Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

New Design of Highly Homogeneous Photopolymer Networks for Shape Memory Materials

Matthieu Retailleau, Ahmad Ibrahim, Céline Croutxé-Barghorn and Xavier Allonas

Laboratory of Macromolecular Photochemistry and Engineering, University of Haute Alsace, 3b rue Alfred Werner, 68093 Mulhouse, France.

1-Materials

Ethoxylated Bisphenol A Diacrylate (SR349) and Irgacure 819 were donated by Sartomer and BASF, respectively. 1,5-diaminopentane (cadaverine) was purchased from Sigma Aldrich (Figure 1). All compounds were used as received without any purification steps.

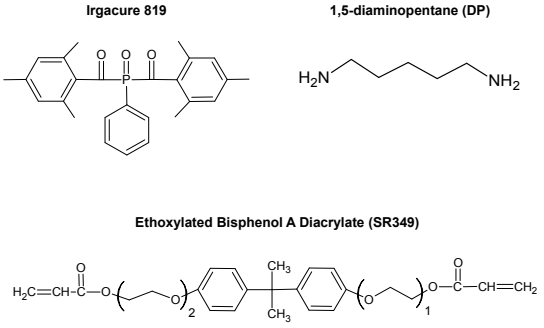

Figure ESI 1 - Chemical structures of the materials used in this study: SR349, 1,5-diaminopentane and Irgacure 819.

2- Preparation of samples

Michael polymerization was carried out by mixing SR349 with 1,5-diaminopentane with amine:acrylate molar ratios of 1:2, 1:4 and 1:8.

For the three-step system, Irgacure 819 (2.5 wt %) was first added to SR349 and then, the mixture was mixed with 1,5-diaminopentane (molar ratio 1:4). After the end of AZ_1 (80 min), the mixture was spread onto a polypropylene film (70 µm thick) and cured using a UV conveyor belt (Phoseon Firejet LED @ 395 nm, light dose of 7 $J.cm^{-2}$).

3- Differential Scanning Calorimetry (DSC)

Thermal properties of the resulting polymers were evaluated using Q200 from TA Instruments. Products were placed in hermetically sealed aluminium pans (between 5 and 10 mg) and heated from -80 to 30 °C (two runs).

In order to ensure proper measurement of the slope of the glass transition temperature, DSC thermograms were derivate as a function of temperature. As a result, the value of the peak minimum was considered as the slope of the glass transition.

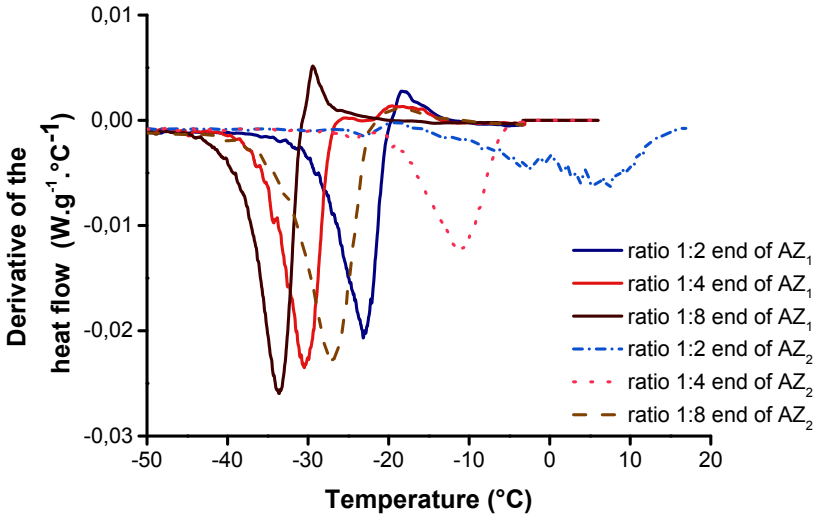

Figure ESI 2 – Derivative of the heat flow vs. temperature for different molar ratios 1:2, 1:4 and 1:8 (straight line: end of AZ_1, dashed line: end of AZ_2).

4- Dynamic Mechanical Analysis (DMA)

Thermomechanical properties

The dynamic thermo-mechanical properties of the UV-cured materials were investigated with a Q800 DMA (TA Instruments) in the tensile configuration. The samples were rectangular (12.8 × 5.3 × 0.070 mm) free films removed from polypropylene substrates. Temperatures ranged from -20 to 100 °C and the heating rate was set at 2 °C/min. The amplitude and frequency of the oscillatory deformations were adjusted to 15 µm and 1 Hz, respectively.

Thermocycling test

Thermomechanical cycle experiments were performed with a TA DMA Q800 instrument with 12.8 × 5.3 × 0.070 mm samples. The parameters used to quantify the shape memory performances are defined below.

- *Shape fixity* (R_f) evaluates the SMP's ability to be fixed by mechanical deformation after successive cooling and unloading.

- *Shape recovery* (R_r) evaluates the ability of the SMP to recover the permanent form during the recovery step after N cycles when reheated to the rubbery state,

- *Recovery rate* (v_r) describes the rate at which the permanent strain is recovered.

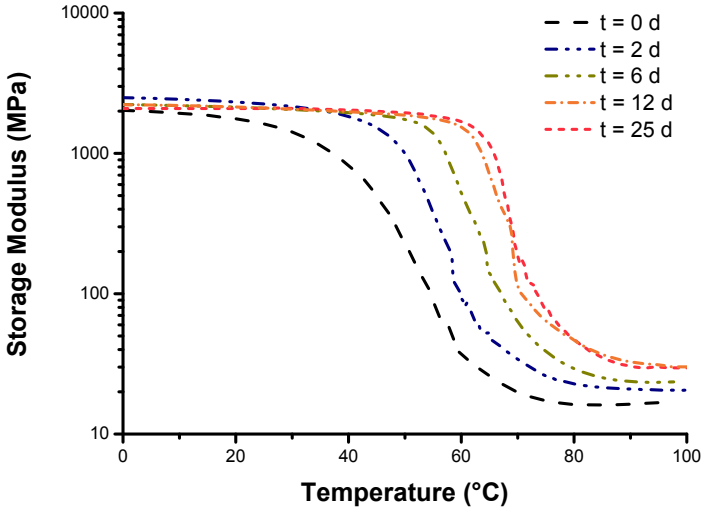

Figure ESI 3 - Storage modulus vs. temperature along AZ_2 progress (in days)

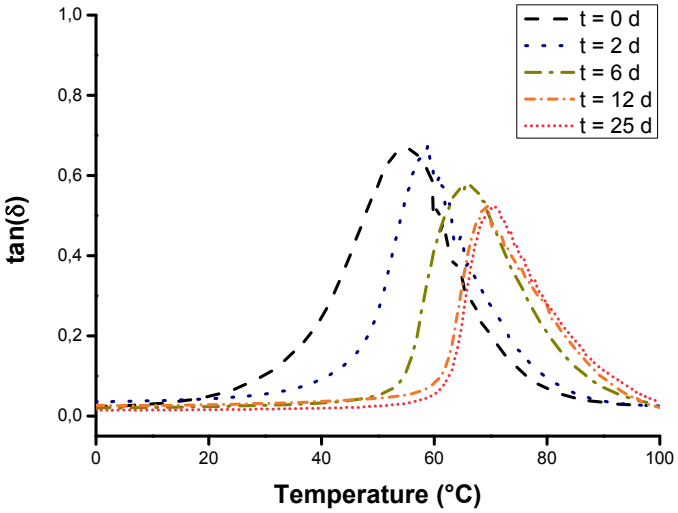

Figure ESI 4 – tan(δ) vs. temperature along AZ_2 progress (in days)

7- Shape memory demonstration

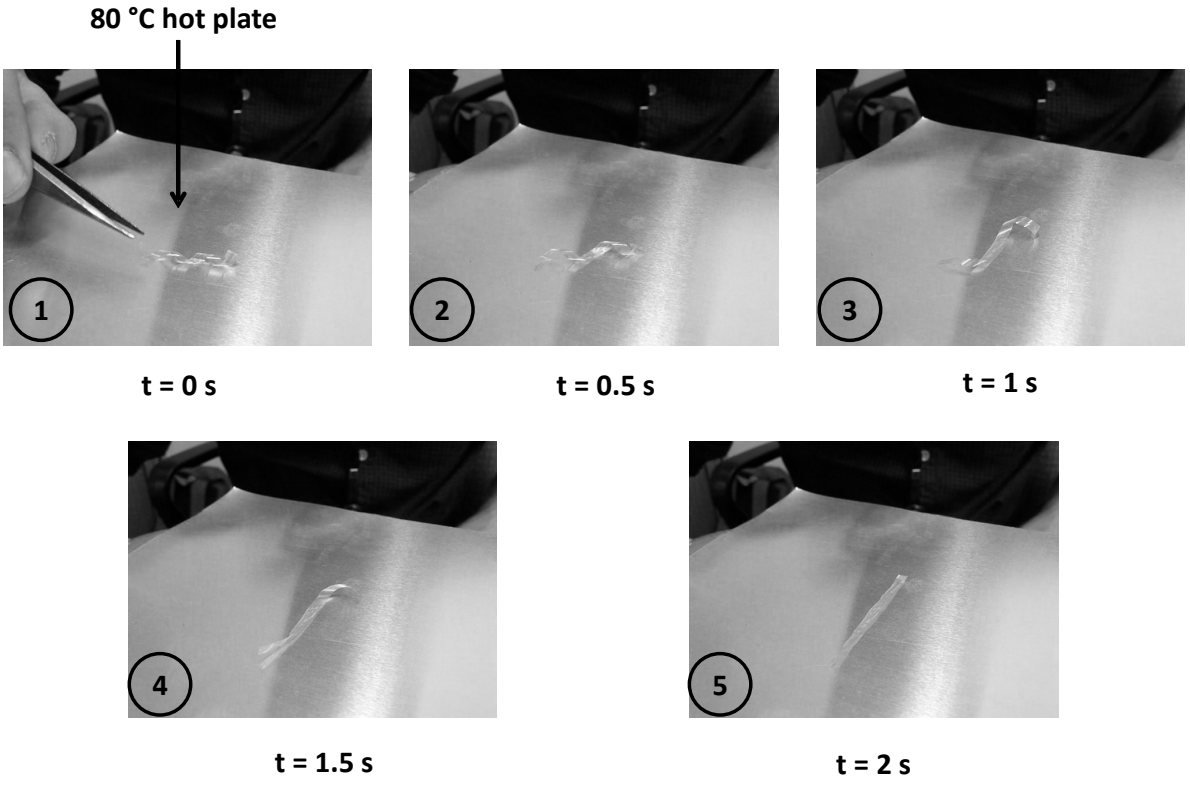

Figure 5 – Shape memory demonstration using double click aza-Michael addition and radical photopolymerization (ratio 1:4)