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Synthesis and radical polymerization of *p*-(2,3-dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate and methacrylate

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Summary

p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate **3a** and methacrylate **3b** were prepared by the reactions of methyl bromocyanoacetate with methyl acryloyloxybenzylidenecyanoacetate **2a** or methyl p-methacryloyloxybenzylidenecyanoacetate **2b**, respectively. Monomers **3a** and **3b** were polymerized with free-radical initiators to obtain polymers with multicyanocyclopropane functionalities in the pendant group. The resulting polymers **4a-b** were soluble in acetone and the inherent viscosities were in the range of 0.15-0.25 dL/g. Solution-cast films were brittle, showing T_g values in the range of 120-150°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 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 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[5] and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,[5-6] 1,1,2-tricyano-2-carbomethoxycyclopropane,[7] 1,1,2,2-tetracyanocyclobutane units,[8] but have not yet obtained film-forming materials. The present report describes the synthesis and radical polymerization of p-(2,3-dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate and methacrylate **3a-b**.

Experimental

Materials

The reagent grade chemicals were purified by distillation or recrystallization before use. p-Hydroxybenzaldehyde was crystallized from water containing a 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. n-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and stored at 5°C. Methyl bromocyanoacetate was prepared according to a literature procedure[9] and purified by fractional distillation.

Measurements

IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. Proton-NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperature (T_g) were measured on a DuPont 910 differential scanning calorimeter in 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 atmosphere. Melting points were measured in Buchi 512 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Preparation of p-Acryloyloxybenzaldehyde **1a**

p-Acryloyloxybenzaldehyde was prepared by the Schotten-Baumann procedure. At 0°C under nitrogen, 18.1 g (0.20 mol) of freshly distilled acryloyl chloride in 30 mL of dry 1,2-dichloroethane was added dropwise to a solution of p-hydroxybenzaldehyde (22.0 g, 0.18 mol), triethylamine (20.2 g, 0.20 mol), and 50 mL of 1,2-dichloroethane with stirring. The resulting solution was stirred for 1 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 23.1 g (73% yield) of **1a**. Mp 17-18°C. Proton-NMR (acetone-d_6) δ 5.88-6.17 (m, 1H), 6.28-6.68 (m, 2H), 7.17-7.46 (m, 2H), 7.70-8.06 (m, 2H), 9.97 (s, 1H): IR (neat) 1743, 1696 (C=0), 1598 (C=C) cm^{-1}. Anal. Calcd for $C_{10}H_8O_3$: C, 68.20: H, 4.54. Found: C, 68.29: H, 4.58.

Preparation of p-Methacryloyloxybenzaldehyde **1b**

The same procedure as described for **1a** is used starting from methacryloyl chloride. The obtained white crystals were collected and washed a few times with cold water to give 37.3 g (70% yield) of **1b**. Mp 23-24°C. Proton-NMR (acetone d_6) δ 1.95-2.23 (m, 3H), 5.73-5.93 (q, 1H), 6.26-6.36 (q, 1H), 7.24-7.55 (m, 2H), 7.84-8.13 (m, 2H), 10.07 (s, 1H); IR (neat) 1742, 1703 (C=0), 1602 (C=C) cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.49; ; H, 5.26. Found: C, 69.40; H, 5.22.

Preparation of Methyl p-Acryloyloxybenzylidenecyanoacetate **2a**

Piperidine (0.27 g, 3.2 mmol) was added to a solution of **1a** (5.28 g, 330 mmol) and methyl cyanoacetate (2.97 g, 30 mmol) in 32 mL of n-butanol with stirring at room temperature. The resulting solution was filtered and washed with cold n-butanol, water containing a small amount of acetic acid, and cold n-butanol. The obtained white product was recrystallized from ethanol-acetone (80/20, vol/vol) to give 5.86 g (75% yield) of **2a** (an isomeric mixture of Z-/E-). Mp 105-107°C. Proton-NMR (acetone-d_6) δ 3.90 (s, 3H), 5.94-6.25 (m, 1H), 6.36-6.85 (m, 2H), 7.28-7.66 (d 2H), 8.02-8.37 (t, 3H); IR (KBr) 2225 (CN), 1754, 1723 (C=0), 1629, 1597, 1573 (C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.39; H, 4.28; N, 5.44. Found: C, 65.48; H, 4.24; N, 5.39.

Preparation of Methyl p-Methacryloyloxybenzylidenecyanoacetate **2b**

Same procedure as for 2a starting from p-methacryloyloxybenzaldehyde **1b**. The obtained white product was recrystallized from ethanol-acetone (80/20, vol/vol) to give 4.34 g (80% yield) of **2b** (an isomeric mixture of Z-/E-). Mp 90-92°C. Proton-NMR (acetone-d_6) δ 1.95-2.15 (d, 3H), 3.90 (s, 3H), 5.76-5.94 (m, 1H), 6.26-6.37 (m, 1H), 7.26-7.59 (d, 2H), 8.01-8.36 (t, 3H); IR (KBr) 2228 (CN), 1742, 1725 (C=0), 1601, 1575 (C=C)cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.44; H, 4.79; N, 5.16. Found: C, 66.38; H, 4.74: N, 5.10.

Synthesis of p-(2,3-Dicyano-2,3-dicarbomethoxy-cyclopropyl)phenyl Acrylate **3a**

Methyl p-acryloyloxybenzylidenecyanoacetate **2a** (1.54 g, 6.0 mmol) and methyl bromocyanoacetate (1.6 g, 9.0 mmol) were dissolved in 20 mL of 85% aqueous ethanol with stirring at 0°C. The resulting solution was stirred for 4 hr at 0°C and 10 hr at room temperature. After filtration of the product, it was rinsed once with 15 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) to give 0.96 g (45% yield) of **3a** (an isomeric mixture of Z-/E-). Mp 112-114°C. Proton-NMR (acetone-d_6) δ 3.86 (s, 6H), 4.14 (s, 1H), 5.89-6.14 (m, 1H), 6.27-6.44 (m, 2H), 7.13-7.76 (m, 4H); IR (KBr) 2266 (CN), 1767, 1750 (C=0), 1638, 1617 (C=C)cm^{-1}. Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.04; H, 3.95; N, 7.91. Found: C, 61.12; H, 3.99; N, 7.96.

Synthesis of p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl Methacrylate **3b**

Same procedure as for **3a** starting from **2b**. The obtained white crystals were recrystallized from ethanol-acetone (90/10, vol/vol) to give 1.47 g (50% yield) of **3b** (an isomeric mixture of Z-/E). Mp 127-129°C. Proton-NMR (acetone-d_6) δ 1.98 (s, 3H), 3.72-3.97 (t, 6H), 4.06-4.26) (d, 1H), 5.71-5.89 (m, 1H), 6.22-6.33 (m, 1H), 7.07-7.76 (m, 4H); IR (KBr) 2248 (CN), 1760, 1743, 1727 (C=0), 1635, 1604 (C=C)cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_2O_6$: C, 61.98; H, 4.35; N, 7.60. Found: C, 61.88; H, 4.30; N, 7.68.

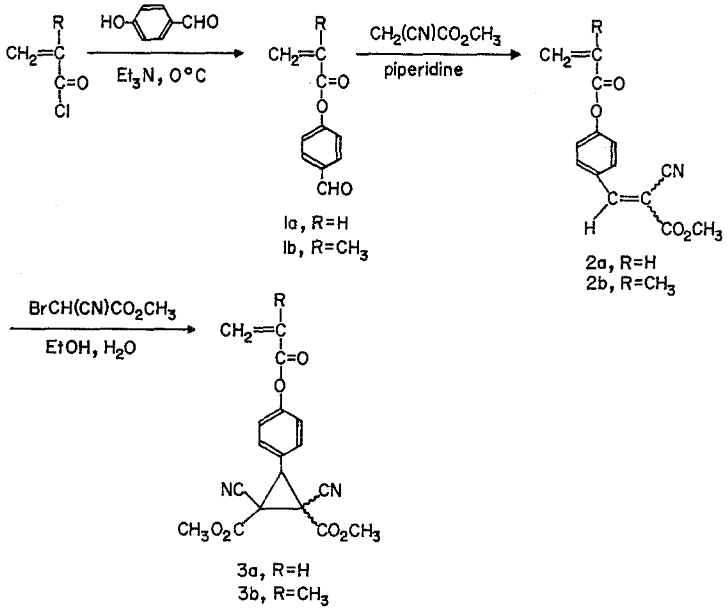
Representative Radical Polymerization of p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl Acrylate and Methacrylate **3a-b**

A γ-butyrolactone (2.0 mL) solution of **3a** (0.71 g, 2.0 mmol) was placed in a polymerization tube, and 3.0 mg (1.8 x 10^{-2} mmol) of AIBN was added under nitrogen. The mixture was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65°C. After 10 hr the polymerization tube was opened and the viscous product was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. **4a**: 0.64 g (90% yield); η_{inh}=0.21 dL/g (0.5 g/dL in acetone at 25°C). Proton-NMR (acetone-d_6) δ 7.31-7.70 (d, 2H), 6.99-7.70 (d, 2H), 4.08-4.28 (s, 1H), 3.58-4.05 (m, 6H), 2.74-3.46 (m, 1H), 2.01-2.60 (m, 2H): IR (KBr) 2244 (CN), 1747 (C=0) cm^{-1}. Anal. Calcd for $(C_{18}H_{14}N_2O_6)_n$: C, 61.04; H, 3.95; N, 7.91. Found: C, 61.12; H, 3.92; N, 5.51. **4b**: Proton-NMR (acetone-d_6) δ 6.93-7.85 (m, 4H), 4.05-4.32 (s, 1H), 3.47-4.12 (m, 6H), 1.88-2.83 (m, 2H), 0.97-1.85 (m, 3H): IR (KBr) 2242 (CN), 1745 (C=0) cm^{-1}. Anal. Calcd for $(C_{19}H_{16}N_2O_6)$n: C, 61.98; H, 4.35; N, 7.60. Found: C, 62.07; H, 4.42; N, 7.52.

Results and Discussion

Syntheses of Monomers 3a-b

p-Acryloyloxybenzaldehyde **1a** and p-methacryloyloxybenzaldehyde **1b** were prepared by the well-known Schotten-Baumann method and condensed with methyl cyanoacetate to yield methyl p-acryloyloxybenzylidenecyanoacetate **2a** and methyl p-methacryloyloxybenzylidenecyanoacetate **2b** respectively.[10] p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate **3a** and p-(2,3-dicyano-2,3-dicarbomethoxycyclopropyl)phenyl methacrylate **3b** were synthesized in moderate yields by cyclopropane formation from methyl bromocyanoacetate and **2a** or **2b**, according to a variation of the Wideqvist reaction.[11] Spectral data indicated that **3a** and **3b** were mixtures of the cis- and trans-isomer.



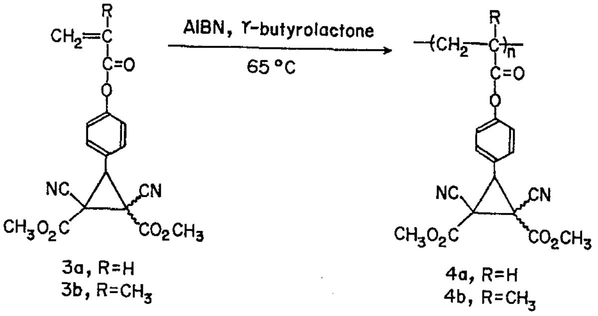
Radical Polymerization of Monomers 3a and 3b

p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate **3a** and p-(2,3-dicyano-2,3-dicarbomethoxycyclopropyl)phenyl methacrylate **3b** were polymerized in solution at 65°C using AIBN as initiator to obtain the polymers **4a** and **4b**. The polymerization results are summarized in Table 1.

Table 1: Free Radical Polymerization of **3** by AIBN[a] at 65°C

Monomer	Solvent (vol/vol)	Monomer/ Solvent (mol/1 L)	Time (h)	Yield (%)	η_{inh}[b] (dL/g)
3a	γ-butyrolactone	1.00	10	90	0.21
3a	γ-butyrolactone	0.38	16	88	0.18
3a	γ-butyrolactone	0.92	12	85	0.18
3a	CH_3CN/C_6H_6, 2.0	0.80	10	83	0.16
3b	γ-butyrolactone	1.00	10	92	0.25
3b	γ-butyrolactone	0.83	12	90	0.22
3b	γ-butyrolactone	0.75	16	92	0.21
3b	CH_3CN/C_6H_6, 2.0	0.60	20	91	0.20

[a] 0.8 mol% AIBN.
[b] Inherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25°C.



Monomers **3a-b** were quite reactive toward free radical initiator and polymerized readily. The polymer structures were determined by proton-NMR and IR spectra. The free radical 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 polymers were soluble in acetone and DMSO, but were not soluble in chloroform and diethyl ether. The inherent viscosity was in the range of 0.15-0.25 dL/g indicating moderate molecular weights. The thermal behavior of the polymers **4a-b** was 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 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 polymers was around 120-150°C. These Tg values are higher than those for poly(methyl acrylate (10°C) and for poly(methyl methacrylate) (105°C). Solution-cast films were cloudy and brittle, which could be due to the rather low molecular and/or high dipole moment, and therefore the piezoelectric behavior has not been measured yet.

Table 2: Thermal properties of Polymer **4a-b**

Polymer	Tg[a], °C	degradation temp, °C[b]			residue[b] at 700°C, %
		5%-loss	20%-loss	40%-loss	
4a	122	286	302	381	31.4
4b	150	272	294	329	28.9

[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 YGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

Conclusion

p-(2,3-Dicyano-2,3-dicarbomethoxycyclopropyl)phenyl acrylate **3a** and p-(2,3-dicyano-2,3-dicarbomethoxycyclopropyl)phenyl methacrylate **3b** were readily polymerized in solution by radical initiator to obtain the polymers with multicyano functions in high yield. The resulting polymers **4a-b** were soluble in acetone and DMSO. The polymers show a double phase degradation pattern in their TGA thermograms due to the presence of two rings in the pendant group. Films cast from the polymer solution were cloudy and brittle, which could be due to the rather low molecular weight and/or the presence of high dipole density in the side chain.

Acknowledgements

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