Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

The synthesis and characterization of processable polyrotaxane based triblock copolymer via "two steps" strategy

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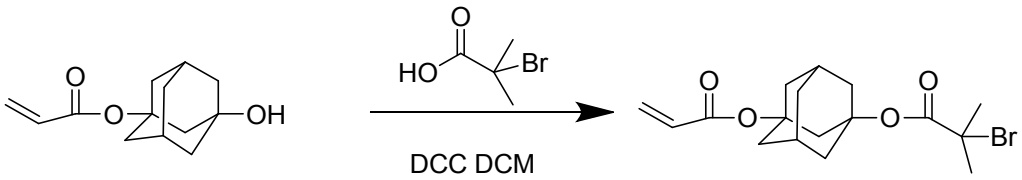
1. The synthesis and characterization of AD stopper



Scheme S-1 The synthetic route of AD stopper.

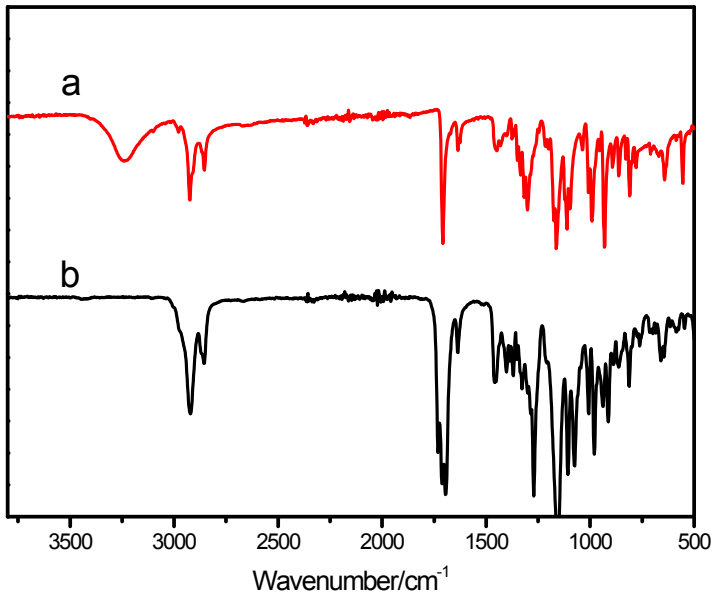


Fig. S-1 FTIR spectra of HADA (a) and AD stopper (b).

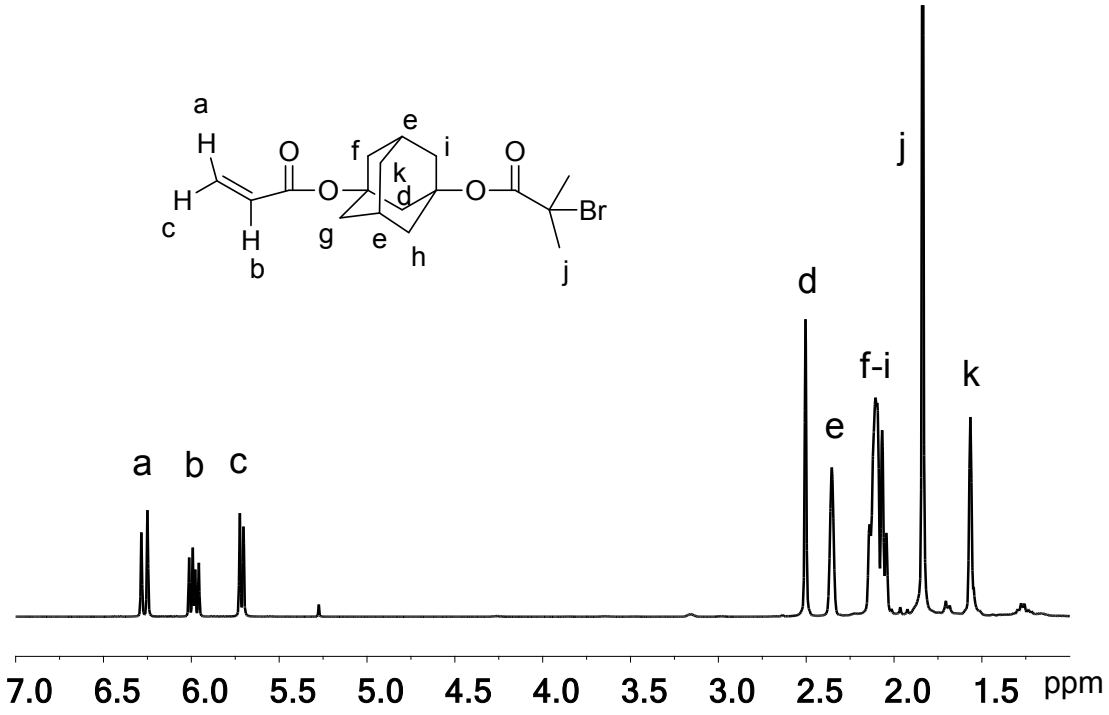
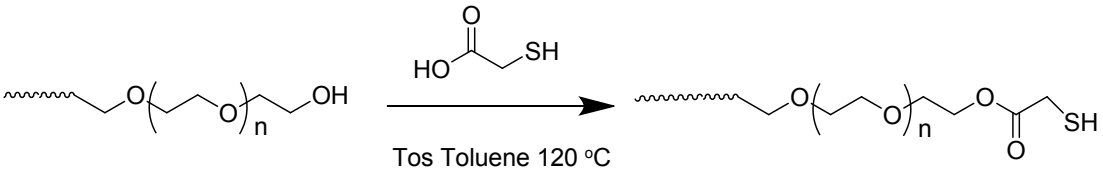


Fig. S-2 ^{1}H NMR spectra of AD stopper in $CDCl_3$.

As shown in Scheme. S-1, the AD stopper was synthesized by esterfication between HADA and 2-bromo-2-methylpropionic acid. The IR spectrum of AD stopper was shown in Fig.S-1. Compared with HADA, the hydroxyl peak at 3400 cm^{-1} disappeared in AD stopper's spectrum while the stretching vibration peak of carbonyl at 1700 cm^{-1} enhanced significantly. Furthermore, the NMR spectrum (Fig.S-2) showed all the resonance peaks were well assigned to the corresponding protons of AD stopper. All the above results implied that AD stopper was synthesized successfully.

2. The synthesis and characterization of SHPEG



Scheme S-2 The synthetic route of SHPEG.

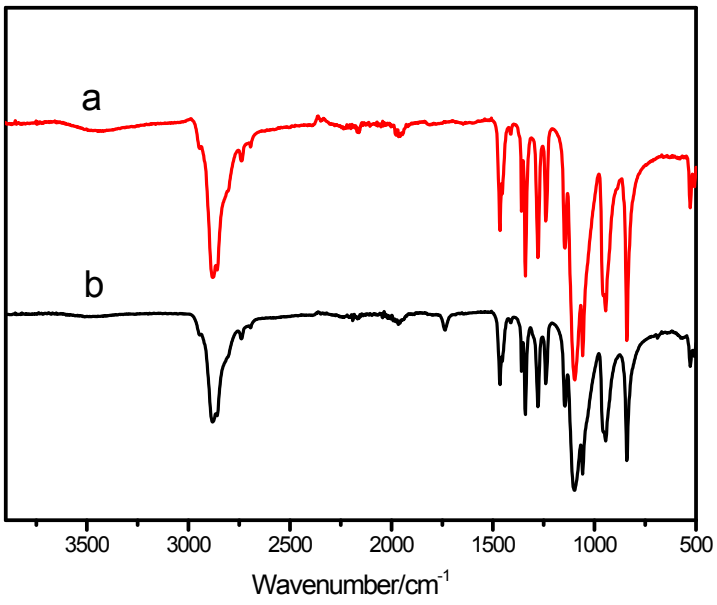


Fig. S-3 FTIR spectras of PEG4000 (a) and SHPEG (b).

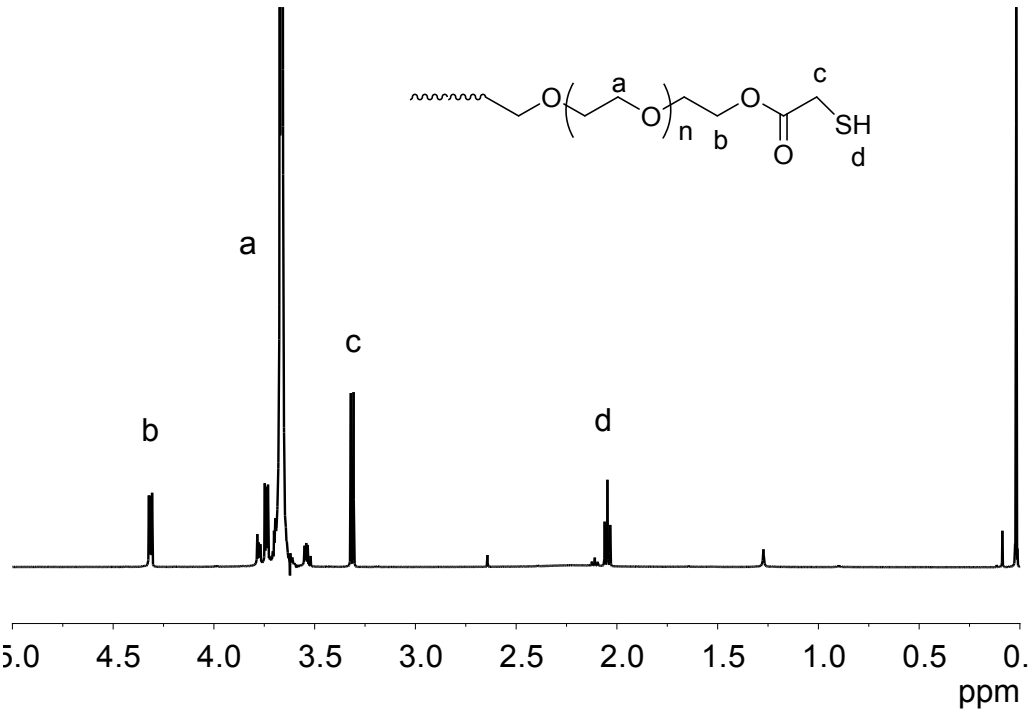
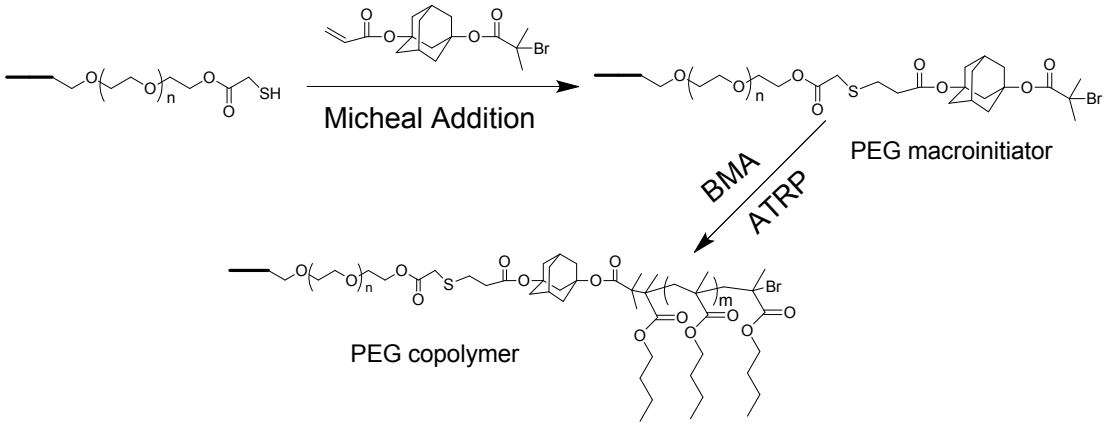


Fig. S-4 ^{1}H NMR spectra of SHPEG in $CDCl_3$.

As described in Scheme. S-2, the thiol terminated PEG(SHPEG) was prepared via the reaction between its hydroxyl and thioglycolic acid. The IR spectrum(Fig.S-3) showed in SHPEG's spectrum the hydroxy's absorption peak in PEG's spectrum disappeared, whereas the carbonyl peak at 1695 cm^{-1} appeared. Furthermore, all the resonance peaks were well assigned to the corresponding protons of SHPEG in Fig.S-4. These results definitely confirmed the SHPEG was synthesized successfully.

3. The synthesis and characterization of PEG based triblock copolymer (PEG copolymer)



Scheme S-3 The synthetic route of PEG copolymer.

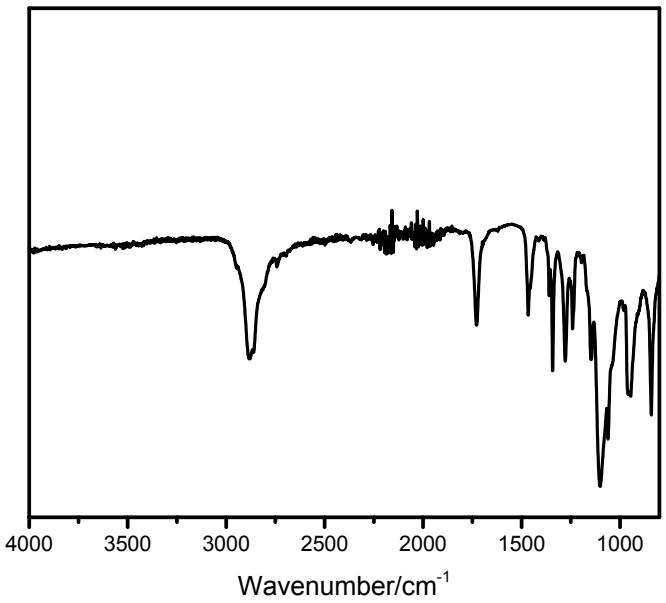


Fig. S-5 FTIR spectrum of PEG macroinitiator

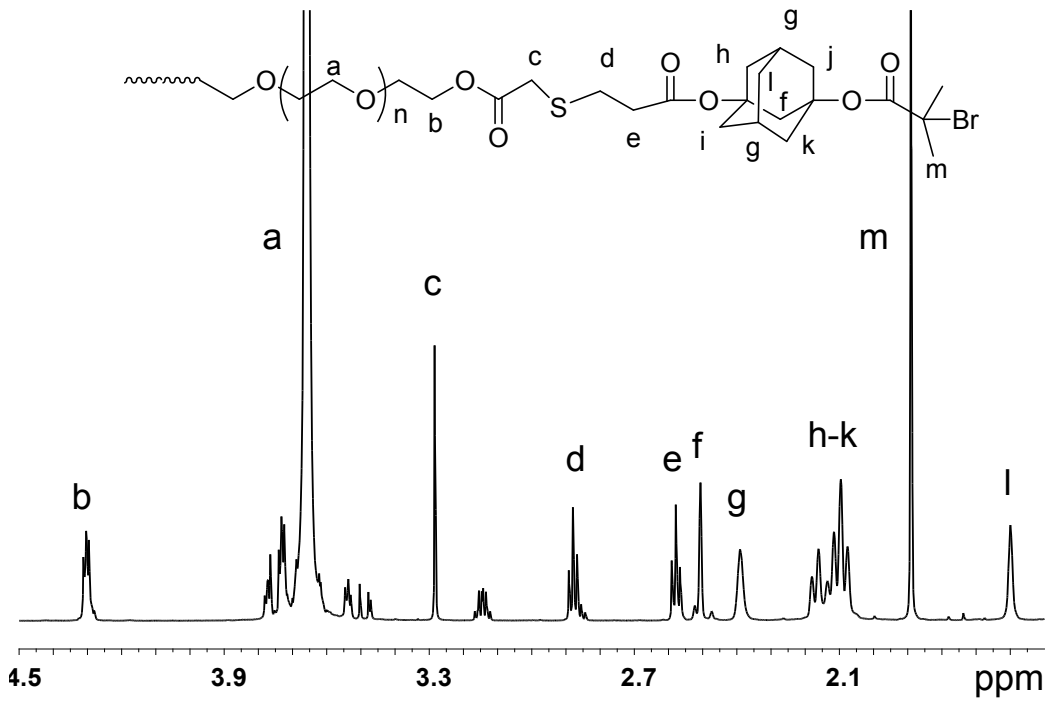


Fig. S-6 ^{1}H NMR spectrum of PEG macroinitiator in $CDCl_3$.

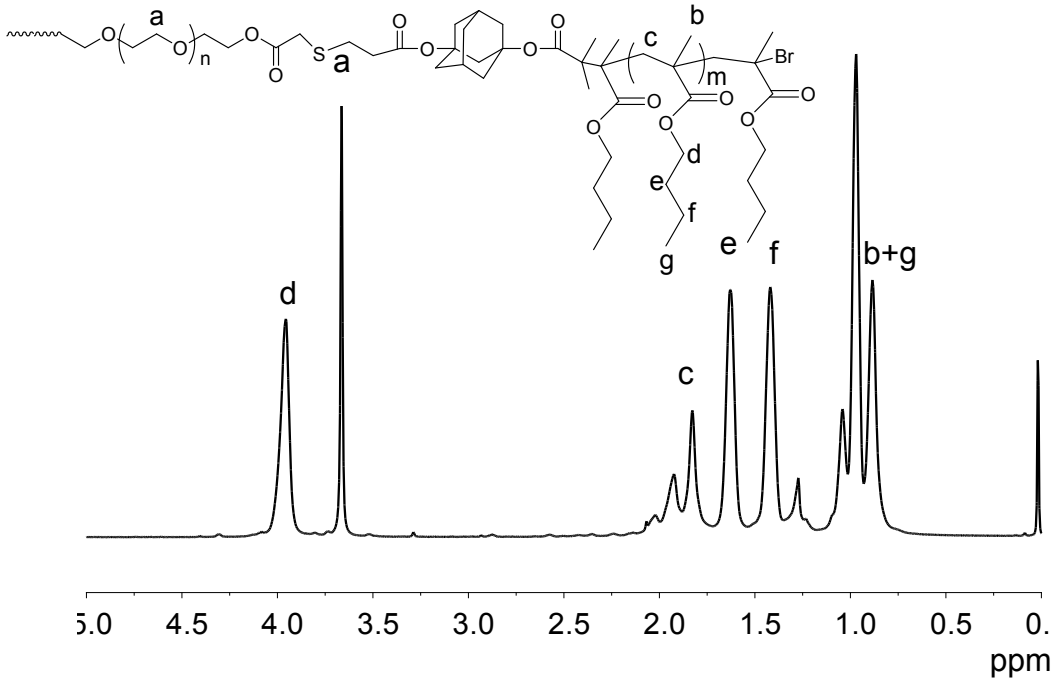


Fig. S-7 ^{1}H NMR spectrum of PEG copolymer in $CDCl_3$.

The synthetic protocol of PEG copolymer was shown in Scheme.S-3. The similar “two steps” strategy was used to synthesize PEG copolymer. The PEG macroinitiator was prepared in first step and then PEG copolymer was synthesized via ATRP of BMA in second step. The IR and NMR spectra of PEG macroinitiator were depicted in Fig.S-5 and S-6, respectively, indicating the successful preparation of PEG macroinitiator. Fig S-7 showed NMR spectrum of PEG copolymer. Both the resonance peaks of PMBA blocks (b-g) and PEG’s methylene axis(a) were found in Fig.S-7. Furthermore, the DP of PBMA can be also calculated according to following equation S-1.

$$DP_{PBMA}=[2DP_{PEG}\times A_{3.90(d)}]/A_{3.50(H\ of\ PEG)} \qquad \text{equation S-1}$$

4. **The characterization of the PR copolymer**

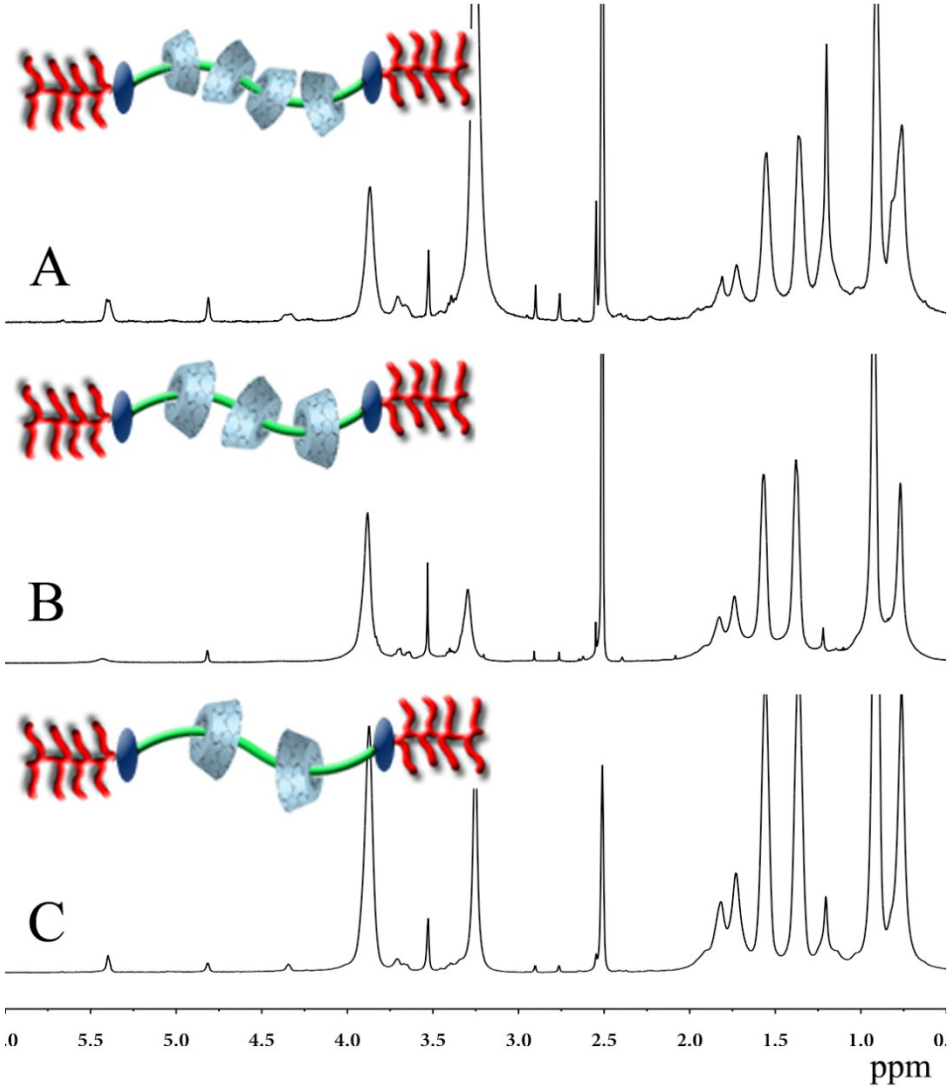


Fig. S-8 ^{1}H NMR spectrum of PR copolymer-8 (A), 7 (B) and 5 (C) in DMSO-d_6 and $CDCl_3$ (v/v=1:1).

The NMR spectra of PR copolymers made from different PR macroinitiator with different CD content were shown in Fig. S-8. The number of threaded CDs in PR copolymer 8,7 and 5 were calculated as 20.1, 16.5 and 13.8 according to equation (1), whereas those in their corresponding PR macroinitiator were 20.3, 17.2 and 14.0 according to Table 1. These results clearly demonstrated the “two steps” strategy in

this study can effectively prevent the de-threading of α-CD so as to prepare the PR copolymers with high CD content.

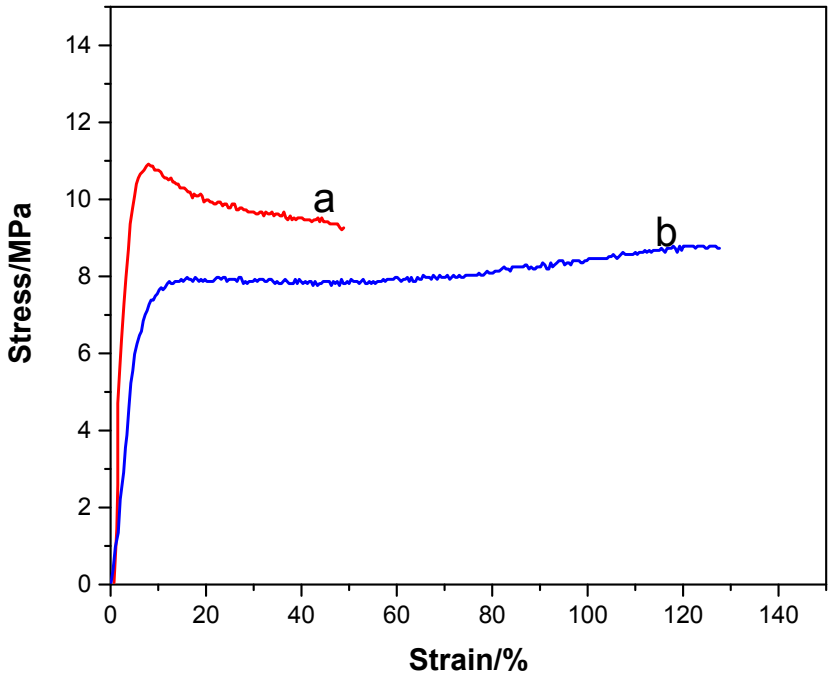


Fig. S-9 The stress-strain curves of PR copolymer 5(b) and 6(a).

The stress-strain curves of PR copolymer 5 and 6 were depicted in Fig. S-7. It showed PR copolymer 6 had higher yield and tensile strength, but lower elongation at break than PR copolymer 6.

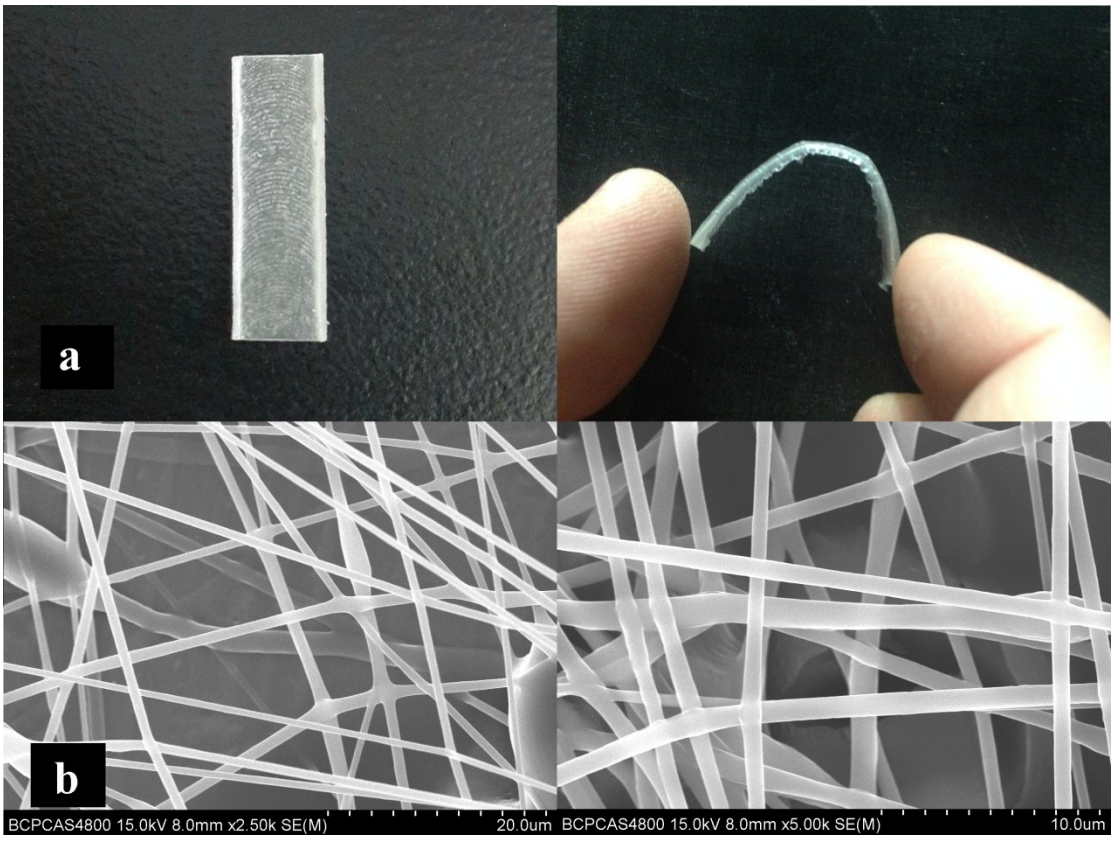


Fig. S-10 (a) The film of PR copolymer-5 by solution casting technique. (b) The SEM images of electrospun of PR copolymer-5 in $CHCl_3$ of 50 mg/mL.

The film made from PR copolymer 5 by solution casting technique was shown in Fig. S-10a, whereas the Fig S-10b showed the SEM images of electrospun mat made from PR copolymer 5.