Crosslinked Side-chain Polyurethanes with Shape Memory Effect

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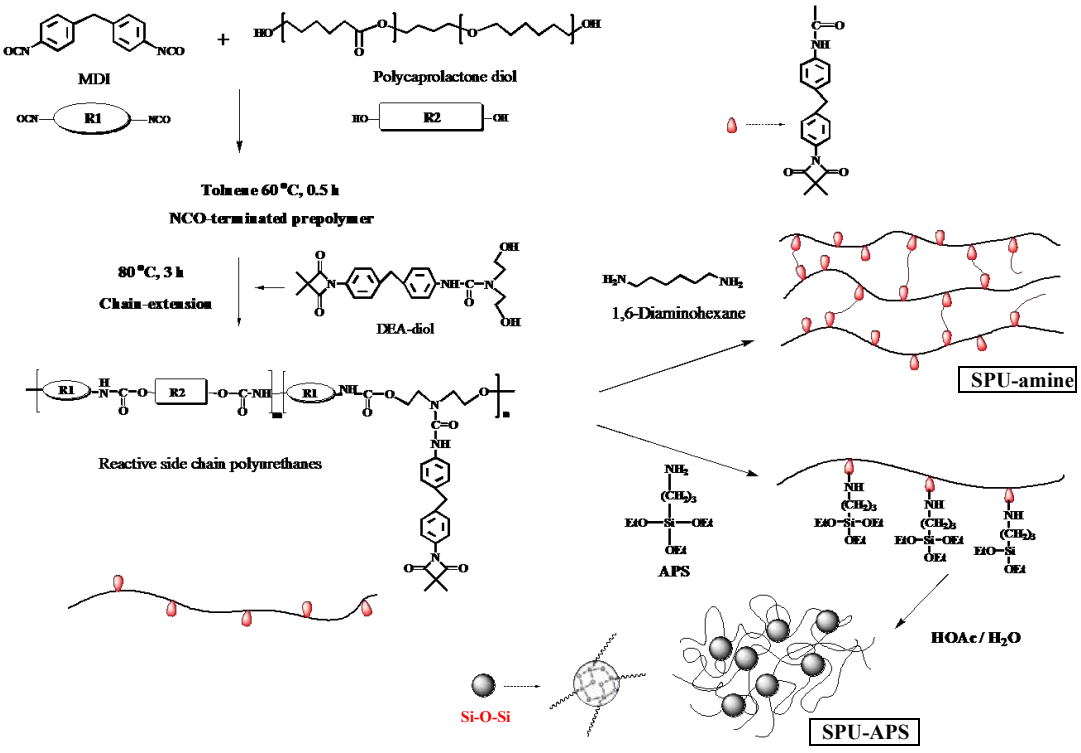
A diol with reactive azetidine-2,4-dione was prepared and introduced onto side-chain polyurethanes (SPUs).[1,2] The SPUs with reactive azetidine-2,4-dione pendants were further crosslinked by aliphatic diamines or 3-aminopropyltriethoxysilanes (APS)[3] (**Scheme 1**). The structure of the polyurethane was characterized by Fourier transform infared spectrometer (FT-IR), X-ray diffraction (XRD) and differential scanning calorimeter (DSC). It is confirmed by FTIR that APS was capable of reacting with the azetidine-2,4-dione containing polyurethane. This resulted in the polyurethane grafted with alkoxysilane. Tensile strengths of SPUs were increased with increasing crosslinking density and hydrolysis degree of alkoxysilane pendants. However, the crystallinity of the polyurethane behaved otherwise by the XRD and DSC investigation. By introducing the crosslinking amine into SPUs, the strong covalent bonds between polymeric chains further enhanced the shape memory effect. In addition, the organic/inorganic hybrid materials exhibited rather strong intermolecular attractions due to the formation of three-dimensional network (Si-O-Si) between polyurethane backbones via the sol-gel reaction of alkoxysline containing polyurethanes.[4-6] The shape recovery efficiencies of all crosslinked SPU-APS samples (**Scheme 1**) were up to 97% during cyclic thermomechanical tensile tests, which exhibited better recovery properties than those of crosslinked SPU-amine samples (**Scheme 1**). Consequently, these novel crosslinked polyurethanes with excellent shape-memory effect have been successfully developed (**Table 1**).



Scheme 1. Preparation of crosslinked side-chain polyurethanes

Table 1. Shape retention and shape recovery of polyurethanes

Sample code	Thermomechanical Tensile Test					
	Shape retention(%)			Shape recovery(%)		
	1st	2nd	3rd	1st	2nd	3rd
LPU45	80.6	66.1	61.2	79.2	69.5	54.0
LPU50	81.3	71.7	70.6	84.3	68.9	67.8
LPU55	76.1	71.7	67.2	88.4	77.8	78.7
SPU45	76.1	72.8	66.1	79.4	77.4	73.4
SPU45-amine-10%	71.7	66.2	61.1	94.0	83.4	78.4
SPU45-amine-20%	81.7	76.1	75.6	97.5	94.8	90.0
SPU50	95.1	92.2	91.1	90.5	72.0	72.5
SPU50-amine-10%	90.3	89.3	87.2	97.9	97.3	92.5
SPU50-amine-20%	86.2	85.6	85.0	98.9	97.8	93.5
SPU55	90.0	87.6	85.6	91.4	87.3	84.4
SPU55-amine-10%	90.5	86.1	85.0	95.5	92.5	92.5
SPU55-amine-20%	87.6	86.7	85.0	99.5	98.4	97.5
SPU55-APS-20%	95.0	92.8	91.5	99.5	97.5	97.5
SPU55-APS-40%	90.0	87.8	87.5	99.8	99.5	99.4
SPU55-APS-60%	85.0	83.6	—	99.8	99.8	—

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