

Supporting Information

Reactivity of poly(alkoxycarbonylmethylene)s under basic conditions: alkylation of main chain carbon atoms *via* a ketene silyl acetal-type intermediate and cleavage of the carbon–carbon main chain

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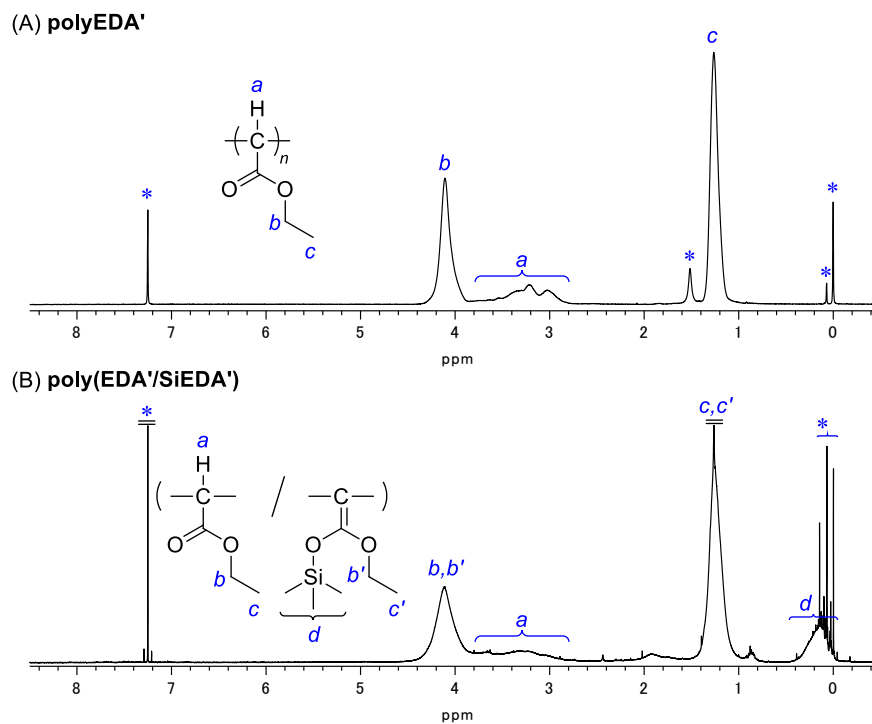


Figure S1. ¹H NMR spectra of (A) **polyEDA'** (run 3 in Table 1, prepolymer) and (B) **poly(EDA'/SiEDA')** (run 3 in Table 1, product) (*: solvent, grease, or water).

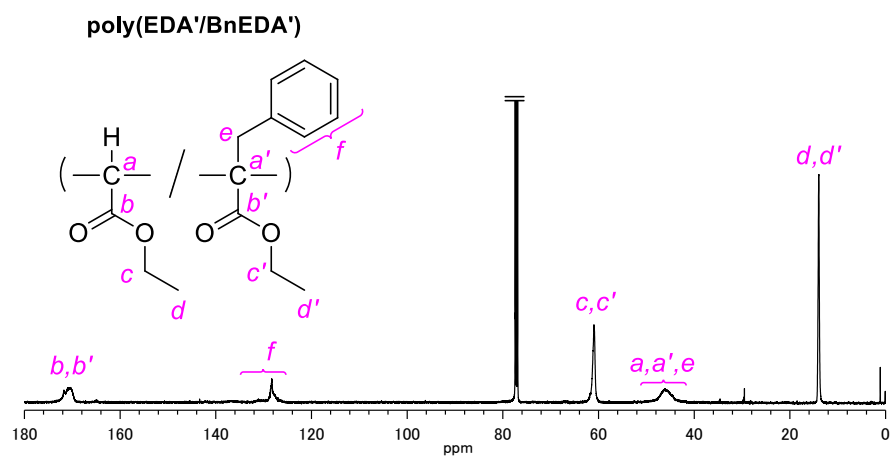


Figure S2. ¹³C NMR spectrum of **poly(EDA'/BnEDA')** (path B in Scheme 3, product).

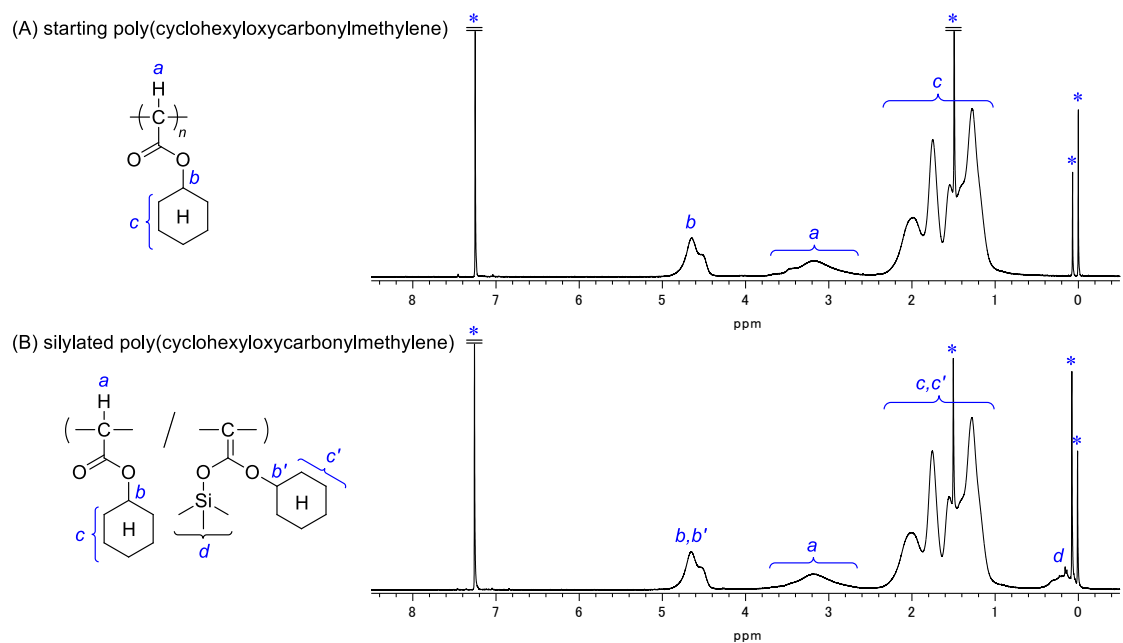
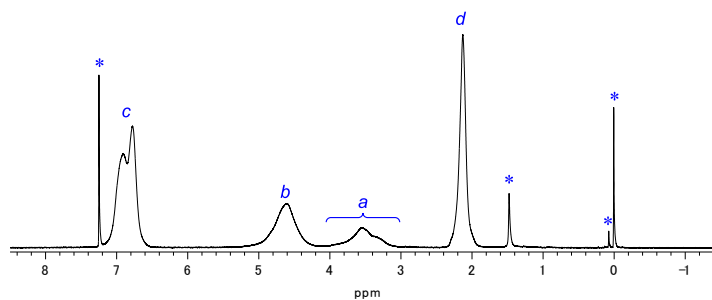
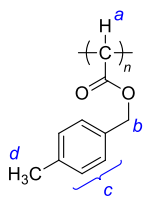
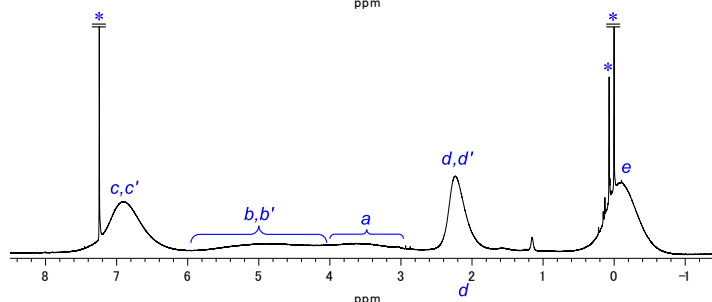
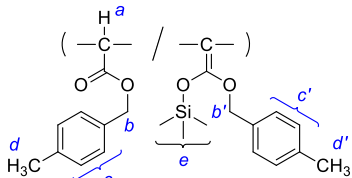


Figure S3. ^1H NMR spectra of (A) starting poly(cyclohexyloxycarbonylmethylene) (run 1 in Table 4, prepolymer) and (B) silylated poly(cyclohexyloxycarbonylmethylene) (run 1 in Table 4, product) (Scheme 6) (*: solvent, grease, or water).

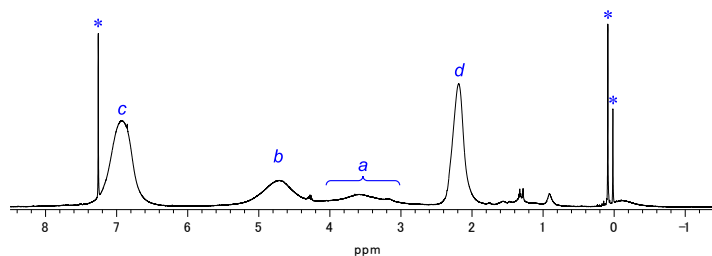
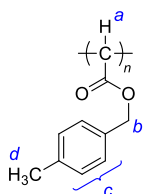
(A) starting **poly(4-Me-BDA)**'



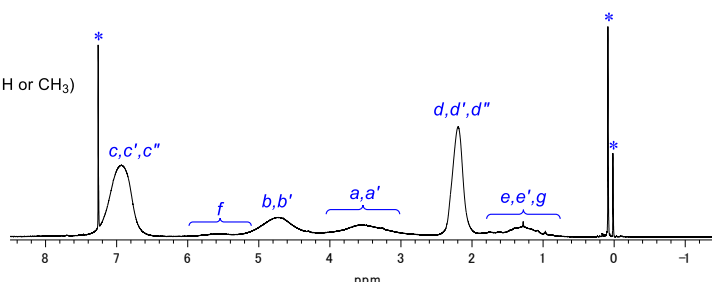
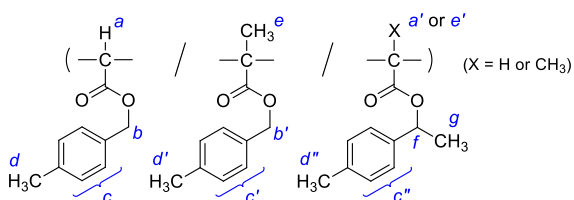
(B) silylated **poly(4-Me-BDA)**'



(C) regenerated **poly(4-Me-BDA)**'



(D) methylated **poly(4-Me-BDA)**'



(E) benzylated **poly(4-Me-BDA)**'

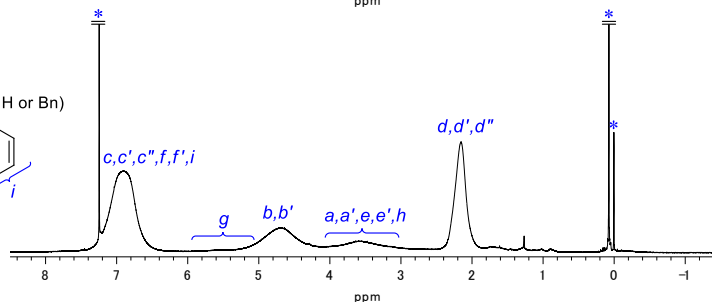
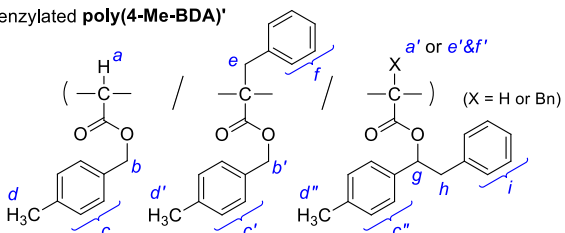
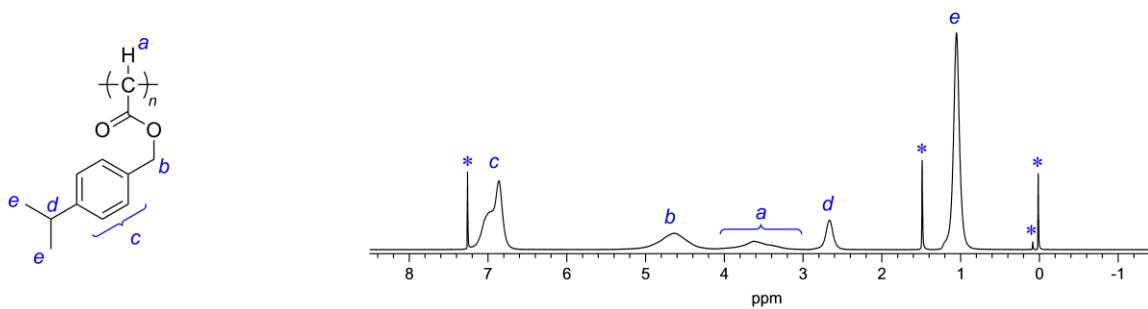
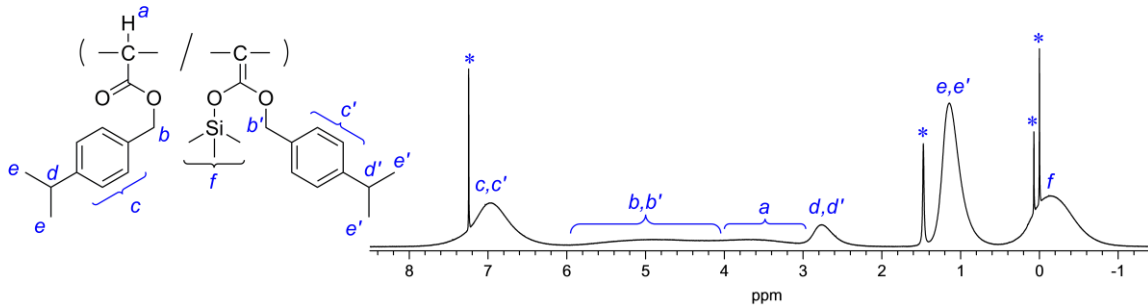


Figure S4. ^1H NMR spectra of (A) starting **poly(4-Me-BDA)**' (run 3 in Table 4, prepolymer), (B) silylated **poly(4-Me-BDA)**' (run 3 in Table 4, product), (C) regenerated **poly(4-Me-BDA)**' (run 2 in Table 5, product), (D) methylated **poly(4-Me-BDA)**' (run 2 in Table 6, product), and (E) benzylated **poly(4-Me-BDA)**' (run 3 in Table 6, product) (*: solvent, grease, or water).

(A) starting **poly(4-*i*-Pr-BDA)'**



(B) silylated **poly(4-*i*-Pr-BDA)'**



(C) regenerated **poly(4-*i*-Pr-BDA)'**

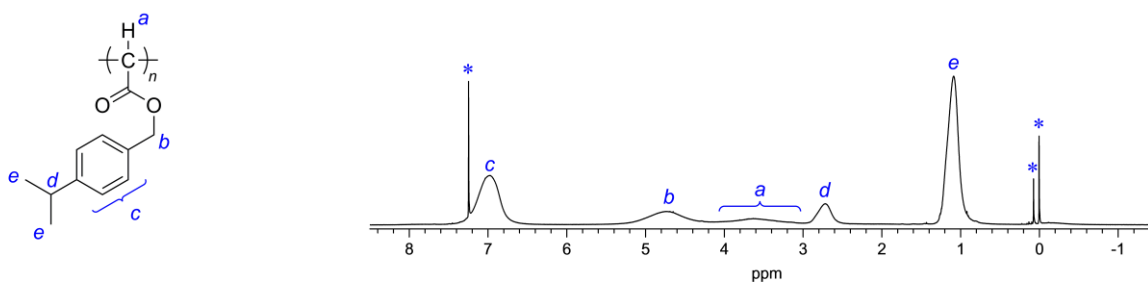


Figure S5. ¹H NMR spectra of (A) starting **poly(4-*i*-Pr-BDA)'** (run 4 in Table 4, prepolymer), (B) silylated **poly(4-*i*-Pr-BDA)'** (run 4 in Table 4, product), and (C) regenerated **poly(4-*i*-Pr-BDA)'** (run 3 in Table 5, product) (*: solvent, grease, or water).

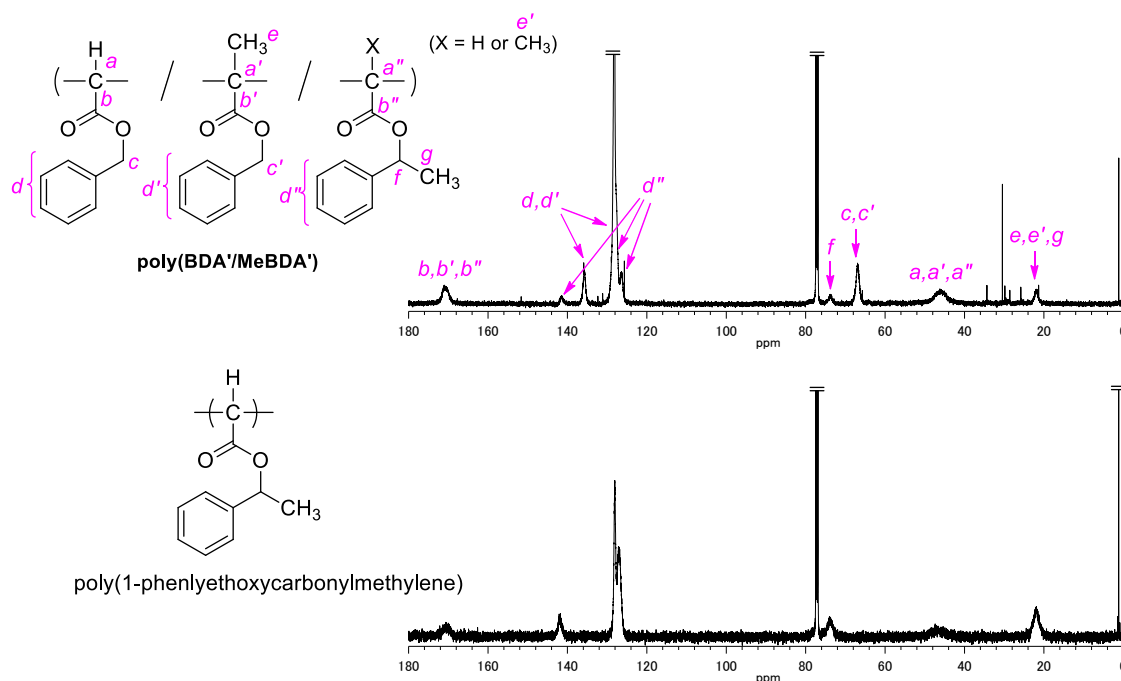


Figure S6. ^{13}C NMR spectra of **poly(BDA'/MnBDA')** (path B in Scheme 7, product) and poly(1-phenylethoxycarbonylmethylene).

Note: Comparing the spectra of **poly(BDA'/MnBDA')** and poly(1-phenylethoxycarbonylmethylene), we realized that methyl group incorporation occurred at not only the main chain carbon but also the side chain benzylic position, although the mechanism is unclear at present.

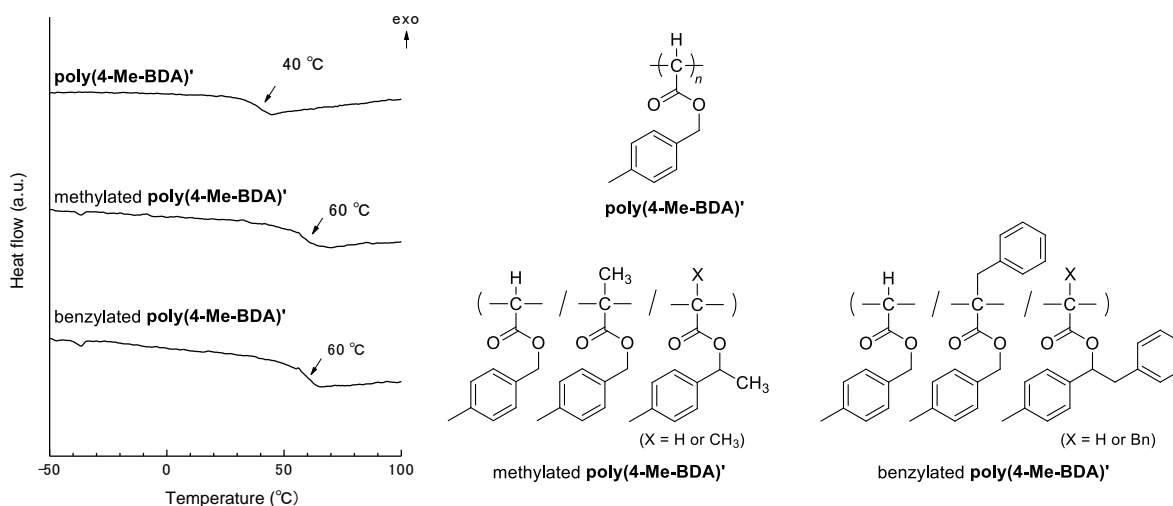


Figure S7. DSC thermograms of **poly(4-Me-BDA)'** ($M_n = 16000$, $M_w/M_n = 1.92$), methylated **poly(4-Me-BDA)'** ($M_n = 5800$, $M_w/M_n = 1.86$, methylation ratio = 17%), and benzylated **poly(4-Me-BDA)'** ($M_n = 5700$, $M_w/M_n = 1.96$, benzylation ratio = 17%).

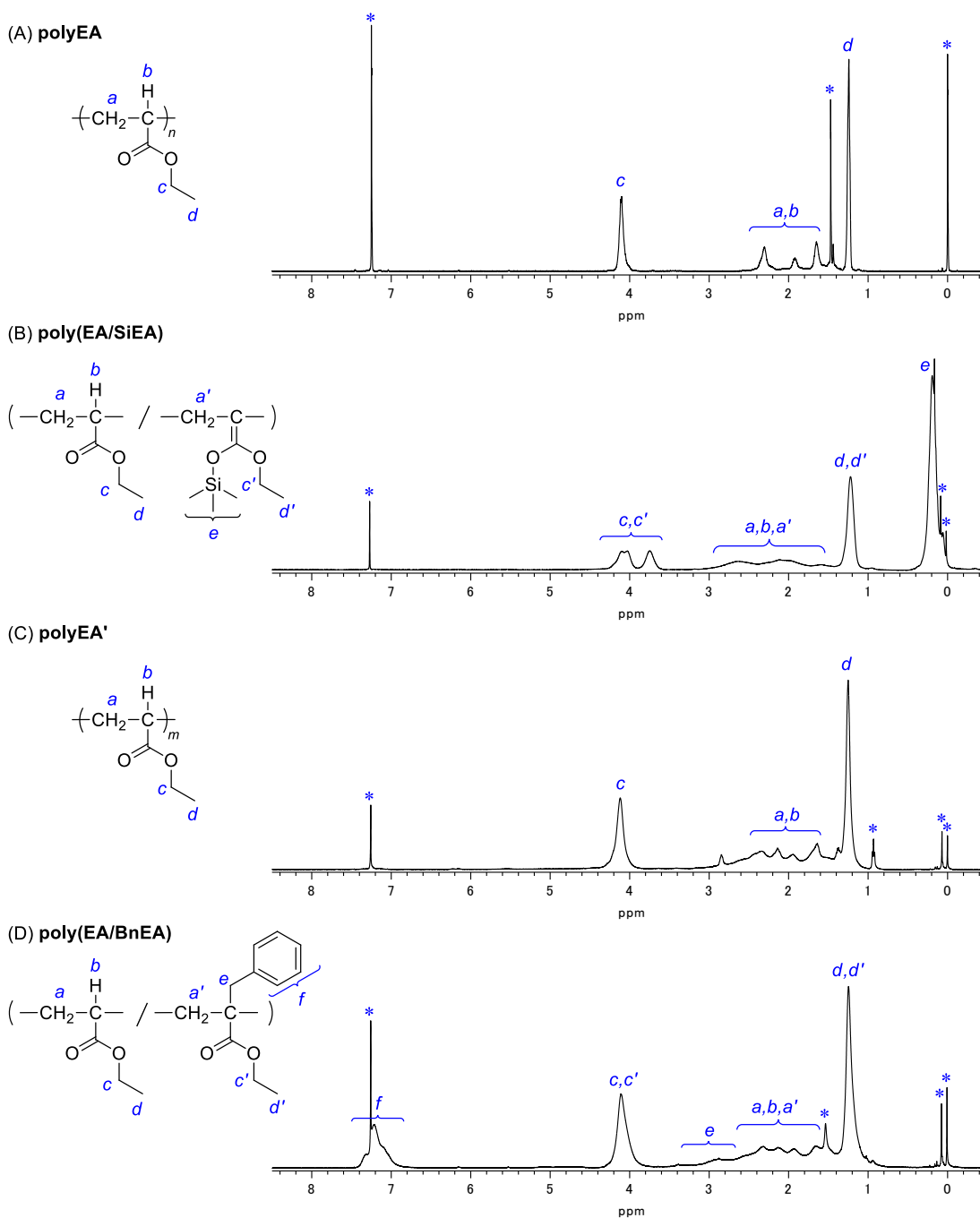


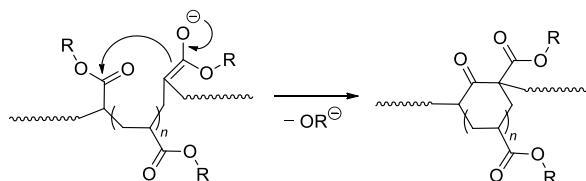
Figure S8. ^1H NMR spectra of (A) **polyEA**, (B) **poly(EA/SiEA)**, (C) **polyEA'**, and (D) **poly(EA/BnEA)** (Scheme 8) (*: solvent, grease, or water).

Note: Comparing the spectra of the starting **polyEA** [Figure S8(A)] and the regenerated **polyEA** [Figure S8(C)], we noticed that they apparently differed in the appearance of the signals for the main chain CH_2 and CH ; there appear many additional broad signals in 1.0–3.0 ppm, which cannot be explained by the tacticity change during the transformation described in the main text for **polyEDA'**. Furthermore, the relative intensity of the whole CH_2 and CH signals with respect to those of OCH_2CH_3 signals is higher than that expected from the **polyEA** structure. We suppose that this phenomenon could be explained by the occurrence of the intramolecular cyclization described in Scheme S1, which accounts for the diminished relative intensities of OCH_2CH_3 signals with the release of the alkoxy

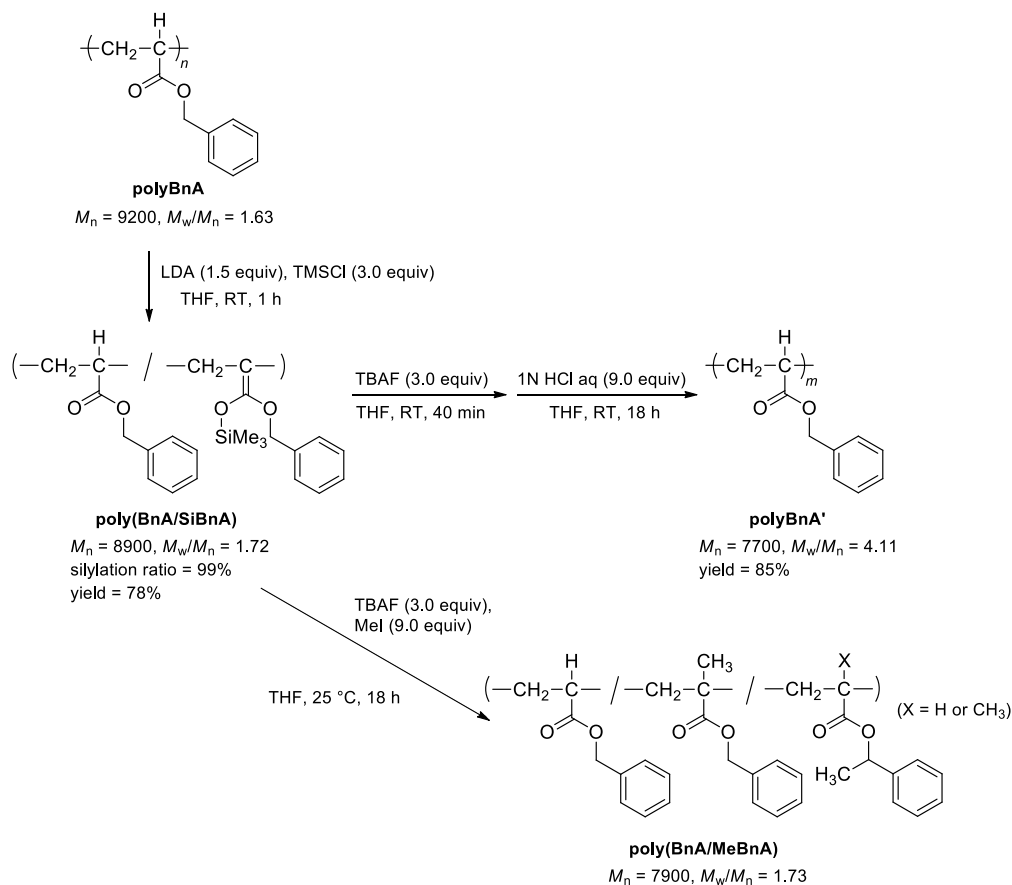
group and the appearance of additional signals in 1.0–3.0 ppm. More importantly, the suppression of the side reaction in the case of **polyEDA'** would be ascribed to the dense packing of the side chain substituents in poly(alkoxycarbonylmethylene).

Likewise, the appearance of the spectrum in Figure S8(D) suggests that the side reaction occurred during the benzylation as well.

Scheme S1. Plausible mechanism for the intramolecular cyclization via enolate formation



Scheme S2. Silylation of **polyBnA** and protonation and methylation of the silylated product



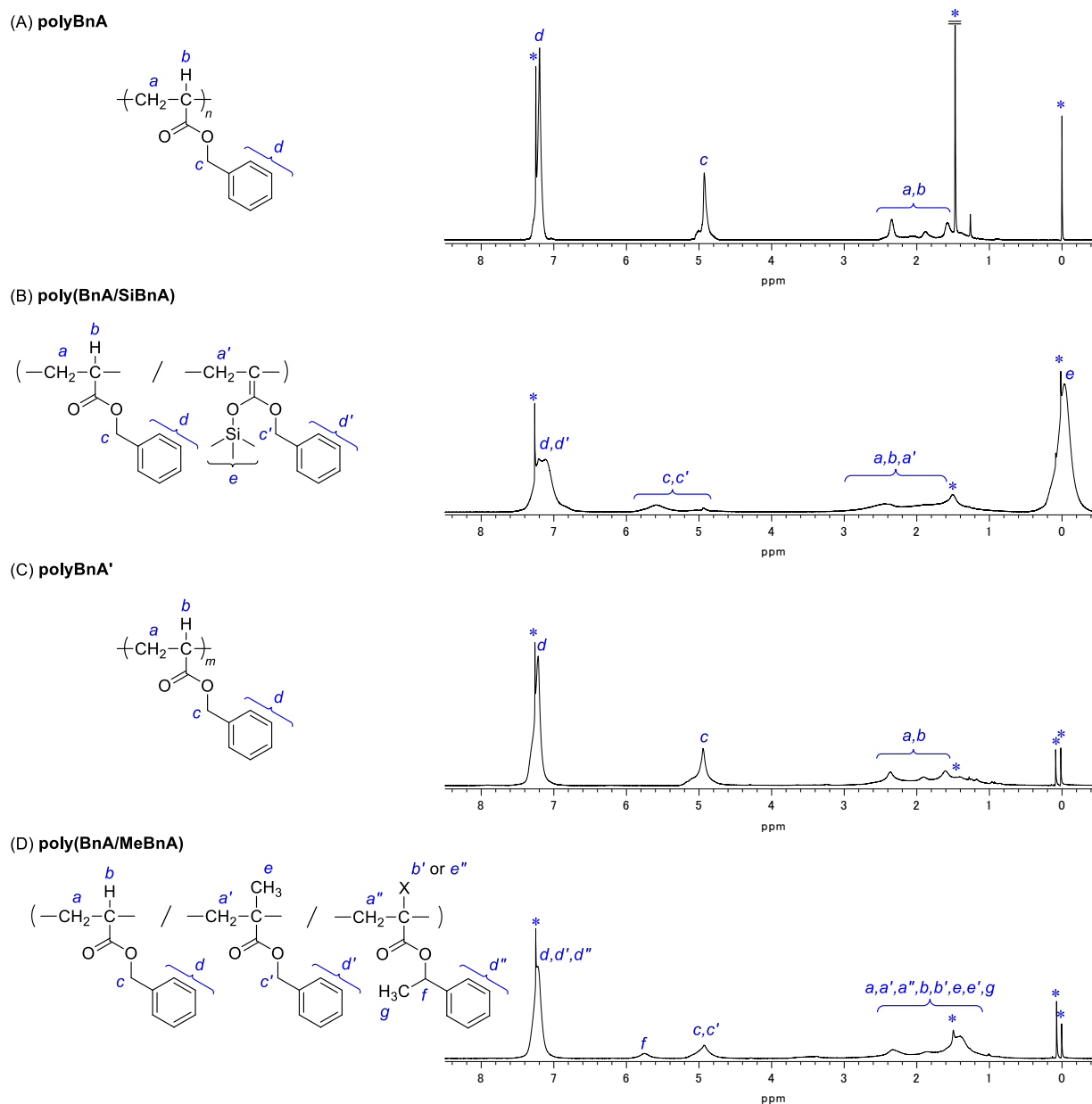


Figure S9. ^1H NMR spectra of (A) **polyBnA**, (B) **poly(BnA/SiBnA)**, (C) **polyBnA'**, and (D) **poly(BnA/MeBnA)** (Scheme S2) (*: solvent, grease, or water).

Note: The signal appearance in the spectra in Figures S9(C) and (D) suggests that the intramolecular cyclization described in the case of **polyEA** also occurred for **polyBnA**. The mol% of the incorporated methyl groups cannot be determined from the spectrum in Figure S9(D) because of the signal overlap.

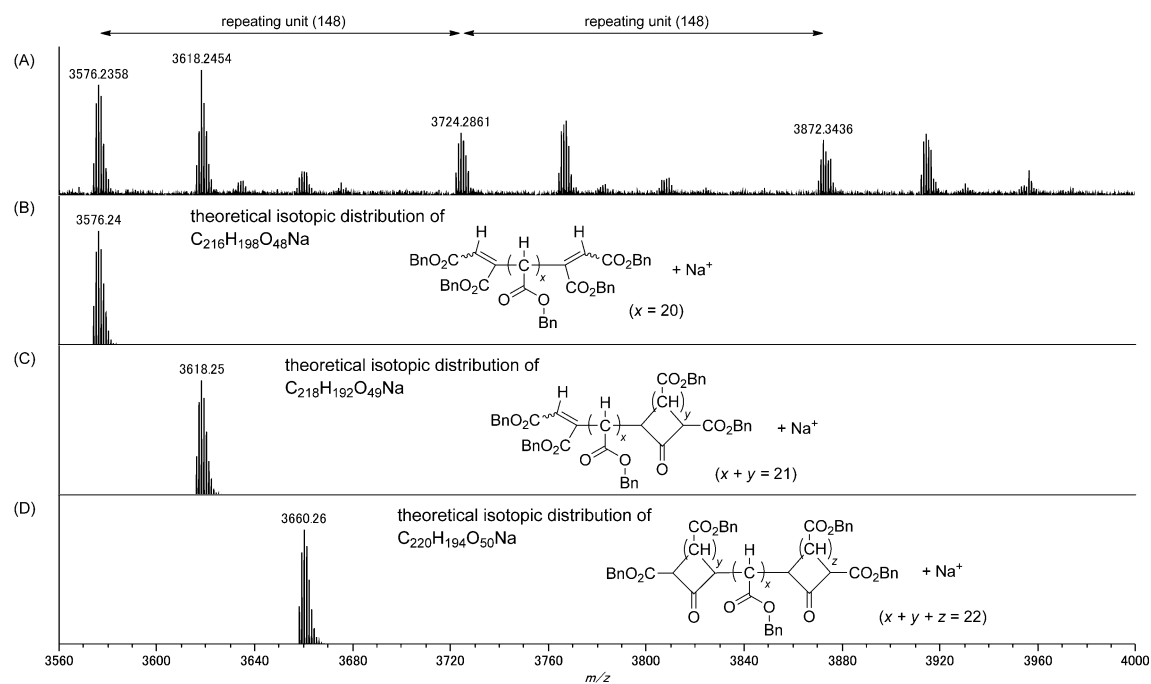


Figure S10. MALDI-TOF-MS spectrum of a product of run 5 in Table 7 (A). Simulated signal appearances of polyBDA' with a combination of C=C and cyclic ketone at polymer chain ends [(B)–(D)].

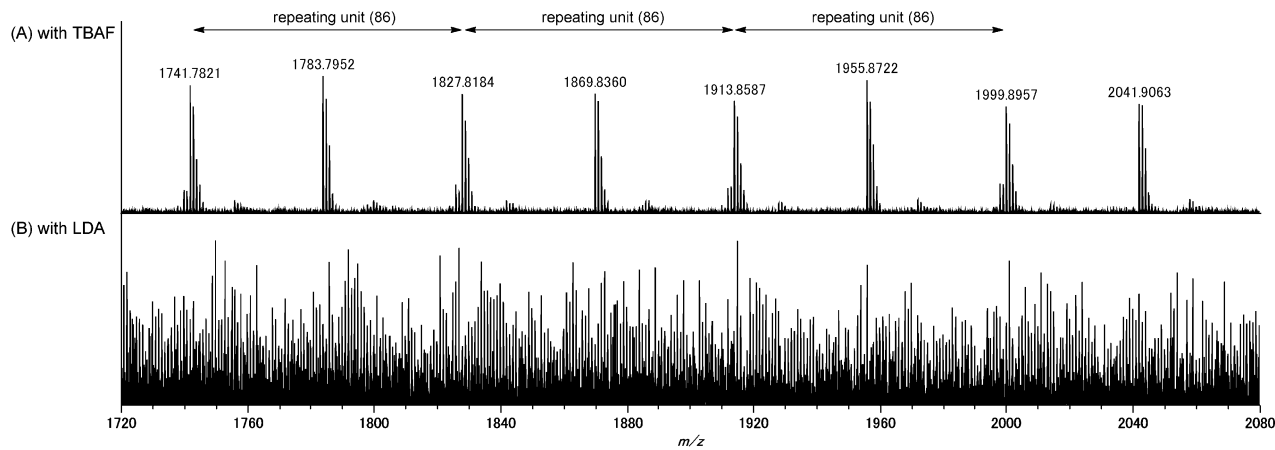


Figure S11. MALDI-TOF-MS spectra of (A) a product of run 2 in Table 7 and (B) a product of run 1 in Table 7.

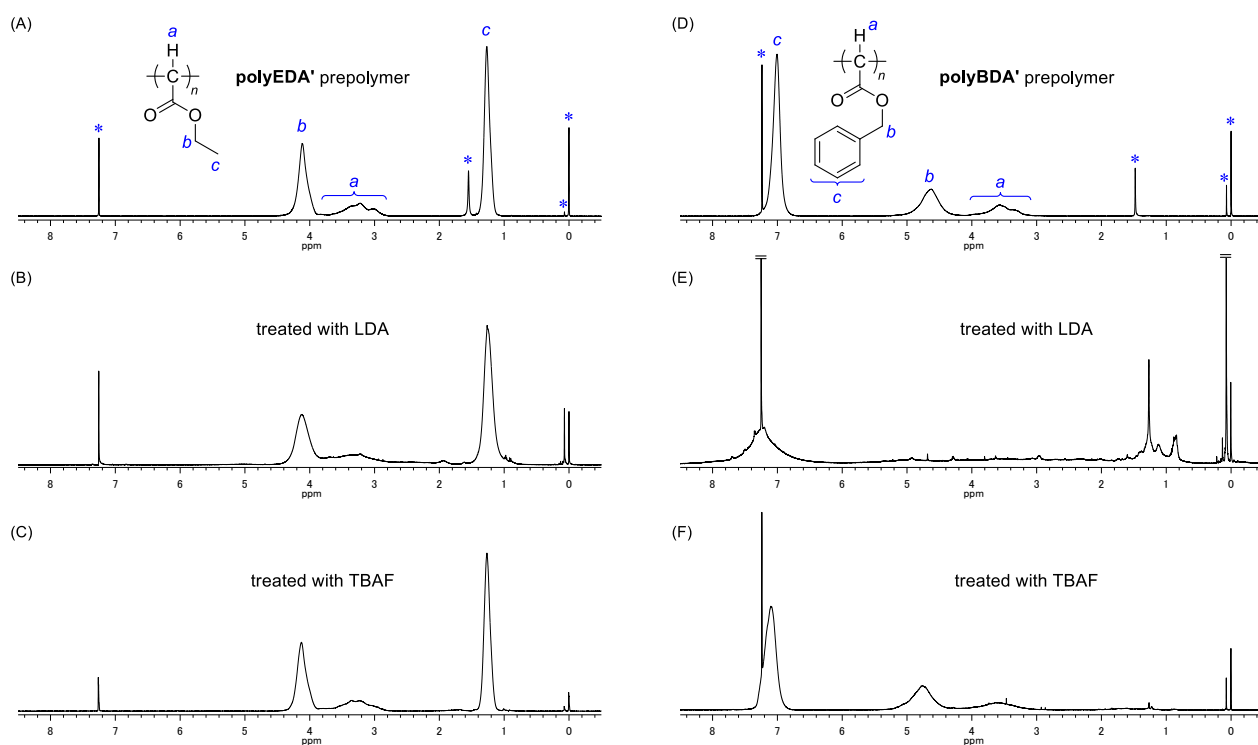


Figure S12. ^1H NMR spectra of **polyEDA'** prepolymer (A) and its degraded products obtained with LDA (B, run 1 in Table 7, product) and TBAF (C, run 2 in Table 7, product), and **polyBDA'** prepolymer (D) and its degraded products obtained with LDA (E, run 4 in Table 7, product) and TBAF (F, run 5 in Table 7, product).

Note: Expected end-groups cannot be observed in the NMR spectra probably because of peak overlap.

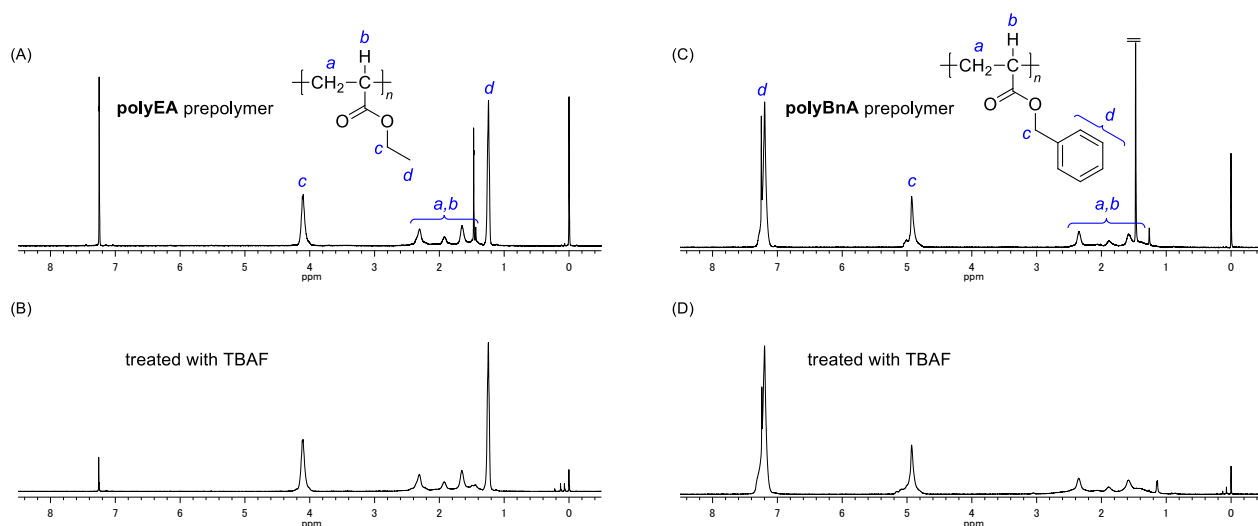


Figure S13. ^1H NMR spectra of **polyEA** prepolymer (A) and its degraded product obtained with TBAF (B, run 3 in Table 7, product), and **polyBnA** prepolymer (C) and its degraded product obtained with TBAF (D, run 6 in Table 7, product).