22 *Macromolecules* **1996,** *29,* 22−25

Spontaneous Copolymerization of the Cyclobutane Adduct of Tetracyanoethylene and Vinyl Ether with Oxiranes

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Received May 23, 1995; Revised Manuscript Received September 11, 1995[⊗]

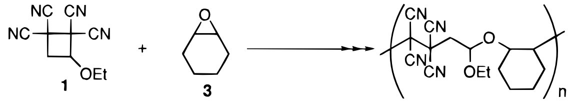
ABSTRACT: Spontaneous copolymerizations of 1,1,2,2-tetracyano-3-ethoxycyclobutane (**1**), which is a cyclobutane adduct of the zwitterionic tetramethylene generated from tetracyanoethylene (TCNE) and ethyl vinyl ether (VE), with oxiranes are described. The cyclobutane adduct **1** reacted with a variety of oxiranes spontaneously at ambient temperature in CH_3CN to yield copolymers. Of the oxiranes, cyclohexene oxide (**3**) resulted in a high molecular weight alternating copolymer of **1** and **3**. In the alternating copolymerization, the polymer yields and molecular weights increased with reaction time, whereas the composition of the copolymers remained constant at 1:1 irrespective of time. Furthermore, the polymer yields and molecular weights became maximum at a feed ratio of 1:1. The reaction of **1** with **3** was quenched with acetic acid in the initial stage to yield the acetic acid adduct (**4**) of the zwitterion generated from **1** and **3**. On the basis of the polymerization behavior and the isolation of **4**, the proposed mechanism of the copolymerization involves the stepwise reaction of the zwitterion generated from **1** and **3**.

Introduction

Copolymers of strong donor olefins and strong acceptor olefins have not been synthesized because those olefins are liable to react with each other spontaneously to generate zwitterionic tetramethylenes, which produce cyclobutane adducts or initiate the cationic homopolymerization of the donor olefins and/or the anionic homopolymerization of the acceptor olefins.[1] Recently, we have been successful in producing the copolymer of vinyl ether (VE) as a strong donor olefin and tetracyanoethylene (TCNE) as a strong acceptor olefin by the ring-opening polymerization of the cyclobutane adduct (**1**) of VE and TCNE with anionic initiators,[2] Lewis acids,[3] and tertiary amines.[4]

The fact that **1** undergoes anionic ring-opening polymerization prompted us to investigate whether zwitterionic copolymerization[5] of **1** with another monomer could take place by using donor monomers instead of anionic initiators (Scheme 1). Thus, if the zwitterion **2** generated from **1** and the donor monomer has enough stability to exist in high concentration, **2** would react with itself to produce a dimeric zwitterion, and growth would continue in a step reaction manner with the formation of different-sized zwitterions to yield the alternating copolymer of **1** and the donor monomer. This copolymerization will provide access to 1:1:1 periodic terpolymers,[6] because **1** is derived from TCNE and VE. Especially using a cyclic monomer as the donor monomer, the copolymerization will permit the production of unprecedented 1:1:1 periodic terpolymers of two olefins and a cyclic monomer.

The present paper reports the spontaneous copolymerizations of the cyclobutane adduct **1** of TCNE and VE with oxiranes. In particular, the copolymerization behavior of **1** with cyclohexene oxide (**3**) is studied in detail to discuss whether the spontaneous copolymerization involves the zwitterion generated from **1** and **3**.



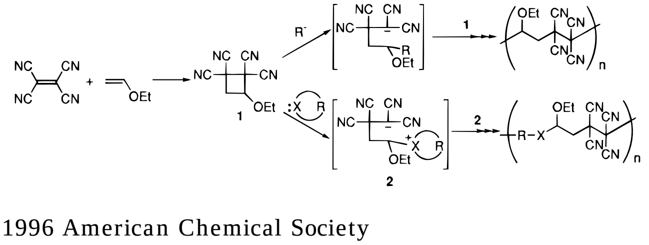
(1)

Results and Discussion

Polymerization Conditions. The cyclobutane adduct **1** reacted with a variety of equimolar oxiranes spontaneously at ambient temperature in CH_3CN to yield polymers (Table 1). Of the oxiranes, cyclohexene oxide (**3**) resulted in a high molecular weight polymer that consisted of **1** and **3** in a ratio of nearly 1:1. This polymer, insoluble in methanol, would be the copolymer of **1** and **3**, because the homopolymers of **1** and **3** are soluble in methanol, respectively. The production of polymers rich in **1** in the reaction with other oxiranes implies that the lower nucleophilicity of other oxiranes compared to **3** causes the homopolymerization of **1** to some extent.

The copolymerizations of **1** with equimolar **3** were next carried out under various conditions. The reaction solvent was found to dramatically affect the polymer molecular weight (Table 2). When the copolymerization was carried out in CH_3CN, the molecular weight of the polymer obtained was about 50 000. Using other solvents, however, the molecular weights were about 10 000 in all cases. Since CH_3CN was regarded as the best solvent for the spontaneous copolymerization of **1** with **3**, polymerizations in CH_3CN were next carried out at 0−80 °C (Table 3). The reaction of **1** with **3** took place even at 0 °C and all of **1** and **3** were consumed, although the methanol-insoluble polymer was not obtained. With increasing reaction temperature above ambient temperature, the polymer molecular weight decreased and

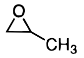
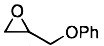
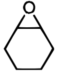
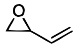
Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

0024-9297/96/2229-0022$12.00/0

Table 1. Spontaneous Copolymerization of 1 with Oxiranes[a]

oxirane	time, h	yield, %[b]	$\overline{M}n$[c]	polymer content[d] 1 : oxirane
	180	8[e]	16500	65 : 35
	180	2[e]	16400	89 : 11
	48	41	51900	54 : 46
	180	33	68600	62 : 38

[a] Polymerization was carried out at room temperature in CH_3CN ($[\mathbf{1}]_0 = [\text{oxirane}]_0 = 1$ M). [b] Insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards. [d] Determined by elemental analysis. [e] Insoluble in diethyl ether.

Table 2. Solvent Effect of Copolymerization of 1 with 3[a]

solvent[b]	yield, %[c]	$\overline{M}_n$[d]	polymer content[e] **1:3**
CH_3CN	40	49600	48:52
CH_3NO_2	2[f]		
THF	0[f]		
DMSO	71[g]	9700	
DMF	84[g]	9400	
DMAc	92[g]	9100	
NMP[h]	19	10000	61:39

[a] Polymerization of **1** with equimolar **3** was carried out at room temperature for 48 h. [b] $[\mathbf{1}]_0 = [\mathbf{3}]_0 = 1$ M. [c] Insoluble in MeOH. [d] Estimated by GPC based on polystyrene standards. [e] Determined by elemental analysis. [f] **1** and **3** were consumed, but the products were soluble in MeOH. [g] Soluble in MeOH, but insoluble in Et_2O. [h] *N*-Methyl-2-pyrrolidone.

Table 3. Effect of Polymerization Temperature on Copolymerization of 1 with 3[a]

temp, °C	yield, %[b]	$\overline{M}_n$[c]	polymer content[d] **1:3**
0	0		
25	40	49600	48:52
60	33	31900	58:42
80	42	29800	68:32

[a] Polymerization of **1** with equimolar **3** was carried out for 48 h in CH_3CN ($[\mathbf{1}]_0 = [\mathbf{3}]_0 = 1$ M). [b] Insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards. [d] Determined by elemental analysis.

Table 4. Spontaneous Copolymerization of 1 with 3[a]

time, h	yield, %[b]	$\overline{M}_n$[c]	polymer content[d] **1:3**
6	0		
12	4	36500	
24	26	45900	50:50
48	41	51900	54:46
144	44	61500	55:45

[a] Polymerization was carried out for at room temperature in CH_3CN ($[\mathbf{1}]_0 = [\mathbf{3}]_0 = 1$ M). [b] Insoluble in MeOH. [c] Estimated by GPC based on polystyrene standards. [d] Determined by elemental analysis.

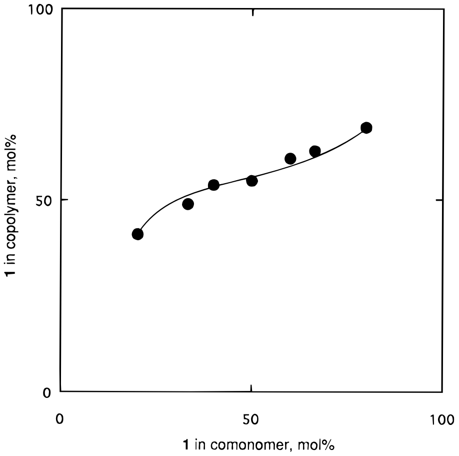


Figure 1. Effects of monomer feed ratio on the polymer composition (in CH_3CN at room temperature for 48 h).

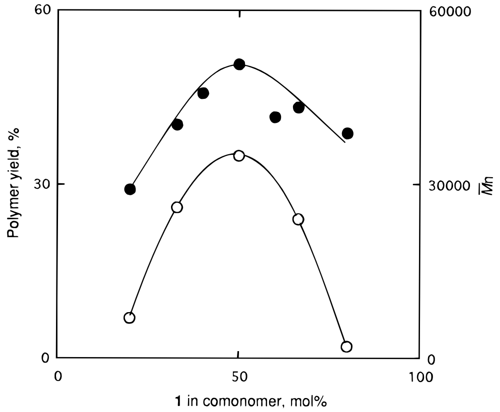


Figure 2. Effects of monomer feed ratio on the polymer yield (○) and on the polymer molecular weight (●) (in CH_3CN at room temperature for 48 h).

the unit of **1** in the copolymer increased. Consequently, the reaction of **1** with **3** in CH_3CN at ambient temperature yielded the highest molecular weight 1:1 copolymer of **1** and **3**.

Copolymerization Behavior and Mechanism. In order to propose a mechanism for the spontaneous copolymerization of **1** with **3**, the polymerization behavior with time or feed ratio was studied. Table 4 shows changes of the polymer yields, molecular weights, and compositions with the reaction time. The yields and molecular weights increased with time, whereas the compositions of the copolymers remained almost constant at 1:1 irrespective of time. These results imply that the alternating copolymer would be produced in a step reaction manner by considering the very low possibility of the production of a random copolymer consisting of **1** and **3** with the ratio 1:1 at any time.

Figure 1 shows the compositions of the copolymers when the reaction was carried out at various feed ratios of **1** to **3**, and Figure 2 the polymer yields and molecular weights. When the feed ratios of **1** in monomers were 33−50 mol %, 1:1 copolymers were obtained. When less than 33 mol % of **1** or more than 50 mol % of **1** was used, copolymers rich in **3** or rich in **1** were produced, respectively. Therefore, even a slight excess of **1** in the feed became favorable for homopolymerization of **1**, whereas for up to 17 mol % excess of **3**, the homopolymerization of **3** was depressed to yield 1:1 copolymer. The polymer yields and the molecular weights became maximum at the 1:1 feed ratio (Figure 2), indicating that the polymerization took place most effectively at the 1:1 feed ratio and could involve a polymerization intermediate generated from equimolar **1** and **3**.

The ^1H NMR spectrum of the 1:1 copolymer showed the signal corresponding to the methine proton of the unit from **1** at 5.4−4.4 ppm, although that signal of the homopolymer of **1** appears at 6.2−5.2 ppm.[3] The signal assignable to the methine proton on a carbon adjacent to an oxygen of the unit from **3** was observed at 4.4−3.2 ppm, and a broad singlet signal of the same methine proton of the homopolymer of **3** was not observed at 3.4

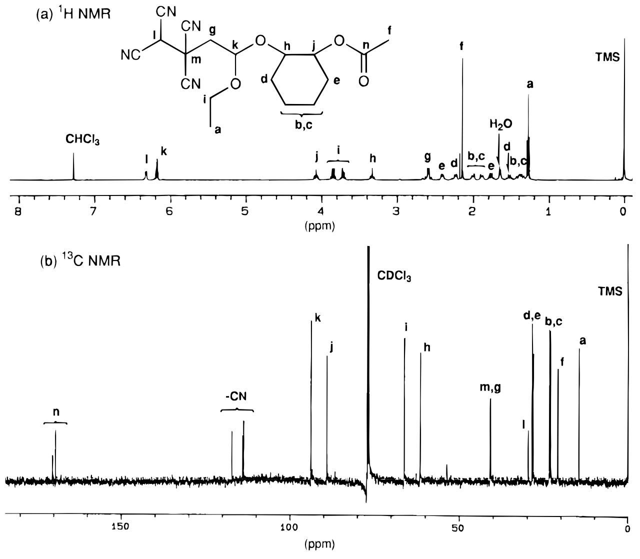
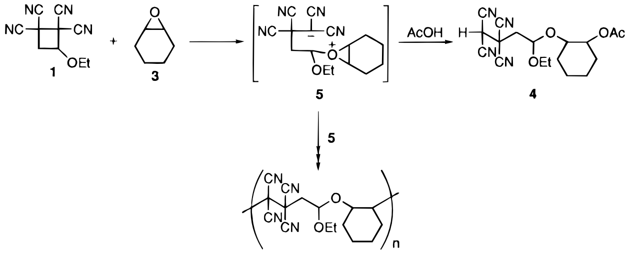


Figure 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **4** in CDCl$_3$ at 28 °C.

Scheme 2



ppm; that means the signal of the copolymer at 4.4–3.2 ppm showed no shoulder at 3.4 ppm. The ^{13}C NMR spectrum of the copolymer in DMSO-d_6 did not show signals even at 120 °C; the reason remains unclear, but the ^{13}C CP/MAS spectra could show the characteristic signal of an acetal carbon at 99.5 ppm in spite of a broad signal.

These NMR spectra are consistent with the alternating structure shown in eq 1. To clarify the copolymer structure, the reaction mixture was quenched with acetic acid just after the addition of **3** to the solution of **1** in CH$_3$CN. Purification of the products by HPLC yielded acetate **4**, consisting of **1** and **3**. The ^{1}H and ^{13}C NMR spectra of **4** are shown in Figure 3 with assignments for various signals; each signal was assigned on the basis of the ^{1}H–^{1}H and ^{13}C–^{1}H COSY NMR spectra. The isolation of **4** confirmed not only the alternating copolymer structure but also the involvement of the zwitterion **5** generated from **1** and **3** as a key intermediate in the copolymerization. On the basis of the above polymerization behavior and the isolation of **4** from the reaction mixture quenched with acetic acid, a zwitterionic mechanism is proposed to describe the alternating copolymerization of **1** with **3** (Scheme 2). Polymerization is initiated by the ring-opening reaction of **1** with **3** at the ethoxy-substituted C-3 to generate the zwitterion **5** containing the acetal moiety. Propagation proceeds by the reaction of **5** with itself and the polycombination of macrozwitterions of the type **5** in a step reaction manner.

It should be noted that the alternating copolymer obtained was the 1:1:1 periodic terpolymer of TCNE, VE, and **3**. These alternating copolymerizations of cyclobutane adducts of strong donor olefins and acceptor olefins with the third monomers would serve as a general method for the preparation of 1:1:1 periodic terpolymers. Since the cyclobutane adducts undergo both anionic[2] and cationic[3] polymerizations, not only donor monomers but also acceptor monomers can be used as the third monomers for the synthesis of 1:1:1 periodic terpolymers. Further work on the spontaneous copolymerization of cyclobutane adducts of strong donor and acceptor olefins with nucleophilic or electrophilic monomers is now in progress.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-200 and α-500 operating in the pulsed Fourier transform (FT) modes, using tetramethylsilane (TMS) as an internal standard. ^{13}C CP/MAS spectra were obtained on a JEOL JNM EX-270 operating in the pulsed FT modes, using adamantane as an external standard (δ 29.5). IR spectra were recorded on a Hitachi R-270-30. Elemental analysis was performed on a Yanaco CHNcorder MT-2. The number-average molecular weights ($\bar{M}_n$) of the polymers obtained were measured with a Tosoh HLC-8020 gel permeation chromatography (GPC) unit (eluent: *N*,*N*-dimethylformamide (DMF), calibration: polystyrene standards) using four TSK-gel columns (2 × GMH$_{XL}$ and 2 × G2000H$_{XL}$). Isolation of acetic acid adduct **4** of the zwitterion was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using JA1GEL-1H and -2H columns.

1,1,2,2-Tetracyano-3-ethoxycyclobutane (**1**) was prepared from tetracyanoethylene (TCNE) and ethyl vinyl ether according to the reported procedure.[7] Oxiranes were purified by distillation over CaH$_2$. Acetonitrile, dimethyl sulfoxide (DMSO), DMF, *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) were distilled over CaH$_2$. Nitromethane was dried overnight with CaCl$_2$ and then distilled. Tetrahydrofuran (THF) was distilled over sodium just before use.

Spontaneous Copolymerization of 1 with Cyclohexene Oxide (3). Cyclobutane adduct **1** was placed in a round-bottomed flask equipped with a three-way stopcock and purged with argon. A solution of equimolar **3** in distilled CH$_3$CN ([**3**]$_0$ = 1 M) was added at room temperature via a syringe under a dry nitrogen flow. After stirring for 48 h, the solution was poured into a large amount of diethyl ether (25 times volume to the CH$_3$CN solution). The precipitated polymer was collected and dried in vacuo: IR (KBr) 2938, 2860, 2212, 1092 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.41–4.39 (br, 1H), 4.39–3.17 (br, 4H), 2.78–2.18 (br, 2H), 1.96–1.52 (br, 4H), 1.52–0.80 (br, 7H).

Trap of Zwitterion Generated from 1 and 3 with Acetic Acid. Cyclobutane adduct **1** (0.200 g, 1.0 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and purged with argon. A solution of equimolar **3** (0.098 g, 1.0 mmol) in distilled CH$_3$CN (0.5 mL) was added at room temperature via a syringe under a dry nitrogen flow. After the mixture became homogeneous (ca. 1 min), acetic acid (1mL) was added and the mixture was stirred for 26 h. The reaction mixture was concentrated in vacuo and the residue was purified by preparative HPLC to yield acetic acid adduct **4** of the zwitterion (0.019 g, 7% yield): mp 82–87 °C; IR (KBr) 2194, 1743, 1371, 1236, 1122, 1145, 1104, 1070, 1047 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.32 and 6.31 (2bs, 1H), 6.17 and 6.16 (2t, J = 5.5 and 5.8 Hz, 1H), 4.06 (tt, J = 3.4 and 11.6 Hz, 1H), 3.85 (dq, J = 7.0 and 9.3 Hz, 1H), 3.71 (dq, J = 7.0 and 9.3 Hz, 1H), 3.32 (tt, J = 2.9 and 11.6 Hz, 1H), 2.68–2.55 (m, 2H), 2.43–2.38 (m, 1H), 2.28–2.20 (m, 1H), 2.14 (s, 3H), 2.04–1.98 (m, 1H), 1.92–1.82 (m, 1H), 1.84–1.73 (m, 1H), 1.60–1.46 (m, 1H), 1.46–1.30 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 170.4, 169.6, 117.3, 114.1, 113.8, 93.9, 89.2, 66.3, 61.6, 41.0, 40.9, 29.8, 28.7, 28.4, 23.6, 23.3, 21.1, 14.8.

Acknowledgment. We gratefully acknowledge financial support of this work under a grant from the Kawasaki Steel 21st Century Foundation. We are also grateful to Professor T. Yamanobe (Gunma University) for obtaining the ^{13}C CP/MAS spectra and for helpful advice.

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MA9506997