

Hydrogen-bonded polymer network—poly(ethylene glycol) complexes with shape memory effect

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Complexes of a poly(methacrylic acid-*co*-methyl methacrylate) network with poly(ethylene glycol) stabilized by hydrogen bonds were prepared. By introducing poly(ethylene glycol), the complexes possessed shape memory effect, due to which a large difference in storage modulus below and above the glass transition temperature occurred. The morphology of the complexes was investigated and the mechanism of the shape memory behavior was discussed. This kind of complexes can be regarded as a novel shape memory network.

Introduction

Polymer complexes are macromolecular structures formed by the noncovalent association of polymers that have an affinity for one another. The major classes of polymer complexes are stereocomplexes, polyelectrolyte complexes, and hydrogen bonded complexes.¹ Among these complexes, the hydrogen bonded complexes have attracted many researchers over the past two decades due to their special character;^{2,3} many biological phenomena such as enzymatic processes, supermolecular assemblies in virus shells, and muscle contraction are related to intermacromolecular complexes governed by hydrogen bonds. The formation of hydrogen bonded complexes between the poly(methacrylic acid) (PMAA) network and poly(ethylene glycol) (PEG) has been much reported.^{4–7} However, research work concerning the mechanical properties of PMAA–PEG complexes has not been presented because the complexes could not provide enough rigidity due to the flexibility of PMAA.

It is known that polymer networks generally could not show satisfactory shape memory behavior since a large difference in modulus below and above the glass transition temperature and a sharp glass-rubber transition cannot be obtained for networks. A reasonable way to produce shape-memorized networks is to prepare networks containing crystallizable polymer chains.^{8–11} In our previous paper,¹¹ we reported the discovery of shape memory effects of poly(acrylic acid-*co*-methyl methacrylate)-cetyltrimethylammonium bromide (P(AA-*co*-MMA)-C₁₆TAB) complexes. The shape memory properties of this complex are based on a reversible order–disorder transition due to the formation of crystalline aggregates among the long alkyl chains of C₁₆TAB in the complex. All networks containing crystallizable polymer chains can exhibit shape memory behavior because their melting transition is sharp and the difference in their modulus below and above the melting transition temperature is large enough.

Based on previous work, we report here another type of shape memory complex that are stabilized by hydrogen bonds even though crystalline aggregates cannot be found in this complex. Complexes form between a chemically crosslinked copolymer of methyl methacrylate (MMA) and methacrylic acid (P(MAA-*co*-MMA)), which acts as a hydrogen bond donor, and PEG, which is a hydrogen bond acceptor. By introducing the PMMA component, the complexes behave as a

hard plastic. We have found that the complex shows shape memory effects due to a high elasticity ratio of the glass state modulus (E_g) to the rubbery modulus (E_r), and the ratio of recovery could reach nearly 100%. Up to now, no similar research work has been reported. Hence, the hydrogen-bonded polymer network–poly(ethylene glycol) complex can be considered as a kind of novel shape memory network. In this study, complexes with different molecular weights of PEG were synthesized to study the relationship between the morphology, dynamic mechanical properties, and shape memory behavior.

Experimental

Materials

Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2'-azobis(isobutyronitrile) (AIBN) and *N,N'*-methylenebis(acrylamide) (MBAA) were analytical grade from the Chengdu Reagent Factory. Samples of poly(ethylene glycol) (PEG) with catalogue number average molecular weights of 1000, 2000, 4000, 8000 (Aldrich) were used as received. MAA and MMA were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from an ethanol solution. MBAA, used as a cross-linker, and PEG were used without further purification.

Preparation

The P(MAA-*co*-MMA) network was prepared by radical copolymerization of 1.0 mol L⁻¹ MAA with 1.0 mol L⁻¹ MMA in the presence of 0.01 mol L⁻¹ AIBN as initiator and 0.02 mol L⁻¹ MBAA as crosslinker in dimethyl sulfoxide. The reaction mixture was bubbled with nitrogen for 15 min to remove oxygen from the mixture, then injected into the space between two glass plates separated by polyethylene spacers (3 mm thick), into a spring shape glass tube of diameter 7 mm, or into a cylindrical glass tube of diameter 7 mm. Gelation was carried out at 60 °C for 24 hours. After polymerization, the crosslinked P(MAA-*co*-MMA) was immersed in a 2000 mL ethanol–water mixture (50 : 50 wt%) for 1 week to remove the monomers and uncrosslinked polymers, then in 5000 mL water for 2 weeks. The sample was divided into two parts. One representing a P(MAA-*co*-MMA) network was immersed in water. The other part was immersed in a different molecular

Table 1 The μ values of complexes of P(MAA-co-MMA) with PEG of various molecular weights

Sample	μ (%)
Complex 1000 ^a	—
Complex 2000	56
Complex 4000	73
Complex 8000	85

^aPEG of molecular mass lower than 1000 does not form a complex with PMMA at room temperature.¹²

weight PEG solution with 16.0 wt% (3 mL of the solution per 1 mg of swollen network). The samples were thermostated at 25 °C for 1 week, then immersed in water for 1 hour to remove PEG absorbed on the surface of the P(MAA-co-MMA)-PEG complex. According to the PEG molecular weight, these samples were represented as complex 1000, complex 2000, complex 4000 and complex 8000, respectively. All specimens were dried under vacuum at room temperature for 3 days.

The characteristics of the prepared complexes are summarized in Table 1. 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 PMAA 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 water (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 (μ) of PEG with the polymer network.

Measurements

FTIR spectra were obtained on a Nicolet 200SXV FTIR spectrometer at a resolution of 2 cm⁻¹. A minimum of 16 scans were signal averaged. The dried samples were examined as pressed KBr disks. The thermal analyses were carried out with a differential scanning calorimeter (Du Pont 9900) over a temperature range of -50 °C to 150 °C at a heating rate of 10 K min⁻¹. The dynamic mechanical analyses (DMA) 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 40 °C to 150 °C using a heating rate of 5 K min⁻¹.

The method of evaluating the shape memory effect of a shape-memory alloy was adopted to investigate that of our specimens. The shape memory effect was examined by a bending test as follows: a straight strip specimen was folded at 100 °C then cooled at a cooling rate of 10 K min⁻¹ to keep the deformation. Then the deformed sample was heated again at a fixed heating rate of 2 K min⁻¹ from 20 to 140 °C and the change in the angle θ_f with temperature was recorded. The ratio of the recovery was defined as $\theta_f/180$.

Results and discussion

Various studies of the mechanism of complexation between the polymer network and PEG have been carried out using pH, viscosity and potentiometric measurements.¹³ These studies show that complexation occurs due to the formation of hydrogen bonds between the carboxy protons of PMAA and the ether group of PEG, and that the hydrophobic interactions between the CH₂ groups of PEG and the CH₃ groups of PMAA stabilize the complex. It should be noted that the P(MAA-co-MMA)-PEG complexes prepared from higher molecular weight PEG have large values of μ , as shown in

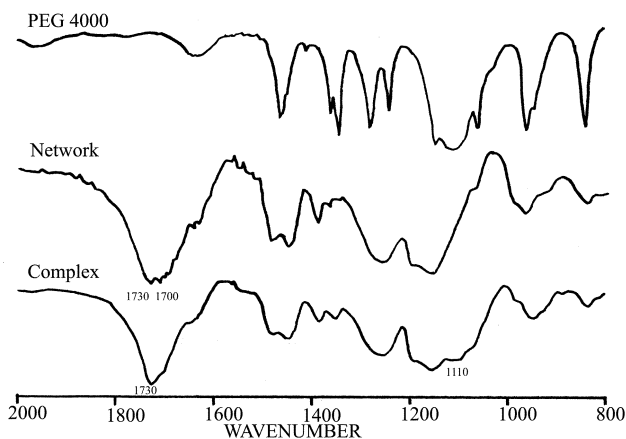


Fig. 1 FTIR spectra of PEG 4000, the P(MAA-co-MMA) network and complex 4000.

Table 1. This is because the stability of the complexes decreases sharply with decreasing length of the PEG macromolecules.¹²

Fig. 1 shows the FTIR spectra of PEG 4000, and the P(MAA-co-MMA) network before and after complexation with PEG 4000. The frequency of the C=O stretching absorption of the carboxylic acids is known to be affected by hydrogen bonding.¹⁴ The C=O stretching absorption of carboxylic acids is observed at 1750 cm⁻¹ in the monomeric state without hydrogen bonds and shifted to 1700 cm⁻¹ for the dimeric structure with hydrogen bonds. On the other hand, the wavenumber of the C=O stretching absorption of carboxylic acids in ether or dioxane usually appears at 1730 cm⁻¹. As shown in Fig. 1, the C=O stretching absorption of carboxylic acids appeared at 1700 cm⁻¹ rather than 1750 cm⁻¹ for the P(MAA-co-MMA) network, indicating that there is no monomeric state for carboxylic acids and that the carboxylic acid groups may have a dimer structure resulting from hydrogen bonds between them. After complexation, the absorption at 1700 cm⁻¹ disappeared, and the C=O stretching absorption was only observed at 1730 cm⁻¹, implying that the C=O stretching absorption of PMAA was overlapped by the C=O stretching absorption of PMMA. This suggests that complexation occurs due to the formation of hydrogen bonds between the PMAA carboxylic protons and the PEG ether group.

The thermograms of the P(MAA-co-MMA)-PEG complex 1000 and the P(MAA-co-MMA)-PEG complex 4000 are shown in Fig. 2. Complex 1000 displayed recrystallization and crystal melting behavior, indicating that a fair amount of PEG 1000 is not complexed with PMAA. This is because the chain length of PEG 1000 is insufficient for cooperative complexation.¹⁵ However, endothermic peaks due to the melting of PEG crystallites are not observed for complex 4000, and only one glass transition was exhibited corresponding to the PEG-PMAA complex. These facts mean the crystalline phase of PEG 4000 is

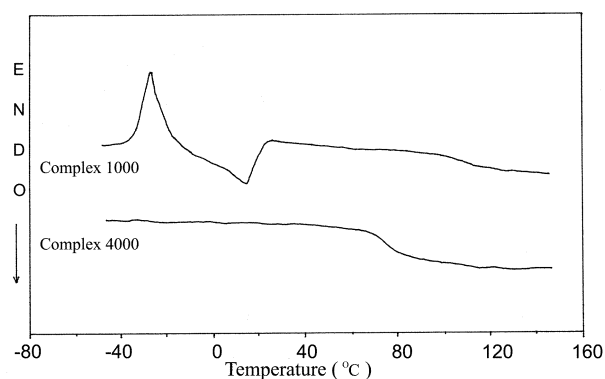


Fig. 2 DSC thermograms of complex 1000 and complex 4000.

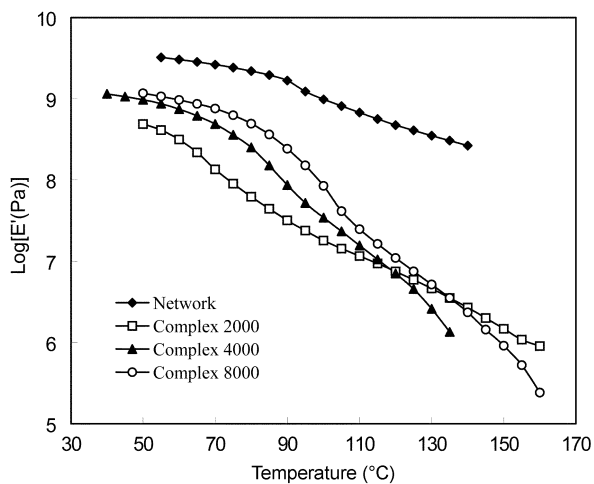


Fig. 3 Temperature dependence of tensile storage modulus E' for complex 2000, complex 4000, complex 8000 and the network.

destroyed in the complex and that there is only the PEG–PMAA complex phase in complex 4000 where the segments are molecularly mixed. The DMA result, discussed later, also suggests that the PEG–PMAA complex phase is amorphous due to a single glass transition. The detection of a single glass transition temperature is generally considered as evidence of compatibility,¹⁶ so we assume the complexes are homogeneous to a few hundred Angstroms and motional heterogeneity does not exist in the complexes.

A high elasticity ratio (E_g/E_r), preferably as much as two orders of magnitude, allows easy shaping at $T > T_g$ (shape memory temperature) and high resistance to deformation at $T < T_g$.¹⁷ However, polymer networks are generally not preferred because their glass transition is not sharp. The storage modulus E' of the P(MAA-co-MMA) network and complex 2000, 4000, 8000 is shown in Fig. 3 as a function of temperature (complex 1000 behaves like a soft elastomer even in the dry state and a DMA result could not be obtained). A pronounced decrease in E' occurred in the T_g region for all complexes, while E' values for the P(MAA-co-MMA) network gradually decrease during the glass transition and only a small difference in storage modulus was discovered. The modulus ratio data are summarized in Table 2. For complexes, we see that the modulus ratio increased with increasing molecular weight of PEG. A large difference in the modulus below and above the transition temperature is the most significant property to render the materials shape memory function. With a large elastic modulus ratio, high temperature deformation becomes easy while keeping high the resistance to low temperature deformation.¹⁷ Thus, P(MAA-co-MMA) complexes show shape memory effects due to this high modulus ratio. We assume the differences in the dynamic mechanical properties between the P(MAA-co-MMA) network and the P(MAA-co-MMA)–PEG complex could be interpreted in terms of cooperative inter-polymer hydrogen bonds which alter the dynamics and structures of the component polymers.

Table 2 The storage modulus ratio (E' ratio)^a and hardness of network and complexes at 25 °C

Sample	E' Ratio	Hardness (Shore D)
Network	3.87	83
Complex 1000	—	15
Complex 2000	17.25	68
Complex 4000	31.26	75
Complex 8000	48.19	80

^aThe storage modulus ratio (E' ratio) was defined as $(E'_{T_g-20^\circ\text{C}}/E'_{T_g+20^\circ\text{C}})$.

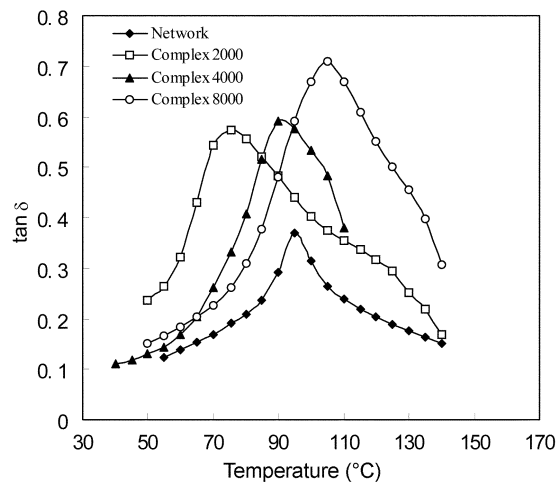


Fig. 4 $\tan \delta$ versus temperature for complex 2000, complex 4000, complex 8000 and the network.

Shape memory 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.¹⁸ Considering the P(MAA-co-MMA)–PEG complex, the fixing phase was the P(MAA-co-MMA) network, while the reversible phase was the PEG–PMAA complex phase. From Fig. 3, it can be seen that the glass modulus increased with increasing PEG molecular weight. This observation is consistent with the hardness measurements of complexes in the glass state as shown in Table 2. This means that the modulus of the glass state of the complex connects with the elastic energy of the amorphous PEG–PMAA complex phase. A high glassy state modulus will provide the materials with high shape retention during cooling and unloading. Thus, reversible phase transformation with a high glassy state modulus is responsible for the absence of elastic recovery.

Fig. 4 shows the $\tan \delta$ –temperature curves of the P(MAA-co-MMA) network and P(MAA-co-MMA)–PEG complexes. It is seen that the magnitude of the $\tan \delta$ peak increased with increasing PEG molecular weight. Since the $\tan \delta$ corresponds to the strain energy dissipated by viscous friction, a large $\tan \delta$ implies that the material is more likely viscous than elastic.

Shape memory behavior is detected in the temperature study, as shown in Fig. 5, and provides a direct comparison of the shape memory effect of P(MAA-co-MMA)–PEG complexes and the P(MAA-co-MMA) network. The data curves, based on the recovery ratio and temperature, are S-shaped. The deformation could be recovered relatively rapidly when the

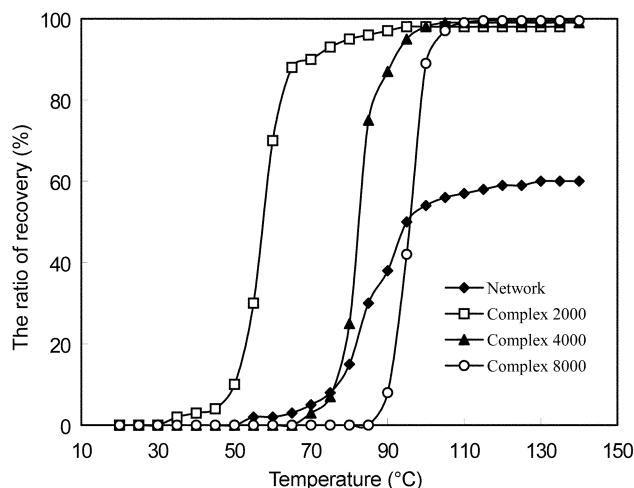


Fig. 5 Shape memory effect of complex 2000, complex 4000, complex 8000 and the network.

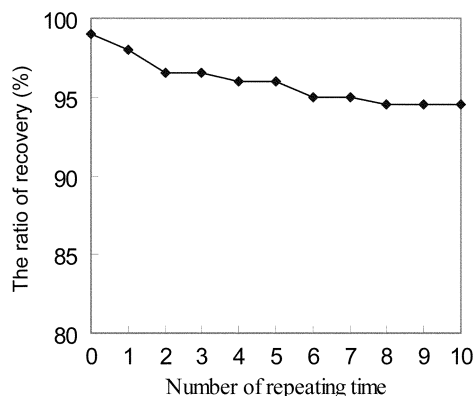


Fig. 6 Relationship between the ratio of recovery and the numbers of tests on complex 4000.

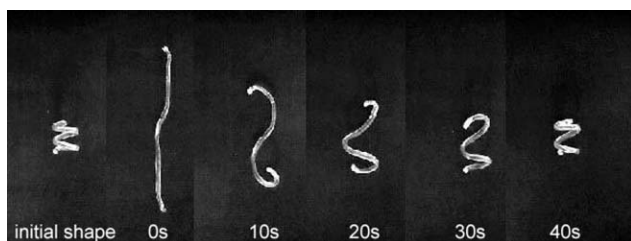


Fig. 7 Shape memory phenomenon of complex 4000. (The initial spring shape sample was heated to 95 °C and deformed as a strip shape, then cooled to room temperature under constrained conditions. After withdrawing the external force, the strip shape sample was put into a glass container kept constant temperature at 95 °C. A snapshot of the sample was captured by a digital camera every 10 seconds.)

deformed complex was heated again to a high temperature. The ratio of recovery could reach nearly 100%; the network showed a slow recovery rate, but there was still residual deformation that was not recovered under the testing process. Complexes with higher PEG molecular weight showed a higher recovery rate than those with a lower PEG molecular weight. These results are in good agreement with the modulus ratio data and $\tan \delta$ of complexes, as discussed above. Fig. 6 shows the results of the influence of the number of testings on the ratio of recovery for complex 4000. The ratio of recovery is slightly reduced and then approximates to a steady value as the number of testings increased. Thus, complex 4000 shows better shape memory behavior after a training process. The loss of recovery may be associated with the dissociation of the complex during the repeated temperature changes.

Fig. 7 shows the shape memory phenomenon of complex 4000. The spring shape sample was heated to 95 °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 95 °C, the complex became soft and recovered its original spring shape. This interesting phenomenon is reversible and cyclically reproduced by repeated temperature changes.

In conclusion, the P(MAA-co-MMA)-PEG complex has

shape memory behavior due to the formation of cooperative inter-polymer hydrogen bonds. The recovery ratio of this complex is nearly 100%, while that of P(AA-co-MMA)-C₁₆TAB complex is about 85%.¹¹ A special feature of the P(MAA-co-MMA)-PEG complex lies in the fact that the shape memory effect can be easily modulated by varying the molecular weight of the PEG, which is very important in real applications. Shape memory polymers are already used in different areas, such as medical instruments, toys and packaging materials.¹⁹ These kinds of complexes may be used in building materials, for example, pipe joints, because different shape memory effects are demanded.

Conclusion

The morphology of the P(MAA-co-MMA)-PEG complexes was studied by DSC, WAXD, and DMA. The results indicated that the fixed phase of this kind of novel shape memory material was the network, and the reversible phase was the amorphous state of the PEG-PMAA complex. The complexes showed shape memory properties due to a large difference in storage modulus below and above the glass transition temperature. When PEG with a higher molecular weight was introduced into the network (1) a higher modulus ratio, (2) a higher glassy state modulus, and (3) a higher recovering rate were obtained.

Acknowledgements

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