

NOTE

1-(1',3'-펜타디에닐)-2,2,3,3-테트라시아노시클로프로판의 합성 및 음이온 중합

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Synthesis and Anionic Polymerization of 1-(1',3'-Pentadienyl)- 2,2,3,3-Tetracyanocyclopropane

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요 약 : 브로모말로노니트릴과 1,1-디시아노-1,3,5-헵타트리엔(1)을 반응시켜 1-(1',3'-펜타디에닐)-2,2,3,3-테트라시아노시클로프로판(2)을 합성하였다. 화합물 1은 2,4-헥사디에날과 말로노니트릴로부터 합성하였다. 단량체 2를 시안화 나트륨과 같은 음이온 개시제로 중합시킨 결과 시클로프로판고리가 개환되어 펜타디에닐기 펜타디에닐기가 치환된 중합체(3)를 얻었다. 중합체 3은 아세톤에 녹았으며 고유점도는 0.05~0.10 dL/g을 보였다.

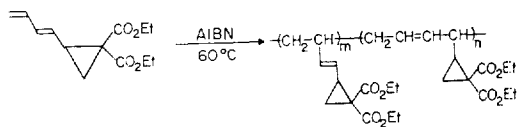
Abstract : 1-(1',3'-Pentadienyl)-2,2,3,3-tetracyanocyclopropane(2) was prepared by the reaction of bromomalononitrile with 1,1-dicyano-1,3,5-heptatriene(1). Compound 1 was prepared from 2,4-hexadienal and malononitrile. Monomer 2 was polymerized by anionic initiators such as sodium cyanide to give the polymer 3 with pentadienyl functionalities in the pendant group. The resulting polymer was soluble in acetone and the inherent viscosities were in the range of 0.05~0.10 dL/g.

INTRODUCTION

Homodienyl 1,1-disubstituted-2-vinylcyclopropanes are polymerizable radically^{1~3} or anionically⁴ in different degrees, depending on the electronic

properties of substituents. Radical initiator attacks vinyl group and radical polymerization usually proceeds via 1,5-mode,¹ but anionic catalyst only attacks cyclopropane to give the polymers with pendant vinyl groups.⁴ However, examples of the po-

lymerization of homotrienyl cyclopropanes are rare. Recently I. Cho and his coworkers have prepared several homotrienes such as 1,1-diethoxycarbonyl-2-(1,3-butadienyl)cyclopropane and investigated their polymerization behavior.⁵ According to their results, butadienylcyclopropane derivatives polymerize in a mixed mode such as 1,2- and 1,4-type with free radical initiators. 1,7-Type polymerization involving both butadienyl group and ring-opening of cyclopropane does not occur. Radical polymerizabilities of those monomers decrease with increasing alkyl substituents in the butadienyl moiety, probably due to the steric hindrance.



In this work we investigated the polymerization behavior of another homotrienyl cyclopropane containing four cyano groups. The present paper describes the synthesis and anionic polymerization of 1-(1',3'-pentadienyl)-2,2,3,3-tetracyanocyclopropane(2). We now report the results of the initial phase of the work.

EXPERIMENTAL

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. 2,4-Hexadienal was distilled before use. Piperidine was dried with calcium hydride and fractionally distilled. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Bromomalnonitrile was prepared according to a literature⁶ and recrystallized twice from chloroform. Anhydrous N,N-dimethylformamide (DMF) packed under nitrogen was purchased from Aldrich Co. and dried over a molecular sieve (4Å). Sodium cyanide was recrystallized from ethanol-water(3 : 1 by volume) and stored in a desiccator. The initiator solution was prepared by dissolving 0.1 g(2.0 mmol) of purified sodium cyanide in 10 mL of dry DMF and was stored in a de-

siccator.

Measurements. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer.¹ H-NMR spectra were taken on a Varian 360 L NMR spectrometer(60 MHz). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperature(T_g) was 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. Melting points were measured in Buchi 512 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Preparation of 1,1-Dicyano-1,3,5-heptatriene(1). Piperidine(0.51 g, 0.006 mol) was added to a solution of malononitrile(3.96 g, 0.06 mol) in 35 mL of n-butanol at room temperature. Then 2,4-hexadienal(3.84 g, 0.04 mol) was added dropwise with stirring at 0°C. The resulting solution was stirred for 5 min at 0°C, followed by standing at 0°C for 12 hr. The product was filtered and washed with cold n-butanol and water containing a small amount of acetic acid. Product thus obtained was sublimed (50°C, 0.5 mmHg) to give 4.16 g(50% yield) of 1 (an isomeric mixture of Z/E-). M.p. 70~72°C. ¹H-NMR(acetone-d₆) δ 1.82~2.01(d, 3H), 6.08~6.87(m, 3H), 7.02~7.48(m 1H), 7.78~8.03(d, 1H); IR(KBr) 3015(olefinic C-H), 2230, 2215(CN), 1633, 1588, 1540(C=C) cm⁻¹.

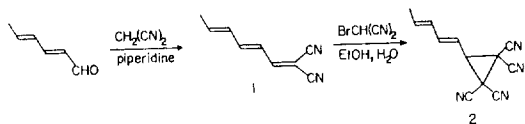
Preparation of 1-(1',3'-Pentadienyl)-2,2,3,3-Tetracyanocyclopropane(2). 1,1-Dicyano-1,3,5-heptatriene(1.73 g, 0.012 mol) and bromomalnonitrile(2.90 g, 0.020 mol) were dissolved in 20 mL of 85% aqueous ethanol with stirring at room temperature. The resulting solution was stirred for 7 hr at room temperature. After filtration of the product, it was rinsed with 20 mL of 85% aqueous ethanol and 20 mL of cold ethanol respectively. The obtained product was sublimed(100°C, 0.5 mmHg). Yield : 1.50 g(60%). M.p. 166~168°C(dec.). ¹H-NMR (acetone-d₆) δ 1.68~1.93(d, 3H), 4.20~4.45(d, 1

H), 5.07~5.54(q, 1H), 5.74~6.55(m, 2H), 6.65~7.16(q, 1H) : IR(KBr) 3030(olefinic C-H), 2255(CN), 1650(C=C) cm⁻¹. Anal. Calcd for C₁₂H₈N₄ : C, 69.22 ; H, 3.87 ; N, 26.91. Found : C, 69.35 ; H, 3.82 ; N, 26.98.

Anionic Polymerization of 2. A DMF(2 mL) solution of **2**(1.04 g, 0.005 mol) was placed in a polymerization tube and dry nitrogen was flushed through it with a long syringe needle for 30 min at room temperature. The solution was cooled in a dry ice-acetone bath and 0.5 mL of sodium cyanide initiator solution was added with a microsyringe under nitrogen. The polymerization tube was then evacuated and sealed under vacuum. The tube was taken out of the dry ice-acetone bath and placed in a bath kept at proper temperatures. After 6 days, the polymerization tube was opened and the polymerization product was poured into 400 mL of diethyl ether. The obtained polymer was collected and reprecipitated from acetone into diethyl ether. Polymer thus obtained was dried in a vacuum oven at 30°C. **3** : 0.57 g(55% yield) ; η_{inh} = 0.10 dL/g(c : 0.5 g/dL in acetone at 25°C). ¹H-NMR(acetone-d₆) δ 0.90~2.05(m, 3H), 2.50~3.70(m, 1H), 5.25~7.40(m, 4H) ; IR(KBr) 2205(CN), 1630(C=C) cm⁻¹.

RESULTS AND DISCUSSION

1-(1',3'-Pentadienyl)-2,2,3,3-tetracyanocyclopropane **2** was prepared by cyclopropane formation from malononitrile and 1,1-dicyano-1,3,5-heptatriene **1** Scheme 1, according to a variation of the Wideqvist reaction.⁷ Compound **1** was prepared by the condensation of bromomalononitrile with 2,4-hexadienal.⁸ The chemical structure of the compounds was confirmed by ¹H-NMR(Fig. 1), IR, and elemental analysis. Spectral data indicated that co-



Scheme 1

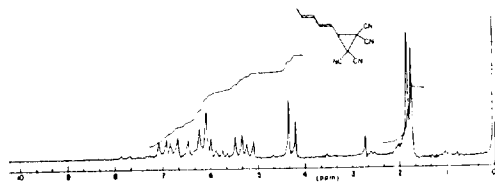
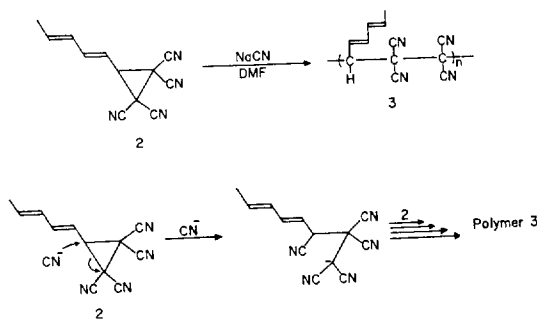


Fig. 1. ¹H-NMR spectrum of 1-(1',3'-Pentadienyl)-2,2,3,3-tetracyanocyclopropane(**2**) taken in acetone-d₆ at room temperature.



Scheme 2

Table 1. Anionic Polymerization of **2**^a by Sodium Cyanide in DMF

Monomer	Monomer /DMF (g/mL)	NaCN (mol%)	Temp. (C)	Time (day)	Conversion (%)	η _{inh} ^b (dL/g)
2	0.50	1.5	15	6	55	0.10
2	0.42	1.2	15	3	48	0.08
2	0.33	1.2	25	5	50	0.06
2	0.35	1.5	25	7	52	0.10

^a **2** = 1-(1',3'-Pentadienyl)-2,2,3,3-tetracyanocyclopropane

^b Concentration of 0.5 g/dL in acetone at 25°C.

mpounds **1** and **2** were mixtures of cis-and trans-isomer. Monomer **2** was quite stable when heated up to 100°C.

Monomer **2** was polymerized by sodium cyanide in dry DMF at different temperatures. With sodium cyanide ion monomer **2** yielded powdery polymer **3**. The anionic polymerization results are summarized in Table 1, which shows that monomer **2** is not as reactive as some of 1,1-disubstituted 2-vinylcyclopropanes,⁴ failing to give high mo-

lecular weight polymers. The inherent viscosities of polymer were in the range of 0.05~0.10 dL/g in acetone.

The chemical structure of polymer **3** was determined by IR(Fig. 2) and $^1\text{H-NMR}$ (Fig. 3) spectra. The striking feature of polymer **3** revealed by spectra is that the polymer does not possess any cyclopropane group. The polymer sample failed to show any resonance peaks attributable to methine proton of cyclopropane ring in its $^1\text{H-NMR}$ spectrum. These spectral evidence seems to indicate that the anionic polymerization proceeded via a ring-opening of cyclopropane as in the case of 1,1-disubstituted-2-vinylcyclopropanes.⁴ In the anionic polymerization(Scheme 2), the cyanide ion initiates the polymerization by attacking the positively characterized carbon rather than the vinyl group, thereby resulting in the formation of an anion which is stabilized by two electron-withdrawing cyano substituents. Thus, the driving force of the

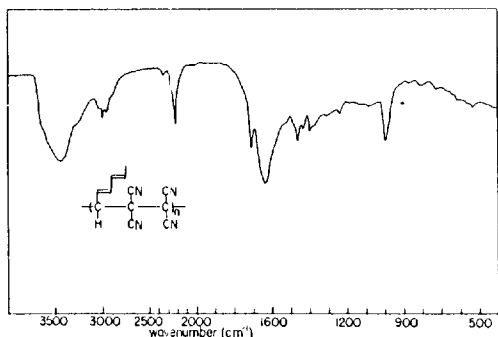


Fig. 2. IR spectrum of polymer **3**.

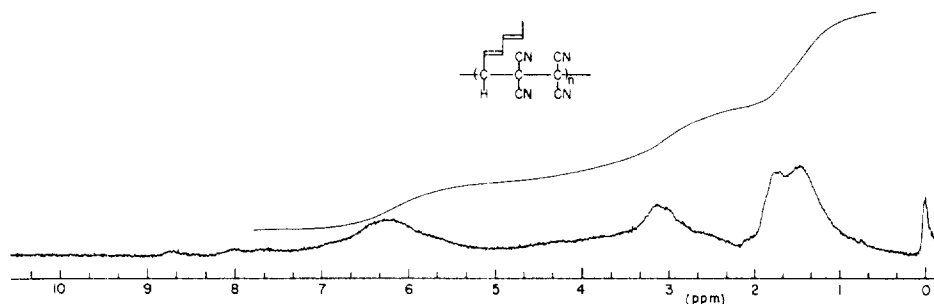


Fig. 3. $^1\text{H-NMR}$ spectrum of polymer **3** taken in acetone- d_6 at room temperature.

Table 2. Thermal Properties of Polymer **3**

Polymer	T_g ($^{\circ}\text{C}$)	Degradation temp.($^{\circ}\text{C}$) ^a			Residue ^a at 700 $^{\circ}\text{C}$ (wt.-%)
		5%-loss	20%-loss	40%-loss	
3	—	216	324	494	13.2

^a Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 atmosphere.

anionic polymerization is probably the stability of ring-opened anion. Vinyl type polymerization without ring-opening is obviously not favored for steric reasons.

Polymer **3** was soluble in acetone but insoluble in chloroform and diethyl ether. Thermal behavior of the polymer was investigated by thermogravimetric analysis(TGA) and differential scanning calorimeter(DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. Polymer **3** appeared to be amorphous and began to decompose at around 220 $^{\circ}\text{C}$ under nitrogen in TGA thermogram. The polymer did not show any characteristic T_g in its DSC thermogram. All the attempts to homopolymerize **2** with various radical catalysts have failed so far.

We are now in the process of polymerization of other homotrienylyl systems and the full accounts of the work will be reported later.

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