Colloquium on Polymer Science and Molecular Engineering Zhejiang University and the University of Chicago
12-16 April 2017

Branched Polytetrahydrofuran and Poly(tetrahydrofuran-co-ε-caprolactone) Synthesized by Janus Polymerization: A Novel Self-healing Material

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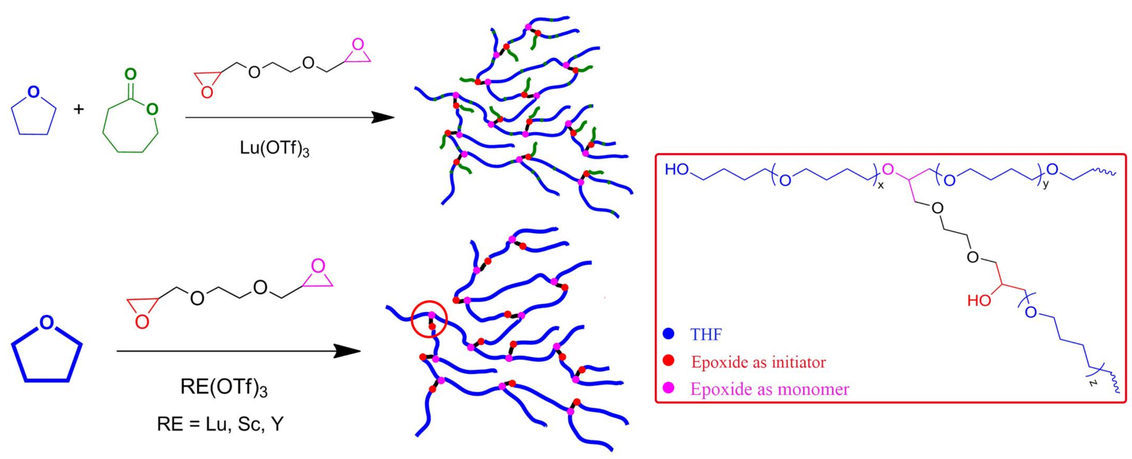
Abstract: The branching of synthetic polymers allows to design a wide range of macromolecules with complex architectures, and the increased number of the end-groups resulting from the branching process allows further modification which potentially increases greater flexibility in targeting applications. The Janus polymerization combines cationic and anionic polymerizations into growing chains with two different chain ends. This provides a novel pathway to produce topologically interesting polymers. Polytetrahydrofuran (PTHF) is a biocompatible soft-segment in thermoplastic polyurethane elastomers because of its low glass-transition temperature (Tg), excellent resiliency, high fungal resistance and hydrolytic stability. However, its intrinsic brittleness due to high crystallinity and low Tg pose considerable challenges, which limits its large-scale applications.Here we report the first synthesis of branched poly(THF-co-ε-caprolactone) (bPTC) and polytetrahydrofuran (bPTHF). Catalyzed by $RE(OTf)_3$ (RE=Lu, Sc and Y), one epoxide group of ethylene glycol diglycidyl ether (EGDE) initiates the Janus polymerization of THF with CL while the other acts as a comonomer. The mechanism and branched topology of the products are discussed in detail. The bPTHF shows unprecedented tensile strength and self-healing properties.

Part I. Polymerization design



Scheme 1. Synthesis of bPTC and bPTHF catalyzed by $Lu(OTf)_3$ and EGDE

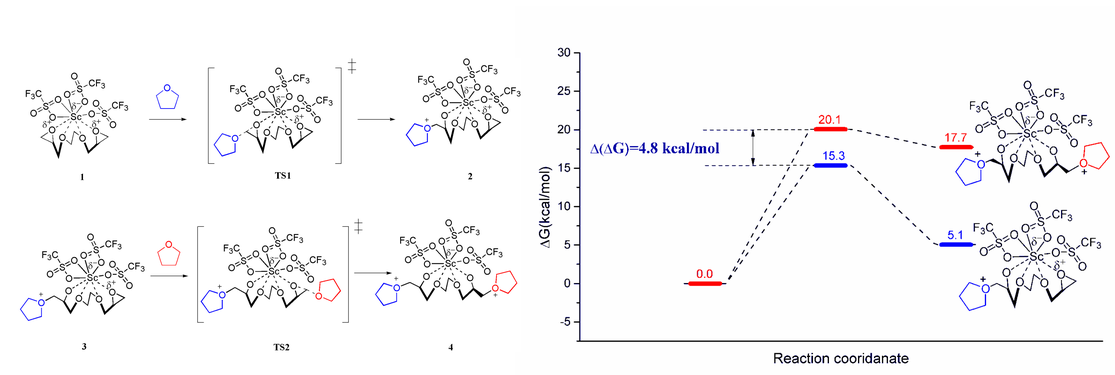


Figure 1. DFT-based Gibbs free energy profiles of the first (blue line) and the second (red line) cationic initiation processes of EGDE by THF in the presence of $Sc(OTf)_3$

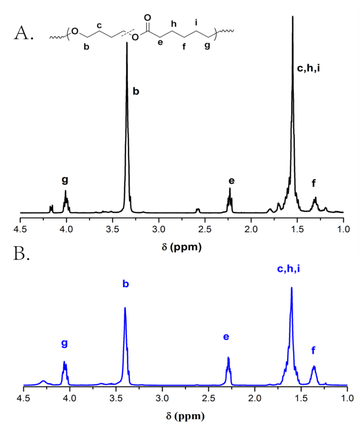


Fig. 2. (A) 1H NMR spectra of bPTC terminated by H_2O (Table 1, #2). The small signals at 4.2, 2.6, 1.8 and 1.7 ppm belong to the remaining CL monomers. (B) 1H NMR spectra of bPTC after degradation with hydrochloric acid in THF.

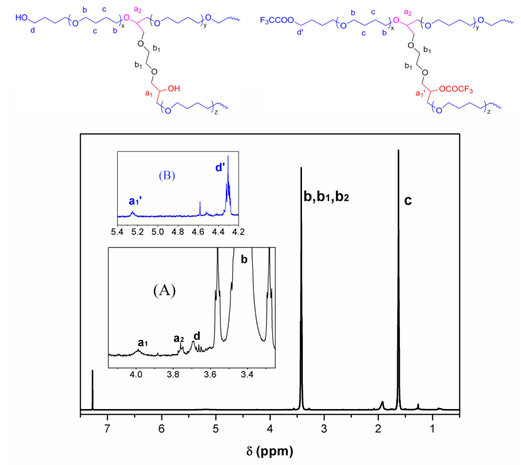


Fig. 3. ^1H NMR spectra of branched PTHF terminated by water (Table 1, #3) with a magnified view in inset A. The inset B shows the corresponding 1H NMR spectrum after the addition of trifluoroacetic anhydride.

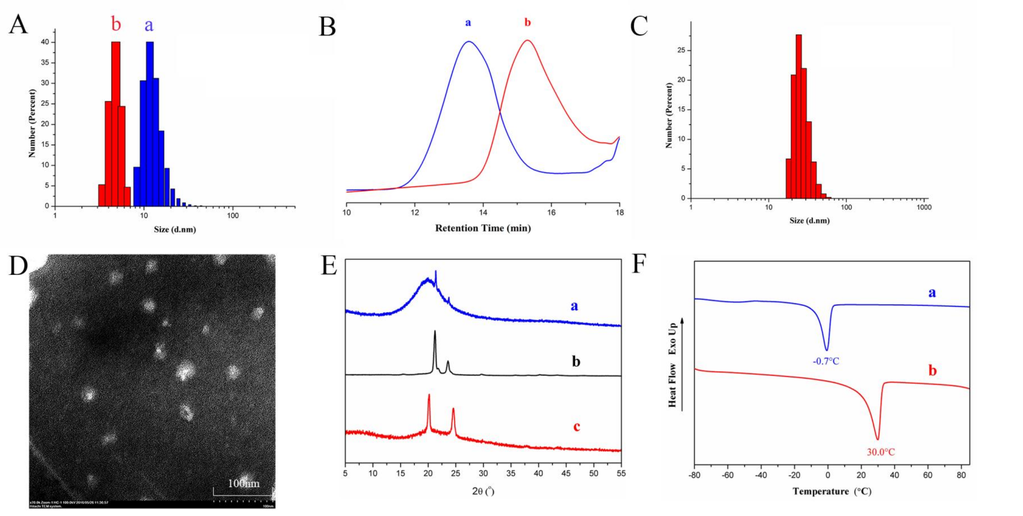


Fig. 4. (A) Size distribution histogram of bPTC (Table 1, #2) before (a) and after degradation by hydrochloric acid in THF (0.5 mg/mL) at 25 °C (b). (B) SEC trace of bPTC (Table 1, #2) before (a) and after degradation by hydrochloric acid in THF (0.5 mg/mL) at 25 °C (b). (C) Size distribution histogram of bPTHF (Table 1, #3) in THF (0.5 mg/mL) at 25 °C. (D) TEM image of bPTHF (Table 1, #3) the scale bar is 100 nm. (E) X-ray diffraction patterns of bPTC (Table 1, #1) (a), homopolymer PCL (Mn = 5 kDa) and (b) bPTHF (Table 1, #3) (c). (F) DSC curves of bPTC (Table 1, #1) (a) and bPTHF (Table 1, #3) (b).

Part II. Synthesis of branched PTC and PTHF

Table 1. Janus polymerization of THF and CL catalyzed by $RE(OTf)_3$ and EDGE at 45 °C.

Run	RE	$RE(OTf)_3$:EDGE: THF:CL (molar ratio in feed)	Time (h)	Yield [a] (%)		H^{a1}/H^{a2} [b] (in polymer)	[THF]/[CL] [b] (in polymer)
				THF	CL		
1	Lu	1: 0.3: 200: 100	4	24.5	9.1	1.1	5.7
2	Lu	1: 0.4: 200: 100	6.5	27.5	16.2	0.9	3.4
3	Lu	1: 0.2: 200: 0	5	63.1	-	0.9	-
4	Lu	1: 0.3: 200: 0	5	79.4	-	0.8	-
5	Sc	1: 0.3: 200: 0	0.33	74.2	-	0.8	-
6	Y	1: 0.3: 200: 0	0.33	57.8 [c]	-	1.0	-
7	Lu	1: 0.5: 200: 0	1	gel	-	-	-

[a] Determined by 1H NMR analysis. [b] Molar ratio determined by 1H NMR analysis. [c] Part of the product did not completely dissolved in THF and is presumably crosslinked.

Part III. Self-healing behavior and Tensile properties

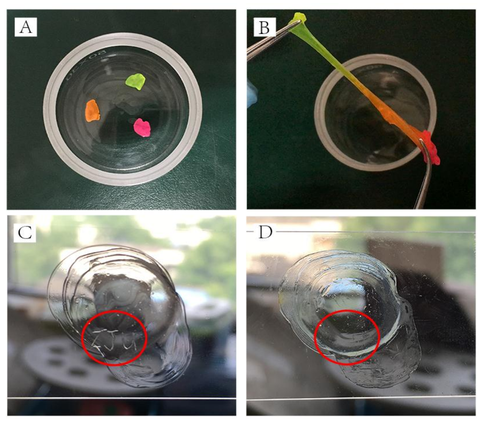


Fig. 5. (A) The bPTHF swollen by acetone with different colors (containing Nile red, DCM and coumarin 6). (B) Five minutes after self-healing. (C) The bPTHF film carved "ZJU" on the surface and (D) recovered surface of the film after the treatment of hot acetone vapor.

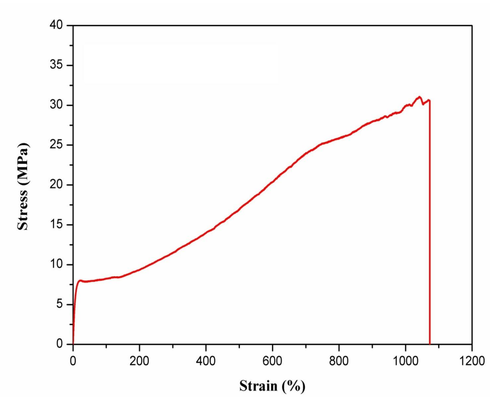


Fig. 6. Stress-strain curves for bPTHF (Table 1, #5).

Conclusions

Janus polymerizations of THF with CL using EGDE as initiator and $RE(OTf)_3$ as catalyst produce novel bPTC and bPTHF polymers for the first time. Both DFT calculation and experimental characterization demonstrate the dual roles of di-epoxide compound EGDE acting as both initiator and comonomer. Introducing CL units into the branched materials provides the capability of degradation. Both semi-crystalline bPTC and bPTHF exhibit the tremendous tensile property superior to the linear PTHF or random poly(THF-co-CL), which contributes to the co-existence of amorphous and crystallized PTHF or PCL regions. The obtained bPTHFs exhibit self-healing behavior with promising applications.

Acknowledgement

Financial support from the Zhejiang Provincial Natural Science Foundation of China (LR15B040001) is acknowledged.

References

(1)L. You, J. Ling, *Macromolecules* **2014**, 47, 2219.
(2)L. You, Z. Shen, J. Kong, J. Ling, *Polymer* **2014**, 55, 2404.