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Cyanoethylation of cyclopentadiene: Isolation of penta- and hexa(β-cyanoethyl)cyclopentadiene and an unexpected acrylonitrile polymer

Lon J. Mathias*, Christopher C. Roberts, and Jeno Muthiah

Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, MS 39406-0076, USA

Summary

The cyanoethylation of cyclopentadiene was examined under a variety of reaction conditions. Approximately 9% of cyclopentadiene was converted to the desired hexa(β-cyanoethyl)cyclopentadiene when the amount of acrylonitrile to cyclopentadiene was increased from 2 to 7 equivalents under phase transfer conditions. The low conversion is due to competitive formation of various unreactive side-products. For example, termination leading to less-highly substituted products was confirmed by isolation of crystalline 1,1,2,3,4-penta(β-cyanoethyl)cyclopentadiene. Another side product isolated and characterized by ^{13}C NMR was an oligomer of acrylonitrile attached to hexa(β-cyanoethyl)cyclopentadiene; the anion (at a β-alkyl position) of the latter apparently acted as anionic initiator. Attempts to induce thermal polymerization and cyclotrimerization of the pendent cyano groups of hexa(β-cyanoethyl)cyclopentadiene were unsuccessful even with added Lewis acid catalysts. Reduction to the hexaamine was only partially successful.

Introduction

Electrophilic substitution of cyclopentadienyl anions is well documented (1). The five-membered aromatic anion readily attacks cyanogen chloride (2), methyl iodide (3) and even t-butyl bromide (4). The mechanism of alkylation has been investigated extensively (2), but there is no data available on the mechanism and product distribution of cyanoethylation via acrylonitrile addition. Bruson (5) showed that hexa(β-cyanoethyl)cyclopentadiene formed even when acrylonitrile was in a 2:1 ratio with the cyclopentadienyl anion. In this paper we describe our efforts to understand the details of the cyanoethylation reaction in the hope of developing a high-conversion process for the hexa(β-cyanoethyl)cyclopentadiene which may have utility for polymer formation directly or through reduced or hydrolyzed derivatives.

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*To whom offprint requests should be sent

Experimental

All reagents and solvents were purchased from Aldrich Chemical Company. Cyclopentadiene was obtained by distillation at 45°C from dicyclopentadiene heated at 165°C. All solvents and remaining reagents were used as obtained. ^{13}C NMR spectra were obtained in DMSO-d_6 on Bruker AC-200 and AC-300 NMR spectrometers. All NMR spectra were processed using Spectra Calc (6) and an in-house Bruker NMR module. A Perkin-Elmer DSC-7 and data station was used for thermal analysis.

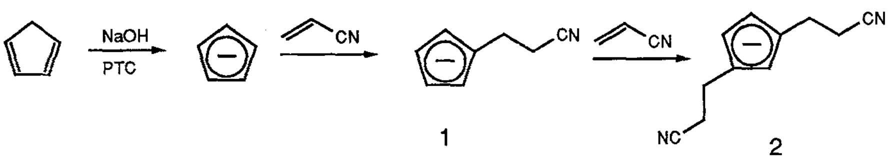
A solution of 0.414 g tetrabutyl ammonium bromide and 1.05 g sodium hydroxide in 5 mL water was added to cyclopentadiene (5.17 g, 0.078 mol) in 20 mL dioxane. This caused the solution to turn dark purple in color. Acrylonitrile (5.6 m, 0.085 mol) was added dropwise over 30 minutes during which the temperature of the reaction mixture rose from 22 to 29°C. The reaction was then allowed to stir for 3 h. The precipitate was removed by filtration through a fritted-glass funnel and washed with 5 mL dioxane. The solid product was extracted with 50 mL of boiling methanol, isolated by hot filtration, and air-dried to give 0.90 g.

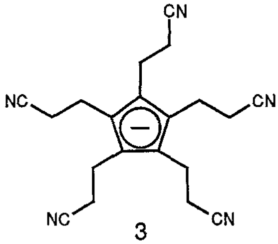
The initial filtrate was returned to the reaction flask, and more acrylonitrile (5.5 mL, 0.084 mol) was added to the solution dropwise over 30 minutes. The same change in temperature was observed for this cycle as in the previous one. The reaction mixture was stirred for 7 hours, and the residue was filtered and washed as before. The yield from this cycle was 1.38 g. The filtrate was again returned to the reaction flask, and acrylonitrile (5.6 mL, 0.085 mol) was added dropwise over 30 minutes. The reaction temperature rose from 22°C to 27°C during the addition. After allowing 5 hours for further reaction, the mixture was filtered and washed as before; yield of dry product was 0.25 g.

A forth reaction cycle was attempted, but no product formed. A total yield of 2.53 g was obtained for three cycles which corresponds to 8.5% conversion of cyclopentadiene to hexa(β-cyanoethyl)cyclopentadiene. The crude product (mp 174°C) may be purified by recrystallization from 2-methoxyethanol; mp 180°C by repeated DSC scans (lit. mp 203°C (5)).

Results and Discussion

Various reaction conditions were altered in an attempt to improve the yield of hexa(β-cyanoethyl)cyclopentadiene **5**. Although higher yields were not obtained, the experiments did give insight into the mechanism of the reaction. The most revealing reaction (given in the experimental) gave yields for each of the cycles of 16%, 21%, and 16%, respectively. This suggests that the reaction proceeds very quickly to the hexa-substituted product and the various terminated by-products. During the last addition, no temperature change or product formation indicated complete conversion of all reactive cyclopentadiene positions had occurred. That is, cyclopentadiene formation ceased despite an overall or average substitution of only three cyanoethyl units per ring (based on 3.3 equivalents of acrylonitrile reacted). Below are shown the first few steps of a possible mechanism for cyanoethylation of cyclopentadiene along with a final intermediate and two isolated products (**4** and **5**).





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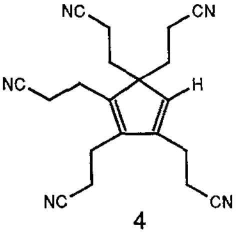

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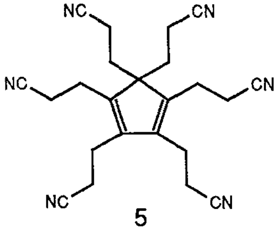

5

A number of by-products are possible from addition to an already substituted carbon that stop further reaction. Such termination gives the di-, tri-, tetra-, or penta-substituted derivatives (the latter possesses structure **4**). Various regioisomers of some of these compounds are possible, although no attempt was made to isolate and separate these materials. Crystallization of **5** from the reaction mixture occurred spontaneously, facilitating its isolation. Cooling the crude reaction mixture after filtration of **5** led to formation of crystalline **4** (contaminated with a small amount of **5**).

The structure of the hexa(β-cyanoethyl)cyclopentadiene obtained was confirmed by ^{13}C NMR (Figure 1). All peak chemical shifts were consistent with values calculated and the off-resonance spectrum showed no splitting of the peak at 60.3 ppm (quaternary sp^3 carbon) and the peaks around 141 ppm (substituted vinyls).

The other major side-product isolated was formed from the anion of the hexa-substituted derivative. If protonation of this species (the β-anion of **5** resulting from the final Michael addition of acrylonitrile) is slow, reaction with more acrylonitrile can occur leading to anionic

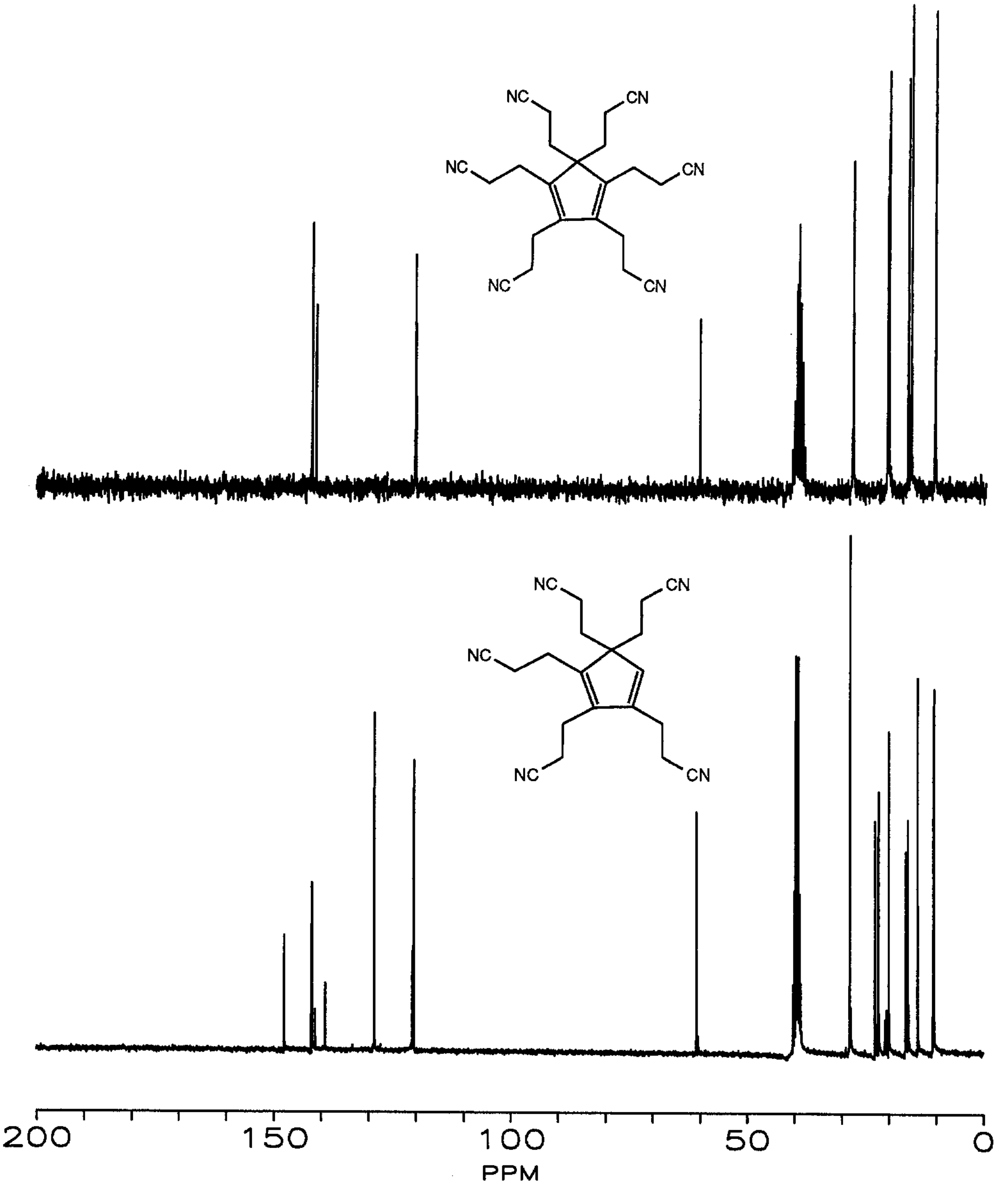

Figure 1. ^{13}C NMR spectra of 4 (bottom) and 5 (top)

polymerization. This results in formation of a polymer or oligomer of acrylonitrile with a terminal hexa(β-cyanoethyl)cyclopentadiene attached. This material is especially favored when excess acrylonitrile is used. Its ^{13}C NMR spectrum shows peaks corresponding to both hexa(β-cyanoethyl)cyclopentadiene and polyacrylonitrile (Figure 2).

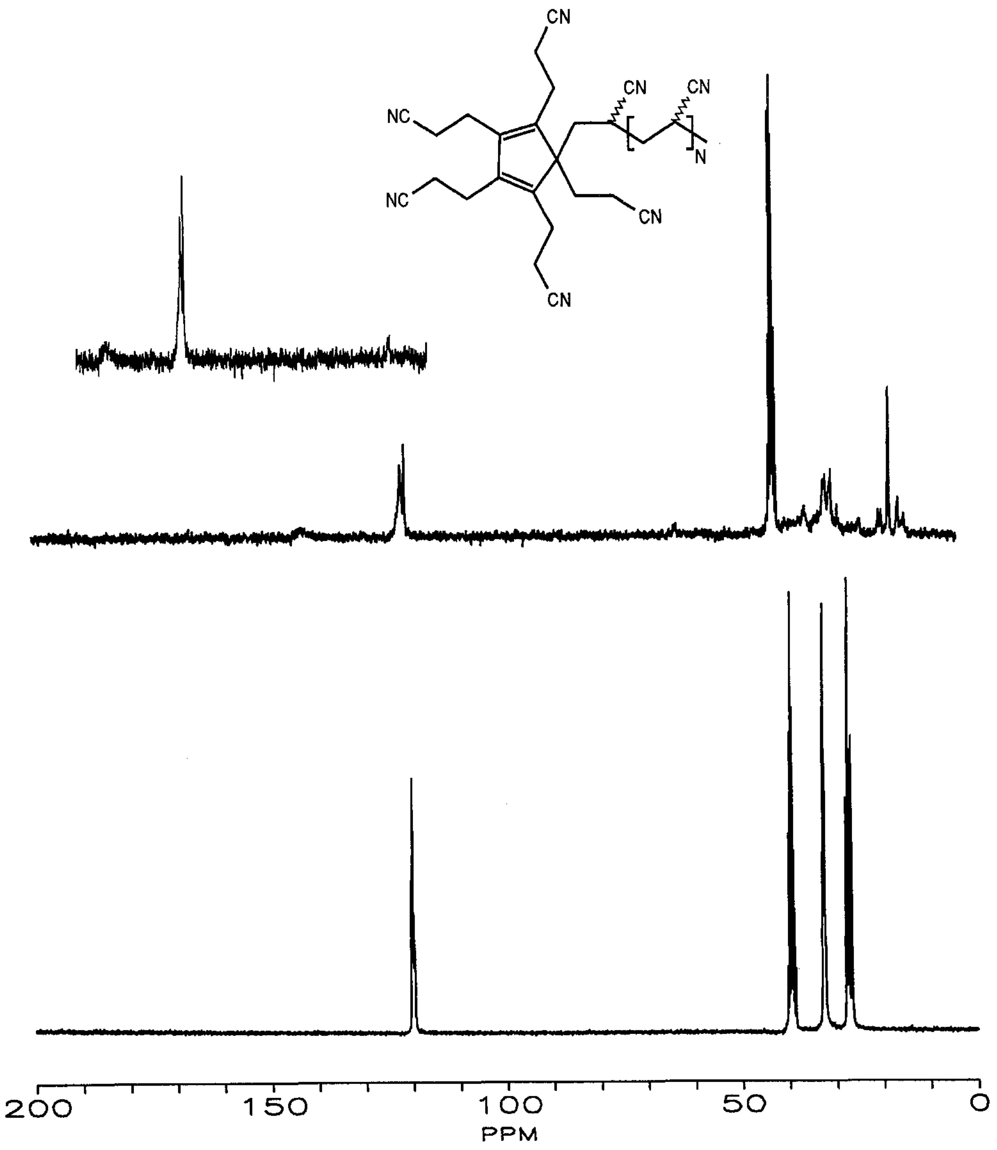

Figure 2. **^{13}C NMR spectra of polyacyrlonitrile (bottom) and 6 with an insert, 50 ppm - 150 ppm (top)**

One goal of this project was evaluation of the ability of **5** to form highly crosslinked matrices containing substituted 1,3,5-triazines. Alkyl nitriles have been reported to undergo cyclotrimerization with ferric chloride, zinc chloride, acetic acid, or aluminum chloride as catalyst (7). Zinc chloride has also been used for crosslinking polymers with cyano groups pendent from a polymer backbone (8). Attempted thermal curing of **5** with 5-12% by weight of zinc chloride, ferric chloride, benzoic acid, and aluminum chloride was monitored by DSC. No cure exotherm was observed below 220°C and repeated scans showed no change in melting point and heat of melting indicating that trimerization was not taking place under these conditions. Recently, a report appeared in which stannous chloride was used for the linear polymerization of cyano groups (9). This catalyst also caused no substantial change in the temperature and heat of melting of **5**.

A second goal of the project was conversion of **5** to reactive derivatives for crosslinking applications and star polymer formation. In fact, the hexacarboxylic acid has been reported to be obtainable by base-catalyzed hydrolysis of **5** (5). We attempted reduction to the hexakis(3-aminopropyl) compound with palladium and ammonium formate (10). However, even with variations of solvent, temperature and concentrations of the substrate, reagents and catalyst, we were not able to cleanly form the hexamine compound. Instead, reduction of the cyclopentadiene ring was accompanied by partial reduction of the nitrile groups (as confirmed by ^{13}C NMR analysis).

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