

Cationic Polymerization of Electron-Donor Monomers by 1, 1, 2, 2-Tetracyanocyclopropylstyrene, A New Electron-Acceptor

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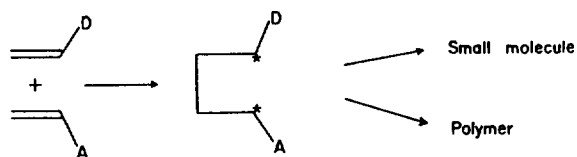
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Poly (N-vinylcarbazole) was obtained spontaneously by 1, 1, 2, 2-tetracyanocyclopropylstyrene(1) in polar solvents such as dichloromethane and acetonitrile at room temperature. The polymerization reactions were faster in more polar solvent and were not proceeded in less polar solvents such as chloroform and diethyl ether. The formation of poly (N-vinylcarbazole) was explained by bond-forming initiation theory, in which the initiating species are zwitterionic tetramethylene intermediates.

Introduction

It is well-known that spontaneous, thermal reactions of electron-rich olefins with electron-poor olefins lead to both small organic molecules and polymers. Most of the small organic compounds are cyclobutanes. On the polymer side, homopolymers of one or both of the electron-rich and electron-poor olefins or alternating copolymers are formed. For example, electrophilic tri- and tetrasubstituted olefins such as methyl tricyanoethylenecarboxylate and dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate initiate cationic homopolymerization of very electron-rich monomers, in particular N-vinylcarbazole.¹⁻⁴ These facile reactions proceed through an electron donor-acceptor (EDA) complex. To explain these results, Hall and his coworkers proposed the Bond-Forming Initiation theory, in which the tetramethylene intermediates are proposed as the initiating species for spontaneous polymerizations.^{5,6} According to the theory, homopolymers as in-



initiated by zwitterionic tetramethylenes, while alternating copolymers are formed by biradical tetramethylenes.

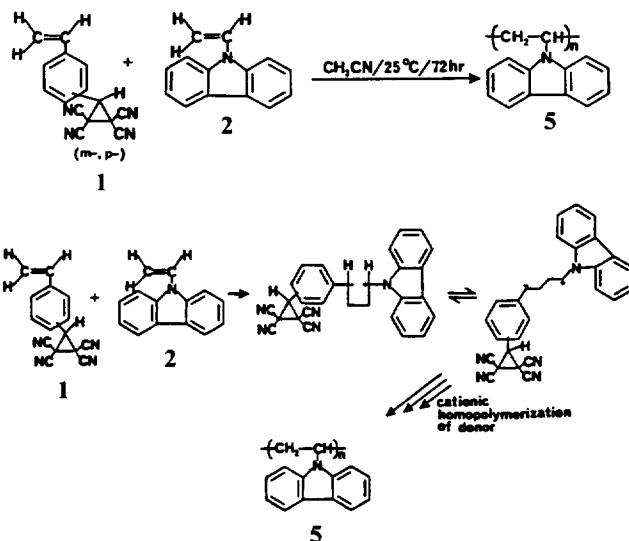
In the course of our study of tetracyanocyclopropanes,^{7,8} we found that 1, 1, 2, 2-tetracyanocyclopropylstyrene (1) is a moderate electron-acceptor, which can initiate cationic homopolymerization of electron-rich monomers. In the present work we report the spontaneous cationic polymerization of N-vinylcarbazole by 1, 1, 2, 2-tetracyanocyclopropylstyrene, a new electron-acceptor. We shall also comment on the polymerization mechanism.

Results and Discussion

1, 1, 2, 2-Tetracyanocyclopropylstyrene (1) was prepared by the Wideqvist reaction for cyclopropane synthesis.⁹⁻¹¹ Vinyl benzaldehyde was synthesized according to a known method

by oxidation of vinylbenzyl chloride¹². Reaction of vinyl benzaldehyde with bromomalononitrile in dilute aqueous ethanol solution gave 1, 1, 2, 2-tetracyanocyclopropylstyrene in good yield at room temperature. The chemical structure was confirmed by ¹H-NMR, IR, ¹³C-NMR spectra, and elemental analysis. ¹H-NMR spectrum showed that compound 1 is a mixture of *m*-isomer (70 mole%) and *p*-isomer (30 mole%).

Reactions of donor olefins N-vinylcarbazole (2), *p*-methoxystyrene (3), and ethyl vinyl ether (4) were carried out in various solvents such as dichloromethane, 1,2-dichloroethane, and acetonitrile. Nothing happened in the reaction of compound 1 with 3 or 4. However, reaction of 2 with acceptor 1 gave the homopolymer (5) of N-vinylcarbazole. The polymerization reactions were carried out at room temperature in various solvents. The reactions were faster in more polar solvents. From acetonitrile, the polymer precipitated as formed. The results of the reactions are summarized in Table 1. The structures of the poly(N-vinylcarbazole) (5) were iden-

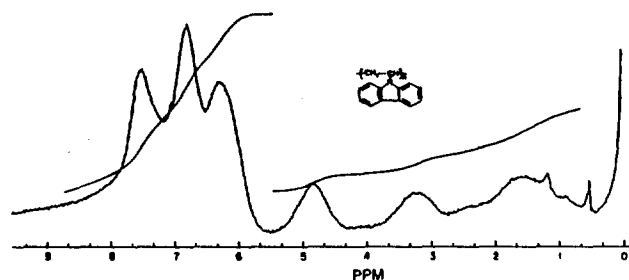
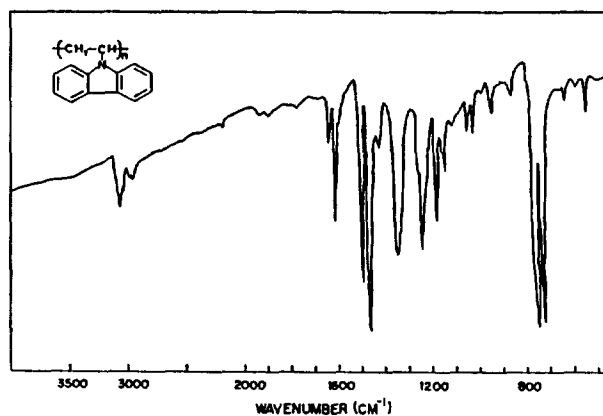


tified by ¹H-NMR (Figure 1) and IR (Figure 2) spectra. The ¹H-NMR spectrum shows all the resonance peaks attributable to the protons of backbone and pendant carbazole group. The IR spectrum confirmed the expected chemical structures, exhibiting all the absorption bands attributable to the

Table 1. Polymerization of Electron-Donor Monomers by 1, 1, 2, 2-Tetracyanocyclopropylstyrene (1) in Various Solvents at Room Temperature

Acceptor ^a	Concn (mole/l)	Donor ^b	Concn (mole/l)	Solvent	Time (h)	Product	Yield (%)	η^c inh (dl/g)
1	0.05	2	0.5	CH ₂ Cl ₂	8	hemopoly-2	69	0.59
1	0.5	2	0.5	CH ₂ Cl ₂	2	hemopoly-2	55	0.29
1	0.05	2	0.5	ClCH ₂ CH ₂ Cl	1	hemopoly-2	36	0.40
1	0.5	2	0.5	ClCH ₂ CH ₂ Cl	1	hemopoly-2	32	0.36
1	0.05	2	0.5	CH ₃ CN	1	hemopoly-2	28	0.22
1	0.5	2	0.5	CH ₃ CN	2	hemopoly-2	19	0.19
1	0.05	3	0.5	CH ₂ Cl ₂	48	nil	—	—
1	0.5	3	0.5	CH ₂ Cl ₂	72	nil	—	—
1	0.5	3	0.5	CH ₃ CN	60	nil	—	—
1	0.5	4	0.5	CH ₂ Cl ₂	72	nil	—	—
1	0.5	4	0.5	CH ₃ CN	72	nil	—	—

^a1 = 1, 1, 2, 2-Tetracyanocyclopropylstyrene (*m*-/*p*- = 70/30, mole/mole). ^b2 = N-vinylcarbazole; 3 = *p*-Methoxystyrene; 4 = Ethyl vinyl ether. ^cInherent viscosity: Concentration of 0.5 g/dl in chloroform at 25°C.

**Figure 1.** ¹H-NMR spectrum of poly(N-vinylcarbazole) (5). 60 MHz, room temperature, arbitrary concentration in CDCl₃.**Figure 2.** IR spectrum of poly(N-vinylcarbazole) (5).

functional groups comprising the poly(N-vinylcarbazole).

The reaction of acceptor 1 with donor 2 gave none of the expected cyclobutane, and poly (N-vinylcarbazole) was not formed in less polar solvent such as chloroform and diethyl ether.

The formation of poly (N-vinylcarbazole) (5) was explained by Bond-Forming Initiation Theory, in which the initiating species are zwitterionic tetramethylene intermediates.^{5,6} Because of steric hindrance and rather weak acceptor character the formation of cyclobutane would not be favored in this situation.

Copolymerization with other monomers are in progress and the results will be reported later.

Experimental

Instrumentation. All melting point temperatures are uncorrected. IR spectra were taken on Hitachi Model 260-30 infrared spectrometer. ¹H-NMR spectra were obtained on a Varian Model 360-L nuclear magnetic resonance spectrometer at 60 MHz. ¹³C-NMR spectra were obtained on a Bruker WM 250 nuclear magnetic resonance spectrometer at 250 MHz. Elemental analyses were performed by Perkin-Elmer 2400 CHN Elemental Analyzer. Viscosity values were obtained by using a Cannon-Fenske viscometer. Melting points were measured in a Buchi-512 melting point apparatus.

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 before use. Dimethyl sulfoxide (DMSO) was dried over 4Å molecular sieves for several days and distilled under vacuum. Acetonitrile was refluxed with calcium hydride and fractionally distilled. Bromomalononitrile was prepared according to a literature procedure¹³ and recrystallized twice from chloroform. N-Vinylcarbazole was recrystallized twice from methanol. Ethyl vinyl ether was dried over sodium metal and distilled under vacuum, taking the middle fraction. *p*-Methoxystyrene was distilled from calcium hydride, and stored under nitrogen at -10°C.

Synthesis of Vinyl Benzaldehyde. A mixture of 6.1 g (0.04 mole) of vinylbenzyl chloride (*m*- and *p*-isomeric mixture) and 11.6 g (0.06 mole) of potassium chromate in 50 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 10 ml of dimethyl sulfoxide. Extraction was performed on the filtrate twice with 50 ml of diethyl ether. The organic layer was washed with 50 ml of water and dried over anhydrous magnesium sulfate. The resulting solution was concentrated by rotary evaporator, followed by fractional distillation gave 3.7 g of vinyl benzaldehyde (70% yield; *m*-/*p*-: 67/33, mole/mole). Bp. 63-64°C/0.5

mmHg. $^1\text{H-NMR}$ (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 $\text{C}_9\text{H}_8\text{O}$: C, 81.82; H, 6.06. Found: C, 81.75; H, 6.03.

Synthesis of 1, 1, 2, 2-Tetracyanocyclopropylstyrene (1). A solution of 3.5 g (0.021 mole) of potassium iodide in 10 ml of water was added slowly to the solution of vinyl benzaldehyde (1.32 g, 0.01 mole) and bromomalononitrile (1.45 g, 0.01 mole) in 10 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 0.73 g (63% yield) of **1** (*m-p*-: 70/30, mole/mole). Mp 157-160°C (dec.). $^1\text{H-NMR}$ (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 (CN), 1631, 1600 (C=C) cm^{-1} ; $^{13}\text{C-NMR}$ (acetone- d_6) δ 23.5 (s, $(\text{CN})_2\text{C}<$), 43.0 (s, $>\text{CH}-$), 109.5 (s, *cis*-CN), 111.2 (s, *trans*-CN), 115.6-116.2 (d, $\text{CH}_2=$), 127.3-130.4 (m, aromatic), 136.4 (s, $=\text{CH}-$), 139.5 (s, $-\text{C}-$). Anal. Calcd for $\text{C}_{15}\text{H}_8\text{N}_4$: C, 73.77; H, 3.28; N, 22.95. Found: C, 73.84; H, 3.23; N, 22.87.

Polymerization of Electron-Donor Monomers by 1, 1, 2, 2-Tetracyanocyclopropylstyrene (1). A representative polymerization procedure was as follows: A dichloromethane (10 ml) solution of N-vinylcarbazole (0.97 g, 5 mmole) and 1,1,2,2-tetracyanocyclopropylstyrene (0.012 g, 0.5 mmole) in 10 ml of dichloromethane were placed separately into a Y-shaped polymerization tube. The system was degassed by a freeze-thaw process under vacuum, and the vessel is filled with nitrogen gas. The two olefin solutions were combined, and the resulting solution was stirred for 8 hr at room temperature. Thus obtained viscous product was poured into

a 400 ml of diethyl ether. The precipitated polymer was collected and reprecipitated from chloroform into diethyl ether. **5**: 0.67 g (69% yield). The homopolymer of N-vinylcarbazole was identified by $^1\text{H-NMR}$, IR, and elemental analysis.

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Kinetics and Mechanism of the Hydrolysis of α , N-Diphenylnitron

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The rate constants of hydrolysis of α , N-diphenylnitron and its derivatives have been determined by UV spectrophotometry from pH 2.0 to 13.5, and a rate equation which can be applied over a wide pH range was obtained.

On the basis of rate equation, hydrolysis product, and general base and substituent effects, a plausible mechanism of hydrolysis has been proposed: Below pH 5, the hydrolysis was initiated by the protonation and followed by the addition of water to α -carbon. However, above pH 11, the hydrolysis was proceeded by the addition of hydroxide ion to α -carbon. In the range of pH 5-11, the addition of water to nitron is rate controlling step.

Introduction

The nucleophilic addition of activated carbon-carbon double bond and carbon-nitrogen double bond has been subjected to extensive mechanistic and synthetic studies.¹⁻⁴

Scott⁵ suggested $\text{S}_{\text{N}}1$ mechanism for the hydrolysis of N-arylbenzhydrazidic bromide in acidic solution. Kim and Lee⁶

pointed out that the hydrolysis of imidoyl chloride proceeds through $\text{S}_{\text{N}}1$ mechanism below pH 7, however, above pH 7.5, the reaction initiated by the attack of hydroxide ion.

Azomethine N-oxides (commonly known as nitrones) have a carbon-nitrogen dipolar double bond and the structure is conveniently viewed as a resonance hybrid of following three canonical forms.