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Shape memory properties of polypeptide hydrogels having hydrophobic alkyl side chains

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ABSTRACT

Polypeptide hydrogels were prepared by crosslinking of hydrophobically-modified poly[N^δ-(2-hydroxyethyl) L-glutamine] having alkyl side chains –C_nH_{2n+1}. Chain length of the alkyl group was n = 8, 16, and 18, and their mole fractions in the polypeptide were varied in the range of 0.05–0.16. Shape memory ability of the prepared polypeptide hydrogels was investigated. After deformation at 60 °C, the hydrogel was cooled in order to fix the temporary deformed shape. It was found that crystallization of the alkyl side chains did not occur, and the fixation ability of the hydrogel at 0 °C was low. In the subsequent heating process, the deformed temporary shape spontaneously recovered to the original shape gradually with increasing temperature, in other words, the shape recovery ratio varied with
depending on the recovery temperature. From these observations, it was proposed that the shape fixation of the polypeptide hydrogel was achieved by strong segregation of the hydrophobic alkyl chains at low temperature, and the shape recovery of the deformed hydrogel was accompanied by the gradual decrease of the segregation strength with the temperature increase.

Keywords: polypeptide / hydrogel / shape memory polymer / alkyl chain / segregation / poly[\(N^\delta\)-(2-hydroxyethyl) L-glutamine]

1. Introduction

Shape memory materials have been attracted much attention because of their applicability as functional materials. Especially in these years, many researches concerning shape memory polymers (SMPs) have been reported [1–7]. In thermo-responsive SMPs, the material remembers its original shape, and can keep the temporary deformed shape at low temperature, and recovers to the original shape spontaneously by heating. The shape memory mechanism is described as follows: in SMP, the polymer chains are chemically or physically cross-linked and the polymer network can recover to the original permanent shape after deformation because of its entropy elasticity. By cooling the deformed material below its crystallization or glass transition temperature, the material cannot recover to the original shape because the segmental motion of the polymer chain is frozen by the phase transition of the constituent polymers. So the material can be fixed at the temporary deformed shape at low temperature. By heating the material above the phase transition temperature, the segmental motion of the polymer chain becomes possible, and the material recovers to the original permanent shape spontaneously. The cross-linking point in SMP is called as a fixing phase, and the component undergoes transition between liquid and solid states is called
as a reversible (switchable) phase.

Osada and coworkers reported a shape memory behavior of hydrogels [8–11]. The hydrogels were synthesized by copolymerization of \( n \)-stearyl acrylate (SA) and acrylic acid (AA) in presence of a cross-linker. Copolymer of SA and AA can be regarded to consist of a water-soluble poly(AA) as main chain and hydrophobic stearyl (octadecyl) chain as side chains. When the SA mole fraction was high, crystallization of the octadecyl chains occurred in the prepared hydrogel, which played a role to fix the temporary deformed shape as the reversible phase, and the obtained gel acted as shape memory hydrogel.

Recently, we have reported association behavior of amphiphilic polypeptides based on water-soluble non-ionic polypeptide, poly[\( N \)-5-(2-hydroxyethyl) L-glutamine] (PHEG), with hydrophobic modification in various manners [12–14]. In graft-type amphiphilic polymers [14], hydrophilic PHEG main chain had some long alkyl chains as hydrophobic side chains, and this structure is similar to the copolymer of SA and AA by Osada et al. Therefore, by cross-linking of the PHEG having alkyl side chains, a shape memory polypeptide hydrogel is expected to be prepared. PHEG hydrogel membrane was reported to be applicable as biomaterials [15–18], therefore, the obtained shape memory polypeptide hydrogel will be possibly used as novel biomaterials and biodegradable materials. Until now, only limited shape memory polypeptide hydrogels have been reported: for example, shape memory behavior of hydrogels consisting of telechelic polypeptide was recently reported by Skrzeszewska et al. [19]

In this paper, we report preparation and shape memory properties of the polypeptide hydrogels consisting of PHEG with alkyl side chains \(-\text{C}_n\text{H}_{2n+1}\) (PHEG-\( \text{C}_n \)). In order to investigate the effect of the alkyl chains on the shape memory property, hydrogels with various side chain lengths (\( n = 8, 16, \) and 18) and side chain mole fraction (\( f_{\text{alkyl}} = 0.05 – 0.16 \)) were prepared. In the hydrogels prepared in this work, crystallization of the alkyl side chains was not confirmed even at 0 °C, as the result, the observed shape memory behavior
was different from that in other normal SMPs. From the experimental results, shape memory mechanism of the PHEG-Cn hydrogels will be discussed.

2. Experimental

2.1. Materials

Triethylamine, 2-aminoethanol, 2-hydroxypyridine, 1,4-dioxane, N,N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF) were fractionally distilled before use. N-carboxyanhydride (NCA) of γ-benzyl L-glutamate (BLG) was prepared by reacting BLG with triphosgene, and purified by recrystallization from tetrahydrofurane/petroleum ether [12]. n-Octyl isocyanate (C8-NCO), n-hexadecyl isocyanate (C16-NCO), n-octadecyl isocyanate (C18-NCO), hexamethylene diisocyanate (HMDI), and di-n-butyltin dilaurate (DBTDL) were commercially purchased and used without further purification.

2.2. Synthesis of polypeptide hydrogels

Preparation of polypeptide hydrogels is described below, and reaction scheme is shown in Scheme 1.
NCA of BLG was polymerized by using triethylamine as initiator in dry 1,4-dioxane at 25 °C for three days. The solution was poured into methanol, and precipitated poly(γ-benzyl L-glutamate) (PBLG) was filtered and dried in vacuum.

The obtained PBLG and 2-hydroxypyridine was dissolved in DMF, 20-fold molar amount of 2-aminoethanol was added, and side-chain exchanging reaction was performed for 48 hours at 37 °C. The reaction solution was poured into excess ethanol/diethyl ether (1/5 v/v) mixed solvent. The precipitated PHEG was filtered and dialyzed against water by using cellulose membrane with nominal fractional molecular weight of 8,000. The aqueous polymer solution was freeze-dried to obtain solid PHEG.

To PHEG (0.1 g) solution dissolved in DMAc (5 ml), n-alkyl isocyanate (Cn-NCO) was added dropwise, and subsequently DBTDL was added as catalyst. The solution was stirred for two hours at room temperature, after that, it was poured into excess diethyl ether, and precipitates were filtered and dried. This polymer corresponds to a random copolymer of \(N^5\)-(2-hydroxyethyl) L-glutamine and \(N^5\)-[2-\((n\text{-alkylcarbamoyloxy})\text{ethyl}]\) L-glutamine, and is designated as PHEG-Cn.
PHEG-C\textsubscript{n} was dissolved in DMAc to obtain 5 wt\% solution. HMDI was added as cross-linker, subsequently DBTDL as catalyst was added and stirred sufficiently. The mixed solution was poured into flat mold with 0.8 mm thickness, and cross-linking reaction was carried out at room temperature. The obtained gel film was immersed in DMAc for three days to remove impurities. Finally, the gel was immersed in distilled water for more than one week to obtain polypeptide hydrogel film.

2.3. Measurements

\textsuperscript{1}H-NMR spectrum of PHEG-C\textsubscript{n} was recorded on an Avance200 (Bruker) with using DMSO-\textit{d}\textsubscript{6} as solvent. Size exclusion chromatography (SEC) was measured on a SD-8022 system (Tosoh) with using DMF containing 1 wt\% lithium bromide as eluent, and standard polystyrene was used for molecular weight calibration. Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer Pyris 1. Wide-angle X-ray diffraction (WAXD) photograph, with using Ni-filtered Cu-K\textsubscript{\alpha} radiation, was recorded on a flat film with a Laue camera. Degree of swelling (\(Q\)) was defined as the weight ratio of swollen gel to dried polymer: \(Q = w_{\text{gel}} / w_{\text{polymer}}\).

Shape memory properties were tested by the following procedure. A hydrogel film in stripe shape was loaded in a uniaxially-stretching machine, and stretched until its strain would be \(\varepsilon_1 = 50\%\) in water bath at 60 °C. With keeping this strain, the sample was cooled at 0 °C in ice-cooled water for 30 min. After the stretched hydrogel was unloaded from the uniaxially-stretching machine, it was continuously cooled at 0 °C and its length was measured after 30 min to evaluate the fixed strain \(\varepsilon_2\). After that, the sample in the water bath was heated with heating speed of 5 °C/min, and the strain at each temperature, \(\varepsilon_3\), was measured. Shape fixity ratio \(R_f\) and shape recovery ratio \(R_r\) were calculated by equations (1) and (2).
\[ R_\varepsilon = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} \times 100\% \quad (1) \]
\[ R_r = \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1} \times 100\% \quad (2) \]

3. Results and Discussion

3.1. Characterization of Polymers and Hydrogels

Weight-averaged molecular weight of the starting PHEG’s, evaluated from SEC chart, were 280,000, 281,000, and 418,000, and their polydispersity index \( (M_w/M_n) \) was 1.3, 1.7, and 1.3, respectively. Characteristics of the obtained samples of PHEG-C\( n \) are listed in Table 1.

In order to investigate the effect of alkyl side chains on shape memory properties, we prepared PHEG-C\( n \) samples with different chain length \( (n) \) of the alkyl chain –C\( n \)H\( 2n+1 \) and alkyl chain mole fraction \( (f_{\text{alkyl}}) \). Values of \( f_{\text{alkyl}} \) were estimated from \(^1\text{H} \) NMR peak area of the methine proton in main chain and the methyl proton in side chain. Typical example of \(^1\text{H} \) NMR spectrum is shown in Fig. 1. Value of side chain fraction \( (100 \times f_{\text{alkyl}}) \) is indicated in parenthesis of sample code as shown in Table 1. For comparison, PHEG homopolymer was also used, and designated as H-PHEG.

<table>
<thead>
<tr>
<th>sample code</th>
<th>( n )</th>
<th>( f_{\text{alkyl}} )</th>
<th>( Q ) at 20 °C</th>
<th>( R_\varepsilon / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-PHEG</td>
<td>—</td>
<td>0</td>
<td>24.7</td>
<td>0</td>
</tr>
<tr>
<td>PHEG-C8(5)</td>
<td>8</td>
<td>0.049</td>
<td>15.8</td>
<td>32</td>
</tr>
<tr>
<td>PHEG-C8(16)</td>
<td>8</td>
<td>0.163</td>
<td>4.1</td>
<td>36</td>
</tr>
<tr>
<td>PHEG-C16(6)</td>
<td>16</td>
<td>0.058</td>
<td>6.2</td>
<td>33</td>
</tr>
<tr>
<td>PHEG-C16(10)</td>
<td>16</td>
<td>0.097</td>
<td>3.8</td>
<td>58</td>
</tr>
<tr>
<td>PHEG-C18(5)</td>
<td>18</td>
<td>0.045</td>
<td>4.5</td>
<td>40</td>
</tr>
<tr>
<td>PHEG-C18(14)</td>
<td>18</td>
<td>0.135</td>
<td>3.1</td>
<td>73</td>
</tr>
</tbody>
</table>
In the cross-linking reaction of PHEG-Cn, we used HMDI having two isocyanate groups as cross-linker, and homogeneous flat gel film could be obtained. However, it was difficult to control the concentration of the cross-linker because of its very tiny amount, so the gelation reaction was continued until the solution lost fluidity.

The obtained gels prepared from polypeptides in Table 1 were immersed in water, and evaluated swelling ratio $Q$ of the hydrogels at 20 °C is shown in Table 1. The values of $Q$ became smaller with increase of $n$ and $f_{alkyl}$. It should be reasonable that the highly hydrophobic alkyl chains tended to segregate in the hydrogel, which induces increase in cross-linking density and decrease in $Q$. In Fig. 2, temperature dependence of $Q$ for the prepared hydrogels is indicated. In water, PHEG chain takes random coil conformation by interaction with water molecules instead of the intramolecular hydrogen bond for formation of $\alpha$-helix [12–15], and PHEG homopolymer was easily dissolved in water in the temperature range in Fig. 2. This result means any significant change in hydration behavior of water molecules with PHEG chain does not occur in this experimental condition. Therefore, the decreasing tendency in $Q$ with heating from 5 °C in Fig. 2 may be due to an activated segmental motion of PHEG chain with increasing temperature. In the hydrogels from H-PHEG, PHEG-C8(5) and PHEG-C16(6), the $Q$ value showed gradual increase by further
heating. A possible reason is that the segregation strength of the alkyl chains, including hexamethylene group in the HMDI cross-linker, became weaker at high temperature in these less-hydrophobic gels, which caused the hydrogels more swollen.

![Fig. 2. Temperature dependence of swelling ratio $Q$ for polypeptide hydrogels of (○) PHEG-C8(5), (●) PHEG-C8(16), (Δ) PHEG-C16(6), (▲) PHEG-C16(10), (▼) PHEG-C18(5), (▲) PHEG-C18(14), and (□) H-PHEG.]

3.2. DSC and WAXD

As pointed out in Introduction, the shape memory poly(SA-AA) gels exhibited side chain crystallization when SA mole fraction ($F$) was high. Here, we performed DSC and WAXD measurements in order to check the crystallization of the alkyl side chains. In DSC thermogram of PHEG-C18(14) hydrogel, there was no transition peak in the range of 5 – 80 °C. WAXD pattern of freeze-dried PHEG-C18(14) hydrogel was measured at room temperature, but it revealed only amorphous halo. These results suggest that the C18 side chains in PHEG-C18(14) hydrogel did not crystallize in the present experimental condition. As shown in Table 1, this hydrogel has highest $f_{alkyl}$ and lowest $Q$ among the prepared
hydrogels, so the crystallization of alkyl chains was most likely to occur. Matsuda et al. reported that the octadecyl chains in poly(SA-AA) were crystallized when $F$ was larger than 0.15, and $Q$ values for these samples were less than 1.9 [8]. Comparison of these results suggests that the alkyl chain concentration in the swollen PHEG-C18(14) hydrogel was lower than the crystallized poly(SA-AA), and this may be the reason why the hydrogels prepared in this report did not exhibit alkyl chain crystallization. Furthermore, the main chain of poly(SA-AA) has carboxylic acid group, which should be more hydrophilic than hydroxyethyl group in PHEG. Therefore, the alkyl chains in PHEG-C$n$ will be segregated much weakly than in poly(SA-AA), which also causes the non-crystalline nature of PHEG-C$n$ hydrogels.

It was difficult to prepare PHEG-C$n$ hydrogel with higher $f_{\text{alkyl}}$ because of the limited solubility of PHEG-C$n$ in DMAc in the cross-linking reaction. The shape memory tests in the following section were performed by using these non-crystalline PHEG-C$n$ hydrogels.

3.3. Shape Memory Properties

All the prepared hydrogels were used for the shape memory test described in the Experimental section. At first, the gel was stretched to $\varepsilon_1 = 50\%$ at 60 °C, and subsequently cooled at 0 °C for 30 min, and strain of the sample was measured in order to evaluate $R_f$. In Table 1, $R_f$ values for various PHEG-C$n$ hydrogels are compared. In case of H-PHEG hydrogel, which has no alkyl side chain, the deformed shape could not be maintained and recovered to the original shape immediately. This behavior is reasonable for normal hydrogel because it has no shape fixing component. When $n = 8$, $R_f$ was less than 40 % and almost independent of $f_{\text{alkyl}}$. This value means that the deformed strain $\varepsilon_1$ could be fixed only partially at 0 °C and recovered to $\varepsilon_2 < 20\%$. In case of $n = 16$ and 18, $R_f$ showed drastic increase with increase of $f_{\text{alkyl}}$. Therefore, the alkyl chain length of $n = 8$ was not enough to fix the deformed temporary shape, and when $n \geq 16$, the shape fixation
ability was improved with increase of \( f_{\text{alkyl}} \). However, as pointed out in the previous section, crystallization of the alkyl chains did not occur even in PHEG-C18(14) hydrogel, so the highest \( R_f \) was at most \( \sim 70 \% \) and complete shape fixation \( (R_f = 100 \%) \) could not be achieved. From these results, it may be supposed that the temporary deformed shape was fixed not by the alkyl chain crystallization but by the segregation of alkyl chains by hydrophobic interaction. Crystallization of alkyl chains to form solid-like domains did not occur because of the low alkyl chain concentration in the prepared PHEG-\( C_n \) hydrogels, which should be the reason of the low shape fixation ability.

After the shape fixation at 0 °C, temperature of the water bath was increased gradually and measured the shape recovery behavior. \( R_r \) values were found to increase gradually with temperature, as shown in Fig. 3. As mentioned above, the less-hydrophobic hydrogels \( (f_{\text{alkyl}} \approx 0.05 \text{ or } n = 8) \) exhibited low \( R_r \), so the starting \( R_r \) values at 0 °C for these samples were in the range of 60–70 %. With increase of temperature, the temporary shape recovered to the original shape gradually, and at 50–60 °C, \( R_r \) value reached to 100 %, means that the original shape was completely recovered. In case of PHEG-C18(14) hydrogel, \( R_r \) increased with temperature from \( \sim 30\% \), and gradually reached to 100 % at 80 °C. In usual SMPs, the temporary deformed shape can be fixed enough \( (R_f \approx 100 \%) \) by solidification of the constituent polymers below phase transition temperatures \( (T_{\text{trans}}) \), and recovers to the original shape abruptly \( (\text{from } R_r \approx 0 \% \text{ to } R_r \approx 100 \%) \) around \( T_{\text{trans}} \) by solid-to-liquid transition. The results in Fig. 3 are obviously different from the shape recovery process of usual SMPs.
Here, it should be commented that the $R_t$ values in some PHEG hydrogels exceeded 100%. As shown in the temperature dependence of $Q$ in Fig. 2, the size of the hydrogel with high $f_{\text{alkyl}}$ at high temperature was smaller than that at lower temperature. Because the strain values in equations (1) and (2) was evaluated on the basis of the size at 20 °C, so the shrinkage at high temperature results in the negative value in $\varepsilon$. Therefore, the larger $R_t$ than 100% at high temperature was caused by the size variation of the hydrogel with temperature.

In Fig. 4, elapsed time dependence of $R_t$ at 30 °C and 50 °C for PHEG-C18(14) hydrogel is presented. At both temperatures, $R_t$ value increased with time in short time region, and became almost constant after 30 min was passed. After that, the change of $R_t$ was negligibly small. Therefore, it can be pointed out that the $R_t$ value of the PHEG-Cn hydrogel was dependent upon the shape recovery temperature.
Fig. 4. Time dependence of $R_t$ of PHEG-C18(14) hydrogel at (○) 30 °C and (●) 50 °C.

From these results, a plausible shape memory mechanism of the PHEG-Cn polypeptide hydrogel can be proposed as shown in the schematic illustration in Fig. 5. In these figures, the random-coiled main chains and crystalline side chains are represented by thick and thin lines, respectively. At high temperature, the alkyl side chains are melted (Fig. 5a) and the shape of the hydrogel can be deformed. In the shape memory gels reported by Osada et al. [8–11], the alkyl chains are in crystalline state after cooling below $T_{\text{trans}}$, as shown in Fig. 5b, and the deformed shape can be fixed. On the other hand, in the PHEG-Cn hydrogel, the alkyl chains are non-crystalline state even at 0 °C, but should be segregated in the gel as suggested by the low $Q$ value in the sample with higher alkyl-chain content (Fig. 5c). As mentioned above, PHEG chain takes random coil conformation in water, so the entropy elastic force will act for recovery from the deformed shape by the chemically cross-linked PHEG. However, the strong segregation of the alkyl chains at low temperature possibly prevents the hydrogel to recover to the original shape. With increasing temperature, the segregation strength becomes weaker and the shape fixation ability becomes lower, so the hydrogel recovers to the original shape gradually. Larger elastic force to shrink at high temperature, as mentioned in section 3.1 and Fig. 2, may also contribute to the gradual
recovery with increasing temperature. The recovery behavior depends on the segregation strength of alkyl chains at each temperature, not on the recovery time, as shown in Fig. 4. This shape memory mechanism is able to describe the gradual shape recovery process observed in Fig. 3.

Fig. 5. Schematic representation of the shape memory mechanism of crystalline shape memory gel and PHEG-Cn hydrogel. (a) Alkyl chains are in melt state at high temperature. (b) In the shape memory gel, alkyl chains are in crystalline state after cooling. (c) In the PHEG-Cn hydrogel, alkyl chains are in non-crystalline state but segregated at low temperature.

In order to confirm the above-proposed mechanism more clearly, a flat hydrogel film of PHEG-C18(14) was deformed to helical shape as shown in photo images in Fig. 6, and shape recovery behavior with increasing temperature was observed. The helical shape deformed at 60 °C was temporary fixed at 0 °C, and gradually recovered to the original shape with increasing temperature, and finally recovered to the flat shape at 80 °C. This temperature dependence of shape recovery process reflects the results of the shape memory test in Fig. 3.
Fig. 6. Photo images of shape recovery behavior of PHEG-C18(14) hydrogel flat film in the heating process from 0 °C to 80 °C.

The shape memory behavior of PHEG-Cₙ hydrogel is compared with a common gel and a conventional shape memory gel in Fig. 7. In a common gel, the deformed shape recovers to the original shape even at low temperature as shown in Fig. 7a, because it has no shape-fixing component. In a conventional shape memory gel, the shape fixation is achieved by phase transition of constituent polymers, which takes place within relatively narrow temperature range around $T_{\text{trans}}$. Therefore, they show sudden shape recovery in the heating scan, as illustrated in Fig. 7b. On the other hand, the PHEG-Cₙ hydrogel cannot fix the temporary shape completely even at low temperature, and shape recovery occurred gradually as shown in Fig. 3 and in illustration of Fig. 7c. The segregated hydrophobic alkyl chains fix the temporary shape only partially, and its segregation strength is weakened gradually as the temperature increase. In this sense, although the shape fixation ability is not good, the PHEG-Cₙ hydrogel can recover to a desired shape by controlling the recovery temperature, because the segregation strength depends on temperature. In other words, the PHEG-Cₙ hydrogel can be used as a shape memory gel having ability to remember multiple shapes at various recovery temperatures, like a shape memory ionomer with broad phase
transition reported by Xie [20].

\[ 16 \]

Fig. 7. Schematic illustration of temperature dependence of \( R_t \) for (a) a normal gel, (b) a shape memory gel, and (c) PHEG-C\( n \) hydrogel.

4. Conclusion

Polypeptide hydrogels were prepared by cross-linking of PHEG having hydrophobic alkyl chains as side chain. The alkyl chain length \( n \) was 8, 16, and 18, its mol fraction in the polypeptide was varied in the range of 0.05–0.16, and these polymers were cross-linked with using HMDI. In the prepared hydrogels, crystallization of the side chains could not be confirmed. Instead of their non-crystalline nature, the hydrogels had the ability to fix the deformed temporary shape, although the absolute value of \( R_t \) was not high. The shape
fixiation ability was enhanced with the increase of hydrophobicity of PHEG-CN. The fixed temporary shape recovered gradually with increasing temperature, in other words, the recovered shape varied with the change of recovery temperature. From these observations, we proposed that the shape fixation was achieved by the segregation of the hydrophobic alkyl chains, and shape recovery occurred as the segregation strength was weakened gradually with heating.

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**References**


Figure captions
Scheme 1. Preparation scheme of PHEG-Cn hydrogel.

Fig. 1. $^1$H NMR spectrum of PHEG-C18(14) by using dimethylsulfoxide-$d_6$ as solvent.

Fig. 2. Temperature dependence of swelling ratio $Q$ for polypeptide hydrogels of (○) PHEG-C8(5), (●) PHEG-C8(16), (△) PHEG-C16(6), (▲) PHEG-C16(10), (▼) PHEG-C18(5), (▼) PHEG-C18(14), and (□) H-PHEG.

Fig. 3. Temperature dependence of shape recovery ratio $R_r$ of the polypeptide hydrogels.
The symbols are indicated in the legend of Fig. 2.

Fig. 4. Time dependence of $R_r$ of PHEG-C18(14) hydrogel at (○) 30 °C and (●) 50 °C.

Fig. 5. Schematic representation of the shape memory mechanism of crystalline shape memory gel and PHEG-Cn hydrogel. (a) Alkyl chains are in melt state at high temperature. (b) In the shape memory gel, alkyl chains are in crystalline state after cooling. (c) In the PHEG-Cn hydrogel, alkyl chains are in non-crystalline state but segregated at low temperature.

Fig. 6. Photo images of shape recovery behavior of PHEG-C18(14) hydrogel flat film in the heating process from 0 °C to 80 °C.

Fig. 7. Schematic illustration of temperature dependence of $R_r$ for (a) a normal gel, (b) a shape memory gel, and (c) PHEG-Cn hydrogel.