Thermoplastic elastomer by Janus polymerization: One-step synthesis of multiblock copolymers

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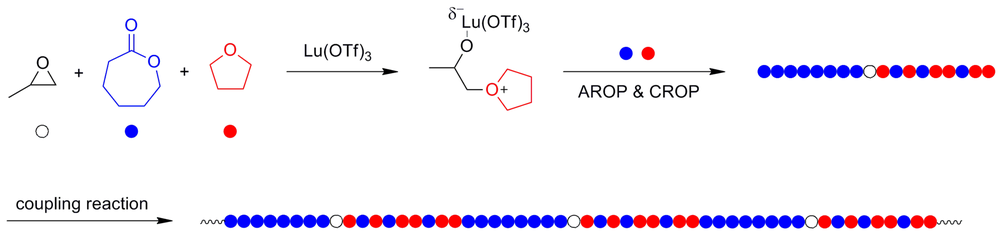
Introduction

Multiblock copolymers (MBCPs) composing of poly(ε-caprolactone) (PCL) and poly(ε-caprolactone-*r*-tetrahydrofuran) (P(CL-*r*-THF)) segments were synthesized in a one-step process by "Janus polymerization",[1] a newly raised synthetic protocol. Janus polymerization included an anionic and a cationic polymerizations on both ends of a single living polymer chain, and finally coupled into multiblock copolymers. In this case, *in-situ* generated lutetium compound initiated anionic ring-opening polymerization (ROP) of CL and cationic ROP of CL with THF at the two chain ends, producing PCL and P(CL-*r*-THF) segments, and followed by coupling reaction of ionic propagation sites. The obtained well-defined MBCPs had relatively high molecular weight up to 131 kg/mol and exhibited thermoplastic elastic property with excellent elongation up to 2610% in tensile tests. The repeating blocks formed interesting phase separation observed by AFM. The novel biodegradable elastomers had negligible cytotoxicity and were promising in medical applications.[2]

Results and Discussion

Part I. Synthesis of MBCPs



Scheme 1. Synthesis of multiblock copolymers: Janus polymerization of CL and THF

Table 1. Janus polymerization of CL and THF

Sample[a]	[Lu]/[PO]/[CL]/[THF]	T (ºC)	$M_{n,\ SEC}$ (k Da)	$Đ_{SEC}$	CL wt% (%)[b]
JCT1	1/1.5/50/200	25	96.6	2.09	53.3
JCT4	1/1.5/100/200	45	131.0	2.06	88.4

[a] Polymerized for 330 h
[b] Determined by ^{1}H NMR in $CDCl_3$ calculated as: $[2I_a \times 114/(2 \times I_a \times 114+I_b \times 72)]$

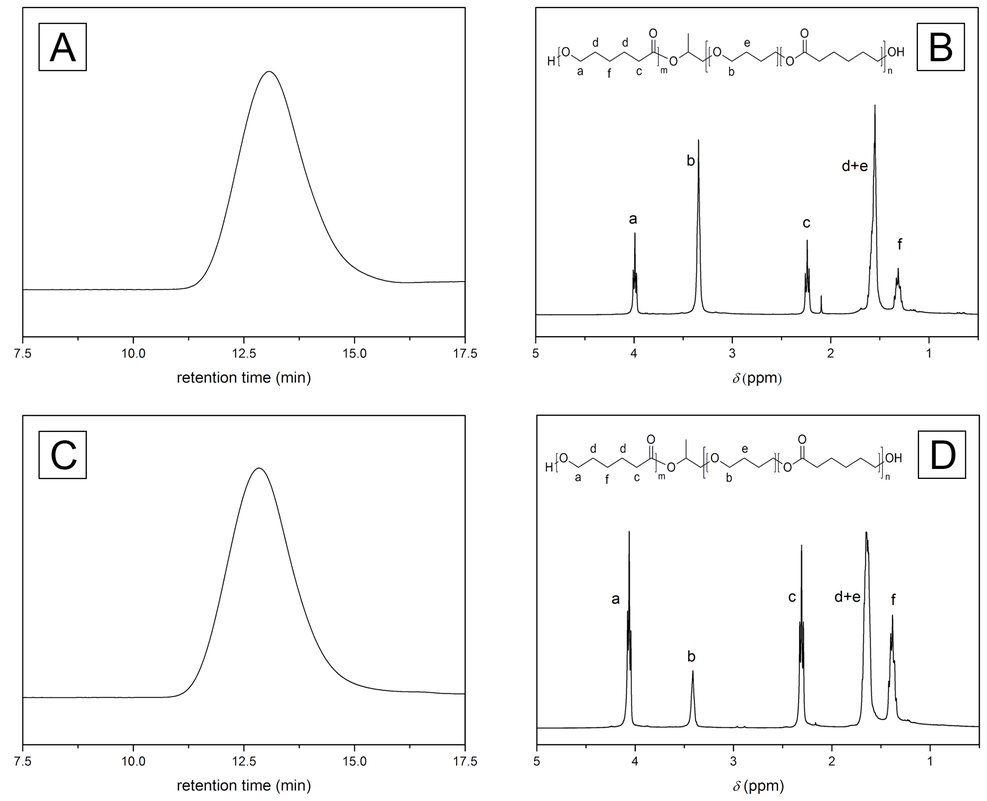


Figure 1. SEC traces and ^{1}H NMR spectra of of **JCT1** (A, B) and **JCT4** (C, D)

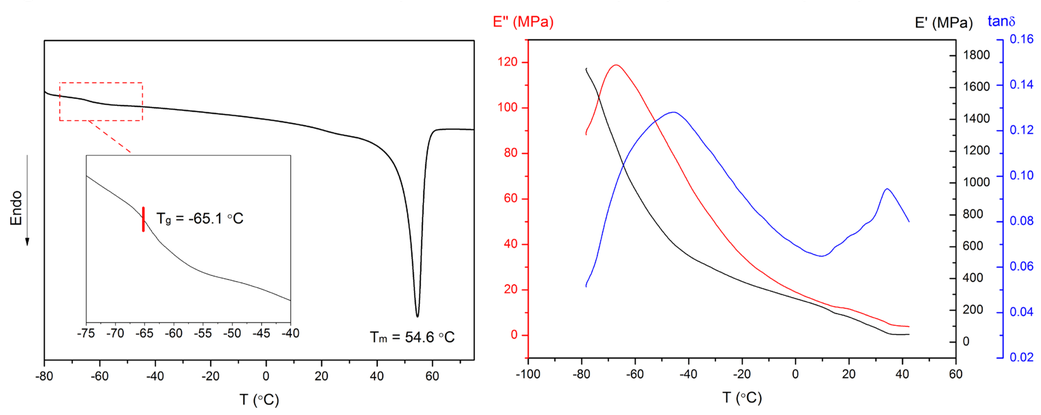


Figure 2. DSC and DMA curves of **JCT1**

Part II. Characterizations of MBCPs

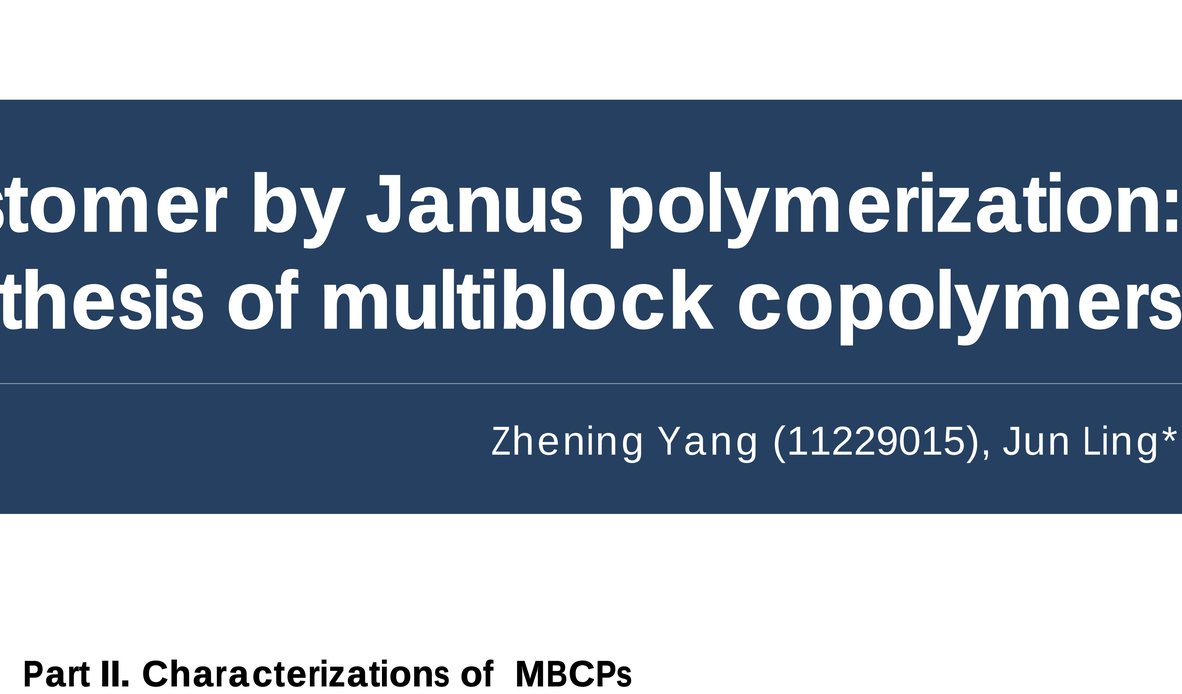


Figure 3. AFM phase images of **JCT1** after (A, B) and before (C, D) annealing

Figure 4. AFM phase images of **JCT4** after (A, B) and before (C, D) annealing

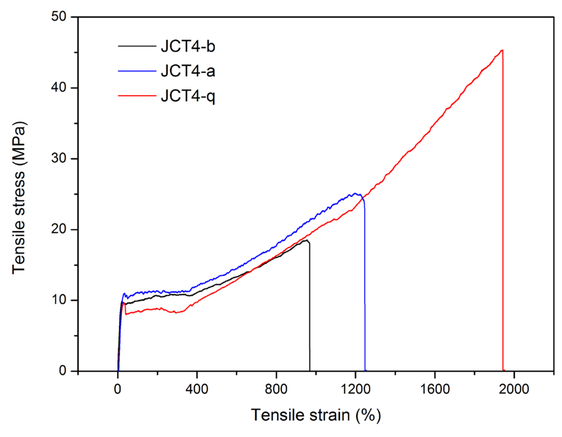


Figure 5. Stress–strain curves of **JCT4**

Table 2. Tensile Data for MBCPs

Sample[a]	Young's modulus (MPa)	tensile stress (MPa)	tensile strain (%)
JCT1-b	41.0	20.0	2610
JCT1-a	32.1	22.5	2268
JCT1-q	24.7	24.0	2545
JCT4-b	124.0	17.1	1020
JCT4-a	82.1	25.1	1246
JCT4-q	76.4	45.4	1942

[a] b: before heat treatment;
a: annealing;
q: quenching.

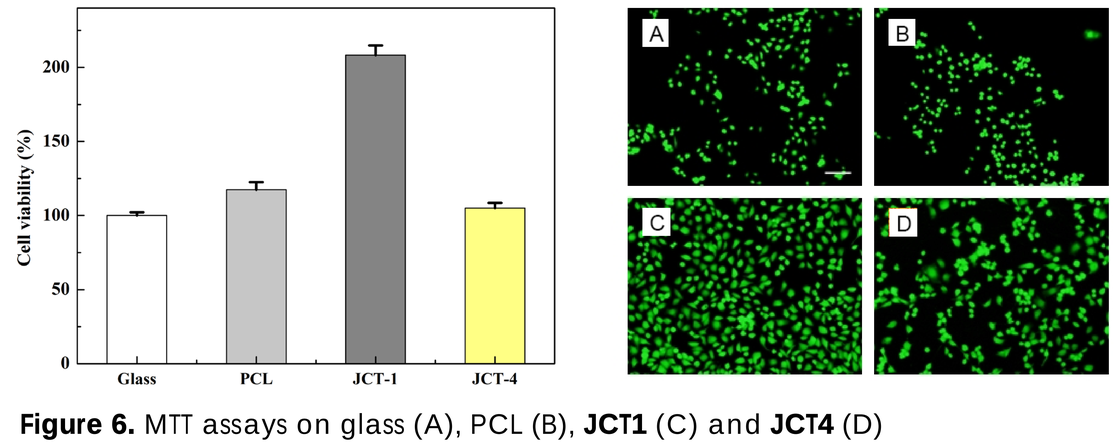


Figure 6. MTT assays on glass (A), PCL (B), **JCT1** (C) and **JCT4** (D)

Conclusion

High molecular weight MBCPs with well-defined structures were synthesized by Janus polymerization, confirmed by ^{1}H NMR and SEC. Their thermal properties were characterized by DSC and DMA, showing a T_g at -65.1 ºC and a T_m at 54.6 ºC of PCL blocks and a T_g at 35 ºC of P(THF-*co*-CL) blocks. For MBCPs with different fractions of CL, different microphase separation behaviors and mechanical properties responding to heat treatments were observed. It is worth mentioning that after quenching, even for CL rich sample JCT4, excellent elongation up to 1942% and strength up to 45.4 MPa were achieved. Accompanying with the biocompatible property concluded from MTT assay, a bright future of materials synthesized by Janus polymerization in applications such as biomedical and tissue engineering is illustrated.

Acknowledgement

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Reference

[1] L. You, J. Ling, *Macromolecules* **2014**, 47, 2219.
[2] J. Lin, W. Chen, Z. Shen, J. Ling, *Macromolecules* **2013**, 46, 7769.