Shape Memory of Hydrogen-Bonded Polymer Network/Poly(ethylene glycol) Complexes

Guoqin Liu, Xiaobing Ding, Yiping Cao, Zhaohui Zheng, and Yuxing Peng*

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China

Received November 15, 2003; Revised Manuscript Received December 30, 2003

ABSTRACT: Because of a large difference in storage modulus below and above the glass transition temperature, poly(acrylic acid-*co*-methyl methacrylate)/poly(ethylene glycol) (P(AA-*co*-MMA)/PEG) complexes show shape memory properties with a recovery ratio of nearly reach 99%. Before the shape memory testing, it was necessary to determine the conformational changes of the P(AA-*co*-MMA) gel induced by complexation with linear PEG. It was found that both the concentration and molecular weight of PEG have a strong effect on the complexation with P(AA-*co*-MMA) gel. In such a system the minimum molecular weight of PEG required for the complex formation lowers to 1000.

Introduction

Poly(carboxylic acid)s can form intermacromolecular complexes with poly(ethylene glycol) (PEG) due to the hydrogen bonding between the carboxy groups of poly(carboxylic acid)s and the ether oxygen atoms of PEG.[1] The formation of this hydrogen-bonded complex is highly sensitive to a change in the concentration or molecular weight of PEG, temperature, and other parameters.[2,3]

The complex formation in the poly(carboxylic acid) networks is quite different from that in linear poly(carboxylic acid)s. The conformational changes of the poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAA) networks in PEG solution were reported in refs 4−7. It was shown that the absorption of PEG leads to the contraction of the gel of PMAA or PAA, and the relative mass of the gel can be lowered by a factor of 1.5−3.0. This may be the reason why research work concerning the mechanical properties of complexes has not been presented previously.

In our previous paper,[8] we reported the observation of shape memory behavior exhibited by poly(acrylic acid-*co*-methyl methacrylate)/cetyltrimethylammonium bromide (P(AA-*co*-MMA)/C_{16}TAB) complexes prepared in our laboratory. The shape memory principle of this type of complex is based on a reversible order−disorder transition due to the formation of crystalline aggregates among the long alkyl chains of C_{16}TAB in the complexes. This gives us a hope to design a hydrogen-bonded polymer network−poly(ethylene glycol) complex for shape memory network. In the present work, the complex of a poly(acrylic acid-*co*-methyl methacrylate) (P(AA-*co*-MMA)) network with PEG stabilized by the hydrogen bonding was prepared. As comonomer with AA, methyl methacrylate (MMA) was selected due to the low glass transition temperature (T_g) of the PEG:PAA complex phase ($T_g = 12$ or 5 °C[9,10]) because a suitable shape recovery temperature (T_s) is required for the real application of shape memory materials (in this case the T_g of the complex phase being T_s). By introducing the PMMA component, a higher T_g can be expected for the complexes. Meanwhile, a large contraction of gel induced by complexation with PEG can be averted. In these complexes, crystalline aggregates cannot be found, although PEG is a semicrystalline polymer, yet good shape memory behavior can be achieved. In fact, the ratio of recovery reaches almost 99%.

Table 1. Notation and Compositions of P(AA-*co*-MMA)/PEG Complexes

	formulations of initial PEG solution	
notation	MW	C_P (%)
C_P series		
B1	6000	2
B2	6000	5
B3	6000	7
B4	6000	11
B5	6000	15
B6	6000	20
B7	6000	30
B8	6000	40
MW[a] series		
C1	400	9
C2	1000	9
C3	2000	9
C4	4000	9
C5	10000	9
C6	20000	9

[a] Molecular weight of PEG.

Experimental Section

Materials. Acrylic acid (AA), methyl methacrylate (MMA), 2,2′-azobis(isobutyronitrile) (AIBN), and *N,N*′-methylenebis(acrylamide) (MBAA) were of analytical grade obtained from the Chengdu Reagent Factory. Samples of poly(ethylene glycol) (PEG) with catalog number-average molecular weights of 400, 1000, 2000, 4000, 6000, 10 000, and 20 000 (Aldrich) were used as received. AA and MMA were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. MBAA, used as a cross-linker, and PEG were used without further purification.

Preparation. The P(AA-*co*-MMA) network was prepared by radical copolymerization of 1.0 mol L^{-1} AA with 1.0 mol L^{-1} MMA in the presence of 0.01 mol L^{-1} AIBN as an initiator and MBAA as a cross-linker in dimethyl sulfoxide. The reaction mixture was bubbled with nitrogen for 15 min to remove the oxygen from the mixture and then injected into the space between two glass plates separated by polyethylene spacers (3 mm thick) or into a cylindrical glass tube with a diameter 7 mm. Gelation was carried out at 55 °C for 24 h. After polymerization, the cross-linked P(MAA-*co*-MMA) was immersed in 2000 mL of an ethanol−water mixture (50/50 wt %) for 1 week to remove the monomers and un-cross-linked polymers and then in a large amount water for 3 weeks until

---

* To whom all correspondence should be addressed. E-mail: yxpeng@cdb.ac.cn or yxpeng@cioc.ac.cn.

10.1021/ma035717w CCC: $27.50

equilibrium was reached. The sample was divided into two parts. One represented as P(MAA-*co*-MMA) network was still immersed into water. The other part was put in PEG solution (3 mL of the solution per 1 mg of swollen network). The formulations of initial PEG solution are summarized in Table 1. The samples were thermostated at 25 °C for 1 week, and then rinsed PEG absorbed on the surface of P(AA-*co*-MMA)/PEG complex with water. According to the formulations of initial PEG solution and compositions of P(AA-*co*-MMA) networks, these complexes were represented as C_P series and MW (molecular weight of PEG) series, respectively. All specimens were dried under vacuum at room temperature for 7 days.

Composition of Complexes. To obtain information on copolymer composition and polymer yield, a sample of the prepared gels was quenched and then dried under vacuum at room temperature for 10 days to remove solvent and unreacted monomers. The weight loss, except for the solvent, during the drying process was negligible, indicating that the monomer-to-polymer conversion was nearly 100% and that the molar ratio of PAA to PMMA in the copolymer was close to 1:1. The composition of the complexes was characterized as follows: by knowing the weight of the dried gel before complexation, the weight of the complexes equilibrated with PEG water solution (the water on the surface of complex disks was adsorbed before weighing) and the weight of the dried complexes, we could calculate the binding degree (θ: molar fraction of PEG/PAA repeating units in the networks) of PEG with the polymer network. The relative mass of the sample was characterized by the m/m_0 ratio, where m is the mass of the complex at the equilibrium state and m_0 is the mass of the gel equilibrated with water.

Differential Scanning Calorimetry (DSC). The thermal analyses were carried out with a differential scanning calorimeter (Du Pont 9900) over a temperature range from −40 to 120 °C at a heating rate of 10 °C/min, purged with nitrogen gas, and quenched with liquid nitrogen. The cell was calibrated using an indium standard; the weight of the sample was 5−10 mg.

Dynamic Mechanical Analysis (DMA). The 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. A sheet of the sample (0.77 cm wide, 0.22 cm thick, 4.2 cm long) was heated from 20 to 100 °C using a heating rate of 3 °C/min. The modulus ratio was obtained by the definition $E'_{50°C}/E'_{90°C}$, where E' was the storage modulus.

Shape Memory Behavior. The method of evaluating the shape memory effect of the shape memory alloy[11] was adopted to investigate that of our specimens. The shape memory effect was examined by a bending test as follows: a straight strip of the specimen was folded at 90 °C and then cooled to keep the deformation. Then the deformed sample was heated again at a fixed heating rate of 2 °C/min from 20 to 130 °C, and the change of the angle θ_f with temperature was recorded. The ratio of the recovery was defined as $\theta_f/180$.

Results and Discussion

Conformational Changes and Composition. When the gel of PAA or PMAA is put in an aqueous solution of PEG, it could change drastically its dimensions with infinitesimal variation of external parameters such as temperature, pH, and the concentration of PEG solution. This phenomenon is called polymer gel collapse. Starodubtzev[6,12] showed that the absorption of PEG leads to the contraction of the gel of PMAA or PAA, and the relative mass of the gel is lowered by a factor of 1.5−3.0. However, a slight contraction of gel can be observed for the gel of P(AA-*co*-MMA). Figure 1 illustrates the dependence of the relative mass of the P(AA-*co*-MMA)/PEG complex A on the initial concentration of PEG 6000 (C_P). We see that the increase of C_P up to 30 wt % leads to a further contraction of the P(AA-*co*-MMA) gel. Then, in the large region of PEG concentration (30−40 wt %), the relative mass of the gel changes insignificantly. It is to be noted that the transition of weakly cross-linked PMAA or PAA gel from a swollen to the collapsed state is observed at low concentrations of PEG solutions (<5 wt %). At rather high concentrations of PEG (5−10 wt %) a reswelling of the collapsed gel of PAA or PMAA is observed.[6,14] This phenomenon does not occur for the P(AA-*co*-MMA) gel due to the difference in hydrophobic character of the network. P(AA-*co*-MMA) is highly hydrophobic compared with PAA because they have MMA component in its backbone chain. The main reason for the contraction of the gel is the intermacromolecular complex formation,[12] and it was suggested[13] that the driving forces of the aggregation of the complex are partly hydrophobic interactions. For P(AA-*co*-MMA)/PEG complexes, MMA units are able to participate in interactions between their hydrophobic group and the main chain of PEG as well as participating in hydrogen bonding, which is the main interacting force.

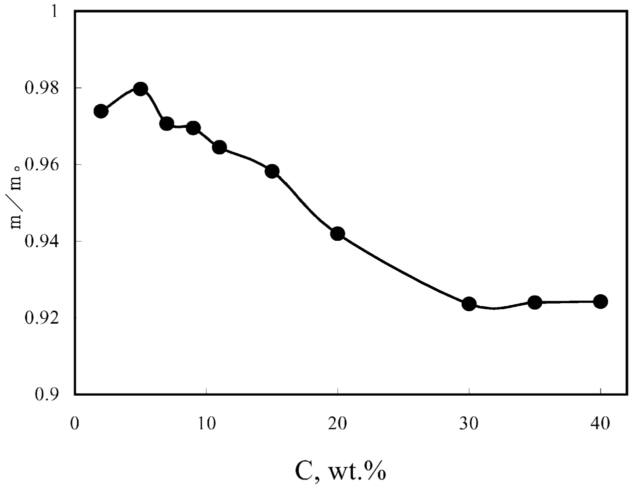

Figure 1. Dependence of the relative mass of the P(AA-*co*-MMA)/PEG complex B on the initial concentration of PEG 6000.

In further experiments, we have studied the influence of the concentration on binding degree (θ). When the concentration of PEG increases to 13 wt %, there is a fair amount of PEG that is not complexed with PMAA or PAA in the gel.[6] It is then interesting to investigate the P(AA-*co*-MMA)/PEG system. DSC and DMA results discussed later suggested that no excess PEG is observed, and there is only the PEG:PAA complex phase even in complex B8 formed in the solution of $C_P = 40$ wt %. Figure 2 illustrates the dependence of θ of complex B on initial concentration of PEG 6000. With increasing C_P of PEG solution, the θ value increased simultaneously.

It would be of interest to study the effects of chain length of PEG on the complexation with the P(AA-*co*-MMA) network, too. Figure 3 shows the dependence of θ of complex C on molecular weight of PEG. The θ value was the highest at MW = 6000 and gradually decreased with the increase of molecular weight of PEG. The above results indicate that PEG with molecular weight of 400 does not interact with the P(AA-*co*-MMA) gel and that in order to form a stable complex it is necessary for PEG to have sufficient long chain. When molecular weight was increased above 6000, the decreasing θ values could be attributed to the steric hindrance from the relatively small mesh size of the polymer network for the long

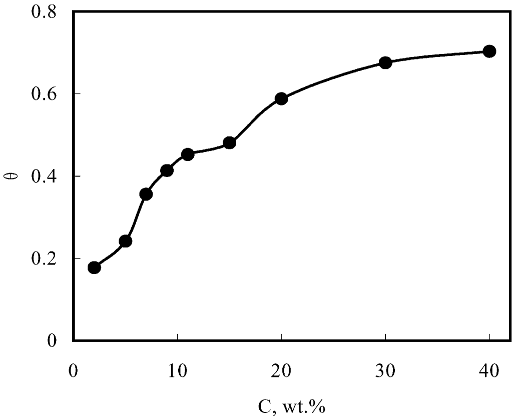

Figure 2. Dependence of θ of the P(AA-*co*-MMA)/PEG complex B on initial concentration of PEG 6000.

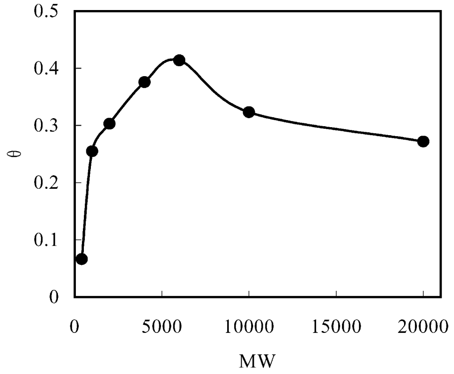

Figure 3. Dependence of θ of the P(AA-*co*-MMA)/PEG complex C on molecular weight of PEG.

PEG chain to interact with PAA, as evidenced by the late experiments that higher cross-linking density (corresponding to smaller mesh size) of P(AA-*co*-MMA) network would hinder the PAA from forming complex with PEG.

It should be remembered here that PEG with molecular weight of 7500 or lower does not form any complexes with linear PAA.[2] For the complexation between cross-linked PAA an linear PEG, there is a definite range of molecular weight of PEG where the stable complexes exist, below and above which the conditions of complete complexation will be disrupted.[4] The lower limit of molecular weight of PEG is equal to 6000, and the upper limit is equal to 100 000. From Figure 3, we notice that PEG with molecular weight of 1000 apparently can form a complex with a three-dimensional network of P(AA-*co*-MMA), despite its short chain length. We believe that there are three possible reasons for this effect: (1) the decrease in apparent dissociation constant of PAA by cross-linking; (2) the local difference concentration of PEG near the P(AA-*co*-MMA) network; (3) the hydrophobic character of PMMA on favoring the equilibrium of the complexation.

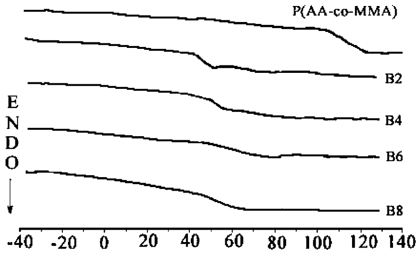

Figure 4. DSC thermograms of the P(AA-*co*-MMA)/PEG complex B formed in the solution of PEG of various initial concentrations.

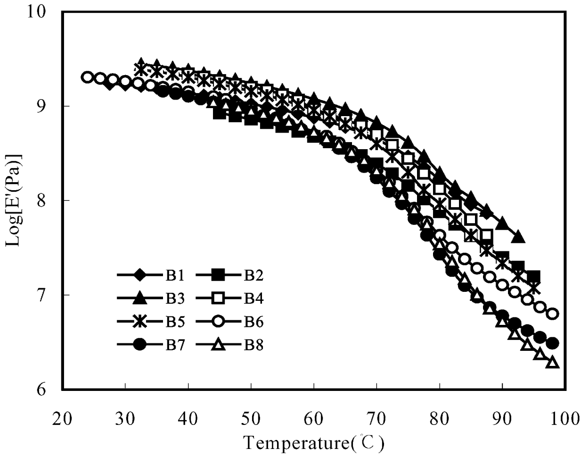

Figure 5. Temperature dependence of tensile storage modulus E' for P(AA-*co*-MMA)/PEG complex B formed in the solution of PEG 6000 of various initial concentrations.

DSC. Differential scanning calorimetry (DSC) is extensively used to investigate miscibility in polymer blends or complexes. A single compositionally dependent glass transition is an indication of full miscibility at a dimensional scale between 20 and 40 nm.[15] Figure 4 shows the DSC scanning curves of the P(AA-*co*-MMA) networks and the P(AA-*co*-MMA)/PEG complex B formed in the solution of PEG of various initial concentrations. The pure amorphous P(AA-*co*-MMA) network exhibits one T_g at 115 °C while the T_gs of P(AA-*co*-MMA) shift to lower temperatures for the complexes. However, endothermic peaks due to the melting of PEG crystallites cannot be observed for all complexes. All P(AA-*co*-MMA)/PEG complexes showed only a single glass transition temperature, suggesting that these are fully miscible complexes with a homogeneous amorphous phase. During the heating process, the molecular chain of the PAA−PEG complex phase acts as amorphous only during the transfer from the glassy state to the rubbery state.

Dynamic Mechanical Analysis (DMA). The storage modulus E' of the P(AA-*co*-MMA) network and P(AA-*co*-MMA)/PEG complex B formed in the solution of PEG 6000 of various initial concentrations as a function of temperature is shown in Figure 5. A pronounced decrease in E' occurred in the T_g region for all P(AA-*co*-MMA)/PEG complexes, while E' values for the P(AA-*co*-MMA) network gradually decreased during the glass transition, and only a small difference in storage modulus was discovered. Modulus ratio data are summarized in Table 2; the storage modulus ratio increased with the PEG concentration, which is in good agreement with the θ results shown in Figure 2. From Figure 5, it can be seen that the rubbery modulus ($E'_{90°C}$) increased with increasing PEG concentration.

The loss tangent for the P(AA-*co*-MMA)/PEG complex B increased with the increasing PEG concentration as shown in Table 2. Complex B8 has a tan δ value as high as 1.086 at the T_g region. Since the tan δ corresponds to the strain energy dissipated by viscous friction, a large tan δ implies that the material is more likely to be viscous than elastic. This type of complexes may be used for vibration control due to their high loss tangent value at T_g region, since impact energy can be effectively abosorbed.[16]

Table 2. Storage Modulus Ratio (E' Ratio)[a] and Maximum tan δ of P(AA-*co*-MMA) Network and P(AA-*co*-MMA)/PEG Complexes

notation	E' ratio	$\tan_{\max}\delta$	notation	E' ratio	$\tan_{\max}\delta$
B1	15.4	0.6486	P(AA-*co*-MMA)	5.4	0.3659
B2	28.1	0.7126	C1		
B3	30.4	0.7405	C2	25.8	0.6133
B4	42.5	0.7567	C3	37.4	0.7208
B5	66.1	0.8597	C4		
B6	89.7	0.8701	C5	51.6	0.8312
B7	145.6	1.036	C6	63.3	0.9866
B8	168.2	1.086			

[a] The storage modulus ratio (E' ratio) was defined as ($E'_{50°\mathrm{C}}/E'_{90°\mathrm{C}}$).

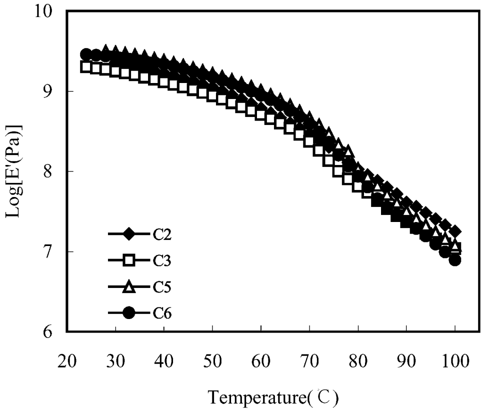

Figure 6. Temperature dependence of tensile storage modulus E' for P(AA-*co*-MMA)/PEG complex C formed in the solution of PEG with various molecular weights.

Figure 6 shows the storage modulus of the P(AA-*co*-MMA)/PEG complex C formed in the solution of PEG with various molecular weights. In Table 2, it can be seen that modulus ratio increased with increasing PEG molecular weight. This result does not coincide with findings in previous θ values as shown in Figure 3. In complex C6, 72.8% of the interacting groups are left unbound, whereas the complex shows a high modulus ratio. The above results allow us to make the assumption that the modulus ratio of the P(AA-*co*-MMA)/PEG complex depends strongly on molecular weight of PEG, not just on θ value. The loss tangent for the P(AA-*co*-MMA)/PEG complex C increased with PEG molecular weight as shown in Table 2, which is in good agreement with the modulus ratio effects.

Shape Memory Behavior. The shape memory effect can be described briefly as the following mathematical model:[18]

$$\text{shape fixity ratio } f^{-}_{\mathrm{f}} = 1 - E_{\mathrm{r}}/E_{\mathrm{g}} \tag{1}$$

$$\text{shape recovery ratio } R_{\mathrm{f}} = 1 - f^{-}_{\mathrm{IR}}/[(1 - E_{\mathrm{r}}/E_{\mathrm{g}})f^{-}_{\infty}] \tag{2}$$

where E_{g} is the glass state modulus, E_{r} is the rubbery modulus, f^{-}_{IR} is the viscous flow strain, and f^{-}_{∞} is the strain when $t \gg \tau'$ (relaxation time). A high elasticity ratio ($E_{\mathrm{g}}/E_{\mathrm{r}}$), preferably with a difference of 2 orders of magnitude, allows for easy shaping at $T > T_{\mathrm{s}}$ (shape memory temperature) and great resistance to deformation at $T < T_{\mathrm{s}}$.[19] One or two of these requirements can be satisfied easily with many of the existing polymeric materials. It is known that polymer networks generally do not show satisfactory shape memory behavior since a large difference in modulus below and above the glass transition temperature,[20] as evidenced by the modulus ratio of P(AA-*co*-MMA) network in Table 2.

In Figure 7 a picture sequence demonstrates impressively the performance of shape memory polymers. The permanent shape of the polymers is that of a rod, which has been deformed to a spiral (temporary shape) during the handling process. Under the influence of hot air having a temperature of 90 °C the permanent shape is recovered as soon as the T_{s} is reached.The permanent shape is recovered with a precision of more than 99%. The shape memory behavior is detected in the temperature study, as shown in Figure 8. The data curves, based on the recoverable ratio and temperature, were S-shaped. The deformation could be recovered relatively rapidly when the deformed P(AA-*co*-MMA)/PEG complexes were heated again to high temperature. This interesting phenomenon is reversible and cyclically reproduced by repeated temperature changes. While the P(AA-*co*-MMA) network showed a slow recovery rate, there was still residual deformation that did not recover under the testing process. On the other hand, the complex with a higher PEG molecular weight showed a higher recovery rate than those with a lower PEG molecular weight. These results were in agreement with the modulus ratio data of the complexes discussed above.

By introducing PEG, the complexes possessed a shape memory effect due to that a large difference in storage modulus below and above the glass transition temperature occurred. A large difference in modulus below and above the transition temperature is the most substantial property to render the material's shape memory func-

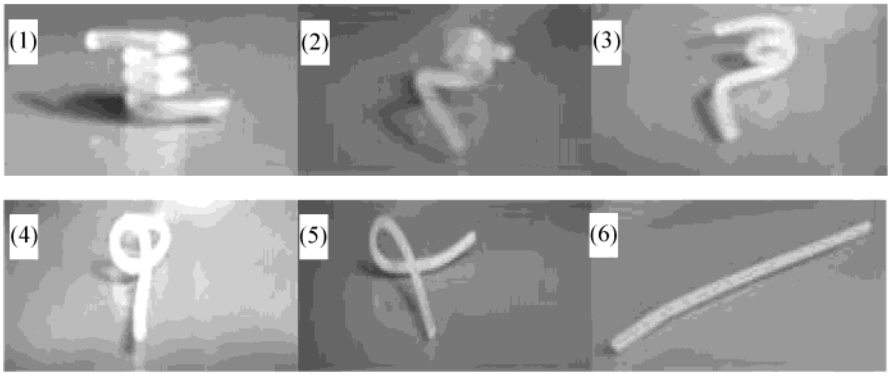

Figure 7. Transition from the temporary shape (spiral) to the permanent shape (rod) for B8 (T_{g}: 70 °C). The recovery process takes 70 s after heating to 90 °C.

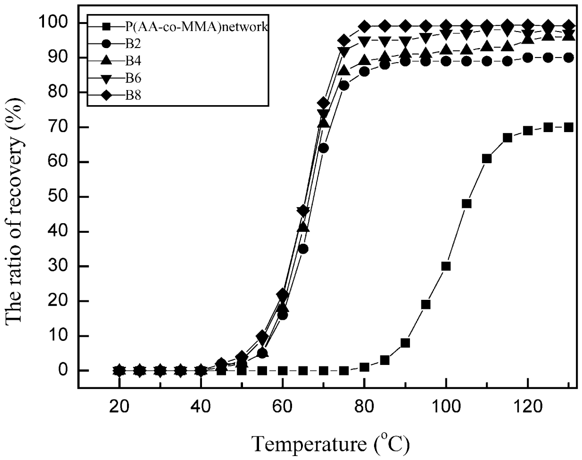

Figure 8. Shape memory effect of P(AA-*co*-MMA)/PEG network and complex B formed in the solution of PEG 6000 of various initial concentrations.

tion. With a large elastic modulus ratio, high-temperature deformation becomes easy while keeping the resistance to low-temperature deformation great.[19]

The principle of shape memory behavior found in the P(AA-*co*-MMA)/PEG complex is that the polymer network restores its random coil conformation when the temperature is elevated about the glass point, which is the same as that of the thermoplastic described in Flory's famous book *Principle of Polymer Chemistry*. This is the reason the shape of the P(AA-*co*-MMA) network without PEG in Figure 8 could be recovered to about 70% in the absence of the interpolymer complex formation.

Shape memory polymers basically contain a fixing phase and a reversible phase.[21] The fixing phase can be chemical or physical cross-linking, imparting a level of rigidity, dimensional stability, and thermal resistance, while the reversible phase can be either crystalline or amorphous and provide properties of elastomers—primarily recovery and energy absorption. Considering the P(AA-*co*-MMA)−PEG complex, the fixing phase is the chemical cross-linked point, while the reversible phase was the PEG:PAA complex phase. Reversible phase transformation is responsible for the shape memory effect.

Conclusion

The complexes show shape memory properties due to a large difference in storage modulus below and above the glass transition temperature. When the PEG with higher molecular weight was introduced into the P(AA-*co*-MMA) network, it had the following results: (1) the higher modulus ratio and (2) a higher recovery rate. Reversible phase transformation is responsible for the shape memory effect.

Acknowledgment. This project (50373045) is supported by the National Natural Science Foundation of China.

References and Notes

(1) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(2) Ikawa, T.; Abe, K.; Tsuchida, E. *J. Polym. Sci., Part A* **1975**, *13*, 1505.
(3) Osada, Y.; Sato, M. *J. Polym. Sci., Part C* **1976**, *14*, 129.
(4) Bekturov, E. A.; Frolova, V. A.; Mamytbekov. G. K. *Macromol. Chem. Phys.* **2000**, *201*, 1031.
(5) Osada, Y. *Adv. Polym. Sci.* **1987**, *82*, 1.
(6) Philippova, O. E.; Karybiants, N. S.; Starodubtzev, S. G. *Macromolecules* 1**994**, *27*, 2398.
(7) Skirda, V. D.; Aslanyan, I. Y.; Philippova, O. E.; Karybiants, N. S.; Khokhov, A. R. *Macromol. Chem. Phys.* **1999**, *200*, 2152.
(8) Guan, Y.; Cao, Y. P.; Peng, Y. X.; Chen, A. S. C. *Chem. Commun.* **2001**, *17*, 1694.
(9) Aubin, M.; Voyer, R. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 419.
(10) Miyoshi, T.; Takegoshi, K.; Hikichi, K. *Polymer* **1997**, *38*, 2315.
(11) Lin, H. C.; Wu, S. K. *Scr. Met.* **1992**, *26*, 959.
(12) Starodubtzev, S. G.; Philippova, O. E. *Vysokomol. Soedin., Ser. B* **1992**, *34*, N7, 72.
(13) Yu, X.; Tanaka, A.; Tanaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1992**, *66*, 514.
(14) Yu, X.; Tanaka, A.; Tanaka, K.; Tanaka, T. *J. Chem. Phys.* **1992**, *97*, 7805.
(15) Kuo, S. W.; Chang, F. C. *Macromolecules* **2001**, *34*, 4089.
(16) Lee, B. S.; Chun, B. C.; Chung, Y. C.; Sul, K. I.; Cho, J. W. *Macromolecules* **2001**, *34*, 6431.
(17) Karybiants, N. S.; Philippova, O. E.; Starodubtzev, S. G.; Khokhov, A. R. *Makromol. Chem. Phys.* **1996**, *197*, 2373.
(18) Wang, S.; Lv, Z.; Zhao, W.; Xu, X.; Li, B. *Polym. Mater. Sci. Eng.* **2000**, *16*, 1.
(19) Kim, B. K.; Lee, S. Y. *Polymer* **1996**, *37*, 5781.
(20) Reyntjens, W. G.; Du Prez, F. E.; Goethals, E. G. *Macromol. Rapid Commun.* **1999**, *20*, 251.
(21) Lin, J. R.; Chen, L. W. *J. Appl. Polym. Sci.* **1999**, *73*, 1305.

MA035717W