Synthesis and Radical Polymerization of the Acrylate and Methacrylate Esters of 1-Methyl-2,2,3,3-tetracyanocyclopropylcarbinol

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ABSTRACT: The acrylate and methacrylate esters of 1-methyl-2,2,3,3-tetracyanocyclopropylcarbinol (**2a** and **2b**) were prepared by the reactions of 2 equiv of bromomalononitrile with acetonyl acrylate (**1a**) or acetonyl methacrylate (**1b**), respectively. Compounds **2a** and **2b** polymerized with free-radical initiators to obtain the polymers with multicyano functionalities in the cyclopropane ring. The resulting polymers were soluble in acetone and tetrahydrofuran, and inherent viscosities in the range of 0.25–0.35 dL/g were obtained. Solution-cast films were clear and brittle, showing T_g values in the range of 72–80 °C.

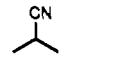
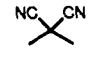
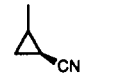
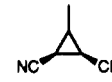
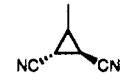
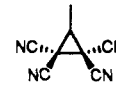
Introduction

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 having large dipole moments can exhibit piezoelectric effects if the main chains have an all-planar zigzag structure. The best known polymer is crystalline poly(vinylidene fluoride).[2] However, amorphous polymers with high concentrations of dipole moments can also exhibit the piezoelectric properties. The copolymer of vinylidene cyanide and vinyl acetate is such a case.[3]

Poly(acrylonitrile) has high concentrations of nitrile dipoles, but the helical structure of the polymer main chains causes the radiating dipoles to cancel each other.[4] Introduction of only a small amount (~5%) of a comonomer greatly increases the internal mobility of polymer segments. The copolymer of acrylonitrile with 7% methyl methacrylate does show piezoelectric behavior after stretching.[5] In the case for poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation and this polymer does indeed show piezoelectric behavior.[6]

Unlike linear chains, for which the dipoles of vicinal cyano groups oppose each other, small rings hold vicinal cyano groups in roughly parallel alignment. Small rings, three- and four-membered, do not undergo large conformational changes found in the larger rings, most notably five- and six-membered rings. To verify this concept, molecular modeling calculations were performed on aliphatic and cyclic nitriles using AM1.[7] These results are summarized in Table I. The largest dipole moment was calculated for a *cis*-dicyanocyclopropane unit. However, these are not easily synthesized. The tetrasubstituted ring also has a large dipole moment and is the topic of this paper. In this report, we describe the initial phase of this research, namely the synthesis and polymerization of two monomers containing the tetracyanocyclopropane unit.

Table I
Calculated Dipole Moments (*D*) from AM1

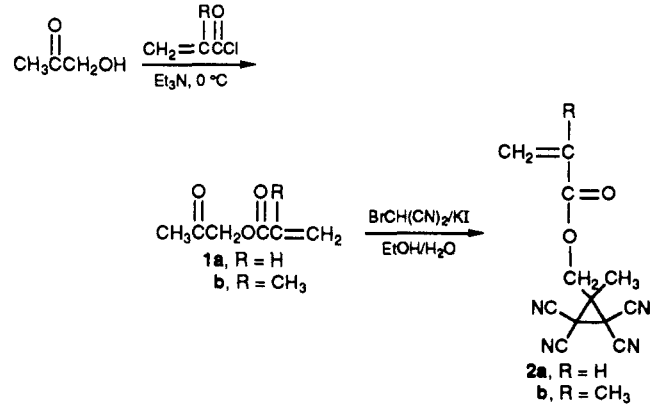
	2.96		3.34
	3.02		4.50
	2.20		3.55

Experimental Section

Materials. The reagent-grade chemicals were purified by distillation or recrystallization before use. Technical-grade acetol was distilled before use. Acryloyl chloride and methacryloyl chloride (Aldrich) were distilled and used immediately. Triethylamine was refluxed over KOH and distilled. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Bromomalononitrile was prepared according to a literature procedure[8] and recrystallized twice from chloroform. 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 molecular sieves under nitrogen. γ-Butyrolactone was dried with anhydrous calcium sulfate and fractionally distilled. α,α′-Azobis(isobutyronitrile) was recrystallized from methanol and stored at 3 °C.

Measurements. All melting point temperatures are uncorrected. IR spectra were taken on a Perkin-Elmer 983 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker WM 250 nuclear magnetic resonance spectrometer at 250 MHz. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Viscosity values were obtained by using a Cannon-Fenske viscometer. Melting points were measured in a Thomas-Hoover melting point apparatus. The glass transition temperatures (T_g) were measured on a Perkin-Elmer DSC-4 differential scanning calorimeter in a nitrogen atmosphere.

Preparation of Acetonyl Acrylate (1a). Acetonyl acrylate and acetonyl methacrylate were prepared by the Schotten–Baumann procedure. At 0 °C under nitrogen, 18.1 g (0.2 mol)



of freshly distilled acryloyl chloride in 40 mL of dry 1,2-dichloroethane was added dropwise to a solution of acetol (hydroxyacetone) (14.8 g, 0.2 mol), triethylamine (23.3 g, 0.23 mol), and 50 mL of 1,2-dichloroethane. The resulting solution was

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Table II
Free-Radical Polymerization of 2a,b by AIBN at 65 °C

monomer[a]	solvent (vol/vol)	monomer, g/mL	initiator to monomer, mol %	temp, °C	time, h	yield, %	η_{inh},[b] dL/g	T_g,[c] °C
2a	C_6H_6/CH_3CN (2.5)	0.20	1.0	65	8	88	0.26	
2a	C_6H_6/CH_3CN (2.0)	0.25	0.9	65	10	86	0.25	
2a	γ-butyrolactone	0.36	0.9	65	20	89	0.33	72
2b	C_6H_6/CH_3CN (1.5)	0.23	1.0	65	10	88	0.29	
2b	C_6H_6/CH_3CN (1.7)	0.16	0.9	65	20	85	0.26	
2b	γ-butyrolactone	0.44	1.0	65	16	92	0.37	80

[a] **2a** = 1-methyltetracyanocyclopropylcarbinol acrylate ester; **2b** = 1-methyltetracyanocyclopropylcarbinol methacrylate ester. [b] Inherent viscosity of polymer: concentration of 0.5 g/dL in acetone at 25 °C. [c] Determined from DSC curves measured on a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 10 °C/min in a nitrogen atmosphere.

stirred for 1 h at 0 °C and 2 h 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 40 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 0.04 g (1.11×10^{-4} mol) of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide as inhibitor was added. Fractional distillation with a Vigreux column yielded 18.9 g of **1a** (74% yield). Bp: 46–47 °C (3 mmHg). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3 H), 4.73 (s, 2 H), 5.82–5.96 (q, 1 H), 6.17–6.29 (q, 1 H), 6.48–6.52 (q, 1 H). IR (neat): 1724 (C=O), 1632 (C=C) cm^{-1}. Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.25. Found: C, 56.07; H, 6.33.

Preparation of Acetonyl Methacrylate (1b). A solution of methacryloyl chloride (41.8 g, 0.4 mol) in dry 1,2-dichloroethane (80 mL) was added dropwise to a solution of acetol (29.6 g, 0.4 mol), dry triethylamine (46.5 g, 0.46 mol), and 100 mL of 1,2-dichloroethane at 0 °C under nitrogen. The resulting solution was stirred for 1 h at 0 °C and 3 h at room temperature. Triethylamine hydrochloride was then filtered off and rinsed with 80 mL of 1,2-dichloroethane. Extractions were performed on the filtrate twice with 100 mL of 1 N HCl, once with 100 mL of water, and twice with 100 mL of saturated sodium bicarbonate. The resulting organic layer was dried over anhydrous magnesium sulfate and filtered. The solution was concentrated, and 0.08 g (2.22×10^{-4} mol) of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide as inhibitor was added. Fractional distillation with a Vigreux column gives 40.9 g (72% yield) of **1b**. Bp: 51–52 °C (3 mmHg) [lit.[8] bp 48–49 °C (2 mmHg)]. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 3 H), 2.15 (s, 3 H), 4.67 (s, 2 H), 5.66 (m, 1 H), 6.21 (m, 1 H). IR (neat): 1723 (C=O), 1613 (C=C) cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.15; H, 7.04. Found: C, 59.30; H, 7.13.

Preparation of the Acrylate Ester of 1-Methyl-2,2,3,3-tetracyanocyclopropylcarbinol (2a). A solution of 21 g (0.13 mol) of potassium iodide in 60 mL of water was added slowly to a solution of acetonyl acrylate (7.68 g, 0.06 mol) and bromomalononitrile (8.70 g, 0.06 mol) in 40 mL of ethanol at room temperature. After the solution was stirred for 5 h at room temperature, the product was filtered and rinsed with cold ethanol (50 mL). The obtained white crystals were recrystallized from chloroform to give 4.68 g (65% yield) of **2a**. Mp: 133–134 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 3 H), 4.56 (s, 2 H), 6.05–6.17 (t, 1 H), 6.20–6.30 (t, 1 H), 6.57–6.64 (d, 1 H). ^{13}C NMR (acetone-d_6): δ 15.8 (CH_3), 26.4 (*C*Me cyclopropane), 41.5 (*C*-$(CN)_2$), 62.9 (CH_2), 109.3, 109.6 (CN), 126.9 (=CH), 129.5 (CH_2=), 164.5 (CO). IR (KBr): (C≡N), 1724 (C=O), 1632 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.33; N, 23.33. Found: C, 59.83; H, 3.20; N, 23.17.

Preparation of Methacrylate Ester of 1-Methyl-2,2,3,3-tetracyanocyclopropylcarbinol (2b). A solution of potassium iodide (17.50 g, 0.11 mol) in 50 mL of water was added slowly to a solution of acetonyl methacrylate (7.10 g, 0.05 mol) and bromomalononitrile (7.25 g, 0.05 mol) in 30 mL of ethanol at room temperature. The resulting solution was stirred for 6 h at room temperature. After filtering, the crude product was rinsed with 40 mL of cold ethanol. The white crystals were recrystallized from chloroform to give 4.45 g (70% yield) of **2b**. Mp: 155–156 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3 H), 2.02 (m, 3 H), 4.54 (s, 2 H), 5.79 (m, 1 H), 6.27 (m, 1 H). ^{13}C NMR (acetone-d_6): δ 15.9 (CH_3 cyclopropane), 18.8 (CH_3 methacrylate), 26.4 (*C*Me cyclopropane), 41.6 (*C* $(CN)_2$), 63.2 (CH_2), 109.4, 109.6 (CN), 127.8 (CH_2=), 134.6 (=C), 165.7 (CO). IR (KBr): 2252 (C≡N), 1713 (C=O), 1632 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_4O_2$: C, 61.42; H, 3.94; N, 22.05. Found: C, 61.26; H, 3.78; N, 22.03.

Radical Polymerization of the Acrylate (2a) and Methacrylate (2b) Esters of 1-Methyl-2,2,3,3-tetracyanocyclopropylcarbinol. A representative free-radical polymerization procedure was as follows: A γ-butyrolactone (1.7 mL) solution of **2a** (0.62 g, 2.6 mmol) was placed in a polymerization tube, and 3.9 mg (2.3×10^{-2} mmol) of AIBN was added under nitrogen. The mixture was degassed by a freeze-thaw process under vacuum. After the mixture was warmed to room temperature, it was placed in an oil bath kept at 65 °C. After 20 h, the polymerization tube was opened and the viscous product was poured into 400 mL of diethyl ether. The precipitated polymer was collected and reprecipitated from acetone into diethyl ether.

3a: 0.55 g (89% yield); η_{inh} = 0.33 dL/g (0.5 g/dL in acetone). ^{1}H NMR (acetone-d_6): δ 1.8 (s, 3 H, CH_3), 2.0 (br s, 2 H, CH_2 backbone), 2.7 (br s, 1 H, CH backbone), 4.6 (br s, 2 H, OCH_2). ^{13}C NMR (acetone-d_6): δ 16.1 (CH_3), 26.5 (*C*Me cyclopropane), 30.0 (CH_2 backbone), 34.8 (CH backbone), 42.0 (*C*$(CN)_2$, 64.7 (CH_2), 109.3, 109.6 (CN), 173.8 (CO). IR (KBr): 2255 (C≡N), 1745 (C=O). Anal. Calcd for $(C_{12}H_8N_4O_2)_n$: C, 60.00; H, 3.33: N, 23.33. Found: C, 59.79; H, 3.19; N, 23.27.

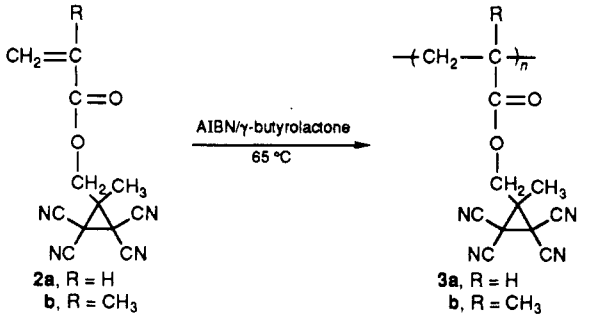
3b: 92% yield, η_{inh} = 0.37 dL/g (0.5 g/dL in acetone). ^{1}H NMR (acetone-d_6): δ 1.2 (br, 3 H, Me backbone), 1.9 (br s, 3 H, Me cyclopropane), 2.2 (v br, 2 H, CH_2 backbone), 4.5 (br, 2 H, OCH_2). ^{13}C NMR (acetone-d_6): δ 16.8 (CH_3 cyclopropane), 18.5, 20.0 (CH_3 methacrylate), 27.0 (*C*Me cyclopropane), 41.7 (*C* $(CN)_2$), 45.9 (CH_2 backbone), 54 (br, CH backbone), 66.1 (OCH_2), 109.8, 110.2 (CN), 177 (CO). IR (KBr): 2250 (CN), 1744 (C=O) cm^{-1}.

Results and Discussion

Syntheses of Monomers 2a and 3b. Acetonyl acrylate and acetonyl methacrylate were prepared by the well-known Schotten–Baumann method. The acrylate (**2a**) and methacrylate (**2b**) esters of 1-methyl-2,2,3,3-tetracyanocyclopropylcarbinol were prepared from bromomalononitrile and acetonyl acrylate or methacrylate, respectively, following established literature procedures.[10–12] In dilute aqueous ethanol solution at room temperature, the title compounds were obtained in high yields. The chemical structure of the compounds was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Both of the tetracyanocyclopropanes **2a** and **2b** were quite stable when heated at 100 °C.

Radical Polymerization of 2a and 2b. The substituted tetracyanocyclopropane monomers **2a** and **2b** were polymerized with free-radical initiator (AIBN) to obtain the polymers **3a** and **3b**. Polymerizations were carried out in solution at 65 °C. Monomers **2a** and **2b** were quite reactive toward radical initiator and polymerized readily. The polymerization results and physical data for the polymers are summarized in Table II. In most cases, conversions were very high (~90% yield).

The chemical structure of the polymers **3a** and **3b** were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and elemental



analyses. The polymers were soluble in acetone and tetrahydrofuran but were not soluble in diethyl ether and chloroform. The inherent viscosities measured in acetone were in the range 0.25–0.35 g/dL. The thermal behavior of the polymers was investigated by DSC at a scanning rate of 10 °C/min, and the glass transition temperatures (T_g) were found to be about 80 °C for both polymers. These T_g values are higher than those for poly(methyl acrylate) (10 °C) and comparable to those for poly(methyl methacrylate) (105 °C). Films cast from polymer solution in acetone or cyclohexanone were brittle, and therefore the piezoelectric activity has not been measured yet.

Conclusion

We prepared two new monomers **2a** and **2b** containing four cyano groups in a small cyclopropane ring. The tetracyanocyclopropane compounds were polymerized radically to obtain the polymers with multicyano functions. The resulting polymers were soluble in acetone and tetrahydrofuran but insoluble in chloroform. The T_g value of the polymer was around 80 °C. Films cast from solution were brittle, which could be due to the rather low molecular weights, as indicated by the inherent viscosities, and/or to the presence of strong dipoles in the side chain. Attempts to obtain higher molecular weights by lowering the initiator concentration and changing solvents failed. Even though we do not see any evidence of radical attack of the tetracyanocyclopropane rings in the NMR spectra of the polymers, these rings could possibly act as weak inhibitors. We have observed a similar effect by tetracyanocyclobutyl groups incorporated in the monomer.[13] It is also known that cyclopropane rings are able to participate in free-radical polymerization if a vinyl group is directly attached to the cyclopropane ring.[14] Copolymerization with other monomers and measurements of piezoelectric activity are in progress, and the results will be reported later.

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References and Notes

(1) Hall, H. K., Jr. *J. Macromol. Sci., Chem.* **1988**, *A25*, 729.
(2) Hasegawa, R.; Takahashi, Y.; Tadokoro, H. *Polym. J.* **1972**, *3*, 600.
(3) Jo, Y. S.; Inoue, Y.; Chujo, R.; Saito, K.; Miyata, S. *Macromolecules* **1985**, *18*, 1850.
(4) Henrici-Olivé, G.; Olivé, S. *Adv. Polym. Sci.* **1975**, *6*, 421.
(5) Von Berlepsch, H.; Kuenstler, W. *Polym. Bull.* **1988**, *19*, 305.
(6) Hall, H. K., Jr.; Chan, R. J. H.; Oku, J.; Hughes, O. R.; Scheinbeim, J.; Newman, B. *Polym. Bull.* **1987**, *17*, 135.
(7) Dewar, M. I. S.; Zoebisch, E. U.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(8) Hesse, B. C. *J. Am. Chem. Soc.* **1986**, *18*, 723.
(9) Veda, M.; Mano, M.; Yazawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2295.
(10) Ramberg, L.; Widequist, S. *Arh. Kem.* **1937**, *12A* (22), 12.
(11) Ramberg, L.; Widequist, S. *Arh. Kem.* **1945**, *20B* (4), 8.
(12) Hart, H.; Freeman, F. *J. Org. Chem.* **1963**, *28*, 1220.
(13) Padias, A. B.; Hall, H. K., Jr. *Polym. Bull.* **1990**, *24*, 195.
(14) Cho, I.; Ahn, K. D. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3169.

Registry No. **1a**, 54545-40-3; **1b**, 44901-95-3; **2a**, 130200-29-2; **2b**, 130200-30-5; **3a** (homopolymer), 130200-31-6; **3b** (homopolymer), 130200-32-7; acetal, 116-09-6; bromomalonitrile, 1885-22-9.