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Ring-Opening Polymerization of the Cyclobutane Adduct of Methyl Tricyanoethylenecarboxylate and Ethyl Vinyl Ether

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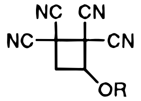
ABSTRACT: For an extension of the work on the ring-opening polymerizations of cyclobutane adducts of strong donor and strong acceptor olefins yielding novel alternating copolymers of those olefins, the ring-opening polymerizations of a cyclobutane adduct **2** of methyl tricyanoethylenecarboxylate (MTCE) and ethyl vinyl ether (EVE) are investigated. The cyclobutane **2** reacted with acetic acid and ethanol at ambient temperature to yield the ring-opened corresponding adducts in good yields. The polymerizations of **2** were carried out with Lewis acids, anionic initiators, tertiary amines, and ammonium halides, respectively, according to the polymerization methods of a cyclobutane adduct **1** of tetracyanoethylene (TCNE) and EVE. All those polymerization catalysts except for ammonium halides were effective for the polymerization of **2**, that yielded an alternating copolymer of MTCE and EVE.

Introduction

Olefins with resonance-stabilizing substituents undergo copolymerization with a variety of olefins in the presence of a radical initiator or without the initiator when they are weak donor and acceptor olefins. However, olefins with strong donor substituents and olefins with strong acceptor substituents cannot be copolymerized because they are liable to react with each other spontaneously to generate zwitterions, which produce cyclobutane adducts or homopolymers of donor and/or acceptor olefins.[1]

We have initiated work with the objectives of establishing a versatile protocol for otherwise difficult synthesis of copolymers of strong donor olefins and strong acceptor olefins. Our basic strategy is the ring-opening polymerization of the cyclobutane adducts of strong donor olefins and strong acceptor olefins. In the previous papers, we have reported the synthesis of copolymers of tetracyanoethylene (TCNE) and vinyl ethers (VE) by the ring-opening polymerizations of cyclobutane adducts **1** of TCNE and VE with Lewis acids,[2] anionic initiators,[3] tertiary amines,[4] and ammonium halides.[5] The polymerization with anionic initiators involves the chain polymerization mechanism, whereas the polymerizations with Lewis acids, tertiary amines, and ammonium halides involve both the chain polymerization mechanism and step polymerization mechanism. However, the ring-opening polymerizations of **1** with four kinds of initiators proceed via cleavage of the bond between the dicyano-substituted C-2 and the alkoxy-substituted C-3 irrespective of the polymerization catalysts, suggesting that two of the cyano groups on the C-2 and the alkoxy group on the C-3 of the cyclobutane adducts play an important role in the ring-opening reaction of the cyclobutane adducts.

Accordingly, we design another cyclobutane undergoing ring-opening polymerization in such a way that the substituents on the C-2 and C-3 remain unchanged and that the substituents on the C-1, which seem to have small influence upon ring-opening reactivity, are replaced. In the present paper, we report the ring-opening polymerization of a cyclobutane adduct **2** of methyl tricyanoethylenecarboxylate (MTCE) and ethyl vinyl ether (EVE), in that the cyano group on the C-1 of **1** is replaced by the methoxycarbonyl group as a little weaker electron-withdrawing group than the cyano group.



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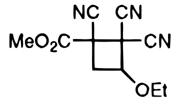
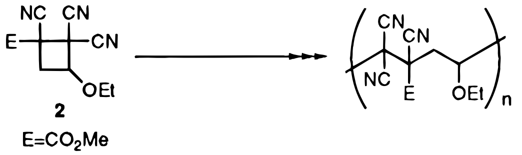


2

Although radical copolymerization of MTCE with *p*-methoxystyrene has been reported,[6] there has been no report on the copolymerization of MTCE and EVE; therefore the polymer obtained by the ring-opening polymerization of **2** will be the first example of the copolymer of MTCE and EVE. The ring-opening polymerizations of **2** are studied by using Lewis acids, anionic initiators, tertiary amines, and ammonium halides in a manner similar to the ring-opening polymerizations of **1**.



Results and Discussion

Preparation of 2. The requisite MTCE was prepared from TCNE and methyl cyanoacetate according to the reported procedure.[6] A solution of EVE in chloroform was slowly added to a solution of MTCE to afford the homopolymer of EVE. An excess amount of EVE was then rapidly added to MTCE to yield a cyclobutane adduct **2**, a dihydropyran adduct **3**,[6] and small amount of the homopolymer of EVE, contrary to the reaction of TCNE and EVE giving only the cyclo-

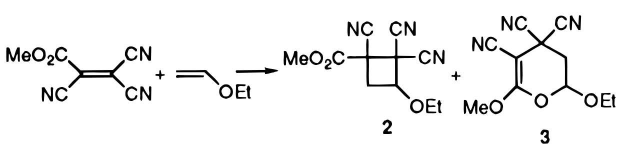


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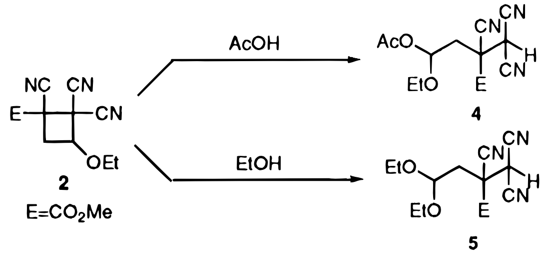
Table 1. Polymerization of 2 with Lewis Acids[a]

Lewis acid[b]	yield, %[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
ZnI_2	7	9600	1.12
BF_3OEt_2	0		
$SnCl_4$	16	9600	1.10
$EtAlCl_2$	25	6500	1.12

[a] Polymerization was carried out at room temperature for 24 h in CH_3NO_2 ($[\mathbf{2}]_0 = 1.0$ M). [b] 5 mol %. [c] Insoluble in diethyl ether. [d] Estimated by GPC based on polystyrene standards.

butane adduct **1**.[7] Considering that chloroform promoted the cationic homopolymerization of EVE, the reaction was carried out in tetrahydrofuran instead of chloroform, but only the homopolymer of EVE was obtained. We tried to isolate cyclobutane **2** from the mixture above by column chromatography on silica gel. When low-polarity eluent was used, it took such a long time that **2** was decomposed in silica gel, whereas **2** could not be separated from **3** by using a high-polarity eluent such as dichloromethane. After all, when a solution of dichloromethane and hexane with volume ratio 9:1 was used, **2** was isolated in the highest yield. The cyclobutane **2** obtained was a *cis*−*trans* mixture. The isomeric ratio was *cis*(ethoxy and ester group *cis*)/*trans* = 73/27 according to the reported ^{1}H NMR spectral data of the isobutoxy analogs.[6]

Reactions of 2 with Acetic Acid or Ethanol. To estimate the ring-opening reactivity of **2**, the reactions of **2** with acetic acid or ethanol were carried out. The cyclobutane **1** derived from TCNE and EVE is known to react with acetic acid and alcohol via cleavage of the bond between the dicyano-substituted C-2 and the ethoxy-substituted C-3 to give the corresponding adducts, respectively.[8] The cyclobutane **2** reacted with acetic acid at ambient temperature to yield the adduct **4** in 75% yield. Similarly, the reaction of **2** with ethanol gave the adduct **5** quantitatively. Both reactions proceeded via cleavage of the bond between the C-2 and the C-3 in a manner similar to that of **1**. Accordingly, **2** having the methoxycarbonyl group as a weaker electron-withdrawing group than the cyano group was shown to have sufficient ring-opening reactivity and expected to undergo both cationic and anionic ring-opening polymerizations since the reactions of **2** with acetic acid and ethanol are regarded as model reactions of cationic and anionic ring-opening polymerizations, respectively.



Polymerizations with Lewis Acids. The polymerizations of **2** with a variety of Lewis acids were carried out in CH_3NO_2 at room temperature in a manner similar to the polymerization of **1**[2] (Table 1). The polymerization of **2** occurred with ZnI_2, the most suitable Lewis acid for the polymerization of **1**,[2] and BF_3OEt_2 did not polymerize **2** similarly to **1**. Surprisingly, however, $EtAlCl_2$ gave the polymer in better yield than ZnI_2 in spite of no polymer in the polymerization of **1**. Although yields of polymer insoluble in diethyl ether were not high, as shown in Table 1, the ether-soluble part was oligomers with similar structures and did not contain the monomer **2**; that is, the conversions were 100% in all cases except for the polymerization with BF_3OEt_2.

Table 2. Polymerization of 2 with Anionic Initiators[a]

initiator[b]	yield, %[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
$NaCEt(CO_2Et)_2$	26	8800	1.20
$NaCH(CO_2Et)_2$	18	6900	1.15
$NaCH(CN)_2$	11	7400	1.19
NaOMe	24	11700	1.24

[a] Polymerization was carried out at room temperature for 24 h in DMF ($[\mathbf{2}]_0 = 1.0$ M). [b] 5 mol %. [c] Insoluble in diethyl ether. [d] Estimated by GPC based on polystyrene standards.

Table 3. Polymerization of 2 with Tertiary Amines[a]

amine[b]	time, h	yield, %[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
Et_3N	24	20	8600	1.25
	48	39	8700	1.22
DBU[e]	48	50	8000	1.18

[a] Polymerization was carried out at room temperature in CH_3CN ($[\mathbf{2}]_0 = 1.0$ M). [b] 10 mol %. [c] Insoluble in diethyl ether. [d] Estimated by GPC based on polystyrene standards. [e] 1,8-Diazabicyclo[5.4.0]undec-7-ene.

The IR spectrum of the polymer showed characteristic absorptions of a cyano group, an ester carbonyl group, and an ether linkage at 2200, 1756, and 1098 cm^{-1}, respectively. In the ^{1}H NMR spectrum, the signals of the methine proton at 4.73 and 4.67 ppm of **2** were shifted to 5.97−5.55 ppm for the polymer, implying that a unit from EVE was between strongly electron-withdrawing units from MTCE in the polymer. In comparison with the ^{1}H NMR spectrum of the polyEVE, which shows signals of the methylene and methine protons of the backbone at 2.00−1.44 and 3.80−3.20 ppm, respectively, the signals due to the methylene and methine protons of the unit from EVE of **2** appeared differently at 4.12−2.47 and 5.97−5.55 ppm, respectively. Furthermore, the ^{13}C NMR spectrum of the polymer was in fair agreement with the spectra of the adducts **4** and **5**. These spectral data support the ring-opening mechanism which yields an alternating copolymer of units from MTCE and EVE.

Polymerization with Anionic Initiators. The anionic polymerizations of **2** were carried out at room temperature in *N*,*N*-dimethylformamide (DMF), that is the optimized conditions for the anionic polymerization of **1**[3] (Table 2). Of carbanions stabilized with two electron-withdrawing groups as initiators, sodium diethyl ethylmalonate was most suitable for obtaining high molecular weight polymer in good yield in a manner similar to the polymerization of **1**.[3] Furthermore, the highest molecular weight polymer was obtained when sodium methoxide was used. The ether-soluble part did not contain monomer **2** but consisted of oligomers in all cases. The number-average molecular weight ($\bar{M}_n$) of the polymer from **2** was similar to that of the polymer from **1** under the same conditions.

The IR and NMR spectra of the polymers showed the same spectra of the polymer obtained with Lewis acids.

Polymerization with Tertiary Amines. The polymerizations of **2** were carried out with Et_3N or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile at room temperature, which were found to be the optimized conditions for the polymerization of **1** with tertiary amines[4] (Table 3). When Et_3N was used, the yields of the polymer increased with time, whereas the molecular weight did not increase. Furthermore, the yield of the polymer with similar molecular weight increased by

Table 4. Polymerization of 2 with TBAI[a]

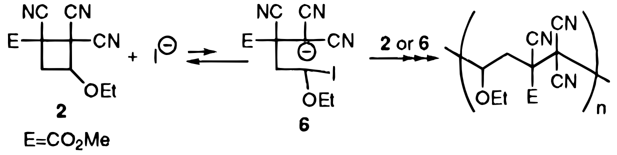
mol % of TBAI	time, h	yield, %[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
2.5	24	3	8200	1.21
10	72	3	9300	1.14

[a] Polymerization was carried out at room temperature in DMAc ($[\mathbf{2}]_0$ = 1.0 M). [b] Insoluble in diethyl ether. [c] Estimated by GPC based on polystyrene standards.

using DBU instead of Et_3N. The $\bar{M}_n$ of the polymer obtained was about half of that of the polymer of **1** obtained with Et_3N.[3] Since the ether-soluble part consisted of oligomers without **2** and the yields increased with time, the low molecular weight of the polymer is probably due to slow intermolecular reactions of different-sized ammonium zwitterions generated from **2** and tertiary amines.

Polymerization with Ammonium Halides. The polymerizations of **2** were carried out with tetrabutylammonium iodide (TBAI) in *N*,*N*-dimethylacetamide (DMAc) at room temperature according to the procedure of the polymerization of **1** with TBAI[5] (Table 4). When 2.5 mol % of TBAI was used, the yield of the polymer was only 3% and the monomer **2** remained. The cyclobutane **2** was then allowed to react with 10 mol % of TBAI for a longer reaction time, but the yield of the polymer did not increase and **2** remained.

The polymerization behavior of **2** with TBAI was distinctly different from that of **1** which yields the high molecular weight polymer quantitatively by using TBAI. The observed difference may be interpreted in terms of the low concentration of iodo-substituted anion **6** in equilibrium with the iodide ion and **2** having a lower ring-opening reactivity than **1**.



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. IR spectra were recorded on a Hitachi R-270-30. 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 × $G2000H_{XL}$).

Methyl tricyanoethylenecarboxylate (MTCE) was prepared from tetracyanoethylene (TCNE) and methyl cyanoacetate according to the reported procedure.[6] Ethyl vinyl ether (EVE) was purified by distillation over sodium. ZnI_2 was used as received; it was vacuum dried at 250 °C in the reaction flask just before use. Commercial $SnCl_4$ and BF_3OEt_2 were distilled. $EtAlCl_2$ (1.0 M solution in hexane) was commercially supplied as a solution. Sodium salts of active methylene or methine compounds were prepared from the corresponding active methylene or methine compounds and sodium hydride and then were vacuum dried over P_2O_5. Sodium methoxide was prepared from methanol and sodium and then was vacuum dried over P_2O_5. Et_3N and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were distilled over CaH_2. Tetrabutylammonium iodide (TBAI) was recrystallized from benzene by adding hexane and then was vacuum dried over P_2O_5. Chloroform was distilled over P_2O_5. Nitromethane was dried overnight with $CaCl_2$ and then distilled. *N*,*N*-Dimethylformamide (DMF), acetonitrile, and *N*,*N*-dimethylacetamide (DMAc) were distilled over CaH_2.

Preparation of 2. Into a solution of MTCE (2.38 g, 14.8 mmol) in chloroform (80 mL) was added a solution of EVE (1.06 g, 14.8 mmol) in chloroform (5 mL) at once, and the reaction mixture was stirred at room temperature for 5 h. Furthermore, a solution of EVE (1.20 g, 16.7 mmol) in chloroform (5 mL) was added into the reaction mixture, followed by stirring for 20 h. After concentration in vacuo, the residue was purified by column chromatography on silica gel (Wakogel C-300, eluent: CH_2Cl_2/hexane = 9/1) to yield **2** (1.53 g, 45% yield, *cis*/*trans* = 73/27): IR (neat) 2980, 2254, 1758, 1443, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) for *cis*-isomer δ 4.73 (t, J = 8.1 Hz, 1H), 4.02 (s, 3H), 3.83−3.68 (m, 2H), 3.19 (dd, J = 8.1 and 13.0 Hz, 1H), 2.94 (dd, J = 8.1 and 13.0 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); ^{1}H NMR ($CDCl_3$) for *trans*-isomer δ 4.67 (dd, J = 7.8 and 9.4 Hz, 1H), 4.00 (s, 3H), 3.83−3.68 (m, 2H), 3.16 (dd, J = 9.4 and 13.3 Hz, 1H), 3.00 (dd, J = 7.8 and 13.3 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) for *cis*-isomer δ 164.0, 113.4, 110.9, 108.9, 77.0, 67.3, 55.6, 41.8, 38.1, 36.5, 14.9; ^{13}C NMR ($CDCl_3$) for *trans*-isomer δ 164.0, 113.4, 110.9, 108.9, 76.0, 67.3, 55.4, 53.8, 43.6, 38.1, 14.8.

Reaction of 2 with Acetic Acid. Cyclobutane **2** (0.233 g, 1.0 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and purged with argon. Acetic acid (1 mL) was added and the mixture was stirred for 23.5 h. The reaction mixture was concentrated in vacuo to give the adduct of acetic acid **4** (0.221 g, 75% yield): IR (neat) 2980, 2256, 1754, 1440, 1012 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.05 and 5.98 (2dd, J = 4.9 and 3.9 Hz, 1H, $C\mathit{H}(OEt)OAc$), 4.77 and 4.67 (2s, 1H, $C\mathit{H}(CN)_2$), 4.00 and 3.99 (2s, 3H, $CO_2C\mathit{H}_3$), 3.84−3.42 (m, 2H, $OC\mathit{H}_2CH_3$), 2.74−2.58 (m, 2H, $C\mathit{H}_2$), 2.12 and 2.15 (2s, 3H, $O_2CC\mathit{H}_3$), 1.26 and 1.21 (2t, J = 7.1 Hz, 3H, $OCH_2C\mathit{H}_3$); ^{13}C NMR ($CDCl_3$) δ 170.1 and 170.0 ($O_2\mathit{C}CH_3$), 164.5 and 164.7 ($\mathit{C}O_2CH_3$), 109.2 (CN), 93.6 and 93.4 ($\mathit{C}H(OEt)OAc$), 66.4 and 66.2 ($O\mathit{C}H_2CH_3$), 55.4 ($CO_2\mathit{C}H_3$), 47.2 and 46.8 ($\mathit{C}(CN)CO_2Me$), 38.2 and 38.6 (CH_2), 29.7 ($\mathit{C}H(CN)_2$), 21.0 ($O_2C\mathit{C}H_3$), 14.7 and 14.8 ($OCH_2\mathit{C}H_3$).

Reaction of 2 with Ethanol. Cyclobutane **2** (0.233 g, 1.0 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and purged with argon. Ethanol (1 mL) was added, and the mixture was stirred for 21 h. The reaction mixture was concentrated in vacuo to give the adduct of ethanol **5** (0.286 g, 100% yield): IR (neat) 2980, 2252, 1760, 1442, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 1H, $C\mathit{H}(CN)_2$), 4.69 (t, J = 4.4 Hz, 1H, $C\mathit{H}(OEt)_2$), 3.95 (s, 3H, $CO_2C\mathit{H}_3$), 3.74−3.36 (m, 4H, $OC\mathit{H}_2CH_3$), 2.57 (d, J = 4.4 Hz, 2H, $C\mathit{H}_2$), 1.25 and 1.20 (2t, J = 7.1 Hz, 6H $O_2CC\mathit{H}_3$); ^{13}C NMR ($CDCl_3$) δ 165.2 (C=O), 115.0 and 109.6 (CN), 99.6 ($\mathit{C}H(OEt)_2$), 64.2 and 63.9 ($O\mathit{C}H_2CH_3$), 55.1 ($CO_2\mathit{C}H_3$), 47.2 ($\mathit{C}(CN)CO_2Me$), 38.2 (CH_2), 29.6 ($\mathit{C}H(CN)_2$), 15.1 and 15.0 ($OCH_2\mathit{C}H_3$).

Polymerization with Lewis Acids. ZnI_2 (0.016 g, 5 mol % to **2**) was dried at 250 °C under vacuum in a round-bottomed flask equipped with a three-way stopcock and cooled at room temperature under an argon atmosphere. Into the flask was added a solution of **2** (0.233 g, 1.0 mmol) in CH_3NO_2 (1 mL) at ambient temperature under dry nitrogen flow. After stirring for 24 h, the polymerization was terminated with methanol containing a small amount of ammonia, and the solution was poured into 25 mL of ether with stirring. The precipitated polymer was collected and dried in vacuo. When other Lewis acids were used, a solution of Lewis acid in CH_3NO_2 (1 mL) was added to the flask containing **2**: IR (KBr) 2976, 2200, 1756, 1438, 1098 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.97−5.55 (br, 1H), 4.12−2.47 (br, 7H), 1.30−0.90 (br, 3H); ^{13}C NMR (acetone-d_6) δ 167.6, 114.5, 77.6, 65.1, 54.3, 49.1, 38.7, 35.9, 15.2.

Polymerization with Anionic Initiators. Into the initiator (5 mol % to **2**) in a round-bottomed flask equipped with a three-way stopcock and filled with argon, was added a solution of **2** (0.233 g, 1.0 mmol) in DMF (1 mL) at ambient temperature under a dry nitrogen flow. After stirring for 24 h, the polymerization was terminated with a small amount of methanol, and the solution was poured into ether (25 mL) with stirring. The precipitated polymer was collected and dried in vacuo.

Polymerization with Tertiary Amines. Cyclobutane **2** (0.233 g, 1.0 mmol) was placed in a round-bottomed flask equipped with a three-way stopcock and purged with argon.

A solution of amine (10 mol % to **2**) in CH_3CN (1 mL) was added at room temperature via a syringe under a dry nitrogen flow. After stirring for 24 or 48 h, the solution was poured into ether (25 mL) with stirring. The precipitated polymer was collected and dissolved in acetone, followed by pouring into 0.5 N hydrogen chloride (25 mL) with stirring. The precipitated polymer was collected and dried in vacuo.

Polymerization with Ammonium Halides. TBAI (2.5 or 10 mol % to **2**) was placed in a round-bottomed flask equipped with a three-way stopcock and filled with argon. Into the flask was added a solution of **2** (0.233 g, 1.0 mmol) in DMAc (1 mL) at ambient temperature under a nitrogen flow. After stirring for 24 or 72 h, the reaction mixture was poured into water (50 mL) with stirring, and the collected precipitates were dissolved in acetone (1 mL) followed by precipitation in aqueous KI solution (25 mL). The collected polymer further purified by dissolution in acetone followed by precipitation in ether (25 mL). The precipitated polymer was collected and dried in vacuo.

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