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Synthesis and radical polymerization of 1,1,2-tricyano-2-carbomethoxycyclopropylstyrene

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Summary

An isomeric mixture (meta- and para-) of 1,1,2-tricyano-2-carbomethoxycyclopropylstyrene 3 was prepared by cyclopropane formation from bromomalononitrile and methyl styrylidenecyanoacetate 2. The substituted styrene monomer 3 was polymerized with free radical initiators to obtain the polymers with multicyano functions in the pendant group. The resulting polymers were soluble in acetone and the inherent viscosities were in the range of 0.20-0.28 dL/g. Solution-cast films were clear and brittle with a T_g of 102°C.

Introduction

Piezoelectric polymers have been the subject of curiosity to polymer chemists and have caused recent interest (1). It is well-known that crystalline polymers such as polyvinylidene fluoride with a large dipole moment exhibit the piezoelectric effect. 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). In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation and this polymer also shows a piezoelectric effect (3).

A potentially piezoelectric polymer must contain a large concentration of dipoles and also be mechanically very strong. These polymers have to be film-forming and be able to withstand high voltages without breakdown. We have recently proposed that three- and four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments (4) and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane (4-5) and 1,1,2,2-tetracyanocyclobutane units (6).

This work is now extended with the synthesis of another polymer containing multicyanocyclopropane rings. The present report describes the synthesis and radical polymerization of 1,1,2-tricyano-2-carbomethoxycyclopropylstyrene 3.

Experimental

Materials

The reagent grade chemicals were purified by distillation or recrystalization before use. Vinylbenzyl chloride (m- and p-isomer mixture) was purchase from Aldrich Co. and distilled under vacuum before use. Dimethyl sulfoxide (DMSO) was dried over 4A molecular sieves for several days and distilled under vacuum. Acetonitrile was 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. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. n-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. 2,2-Azobisisobutyronitrile was recrystallized from methanol and stored at 5°C. Bromomalononitrile was prepared according to a literature procedure (7) and recrystallized twice from chloroform. 1,1,2,2-Tetracyanocyclopropane was synthesized by a known method from malononitrile and 37% formalin (8).

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. Viscosity values were obtained by using a Cannon-Fenske viscometer. Melting points were measured in a Buchi 512 melting point apparatus and are corrected.

Preparation of Vinyl benzaldehyde 1

Compound 1 was prepared, according to a literature method (9), by oxidation of vinylbenzyl chloride. Yield: 70% (m-/p-: 67/33, mole/mole). Bp 63-64°C/ 0.5 mmHg. Proton-NMR ($CDCl_3$) δ 5.36-5.48 (q,1H), 5.83-5.97 (q,1H), 6.73-6.83 (q,1H), 7.45-7.94 (m,4H), 9.97-10.03 (d,1H); IR (neat) 1698 (C=0), 1627, 1600 (C=C) cm^{-1}. Anal. Calcd for C_9H_8O: C, 81.82; H, 6.06. Found: C. 81.87; H, 6.03.

Preparation of Methyl styrylidenecyanoacetate 2

Sodium acetate (0.40 g, 4.9 mmole) was added to a solution of vinyl benzaldehyde (5.31 g, 40 mmole) and methyl cyanoacetate (3.99 g, 40 mmole) in 30 mL of n-butanol with stirring at room temperature. After stirring for 2 hr at room temperature, the product was filtered and washed with water containing a small amount of acetic acid. The obtained white product was recrystallized from ethanol-acetone (90/10, vol/vol) mixtures to give 3.58 g (42% yield) of 2 (an isomeric mixture of m-/p- and Z-/E-). Mp 103-104°C. Proton-NMR (acetone-d_6) δ 3.87 (s,3H), 5.23-3.57 (m,1H), 5.72-6.22 (m,1H), 6.60-7.15 (m,1H), 7.52-8.42 (m,5H); IR (KBr) 2210 (CN), 1720 (C=0), 1595 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.24; H, 5.16; N, 6.57. Found: C, 73.33; H, 5.13; N, 6.52.

Synthesis of 1,1,2-Tricyano-2-carbomethoxycyclopropylstyrene 3

Methyl styrylidenecyanoacetate (1.07 g, 5.0 mmole) and bromomalononitrile (1.74 g, 12.0 mmole) were dissolved in 32 mL of 85% aqueous ethanol at room temperature. After stirring for 12 hr at room temperature, the product was filtered and rinsed with cold ethanol. The obtained white crystals were recrystallized from ethanol to give 1.25 g (90% yield) of 3 (an isomeric mixture of m-/p-). Mp 130-132°C. Proton-NMR (acetone-d_6) δ 4.01 (s,3H), 4.29 (s,1H), 5.28-5.53 (m,1H), 5.78-6.15 (m,1H), 6.63-7.17 (q,1H), 7.55-8.03 (m,4H); IR (KBr) 2252 (CN), 1760 (C=0), 1628, 1606 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_2$: C, 69.31; H, 3.97; N, 15.16. Found: C, 69.24; H, 3.93; N, 15.20.

Radical Polymerization of 1,1,2-Tricyano-2-carbomethoxycyclopropylstyrene 3

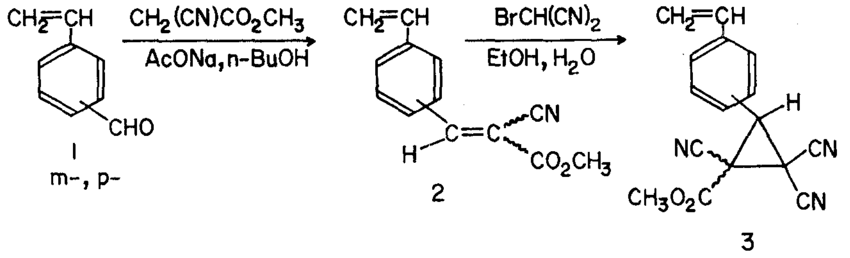
A representative free radical polymerization procedure was as follows:

A δ-butyrolactone (2.5 mL) solution of 3 (0.83 g, 3.0 mmole) was placed in a polymerization tube and 3.95 mg (2.40 x 10^{-2} mmole) of AIBN was added under nitrogen. The mixture was flushed with dry nitrogen for 20 min. It was placed in an oil bath kept at 65°C. After 13 hr, the polymerization tube was opened and the viscous product was poured into 300 mL of methanol. The precipitated white polymer was collected and reprecipitated from acetone into methanol. 4: 0.71 g (85% yield); η_{inh} = 0.26 dL/g (0.5 g/dL in acetone at 25°C). Proton-NMR (acetone-d_6) δ 0.83-2.57 (m,3H), 3.60-4.43 (s,4H), 6.13-7.83 (m,4H); IR (KBr) 2250 (CN), 1758 (C=O), 1604 (aromatic C=C) cm^{-1}. Anal. Calcd for ($C_{16}H_{11}N_3O_2$): C, 69.31; H, 3.97; N, 15.16. Found: C, 69.38; H, 3.99; N, 15.12.

Results and Discussion

Synthesis of Monomer 3

1,1,2-Tricyano-2-carbomethoxycyclopropylstyrene 3 was prepared by cyclopropane formation from methyl styrylidenecyanoacetate 2 and bromomalononitrile, according to a variation of the Widequist reaction (10). Methyl styrylidenecyanoacetate 2 was prepared by the condensation of vinyl benzaldehyde with methyl cyanoacetate in n-butanol (11). The chemical structure of the compounds was confirmed by proton-NMR, IR, and elemental analysis. Monomer 3 was quite stable when heated up to 100°C.



Radical Polymerization of Monomer 3

1,1,2-Tricyano-2-carbomethoxycyclopropylstyrene 3 was polymerized by free radical mechanism using AIBN as initiator to obtain poly(1,1,2-tricyano-2-carbomethoxycyclopropylstyrene) 4. Polymerization reactions were carried out in solution at 65°C. The polymerization results are summarized in Table 1. Monomer 3 was quite reactive toward 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 in the case of 1,1,2,2-tetracyanocyclopropylstyrene (4).

To check if the multicyanocyclopropane ring has an inhibiting effect on the radical polymerization, standard radical styrene polymerizations were carried out in the presence of 1,1,2,2-tetracyanocyclopropane. It was shown to somewhat inhibit the radical polymerization resulting in slightly lower yields and viscosities, as shown in Table 1. A similar inhibiting effect was shown in the radical polymerization of tetracyanocyclobutylstyrene (6).

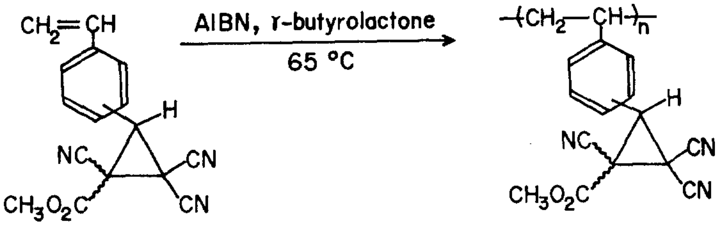
Table 1. Free Radical Polymerization of 3[a] by AIBN at 65°C.

Monomer	Solvent (vol/vol)	Monomer/ Solvent (g/mL)	Time (h)	Yield (%)	η_{inh}[b] (dL/g)
3	C_6H_6/CH_3CN, 1.0	0.30	10	75	0.20
3	C_6H_6/CH_3CN, 0.5	0.25	16	72	0.18
3	ethyl acetate	0.36	10	86	0.28
3	γ-butyrolactone	0.30	13	85	0.24
3	γ-butyrolactone	0.42	12	80	0.25
3	γ-butyrolactone	0.20	20	88	0.28
St[c]	γ-butyrolactone	0.30	12	86	0.38
St	γ-butyrolactone	0.30	12	82	0.32
St/3 9/1	γ-butyrolactone	0.30	12	68	0.24
St/3 9/1	γ-butyrolactone	0.30	12	70	0.28

[a] 3 = 1,1,2-Tricyano-2-carboethoxycyclopropylstyrene (isomer mixtures of meta- and para-isomer), 0.8 mole% AIBN.

[b] Inherent viscosity of polymer: concentration of 0.5 g/dL in acetone at 25°C.

[c] St = styrene



3

4

The chemical structure of polymer 4 was confirmed by proton-NMR, IR spectra, and elemental analyses. The polymer was soluble in acetone and DMSO, but was not soluble in chloroform and diethyl ether. The inherent viscosity, measured in acetone at 25°C, was in the range of 0.20-0.28 dL/g.

The thermal behavior of the polymer 4 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 polymer shows a double phase degradation pattern in its TGA thermogram, probably due to the presence of two rings in the pendant group. The glass transition temperature was 102°C.

Solution-cast films were clear and brittle, which could be due to the rather low molecular weight and high dipole moment. The piezoelectric behavior has not been measured yet.

Table 2. Thermal Properties of Polymer 4

Polymer	T_g[a], °C	degradation temp, °C[b]			residue[b] at 700°C, %
		5%-loss	20%-loss	40%-loss	
4	102	264	357	611	55.5

[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 TGA curves measured with a heating rate of 10°C/min under nitrogen atmosphere.

Conclusion

We prepared a meta- and para-isomeric mixture of 1,1,2-tricyano-2-carbomethoxycyclopropylstyrene. The substituted styrene was polymerized by radical initiator such as AIBN to obtain the polymers with multicyanocyclopropane groups. The glass transition temperature was 102°C. The polymer shows a double phase degradation pattern due to the presence of two rings in the pendant group. Films cast from the polymer solution were clear and brittle, which could be due to the rather low molecular weight and the presence of high dipole density in the side chain. Attempts to obtain high molecular weights failed partly because of the inhibiting effect of multicyanocyclopropane group to the radical polymerization.

Acknowledgements

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