

^{13}C NMR (CDCl_3) δ 19.55, 22.36, 26.05, 50.53, 119.30, 122.78, 128.70, 151.48, 171.20; MS m/z 175 (29), 160 (30), 132 (100), 118 (90), 77 (82); IR (neat) $\nu_{\text{C}=\text{N}}$ 1663 (cm^{-1})

Acetone benzylimine (5). bp 68 °C (1.5 torr); ^1H NMR (CDCl_3) δ 1.92 (s, 3H), 2.08 (s, 3H), 4.44 (s, 2H), 7.19-7.35 (m, 5H); ^{13}C NMR (CDCl_3) δ 18.66, 29.35, 55.33, 126.41, 127.70, 128.14, 140.24, 168.08; MS m/z 147 (16), 91 (100); IR (neat) $\nu_{\text{C}=\text{N}}$ 1663 (cm^{-1})

2-Butanone benzylimine (6). bp 81 °C (1.5 torr); ^1H NMR (CDCl_3) δ 1.14 (t, 3H, $J=3.3$ Hz), 1.89 (s, 3H), 2.30 (q, 2H, $J=5.2$ Hz), 4.48 (s, 2H), 7.19-7.33 (m, 5H); ^{13}C NMR (CDCl_3) δ 10.78, 17.22, 35.65, 54.90, 126.31, 127.53, 128.23, 140.49, 171.94; MS m/z 161 (20), 91 (100); IR (neat) $\nu_{\text{C}=\text{N}}$ 1663 (cm^{-1})

2-Butanone *m*-tolylimine (7). bp 50 °C (1.0 torr); ^1H NMR (CDCl_3) δ 1.15 (t, 3H, $J=7.5$ Hz), 1.74 (s, 3H), 2.29 (s, 3H), 2.35 (q, 2H, $J=7.5$ Hz), 6.46-7.17 (m, 4H); ^{13}C NMR (CDCl_3) δ 10.43, 19.06, 21.29, 34.46, 116.35, 119.99, 123.50, 128.52, 138.42, 151.53, 172.36; MS m/z 161 (42), 146 (30), 132 (100), 91 (68); IR (neat) $\nu_{\text{C}=\text{N}}$ 1667 (cm^{-1})

2-Methylcyclohexanone benzylimine (8). bp 118 °C (1.8 torr); ^1H NMR (CDCl_3) δ 1.13 (d, 3H, $J=6.7$ Hz), 1.30-2.68 (m, 9H), 4.59 (s, 2H), 7.18-7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 17.12, 24.45, 27.45, 28.06, 35.87, 42.00, 53.28, 125.97, 127.11, 127.95, 140.73, 176.13; MS m/z 201 (34), 186 (11), 91 (100); IR (neat) $\nu_{\text{C}=\text{N}}$ 1659 (cm^{-1})

2-*tert*-Butylcyclohexanone benzylimine (9). bp 131 °C (2.0 torr); ^1H NMR (CDCl_3) δ 1.05 (s, 9H), 1.47-2.55 (m, 9H), 4.58 (s, 2H), 7.18-7.37 (m, 5H); ^{13}C NMR (CDCl_3) δ 25.09, 27.22, 28.69, 29.13, 29.41, 33.35, 53.95, 57.14, 126.14, 127.58, 128.19, 141.39, 175.36; MS m/z 243 (4), 186 (28), 91 (100); IR (neat) $\nu_{\text{C}=\text{N}}$ 1659 (cm^{-1})

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Synthesis and Cationic Polymerization of 2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy] ethyl Vinyl Ether

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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, in case of the polymer of vinylidene cyanide and vinyl acetate.² Poly(acrylonitrile) 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- or four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments⁵ and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,⁵⁻⁷ 1,1,2-tricyano-2-carbomethoxycyclopropane,^{8,9} 1,2-dicyano-1,2-dicarbomethoxycyclopropane units,¹⁰ but have not yet obtained film-forming materials. In this work we investigated the poly(ethyl vinyl ether) containing *p*-(2,2,3,3-tetracyanocyclopropyl) phenoxy group. The present report describes the synthesis and cationic polymerization of 2-[*p*-(2',2',3',3'-tetracyanocyclopropyl) phenoxy] ethyl vinyl ether 4.

2-Iodoethyl vinyl ether 1 was prepared by the well known halogen exchange reaction¹¹ from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4-hydroxybenzaldehyde to yield *p*-(2-vinyloxyethoxy) benzaldehyde 2.¹² Compound 2 was condensed with malononitrile with a small amount of piperidine to give *p*-(2-vinyloxyethoxy) benzylidenemalononitrile 3.¹³ 2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl) phenoxy] ethyl vinyl ether 4 was synthesized in moderate yield by cyclopropane formation from bromomalononitrile and 3 in the presence of triethylamine, according to a variation of the Wideqvist reaction.¹⁴ The chemical structure of the compounds was confirmed by ^1H NMR (Figure 1a), IR spectra, and elemental analyses.

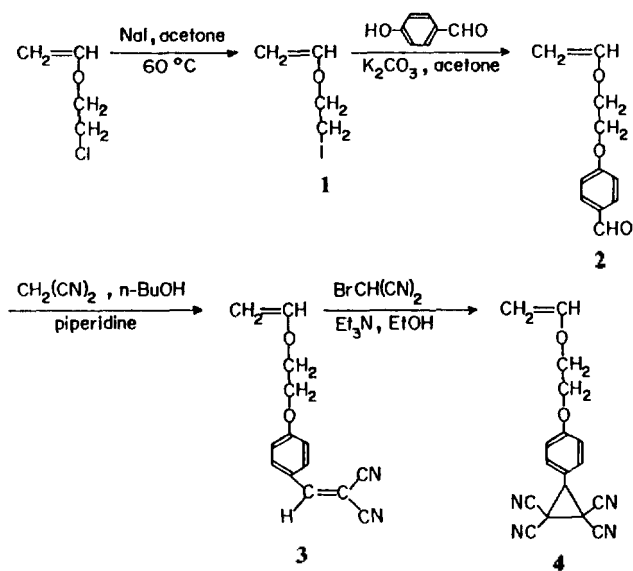
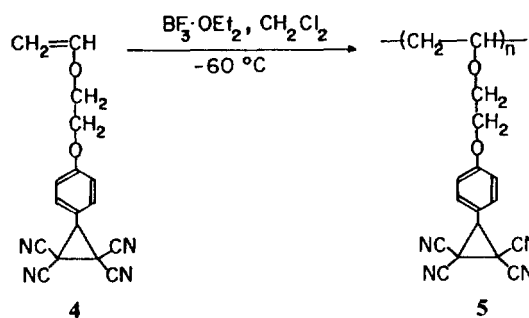
2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy]ethyl vinyl ether 4 was polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiator to obtain the polymer 5. The polymerization results are summarized in Table 1.

Monomer 4 was quite reactive toward cationic initiator and polymerized readily. The chemical structure of the polymer 5 was confirmed by ^1H NMR (Figure 1b), IR spectra

Table 1. Cationic Polymerization of **4** under Various Conditions

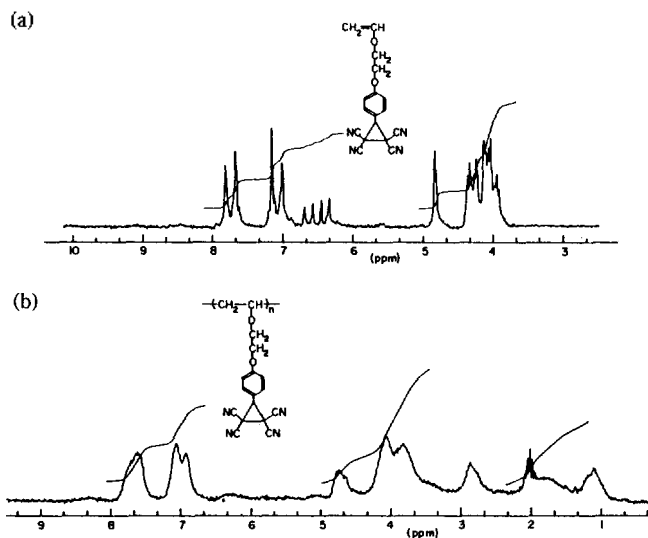
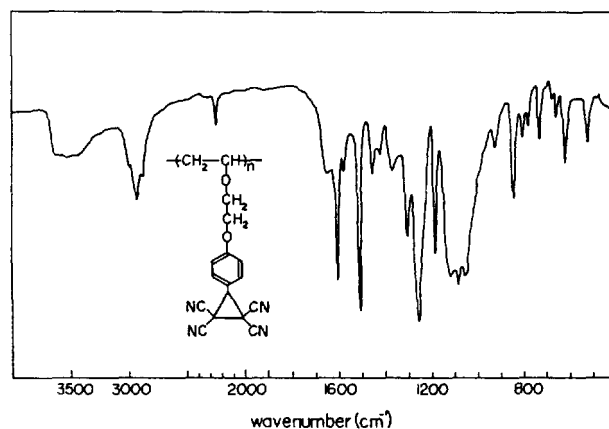
Monomer	Solvent (vol/vol)	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Temp (°C)	Time (h)	Yield (%)	η_{inh}^a (dL/g)
4	CH ₃ CN/CH ₂ Cl ₂	0.65	0.70	-60	10	85	0.18
4	CH ₃ CN/CH ₂ Cl ₂	0.48	0.82	-60	15	88	0.16
4	CH ₃ CN/CHCl ₃	0.50	0.50	-30	20	82	0.15
4	CH ₃ CN/CHCl ₃	0.40	0.57	-30	12	80	0.20

^aInherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 °C.

**Scheme 1.****Scheme 2.**

(Figure 2), and elemental analyses. The cationic initiator did not attack the cyclopropane ring during the polymerization. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities.

The polymer **5** was soluble in acetone and DMSO, but were not soluble in chloroform and diethyl ether. The inherent viscosity was in the range of 0.15–0.20 dL/g indicating moderate molecular weights. The thermal behavior of the polymer **5** 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.

**Figure 1.** ¹H NMR spectrum (60 MHz) of monomer **4** (a) and polymer **5** (b) taken in acetone-*d*₆ at room temperature.**Figure 2.** IR spectrum of polymer **5**.

The polymers show a double phase degradation pattern in their TGA thermograms, probably due to the presence of two rings in the pendant group. The glass transition temperature (T_g) of the polymer **5** was around 73 °C, as shown in Table 2. These T_g values are higher than those of poly(ethyl vinyl ether) (-43 °C), probably because of the presence of polar pendant group. Solution-cast films were clear and brittle, which could be due to the rather low molecular weight

Table 2. Thermal Properties of Polymer 5

Polymer	T_g , °C	Degradation temp., °C ^b			Residue ^b at 700°C, %
		5%-loss	20%-loss	40%-loss	
5	73	208	354	563	44.4

^aDetermined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere. ^bDetermined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

and/or high concentration of dipole moment.

In conclusion, we prepared a new monomeric ethyl vinyl ether 4 containing four cyano groups in a small cyclopropane ring. The tetracyanocyclopropane-substituted ethyl vinyl ether was polymerized cationically to obtain the polymers with multicyno functions. Monomer 4 was quite reactive toward cationic initiators such as boron trifluoride etherate, polymerizing readily in high conversion. Copolymerization with other monomers and measurements of piezoelectric activity are in progress, and the results will be reported later.

Experimental

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. Bromomalononitrile was prepared according to a literature procedure¹⁵ and recrystallized twice from chloroform.

2-Iodoethyl Vinyl Ether (1). Anhydrous sodium iodide (45 g, 0.30 mol) was dissolved in 320 ml of dry acetone contained in a 500 ml round-bottom flask fitted with a reflux condenser protected by a calcium chloride tube, and heated on a heating mantle for 1 h with stirring. 2-Chloroethyl vinyl ether (25.0 g, 0.23 mol) was added to the mixture, and refluxed for an additional 25 h with stirring to complete the reaction. The resulting solution was cooled to room temperature and filtered with suction. The sodium chloride on the filter was washed with 55 ml of acetone and the filtrate was concentrated by distillation of the solvent. The residue was poured into 260 ml of water contained in a separate funnel, which was shaken. The lower layer was washed successively with 55 ml of 10% sodium bisulfite solution, 55 ml of 5% sodium bicarbonate, and 30 ml of water. It was dried with anhydrous magnesium sulfate (1.8 g) and fractionated under reduced pressure to give 32.8 (72% yield) of 1. Bp: 50-52 °C (20 mmHg). ¹H NMR (CDCl₃) δ 6.22-6.57 (q, 1H, =CH-O-), 3.50-4.37 (m, 4H, CH₂= and -O-CH₂-), 2.82-3.47 (t, 2H, -CH₂-I). IR (neat) 3105, 3034, 2960, 2922, 2845 (C-H), 1635, 1612 (C=C) cm⁻¹.

***p*-(2-Vinyloxyethoxy)benzaldehyde (2).** 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 h 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 2. Bp: 72-74 °C (0.2 mmHg). Compound 2 was crystallized in the refrigerator (6 °C). ¹H NMR (acetone-d₆) δ 9.89 (1H, s, -CH=O), 7.63-7.99 (2H, m, aromatic), 6.87-7.28 (2H, m, aromatic), 6.32-6.73 (1H, q, =CH-O-), 4.18-4.48 (2H, m, CH₂=), 3.70-4.17 (4H, m, -O-CH₂-CH₂-O-). IR (neat) 3119, 3068, 2940, 2878, 2833 (C-H), 1694, 1603, 1579 (C=C) cm⁻¹.

***p*-(2-Vinyloxyethoxy)benzylidenemalononitrile (3).**

Piperidine (0.13 g, 1.5 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde 2 (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 ml of *n*-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 *n*-butanol (80 ml), water (30 ml), and cold *n*-butanol (20 ml). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.38 g (80% yield) of 3. Mp: 80-82 °C. ¹H NMR (acetone-d₆) δ 7.75-8.13 (3H, m, aromatic and -C=C(CN)₂), 6.83-7.28 (2H, m, aromatic), 6.30-6.73 (1H, q, =CH-O-), 4.20-4.51 (2H, m, CH₂=), 3.76-4.21 (4H, m, -O-CH₂-CH₂-O-). IR (KBr) 3105, 3067, 2938, 2869 (C-H) 2230 (CN), 1628, 1603, 1579 (C=C) cm⁻¹. Anal. Calcd for C₁₄H₁₂N₂O₂: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.08; N, 11.58.

2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy]ethyl Vinyl Ether (4).

Bromomalononitrile (1.30 g, 9 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzylidenemalononitrile 3 (1.44 g, 6 mmol) and triethylamine (0.91 g, 9 mmol) in 20 ml of absolute ethanol with stirring at 0 °C under nitrogen. The reaction mixture was stirred for 5 min at 0 °C and 12 h at room temperature. The resulting solution was cooled in an ice bath for 2 h. After filtration of the product, it was rinsed with 100 ml of water and 20 ml of cold ethanol. The obtained white product was recrystallized from ethanol-acetone (90/10, vol/vol) mixture to give 1.05 g (58% yield) of 4. Mp: 124-126 °C (dec). ¹H NMR (acetone-d₆) δ 7.52-7.92 (2H, m, aromatic), 6.81-7.25 (2H, m, aromatic), 6.27-6.75 (1H, q, =CH-O-), 4.83 (1H, s, benzyliccyclopropyl), 4.17-4.42 (2H, m, CH₂=), 3.76-4.16 (4H, m, -O-CH₂-CH₂-O-). IR (KBr) 3062, 2988, 2910, 2865 (C-H), 2260 (CN), 1613, 1579 (C=C) cm⁻¹. Anal. Calcd for C₁₇H₁₂N₄O₂: C, 67.10; H, 3.97; N, 18.41. Found: C, 67.18; H, 3.92; N, 18.35.

Cationic Polymerization of 2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy]ethyl Vinyl Ether (4). A representative cationic polymerization procedure was as follows: A solution of 4 (0.91 g, 3 mmol) in acetonitrile (1.7 ml) and dichloromethane (2.6 ml) was placed in a rubber septum stopper capped glass ampule under nitrogen. The resulting solution was flushed with nitrogen for 20 min. The ampule was then placed in an ethanol-acetone bath kept at -60 °C under nitrogen, and 0.0035 ml (0.03 mmol) of boron trifluoride etherate was added to the solution. After 10 h the ampule was taken out and the polymerization mixture was poured into 500 ml of diethyl ether. The precipitated polymer was collected and reprecipitated from acetone into diethyl ether. Thus obtained polymer was then dried in a vacuum oven. 5 : 0.77 g (85% yield); η_{inh} = 0.18 dL/g (0.5 g/dL in acetone at 25 °C). ¹H NMR (acetone-d₆) δ 7.37-7.89 (2H, m, aromatic), 6.75-7.33 (2H, m, aromatic), 4.52-4.93 (1H, s, benzyliccyclopropyl), 3.43-4.37 (5H, m, -CH-O-CH₂-CH₂-O-), 1.31-2.26 (2H, m, -CH₂-). IR (KBr) 2996, 2938, 2865 (C-H), 2250 (CN), 1646, 1608, 1577 (C=C) cm⁻¹. Anal. Calcd for (C₁₇H₁₂N₄O₂)_n: C, 67.10; H, 3.97; N, 18.41. Found: C, 67.21; H, 3.85; N,

18.49.

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