

Polybutadiene–Poly(styrene-*co*-4-vinylpyridine)-Based Supramolecular Shape Memory Elastomers Using Metal Coordination Interactions

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A shape memory polymer (SMP) is a smart polymeric material that can recover its original shape from a temporary shape when exposed to an external stimulus. The theory and experimental studies of SMP shows profound theory and practical significances. Thermal responsive SMPs have a permanent shape, but can be programmed into a temporary shape above a critical, switching temperature (T_c), which can be fixed and stored below T_c , and later be converted back to the permanent shape when reheated above T_c . For the majority of SMPs, T_c is based on the glass transition or a melting transition, but other chemistries, such as reversible Diels-Alder reactions[1, 2], and supramolecular bonds, such as hydrogen bonds[3, 4], ionic interactions[5, 6] and hydrophobic interactions[7] have more recently received attention. Metal coordination interactions have been used to design functional soft materials[8, 9], including SMPs[10, 11].

Aiming at an easy-processing metallo-supramolecular polymer which possesses the shape memory property and large deformation ability, we designed a simple metal coordination complex, the blends of zinc-neutralized carboxyl terminated polybutadiene and poly(styrene-*co*-4-vinylpyridine) (PSVP). This transition metal coordinated shape memory elastomer was investigated in the terms of synthesis mechanism, formability, micro morphology, thermal properties, mechanical properties and shape memory behaviors in this paper. The microstructure and chemical composition of shape memory elastomer were characterized by small angle X-ray scattering analysis and Fourier transform infrared spectroscopy. The mechanical properties of these materials were studied by rheological analysis, dynamic mechanical analysis, and tensile test. The thermal performance of these materials were investigated by differential scanning calorimetry and thermogravimetric analysis. The shape memory performance of these materials was investigated by bent-unfold and stretch-shrink test, respectively.

Carboxyl-terminated polybutadiene (CTB, Hypro 2000×162 CTB) was supplied by CVC Thermoset Specialties, Emerald Performance Materials, LLC. Poly(styrene-

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co-4-vinylpyridine) (PSVP) was purchased from Scientific Polymer Products, Inc. Toluene, methanol, and zinc acetate dihydrate were purchased from Sigma-Aldrich Co. LLC. All chemicals were used as received.

The samples were prepared according to the following procedure. The ZnCTB was prepared by mixing a solution of zinc acetate dihydrate in a 1:1 (v/v) mixture of deionized water and methanol and a solution of CTB in toluene. The stoichiometric ratio of Zn²⁺ and carboxylic acid was 1:2 and the resulting ZnCTB was recovered by evaporating the solvent in air, drying at 50°C for 24 h and drying under vacuum at 50°C for 24 h. Blends of ZnCTB and PSVP were prepared by mixing both components in a common solution of toluene and stirring for 48 hours at room temperature. The blend was air dried at 50°C for 3 days to remove most of the solvent and then vacuum dried at 50°C for 24 hs to remove all the solvent. The ZnCTB–PSVP blend formed a transparent and free-standing, flexible elastomer that had a tunable transition temperature between 77°C to 121°C, depending on the composition. Five blends were prepared, which are denoted as ZnCTBPSVP-1:x (x=1, 1.5, 2, 4, 8), corresponding to of the ratio of carboxyl groups and pyridine groups of 1:1, 1:1.5, 1:2, 1:4, and 1:8, respectively. A blend of an un-neutralized CTB (i.e., the free-acid derivative) and PSVP was also prepared as a controlled sample, and that sample is referred to as CTBPSVP-1:1.

The supramolecular shape memory elastomer was designed and synthesized using a blend of functionalized polybutadiene oligomers and functionalized poly(styrene-*co*-vinyl pyridine)(PSVP) where a physically crosslinked network was produced by a transition metal complex between Zn²⁺ ions from carboxylated telechelic polybutadiene and the pyridine group of the PSVP. The elastomer had reasonably good formability and was thermoplastic.

Shape memory was achieved by tuning the intermolecular complex and using the microphase separation as a permanent network. The shape memory elastomer exhibited good shape memory properties for large deformations. The shape fixing and recovery efficiencies were as high as 95% and 81%, respectively for the first shape memory cycle, and were 93% ±0.7% and 97%±1% respectively in the following seven cycles. In addition, the shape memory elastomer showed excellent triple-shape memory effect, which is applicable to variable deformations, including stretching, twisting and rolling.

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