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Synthesis of potentially piezoelectric polymers containing tetracyanocyclobutyl side groups

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ABSTRACT

Three new monomers containing the tetracyanocyclobutyl substituents were synthesized: p-(tetracyanocyclobutyl)styrene 1, p-(1'-methyl-2',2',3',3'-tetracyanocyclobutyl)-α-methylstyrene 2 and [p-(tetracyanocyclobutyl)phenyl] acrylate 3, with the aim of obtaining potentially piezoelectric polymers which contain substituents with high dipole moments. Moderate molecular weight polymers were obtained from monomer 1 only, 2 and 3 did not polymerize. The inhibiting effect of the tetracyanocyclobutyl group was responsible for the molecular weights as demonstrated by model experiments.

INTRODUCTION

The most commonly used and most widely studied piezoelectric polymers are poly-vinylidene fluoride (1) and the copolymer of vinylidene cyanide/vinyl acetate.(2) The latter is amorphous and has to be poled to induce the piezoelectric behavior. A potentially piezoelectric polymer has to 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.

The cyano group has a large dipole moment (3.9 D) and is therefore a good candidate for designing potentially piezoelectric polymers. The question then arises of how to incorporate the dipoles in the polymer. One option is to use multicyano substituted small rings, such as cyclopropane or cyclobutanes. . In larger rings, the substituents can be axial or equatorial and they can interchange. In small rings the substituents are roughly pointed in the same direction, and the conformations are much more restricted. These intuitive ideas have been confirmed by AM1 calculations of the dipole moments of multicyano-substituted small rings, as shown in Table 1.

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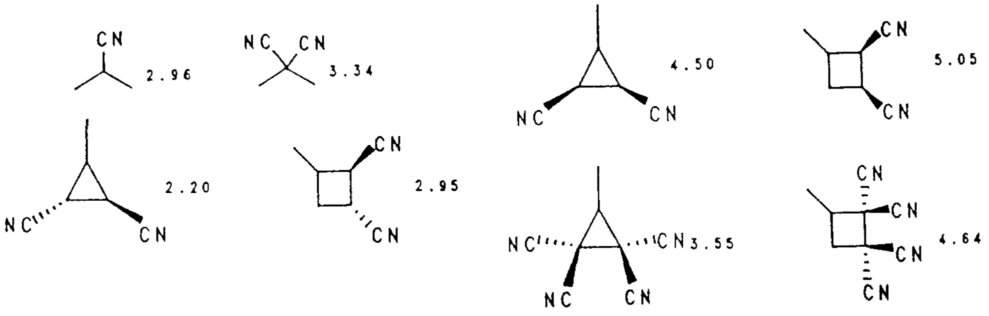
Table 1.: Calculated Dipole Moments (Debye) from AM1



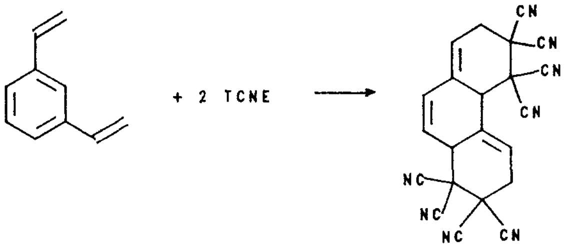
In a related study, our group has reported the synthesis and polymerization of several tetracyanocyclopropyl-containing monomers.(3-4) In this work we will investigate the synthesis of monomers containing a multicyano-cyclobutyl functionality. More specifically, this group will be attached to a styrene or to a phenyl acrylate functionality.

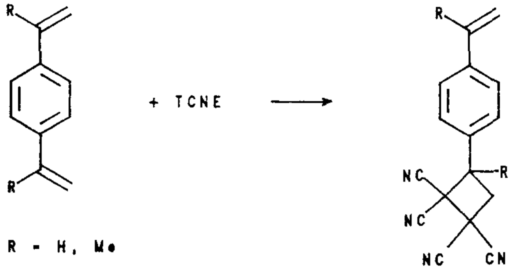
RESULTS AND DISCUSSION

Monomer Synthesis

Although divinylbenzenes are very well-known to polymer chemists as cross-linking agents, these compounds had not been investigated thoroughly in cycloaddition reactions. Moreover, commercial divinylbenzene, DVB, is roughly a 1:1:1:1 mixture of both para-DVB and meta-DVB, and para- and meta-ethyl styrene. Reaction of commercial DVB with tetracyanoethylene (TCNE) in acetonitrile at room temperature yields a 2:1 Diels-Alder type adduct. The same adduct is obtained from the reaction of pure meta-DVB with TCNE,(5) so only the meta component of commercial DVB reacts. The two vinyl groups of meta-DVB react consecutively as part of two diene systems, resulting in the destruction of the aromatic system. This adduct however cannot be used for polymerization.

Pure para-DVB, synthesized from terephthalaldehyde, is much less reactive than the meta isomer. The cycloaddition of para-DVB with TCNE leads to the desired cyclobutane adduct 1 after 48 hours at 28°C; inhibitor is added to these reactions as para-DVB is very susceptible to spontaneous polymerizations. No [4+2] cycloadduct is obtained in this case. para-Diisopropenyl benzene, para-DIB, with TCNE also leads to the corresponding cyclobutane adduct 2 in quantitative yield after 4 hours at 28°C.

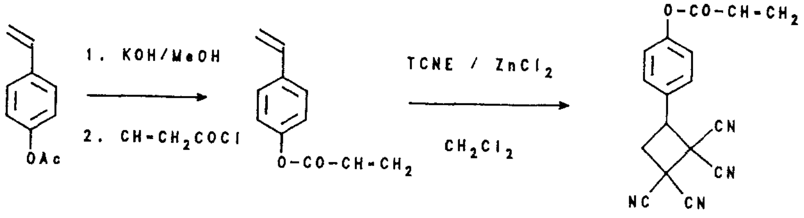




1 R = H

2 R = Me

Another similar monomer, which incorporates the tetracyanocyclobutane ring, is p-(tetracyanocyclobutane)phenyl acrylate 3. This monomer can be synthesized starting from p-acetoxystyrene, which is converted to p-hydroxy-styrene in methanol in the presence of a trace of base. The latter is immediately esterified with acryloyl chloride. p-Acryloyloxystyrene alone does not react with TCNE. However, in the presence of zinc chloride, TCNE is activated and the desired cyclobutane adduct 3 is obtained. This monomer is difficult to purify and might still contain traces of TCNE.



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Polymerizations

Standard conditions for radical polymerization were used with monomers 1-3: AIBN at 60°C for 16 hours under Argon atmosphere after degassing. The data are summarized in Table 2.

Table 2: Polymerizations Data.[a]

Monomer	Comonomer	Solvent	Yield	Polymer Composition
1	-	CH_3CN	37%	homopolymer
1	-	EtOAc	69%	homopolymer[c]
1	AN	CH_3CN	17%	homopolymer
1	p-MeOSt	CH_3CN	0	
1	St	CH_3CN	trace	
1	MMA	CH_3CN	90%	homopolymer
2	-	CH_3CN	0%[b]	
2	St	CH_3CN	0	

a. Concentration 0.5M, Initiator AIBN, Ar atmosphere, 60°C, 16 hours.
b. Also attempted at 0°C with UV light or using EtOAc as solvent.
c. ηinh = 0.2 dl/g in THF at 30°C.

Monomer 1 could be homopolymerized in acetonitrile and a 37% yield was obtained. The best polymer was obtained in ethyl acetate with an inherent viscosity of 0.2dl/g. The other polymers were lower molecular weight, as they were more difficult to precipitate. No size exclusion chromatograms could be obtained due to the low solubility of these homopolymers.

All attempts to copolymerize 1 with other vinyl monomers such as acrylonitrile, vinyl acetate and methyl methacrylate failed and only homopolymers were obtained, as shown in Table 2. In some cases, no polymer was obtained, for example in the presence of p-methoxystyrene. With styrene a trace homopolymer was found. The highest molecular weights were obtained in the presence of ester groups.

As far as the α-methylstyrene derivative 2 is concerned, we have not been able to obtain homo- or copolymer. This could be due to a ceiling temperature effect, in analogy with α-methylstyrene itself. But even at 0°C, using UV light to decompose AIBN, no polymer was obtained.

The tetracyanocyclobutylphenyl acrylate 3 did not homopolymerize either in the presence of radical initiators in acetonitrile.

Due to the odd reluctance of these monomers to polymerize, the question arose if there was an inhibiting effect by the tetracyanocyclobutyl groups. Therefore standard radical polymerizations were run in the presence of two tetracyanocyclobutane derivatives: 3-(p-methoxyphenyl)- and 3-isobutoxy-1,1,2,2-tetracyanocyclobutane.(6-7) When either one of these compounds was added to an AIBN-initiated polymerization of styrene or acrylonitrile, they completely inhibited the polymerization. The p-methoxyphenyl derivative also completely inhibited the polymerization of methyl acrylate, while the isobutoxy derivative reduced the polymer yield from 66% for the blank to 25%.

These results clearly show that the tetracyanocyclobutyl substituent inhibits or hampers the radical polymerization of these novel monomers. Another approach to these potentially piezoelectric polymers, which is under study, would be to attach the tetracyanocyclobutyl functionality to an already formed polymer backbone.

EXPERIMENTAL

Methods

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Model 983 spectrophotometer. NMR spectra were recorded on a Bruker WM 250 spectrometer at 250MHz. Elemental analyses were performed by Desert Analytics, Tucson AZ.

General procedure for cycloaddition reactions

p-DVB (1.5 mmole, 195 mg) was dissolved in 4 mL of dry acetonitrile in a septum-capped flask under Argon atmosphere. TCNE (1.5 mmole, 192 mg) was added and the red color of the CT-complex was observed. The mixture was stirred at room temperature (28°C) under Ar and the red color faded after 48 hours. The product can be recrystallized from toluene or ether.

Cyclobutane adduct of TCNE and p-DVB 1

Yield: 84%. Mp 172°. ^{1}H NMR (acetone-d_6): δ 6.82 (dd), 5.92 (dd), 5.34 (dd, $^3J_{trans} = 17.6$ Hz, $^3J_{cis} = 10.9$ Hz, $^2J_{gem} = 0.6$ Hz), 5.09 (dd), 3.92 and 3.66 (2 dd, $^3J = 8.9$ Hz, 12.1 Hz, $^2J_{gem} = 12.9$ Hz). ^{13}C-NMR: δ 206.3, 139.9, 136.8, 128.9, 127, 115.9 (aromatic), 112.8, 112.2, 112.1, 110.5 (CN), 47.7, 45.5, 36.1, 34.8 ppm. IR (KBr): 3054, 2257, 2219, 1630, 1512, 1410, 1146, 988, 918, 844 cm^{-1}. Chem. Anal. Calcd. 74.40%C, 3.90%H, 21.70%N; Found: 74.49%C, 3.78%H, 21.37%N.

Cyclobutane adduct of TCNE and p-DIB 2

Yield 25%. Mp 183-184°C. NMR (acetone-d_6): δ 7.66 (AB, J = 8.6 Hz), 7.42 (AB), 5.52 (q, $^3J = 0.7$ Hz), 5.19 (q, $^3J = 1.4$ Hz), 4.09 (AB, J = 13.8 Hz), 3.61 (AB), 2.20 (m), 2.10 (s) ppm. IR (KBr): 2980, 1624, 1518, 1436, 1262, 893, 839, 823 cm^{-1}. Chem. Anal. Calcd.: 75.50% C, 4.93% H, 19.57% N; Found: 75.61% C, 4.87% H, 19.54% N.

p-(Tetracyanocyclobutyl)phenyl Acrylate 3

p-Acetoxystyrene (23g, 0.14 mole) is dissolved in methanol under Argon atmosphere and 0.1g KOH is added. The reaction mixture is stirred for 20 hours at 28°C and neutralized with

CO_2 Evaporation of the solvent yields p-hydroxystyrene, which is immediately dissolved in 100 mL of chloroform.
Triethylamine (25 mL, 0.25 mole) is added and the mixture is cooled to 0°C.
Acryloyl chloride (13.5 g, 0.15 mole) is added and the mixture is stirred 3-4 hours at 28°C. The organic layer is extracted with water, dried and the solvent evaporated. The residue is distilled at 87-95°/0.5 mmHg. Yield: 17g (70%) p-acryloxystyrene.

Zinc chloride (4g) is heated to 300°C under an Ar flow and cooled. Chloroform (100 mL), diethyl ether (2 mL) and TCNE (0.03 mole, 3.84g) are added. Then p-acryloxystyrene (5.22g, 0.03 mole) is added and the heterogeneous mixture is stirred overnight. Water is added and the precipitate is filtered off and recrystallized from toluene. Yield: 20%. M.p. 169°C. NMR (acetone-d_6: δ 7.72 and 7.40 (AB system, J= 8.6 Hz, 4 aromatic H), 6.59 (dd, J_{cis} = 10.2 Hz, J_{trans} = 17.2 Hz, vinyl H), 6.40 (dd, J_{gem} = 1.5 Hz, vinyl H trans to -H), 6.13 (dd, vinyl H cis), 5.13 (dd, J = 12.2 and 9.1 Hz, cyclobutyl H to Ph), 2.95 (dd, J_{gem} = 12.9 Hz, Cb H), 2.70 (dd, Cb H) ppm. IR: 2254, 1737, 1631, 1602, 1506, 1403, 1290, 1206, 1153, 908 cm^{-1}.

Polymerization Procedure

The polymerizations were performed in dry solvent in the presence of AIBN. The mixtures were degassed using two freeze-thaw cycles. The polymerizations were run in a thermostatted bath, and precipitated in methanol. The polymers were filtered, dried and weighed.

ACKNOWLEDGEMENTS

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