

## **Facile Synthesis of Unsaturated Polyester-Based Double-Network Gels via Chemoselective Cross-Linking using Michael Addition and Subsequent UV-Initiated Radical Polymerization**

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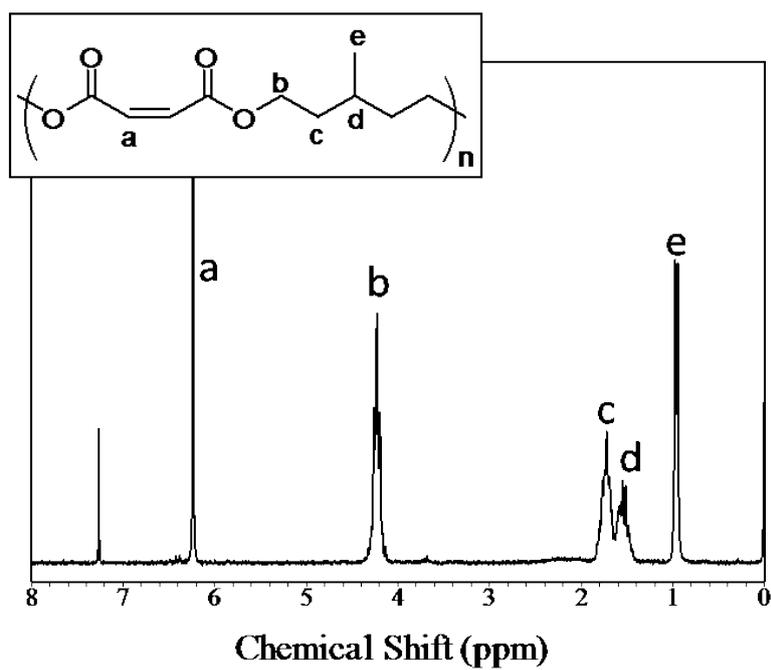


Figure S1. <sup>1</sup>H NMR spectrum of poly(MAn-*alt*-MPD).

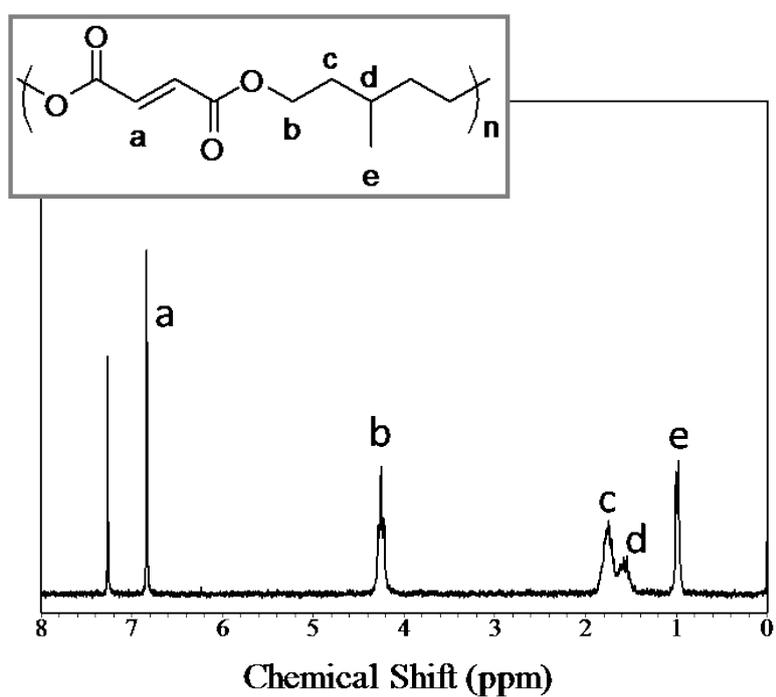


Figure S2. <sup>1</sup>H NMR spectrum of poly(FA-*alt*-MPD) (after isomerization of poly(MAn-*alt*-MPD) in DMF for 12 h.

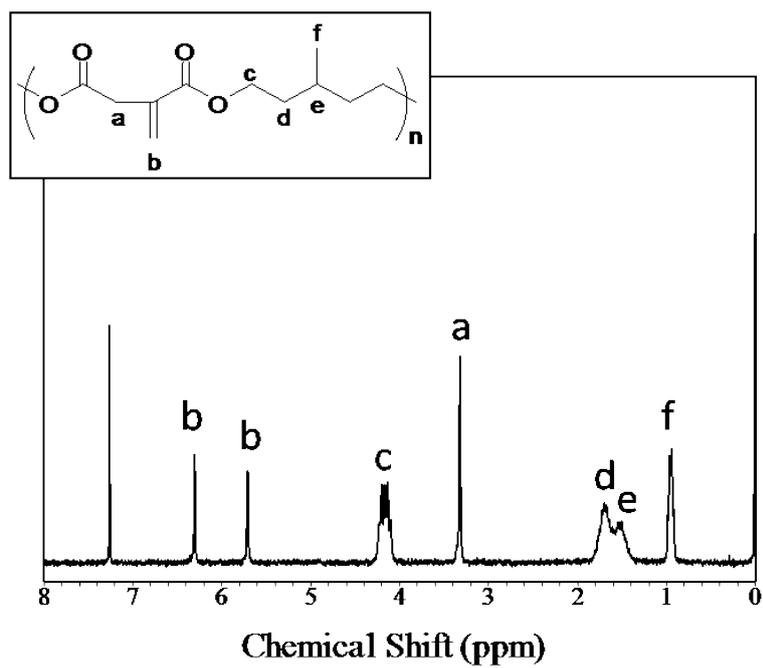


Figure S3. <sup>1</sup>H NMR spectrum of poly(IAn-*alt*-MPD).

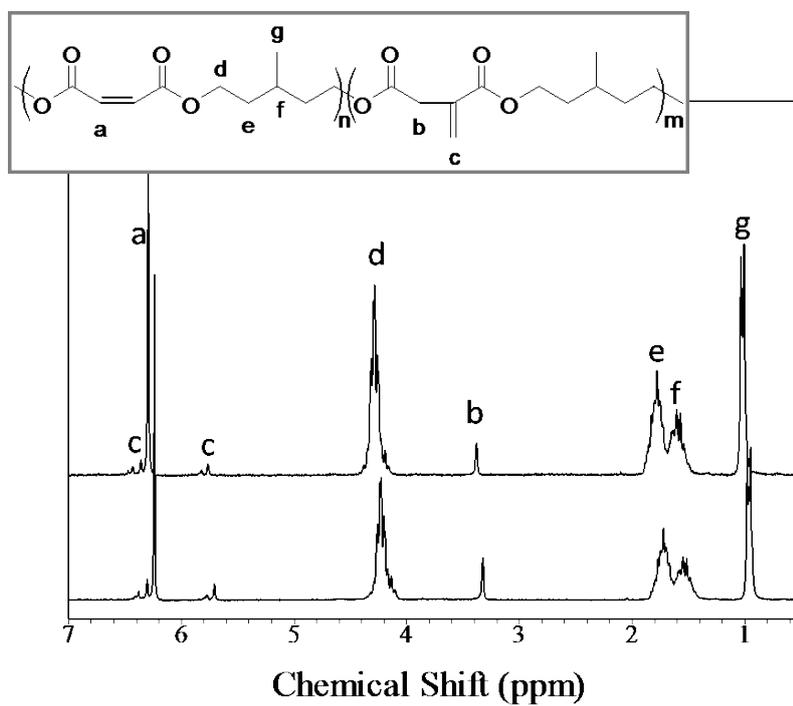


Figure S4. <sup>1</sup>H NMR spectra of poly(IAn-*co*-MAN-*co*-MPD)(upper, [IAn]<sub>0</sub>: [MAN]<sub>0</sub>=1:8; lower, [IAn]<sub>0</sub>: [MAN]<sub>0</sub>=1:4).

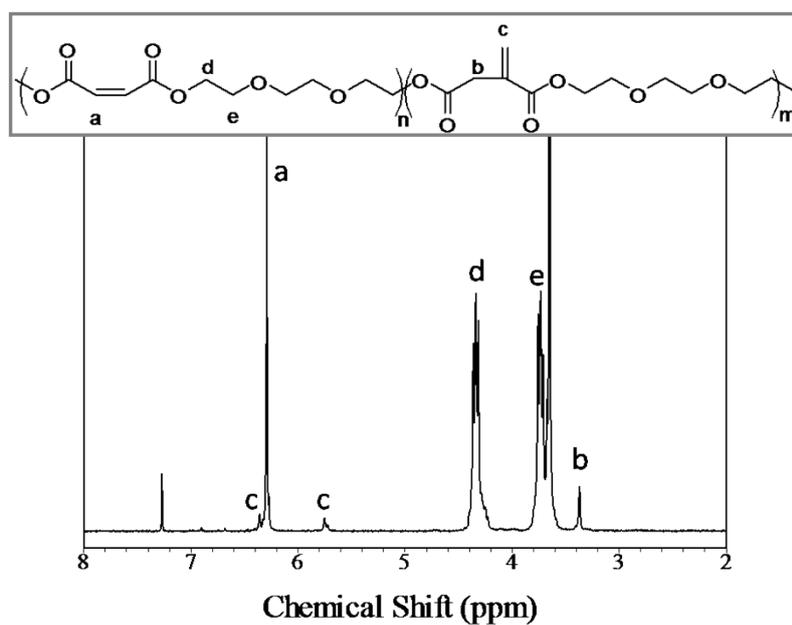


Figure S5. <sup>1</sup>H NMR spectrum of poly(IAn-co-MAN-co-TEG).

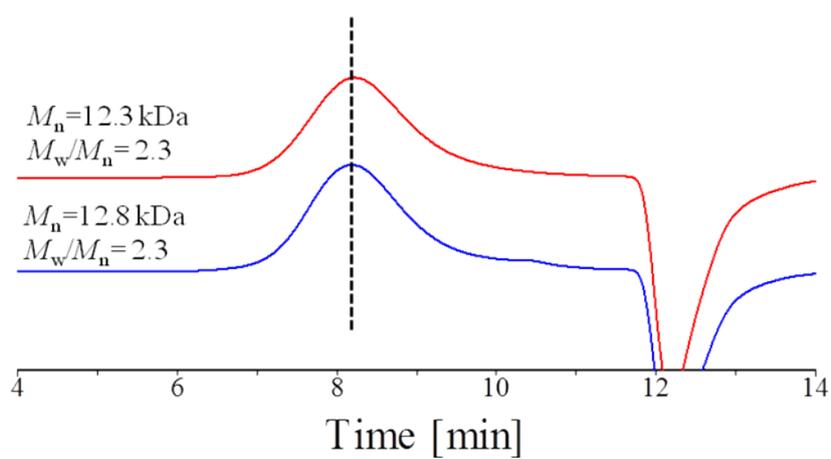
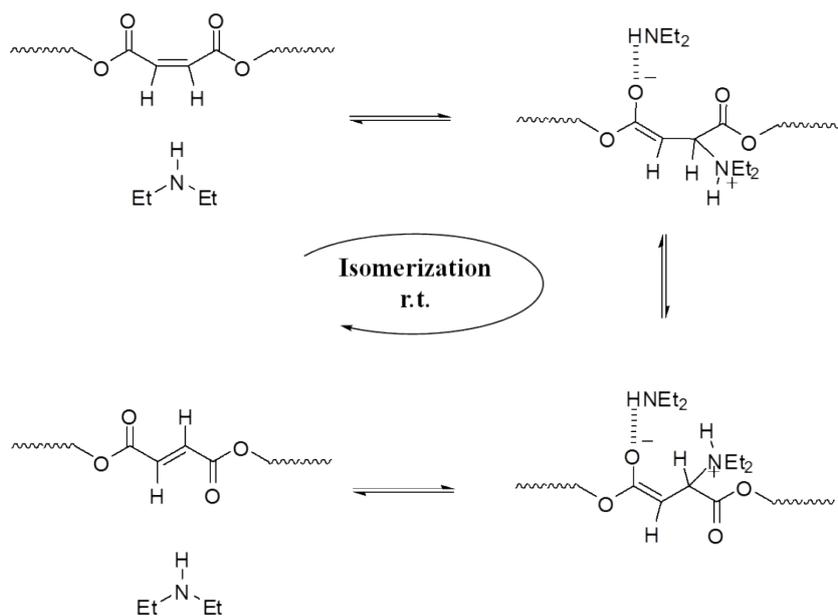
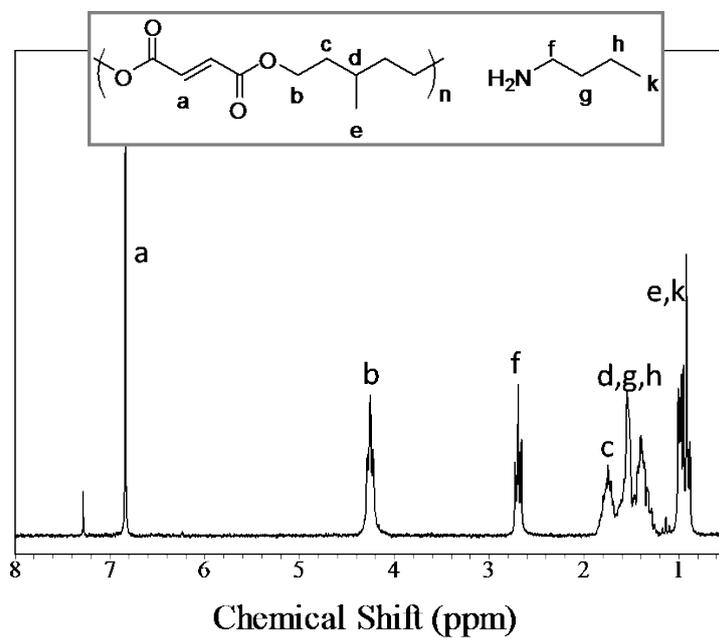


Figure S6. SEC curves of maleate polyester (blue line) and fumarate polyester after isomerization in DMF for 12 h (red line).



**Figure S7. Mechanism of isomerization of maleate double bonds to fumarate double bonds.**



**Figure S8.  $^1\text{H}$  NMR spectrum of product from reaction of poly(FA-*alt*-MPD) and *n*-butylamine at room temperature for 20 min (Table 3, entry 1).**

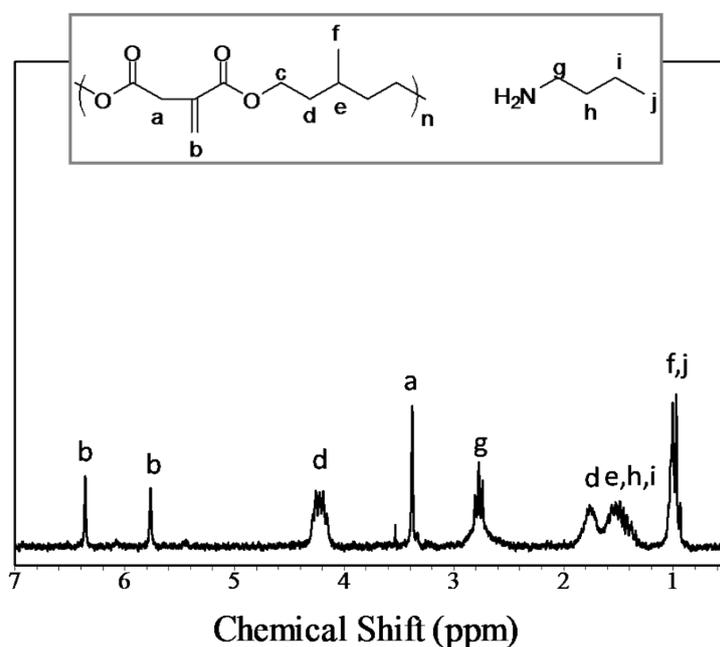


Figure S9.  $^1\text{H}$  NMR spectrum of product from reaction of poly(IAn-*alt*-MPD) and *n*-butylamine at room temperature for 20 min (Table 3, entry 2).

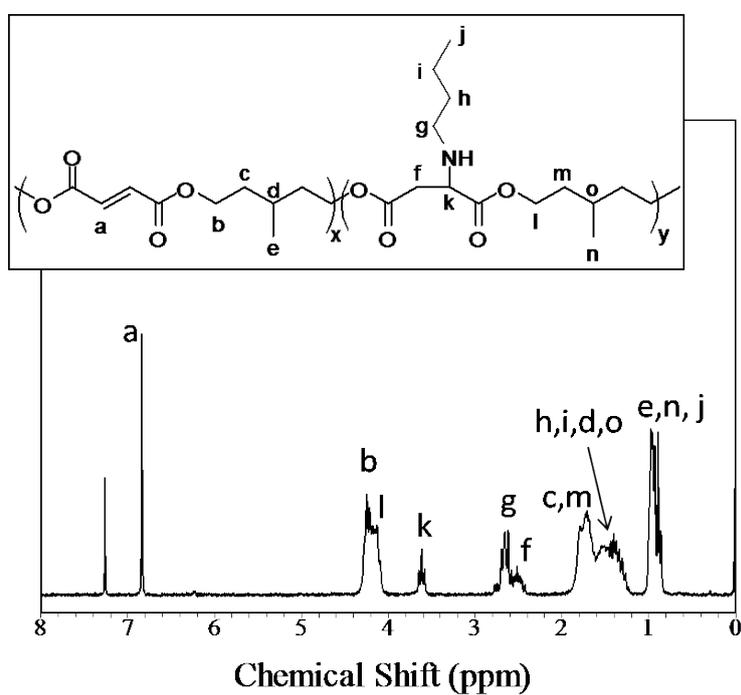


Figure S10.  $^1\text{H}$  NMR spectrum of poly(amino-ester) prepared by Michael addition of poly(MAN-*alt*-MPD) with *n*-butylamine at room temperature.

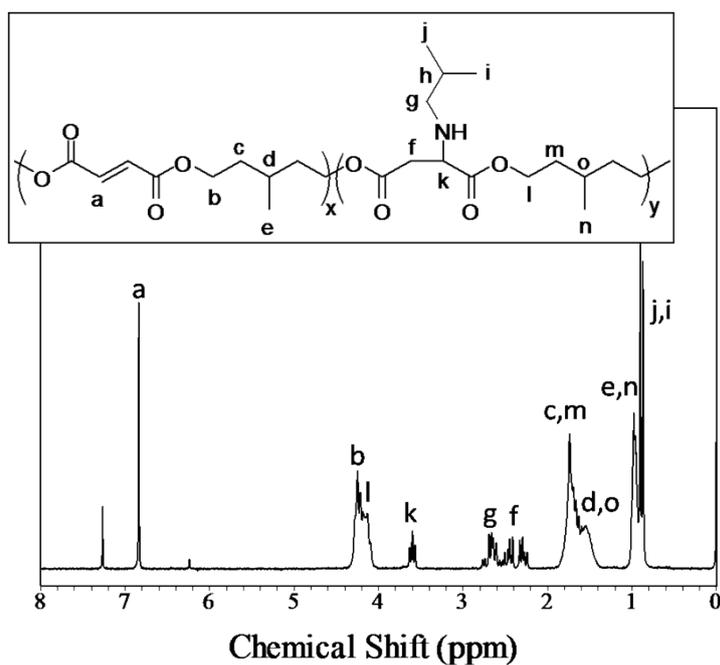


Figure S11. <sup>1</sup>H NMR spectrum of poly(amino-ester) prepared by Michael addition of poly(MAN-*alt*-MPD) with isobutylamine at room temperature.

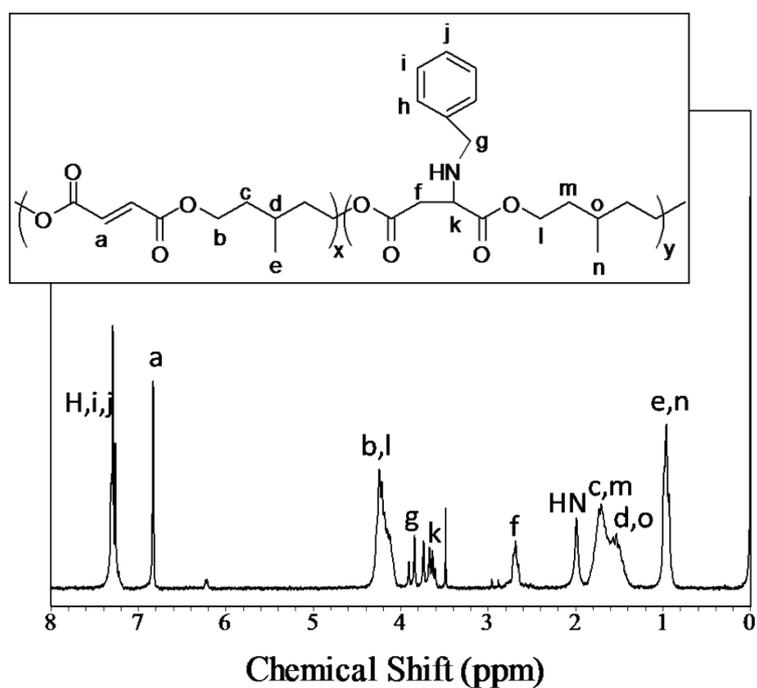
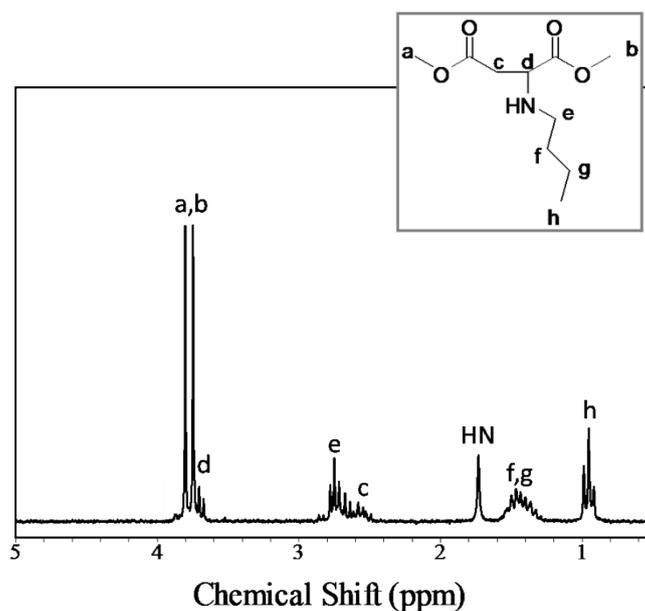
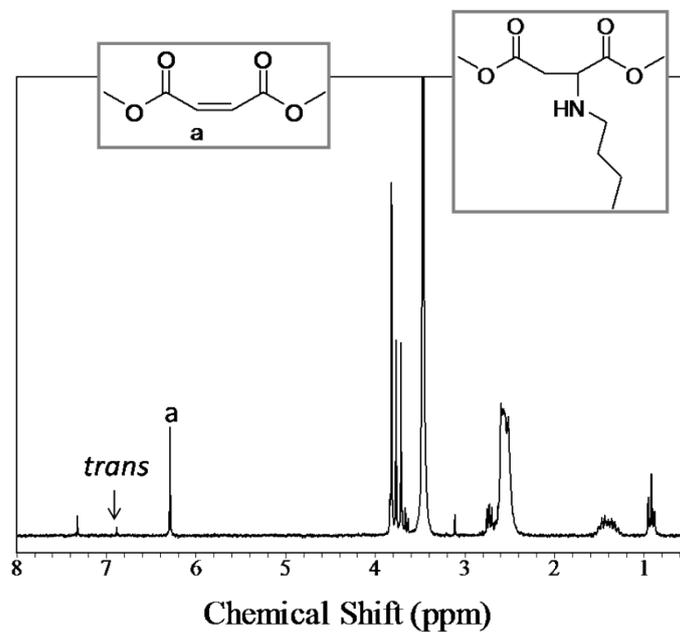


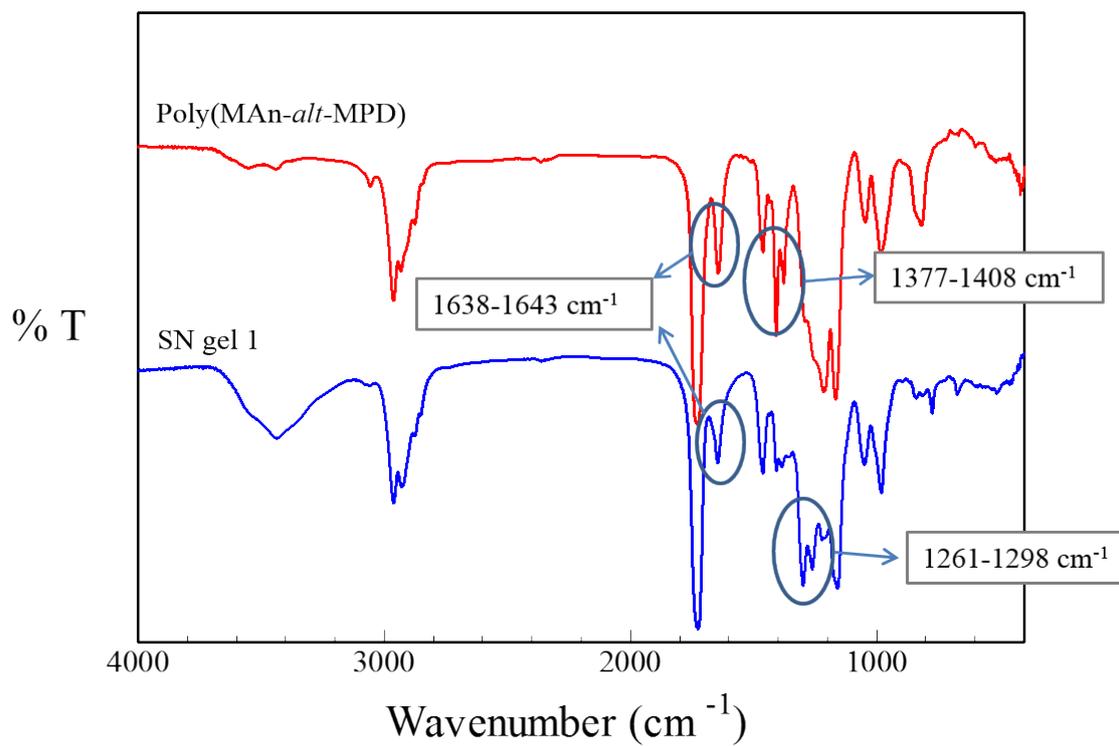
Figure S12. <sup>1</sup>H NMR spectrum of poly(amino-ester) prepared by Michael addition of poly(MAN-*alt*-MPD) with benzylamine at room temperature.



**Figure S13.**  $^1\text{H}$  NMR spectrum of dimethyl 2-(butylamino)butanedioate synthesized by Michael addition of dimethyl maleate with *n*-butylamine.



**Figure S14.**  $^1\text{H}$  NMR spectrum of model reaction. Dimethyl 2-(butylamino)butanedioate reacted with dimethyl maleate for 24 h, and only 4% of *cis* double bonds isomerized to *trans* double bonds.



**Figure S15.** FT IR spectra of poly(MAn-*alt*-MPD) before (red) and after (blue) cross-linked by 1,2-ethanediamine. The peaks at 1377-1408 cm<sup>-1</sup> ascribed to *cis* double bonds and the peaks at 1261-1298 cm<sup>-1</sup> assigned to *trans* double bonds.