JOURNAL OF Applied Polymer SCIENCE

Preparation and Microstructural Analysis of Poly(ethylene oxide) Comb-Type Grafted Poly(*N*-isopropyl acrylamide) Hydrogels Crosslinked by Poly(ε-caprolactone)

Lei Miao,[1,2] Mangeng Lu,[1] Chaolong Yang,[1,2] Yunfei Zhang,[1,2] Tengfei Shen,[1,2] Jianying Ma[1,2]

[1]Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

[2]Graduate School of Chinese Academy of Sciences, Beijing, PR China

Correspondence to: M. Lu (E-mail: mglu@gic.ac.cn)

ABSTRACT: Poly(*N*-isopropyl acrylamide) (PNIPAAm)-*graft*-poly(ethylene oxide) (PEO) hydrogels crosslinked by poly(ϵ-caprolactone) diacrylate were prepared, and their microstructures were investigated. The swelling/deswelling kinetics and compression strength were measured. The relationship between the structure and properties of hydrogel are discussed. It was found that the PEO comb-type grafted structure reduced the thermosensitivity and increased the compression strength. The addition of poly(ϵ-caprolactone) (PCL) accelerated the deswelling rate of the hydrogels. Meanwhile, the entanglement of PCL chains restrained the further swelling of the network of gels. The PCL crosslinking agent and PEO comb-type grafted structure made the behavior of the hydrogels deviate from the rubber elasticity equations. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: grafting; hydrogels; hydrophilic polymers

Received 17 February 2012; accepted 8 June 2012; published online
DOI: 10.1002/app.38172

INTRODUCTION

It is widely recognized that poly(*N*-isopropyl acrylamide) (PNIPAAm) demonstrates a lower critical solution temperature (LCST) (32°C) in aqueous solutions and shows an abrupt coil-to-globule change as the external temperature cycles around this critical temperature.[1–9] In recent years, many studies have been executed to improve the limitations of PNIPAAm hydrogels; these include slow response rates, weak mechanical properties, and nonbiodegradability.[10–14] Among of them, the creation of a comb-type grafted hydrogel is a promising method for preparing a better performance hydrogel. Kaneko et al.[15] first prepared a poly(ethylene oxide) (PEO) comb-type grafted PNIPAAm hydrogel; it was obtained by the reaction of a PEO macromolecular monomer with micromolecules of *N*-isopropyl acrylamide (NIPAAm) and *N,N′*-methylene bisacrylamide. The deswelling process of this type of hydrogel was accelerated extraordinarily.

Recently, PEO, which is highly water-soluble and has a high gelability and low toxicity, has been applied in extended drug-release systems as a crosslinking polymer or macromolecular monomer in the pharmaceutical field.[16–19] The thermal behaviors of PEO and PEO-*g*-PNIPAAm were also studied in the past few years. It was demonstrated that a hydration structure indeed exists between the PEO chains. Kitano et al.[20] and Tasaki[21] discussed the hydrogen bonding about PEO–water and water–water with IR and NMR, respectively. Furthermore, Tajiri et al.[22] investigated a drastic conformational change in a PEO chain during the hydrogelation process with IR spectroscopy and used quantum chemical calculations. Chen et al.[23] found that PEO-*g*-PNIPAAm formed a core–shell structure at high temperatures. Even more, for methoxypoly(ethylene glycol)s (MPEG), Zhu[24] found that the methyl groups aggregated when the collapse of the PNIPAAm backbone occurred. However, the effect and behavior of the PEO chains in the PNIPAAm hydrogel have not been investigated well. Meanwhile, as we know, the mechanical strength of PEO comb-type grafted hydrogels has not yet been discussed. Thus, we needed to investigate this compound's inherent physical properties to better understand the relationship between its structure and properties.

To determine the effect between free PEO chains and PNIPAAm chains in a comb-type grafted hydrogel and to improve the mechanical properties and biodegradability, we synthesized PEO comb-typed grafted hydrogels crosslinked by poly(ϵ-caprolactone) (PCL). Through attenuated total reflection IR spectra, we demonstrated a hydration structure existed in the hydrogel, not only between PEO chains but also between the PNIPAAm chains. We measured the equilibrium swelling ratio (ESR or *Q*) and swelling/deswelling behavior at different PEO contents. In addition, a compression test was conducted to investigate the influence of different PEO and PCL contents.

Table I. Feed Compositions of the PNIPAAm-*g*-PEO Hydrogels

Sample no.	NIPAAm (g)	MPEGAc (g)	PCLDAc (g)	Conversion (%)[a]	Approximate molar ratio (NIPAAm/MPEGAc/PCLDAc)[b]
1	0.2	0.0667	0.0333	95.3	106.7 : 4:1
2	0.2	0.1077	0.0333	95.7	107.2 : 6.5 : 1
3	0.2	0.1333	0.0333	96.2	107.8 : 8: 1
4	0.2	0.1077	0.025	92.5	137.6 : 8.6 : 1
5	0.2	0.1077	0.04	96.3	89.2 : 5.4 : 1
6	0.2	0	0.025	92.2	137.1 : 0: 1

[a]The composition (%) was calculated as follows: $(W/W_0) \times 100\%$, where W is the weight of the dry gel and W_0 is the sum of the weights of PCLDAc, MPEGAc, and NIPAAm, [b]M_w of MPEGAc was approximately 1050 Da, and M_w of PCLDAc was approximately 2100 Da.

EXPERIMENTAL

Materials

NIPAAm was purchased from TCI (Shanghai, Chuo-ku, Tokyo, Japan) Development Corp. and was recrystallized twice with *n*-hexane before use. MPEG was dried *in vacuo* at 70°C. Dichloromethane was stirred with CaH_2 at room temperature overnight and was distilled before use. 1,4-Dioxane was treated with a molecular sieve before use. 4-Methoxyphenol, *N,N*-dicyclohexylcarbodiimide, 4-dimethyl aminopyridine, polycaprolactone diol [purchased from Mitsubishi Chemical Corp., Chiyoda-ku, Tokyo, Japan weight-average molecular weight (M_w) = 2000], acrylic acid (AAc), triethylamine (TEA), and acryloyl chloride were purchased from Aladdin-Agent, Shanghai, China and had no treatment. The other reagents were also used as received.

Structural measurements

^{1}H-NMR spectra (400 MHz) were recorded on a DRX-400 NMR spectrometer (Bruker, Germany, Fahrenheitstraβe, Bremen, Germany) with $CDCl_3$ as the solvent. Fourier transform infrared measurements were taken on a TENSOR 27 spectrometer (Bruker).

Synthesis of poly(caprolactone diacrylate) (PCLDAc)

PCL (5 g, M_w = 2000), AAc (2 mL), and 4-dimethyl aminopyridine (0.1 g) were dissolved in 80 mL of CH_2Cl_2. Until they dissolved completely, 8 g of *N,N*-dicyclohexylcarbodiimide was added dropwise into the reactor at 0°C. Then, the flask was sealed, and the reaction was stirred at room temperature for 48 h. After the filtration of insoluble impurities and reduced-pressure distillation, the product was obtained by three precipitations into mineral ether and was dried in a vacuum oven at 40°C.

Synthesis of methoxypoly(ethylene glycol) acrylate (MPEGAc)

MPEGAc was synthesized by the meliorative method based on previous work.[15] 10 g of MPEG (M_w = 1000), 1.4 mL of TEA, and 0.1 g of MEQH was dissolved completely in 30 mL of CH_2Cl_2. Then, the flask was removed to a salt–ice bath. About 5 mL of acryloyl chloride in 20 mL of CH_2Cl_2 was dripped slowly into the reactor through a constant-pressure funnel. After this addition, the reactor was sealed, and the reaction was carried out at 40°C for 24 h. After the filtration of undissolved TEA salt and concentration by reduced-pressure distillation, the crude product was obtained by the pouring of the mixture into cold ethyl ether. The crude product was dissolved in CH_2Cl_2 and was washed twice with a little 5% NaOH (w/w) solution. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Then, the MPEGAc was dried *in vacuo* at room temperature.

Preparation of the comb-type grafted hydrogels

To prepare the comb-type grafted PNIPAAM-*g*-PEO gel, a mixture of NIPAAm, PCLDAc, MPEGAc, AIBN, and 1, 4-dioxane was put into a glass tube. After the tube was degassed and sealed, the polymerization was conducted at 60°C for 36 h. To remove the unreacted monomer, the obtained gels were immersed in deionized water for 5 days at 4°C, and water was replaced every day. Then, it was dried *in vacuo* at 50°C for 48 h. The contents of each component are summarized in Table I.

Grafting ratio of the PEO chains

The grafting number of the PEO chains in each network element was obtained through calculation. Each network element actually contained one PCLDAc crosslinking point and two PNIPAAm chains. The repeat unit's number of the two PNIPAAm chains in every network element is listed in Table I. Also, every PNIPAAm chain contained different numbers of PEO chains. The numbers of PEO chain in every network element is also listed. The grafting ratio was defined as the ratio of grafting units and the whole units in one PNIPAAm chain. The formula used to calculate this is as follows:

$$n_{\mathrm{MPEG}} \times 100/(n_{\mathrm{MPEG}} + n_{\mathrm{NIPAAm}})$$

where nMPEG, the molar quantities of MPEG; nNIPAAm, the molar quantities of NIPAAm.

Measurements of the ESR of the hydrogels

The gels were cut into disks (10 mm in diameter and 5 mm in thickness) and equilibrated in deionized water at a higher temperature (60°C). After the excess water was wiped from the gel's surface with filter paper, the mass of the gels was obtained by weighing. Then, the temperature was lowered, and the gels were equilibrated to reach swollen conditions at this temperature. This process was repeated until the temperature reached 20°C. ESR (Q) was calculated by the following equation:

$$Q = (W_T - W_0)/W_0 \quad (1)$$

where W_T is the weight of the gel at a certain temperature (°C) and W_0 is the dry weight of the gel.

Measurements of the swelling and deswelling kinetics of the hydrogels

The swelling and deswelling kinetics were determined by measurement of the temporal weight changes of the gels. For the kinetic studies, disk-shaped gels were first equilibrated in deionized water at a predetermined temperature (25°C). The gels were weighed at each given time. The swelling kinetics was calculated as follows:

$$(W_t - W_0)/W_0$$

where W_t is the weight of the gel at a certain time. After confirming that no further changes occurred in the swelling ratios over time, we quickly transferred the gels into water at 40°C. At specific time points, these gels were removed from the water and weighed. The swelling degree was calculated as $(W_t - W_0)/(W_t - W_0)$.

Measurements of the compression properties of the hydrogels

The compression properties were measured by a CT3 texture analyzer (Brookfield, New York, U.S.). The disk-shaped gels were equilibrated in deionized water (25°C) for 2 days to confirm that the weight of gel would not change. After we wiped the excess water from the gel's surface with filter paper, compression mechanical testing was conducted at 25°C. The swollen gels were tested by the CT3 texture analyzer. The compression modulus (G) of each gel could be calculated by the following equation:[25]

$$\tau = -G\left(\lambda - \lambda^{-2}\right) \quad (2)$$

where τ is the compression stress. The Young's modulus (E) of the gels could be calculated as follows:

$$E = -\tau/(\lambda - 1) \quad (3)$$

where λ is the compression strain (L is the deformed sample thickness L/L_0) and L_0 is the undeformed sample thickness. The effective crosslinking density (ρ_x) could be calculated from G and the polymer Q as follows:[26]

$$\rho_x = GQ^{1/3}/RT \quad (4)$$

where R is the gas constant (8.48×10^4 g cm mol^{-1} K^{-1}) and T is the absolute temperature (293 K).

Interior morphology of the hydrogels

The gels were equilibrated in deionized water at 25°C for 2 days to confirm that the weight of gel would not change and were then freeze-dried. After they were covered with gold on an aluminum holder, the dried hydrogel morphologies were analyzed by JSM-6360LV (JEOL, Japan, Tachikawa, Tokyo, Japan).

RESULTS AND DISCUSSION

Synthesis of the PNIPAAm-*g*-PEO hydrogels

Unlike PCL, the same reaction system was not suitable for MPEG and AAc because the impurities were difficult to remove clearly enough to process the next reaction. From the H-NMR spectra, we found that the peaks at 5.668–5.699, 6.145–6.186, and 6.278–6.324 ppm in Figure 1(a) and the peaks at 5.791–5.817, 6.084–6.153, and 6.369–6.413 ppm in Figure 1(b) indicated the MPEG macromolecular monomer and PCL macromolecular crosslinker were prepared successfully. As calculated from the integral area of the H-NMR spectrum, the extent of the reaction exceeded 90%.

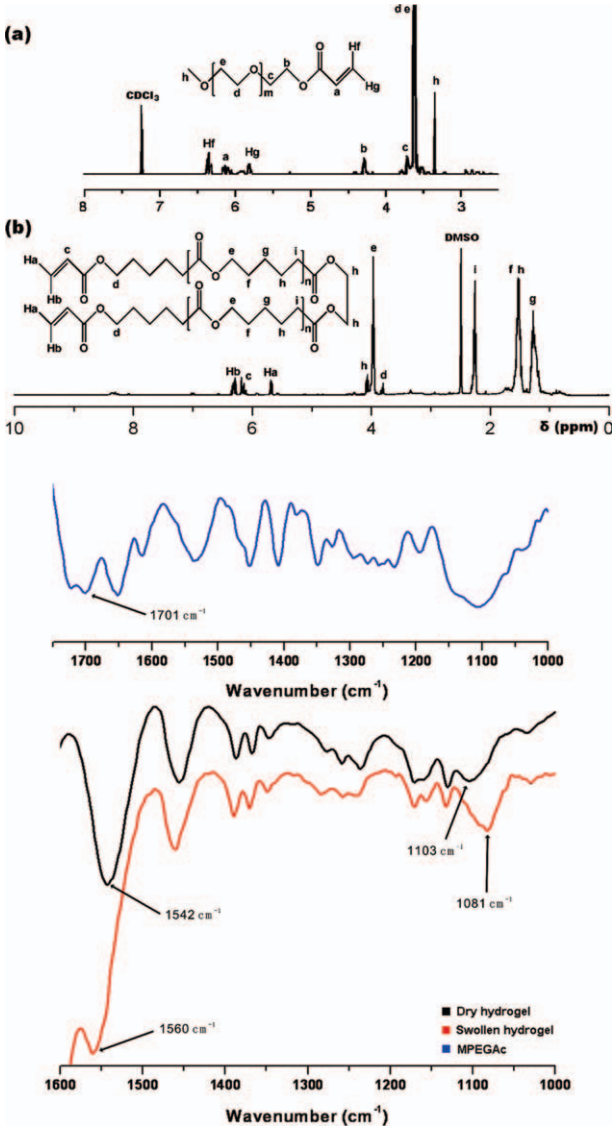

Figure 1. H-NMR spectra (upside) of (a) PCLDAc and (b) MPEGAc and IR spectra (downside) of MPEGAc (KBr disk), the dry gels, and the swollen hydrogels. In the bottom of the figure, the blue/top curved line indicates MPEGAc, the black/middle line represents the dry hydrogel, and the red/bottom line represents the swollen hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Fourier transform infrared spectrum (the blue line in Figure 1) showed a characteristic peak at 1701 cm^{-1}, which was assigned to the carbonyl group of MPEGAc. The attenuated total reflection IR spectra of the swollen hydrogel and dry hydrogel are also shown in Figure 1. The absorption peaks at 1560 cm^{-1} (red line) and 1542 cm^{-1} (black line) were assigned to the amide II of PNIPAAm. We compared the red line with the black line because the hydrogen bond made the flexural vibrations of the

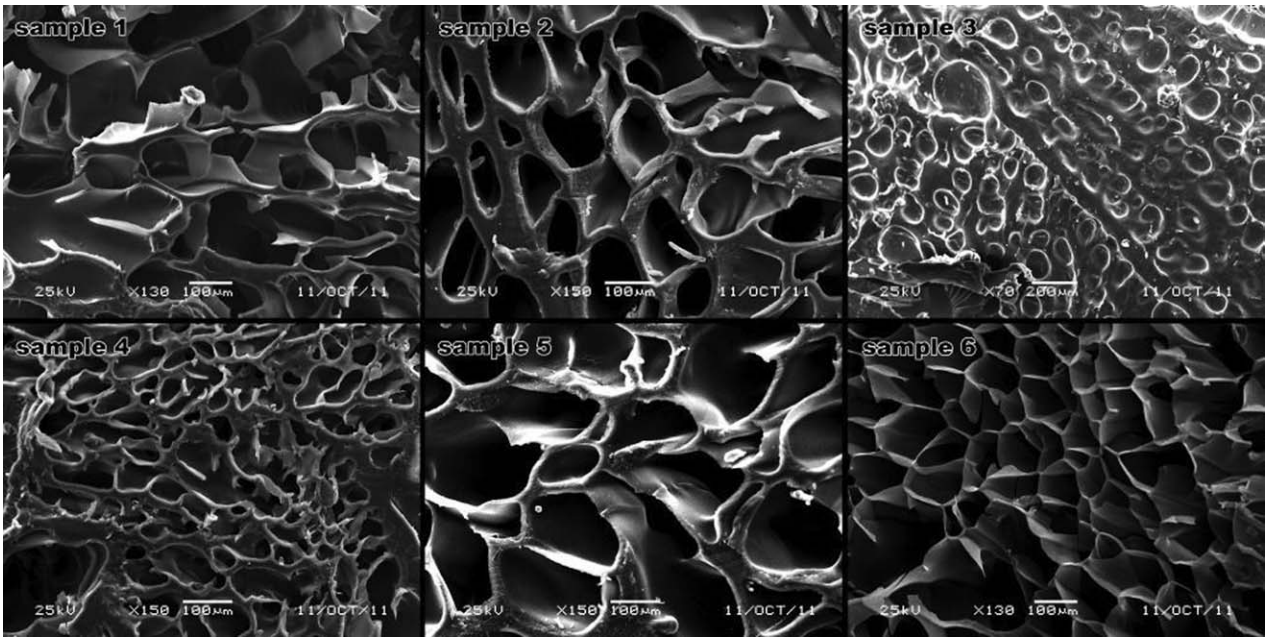

Figure 2. SEM micrographs of the comb-type grafted PNIPAAm hydrogels.

amide groups difficult, and the amide II of PNIPAAm was removed at a wave number about 20 cm^{-1} lower. At the same time, the stretching vibration of —C—O— rose about 20 cm^{-1}. The reason was that the formation of hydrogen bonds made the electron cloud more average and decreased the force constant of the —C—O— bonds. This indicated that there were H bonds in the hydrogel.

Interior morphology of the hydrogels

The morphologies of the comb-type grafted PNIPAAm hydrogels under swollen conditions are shown in Figure 2. The swollen PNIPAAm hydrogels were frozen in a refrigerator and then freeze-dried before SEM morphological investigation. Although this treatment can lead to structural artifacts in the specimens, the dramatic differences in the morphologies observed in these hydrogels were presumably of an intrinsic nature. The fixation procedures were identical among all of the gel specimens. From the photos of samples 6, 1, 2, and 3, it was easy to determine that the walls of the pores thickened in sequence. Because the dangling PEO chains tended to attach to the walls of the three-dimensional network, a higher PEO content made the walls thicker. Meanwhile, with increasing PCL content, the sizes of the pores also enlarged (the photos of samples 5, 2, and 4). The hydrophobia of PCL may have aggravated the phase separation.

ESRs of the hydrogels

Unlike the *N,N′*-methylene bisacrylamide crosslinking comb-type grafted hydrogel,[27] the PCL crosslinking comb-type grafted hydrogel could not absorb several times or even more water than its own weight. As shown later in Figure 4, the ESRs of samples 1–6 were generally under 3.0 at 30–40°C. The introduction of PCL led to the low ESR. As a hydrophobic polymer, the entanglement of the PCL chains restrained the further swelling of the network of gels. Besides the hydrophobicity of PCL, there were three factors that affected the ESR: the content of MPEG, chemical ρ_x, and temperature.

A lower chemical ρ_x resulted in a higher ESR. Also, when the temperature was higher than LCST, the main factor was the MPEG content because of the hydrophilicity of the PEO chains. As Figure 3 shows, the PEO chains could hold water through hydration and could restrain the collapse of the network at a certain extent. The MEPG content was in accordance with the ESR of each sample at 40–60°C (Figure 4).

When the temperature decreased below the LCST, the function of the hydrogen bonds strengthened gradually. The hydrophobic PNIPAAm chains transferred to hydrophilic, so the ESR values of all of the samples increased. However, the ESR of sample 3 increased more tenderly than others. The main reason was perhaps that the hydrogen bonds between the PNIPAAm chains and PEO chains were also strengthened when the temperature

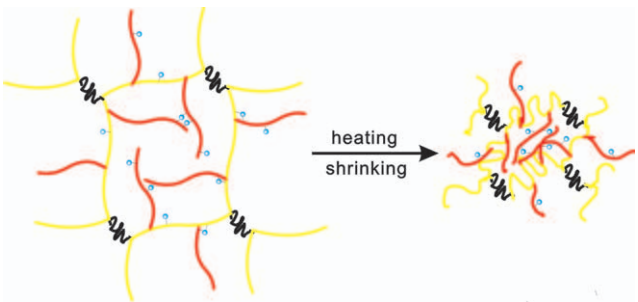

Figure 3. Schematic illustration of the structure of PNIPAAm-*g*-PEO hydrogels (the yellow/light lines stand for the PNIPAAm chains, the red/dark lines stand for the PEO chains, the black dash lines stand for hydrogen bonds, the black dots stand for methyl groups, and the blue balls stand for water molecules). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

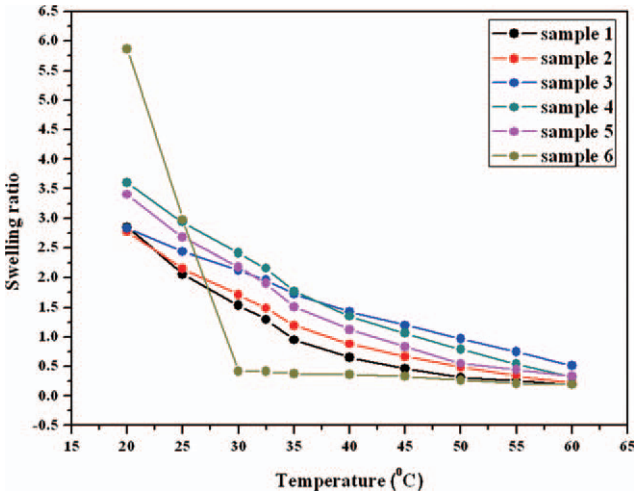

Figure 4. ESR of the hydrogels as a function of the temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased. Meanwhile, the excess of PEO chains adhering to the PNIPAAm chains made the swelling of the network difficult.

Unlike the traditional PNIPAAm gels, the PNIPAAm-*g*-PEO gels did not lose water thoroughly when the temperature was higher than LCST. For the motion of PNIPAAm chain was restrained by PEG's ability to bind to water,[28] so the volume phase transition of the PNIPAAm-*g*-PEO gels was not drastic, as seen in sample 6 in Figure 4. The MPEG content led to a small amount of saltation. These results corresponded to those of the previous work.[29]

Swelling and deswelling kinetics of the hydrogels

The swelling kinetic curves of the hydrogels are shown in Figure 5. As shown, the sample hydrogels all took over 10 h to reach their equilibrium states. Samples 3, 4, and 5 needed even longer times to reach the equilibrium state. The presence of PEO dangling chains did not improve the swelling kinetics of the gels compared with sample 6. The swelling process of comb-type grafted hydrogels was mainly controlled by two steps. First, the PEO dangling chains, which adhered to collapsed network bones, diffused into water. Then, the network bones and water processed synergy diffusion. The first step was determined by the content of MPEG. Thus, the swelling rate of sample 1 was greater than that of sample 2, which was greater than that of sample 3. Only when the adherent PEO chains were in sufficient contact with water molecules was the restraint of the PNIPAAm bones removed and more water molecules entered into the network. The speed of second step was dependent on the chemical ρ_x (Sample 4 > Sample 2 > Sample 5).

The deswelling ratios of the PNIPAAm-*g*-PEO gels were mainly related to two factors. These were the content of the hydrophobic PCL component and the content of dangling PEO chains. Excess PCL increased the heterogeneous degree. The hydrophobic component formed a porous structure on the surface and insides of the hydrogels, so the dehydration rate of sample 5 was greater than that of sample 2, which was greater than that of sample 4. As shown in Figure 5, we observed that the influence of PEO dangling chains was greater than that of the PCL crosslinker. Because of the mixing of most PEO chains and PNIPAAm, the collapse of sample 3 was almost prevented.[30] In contrast to sample 3, sample 1 exhibited a good deswelling rate. In another words, a higher content of PEO resulted in a lower dehydration rate, so the deswelling rate of sample3 was less than sample5, and those of samples 2 and 4 were less than that of sample 1. Because it lacked PEO, sample 6 deswelled faster than comb-type grafted hydrogels.

Compression properties of the hydrogels

Figures 6 and 7 illustrate τ versus $-(\lambda - \lambda^{-2})$ plots and τ versus $-(\lambda - 1)$ of the PNIPAAm-*g*-PEO hydrogels, respectively, with different PEO and PCL contents in the equilibrium swollen state at 25°C. τ denotes the applied compressive force per unit cross-sectional area of the undeformed swollen hydrogel specimen, and λ is the ratio of the deformed length (l) to the undeformed length (l_0) of the hydrogel. So the strain was $-(\lambda - 1)$, and the $-(\lambda - \lambda^{-2})$ was defined as compression deformation factor. The rubber elasticity theory was used here to derive the network parameters based on the τ–strain measurements:

$$G = RT\rho_x/Q^{1/3} \quad (5)$$

The network parameters G and ρ_x are summarized in Table II. We observed that the addition of MPEG enhanced the compression mechanical properties (G of sample 1 > G of sample 2 > G of sample 3; meanwhile, G of sample 4 > G of sample 5). The theoretical ρ_x was calculated as follows:

Table II. Network Parameters of the PNIPAAm-*g*-PEO Hydrogels

Sample no.	Q (g/g) at 25°C	G (g/cm^2)	$\rho_x \times 10^{-5}$ (mol/cm^3)	Theoretical $\rho_x \times 10^{-5}$ (mol/cm^3)	Mean side length of each network element (nm)[a]	Grafting ratio in each PNIPAAm chain (%)
1	2.06	455.77	2.29	0.56	17.25	3.61
2	2.15	797.65	4.38	0.55	17.25	5.72
3	2.44	1046.48	5.57	0.53	17.25	6.91
4	2.93	624.81	3.54	0.42	23	5.88
5	2.68	994.84	5.08	0.66	14.32	5.71

[a]The mean side length of each network element was calculated to be 0.154 × 2 × (the molar quantities of NIPAAm/the molar quantities of PCLnm. The PEO length was calculated as 3 × 0.143 × M_w(MPEG)/44 nm.

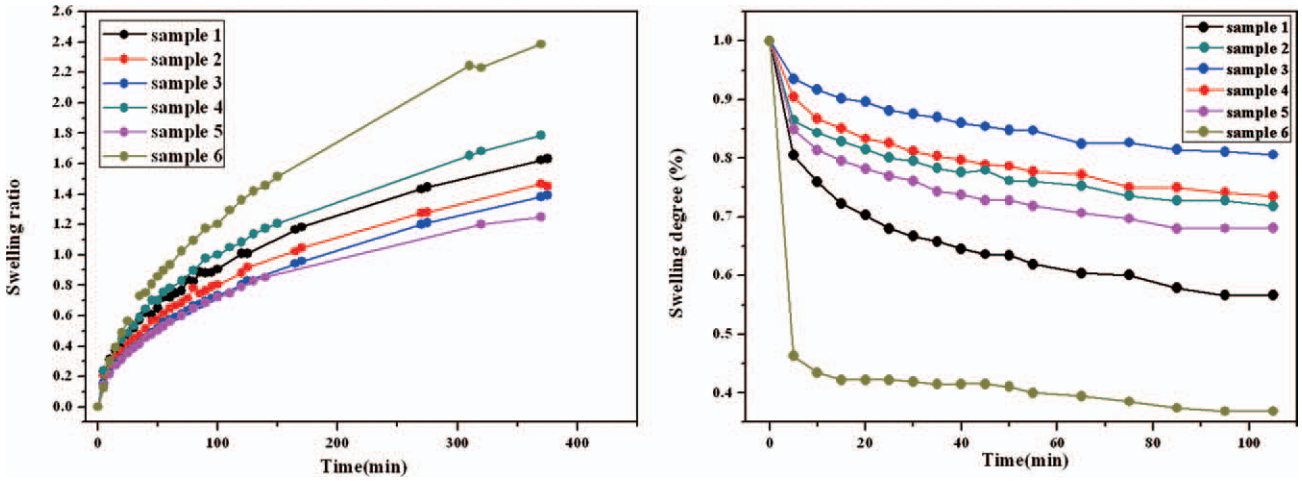

Figure 5. Swelling kinetics curves (left) of the hydrogels (25°C) and deswelling kinetics curves (right) of the hydrogels (from 25 to 40°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

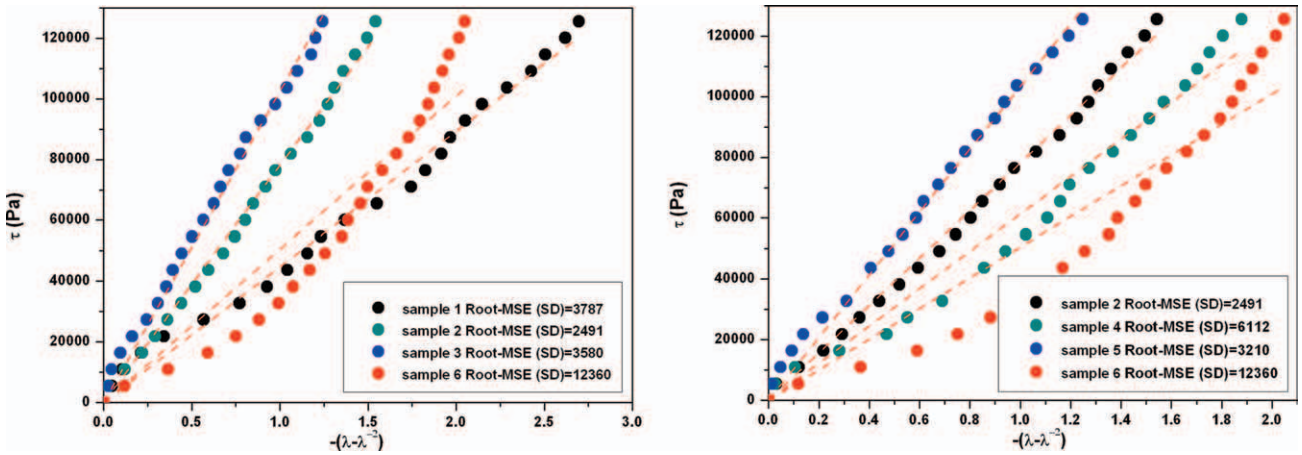

Figure 6. τ versus $-(\lambda - \lambda^{-2})$ plots for the swollen hydrogels with various MPEG contents and PCL contents in the equilibrium swollen state at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

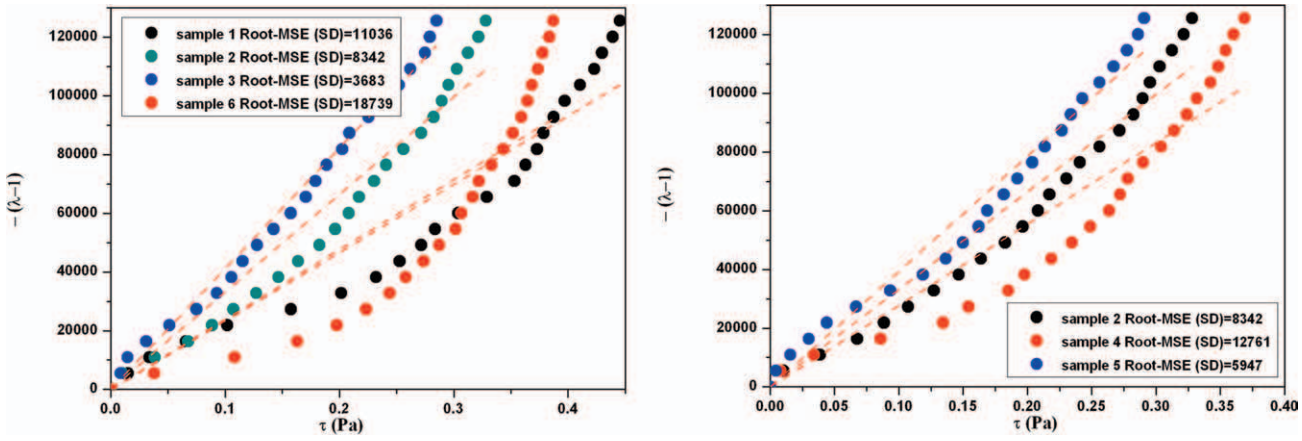

Figure 7. τ versus strain $[-(\lambda - 1)]$ plots for swollen hydrogels with various MPEG contents and PCL contents in the equilibrium-swollen state at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

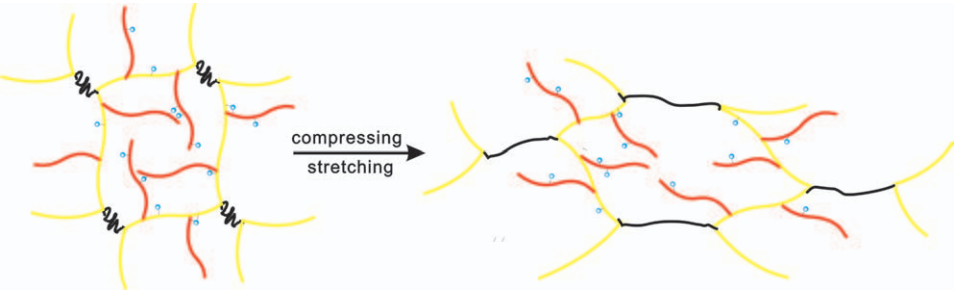

Figure 8. Schematic of the variation in the compressing process (the yellow/light lines stand for the PNIPAAm chains, the dark/red lines stand for the PEO chains, the black dashed lines stand for hydrogen bonds, the black dots stand for methyl groups, and the blue balls stand for water molecules.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\rho_x = m_{\mathrm{PCLAc}}/M_w V \tag{6}$$

where m_{PCLAc} is the mass of PCLAc, M_w is the weight-average molecular weight of PCLAc ($M_w \approx 2000$), and V is the volume of the hydrogel.

As shown in Table II, the PNIPAAm-*g*-PEO hydrogels exhibited outstanding compression properties. The PCL macromolecular crosslinker and PNIPAAm bones constituted the hydrogel's network. The hydrogen bonds between PEO/PNIPAAm chains and water molecules strengthened the three-dimensional network structure. Meanwhile, as shown in the curves in Figure 7, the presence of PCL resulted in the hydrogel deviating from the equations as follows:

$$\tau = -E(\lambda - 1) \tag{7}$$

As Figure 7 shows, we observed that the addition of PCL and PEO enhanced E.

The theoretical ρ_x could be calculated by eq. (6), and the practical ρ_x could be calculated by eq. (5). The results are also listed in Table II. It was easy to observe that the practical ρ_x's were several times than the theoretical ρ_x. Thus, we concluded that there was not only chemical crosslinking in the gels but also physical crosslinking. The physical crosslinking included hydrogen bonding of the PEO chains and the entanglement of the PCL chains.

The mean side lengths of each network element are listed in Table II. The length of the PEO chains was about 9.75 nm. When the mean side length was shorter than 19.5 nm (double the length of the PEO chains), this implied that the PEO chains had more chances to contact each other in one network element. Accordingly, the sample exhibited a higher compressive strength. It explained why G of sample 5 was greater than that of sample 2, which was greater than that of sample 4.

As Figures 6 and 7 show, the kinetics curves showed a pronounced deviation from linearity. The E values of all of the samples (except sample 6) decreased at the beginning and then increased. It might have been that part of hydration was destroyed first, and then, the frizzy PCL chains were stretched with increasing pressure. The increased E in sample 6 demonstrated that the PCL chains indeed were stretched at first without the hydration of PEO. Figure 8 shows the variation of the microcosmic structure of the hydrogels when they were compressed.

CONCLUSIONS

In this study, we synthesized comb-type grafted hydrogels by the copolymerization of NIPAAm and MPEGAc with PCLAc as a crosslinker and measured the parameters of the hydrogels. The results show that the thermosensitivity of the hydrogels decreased with PEO content. Compared with the traditional PNIPAAm hydrogel, the comb-type grafted hydrogel needed more time to achieve equilibrium because it went through two steps, dangling chain diffusion and network bones and water-processed synergy diffusion. The addition of PCL accelerated the deswelling rate because of the porous structure. However, the addition of PEO was not to the benefit of the deswelling process for the hydration of PEO. For the hydrogen bonds and the stretching of PCL, the compression properties of the gels were strengthened. Meanwhile, the compression properties were related to the grafting ratio and the size of the network element. In addition, the addition of PCL made the hydrogel deviate from the rubber elasticity equations.

ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of Guangdong Province of China under contract grant number 8251065004000001.

REFERENCES

1. Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984,** *81*, 6379.
2. Sasaki, S.; Kawasaki, H.; Maeda, H. *Macromolecules* **1997,** *30*, 1847.
3. Lele, A. K.; Hirve, M. M.; Badiger, M. V.; Mashelkar, R. A. *Macromolecules* **1997,** *30*, 157.
4. Ito, K.; Ujihira, Y.; Yamashita, T.; Horie, K. *Polymer* **1999,** *40*, 4315.
5. Suetoh, Y.; Shibayama, M. *Polymer* **2000,** *41*, 505.
6. Norisuye, T.; Shibayama, M.; Nomura, S. *Polymer* **1998,** *39*, 2769.
7. Tokuhiro, T.; Amiya, T.; Mamada, A.; Tanaka, T. *Macromolecules* **1991,** *24*, 2936.
8. Zeng, F.; Tong, Z.; Feng, H. Q. *Polymer* **1997,** *38*, 5539.
9. Zeng, F.; Zheng, X.; Tong, Z. *Polymer* **1998,** *39*, 1249.
10. Liu, Q. F.; Zhang, P.; Qing, A. X.; Lan, Y. X.; Lu, M. G. *Polymer* **2006,** *47*, 2330.

11. Zhang, P.; Liu, Q. F.; Qing, A. X.; Shi, J. B.; Lu, M. G. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 3312.
12. Zhu, D.; Lu, M.; Guo, J.; Liang, L.; Lan, Y. *J. Appl. Polym. Sci.* **2011,** *124*, 155.
13. Misra, G. P.; Singh, R. S. J.; Aleman, T. S.; Jacobson, S. G.; Gardner, T. W.; Lowe, T. L. *Biomaterials* **2009,** *30*, 6541.
14. Xu, X. D.; Chen, C. S.; Lu, B.; Wang, Z. C.; Cheng, S. X.; Zhang, X. Z.; Zhuo, R. X. *Macromol. Rapid Commun.* **2009,** *30*, 157.
15. Kaneko, Y.; Nakamura, S.; Sakai, K.; Kikuchi, A.; Aoyagi, T.; Sakurai, Y.; Okano, T. *Polym. Gels Networks* **1998,** *6*, 333.
16. Graham, N. B.; McNeill, M. E. *Biomaterials* **1984,** *5*, 27.
17. Kim, C. J. *J. Pharm. Sci.* **1995,** *84*, 303.
18. Sako, K.; Nakashima, H.; Sawada, T.; Fukui, M. *Pharm. Res.* **1996,** *13*, 594.
19. Kojima, H.; Yoshihara, K.; Sawada, T.; Kondo, H.; Sako, K. *Eur. J. Pharm. Biopharm.* **2008,** *70*, 556.
20. Kitano, H.; Ichikawa, K.; Ide, I.; Fukuda, M.; Mizuno, W. *Langmuir* **2001,** *17*, 1889.
21. Tasaki, K. *J. Am. Chem. Soc.* **1996,** *118*, 8459.
22. Tajiri, T.; Morita, S.; Ozaki, Y. *Polymer* **2011,** *52*, 5560.
23. Chen, H. W.; Li, W. W.; Zhao, H.; Gao, J. G.; Zhang, Q. J. *J. Colloid Interface Sci.* **2006,** *298*, 991.
24. Zhu, P. W. *J. Mater. Sci. Mater. Med.* **2004,** *15*, 567.
25. Deyao, K.; Peng, T.; Feng, H. B.; He, Y. Y. *J. Polym. Sci. Part A: Polym. Chem.* **1994,** *32*, 1213.
26. Lee, W. F.; Chen, Y. J. *J. Appl. Polym. Sci.* **2001,** *82*, 2487.
27. Liu, Q. F.; Zhang, P.; Lu, M. G. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 2615.
28. Cheng, V.; Lee, B. H.; Pauken, C.; Vernon, B. L. *J. Appl. Polym. Sci.* **2007,** *106*, 1201.
29. Drapala, P. W.; Brey, E. M.; Mieler, W. F.; Venerus, D. C.; Derwent, J. J. K.; Perez-Luna, V. H. *J. Biomater. Sci. Polym. Ed.* **2011,** *22*, 59.
30. Virtanen, J.; Baron, C.; Tenhu, H. *Macromolecules* **2000,** *33*, 336.