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Complex of polyelectrolyte network with surfactant as novel shape memory networks

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Poly(acrylic acid-*co*-methyl methacrylate)–cetyltrimethylammonium bromide (P(AA-*co*-MMA)–C_{16}TAB) complex has shape memory behavior due to the formation of crystalline aggregates among the long alkyl chains of C_{16}TAB in the complex, and can be regarded as a novel shape memory network.

During recent years, shape memory materials have received increasing attention on account of their interesting properties and potential applications, especially thermally stimulated shape memory materials.[1–3] The mechanism of shape memory behavior with temperature can be schemed briefly as outlined below where L is the initial state of material and L′ is the

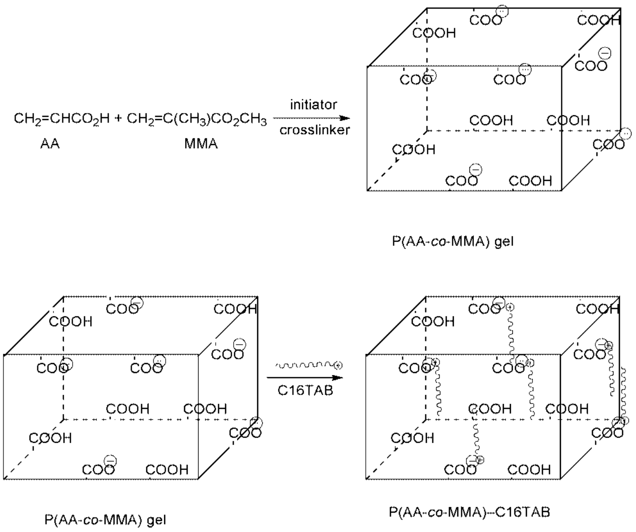
$$\mathrm{L}\xrightarrow[\text{deformation}]{T>T_g \text{ or } T>T_m}\mathrm{L}+\mathrm{L}'\xrightarrow[\text{fixation}]{T<T_g \text{ or } T<T_m}$$
$$\mathrm{L}+\mathrm{L}'\xrightarrow[\text{recovery}]{T>T_g \text{ or } T>T_m}$$

deformation of material. These materials have a two phase structure, namely, the fixing phase remembers the initial shape and the reversible phase shows a reversible soft and rigid transition with temperature. Based on this principle, some polymers were discovered that had shape memory behavior.[4–9]

Among shape memory materials, copolymer networks[6,7] containing long alkyl side chains were reported due to a reversible order–disorder transition of long alkyl side chains. Below the transition temperature, these side chains form a crystalline aggregate structure, and behave as hard plastic. While above this temperature they transfer to the amorphous state and the material abruptly becomes soft and flexible.

It is well known that many beneficial properties of polyelectrolyte–surfactant complexes[10,11] result from the highly ordered structures[12–14] formed by the self-assembly of surfactant molecules inside the complexes. The supermolecular formation was driven by both electrostatic interactions between charged components and hydrophobic interactions between the polymer backbones and the surfactant alkyl chains.

The research works mentioned above served as a great source of inspiration to us in designing the polyelectrolyte network–surfactant complexes for shape memory networks. Up to now, any similiar research work has not been reported. Hence the polyelectrolyte network–surfactant complexes may broaden the list of shape memory polymers. In this paper, we synthesized poly[(acrylic acid)-*co*-(methyl methacrylate)] (P(AA-*co*-MMA)) networks and the complex of P(AA-*co*-MMA)–(cetyltrimethylammonium bromide) (P(AA-*co*-MMA)–C_{16}TAB). The composition and the structure of the network and complex were characterized. And the surface microstructure before and after deformation was also studied.



Scheme 1 Synthesis of P(AA-*co*-MMA)–C_{16}TAB complex.

Scheme 1 shows the synthesis and the expected structure of P(AA-*co*-MMA)–C_{16}TAB. The crosslinked P(AA-*co*-MMA) network was designed as the fixed phase, while C_{16}TAB was designed as the reversible phase for shape memory networks. Fig. 1 is the FTIR spectra of P(AA-*co*-MMA) before and after complexation with C_{16}TAB. The curves of P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB both give a wide peak from 3100 to 3600 cm^{-1} indicating the stretching of –OH groups of polyacrylic acid (PAA). The relative intensity of the peak at 2955 cm^{-1} due to the stretching of the –CH_2 groups of P(AA-*co*-MMA)–C_{16}TAB is slightly higher than that of P(AA-*co*-

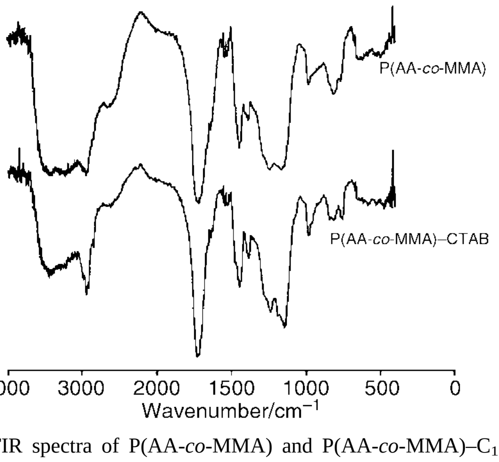


Fig. 1 FTIR spectra of P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB complex.

MMA). Comparing the C or H content between P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB, the C_{16}TAB : AA ratio can be calculated from eqn. (1) where n_{CTAB} and n_{AA} is the mole content of C_{16}TAB and AA in the complex, respectively.

$$n_{\mathrm{CTAB}}/n_{\mathrm{AA}} = 0.432 \times [(\%_{\mathrm{complex}} - \%_{\mathrm{P(AA\text{-}\mathit{co}\text{-}MMA)}})/(\%_{\mathrm{CTAB}} - \%_{\mathrm{complex}})] \times 100\% \qquad (1)$$

$\%_{\mathrm{complex}}$, $\%_{\mathrm{P(AA\text{-}\mathit{co}\text{-}MMA)}}$ and $\%_{\mathrm{CTAB}}$ are the C or H content of P(AA-*co*-MMA)–C_{16}TAB, P(AA-*co*-MMA) and C_{16}TAB, respectively. The calculated value of $n_{\mathrm{CTAB}}/n_{\mathrm{AA}}$ was 15.4%, which is higher than the pK_a of the PAA segment which is *ca.* 5.[15] Hence, the complexation of C_{16}TAB with P(AA-*co*-MMA) was driven not only by electrostatic interactions but hydrophobic interactions among long alkyl chains of C_{16}TAB and between C_{16}TAB and polymer chains of the network.

The most important key to a shape memory network for P(AA-*co*-MMA)–C_{16}TAB is whether the long alkyl chain of C_{16}TAB could form a highly ordered structure or crystalline phase in the P(AA-*co*-MMA) network. Table 1 gives the DSC data for P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB. A glass transition temperature (T_g) attributed to the PAA segment was obtained for both the polymer network and complex. A melting point (T_m) and crystalline point (T_c) was found only in complex. These facts mean the long alkyl side chains of C_{16}TAB form a crystalline phase in P(AA-*co*-MMA)–C_{16}TAB. This is the necessary condition for P(AA-*co*-MMA)–C_{16}TAB to adopt a shape memory network.

The T_g should be greater than or equal to the melting point of P(AA-*co*-MMA)–C_{16}TAB, 98.26 °C. Hence, 100 °C was chosen to observe the deformation and recovery of the complex. Fig. 2 shows the shape memory phenomenon of P(AA-*co*-MMA)–C_{16}TAB. The straight strip sample was heated to 100 °C, deformed as an ‘e’ shape and then cooled to rt. The complex is rigid and retains the ‘e’ shape. On heating again to 100 °C, the complex becomes soft and recovers it’s original strip shape. This phenomenon may be attributed to the formation of crystalline aggregates among the long alkyl chains of C_{16}TAB in the complex that locks the new shape. When the deformed complex is heated again above T_g, the crystalline aggregates become amorphous and the complex recovers its original size and shape.

In order to give further support for the shape memory behavior of P(AA-*co*-MMA)–C_{16}TAB, the surface variation of P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB before and after deformation were also observed on an optic microscope and recorded by a PC digital camera. Fig. 3 shows the microphotographs of P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB under different conditions. The initial surface of P(AA-*co*-MMA)–C_{16}TAB is rougher than that of P(AA-*co*-MMA). Those concavo-convex flecks on the surface of P(AA-*co*-MMA)-C_{16}TAB are due to the shrinkage caused by the complexation of P(AA-*co*-MMA) with C_{16}TAB. The surface of P(AA-*co*-MMA) after deformation shows many tiny streaks, while the surface of P(AA-*co*-MMA)-C_{16}TAB shows the extension flecks along the tensile direction. The surface of P(AA-*co*-MMA) is significantly different after recovery from the initial state, which means P(AA-*co*-MMA) cannot recover its initial microstructure. In contrast, the surface of P(AA-*co*-MMA)–C_{16}TAB is very similiar in both the initial and recovery states. In other words, the complex can recover its initial microstructure. The recovery ratio is about 85%, calculated from the difference in length of the test sample in the initial and recovered states.

Table 1 DSC data of P(AA-*co*-MMA) and P(AA-*co*-MMA)–C_{16}TAB

Sample	$T_m{}^a$/°C	$T_c{}^b$/°C	$T_g{}^c$/°C
P(AA-*co*-MMA)	—	—	115.54
P(AA-*co*-MMA)–C_{16}TAB	98.26	68.98	128.12

[a] Melting point. [b] Crystalline point. [c] Glass transition temperature.

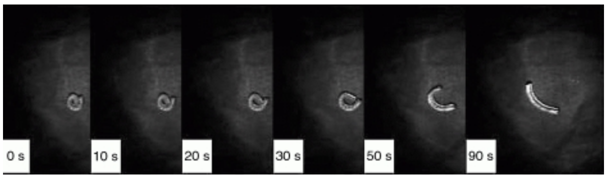


Fig. 2 Shape memory phenomenon of P(AA-*co*-MMA)–C_{16}TAB. (The initial straight stripe was heated to 100 °C and deformed as an ‘e’ alphabet, then cooled to room temperature under constrained conditions. After withdrawal of the external force, the ‘e’ shape sample was put into a glass container and kept at a constant temperature of 100 °C. At the same time the snapshot was captured by a digital camera every 2 s.)

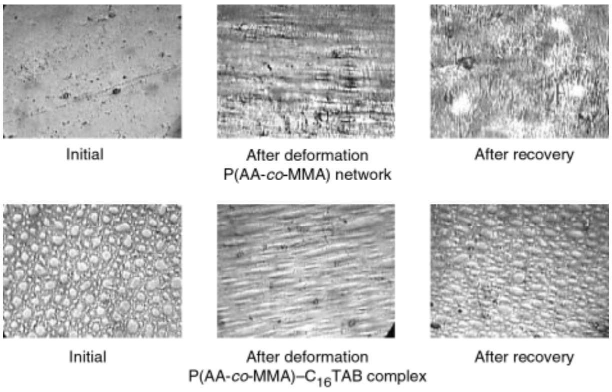


Fig. 3 Microphotographs of the surface of (a) P(AA-*co*-MMA) and (b) P(AA-*co*-MMA)–C_{16}TAB under different conditions at rt. (The enlargement multiple was 160. Initial: initial state of sample. After deformation: sample were drawn at 100 °C under a constant tensile force of 0.05 N until the elongation rate was 150% and then cooled to room temperature. After recovery: samples after deformation were heated to 100 °C and kept at constant temperature for 30 min, then cooled to room temperature.)

In conclusion, although the reversible temperature is high, 100 °C, and the recovery ratio is not 100%, the shape memory phenomenon of P(AA-*co*-MMA)–C_{16}TAB shows that the well designed polyelectrolyte network–surfactant complex can be considered as a kind of novel shape memory network.

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