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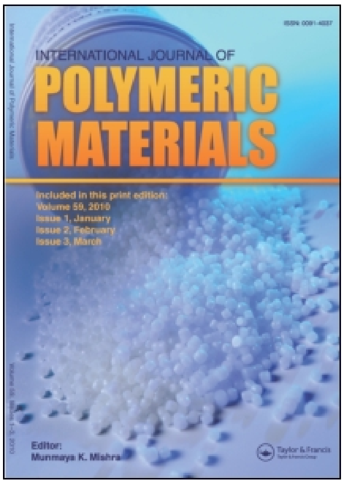

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POLYELECTROLYTE NETWORK-SURFACTANT COMPLEXES WITH SHAPE MEMORY EFFECT

Yiping Cao[a]; Ying Guan[a]; Wenchuan Zhang[a]; Yuxing Peng[a]; Pei Li[b]; Albert S. C. Chan[b]
[a] Chinese Academy of Sciences, Chengdu, China [b] Department of Applied Biology and Chemical Technology, Kowloon, Hong Kong, China

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POLYELECTROLYTE NETWORK-SURFACTANT COMPLEXES WITH SHAPE MEMORY EFFECT

Yiping Cao
Ying Guan
Wenchuan Zhang
Yuxing Peng
Institute of Organic Chemistry,
Chinese Academy of Sciences, Chengdu, China

Pei Li
Albert S. C. Chan
Department of Applied Biology and Chemical Technology,
Hong Kong Polytechnic University, Hung Hom,
Kowloon, Hong Kong, China

The complex of Poly(acrylic acid-co-acrylamide) network with cetyltrimethylammonium bromide (P(AA-co-Am)-C_{16}TAB) was synthesized. It has shape memory behavior due to the formation of thermodynamically homogeneous structure. A specific feature of this type of shape memory complex is that the transition temperature at which the complex abruptly becomes soft and deforms can be controlled by changing the degree of cross-linkage, which enables one to adjust the shape memory effect at desired temperature. Mechanism and process of the shape memory behavior were discussed.

Keywords: poly(acrylic acid-co-acrylamide), cetyltrimethylammonium bromide, complexes, shape memory, networks, polyelectrolyte

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Address correspondence to Yuxing Peng, Institute of Organic Chemistry, Chinese Academy of Sciences, P. O. Box 415, Chengdu 610041. P. R. China. E-mail: yxpeng@mail.com

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INTRODUCTION

Since the first shape memory polymer, norbornene polymer, was reported by the CdF-Chimie Company in France in 1984, 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 morphology of shape memory polymers should contain two phases, namely, the fixing phase remembers the initial shape and the reversible phase shows a reversible soft and rigid transition with temperature. The fixing phase may contain chemical and physical crosslinks, imparting a level of rigidity, dimensional stability, while the reversible phase can be either crystalline or amorphous, and provide properties of elastomers—primarily recovery and energy absorption. Based on this principle. Some polymers were discovered having shape memory behavior [4–9].

As is well known, many beneficial properties of polyelectrolyte-surfactant complexes result from their ordered structures [10–13] 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.

Following the above research works, we have recently discovered the shape memory effect of Poly(acrylic acid-co-methyl methacrylate)-cetyltrimethylammonium bromide (P(AA-co-MMA)-C_{16}TAB) complex [14]. The principle of this phenomenon is based on a reversible ordered-disorder transition due to the formation of crystalline aggregates among the long alkyl chains of C_{16}TAB in the complex. The transition temperature of this complex almost does not vary with the water content due to the hydrophobicity of MMA units.

We report here another type of shape memory complexes where acrylamide(Am) instead of methyl methacrylate is used as a comonomer. Unlike crystalline aggregates of the (P(AA-co-MMA)-C_{16}TAB) complex, the reversible phase of the P(AA-co-Am)-C_{16}TAB complex is AA-C_{16}TAB segments formed by the electrostatic interactions between them, and the fixing phase is network, i.e., the gel network restores its random coil conformation when the temperature is elevated about the glass point. A specific feature of this type of shape memory complexes is that the transition temperature can be controlled by changing the degree of cross-linkage. This is because Am units are substantially hydrated in water, and water content can be controlled by the degree of cross-linkage (DCL). This is important from a practical viewpoint, since one can activate the shape effect at a desired temperature. The composition and the structure of network and complex are characterized, and the mechanism of shape memory behavior with temperature is discussed.

EXPERIMENTAL PART

Materials

Acrylic acid (A.R.), acrylamide (C.P.), potassium persulfate ($K_2S_2O_8$) (C.P.) and N,N′-methylenebis(acrylamide) (MBAA) were commercially available. Acrylic acid was distilled at 313 K under reduced pressure before use. Acrylamide was recrystallized from ethanol solution. Potassium persulfate, used as a radical initiator, was also recrystallized from water. N,N′-methylenebis(acrylamide), used as a cross-linker, and cetyltrimethylammonium bromide were used without further purification.

Preparation

P(AA-co-Am) network was prepared by radical copolymerization of 1.0 mol/L acrylic acid (AA) with 1.0 mol/L acrylamide (Am) in the presence of 0.01 mol/L ($K_2S_2O_8$) and N, N′-methylenebis(acrylamide) in water at 60°C for 24 hours. The degree of cross-linkage (DCL) was simply calculated as a molar ratio of cross-linker to the total monomer. After polymerization, the gel was immersed in a large amount of water for 2 weeks. The sample was divided into two parts. One represented as P(AA-co-Am) network was still immersed into water. The other one was immersed into 0.01 mol/L cetyltrimethylammonium bromide (C_{16}TAB) solution that was changed every week at 25°C for 4 weeks, then immersed into water to remove C_{16}TAB absorbed on the surface of P(AA-co-Am)-C_{16}TAB complex. This sample was represented as P(AA-co-Am)-C_{16}TAB complex. These two samples were dried at room temperature in vacuum.

Measurements

The glass transition temperature was measured using a differential scanning colorimeter (PERKIN ELMER-7) from 40°C to 120°C. The heating rate and cooling rate were 10°C/min. Dynamic mechanical analyses were carried out with a Du Pont 983 DMA at a fixed oscillation amplitude of 0.1 mm and under nitrogen gas purging. The measured specimens were heated from 40°C to 120°C using a heating rate of 5°C/min.

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The shape memory effect was examined by a bending test as follows: A straight strip specimen was folded at 100°C and cooled to kept the deformation. Then the deformed sample was heated again at a fixed heating rate of 2°C/min from 10 to 140°C and the change of the angle θ_f with temperature was recorded. The ratio of the recovery was defined as $\theta_f/180$. This process was designated as a temperature series test hereafter.

In addition, the relation between the time of shape recovery and water content was investigated. The time of shape recovery was measured as follows: the straight strip was treated as above, then the time of $\theta_f = 90°$ was recorded. Water content (Wt, %) was defined as follows:

$$\mathrm{Wt}(\%) = 100 \times (\mathrm{W_f} - \mathrm{W_d})/\mathrm{W_f}$$

Where $\mathrm{W_f}$ = weight of the swelled complex, $\mathrm{W_d}$ = weight of the complex after vacuum dried.

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RESULTS AND DISCUSSION

It is well known that the dynamic mechanical analysis, which is sensitive to the molecular motion in polymers, could provide important information on thermal motions of amorphous state. Figure 1 shows

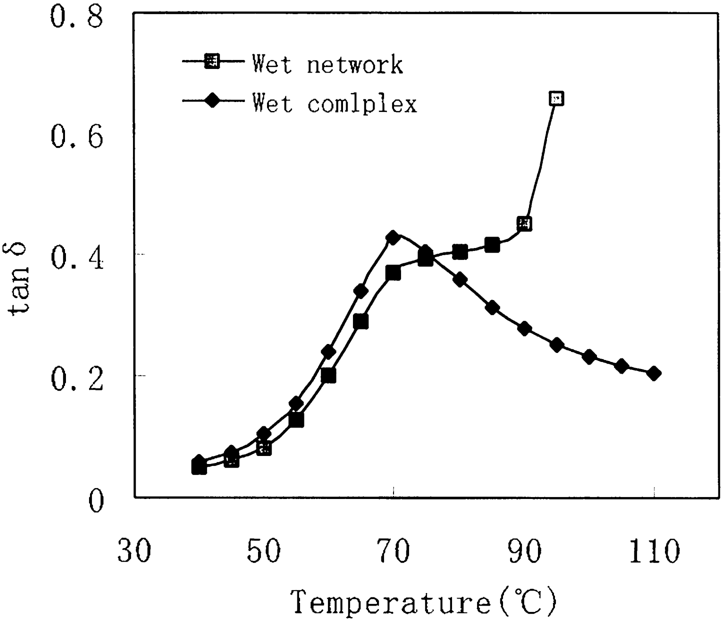

FIGURE 1 DMA analysis of complex and network.

the results of the DMA of the wet network with DCL = 3% and its complex. A loss tan δ peak at 70°C associated with the glass transition of AA units was found in the network. With further rise of temperature, the value of tan δ increased slowly due to the breakdown of hydrogen bond and the motion of lateral group caused by the imperfection of network. However, a typical peak for α-relaxation of amorphous polymer was obtained for the complex. The peak for α-relaxation was associated with the motion of AA-surfactant segments, indicating the thermodynamic homogeneity of the complex. We assume the thermodynamic homogeneity could be connected with the hydrophobic interactions, which can stabilize the complex. Thus the complex was homogeneous to a few hundred angstroms and motional heterogeneity did not exist in the complex. The thermodynamic homogeneity brought a reversible glass-rubber transition, which is responsible for the shape memory effect of the complex.

In order to obtain further information on thermal motion of the complex, DSC measurements were made. The transition temperature (T_g) depended much on the water content, as shown in Figure 2.

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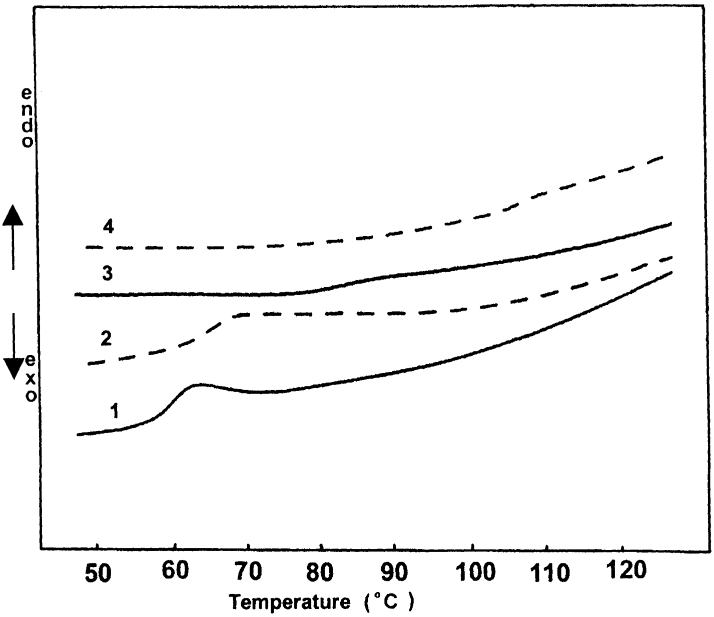

FIGURE 2 DSC thermograms of P(AA-co-Am)-C_{16}TAB complex and P(AA-co-Am) network: (1) complex, DCL = 1% WR = 10% (2) complex, DCL = 3% WR = 10% (3) dry complex, DCL = 3% (4) dry network, DCL = 3%.

Obviously, this is because the water plays a role of plasticizer in the complex. At the same time the T_g of the complex shifted to high temperature with increasing DCL. This shift might be associated with the fact that the AA-surfactant segments inside the complex become less active. Wet complex had a lower T_g than the dry one due to the hydrophilic property of network. Furthermore, the T_g of the complex was higher than that of the network itself, due to the flexibility of hydrophobic long-chain molecules of surfactant.

To give a direct support of shape memory effect of P(AA-co-Am) complex, the shape memory behavior of the network and its complex was detected in the temperature study, as shown in Figure 3. The deformed complex would recover the deformation rapidly when it was heated to high temperature. The ratio of recovery can reach 90%. While the network showed a slow recovery rate, there was residual deformation that could not recover under the testing process.

By the study above, the shape memory behavior of the complex was found. It would keep the deformation at the temperature range, which was lower than the T_g of AA-surfactant segment and recover to the original shape under the heating process.

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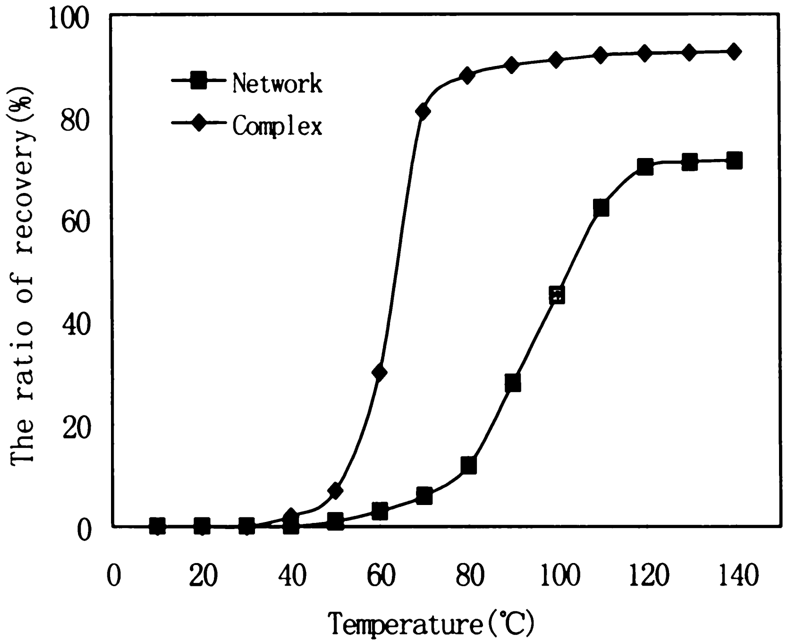

FIGURE 3 Shape-memory behavior of dry complex and dry network in the temperature series study.

The shape memory behavior of the complex based on the different DCL was investigated in a water content series study, as shown in Figure 4. Initially the complex with DCL of 1% showed a slow recovery rate. Next, the rate gradually shifted to high level when the water content decreased until the maximum value was obtained. Subsequently, the effect of shape memory gradually declined again. The reason is as follows: when the deformed complex was heated again above the transition temperature, the reversible phase of AA-surfactant segments became soft, and the molecular segments disoriented. The complex gradually reached a thermodynamic equilibrium under the elastic force of network, that is to say, the recovering rate of complex was dictated by the elastic force of network, which means the motions of chain segments in the network. A unit of the complex was strongly hydrophilic in nature, capable of adsorbing large amounts of water, which provided enough space for the motions of chain segments. Hence, water is important for the recovery rate. A similar tendency but a higher water content corresponding to the maximum value of recovery rate also occured for the complex of DCL = 3%. This is because much more water was needed for maintaining the motion of chain segments of network. Consequently, the recovery rate of the

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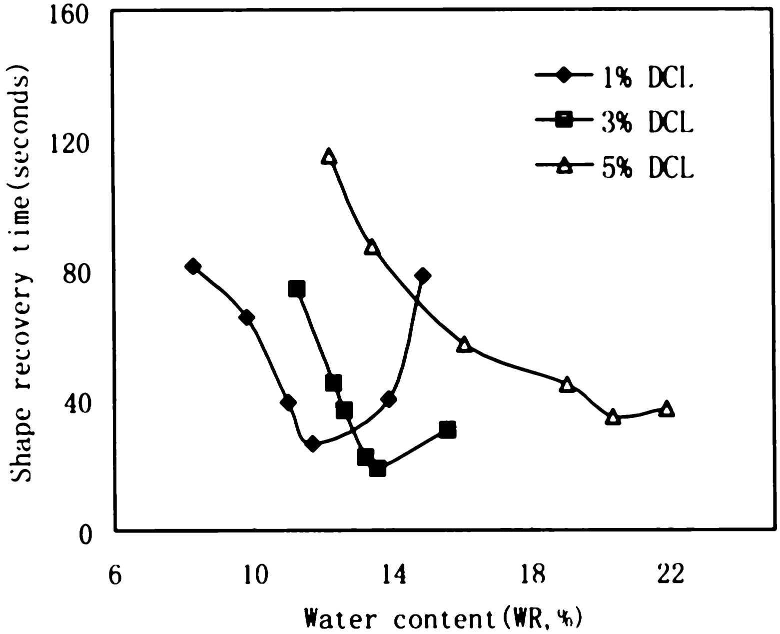

FIGURE 4 Water content dependence of shape memory ratio of complex.

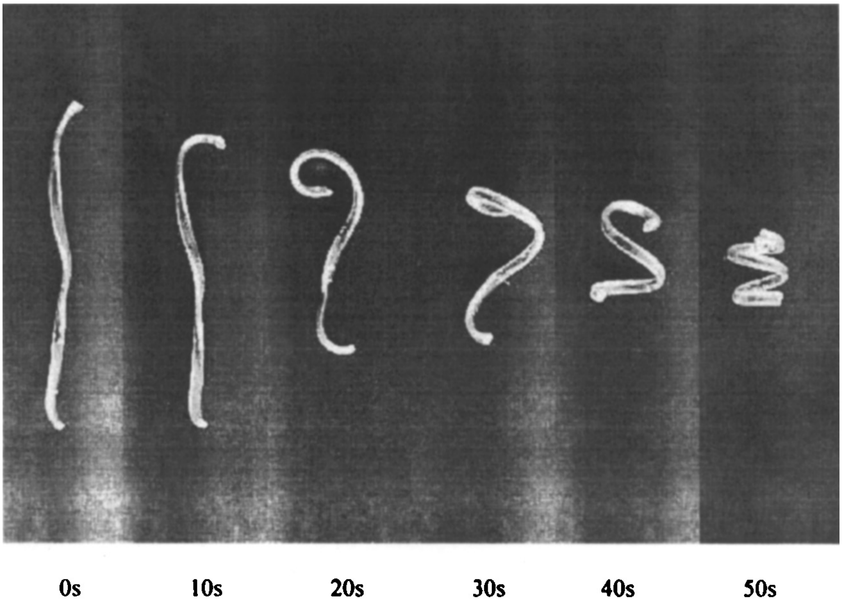

FIGURE 5 Shape memory phenomenon of P(AA-co-Am)-C_{16}TAB complex.

complex of DCL = 5% nearly reached its maximum when the shape memory effect appeared.

Figure 5 shows the shape memory phenomenon of P(AA-co-Am)-C_{16}TAB complex. The spring shape sample was heated to 90°C, then deformed as a strip shape and cooled to room temperature. The complex was rigid and retained the strip shape. On heating again to 90°C, the complex became soft and recovered its original spring shape.

In conclusion, the P(AA-co-Am)-C_{16}TAB complex has shape memory behavior due to the formation of thermodynamically homogeneous structures. The special feature of the P(AA-co-Am)-C_{16}TAB in contrast to the P(AA-co-MMA)-C_{16}TAB) complex lies in the potential capability for modulating its transition temperature, which is very important in the real application of this polymer property. Detailed experimental and theoretical analyses of the aggregate are now in progress.

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