Electronic Supplementary Information for:

Polyaddition of Vinyl Ethers and Phthalaldehydes via Successive Cyclotrimerization Reactions: Selective Model Reactions and Synthesis of Acid-Degradable Linear Poly(Cyclic Acetal)s

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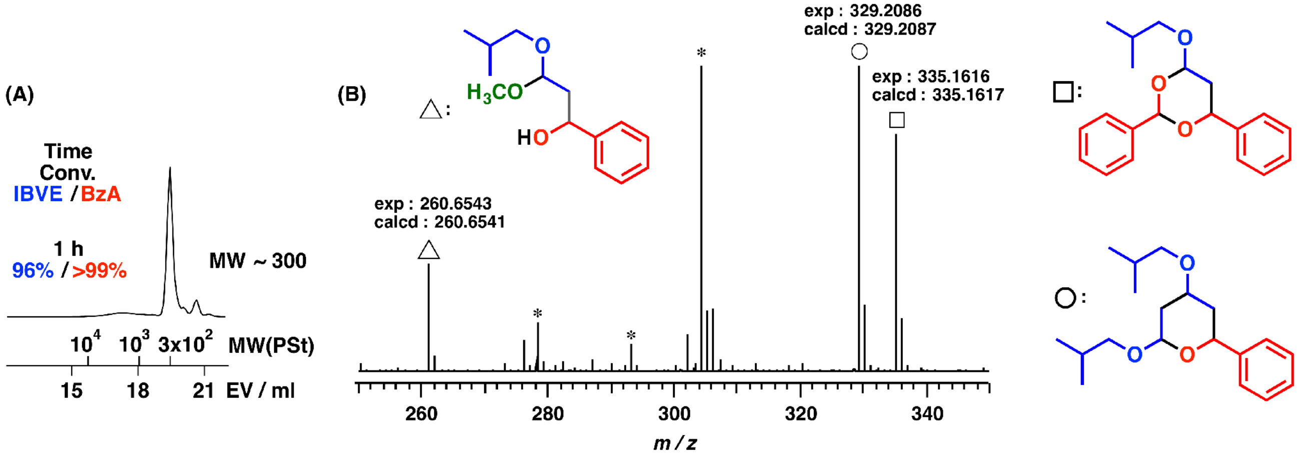


Figure S1. (A) MWD curve and (B) ESI-MS spectrum of the product obtained by the reaction of IBVE and BzA (entry 2 in Table 1).

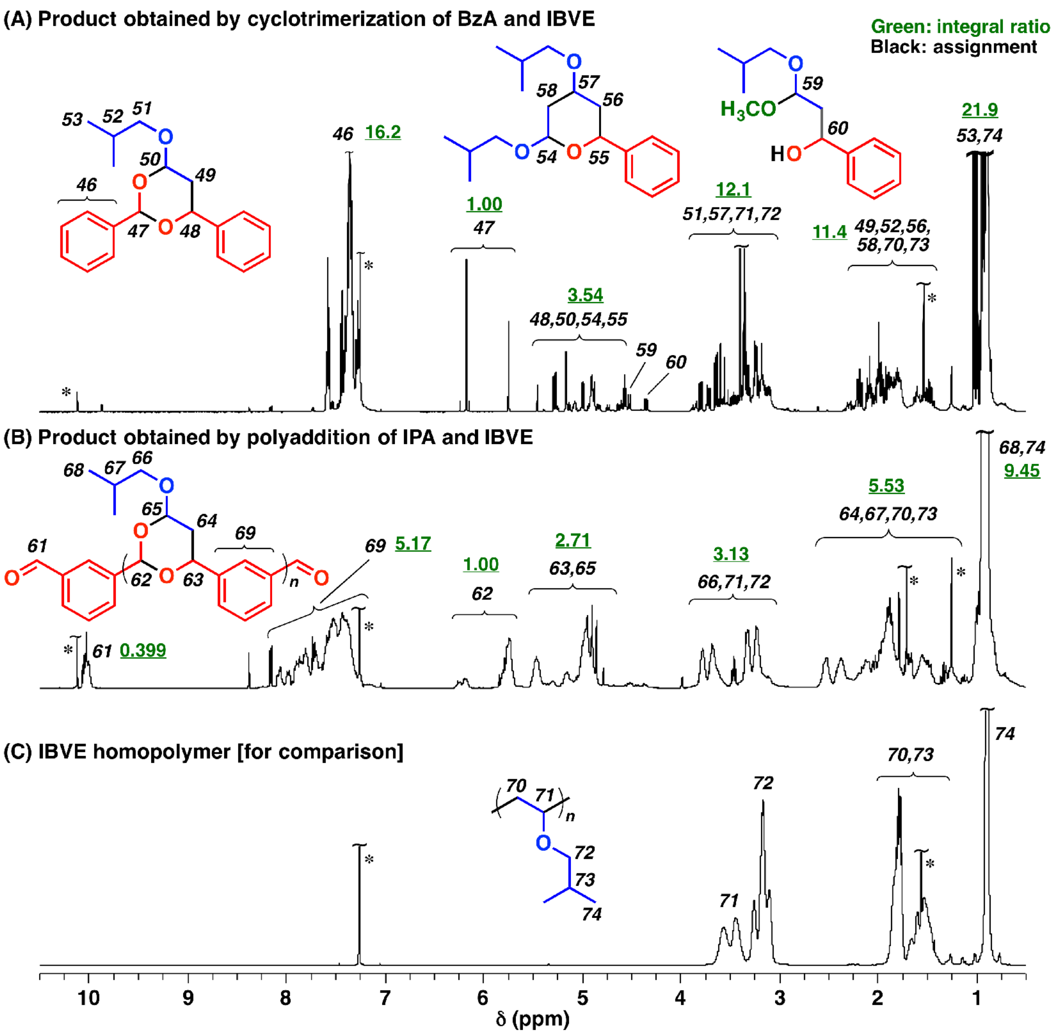


Figure S2. ^{1}H NMR spectra of (A) the product obtained by the cyclotrimerization of BzA and IBVE (entry 2 in Table 1), (B) the product obtained by polymerization of IPA and IBVE (entry 3 in Table 2), and (C) IBVE homopolymer (* solvent, residual monomer, water, etc.; number written in green: integral ratio).

Notes for Figures S2 and S3:

The ratios of a cyclic trimer consisting of two BzA and one VE, a cyclic trimer consisting of one BzA and two VE, and other byproducts, which are listed in Table 1, were calculated from the integral ratios of peaks 47, 48, 50, 53, 54, 55, and 74 for IBVE (Figure S2) and peaks 76, 77, 79, 81, 82, 83 and 100 for IPVE (Figure S3). The ratio of products other than the cyclic trimers was standardized based on the numbers of IPVE units (e.g., the ratio is 1/1/8 when equal amounts of a cyclic trimer consisting of two BzA and one VE, a cyclic trimer consisting of one BzA and two VE, and a homopolymer composed of 8 units of IPVE are generated).

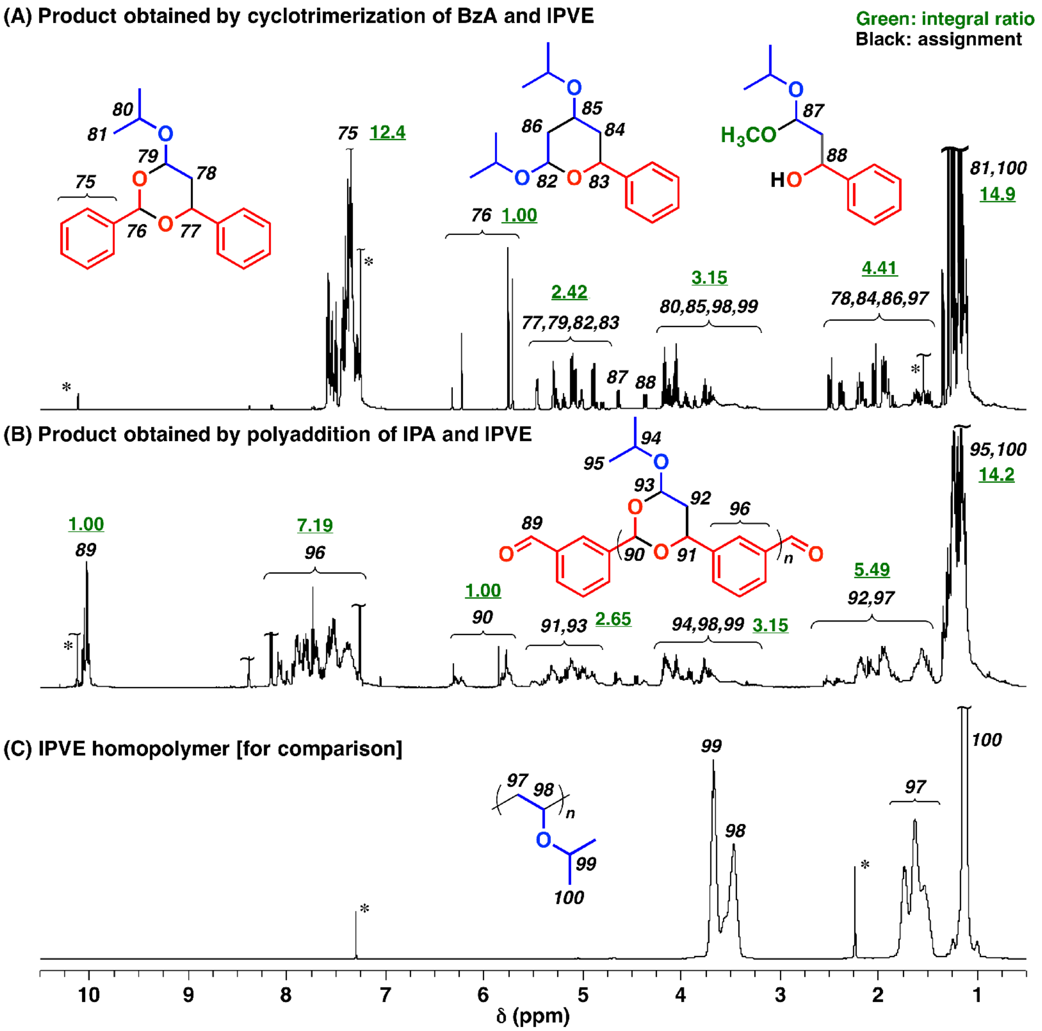


Figure S3. ^{1}H NMR spectra of (A) the product obtained by the cyclotrimerization of BzA and IPVE (entry 3 in Table 1), (B) the product obtained by polymerization of IPA and IPVE (entry 4 in Table 2), and (C) IPVE homopolymer (* solvent, residual monomer, or water; number written in green: integral ratio).

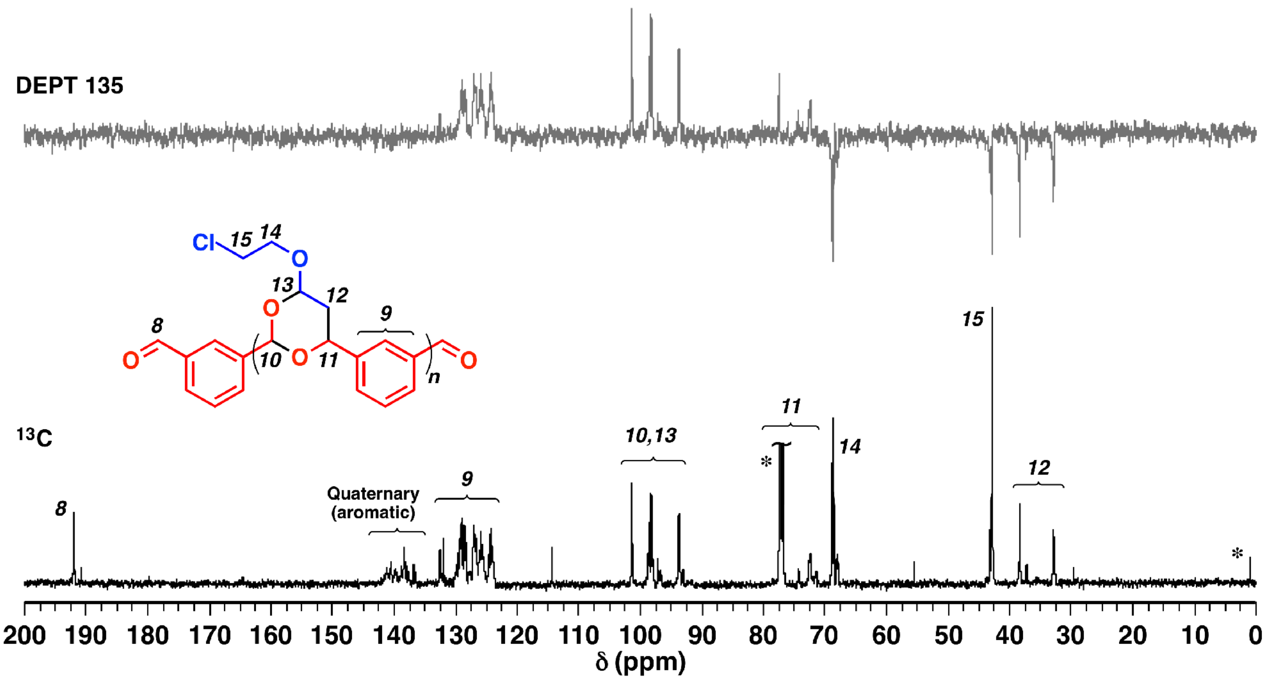


Figure S4. ^{13}C and DEPT 135 NMR spectra of the product obtained by the copolymerization of CEVE and IPA (in $CDCl_3$ at 30 ºC; $[TPA]_0 = 0.50$ M, $[CEVE]_0 = 0.50$ M, $[EtAlCl_2]_0 = 50$ mM, [THF] = 1.0 M, in dichloromethane at 0 ºC; a different sample from those shown in Figures 2 and 3; reprecipitated from methanol; * solvents or grease).

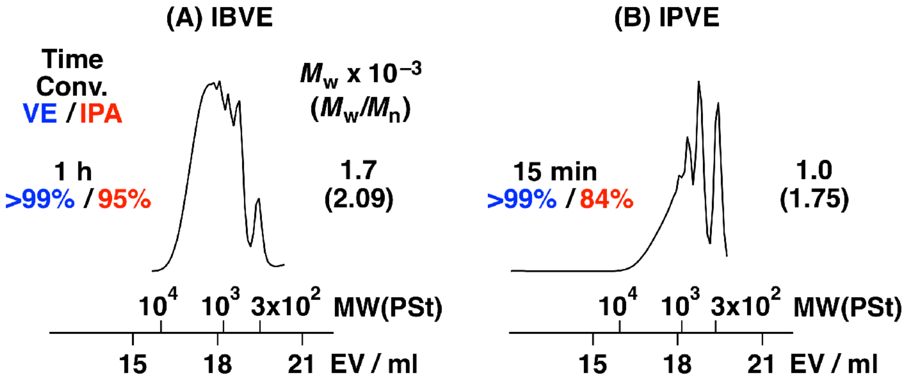


Figure S5. MWD curves of the products obtained by the polymerization of IPA with (A) IBVE (entry 3 in Table 2) or (B) IPVE (entry 4).

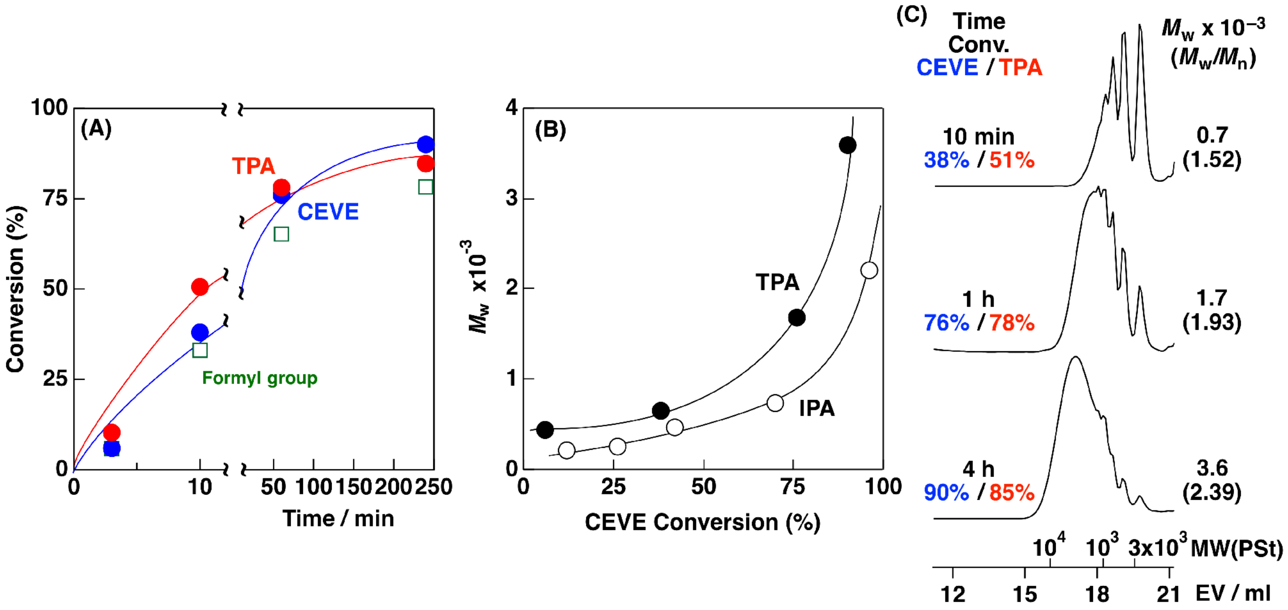


Figure S6. (A) Time–conversion curves of polyaddition of CEVE and TPA, (B) M_w values (the values for IPA are the same to those shown in Figure 3B), and (C) MWD curves of the products obtained (entry 2 in Table 2; $[TPA]_0 = 0.50$ M, $[CEVE]_0 = 0.50$ M, $[EtAlCl_2]_0 = 50$ mM, [THF] = 1.0 M, in dichloromethane at 0 ºC).

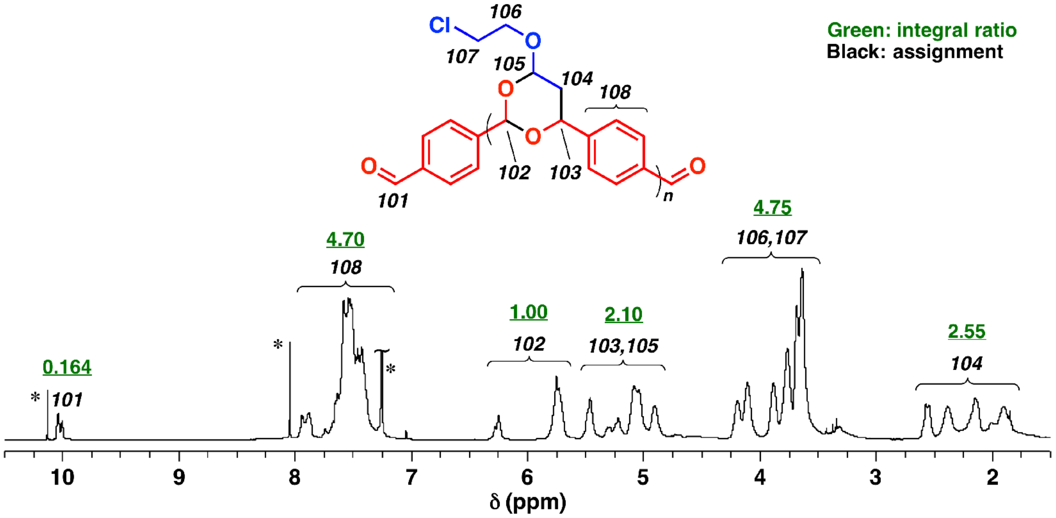


Figure S7. ^{1}H NMR spectrum of the polymer obtained by the polyaddition of CEVE and TPA (the bottom curve in Figure S6C; * solvent or residual monomer; number written in green: integral ratio).

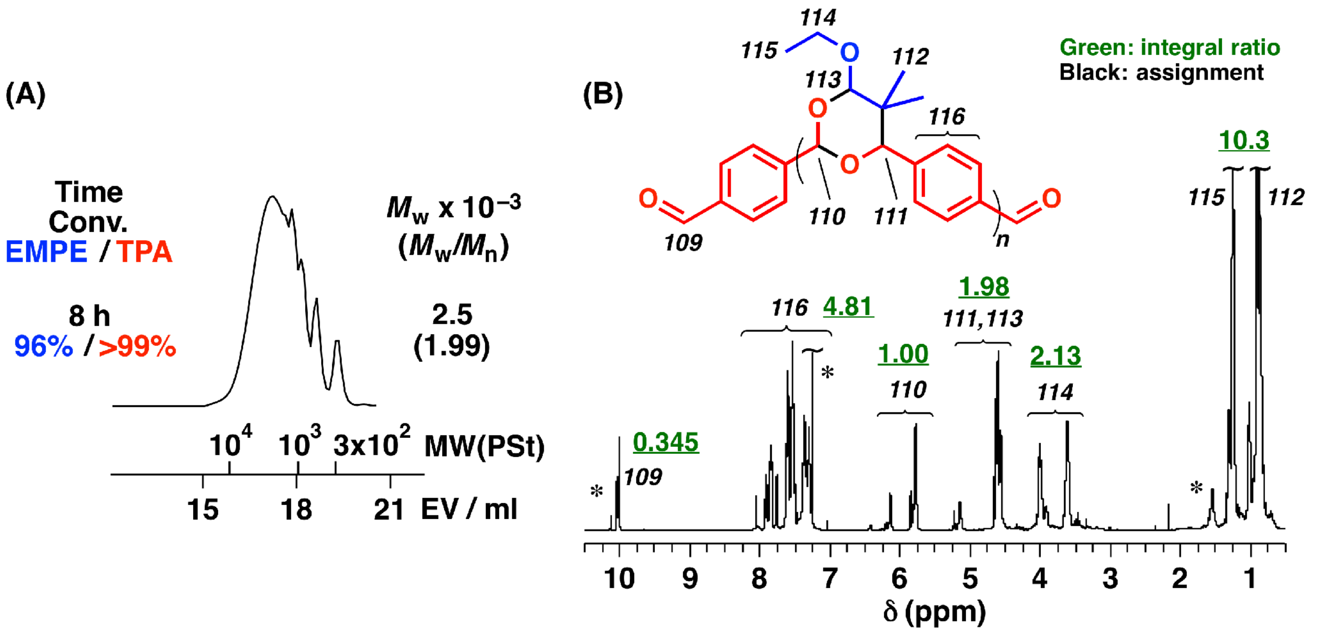


Figure S8. (A) MWD curve and (B) ^{1}H NMR spectrum of the product obtained by the polyaddition of EMPE and TPA ($[TPA]_0$ = 0.50 M, $[EMPE]_0$ = 0.50 M, $[EtAlCl_2]_0$ = 50 mM, [THF] = 1.0 M, in dichloromethane at 0 °C; * solvent, residual monomer, or water; number written in green: integral ratio).

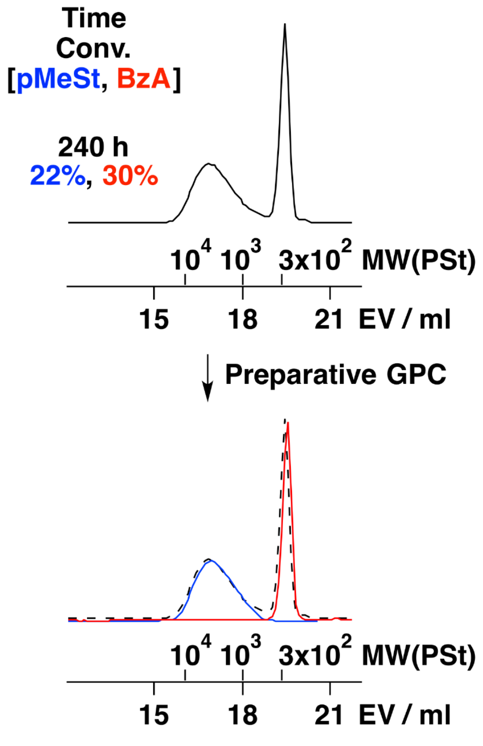


Figure S9. MWD curves of the product obtained by the reaction of pMeSt and BzA (upper) and the high- (blue) and low- (red) molecular-weight portions (lower) separated by preparative GPC ($[pMeSt]_0$ =0.20 M, $[BzA]_0$ = 0.20 M, $[GaCl_3]_0$ = 5.0 mM, [DTBP] = 1.8 mM, in toluene at 0 °C).

Note for Figure S9: The ratio of the low-molecular-weight portion was larger than the sample obtained in the absence of DTBP (entry 8 in Table 1). This sample was used for the analysis (see Figure S10) of the low-molecular-weight portion after separated by preparative GPC.

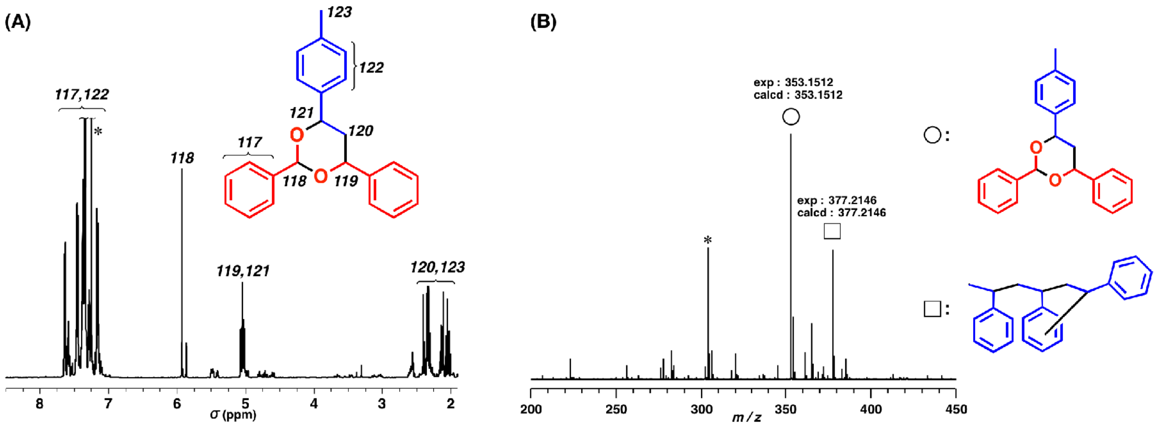


Figure S10. (A) ^{1}H NMR (in $CDCl_3$ at 30 °C; * $CHCl_3$) and (B) ESI-MS spectra of the low-molecular-weight portion of the product obtained by the reaction of pMeSt and BzA (the low-molecular-weight portion of the sample shown in Figure S9).

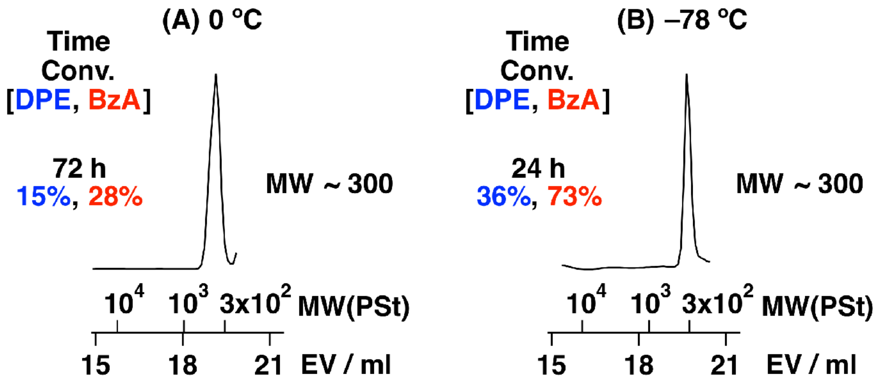


Figure S11. MWD curves of the products obtained by the reaction of DPE and BzA at (A) 0 (entry 10 in Table 1) or (B) –78 (entry 11) °C.

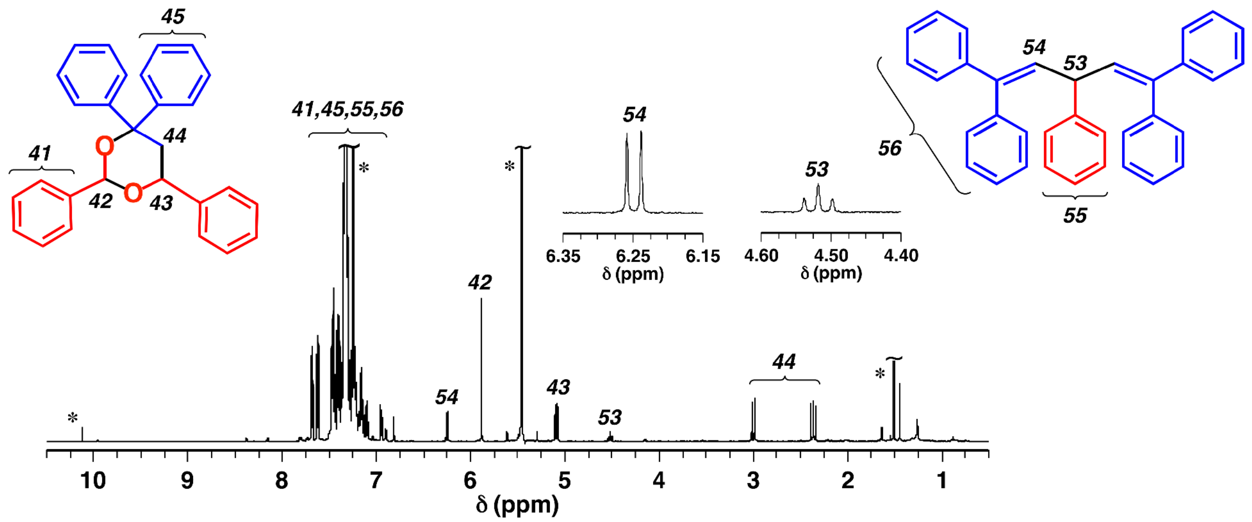
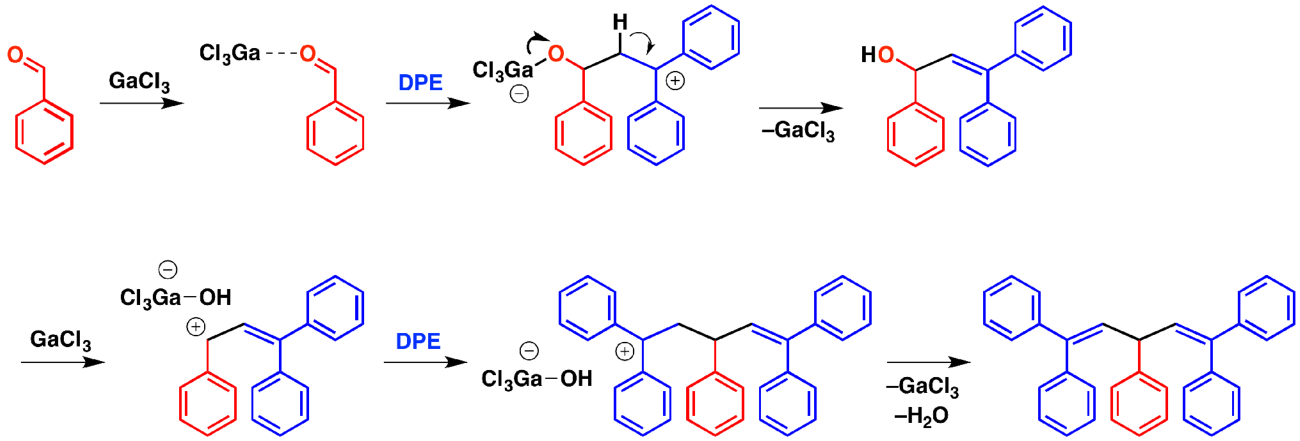


Figure S12. ^{1}H NMR spectrum of the product obtained by the reaction of DPE and BzA at 0 °C (entry 10 in Table 1; in $CDCl_3$ at 30 °C; the assignment of 1,1,3,5,5-pentaphenylpenta-1,4-diene is based on reference 27; * solvents, residual monomer, or water).



Scheme S1. Plausible mechanism of the generation of 1,1,3,5,5-pentaphenylpenta-1,4-diene in the reaction of DPE and BzA.

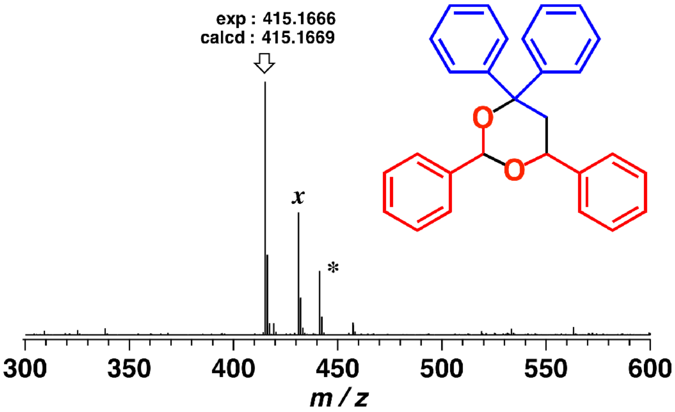


Figure S13. ESI-MS spectrum of the product obtained by the reaction of DPE and BzA at –78 ºC (similar conditions to those for entry 11 in Table 1; $[GaCl_3]_0$ = 5.0 mM unlike entry 11; * Contamination. The same signal was detected when solvents were analyzed). Peak *x* is assigned to a species with a composition of $C_{31}H_{20}O$; however, it is unlikely to generate such a species from DPE and BzA. Thus, the peak may be due to contamination.