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Anionic Polymerization of Z,Z-2,4-Hexadienedinitrile

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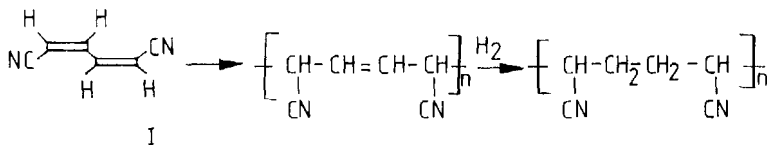
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ABSTRACT

Z,Z-2,4-Hexadienedinitrile, synthesized by the oxidative cleavage of o-phenylenediamine, was found to undergo anionic polymerization with n-BuLi in DMF at room temperature or below. The polymerization behavior appears to be similar to that of acrylonitrile polymerization using n-BuLi as initiator. Infra-red and NMR analysis of the polymer indicate the presence of both 1,4 and 1,2 linkages, with the latter predominating.

INTRODUCTION

The synthesis and characterization of polymers with structural defects such as head-to-head linkages have been the subject of a number of recent investigations [1]. Such defect structures have been reported to influence the thermal properties of poly(vinyl chloride) [2] and poly(acrylonitrile) [3]. However, synthesis of well-defined head-head poly(acrylonitrile) has not been reported so far. We reasoned that the polymerization of Z,Z-2,4-hexadienedinitrile (cis,cis-muconitrile or 1,4-dicyanobutadiene) (I) in a 1,4 fashion followed by hydrogenation could afford a route to such structures:



A literature search showed no available information on the polymerization of Monomer I. A patent report exists on the 1:1 copolymerization of I with vinyl and diene monomers [4]. The copolymer with styrene was reported to be useful for the preparation of adhesives and coatings. More recently, the synthesis and polymerization of 1,3-dicyanobutadiene has been reported [5].

We report in this paper the anionic polymerization of Z,Z-2,4-hexadienedinitrile and the characterization of a polymer derived therefrom. The results are compared with the polymerization of acrylonitrile under similar conditions.

EXPERIMENTAL

Monomer I was prepared by the oxidative cleavage of o-phenylenediamine using cuprous chloride and pyridine as oxygen carriers [6]. The product as recrystallized from diethyl ether had a mp of 128–129°C. The monomer was dried over acetone vapors in a drying pistol for 4 h in vacuo prior to using it in polymerization reactions. Acrylonitrile was purified using standard procedures. DMF was made dry using methods reported [7]. Sodium cyanide was dried over silica gel in a vacuum dessicator for 48 h. A saturated solution in DMF (1% by weight) was prepared. n-BuLi (Fluka A-G, 2 M in n-hexane) was estimated titrimetrically and appropriately diluted in n-hexane.

Polymerization was conducted using thoroughly dried glasswares fitted with a rubber septum for charging. All manipulations involving initiators, solvents, and liquid monomers were performed using a hypodermic syringe under a positive pressure of high purity nitrogen. Polymerization was terminated using acidified water. The recovered polymer was freed from unreacted monomer by washing with diethyl ether and then dried in vacuo.

Infrared analysis was performed on a Beckman 4220 spectrometer and NMR on a JEOL FX-100 instrument. Thermal analysis was performed on a Dupont model 910 analyzer. Intrinsic viscosity was determined using an Ubbelohde viscometer in DMF at 35°C. The average molecular weight was calculated from [8]

$$[\eta] = 2.78 \times 10^{-4} \bar{M}_w^{0.76}$$

RESULTS AND DISCUSSION

The monomer was characterized as the Z,Z-isomer by its characteristic A_2B_2 1H NMR pattern [6]. The spectrum also showed a pronounced solvent-induced shift in DMSO- d_6 relative to $CDCl_3$ ($\Delta\delta = \delta_{DMSO-d_6} - \delta_{CDCl_3} = 0.47$ for 2-H and 0.03 for 3-H). This is presumably due to charge transfer interaction between DMSO and the electron deficient monomer. The ^{13}C NMR of the monomer showed three resonance lines at (δ) 106.7 (C_2), 115.4 ($-CN$), and 143.1 (C_3).

Attempts to homopolymerize I by free radical initiators using AIBN ($80^\circ C$), dicumylperoxide ($120^\circ C$), and ammonium persulfate in DMF ($50^\circ C$) failed and the monomer was recovered quantitatively.

However, anionic initiators were capable of initiating the polymerization of I in DMF at room temperatures or below (Table 1). $n-BuLi$ was found to be more efficient than $NaCN$. The anionic polymerization of I was similar to that of acrylonitrile and in conformity with previously reported studies [9]. The molecular weight of polymer increased with increasing monomer concentration and decreasing initiator concentration. However, solubility limitations precluded it from attaining concentrations higher than 1.7 M in the case of I. Unlike acrylonitrile, conversions in the case of I were limited to 30%. The effect of TMEDA on polymerization was at best marginal for both monomers.

The polymers from I were deep green in appearance and dissolved in DMF to form a dark green solution. Interestingly, it was observed that the recovered monomer in all cases was the pure Z,Z-isomer, implying that propagation was much faster than initiation.

The infrared spectrum of the polymers from I showed (in KBr) two peaks, one at $2250 \pm 10\text{ cm}^{-1}$ and the other at $2200 \pm 10\text{ cm}^{-1}$. This is in contrast to the single nitrile peak for the monomer at 2220 cm^{-1} . Poly(acrylonitrile) also showed the same two peaks. This indicates the presence of two dissimilar cyano groups in the polymer: one in which no conjugation exists and which absorbs at higher frequencies (IIa, IIIa), and the other which is conjugated and absorbs at lower frequencies (IIb) [10].

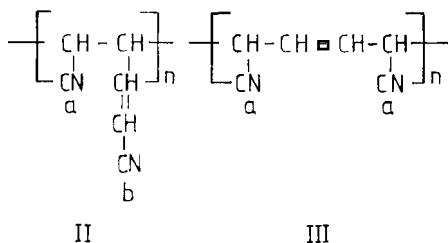


TABLE 1. Anionic Polymerization of Z,Z-2,4-Hexadienedinitrile and Acrylonitrile in DMF^a

Expt. no.	Monomer		Initiator (mmol)	M/I	Yield (g)	Conversion (%)	\bar{M}_w
	mmole	mol/L					
	<u>Z,Z-2,4-Hexadienedinitrile</u>						
8 ^b	40	2.0	NaCN (0.2)	200	0.20	5	-
10 ^c	40	2.0	NaCN (0.2)	200	0.26	6.5	-
16	20	1.0	n-BuLi (0.0625)	320	0.6	30	7,782
17	20	1.0	n-BuLi (0.3125)	64	0.6	30	2,934
18	20	1.0	n-BuLi (0.3125) TMEDA (0.625)	64	0.5	25	4,281
19	17	1.7	n-BuLi (0.0625)	272	0.5	30	12,450
20	17	1.7	n-BuLi (0.3125)	54	0.5	30	5,370
14 ^d	20	1.0	n-BuLi (0.2) TMEDA (0.4)	100	0.7	35	6,039

	Acrylonitrile						
1 ^c	30	2.5	NaCN (0.1)	300	0.25	16	-
22	20	1.0	n-BuLi (0.0625)	320	0.4	36	2,924
23	20	1.0	n-BuLi (0.0625) TMEDA (0.125)	320	0.8	72	3,591
20	20	1.0	n-BuLi (0.3125)	64	1.1	100	1,443
21	20	1.0	n-BuLi (0.3125) TMEDA (0.625)	64	1.1	100	1,179
9	45	2.25	n-BuLi (0.0625)	720	2.5	100	34,850
12	45	2.25	n-BuLi (0.3125)	144	2.0	83	4,281
f	90	1.80	n-BuLi (0.125)	720	4.1	85	31,600

^a10°C, 15 min.

^b20°C, 6 h.

^c100°C, 6 h.

^d10°C, 2 h.

^e20°C, 1.5 h.

^fRef. 9, 0°C, 15 min.

A comparison of the relative intensities of the two peaks for both poly(acrylonitrile) ($I_{2250 \text{ cm}^{-1}}/I_{2200 \text{ cm}^{-1}} = 5.0$) and poly(Z,Z-2,4-hexadienedinitrile) ($I_{2250 \text{ cm}^{-1}}/I_{2200 \text{ cm}^{-1}} = 0.23$) shows that 1,2 polymerization predominates in the latter. The ^1H NMR spectrum of the polymer in DMSO- d_6 was characterized by broad resonances. The peaks at (δ) 7.26 and 6.10 were assigned to the olefinic hydrogens, at 3.38 to the hydrogen α to the cyano group, and at 2.15 to the saturated hydrogen α to the double bond. In addition, resonance signals from initiator end groups (butyl) were detected at (δ) 1.40 (CH_2) and 0.90 (CH_3). The signal at (δ) 2.80 could not be definitively assigned. The NMR spectrum confirmed that both 1,4 and 1,2 linkages are present in the polymer derived from I. The polymers showed no melting behavior in DSC (N_2 , heating rate $5^\circ\text{C}/\text{min}$) and suffered about 40% weight loss at temperatures below 500°C .

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