

Bio-based shape memory polyurethanes (Bio-SMPUs) with short side chains in soft segment

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Synthesis of polyester diol and preparation of bio-based SMPUs

Then, the reaction mixture was charged into the 250 mL three-necked flask. Hydroquinone (0.4 wt % relative to total of reactants) was used as the free radical inhibitor. The mixture with 0.5 wt % p-TSA was pre-condensated under nitrogen atmosphere at 160 °C for 1 h. Then, TBT (0.5 wt% relative to total of reactants), used as the catalyst, was added. After gradually heating to 180 °C under vacuum, the condensation polymerization lasted for 5 h. The products were purified by dissolving in chloroform and precipitating in methanol. The precipitate was then filtered, washed with methanol, and vacuum-dried at 50 °C.

A typical reaction is as follows: the prescribed amount of Bio-Polyol-50 and IPDI were charged into a 250 mL three necked round-bottomed flask which was equipped with a mechanical agitator, a dry nitrogen inlet, and a reflux condenser. DBTDL with the amount of 0.5wt% was added and used as catalyst. Under nitrogen protection, the reaction mixture was then stirred at 65 °C for 3 h to form the pre-polymer. Pre-polymer isocyanate (NCO) content after synthesis was determined by titration with *N,N'*-dibutylamine. The pre-polymer was then chain extended to form a high molecular weight polymer by adding equivalent BDO to the reaction mixture and stirring at 85 °C for 3 ~5h. The reaction was terminated when the isocyanate peak (2260 cm⁻¹) disappeared on the Fourier transform infrared spectra. After that the reaction mixture was poured into a rectangular mold which is made from polytetrafluoroethylene (PTFE) to prepare the polyurethane film for testing.

S-Table 1 The recovery property of Bio-SMPUs with 300% strain of the cyclic tensile testing at room temperature (25 °C).

	$R_r(1)$	$R_r(2)$	$R_r(3)$	$R_r(4)$	$R_r(5)$
Bio-SMPU121	85±0.1	96±0.5	98±0.6	98±0.4	98±0.1
Bio-SMPU132	85±0.1	94±0.6	96±0.3	97±0.6	98±0.4
Bio-SMPU143	76±3.7	92±1	95±1	95±0.8	97±0.3
Bio-SMPU154	62±1	91±1	95±2	96±1	97±0.1
Bio-SMPU165	32±1	87±3.7	93±1.5	95±0.4	96±1.3