78.

Radical polymerization of monomer 5. A representative radical polymerization procedure was as follows: In a polymerization tube were placed 1.33 g (4.0 mmol) of **5**, 3.94 mg (0.024 mmol) of AIBN, and 4.0 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 500 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. The obtained polymer was dried under vacuum to give 1.00 g (75% yield) of polymer **6**: η_{inh} =0.30 dL/g (c. 0.5 g/dL in acetone at 25 °C). ¹H NMR (acetone-*d*₆) δ 1.50-1.95 (br, 2H, -CH₂-), 2.48-2.70 (br, 1H, -CH-CO-), 3.95-4.79 (br, 5H, cyclopropyl, -O-CH₂-CH₂-OCO-), 6.96-7.16 (br, 2H, aromatic), 7.66-7.81 (br, 2H, aromatic). IR (KBr) 2959, 2885 (m, C-H), 2258 (m, CN), 1732 (vs, C=O), 1608, 1582 (s, C=C) cm⁻¹. Anal. Calcd for (C₁₈H₁₂N₄O₃)_n: C, 65.06; H, 3.64; N, 16.85. Found: C, 65.18; H, 3.73; N, 16.92.

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 malononitrile *via* Knoevenagel condensation to give methyl *p*-(2-vinyloxyethoxy)benzylidenemalononitrile **2**.¹⁵ Compound **2** was hydrolyzed to give acetaldehyde and *p*-(2-hydroxyethoxy)benzylidenemalononitrile **3**. *p*-(2-Acryloyloxyethoxy)benzylidene malononitrile **4** was prepared from compound **3** and acryloyl chloride by the well-known Schotten-Baumann method. *p*-(2,2,3,3-Tetracyanocyclopropyl)phenoxy ethyl acrylate **5** was prepared by the reaction of bromomalononitrile with *p*-(2-acryloyloxyethoxy)benzylidenemalononitrile **4**, according to a variation of the Wideqvist reaction.¹⁶ In 85% aqueous ethanol solution at room temperature, monomer **5** was obtained in moderate yields. The chemical structure of the compounds was confirmed by ¹H NMR, IR spectra, and elemental analysis. The signal at 3.95 ppm of the ¹H NMR spectrum assigned to the cyclopropyl proton indicates the formation of tetracyanopropyl ring.

Radical polymerization of monomer 5. *p*-(2,2,3-Tetracyanocyclopropyl)phenoxy ethyl 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. Monomer **5** was quite reactive toward free radical initiator and polymerized readi-



Scheme 1

ly. 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. The resulting polymer was reprecipitated from acetone into methanol. 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 well consistent with the proposed polymer structures. We now have well defined polymer **6** and investigate their properties.

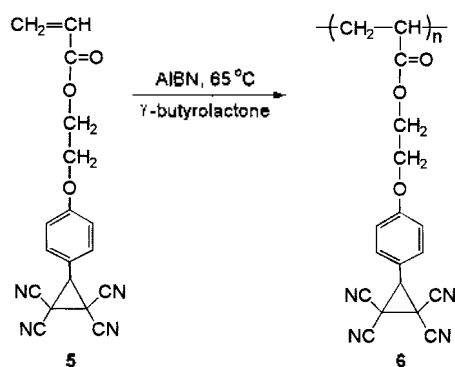
Properties of polymers. The polymers were soluble in chloroform, acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosity measured in acetone at 25 °C was in the range of 0.25-0.30 dL/g. The thermal behavior of the polymer **6** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pat-

tern and glass transition temperature (T_g). The resulting polymer showed a thermal stability up to 320 °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 140 °C, and these T_g values are higher than those for poly(tricyanocyclopropyl acrylate) (132 °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 elsewhere.

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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	0.30
5	0.67	1.0	24	80	0.25
5	1.00	1.0	24	84	0.28

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