Electronic Supplementary Material (ESI) for Polymer Chemistry.

Cheap and Fast: Oxalic Acid Initiated CO_2-based Polyols Synthesized by A Novel Preactivation Approach

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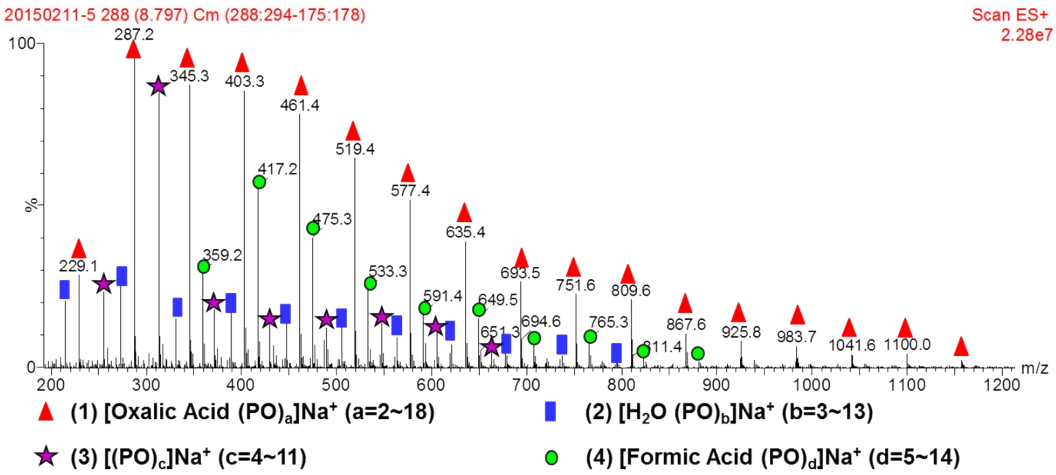

Figure S1. ESI-MS spectrum of copolymerization products at 10 min, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

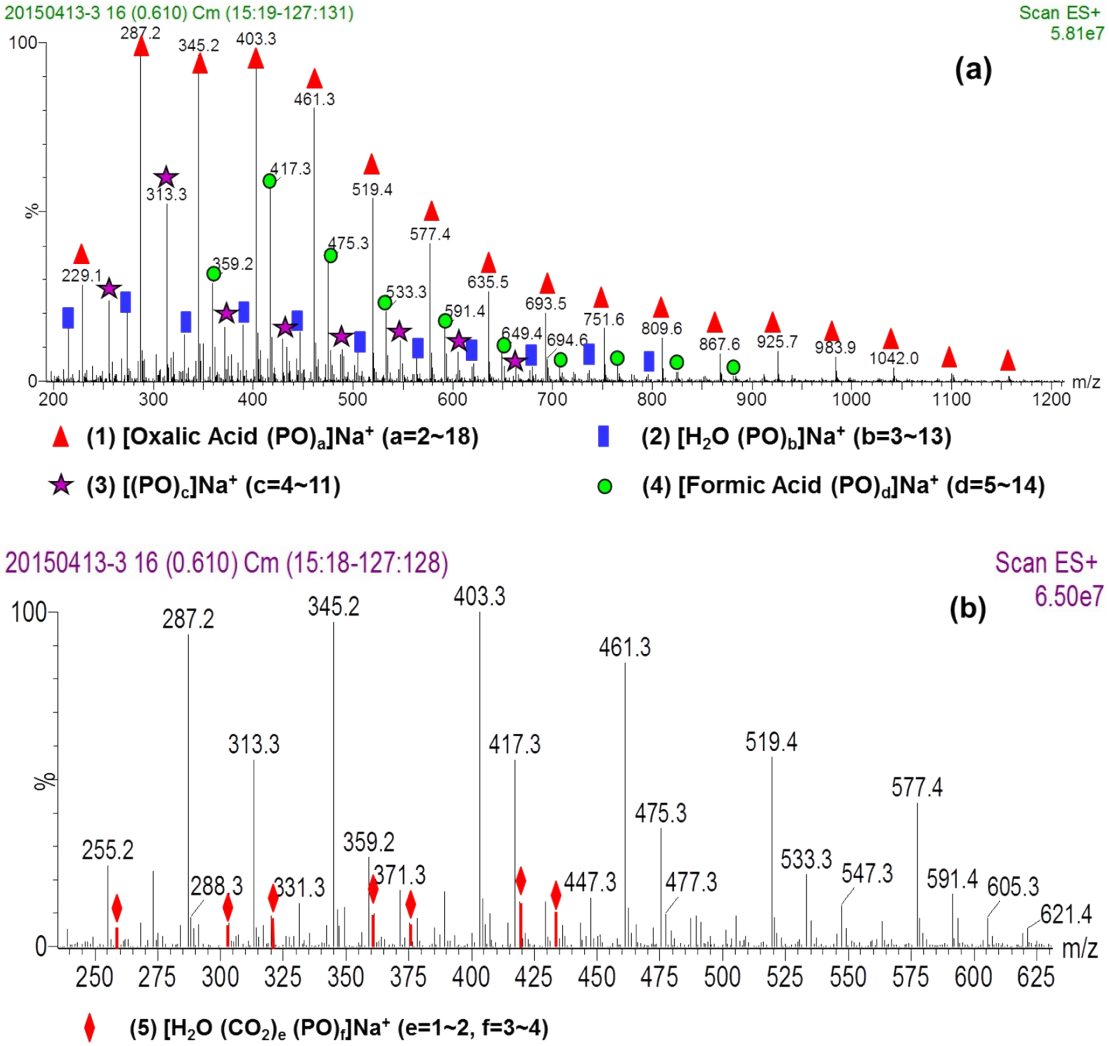

Figure S2. ESI-MS spectrum of copolymerization products at 15 min, a) full spectrum, b) magnified spectrum, m/z: 250~625. The copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

Apart from the same four species (Figure 1a in the main text), new species *(5)*, H_2O initiated CO_2 copolymer appeared with rather low relative abundance at the reaction time of 15 min (Figure S2b). This demonstrated that H_2O began to participate in the copolymerization, thus the induction period of H_2O system was about 15 min in present condition according to our previous definition.[1] Moreover, the observation of H_2O-reacted copolymer, $HO(CO_2)_1(PO)_3H$ and $HO(CO_2)_1(PO)_4H$ suggested that the incorporation of CO_2 happened first on the low molecular weight $HO(PO)_nH$ (n=3-4), though many oligo-ether diols existed in the copolymerization system (Figure S2b).

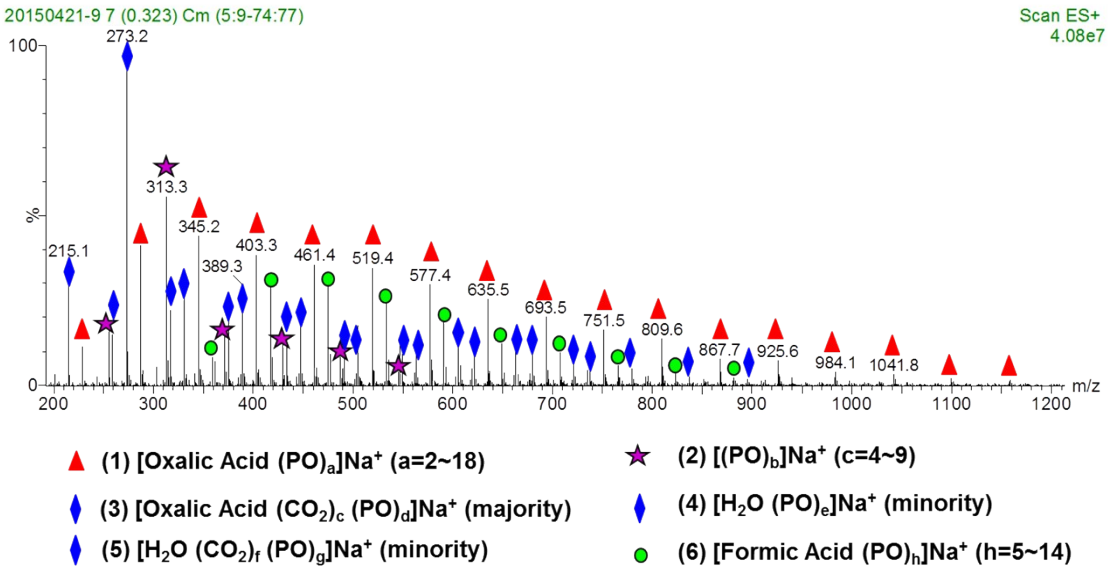

Figure S3. ESI-MS spectrum of copolymerization products at 60 min, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

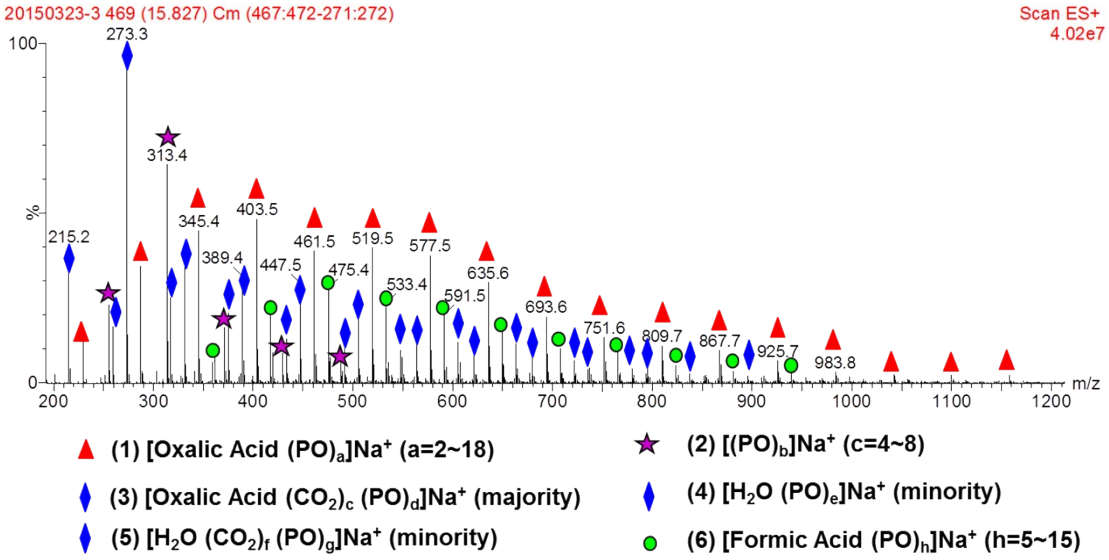

Figure S4. ESI-MS spectrum of copolymerization products at 120 min, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

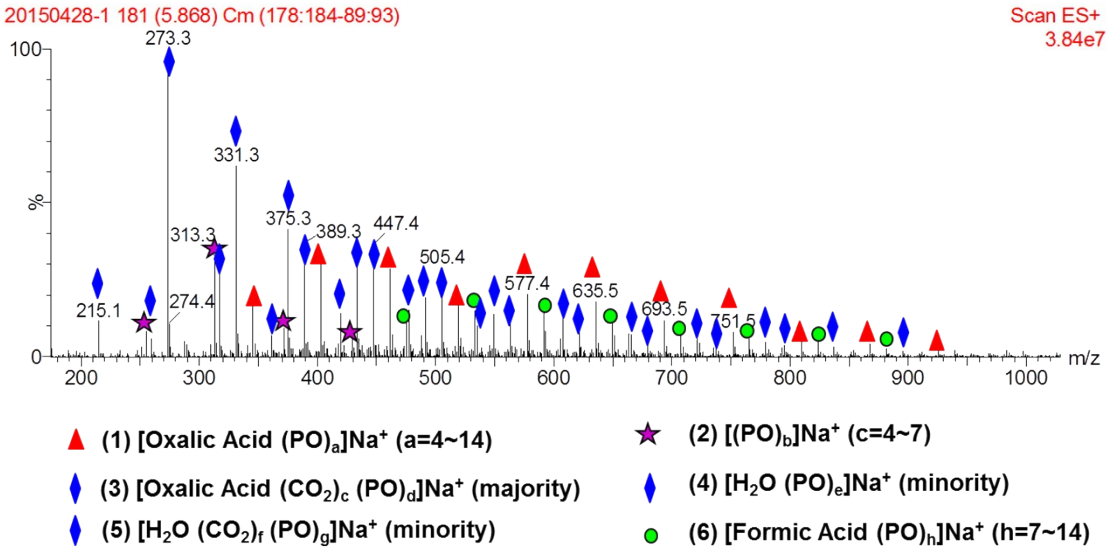

Figure S5. ESI-MS spectrum of copolymerization products at 140 min, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

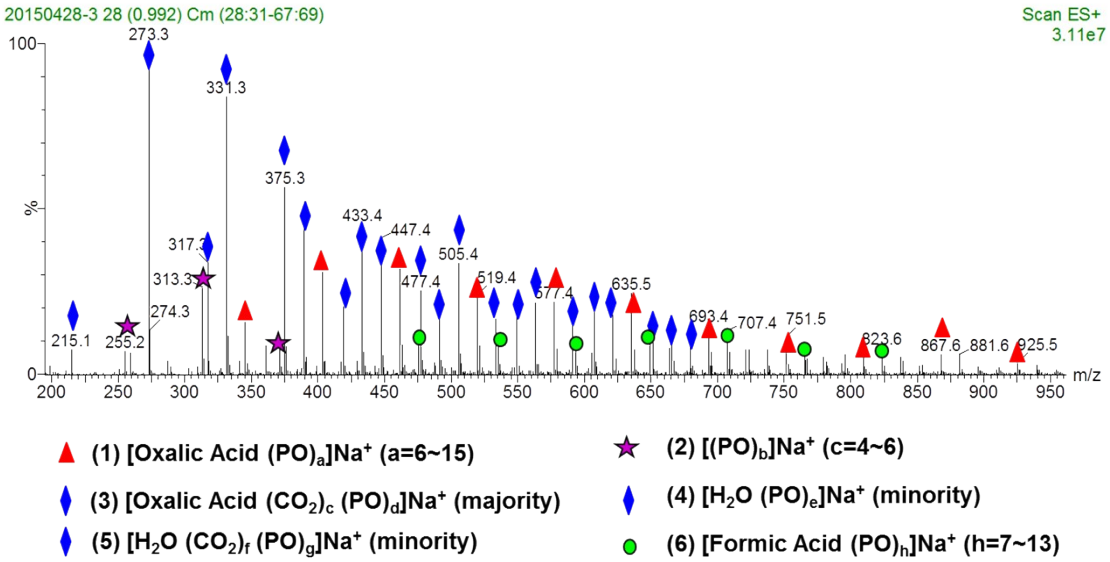

Figure S6. ESI-MS spectrum of copolymerization products at 160 min, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

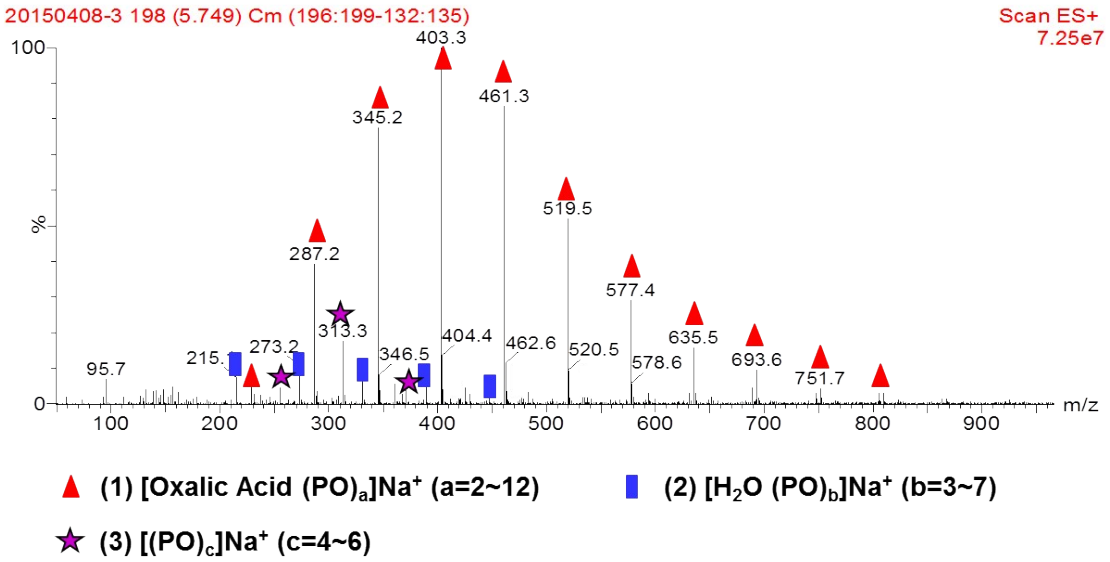

Figure S7. ESI-MS spectrum of reaction product of oxalic acid and PO, where the copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid and 10 ml PO.

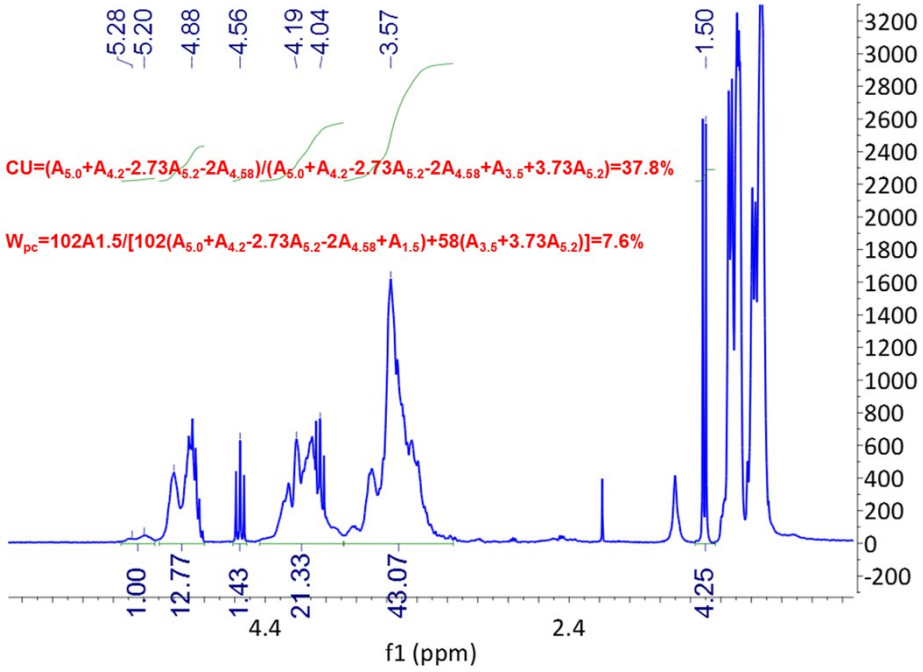

Figure S8. ^{1}H NMR spectrum of oxalic acid based oligo(carbonate-ether)diol with complete monomer conversion (diol comes from entry 10, Table 1).

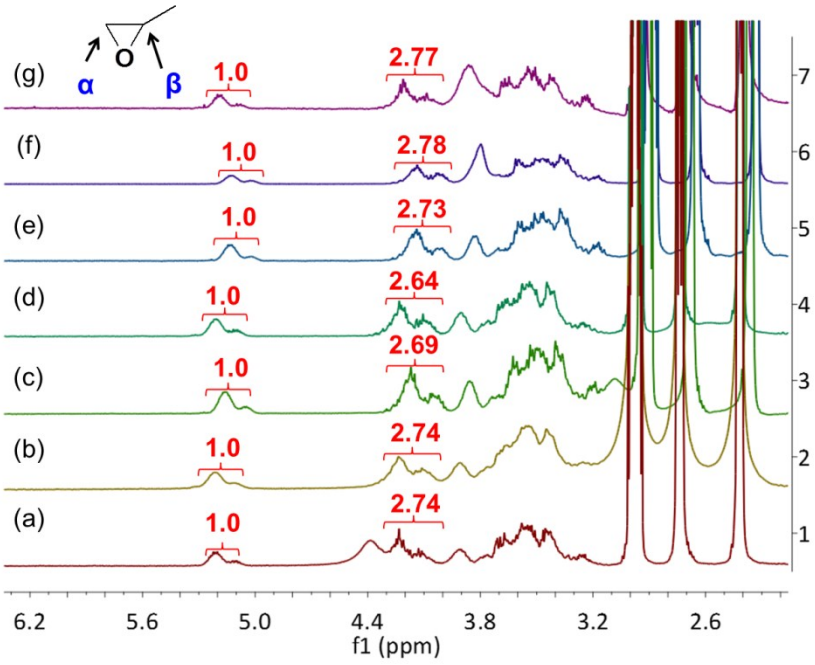

Figure S9. ^{1}H NMR spectra of products at different reaction times, (a) 15 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, where the reactions were carried out at 80 ^{o}C using 0.32 g oxalic acid, 10 ml PO. (f) and (g) were reacted for 15 min at the same conditions as above, except that 0.4g and 0.2 g oxalic acid were used, respectively.

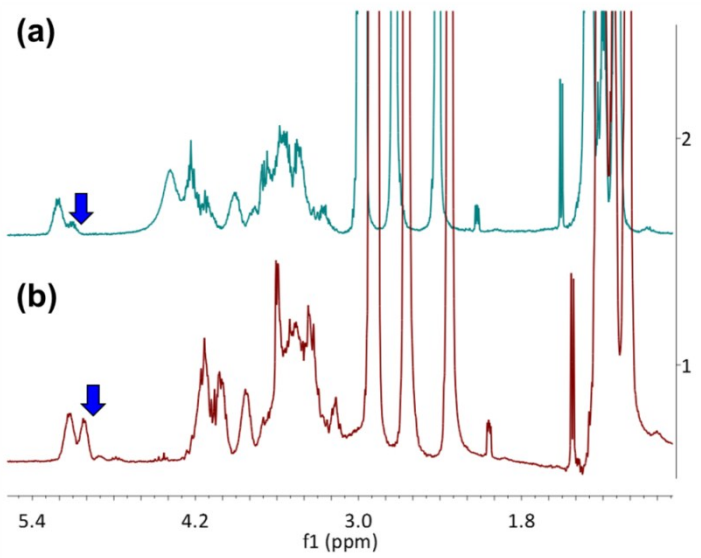

Figure S10. ^{1}H NMR spectra of (a) the product of pre-activation for 15 min, (b) the product of copolymerization for 0 min (preheating for 5 min) after the pre-activation for 15 min. The copolymerization reaction was carried out with 0.32 g oxalic acid, 20 mg DMC, 10 ml PO at 80 ^{o}C, 4 MPa CO_2 pressure.

1. S. J. Liu, Y. S. Qin, X. S. Chen, X. H. Wang and F. S. Wang, *Polymer Chemistry*, 2014, **5**, 6171-6179.