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Synthesis of Terpolymers by Spontaneous Copolymerization of the Cyclobutane Adducts of Electron-Acceptor Olefins and Vinyl Ether with 2-Oxazolines

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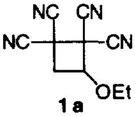
Abstract: Spontaneous copolymerizations of the cyclobutane adducts of strong donor olefins and strong acceptor olefins, 1,1,2,2-tetracyano-3-ethoxycyclobutane (**1a**) and dimethyl 2,2-dicyano-3-ethoxycyclobutane-1,1-dicarboxylate (**1b**), with 2-oxazolines (**2**) are described. In the reaction of **1b** with 2-methyloxazoline (**2b**), the alternating copolymer of **1b** and **2b**, the 1:1:1 periodic terpolymer of dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate, vinyl ether, and **2b**, was obtained. Cyclobutane **1a** also reacted with **2b** to yield copolymer rich in **1a** © 1997 Elsevier Science Ltd.

INTRODUCTION

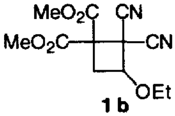
Alternating copolymers are one example of sequence-controlled polymers, and the literature on their synthesis is extensive.[1] For example, radical[2] or spontaneous[3] copolymerization of electron-donor olefins with electron-acceptor olefins is known to yield alternating copolymers. Saegusa and Kobayashi,[4] and other many groups[5] have found a variety of combinations of nucleophilic and electrophilic monomers which give rise to alternating copolymers via zwitterionic intermediates. In coordination polymerization, the alternating copolymer of butadiene and ethylene was synthesized.[6] Inoue and Aida have reported the living alternating copolymerizations of epoxide with carbon dioxide[7] or phthalic anhydride.[8] Recent advances in the insertion monomers into the backbone of homopolymers afford another interesting access to alternating copolymers.[9] Cho and we have reported otherwise difficult synthesis of alternating copolymers of strong donor olefins and strong acceptor olefins by the ring-opening polymerization of their dihydropyran adducts[10] and cyclobutane adducts,[11] respectively.

However, there are few documented examples of synthesis of 1:1:1 periodic terpolymers except for Saegusa and Kobayashi's work of the terpolymerization of ethylene phenyl phosphonite, methyl acrylate, and carbon dioxide via a zwitterionic intermediate,[12] and Hsieh's work of the terpolymerization of tetrahydrofuran, epichlorohydrin, and phthalic anhydride.[13] During the course of our research on the ring-opening polymerization of the above cyclobutane adducts, we have found that the alternating copolymerization of the cyclobutane adduct **1a** of tetracyanoethylene (TCNE) and vinyl ether (VE) with oxirane via a zwitterionic intermediate permits the production of unprecedented 1:1:1 periodic terpolymer of TCNE, VE, and oxirane.[14] This alternating copolymerization is expected to be a versatile attractive route to 1:1:1 periodic terpolymers by using a variety of donor olefins, acceptor olefins, and the third nucleophilic or electrophilic monomers.

Accordingly, the copolymerization of another cyclobutane adduct **1b** of dimethyl dicyanoethylenedicarboxylate (DDED) and VE with oxirane was attempted. However, the polymerization did not occur even at 80 °C. This seems to be because **1b** has the lower ring-opening reactivity compared to **1a**, as shown in the homopolymerization behavior of **1b**.[11f] More nucleophilic comonomers than oxiranes would be required for the spontaneous copolymerization of **1b**. In this paper we report the spontaneous copolymerization of **1b** with 2-oxazolines (**2**) for the synthesis of unprecedented 1:1:1 periodic terpolymers of DDED, VE, and **2**. The copolymerization of more reactive **1a** with **2** is also studied to compare with the copolymerization of **1b** with **2** or of **1a** with oxiranes. On the basis of copolymerization behaviors and the isolation of derivatives of polymerization intermediates, whether zwitterionic intermediates are responsible for these spontaneous copolymerizations are discussed, respectively.



1a



1b

RESULTS AND DISCUSSION

Polymerization Conditions of 1b with 2

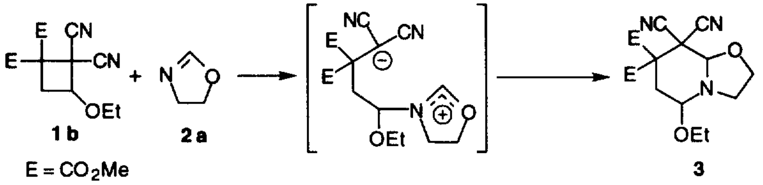
The spontaneous reactions of **1b** with a variety of 2-oxazolines (**2**) were carried out in CH_3CN at ambient temperature for 48 h (Table 1). The substituent at the 2-position of **2** strongly affected the reaction. The methyl- (**2b**) and ethyl-substituted oxazoline (**2c**) resulted in polymer, whereas the phenyl-substituted one **2d** did not react with **1b**, and **2d** and **1b** were recovered. The reaction of unsubstituted **2a** with **1b** proceeded; however not polymer but bicyclo compound **3** was obtained. This product would be formed by an intramolecular reaction of a zwitterion intermediate generated from **1b** and **2a** (Scheme 1). The production of **3** implies that zwitterionic intermediates are also responsible for the copolymerizations of **1b** with **2b** or **2c**. The polymer obtained from **1b** and **2b** was not soluble in diethyl ether and not in water, either, although the homopolymer of **1b** was soluble in

Table 1. Spontaneous Copolymerization of **1b** with **2**[a]

2	yield, %[b]	M_n[c]	M_w/M_n[c]
2a	0[d]		
2b	67	5000	1.39
2c	19	5900	1.29
2d	0[e]		

[a] Polymerization was carried out in CH_3CN ($[\mathbf{1b}]_0 = [\mathbf{2}]_0 = 1$ M) at room temperature for 48 h. [b] Insoluble in Et_2O. [c] Estimated by GPC based on polystyrene standards. [d] Bicyclo compound **3** was obtained in 45% yield (see, Scheme 1). [e] No reaction.

diethyl ether and that of **2b** was soluble in water. Therefore, the polymer obtained from **1b** and **2b** would be a copolymer.



Scheme 1

The copolymerizations of **1b** with equimolar **2b** were carried out under various conditions. The reaction solvent was found to affect the copolymer composition (Table 2). When polymerizations were carried out in most of the aprotic polar solvents including CH_3CN, which was the most suitable solvent for the spontaneous alternating copolymerization of **1a** with oxiranes,[14] copolymers rich in **1b** were obtained. However, only the reaction in CH_3NO_2 yielded 1:1 copolymer. Polymerization in CH_3NO_2 was then carried out at 0-100 °C (Table 3). Polymerization took place even at 0 °C to yield similar molecular weight polymer compared to polymerization at 25 °C, although the polymer yield decreased. Polymerization behavior at 40 °C was not essentially different from that at 25 °C. It seemed at first sight strange that the units of **1b** in the copolymer increased at 60 °C and decreased at 100 °C. In polymerization at 100 °C, the adduct **4** of methanol to **1b** was isolated in 4% yield besides polymer (Scheme 2). The methoxy group of **4** was assumed to be derived from the methoxycarbonyl group via the anionic chain transfer reaction described in the previous paper.[11f] Accordingly, increase in temperature would cause the anionic homopolymerization of **1b** to afford the copolymer rich in **1b**, but at 100 °C the anionic chain transfer reaction in the homopolymerization of **1b** might be also accelerated to yield **4** and decrease **1b**, resulting in the copolymer rich in **2b**.

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

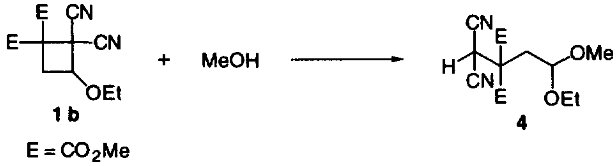
solvent[b]	yield, %[c]	M_n[d]	M_w/M_n[d]	polymer content[e] **1b** : **2b**
THF	10	4200	1.27	77 : 23
CH_3CN	67	5000	1.39	61 : 39
CH_3NO_2	62	5400	1.24	52 : 48
DMF	70	5500	1.29	65 : 35
DMAc	65	5500	1.28	69 : 31
DMSO	56	5800	1.28	57 : 43
NMP[f]	67	5800	1.29	55 : 45
HMPA	55	5300	1.24	71 : 29

[a] Polymerization was carried out at room temperature for 48 h. [b] $[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = 1$ M. [c] Insoluble in Et_2O. [d] Estimated by GPC based on polystyrene standards. [e] Determined by ^1H NMR. [f] *N*-Methyl-2-pyrrolidone.

Table 3. Effect of Polymerization Temperature on Copolymerization of **1b** with **2b**[a]

temp, °C	yield, %[b]	M_n[c]	M_w/M_n[c]	polymer content[d] **1b** : **2b**
0	20	5400	1.16	49 : 51
25	62	5600	1.24	52 : 48
40	69	5800	1.25	53 : 47
60	68	6900	1.31	60 : 40
100	64	7100	1.44	42 : 58

[a] Polymerization was carried out in CH_3NO_2 ($[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = 1$ M) at room temperature for 48 h. [b] Insoluble in Et_2O. [c] Estimated by GPC based on polystyrene standards. [d] Determined by ^1H NMR.



Scheme 2

Copolymerization Behavior and Mechanism of ***1b*** *with* ***2b***

To propose a mechanism for the spontaneous copolymerization of **1b** with **2b**, polymerization behavior with time or feed ratio was studied. Figure 1 shows the conversions of **1b** and **2b** against time in polymerization at room temperature in CH_3NO_2. Two monomers **1b** and **2b** were consumed at almost the same rate. If **1b** and

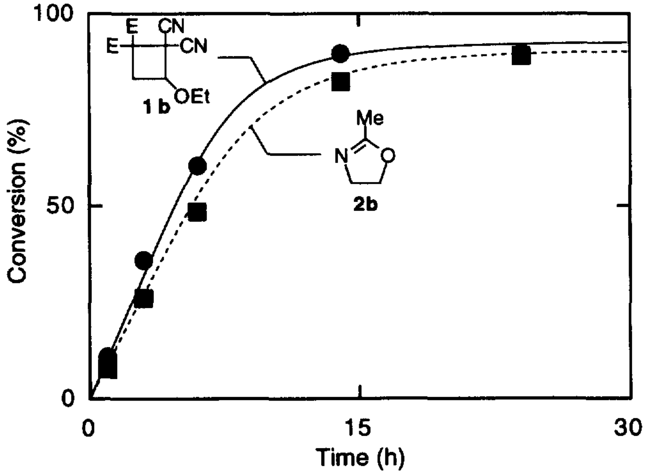


Fig. 1. Time-conversion curves for the copolymerization of **1b** with **2b** in CH_3NO_2 at 25 °C: $[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = 1.0$ M.

Table 4. Spontaneous Copolymerization of **1b** with **2b**[a]

time, h	yield, %[b]	M_n[c]	M_w/M_n[c]	polymer content[d] **1b** : **2b**
1	0			
3	8	3400	1.21	48 : 52
6	20	3600	1.18	50 : 50
12	33	3500	1.18	50 : 50
24	45	3800	1.19	50 : 50
48	56	4400	1.18	49 : 51
72	53	4800	1.19	53 : 47
120	64	5100	1.18	53 : 47

[a] Polymerization was carried out in CH_3NO_2 ($[\mathbf{1b}]_0 = [\mathbf{2b}]_0 = 1$ M) at room temperature. [b] Insoluble in Et_2O. [c] Estimated by GPC based on polystyrene standards. [d] Determined by ^{1}H NMR.

2b were converted to only polymer without other side reaction products, the consumption of **1b** and **2b** at the same rate implies that alternating copolymerization could take place. Table 4 shows the polymer yields, molecular weights, and compositions with reaction time. The yields and molecular weights increased with time, whereas the compositions of copolymers remained almost constant at 1:1 irrespective time. These results also imply that 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 **1b** and **2b** with the ratio 1:1 at any time.

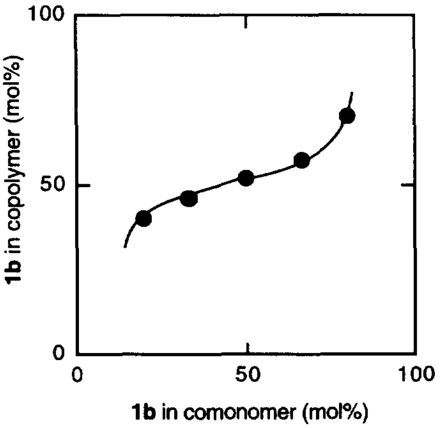


Fig. 2. Effects of monomer feed ratio on the polymer composition in the copolymerization of **1b** with **2b** at 25 °C in CH_3NO_2 for 3 h: $[\mathbf{1b}+\mathbf{2b}]_0 = 2$ M.

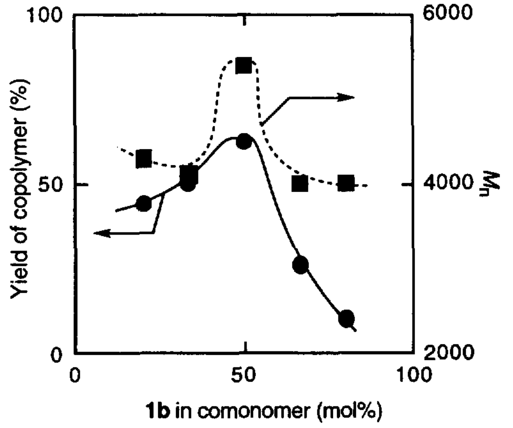
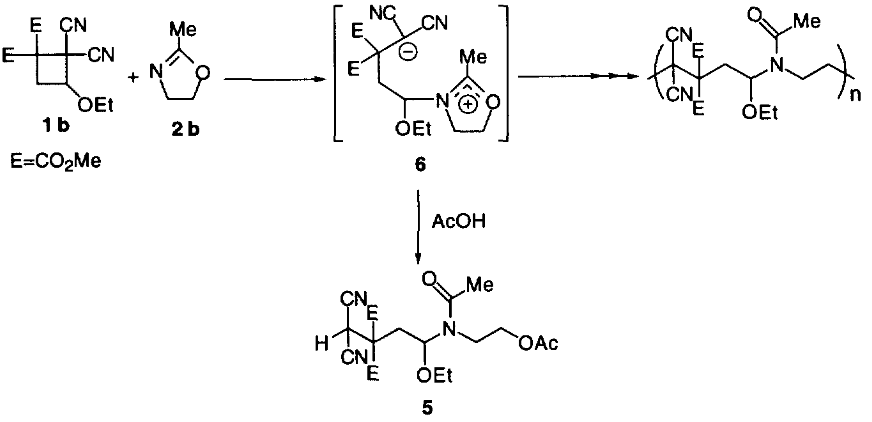


Fig. 3. Effects of monomer feed ratio on the polymer yield and M_n in the copolymerization of **1b** with **2b** at 25 °C in CH_3NO_2 for 24 h: $[\mathbf{1b}+\mathbf{2b}]_0 = 2$ M.

Figure 2 shows the compositions of copolymers when reactions were carried out at various feed ratios of **1b** to **2b**, and Figure 3 the polymer yields and molecular weights. The horizontal-like curve at the 50 mol% of **1b** in copolymer in Figure 2 indicates strong tendency of alternating copolymerization. The polymer yields and molecular weights became maximum at the 1:1 feed ratio (Figure 3), implying that polymerization took place most effectively at the 1:1 feed ratio and could involve a polymerization intermediate generated from equimolar **1b** and **2b**.

Furthermore, the reaction mixture was quenched with acetic acid after 2 h to yield acetate **5** composed of equimolar **1b** and **2b** in 28% yield, as well as the adduct of acetic acid to **1b**. Since the conversion of **1b** and **2b** were about 30% for 2 h in Figure 1, **5** was seemed to be formed almost quantitatively. The isolation of **5** confirmed the involvement of zwitterionic intermediate **6** generated from **1b** and **2b** as a key intermediate in the copolymerization. The ^{13}C NMR spectra of **5** and copolymer are shown in Figure 4 with assignments for various signals; each signal was assigned on the basis of the ^{1}H-^{1}H and ^{13}C-^{1}H COSY, ^{13}C DEPTD, and HMBC NMR spectra. Each carbon of **5** has two kinds of signals in the spectrum because of the *N,N*-dialkylamide moiety in **5**. The spectrum of copolymer was in fair agreement with that of **5** except the acetoxy group. Consequently, the copolymer has alternating structure as shown in Scheme 3, and the following polymerization mechanism may be proposed. Polymerization is initiated by the ring-opening reaction of **1b** with **2b** at the ethoxy-substituted C-3 to generate zwitterion **6**. Propagation proceeds by the reaction of **6** with itself and the polycombination of macrozwitterion of the type **6** in a step polymerization manner.



Scheme 3

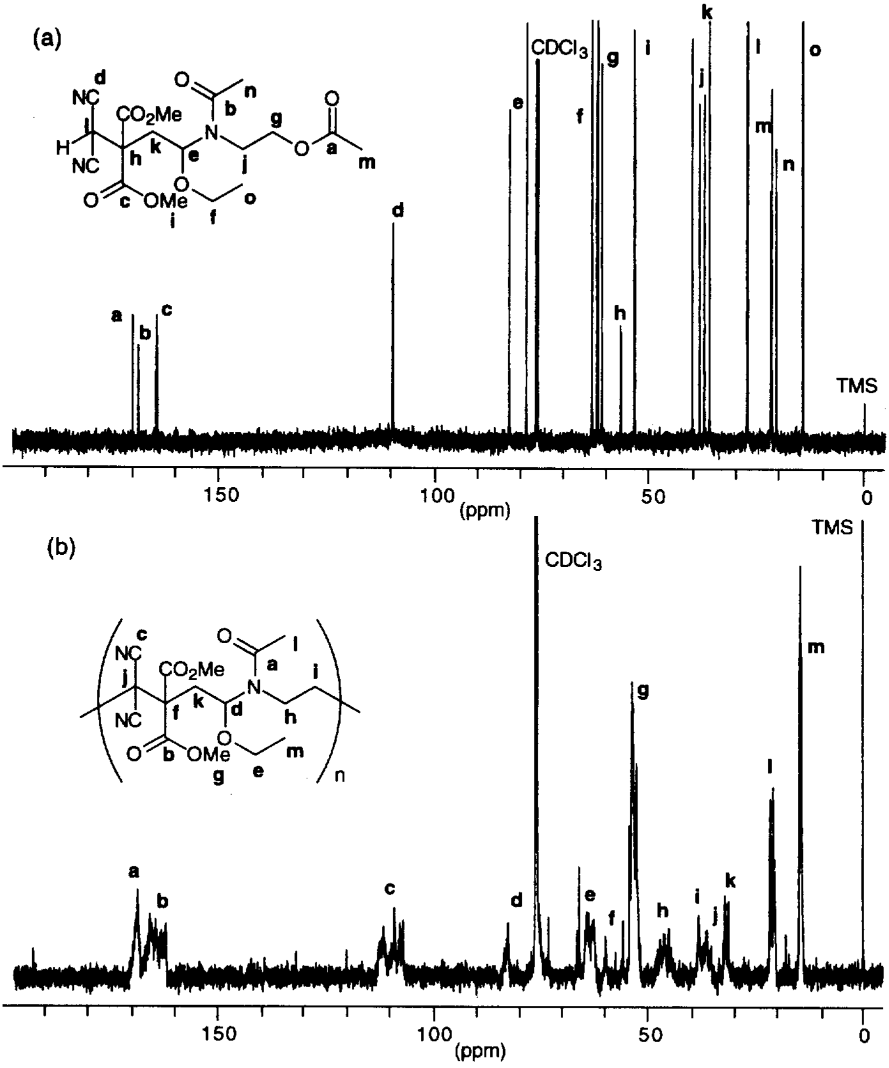


Fig. 4. ¹H NMR spectra in $CDCl_3$ at 28 °C: (a) acetic acid-adduct **5** of zwitterion generated from **1b** and **2b**. (b) copolymer of **1b** and **2b**.

Copolymerization Behavior and Mechanism of 1a with 2b

The spontaneous copolymerization of **2b** with more reactive cyclobutane **1a** was carried out under similar conditions.[15] Figure 5 shows the conversions of **1a** and **2b** with time in polymerization at room temperature in CD_3NO_2. Cyclobutane **1a** was consumed faster than **2b**, contrary to the polymerization behavior of **1b** with **2b**. The polymer yields, molecular weights, and compositions with time are shown in Table 5. The yields and molecular weights increased with time. The **1a** units in copolymer gradually decreased from about 70 to 60 mol% with time; 1:1 copolymer was not obtained. Figure 6 shows the compositions of copolymers when reactions were carried out at various feed ratios of **1a** to **2b**. The horizontal curve at the 50 mol% of **1a** in copolymer was not observed, indicating lack of tendency of alternating copolymerization.

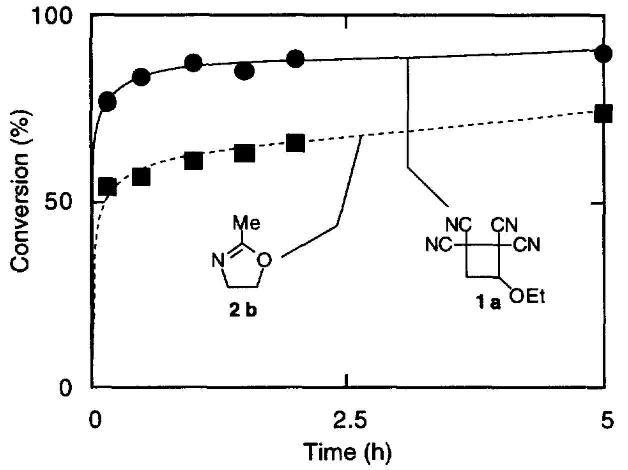


Fig. 5. Time-conversion curves for the copolymerization of **1a** with **2b** in CD_3NO_2 at 25 °C: $[\mathbf{1a}]_0 = [\mathbf{2b}]_0 = 1.0$ M.

Reaction intermediates were attempted to be trapped with acetic acid, but the acetic acid-adducts of zwitterionic intermediates like **5** were not isolated. Reaction was then carried out in CD_3NO_2, and the intermediates were directly observed by ^1H NMR. Figure 7 is the spectrum of the reaction mixture for 10 min. Besides the signals of **1a** and **2b**, the signals of oxazolinium were observed; especially the signal of the methyl protons of oxazolinium appeared at δ 2.8 ppm without overlapping of other signals. From the intensities of these signals, Figure 8 shows the changes of the concentrations of **1a**, **2b**, and oxazolinium in the reaction mixture with time. The concentration of oxazolinium rapidly increased for 10 min, as **1a** and **2b** were rapidly consumed; **1a** was consumed faster than **2b**. After 10 min, the concentration of oxazolinium decreased to almost 0 in 80 min, whereas **1a** and **2b** were gradually consumed.

Table 5. Spontaneous Copolymerization of **1a** with **2b**[a]

time, h	yield, %[b]	M_n[c]	polymer content[d] **1a** : **2b**
1	26	4700	69 : 31
3	76	4900	66 : 34
6	79	5000	65 : 35
12	73	5100	64 : 36
24	81	5300	61 : 39
48	84	5400	59 : 41
96	90	5400	57 : 43

[a] Polymerization was carried out in CH_3NO_2 ($[\mathbf{1a}]_0 = [\mathbf{2b}]_0 = 1$ M) at room temperature. [b] Insoluble in Et_2O. [c] Estimated by GPC based on polystyrene standards. [d] Determined by ^1H NMR.

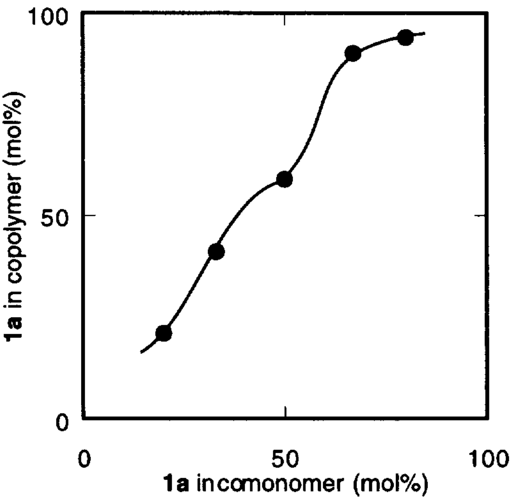


Fig. 6. Effects of monomer feed ratio on the polymer composition in the copolymerization of **1a** with **2b** at 25 °C in CH_3NO_2 for 48 h: $[\mathbf{1a}+\mathbf{2b}]_0 = 2$ M.

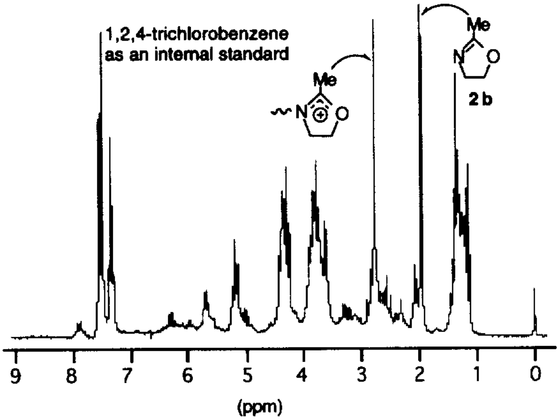


Fig. 7. ^{1}H NMR spectrum of the reaction mixture of **1a** with **2b** in CD_3NO_2 at 25 °C after 10 min.

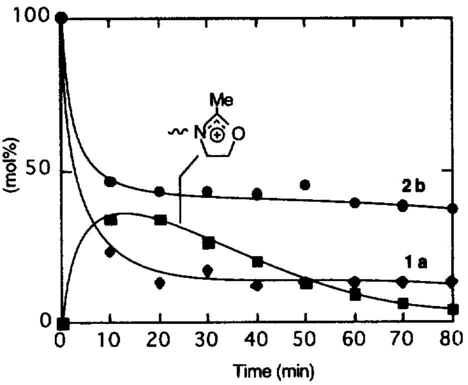
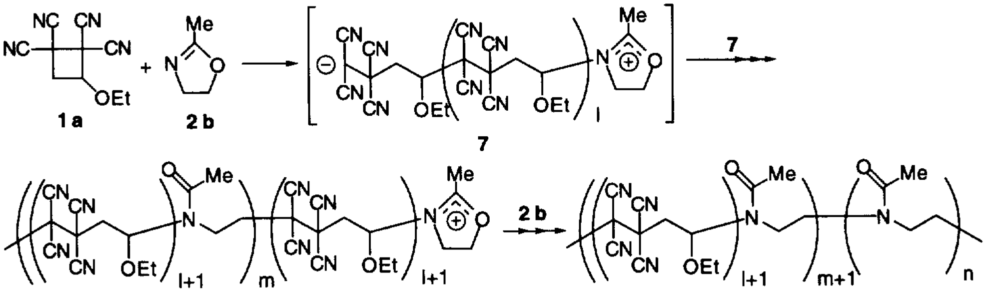


Fig. 8. Course of polymerization of **1a** with **2b** in CD_3NO_2 at 25 °C: $[\mathbf{1a}]_0 = [\mathbf{2b}]_0 = 1.0$ M.

On the basis of the above polymerization behavior, the reaction of **1a** with **2b** can be explained by the following mechanism. The first step is the formation of zwitterionic intermediates **7** consisting of a few molecules of **1a** and a molecule of **2b**, containing the oxazolinium site. The second step is the reaction of **7** with itself in a step polymerization manner. The third step is the polymerization of residual **2b** from the oxazolinium site of macrozwitterion in a chain polymerization manner (Scheme 4).



Scheme 4

CONCLUSION

Spontaneous copolymerization of the cyclobutane adducts **1** of strong donor olefins and strong acceptor olefins with 2-oxazolines **2** was investigated for the synthesis of unprecedented 1:1:1 periodic terpolymers of the two olefins and **2**. The cyclobutane adduct **1b** of dimethyl dicyanoethylenedicarboxylate (DDED) and vinyl ether (VE) spontaneously reacted with 2-methyloxazoline (**2b**) in CH_3NO_2 at ambient temperature to yield the alternating copolymer of **1b** and **2b**, which is the 1:1:1 periodic terpolymer of DDED, VE, and **2b**. On the basis of polymerization behavior and the isolation of the acetic acid-adduct **5** of polymerization intermediate, the zwitterion generated from **1b** and **2b** was responsible for initiation and propagation in the copolymerization. More reactive cyclobutane adduct **1a** of tetracyanoethylene (TCNE) and VE also spontaneously reacted with **2b** in CH_3NO_2 at ambient temperature. However, not the alternating copolymer of **1a** with **2b** but copolymers with higher **1a** contents were obtained. This is ascribed to the involvement of generation of zwitterions composed of a few molecules of **1a** and a molecule of **2b**. Further work on the spontaneous copolymerization of the cyclobutane adducts of strong donor and acceptor olefins with nucleophilic or electrophilic monomers is now in progress.

EXPERIMENTAL

Measurements

^{1}H-NMR spectra were obtained on a JEOL FX-200 and α-500 operating in the pulsed Fourier-transfer (FT) modes, using tetramethylsilane (TMS) as an internal standard. ^{13}C-NMR spectra were obtained on a JEOL FX-200 and α-500 operating in the pulsed FT modes, using TMS as an internal standard. IR spectra were recorded on a HITACHI 270-30. Elemental analysis was performed on a Yanaco CHNcorder MT-2. The number-average molecular weights (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 bicyclo compound **3** and the acetic acid-adduct **5** of zwitterion was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform) using JA1GEL-1H and 2H columns.

Materials

1,1,2,2-tetracyano-3-ethoxycyclobutane (**1a**) was prepared from tetracyanoethylene (TCNE) and ethyl vinyl ether according to the reported procedure.[16] Dimethyl 2,2-dicyano-3-ethoxycyclobutane-1,1-dicarboxylate (**1b**) was prepared from dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate (DDED)[17] and ethyl vinyl ether according to the reported procedure.[17] Unsubstituted 2-oxazoline (**2a**) was prepared by the reaction of *N*-(2-chloroethyl)formamide with 50% KOH according to the reported procedure.[18] 2-Methyl-, ethyl-, and phenyl-2-oxazoline (**2b**, **c**, **d**) were purified by distillation over CaH_2. Acetonitrile, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA) were distilled over CaH_2. Nitromethane was dried overnight with $CaCl_2$ and then distilled. Tetrahydrofuran (THF) was distilled over sodium just before use.

Reaction of 1b with 2a

Cyclobutane adduct **1b** (0.266 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 **2a** (0.073 g, 1.0 mmol) in distilled CH_3NO_2 (1.0 mL) was added at room temperature via a syringe under dry nitrogen flow. After stirring for 24 h, the reaction mixture was concentrated in vacuo to give crude bicyclo compound **3** (0.321 g), and 0.300 g of crude **3** was purified by preparative HPLC to yield **3** (0.135 g, 45% yield): mp 82-87 °C; IR (KBr) 2974, 2902, 2254, 1746, 1176, 1104, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.17 (s, 1H), 4.60 (t, J = 2.6 Hz, 1H), 4.06-4.29 (m, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 3.42-3.57 (m, 2H), 3.22-3.40 (m, 2H), 2.77 (dd, J = 2.6 and 14.9 Hz, 1H), 2.44 (dd, J = 2.6 and 14.9 Hz, 1H), 1.13 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.9 and 166.2, 112.0 and 112.4, 85.4, 82.9, 66.8, 64.3, 57.1, 53.6 and 54.3, 46.6, 43.3, 32.3, 15.1. Anal. Calcd for $C_{15}H_{19}N_3O_6$: C, 53.41; H, 5.68; N, 12.46. Found: C, 52.98; H, 5.48; N, 12.51.

Spontaneous copolymerization of 1b with 2b

Cyclobutane adduct **1b** (0.266 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 **2b** (0.085 g, 1.0 mmol) in distilled CH_3NO_2 (1 mL) was added at room temperature via a syringe under dry nitrogen flow. After stirring for 48 h, the solution was poured into a large amount of diethyl ether (50 mL). Precipitated polymer was collected and dried in vacuo: IR (KBr) 2984, 2172, 1746, 1648, 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.20-5.70 (br, 1H), 3.00-4.08 (br, 12H), 1.90-2.80 (br, 5H), 0.95-1.40 (br, 3H).

Trap of zwitterion 6 generated from 1b and 2b with acetic acid

Cyclobutane adduct **1b** (0.266 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 **2b** (0.085 g, 1.0 mmol) in distilled CH_3NO_2 (1.0 mL) was added at room temperature via a syringe under dry nitrogen flow. After stirring for 2 h at ambient temperature, a solution of acetic acid (0.120 g, 2.0 mmol) in CH_3NO_2 (0.2 mL) was added and stirred for 160 h. The reaction mixture was concentrated in vacuo and the residue was purified by preparative HPLC to yield the acetic acid-adduct of **1b** (0.063 g, 28% yield) and the acetic acid-adduct **5** of zwitterion **6** (0.075 g, 27% yield). Acetic acid-adduct of **1b**: IR (neat) 2932, 2260, 1758; ^1H NMR ($CDCl_3$) δ 5.98 (dd, J = 3.6 and 5.9 Hz, 1H), 4.84 (s, 1H), 3.88 and 3.89 (2s, 6H), 3.45-3.79 (m, 2H), 2.73 (dd, J = 3.6 and 15.4 Hz, 1H), 2.57 (dd, J = 5.9 and 15.4 Hz, 1H), 2.11 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). **5**: IR (neat) 2962, 2254, 1737, 1653, 1119, 1056 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (dd, J = 2.7 and 9.5 Hz, 0.5H), 5.24 (d, J = 7.8 Hz, 0.5H), 4.80 and 4.95 (2s, 1H), 4.16-4.24 (m, 2H), 3.90 and 3.91 (2s, 6H), 3.31-3.64 (m, 4H), 2.32-2.27 (m, 2H), 2.19 (s, 3H), 2.08 and 2.11 (2s, 3H), 1.15-1.24 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 171.9, 170.4 and 170.5 and 170.6, 166.0 and 166.2 and 166.4, 110.7 and 110.9, 79.5 and 83.5, 63. 0 and 64.2, 61.8 and 62.7, 57.2 and 57.5, 54.0 and 54.2 and 54.3, 38.8 and 40.5, 36.4 and 37.6, 27.3 and 27.6, 21.7 and 22.0, 20.6 and 20.7, 14.3 and 14.5.

Spontaneous copolymerization of 1a with 2b

Cyclobutane adduct **1a** (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 **2b** (0.085 g, 1.0 mmol) in distilled CH_3NO_2 (1 mL) was added at room temperature via a syringe under dry nitrogen flow. After stirring for 48 h, the solution was poured into a large amount of diethyl ether (50 mL). Precipitated polymer was collected and dried in vacuo:

IR (KBr) 2974, 2194, 1632, 1611, 1422, 1374, 1335, 1245, 1095 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 4.78-5.00 (br), 4.04-4.32 (br), 3.00-3.90 (br), 1.89-2.11 (br), 0.95-1.40 (br).

*^{1}H NMR analysis of copolymerization of **1a** with **2b***

Cyclobutane adduct **1a** (0.098 g, 0.5 mmol) was placed in a round bottomed-flask equipped with a three-way stopcock and purged with argon. A solution of equimolar **2b** (0.042 g, 0.5 mmol) and 1,2,4-trichlorobenzene (0.089 g, 0.05 mmol) as an internal standard in CD_3NO_2 (0.5 mL) was added at room temperature via a syringe under dry nitrogen flow. After the mixture became homogenous, it was injected into the NMR tube under dry nitrogen flow. Spectra were measured for each 10 min, and the amounts of **1a**, **2b**, and oxazolinium were calculated by their signal intensity ratios to that of the internal standard.

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