

# Multiscale-structuring of rapid response shape memory polymers based on self-assembly reverse micelles



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## ABSTRACT

How to reasonably fabricate shape memory polymers (SMPs) with rapid response without sacrificing the shape fixity and recovery are a critical issue but remains a challenge. Inspired by the relation between biological structure and function, a multiscale design of SMPs is reported by constructing a two-phase architecture via embedding self-assembly “reverse micelles” as elastic region into stiff matrix to enhance the elastic recovery. As a result of the two-phase architecture, the single polymer network exhibits a combination of perfect shape fixity and recovery, rapid and strong response and outstanding cycle life. The mechanism on quick response of the material is analyzed and confirmed by the study about the stress relaxation and recovery stress. Such a shape memory material may be an ideal candidate for potential applications as actuator and biomedical devices.

## 1. Introduction

Shape memory polymers (SMPs) are a class of smart materials that can recover to original shapes from preprogrammed temporary shapes in response to an external stimulus [1]. SMPs have attracted significant interest due to their highly recoverable strain, tunable multi-shape memory effect, light weight, easier processing and biocompatibility, compared with shape memory alloy (SMA) counterparts [2–4]. Nowadays, SMPs hold great potential for a growing list of applications from textiles, aerospace, electronics, biomedicine to 4D printing [5–9].

Typically, the majority of SMPs are triggered thermally by heating above a certain transition temperature ( $T_{trans}$ ). However, whether  $T_{trans}$  is a glass or a melting transition, the thermal transition usually stretches over a broad temperature range [10,11]. Hence, thermally induced SMPs usually suffer from a long recovery time, which is much greater than the tens of milliseconds for SMAs with comparable size [12]. Especially, the shape recovery of SMPs activated by light, water and electric field and most shape-memory hydrogels would take more time [13–16]. This significantly restricts its widespread applications that require fast response, such as medical devices, fluidics devices, actuators and safety systems, etc.

In general, the width of the thermal transition is governed by the distribution of relaxation times associated with molecular mobility, which in turn depends on chain length, microstructure, molecular interactions, and constraints [12]. Thus, the recovery time can be essentially decreased by optimizing the polymer chemistry and network structure. For example, Lendlein's group introduced the end-

crosslinking of telechelic star prepolymer and AB-polymer networks structure into the design of SMPs [17–19]. The resulting SMPs showed a narrower temperature interval of strain recovery and faster recovery, compared to the conventional SMPs. SMPs cross-linked by thiol-ene reaction exhibited a rapid actuation response because the thiol-ene reaction can form a more homogeneous polymer network that results in a relatively narrow glass transition range [20–22]. For instance, the recovery speed of a well-defined shape memory poly(D, L-lactide) networks prepared by thiol-norbornene photopolymerization was as high as 27%/°C within a very narrow transition region [23]. In our previous work, we have demonstrated that poly(methyl methacrylate)/star poly(ethylene glycol) (PMMA/SPEG) composites exhibited rapid and full shape recovery by synergistic effect of star structure and lower level of heterogeneity in polymer network [24,25].

Natural structural materials (nacre, spider silks and mussel byssus) usually comprise hard and soft phases arranged in complex multiscale architectures [26,27]. This structural hierarchy can play a large part in determining the bulk material properties and functions. Typically, extraordinary combination of mechanical strength and elasticity of spider silk results from a combination of highly ordered  $\beta$ -sheet nanocrystals from alanine-rich segments via H-bond self-assembly as a reinforcement and amorphous domains that provide elasticity [28,29]. Similarly, the embedded granules from the coordination self-assembly between 3, 4-dihydroxyphenylalanine and iron ion into the soft cuticle contribute to a combination of high hardness and high extensibility of mussel byssus [30]. These structural materials are all characterized by embedding hard phases into loosely soft matrix, which serves as the sacrifice

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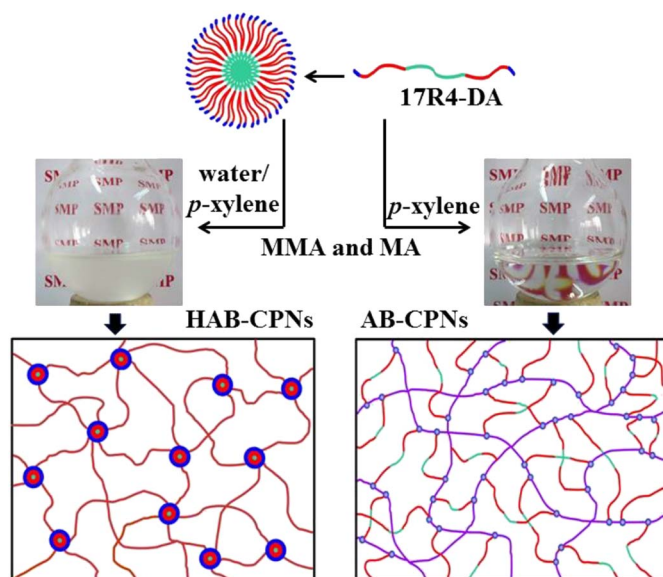


Fig. 1. Schematic structures of 17R4-DA micelles consisting of a hydrophilic PEG core (green) and a hydrophobic PPG shell (red) with vinyl groups (blue) on surface and synthesis of HAB-CPNs (line: MA-co-MA chains) and AB-CPNs (purple line: MA-co-MA chains). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

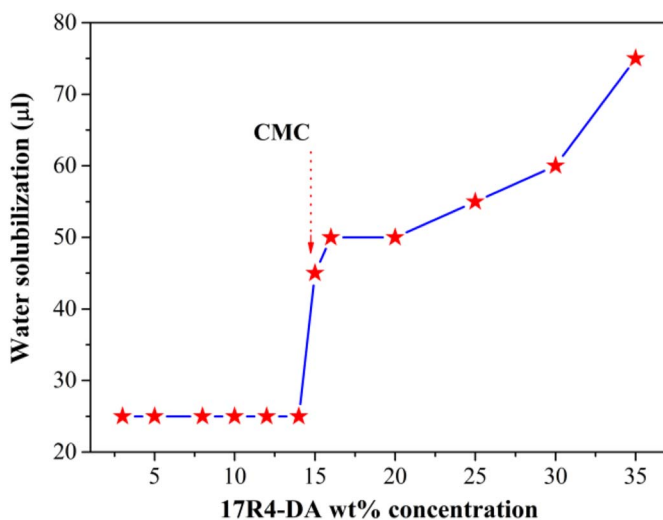


Fig. 2. Water solubilization in 5 g *p*-xylene with various mass fractions of 17R4-DA at 35 °C.

network and effectively absorbs the crack energy to achieve the unique blend of hardness and extensibility.

Unlike the above materials, irreversible fracture of covalent bonds in the SMP network can reduce the amount of recoverable elastic energy and seriously undermines shape memory properties. Inspired by above nature's design principles, from a contrarian view we designed a multiscale SMP system via embedding self-assembly soft phases as elastic region into stiff matrix with high chain density and high glass transition temperature ( $T_g$ ) to enhance the elastic recovery. Herein, AB copolymer networks (AB-CPNs) from copolymerization of macrodimethacrylates and comonomer serve as the control network. As shown in Fig. 1, the acrylated amphiphilic triblock copolymers (poly(propylene glycol)<sub>14</sub>-*block*-poly(ethylene glycol)<sub>24</sub>-*block*-poly(propylene glycol)<sub>14</sub>, PPG<sub>14</sub>-PEG<sub>24</sub>-PPG<sub>14</sub>, 17R4) can self-assemble into "reverse micelles" consisting of a hydrophilic PEG core and a hydrophobic PPG shell with vinyl groups on surface in an appropriate organic solvent. The 17R4 diacrylate (17R4-DA) reverse micelles with spherical

core-shell structure as nano-scale structure were polymerized with the methyl methacrylate (MMA) and methyl acrylate (MA) as comonomer, resulting in AB copolymer networks (HAB-CPNs) with two-phase architecture.

## 2. Experimental section

### 2.1. Materials

Acryloyl chloride and 2,2-dimethoxy-2-phenylacetophenone were obtained from TCI Co. (Japan). 17R4 and triethylamine were purchased from Sigma-Aldrich Co. (USA). Methyl methacrylate (MMA) and methyl acrylate (MA) were of analytical grade and obtained from the Chengdu Reagent Factory (China). MMA and MA were distilled under reduced pressure before use.

### 2.2. Synthesis of 17R4-DA

In a 250 mL three-neck round-bottom flask, 10.0 g 17R4 (after drying at 80 °C for 4 h under vacuum) was dissolved in 80 mL dry dichloromethane. After 10 min stirring in ice bath under argon, 1.12 g triethylamine was added, and then 1.01 g acryloyl chloride in a dropping funnel was added dropwise. The reaction continued for 2 h at 0 °C and for another 48 h at room temperature under stirring. Finally, the freezing mixture was centrifugated to remove the precipitated salt and then was precipitated by adding into anhydrous diethyl ether. The product was redissolved in toluene and a small amount of triethylamine hydrochloride was filtered out. The filtrate was precipitated by adding into anhydrous diethyl ether. The resulting product was dried under vacuum at 30 °C for 24 h. <sup>1</sup>H NMR analysis was used to calculate the degree of esterification (> 95%). <sup>1</sup>H NMR: (CDCl<sub>3</sub>, 300 MHz: δ: 1.1 (–O–CH(–CH<sub>3</sub>)–), 3.3 (–O–CH(–CH<sub>3</sub>)), 3.4 (–O–CH(–CH<sub>3</sub>)–CH<sub>2</sub>–), 3.5–3.6 (–CH<sub>2</sub>–CH<sub>2</sub>–O–), 5.8 (CH<sub>2</sub>=CH–), 6.1 and 6.3 (CH<sub>2</sub>=CH–) ppm); FTIR: (–C=O, 1724 cm<sup>–1</sup>; –CH=CH<sub>2</sub>, 986 cm<sup>–1</sup>).

### 2.3. Synthesis of HAB-CPNs and AB-CPNs

HAB-CPNs were synthesized by radical polymerization of a mixture containing 5 g 17R4-DA, 7 g MMA, 3 g MA, 80 µL deionized water, 0.08 g 2,2-dimethoxy-2-phenylacetophenone and 10 g *p*-xylene in a mold defined by two glass slides. Before the reaction, above mixture was mixed by a vortex mixer for 30 min. The mixture was then irradiated under a UV light intensity of 30 mW/cm<sup>2</sup>. The obtained HAB-CPNs film was vacuum-dried at 100 °C overnight. AB-CPNs were synthesized just like HAB-CPNs. The only difference is free from 80 µL deionized water.

### 2.4. Characterization

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300 NMR spectrometer at 300 MHz. Tetramethylsilane (TMS) was used as an internal standard for the analysis of chemical shifts.

Fourier transform infrared (FTIR) spectra of the samples were measured using a Nicolet MX-1E spectrometer (Thermo Fisher Scientific, America) in the range of 400–4000 cm<sup>–1</sup>.

The dynamic mechanical properties were determined on a Dynamic Mechanical Analysis (DMA) tester (TA Instruments, DMA Q800) equipped with tensile film clamps. The heating rate was 3.0 °C/min. A frequency of 1 Hz and an amplitude of 20 µm were applied.

The size and its distribution of 17R4-DA micelles were measured by dynamic light scattering (DLS) using a Malvern Nano-ZS analyzer.

The phase morphology of samples was investigated by JSM-7500F (JEOL) scanning electron microscope (SEM).

Quantitative assessment of the shape memory properties was

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