

Electronic supplementary information for:

Alternating cationic copolymerizations of vinyl ethers and sequence-programmed cyclic trimer consisting of one vinyl ether and two aldehydes for ABCC-type periodic terpolymers

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Materials

CEVE (TCI; >97.0%), pMeSt (Sigma-Aldrich; 96.0%), IBVE (TCI; >99.0%), and IPVE (Wako; >97.0%) were washed with 10% sodium hydroxide solution and then water and distilled twice over calcium hydride under reduced (CEVE and pMeSt) or atmospheric (IBVE and IPVE) pressure. BzA (Wako; >98.0%), NNE (TCI; > 95.0%), and DPE (TCI; >98.0%) were distilled over calcium hydride twice under reduced pressure before use. EA was distilled twice over calcium hydride. 1,4-DO (Nacalai Tesque; >99.5%) and THF (Wako; >99.5%) were distilled over calcium hydride and then lithium aluminum hydride. The adduct of IBVE with acetic acid (IBEA) was prepared from the addition reaction of IBVE and acetic acid. TiCl₄ (Sigma-Aldrich; 1.0 M solution in toluene), SnCl₄ (Sigma-Aldrich; 1.0 M solution in heptane), EtAlCl₂ (Wako, 1.0 M solution in hexane), and Bi(OTf)₃ (Sigma-Aldrich) were used as received. GaCl₃ (Strem; ≥99.99%) was used without further purification after preparing stock solutions in *n*-hexane. Toluene (Wako; super-dehydrated), dichloromethane (Wako; super-dehydrated), and *n*-hexane (Wako; >96.0%) were dried by passage through solvent purification columns (Glass Contour). Hydrochloric acid (Nacalai Tesque) and sodium hydroxide (Nacalai Tesque) for acid methanolysis were used as received.

Characterization

The MWD of the polymers was measured by GPC in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH_{HR}-M × 2 (exclusive limit molecular weight = 4×10^6 ; bead size = 5 μm; column size = 7.8 mm I.D. × 300 mm); flow rate = 1.0 mL min⁻¹] connected to a JASCO PU-4580 pump, a Tosoh CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average molecular weight (M_n) and the polydispersity ratio (weight-average molecular weight/number-average molecular weight [M_w/M_n]) were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; $M_n = 5.0 \times 10^2$ — 1.09×10^6 , $M_w/M_n \leq 1.1$). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ¹H and 125.77 MHz for ¹³C) spectrometer. ESI-MS spectra were recorded using an LTQ orbitrap XL spectrometer (Thermo Scientific).

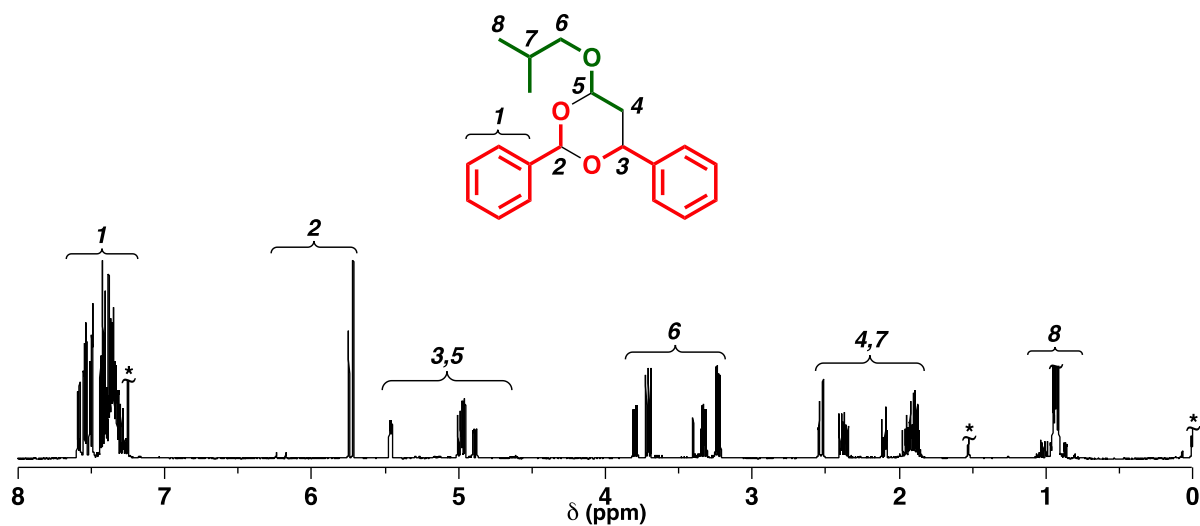


Figure S1. ^1H NMR spectrum of the product obtained in the cyclotrimerization of IBVE and BzA (entry 1 in Table 1; in CDCl_3 at 30°C ; * CHCl_3 , water, or TMS).

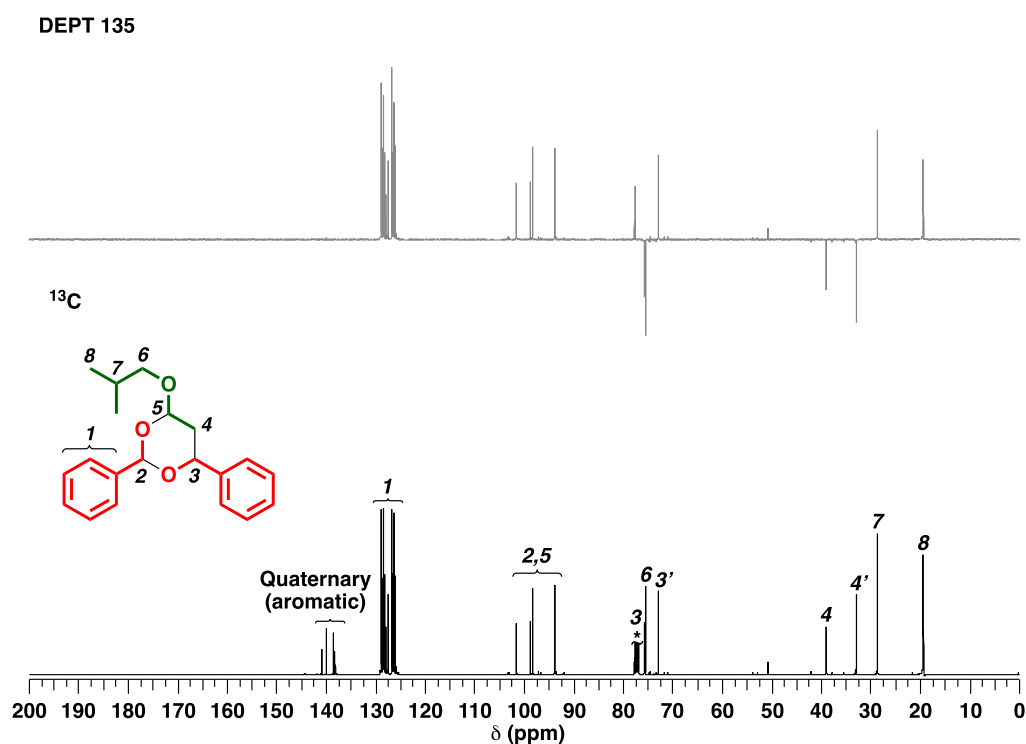


Figure S2. ^{13}C and DEPT 135 NMR spectra of the product obtained in the cyclotrimerization of IBVE and BzA [entry 1 in Table 1; the same sample as that for ^1H NMR analysis (Figure S1); in CDCl_3 at 30°C ; * CDCl_3].

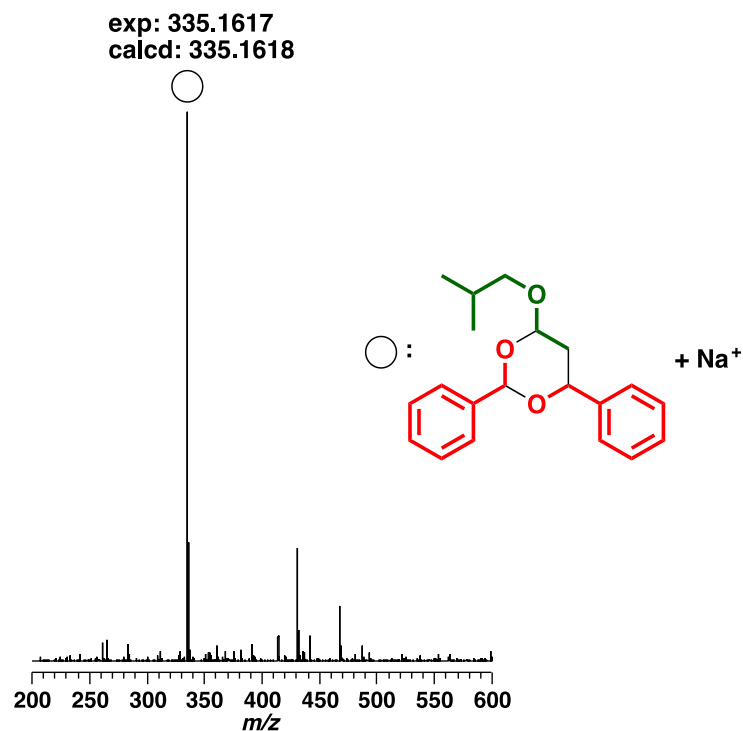


Figure S3. ESI-MS spectrum of the product obtained in the cyclotrimerization of IBVE and BzA [entry 1 in Table 1; the same sample as that for ¹H NMR analysis (Figures S1)].

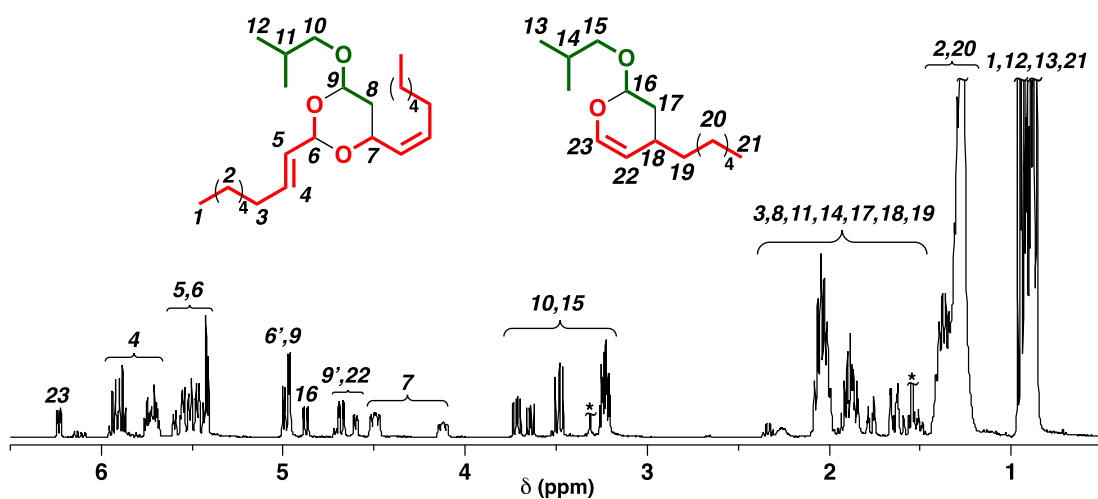


Figure S4. ¹H NMR spectrum of the product obtained by the cyclotrimerization of IBVE and NNE (entry 2 in Table 1; in CDCl₃ at 30 °C; * water or methanol).

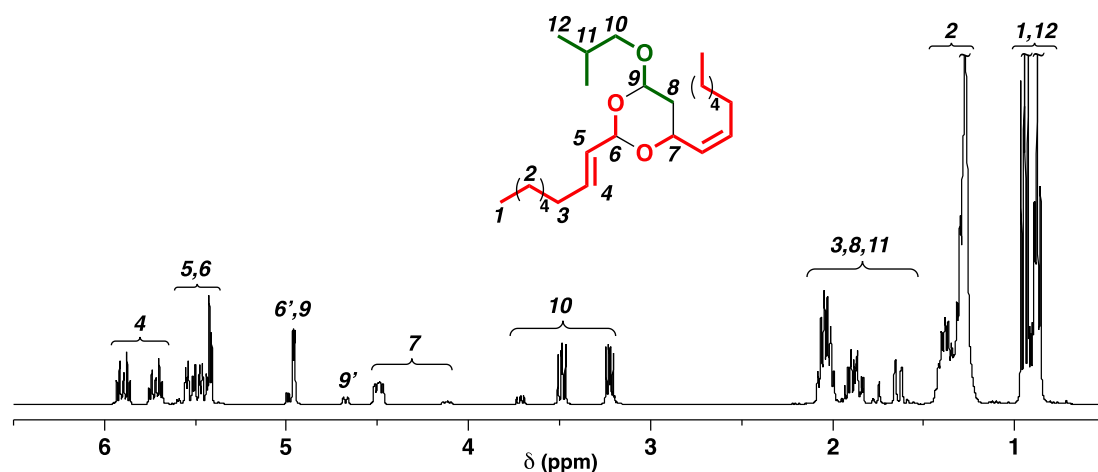


Figure S5. ^1H NMR spectrum of the cyclic trimer consisting of IBVE and NNE separated by silica gel column chromatography ($[\text{IBVE}]_0 = 0.50 \text{ M}$, $[\text{NNE}]_0 = 0.99 \text{ M}$, $[\text{IBVE}]_{\text{add}} = 0.50 \text{ M}$, $[\text{EtAlCl}_2]_0 = 50 \text{ mM}$, $[\text{THF}] = 1.0 \text{ M}$, in dichloromethane at $0 \text{ }^\circ\text{C}$; in CDCl_3 at $30 \text{ }^\circ\text{C}$).

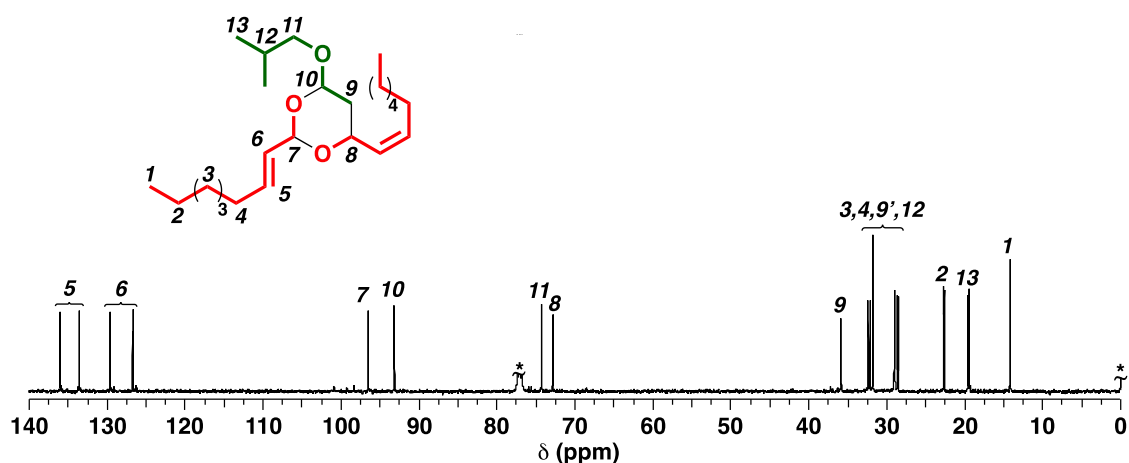


Figure S6. ^{13}C NMR spectrum of the cyclic trimer consisting of IBVE and NNE separated by silica gel column chromatography [the same sample as that for ^1H NMR analysis (Figure S5); in CDCl_3 at $30 \text{ }^\circ\text{C}$; * CDCl_3 or TMS].

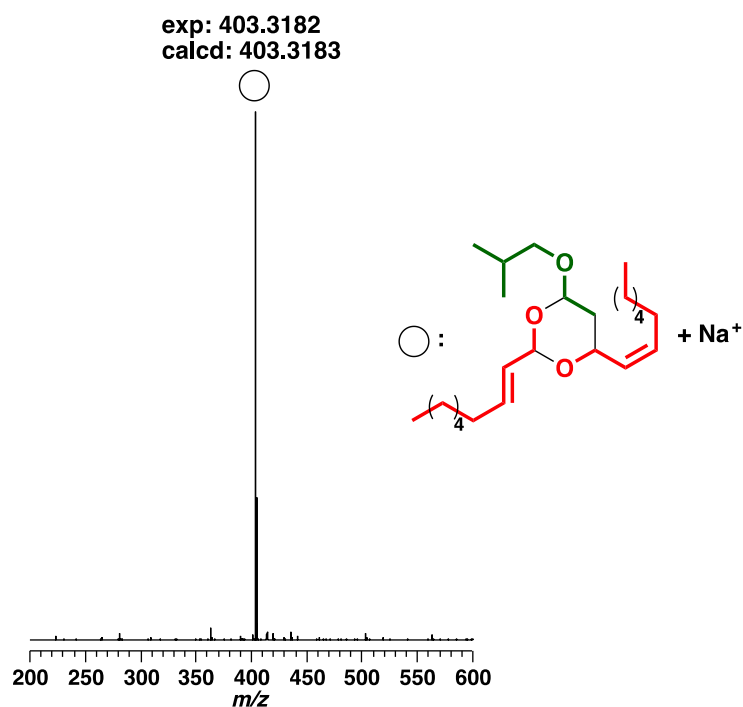


Figure S7. ESI-MS spectrum of the cyclic trimer consisting of IBVE and NNE [a different sample as that for ¹H NMR analysis (Figure S5)].

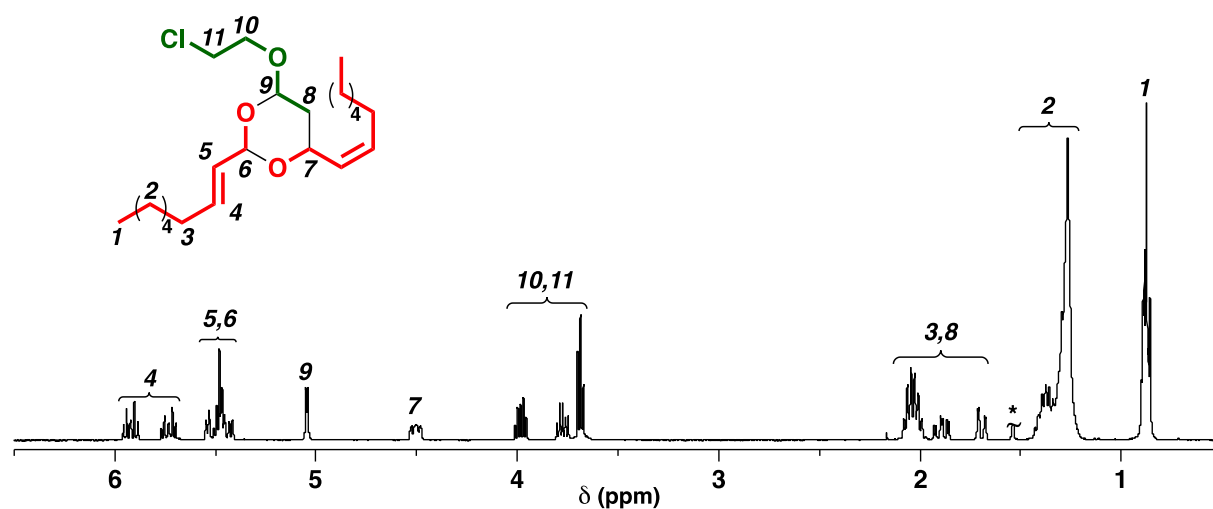


Figure S8. ¹H NMR spectrum of the cyclic trimer consisting of CEVE and NNE separated by silica gel column chromatography ([CEVE]₀ = 0.49 M, [NNE]₀ = 1.0 M, [CEVE]_{add} = 0.49 M, [EtAlCl₂]₀ = 50 mM, [THF] = 1.0 M, in dichloromethane at 0 °C; in CDCl₃ at 30 °C; * water).

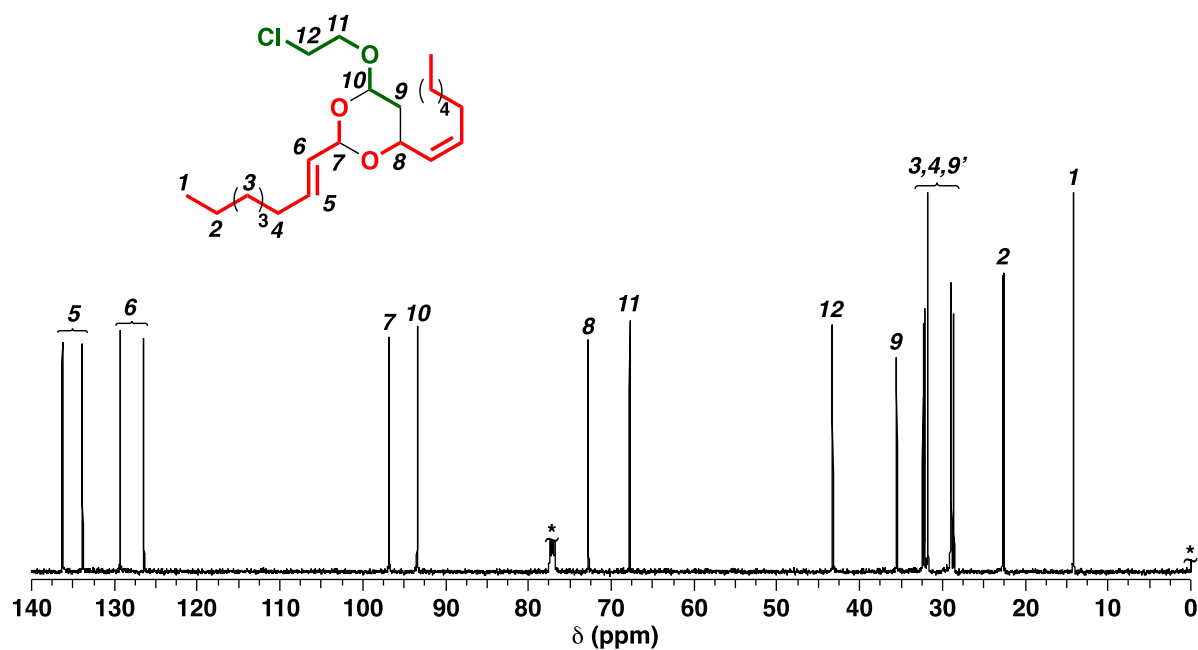


Figure S9. ^{13}C NMR spectrum of the cyclic trimer consisting of CEVE and NNE separated by silica gel column chromatography [the same sample as that for ^1H NMR analysis (Figure S8); in CDCl_3 at 30°C ; * CDCl_3 or TMS].

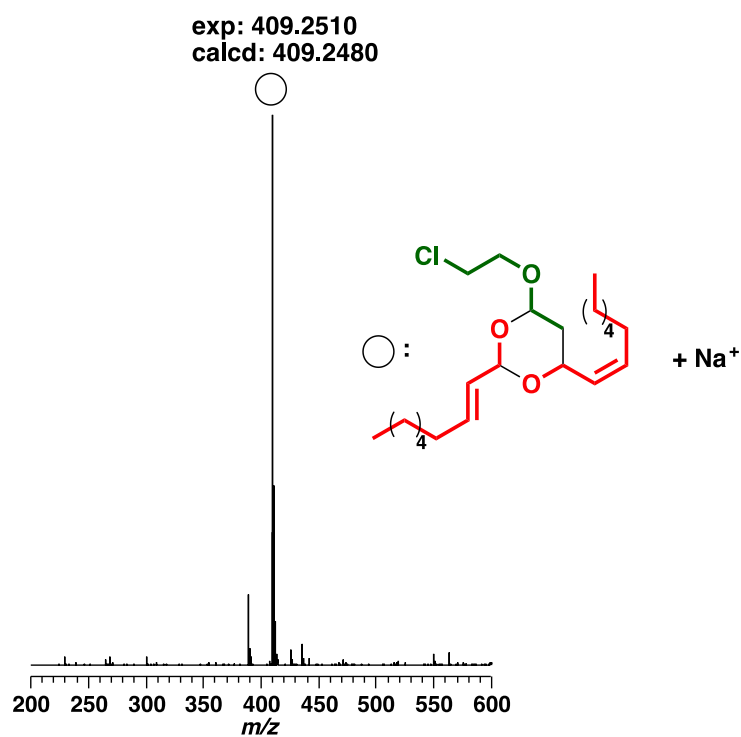


Figure S10. ESI-MS spectrum of the cyclic trimer consisting of CEVE and NNE [a different sample as that for ^1H NMR analysis (Figure S8)].

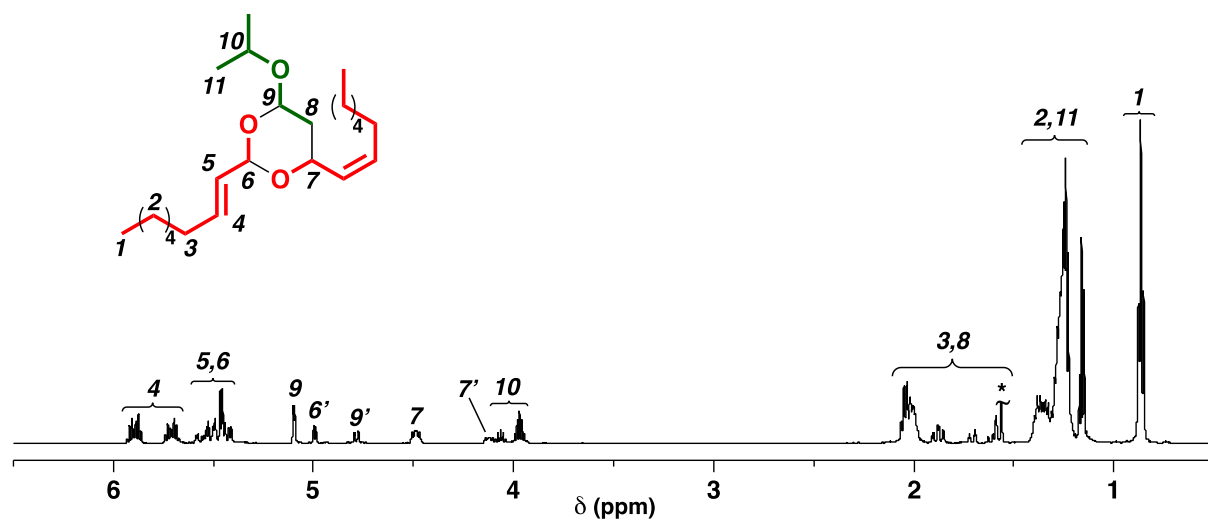


Figure S11. ^1H NMR spectrum of the cyclic trimer consisting of IPVE and NNE separated by silica gel column chromatography ($[\text{IPVE}]_0 = 0.52 \text{ M}$, $[\text{NNE}]_0 = 0.85 \text{ M}$, $[\text{IPVE}]_{\text{add}} = 0.52 \text{ M}$, $[\text{EtAlCl}_2]_0 = 50 \text{ mM}$, $[\text{THF}] = 1.0 \text{ M}$, in dichloromethane at $0 \text{ }^\circ\text{C}$; in CDCl_3 at $30 \text{ }^\circ\text{C}$; * water).

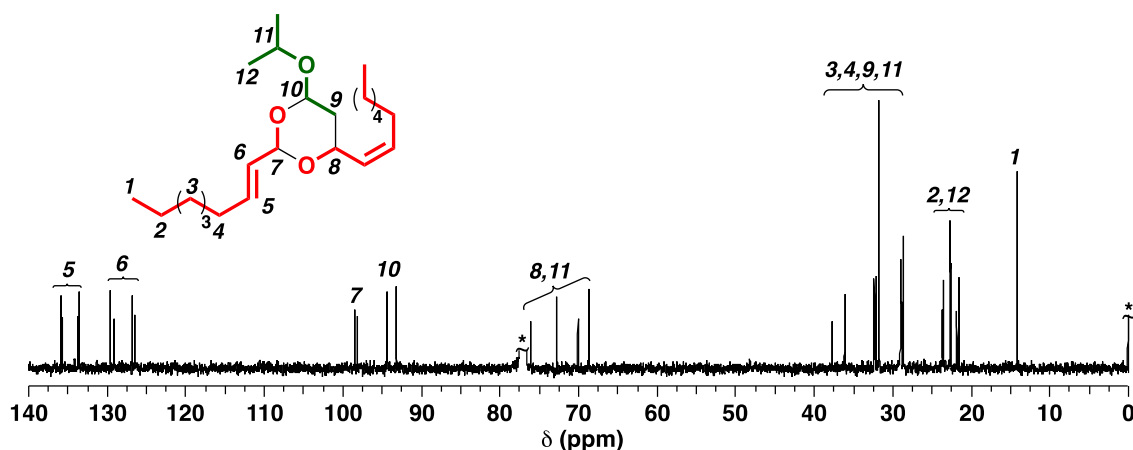


Figure S12. ^{13}C NMR spectrum of the cyclic trimer consisting of IPVE and NNE separated by silica gel column chromatography [the same sample as that for ^1H NMR analysis (Figure S11); in CDCl_3 at $30 \text{ }^\circ\text{C}$; * CDCl_3 or TMS].

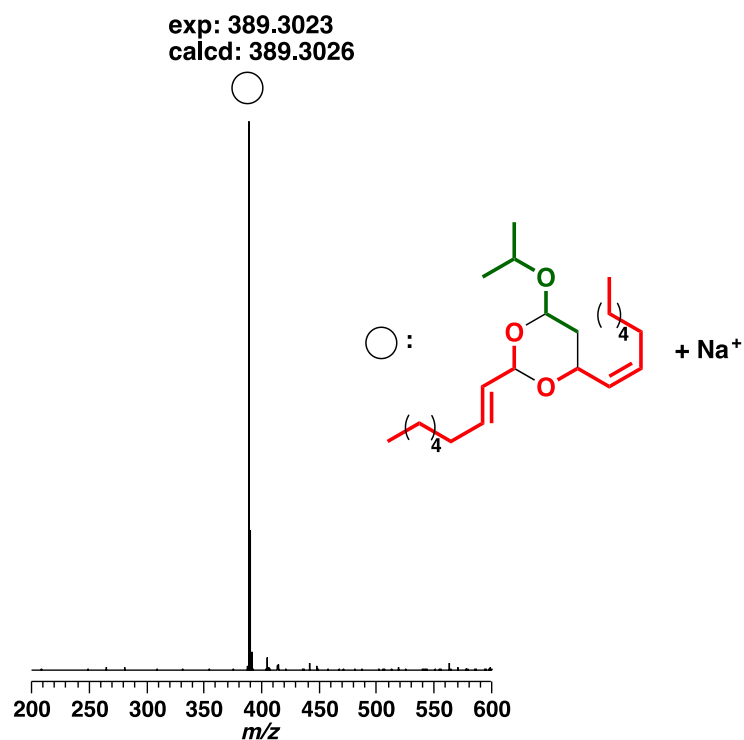


Figure S13. ESI-MS spectrum of the cyclic trimer consisting of IPVE and NNE [a different sample as that for ^1H NMR analysis (Figure S11)].

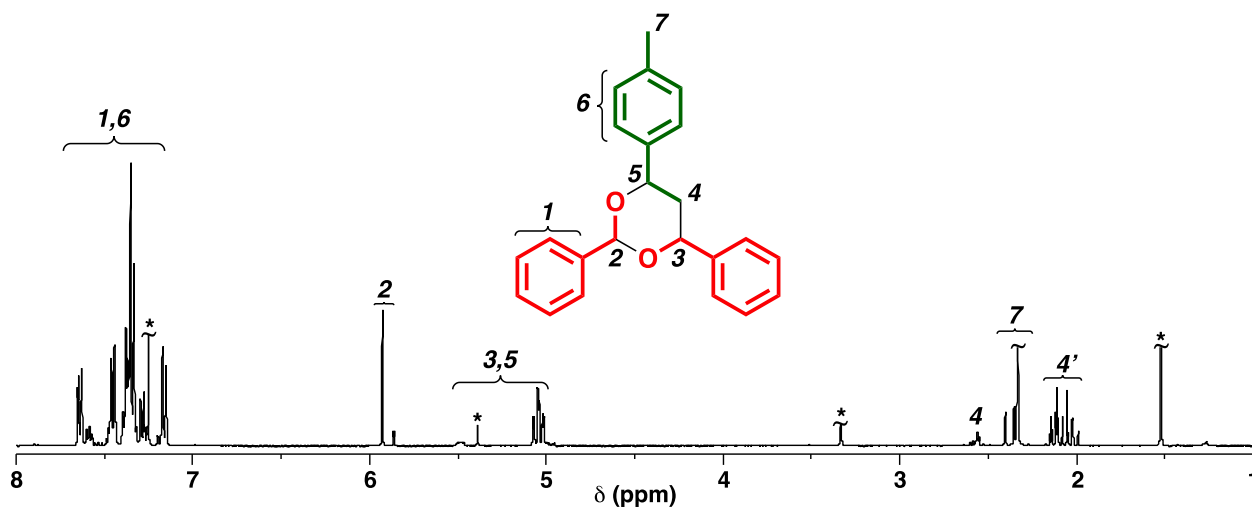


Figure S14. ^1H NMR spectrum of the cyclic trimer consisting of pMeSt and BzA separated by silica gel column chromatography (entry 5 in Table 1; in CDCl_3 at 30 $^\circ\text{C}$; * CDCl_3 , water, or others).

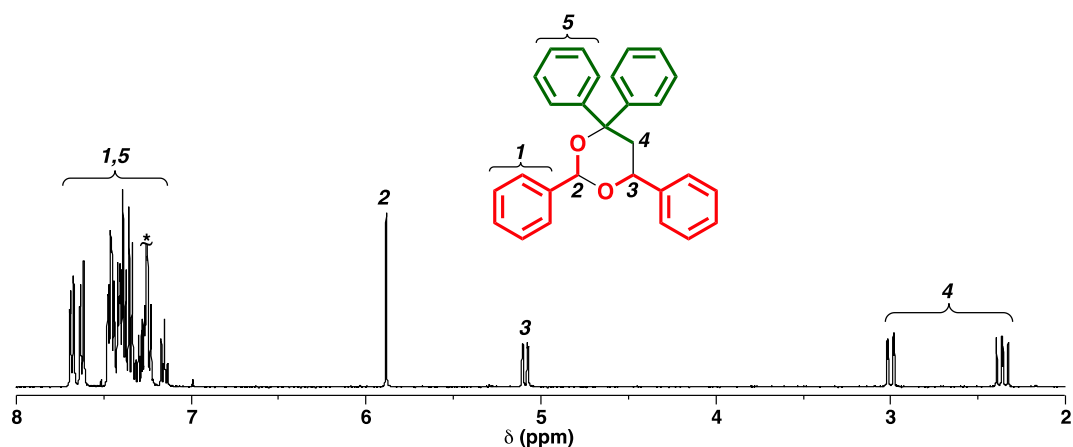


Figure S15. ^1H NMR spectrum of the cyclic trimer consisting of DPE and BzA after purified by reprecipitation in methanol (entry 6 in Table 1; in CDCl_3 at $30\text{ }^\circ\text{C}$; * CHCl_3).

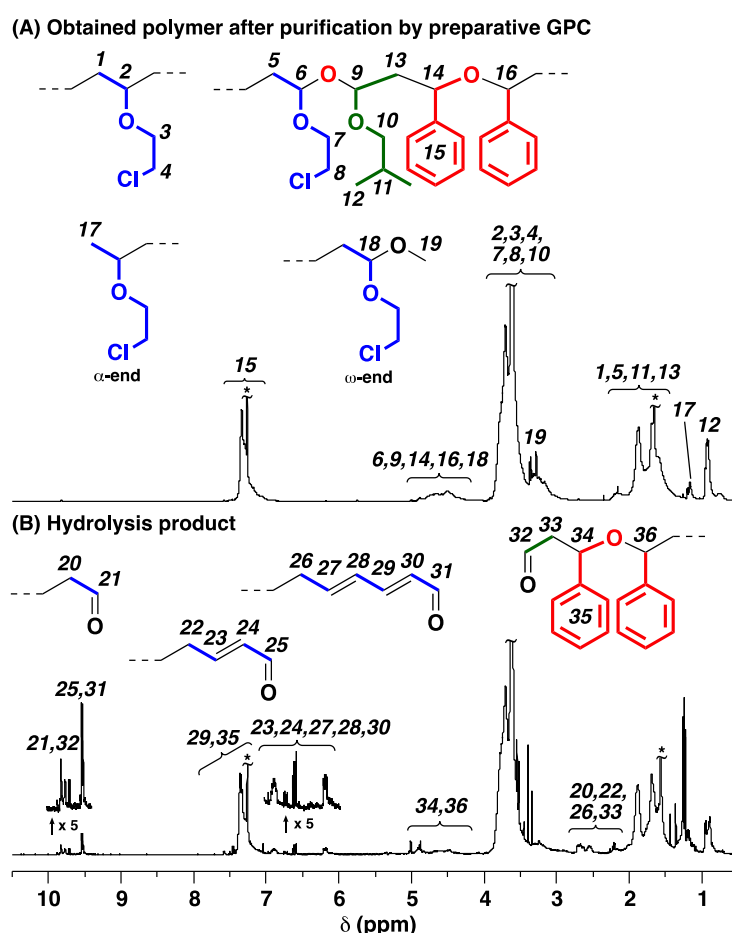


Figure S16. ^1H NMR spectra of (A) the obtained polymer by the cationic copolymerization of CEVE and the cyclic trimer consisting of IBVE and BzA (entry 2 in Table 2) and (B) its acid hydrolysis product [in CDCl_3 at $30\text{ }^\circ\text{C}$; $M_n(\text{GPC}) = 2.2 \times 10^3$, $M_w/M_n(\text{GPC}) = 1.43$; after purification by preparative GPC; * CHCl_3 or water; only ABCC-type monomer sequences were drawn; acid hydrolysis condition: 0.9 M HCl in 1,2-dimethoxyethane at room temperature for 2 h. Other procedures were conducted in similar to that in methanolysis].

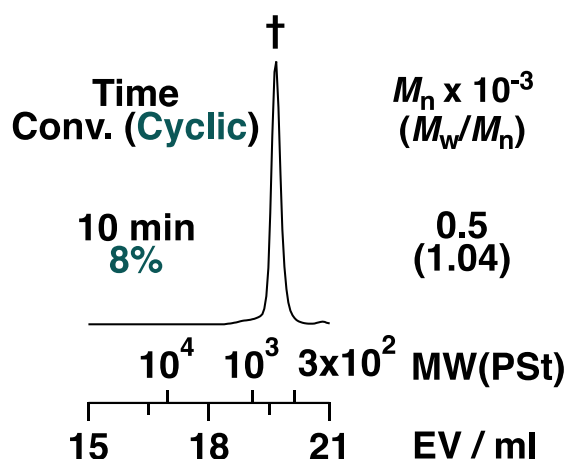


Figure S17. MWD curve of the product obtained in the cationic homopolymerization of the cyclic trimer consisting of IBVE and NNE ($[\text{cyclic trimer (IBVE-NNE)}]_0 = 1.0 \text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 10 \text{ mM}$, in toluene/*n*-hexane (6/4 v/v) at $-78 \text{ }^\circ\text{C}$; † unreacted cyclic trimer).

Note for Figure S17. Peaks assigned to polymer products were not observed, which indicates that the homopolymerization of the cyclic trimer consisting of IBVE and NNE did not proceed.

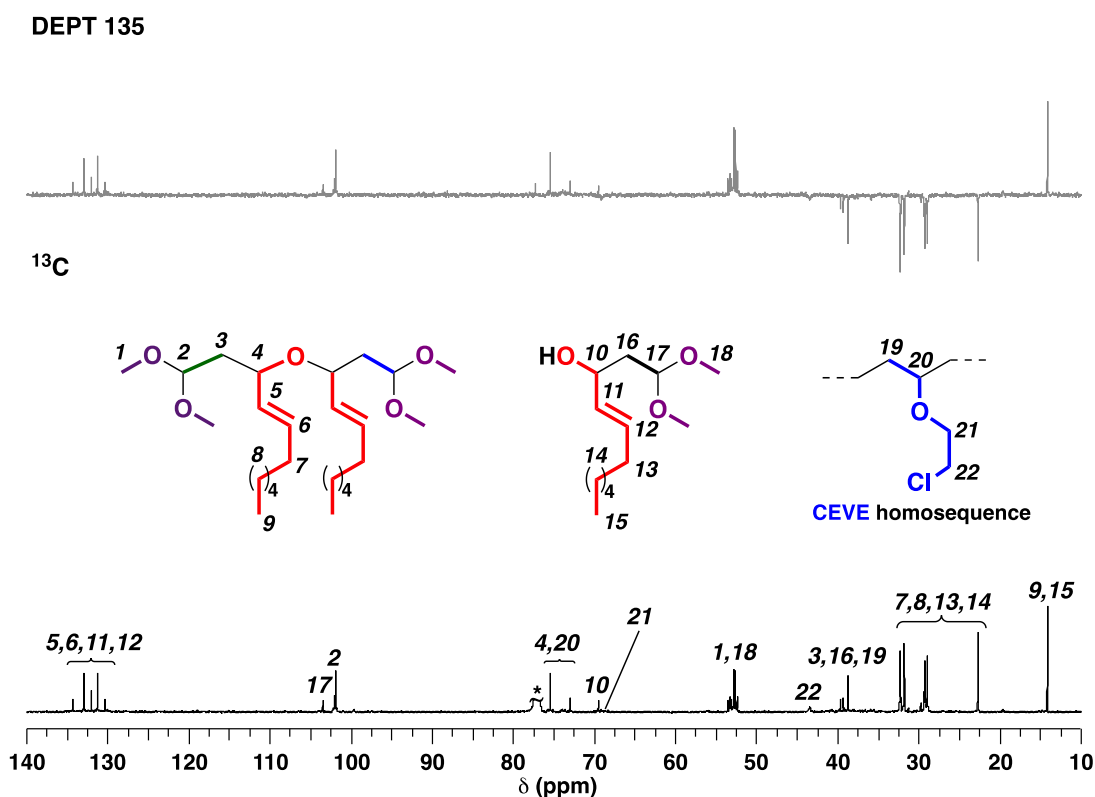


Figure S18. ^{13}C and DEPT 135 NMR spectra of the acid methanolysis product of the polymer obtained by the copolymerization of CEVE and the cyclic trimer (IBVE-NNE) [entry 2 in Table 3; the same sample as that for ^1H NMR analysis (Figure 5, lower); in CDCl_3 at $30 \text{ }^\circ\text{C}$; * CDCl_3].

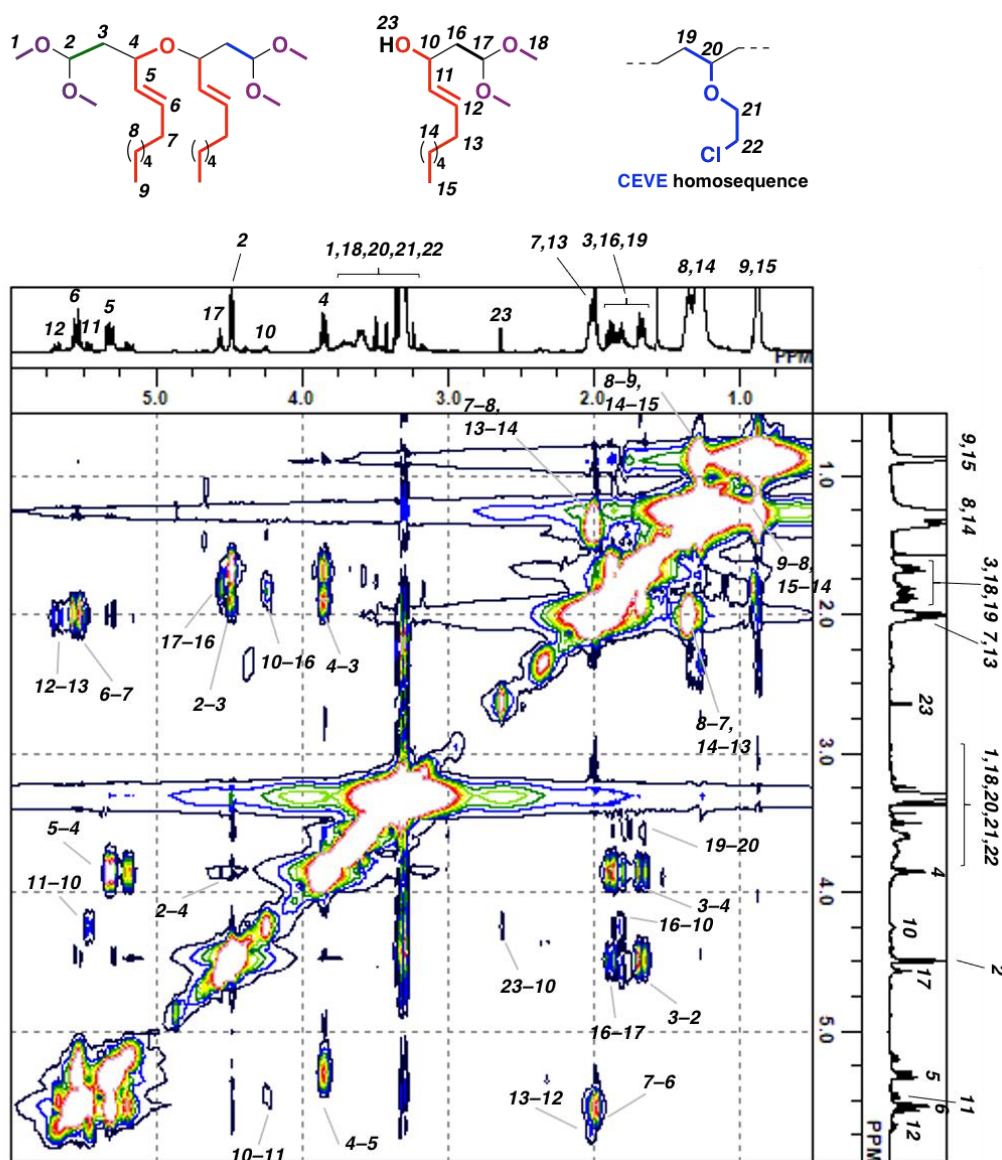


Figure S19. ^1H - ^1H COSY spectrum of the acid methanolysis product of the obtained polymer by the copolymerization of CEVE and the cyclic trimer (IBVE-NNE) (entry 2 in Table 3; in CDCl_3 at 30°C).

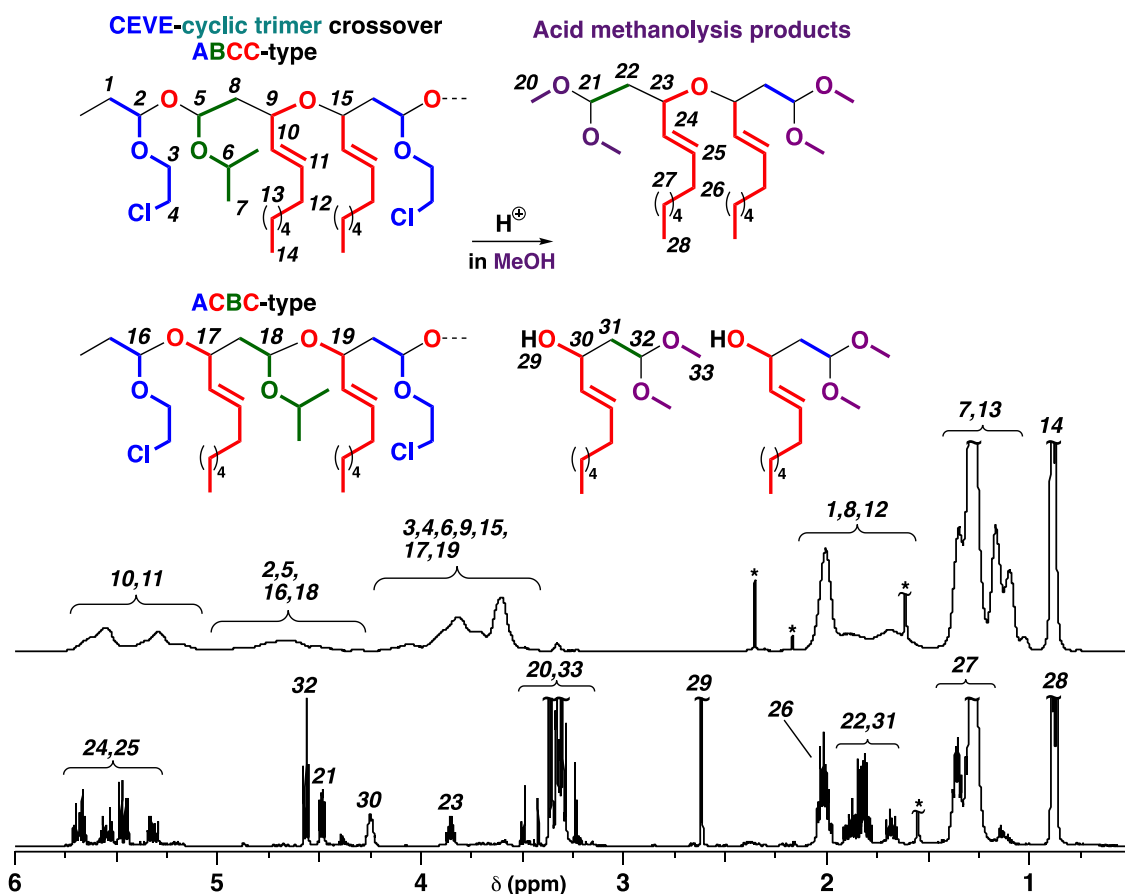


Figure S20. ^1H NMR spectra of the polymer obtained by the cationic copolymerization of CEVE and the cyclic trimer consisting of IPVE and NNE and its acid methanolysis product (entry 7 in Table 3; after purification by preparative GPC; in CDCl_3 at 30°C ; * water or others).

Note for Figure S20. The peak intensities of the acid methanolysis product derived from ACBC-type monomer sequences (peaks 29, 30, and 32) were larger than those obtained by the copolymerization of CEVE and the cyclic trimer consisting of IBVE and NNE (Figure 5, lower).

Table S1. Cationic copolymerization of CEVE and cyclic trimer consisting of IBVE and NNE ^a

entry	CEVE (M)	cyclic trimer	(M)	temp. (°C)	solvent (v/v)		conv. (%) ^b			units per block ^d			ABCC/ACBC ratio ^e
					toluene/hexane	time (min)	CEVE	cyclic trimer	$M_n \times 10^{-3}{}^c$	$M_w/M_n{}^c$	CEVE	cyclic trimer	
1	0.10	IBVE-NNE	1.0	-40	6/4	5	>99	19	1.3	1.41	1.0 ₀	1.0	67/33
2	0.10	IBVE-NNE	1.0	-60	6/4	5	>99	10	2.5	1.52	1.0 ₇	1.0	79/21
3	0.051	IBVE-NNE	0.51	-100	9/1	30	>99	15	3.6	1.68	1.0 ₀	1.0	67/33

^a [EtSO₃H]₀ = 4.0 (entries 1 and 2) or 2.0 (entry 3) mM, [GaCl₃]₀ = 10 mM, at -78 °C. ^b Determined by the ¹H NMR analysis of quenched reaction mixtures. ^c Determined by GPC (polystyrene standards). ^d Estimated by the ¹H NMR analysis of the obtained products after purification by preparative GPC. ^e Determined by the ¹H NMR analysis of the acid methanolysis products.

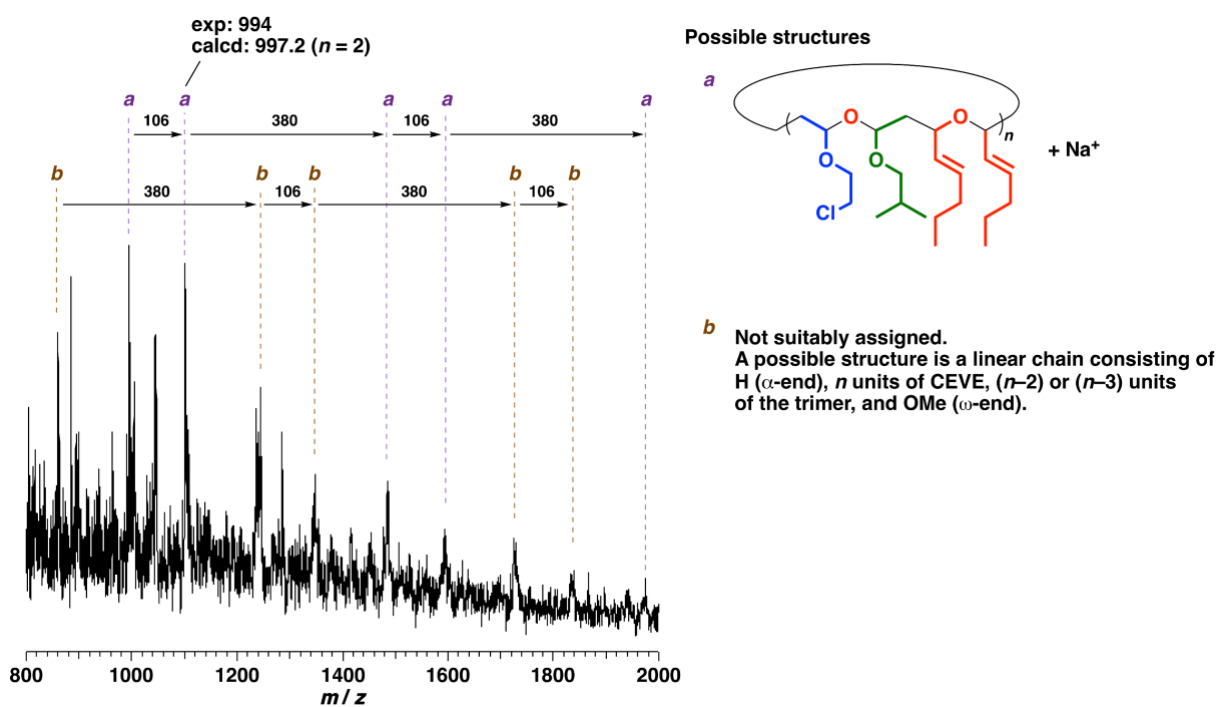


Figure S21. MALDI-TOF-MS spectrum of the polymer obtained by the alternating cationic copolymerization of CEVE and the cyclic trimer consisting of IBVE and NNE (entry 3 in Table 3). The ABAC-type sequences were ignored. Linear chains with a proton at the α -end and an olefin structure resulting from β -proton elimination reaction at the ω -end also have the same mass values as those of the cyclic structure (series *a*); however, such olefin structures were not observed in the ¹H NMR spectrum.