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Synthesis and radical polymerization of 1,1,2,2-tetracyanocyclopropylstyrene

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Synopsis

An isomeric mixture (m-/p-: 70/30, mole/mole) of 1,1,2,2-tetracyanocyclopropylstyrene 2 was prepared by cyclopropane formation from bromomalononitrile and vinyl benzaldehyde. The substituted styrene compound 2 was polymerized with free radical initiator to obtain the polymers with multicyano functions in the pendant group. The resulting polymers were soluble in acetone and dimethyl sulfoxide (DMSO) and the inherent viscosities were in the range of 0.27-0.32 dL/g. Solution-cast films were clear and brittle, showing Tg value of 112°C.

Introduction

Amorphous polymers with a high concentration of dipole moments exhibit piezoelectric properties if the main chain has an all planar zigzag conformation. The copolymer of vinylidene cyanide and vinyl acetate is such a case (1). Poly(1-bicyclobutanecarbonitrile), because the rigid ring structure prevents a helical structure, also shows a piezoelectric effect (2).

We proposed recently that three- and four-membered rings with several cyano groups held rigidly would have large dipole moment (3-4). In this report, we describe the synthesis and radical polymerization of substituted styrene containing the 1,1,2,2-tetracyanocyclopropane unit.

Experimental

Materials

The reagent grade chemicals were purified by distillation or recrystallization before use. Vinylbenzyl chloride (m- and p-isomeric mixture) was purchased from Kodak Co. and distilled under vacuum before use. Dimethyl sulfoxide (DMSO) was dried over 4 Å 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 4 Å molecular sieves under nitrogen. γ-Butyrolactone was dried with anhydrous calcium sulfate and fractionally distilled. Bromomalononitrile was prepared according to a literature procedure (5) and recrystallized twice from chloroform. 2,2′-Azo-bisisobutyronitrile was recrystallized from methanol and stored at 5°C.

Measurements

All melting point temperatures are uncorrected. IR spectra were taken on Perkin-Elmer 983 spectrometer. ^{1}H-NMR 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 (Tg) were measured on a Perkin-Elmer DSC-4 differential scanning calorimeter in a nitrogen atmosphere.

Preparation of Vinyl Benzaldehyde 1

A mixture of 12.2 g (0.08 mole) of vinylbenzyl chloride (m- and p-isomeric mixture) and 23.3 g (0.12 mole) of potassium chromate in 100 ml of dimethyl sulfoxide was refluxed with vigorous stirring at 120°C for 2 hr under nitrogen. The resulting black solution was filtered on Celite and rinsed with 20 ml of DMSO. Extraction was performed on the filtrate twice with 100 ml of diethyl ether. The organic layer was washed twice with 100 ml of water and dried over anhydrous magnesium sulfate. The resulting solution was concentrated by rotary evaporator, followed by fractional distillation, which yielded 7.6 g of 1 (72% yield; m-/p-: 67/33 mole/mole). Bp 63-64°C/0.5 mmHg. ^{1}H-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=O), 1627, 1600 (C=C) cm^{-1}. Anal. Calcd for C_9H_8O: C, 81.82; H, 6.06. Found: C, 81.76; H, 6.02.

Synthesis of 1,1,2,2-Tetracyanocyclopropylstyrene 2

A solution of 7 g (0.042 mole) of potassium iodide in 20 ml of water was added slowly to the solution of vinyl benzaldehyde (2.64 g, 0.02 mole) and bromomalononitrile (2.90 g, 0.02 mole) in 20 ml of ethanol at room temperature. After stirring for 1 hr. at room temperature, the product was filtered and rinsed with 20 ml of cold ethanol. The obtained white crystals were recrystallized from 95% ethanol to give 1.54 g (63% yield) of 2 (m-/p-: 70/30, mole/mole). Mp 157°-160° (dec.). ^{1}H-NMR (acetone-d_6) δ 4.98-5.02 (d, 1H), 5.32-5.40 (m, 1H), 5.88-6.01 (m, 1H), 6.77-6.89 (q, 1H), 7.50-8.08 (m, 4H): IR (KBr) 2259 (C≡N), 1631, 1600 (C=C) cm^{-1}; ^{13}C-NMR (acetone-d_6) δ 23.5 (s, ${}^{NC}_{NC}{>}C{<}$), 43.0 (s, ${>}C{<}_H$), 109.5 (s, cis-CN), 111.2 (s, trans-CN), 115.6-116.2 (d, CH_2=), 127.3-130.4 (m, aromatic), 136.4 (s,=CH-), 139.5 (s, -C<). Anal. Calcd for $C_{15}H_8N_4$: C, 73.77; H, 3.28; N, 22.95. Found: C, 73.83; H, 3.21; N, 22.85.

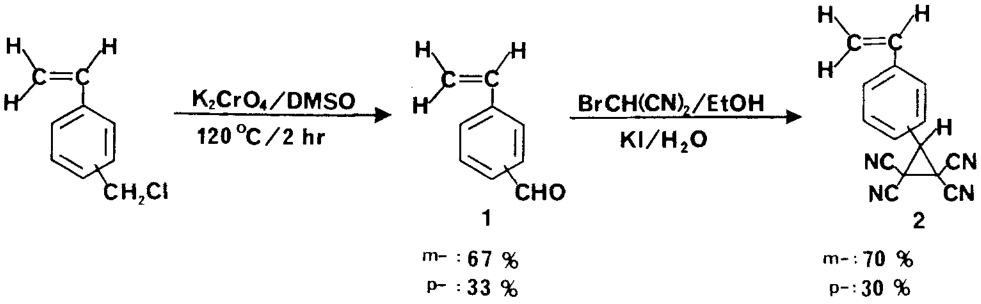
Radical Polymerization of 1,1,2,2-Tetracyanocyclopropylstyrene 2

A representative free radical polymerization procedure was as follows: A γ-butyrolactone (2.0 ml) solution of 2 (0.61 g, 2.5 mmole) was placed in a polymerization tube and 4.1 mg (2.5×10^{-2} mmole) of AIBN was added under nitrogen. The mixture was degassed by a freeze-thaw process under vacuum. After warming to room temperature, 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 a 350 ml of diethyl ether. The precipitated polymer was collected and reprecipitated from acetone into diethyl ether. 3: 0.54 g (89% yield); η_{inh}=0.30 dL/g (0.5 g/dL in acetone at 25°C). ^{1}H-NMR (acetone-d_6) δ 1.10-1.95 (s, 3H), 4.35-4.80 (s, 1H), 6.25-7.65 (m, 4H); IR (KBr) 2256 (C≡N), 1604 (aromatic C=C); ^{13}C-NMR (acetone-d_6) δ 23.0 (s, $^{NC}_{NC}{>}C{<}$), 40.5-41.0 (m,$-CH_2-$), 41.1-42.0 (m,-CH-), 42.4-43.5 (m, $>C<_H$), 109.3 (s, cis-CN), 110.5 (s, trans-CN), 123.4-132.5 (m, aromatic). Anal. Calcd for $(C_{15}H_8N_4)n$: C, 73.77; H, 3.28; N, 22.95. Found C, 73.68; H, 3.22; N, 22.86.

Results and Discussion

Synthesis of Monomer 2

1,1,2,2-Tetracyanocyclopropylstyrene 2 was prepared using the Wideqvist method for cyclopropane synthesis (6-8). Vinyl benzaldehyde was synthesized, according to a known method (9), by oxidation of vinylbenzyl chloride. The latter is purchased as a 70/30 mixture of the meta- and para-isomers. Reaction of vinylbenzaldehyde with bromomalononitrile in diluted aqueous ethanol solution led to tetracyanocyclopropylstyrene in good yield at room temperature. The chemical structure was confirmed by ^{1}H-NMR, IR, ^{13}C-NMR spectra, and elemental analysis. ^{1}H-NMR spectrum showed that tetracyanocyclopropylstyrene 2 is a mixture of m-isomer (70 mole %) and p-isomer (30 mole %). Compound 2 was quite stable when heated to 100°C.



Radical Polymerization of Tetracyanocyclopropylstyrene 2

Tetracyanocyclopropylstyrene 2 was polymerized by free radical initiator such as AIBN to obtain the polytetracyanocyclopropylstyrene 3. Radical polymerizations were carried out in solution at 65°C. Monomer 2 was quite reactive toward radical initiator and polymerized readily. The free radical initiator did not attack the tetracyanocyclopropane ring during polymerization. The polymerization results are summarized in Table 1. In most cases, conversions were very high, but the molecular weights were rather low.

The chemical structure of polymer 3 was confirmed by IR, ^1H-NMR, ^{13}C-NMR spectra, and elemental analyses. The polymer was soluble in acetone and DMSO, but was not soluble in diethyl ether and chloroform. The inherent viscosity measured in acetone at 25°C was in the range 0.27-0.32 dL/g. The thermal behavior of the polymer was investigated by DSC at scanning rate of 10°C/min to determine the glass

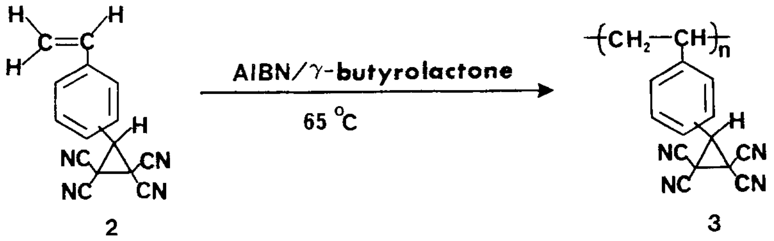


Table 1. Free Radical Polymerization of 2[a] by AIBN at 65°C.

Solvent (vol/vol)	2/Solvent (g/mL)	Time (h)	Yield (%)	η_{inh}[b] (dL/g)	Tg[c] (°C)
C_6H_6/CH_3CN, 0.5	0.20	14	90	0.27	--
C_6H_6/CH_3CN, 0.4	0.22	12	86	0.29	--
C_6H_6/CH_3CN, 0.5[d]	0.20	20	88	0.31	--
γ-butyrolactone	0.31	13	89	0.30	112
γ-butyrolactone	0.41	16	90	0.32	--

[a] 2 = 1,1,2,2-tetracyanocyclopropylstyrene (m-/p-: 70/30, mole/mole), 1 mole % AIBN.
[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.
[d] Catalytic amount of glacial acetic acid was added.

transition temperature (Tg). The Tg value was higher than that of polystyrene. Films cast from the polymer solution were brittle, which could be due to the rather low molecular weight and high dipole density. The piezoelectric activity has not been measured yet.

Conclusion

We synthesized a m- and p-isomeric mixture of tetracyanocyclopropylstyrene containing cyclopropane ring with tetracyano groups. The substituted styrene was polymerized by radical initiator (AIBN) to obtain the polymers with multicyano functions. The resulting polymer was soluble in acetone and DMSO, but insoluble in chloroform. The Tg value of the polymer was higher than that of polystyrene. Films cast from the polymer solution were brittle, which could be due to the rather low molecular weight as indicated by the inherent viscosities, and/or to the presence of strong dipoles in the side chain. Attempts to obtain higher molecular weights failed. The tetracyanocyclopropane ring could act as weak inhibitors. Copolymerization with other monomers and measurements of piezoelectric activity are in progress and the full accounts of the results will be reported later.

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