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# Synthesis and properties of thermo- and pH-sensitive poly(diallyldimethylammonium chloride)/poly(*N*,*N*-diethylacrylamide) semi-IPN hydrogel

Jun Chen, Mingzhu Liu*, Hongliang Liu, Liwei Ma, Chunmei Gao, Siying Zhu, Shaopeng Zhang

*State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China*

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ABSTRACT

In this study, a novel semi-interpenetrating polymer network (semi-IPN) hydrogel of poly(diallyldimethylammonium chloride)/poly(*N*,*N*-diethylacrylamide) (PDADMAC/PDEA) was prepared using ammonium persulfate as an initiator and *N*,*N*,*N*′,*N*′-tetramethylethylenediamide as an accelerator at room temperature. The influence of this additive on the property of resulting PDEA hydrogels was investigated and characterized. The interior morphology by scanning electron microscopy (SEM) revealed that PDADMAC introduced PDEA hydrogels have large and interconnected porous network structures. Differential scanning calorimetry (DSC) studies showed the difference in the state of the water between PDEA and semi-IPN hydrogels. The incorporating of PDADMAC significantly improved the equilibrium swelling ratio of modified hydrogels when comparing with a normal PDEA hydrogel. The semi-IPN hydrogels exhibited improved thermosensitive characteristics, such as faster deswelling and swelling rates and great oscillating deswelling–swelling behavior, and the level of improvement depended on the PDADMAC content. The swelling dynamic transport of the hydrogels was analyzed based on the Fickian equation.

## 1. Introduction

Intelligent hydrogel can undergo abrupt volume or phase transition in response to small changes in environmental parameters such as temperature [1], pH [2], light [3], ion [4], and electric field [5]. Among those external stimuli, temperature and pH are important triggering signals for phase transitions in hydrogels because they are important environment factors in biomedical and other systems. The hydrogels have been utilized in a variety of applications such as controlled drug delivery [6], separation [7] and tissue engineering [8]. Poly(*N*,*N*-diethylacrylamide) (PDEA) hydrogel is a typical thermosensitive polymeric network, which exhibits a transition temperature ($T_{tr}$) or lower critical solution temperature (LCST) at about 31 °C [9,10]. It absorbs water to a swollen state at a temperature below the $T_{tr}$, and shrinks with an abrupt volume decrease when the temperature goes above the $T_{tr}$ because of the rapid alteration in hydrophilicity and hydrophobicity. pH-sensitive hydrogels may be synthesized by crosslinking weak or strong ionized polyelectrolyte. pH of the swelling medium induces a change in the degree of ionization of the polyelectrolyte and therefore in the swelling capacity of the hydrogel.

However, the main limitations of the conventional PDEA hydrogel are the slow rate of response to external environment change. So far, several strategies have been proposed in attempts to improve the response rate of PDEA hydrogel. Introducing another polymer into PDEA hydrogel to form interpenetrating polymer network (IPN) is one of the promising and exciting choice to obtain the improvement on the properties. IPNs are conventionally defined as intimate combination of two polymers, at least one of which is synthesized or crosslinked in the immediate presence of the other [11]. If one polymer is linear and penetrates another crosslinked network without any other chemical bonds between them, it is called a semi-IPN [12]. By using IPN method thermodynamic incompatibility can be overcome due to permanent interlocking of network segments and IPNs with limited phase separation can be obtained. The interlocked structures of the crosslinked IPNs components are believed to ensure stability of the bulk and surface morphology [13,14]. Moreover, the method has been reported to present some possible advantages. For example, the process of preparation is simple and feasible, and the combination of temperature response with other properties can retain its individual response behavior [15–17].

Poly(diallyldimethylammonium chloride) (PDADMAC), the first synthetic polymer to be approved by the U.S. Food and Drug Administration for the use in potable water treatment, possesses a backbone of cyclic units and highly hydrophilic permanently charged quaternary ammonium groups. It is safe for human

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* Corresponding author. Tel.: +86 931 8912387; fax: +86 931 8912582.
*E-mail address:* mzliu@lzu.edu.cn (M. Liu).

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health and has been widely used in many industrial and biological applications, such as flocculent in wastewater treatment, antimicrobial biocide and biocatalyst agents in biological, medical, food applications and layer-by-layer assembly [18]. Moreover, it is also strong cationic polyelectrolyte with antibacterial properties [19]. The kinetics and mechanism of homo- and copolymer syntheses, chemical structures, polyelectrolyte behavior in solution, molecular characterization and interactions in solution and at interfaces have been reviewed [20]. A series of IPN hydrogels with poly(diallyldimethylammonium chloride) (PDADMAC) and other components, such as poly(vinyl alcohol)[21,22], chitosan [23], acrylic acid [24], alginate [25], are synthesized. The hydrogels exhibited changes in their swelling ratio in response to external stimuli, such as temperature, pH, electric and ionic concentration. And these hydrogels swelled rapidly. However, the deswelling and oscillating deswelling–swelling behaviors with the changing content of PDADMAC in the hydrogels are not analyzed. Hence, the synthesis and characterization study on the rapid deswelling and oscillating deswelling–swelling behaviors would provide novel ideas on the design of the stimuli-responsive semi-IPN hydrogels and elucidation on the responsive behavior of the hydrogels with different structures.

In this paper, a series of PDADMAC/PDEA semi-IPN hydrogels with different compositions were fabricated, which combined the advantages of PDADMAC and PDEA to prepare a new kind of material. Fourier transform infrared (FTIR) spectroscopy was used to characterize the hydrogel composition, and scanning electron microscope (SEM) was used to observe their interior morphology, and differential scanning calorimetry (DSC) was used to analyzed the state of water in the hydrogels. The thermo- and pH-responsive behaviors of these hydrogels were studied. The deswelling and swelling kinetics of the different composition ratios of PDADMAC to DEA on the semi-IPN hydrogels were also investigated in detail.

## 2. Experimental

### 2.1. Materials

Poly(diallyldimethylammonium chloride) (PDADMAC) solution (20 wt%), with the molecular weight range of 200,000–350,000, was purchased from Aldrich, which was diluted to 5 wt% in this work. *N*,*N*-Diethylacrylamide (DEA) was synthesized according to the literature [9]. Ammonium persulfate (APS) (Tianjin Chemical Company, China) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamide (TEMED) (Fluka Co. Ltd.) were analytical grade and used without further purification. *N*,*N*′-Methylenebisacrylamide (NNMBA) (Shanghai Chemical Co. Ltd., China) was purified by recrystallization in ethanol. All other reagents were analytical grade and used without further purification. Double distilled water was used for preparing all the solutions of the swelling and deswelling experiment.

### 2.2. Preparation of the PDADMAC/PDEA semi-IPN hydrogels

Polymerization reactions were performed in glass tubes with the inner diameters of 1.2 cm, and lengths of 10 cm. In preparation of the PDADMAC/PDEA semi-IPN hydrogels, the monomer, DEA, the crosslinker, NNMBA, and the various contents of PDADMAC were fully dissolved in water at room temperature. The solution was bubbled with nitrogen for 20 min to remove the dissolved oxygen that would act as an inhibitor for the reaction, and then a given amount of APS and TEMED used as a pair of redox initiator was dropped into the solution to initiate the polymerization reaction [21,22]. The free-radical polymerization was carried out at room temperature for 24 h. At the end of the reaction, the glass tubes were broken carefully without destroying the cylindrical hydrogels. The resulting hydrogels were sliced into small cylinders with lengths of 2 mm and then immersed in distilled water for 5 days, and the water was refreshed four times every day in order to remove the residual unreacted monomer and the sol fraction of the product. The pure PDEA hydrogel was prepared under the same condition. The detailed feed compositions and samples codes of hydrogels are summarized in Table 1.

**Table 1**
The feed compositions and sample codes of the hydrogels.

| Compositions | Sample ID | | | | |
|---|---|---|---|---|---|
| | PDEA | Semi-IPN1 | Semi-IPN2 | Semi-IPN3 | Semi-IPN4 |
| DEA (ml) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| PDADMAC (ml) | 0 | 0.5 | 1.0 | 2.0 | 2.8 |
| NNMBA (mg) | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| APS (mg) | 18.0 | 18.0 | 17.9 | 18.1 | 17.9 |
| TEMED (μl) | 20 | 20 | 20 | 20 | 20 |
| $H_2O$ (ml) | 5.0 | 4.5 | 4.0 | 3.0 | 2.2 |

The composition of the gels was determined from the measure of nitrogen content using elemental analysis method. The weight percent of the DEA in the gel was defined as follows:

$$W_{\mathrm{DEA}} \times 11.02\% + (W_{\mathrm{gel}} - W_{\mathrm{DEA}}) \times 8.67\% = W_{\mathrm{gel}} \times N\% \qquad (1)$$

where $W_{\mathrm{DEA}}$ is the weight of the DEA in gel and $W_{\mathrm{gel}}$ is the weight of the gel.

### 2.3. FTIR analysis

The samples were analyzed using a Fourier transform infrared (FTIR) spectroscope (Nicolet 670 FTIR, USA) in the region of 4000–400 $\mathrm{cm}^{-1}$. Prior to the measurement, the samples were dried under vacuum until reaching a constant weight. The dried samples were pressed into the powder, mixed with 10 times as much KBr powder, and then compressed to make a pellet for FTIR characterization.

### 2.4. Interior morphology of the hydrogels

The hydrogels, after reaching their equilibrium swelling ratio in water at room temperature, were quickly frozen in liquid nitrogen and then freeze-dried under vacuum for 15 h with Labconco Freeze Dry system until all water was sublimed. The freeze-dried samples were fractured carefully and mounted onto aluminum stubs and coated with gold. The interior morphology was investigated using a scanning electron microscope (SEM) (JSM-5600LV SEM, Japan).

### 2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements (Pyris Sapphire DSC, USA) were carried out in a nitrogen atmosphere to analyze the state of the water in the PDADMAC/PDEA semi-IPN hydrogels swollen at 20 °C. The experiments were performed from −30 to 30 °C at a heating rate of 2 °C $\mathrm{min}^{-1}$ under a nitrogen atmosphere (20 ml $\mathrm{min}^{-1}$).

### 2.6. Temperature dependence of the equilibrium swelling ratio of the hydrogels

The classical gravimetric method was used to measure the equilibrium swelling ratios of the hydrogels. For the temperature dependence of the equilibrium swelling ratio study, the hydrogel samples were equilibrated in water at a predetermined temperature ranging from 20 to 50 °C, which covered the expected range of the $T_{\mathrm{tr}}$ of the hydrogel samples. The hydrogels were immersed in water to reach a swollen equilibrium at each predetermined temperature. The hydrogel samples were taken out, and excess water on the sample surface of the wet hydrogel was removed with wet filter papers and then weighed until a constant weight. After the weight measurement, the hydrogel was re-equilibrated in water at another predetermined temperature and then weighed using the same method as above. The weight of each dried sample was finally measured after drying under vacuum at 25 °C to reach a constant weight. Each sample was measured three times and the average value of three measurements was taken. The equilibrium swelling ratio, ESR, was defined as follows:

$$\mathrm{ESR} = \frac{W_s - W_d}{W_d} \qquad (2)$$

where $W_s$ is the weight of the hydrogel sample in the swollen equilibrium and $W_d$ is the weight of the dried gel.

### 2.7. Deswelling kinetics of the hydrogels

The gravimetric method was also employed to study the temperature response kinetics of hydrogel. The hydrogels were first immersed in water at 20 °C until equilibrium. The equilibrated hydrogels were then quickly transferred into a water bath at 50 °C. At predetermined time intervals, the hydrogels were taken out from the hot water and weighed after removing the excess water on the sample surface with wet filter paper. Each sample was weighted three times and the average value of three measurements was taken. The water retention (WR) was defined as follows:

$$\mathrm{WR} = \frac{W_t - W_d}{W_s - W_d} \times 100 \qquad (3)$$

where $W_t$ is the weight of wet hydrogel at regular time intervals, $W_s$ is the weight of hydrogel in the swollen equilibrium at 20 °C and the other symbol is the same as defined above.

### 2.8. Swelling kinetics of the hydrogels

The same method as above was utilized to record the swelling kinetics. The dried gels were immersed in water at 20 °C, and the samples were taken out from water at regular time intervals. After removing the water on the sample surface with wet filter paper, the sample weights were recorded as the average value of three measurements. The water uptake (WU) at time $t$ was defined as follows:

$$\mathrm{WU} = \frac{W_t - W_d}{W_d} \qquad (4)$$

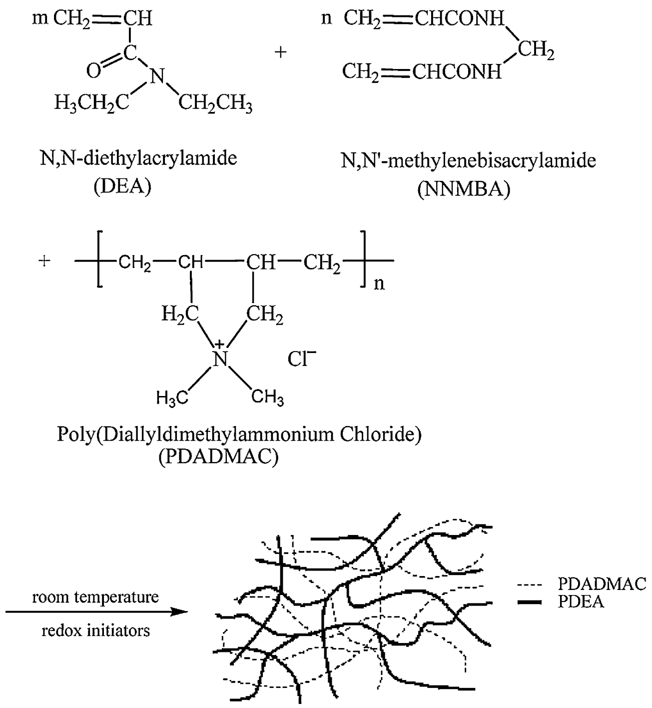
where $W_t$ is the weight of the wet hydrogel at time $t$ and other symbols are the same as defined above.

### 2.9. Study on oscillating deswelling–swelling kinetics of the hydrogels

The oscillating deswelling–swelling kinetics of the hydrogels was also studied in water on cycling the temperature between 25 (below $T_{tr}$) and 40 °C (above $T_{tr}$). The hydrogel samples were first immersed in distilled water at 25 °C till it reached equilibrium. The hydrogel sample was then quickly transferred to distilled water at 40 °C and the sample exhibited deswelling behavior. After 5 min, the sample was taken out of the 40 °C water bath and its wet weight after blotting the excess water on the hydrogel surface by a wet filter paper was weighted and recorded. The sample was then transferred back to 25 °C distilled water for another 5 min swelling and weighted. This 10 min cycle (5 min for deswelling from 25 to 40 °C and 5 min for swelling from 40 to 25 °C) was continued for several cycles in order to determine the oscillatory deswelling–swelling kinetics of the hydrogels. The oscillatory shrinking–swelling kinetics of the hydrogels was studied by monitoring the change of the hydrogel weight in the different temperature, expressed as follows:

$$\mathrm{SR} = \frac{W_t - W_d}{W_d} \qquad (5)$$

where all symbols are the same as defined above.



**Scheme 1.** The synthesis route of the semi-IPN hydrogel.

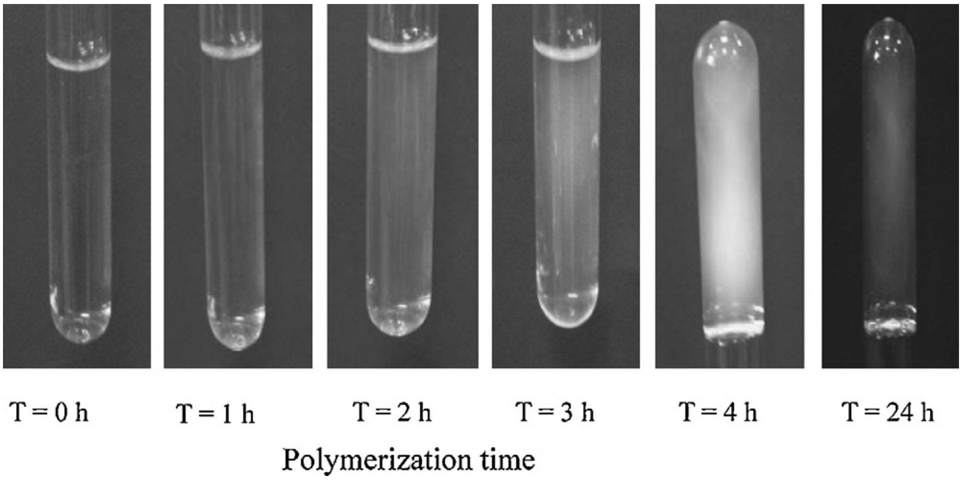
### 2.10. Study on the pH-sensitivity of the hydrogels

The measurement of the equilibrium swelling ratio for the hydrogels under various pH solutions was the same to that in water. The desired pH was adjusted by NaOH and/or HCl solutions, and sodium chloride was used to adjust the ionic strength of solutions to 0.1 M. The pH values were precisely checked by a pH-meter (pHS-3B, China). The hydrogel samples were immersed, respectively, in buffer solutions with different pH values at room temperature for at least 24 h to reach equilibrium. The weights of the samples were measured by gravimetrical method and the equilibrium swelling ratio at each pH value was calculated according to Eq. (2).

## 3. Results and discussions

### 3.1. Synthesis of PDADMAC/PDEA semi-IPN hydrogels

The structures of PDADMAC, DEA and the synthesis route of the PDADMAC/PDEA semi-IPN hydrogel are shown in Scheme 1, respectively. The PDADMAC/PDEA semi-IPN hydrogels are prepared from DEA in PDADMAC aqueous solutions via radical polymerization in the presence of crosslinker, NNMBA. In this work, APS/TEMED as a pair of redox initiators is utilized to initiate the radical polymerization, and the DEA and NNMBA for one network are polymerized/crosslinked. It is well-known that APS and TEMED have been widely used for many advantages, such as high initiation efficiency and fast polymerization rate [10,12,14,21]. The components of the redox system and the reactants formed homogeneous and transparent solution. The resulting hydrogels are composed of the crosslinked PDEA and the linear PDADMAC, which interpen-



**Scheme 2.** Photographs of reaction vials for semi-IPN3 hydrogel (polymerization vs. time).

etrate each other to form semi-interpenetrating network. All the semi-IPN hydrogels are transparent, regardless of PDADMAC content. The polymerization reaction was conducted in test tubes and closely monitored by taking the photographs at regular intervals. These photographs are presented in Scheme 2. In all the formulations, the gelation process of PDEA hydrogels took place within 9 min after addition of the redox initiators, and the gelation time of semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 is about 1.5, 2.5, 3.7 and 8.2 h, respectively. As the polyampholyte of PDADMAC is introduced into the system, the accelerated effect of the TEMED would be partly restrained, and the decomposed rate of the initiator would decrease. On the other hand, the large viscosity would hinder the movement of the radicals. Therefore, the polymerization rate slows down and the formation of the integrated network needs long time.

The *N*% of the PDEA, semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 gel is 11.01%, 10.82%, 10.69%, 10.46% and 10.24%, respectively. The DEA percent of the semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 gel is 91.49%, 85.96%, 76.17% and 66.81%, respectively.

### 3.2. FTIR

The molecular structure of the semi-IPN gel is investigated using FTIR. Fig. 1 shows the FTIR spectra of PDADMAC, PDEA and the PDADMAC/PDEA semi-IPN xerogel. The pure PDADMAC shows the characteristic peaks at 1640 and 1465 cm$^{-1}$, which related to the stretching vibration of NR$_4$ and C(CH$_3$)$_2$$^+$, respectively. The FTIR spectrum of PDEA (Fig. 1c), significant peak at 1636 cm$^{-1}$, can be attributed to the characteristic peaks of C=O. A mixture of absorption band from the PDADMAC and PDEA portions of the semi-IPN xerogel is evident. The characteristic absorptions of both PDADMAC and PDEA can be found in the semi-IPN xerogel. Moreover, the wide-strong absorption bands at 2972, 2932 and 2876 cm$^{-1}$ are resulting from C–H stretching vibrations of –CH$_3$ and –CH$_2$– groups. 1380 and 1457 cm$^{-1}$ bands are also due to symmetrical C–H bending, which belong to the PDEA and PDADMAC components in the xerogel. The peak at 1136 cm$^{-1}$ corresponds to stretching of C–N. As a result, it can be concluded that the PDADMAC/PDEA semi-IPN hydrogel is successfully prepared.

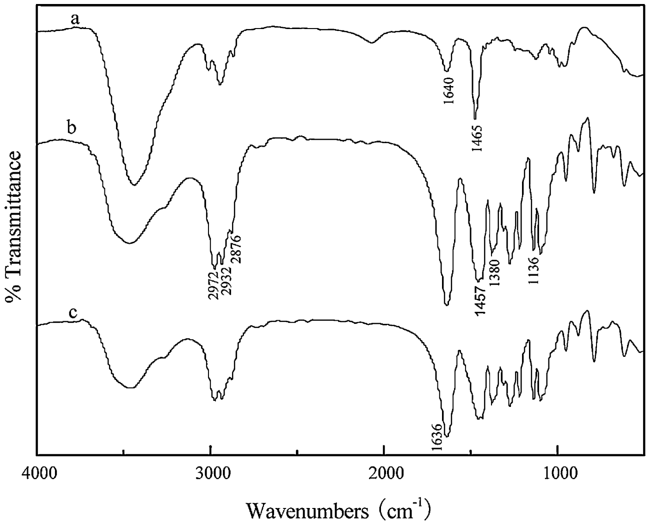


**Fig. 1.** FTIR spectra of PDADMAC (a), semi-IPN4 xerogel (b) and PDEA xerogel (c).

### 3.3. Interior morphology of the hydrogels

The interior morphology of the hydrogels is shown in Fig. 2. The data clearly illustrate the dependence of interior morphology on the composition ratio of PDADMAC to DEA. As shown in Fig. 2, it could be seen that these hydrogel networks have a different interior porous structure. From the size of bar, the average diameter of the pores tends to increase with the increase of PDADMAC content. For example, semi-IPN4 has the largest pore size in the range of 110–155 μm, while PDEA has the smallest one in the range of 5–15 μm. Moreover, the pore of the semi-IPN hydrogels is interconnection, while the distance of PDEA hydrogel is long. As shown in Scheme 1, PDADMAC contains extra tetra-ammonium cations. A highly expanded network can be generated by electrostatic repulsion among tetra-ammonium cations during the polymerization process. Therefore, with the content of PDADMAC increasing, the pore size of the hydrogel becomes larger. The similar phenomenon is also reported [10].

Due to numerous interconnected pores in the hydrogel network, water molecules can easily diffuse. Therefore, incorporating PDADMAC into the PDEA hydrogel network could enhance the rate of the swelling and deswelling processes. The porous and thermosensitive hydrogels have potential applications in the controlled release of drug since the porous network may be able to provide enough space for the loading and releasing of drug, and would also be beneficial to the diversion the fluid when they are used in biomaterial.

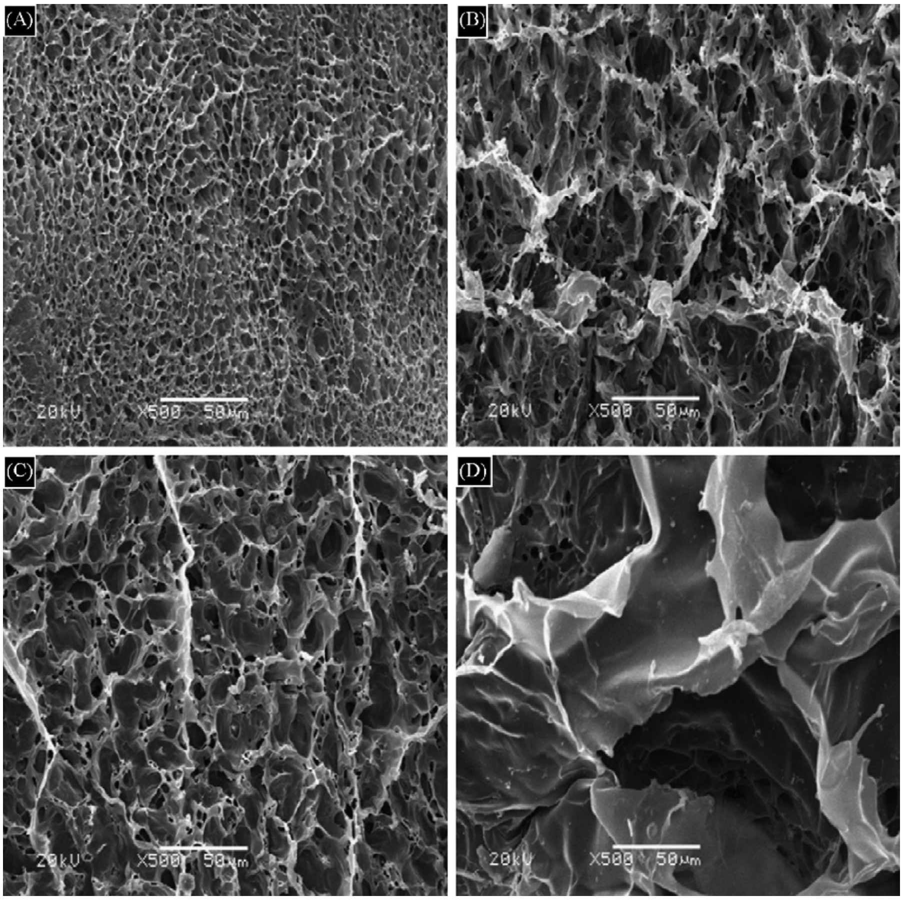


**Fig. 2.** SEM images of the hydrogels: (A) PDEA hydrogel; (B) semi-IPN2 hydrogel; (C) semi-IPN3 hydrogel and (D) semi-IPN4 hydrogel.

### 3.4. State of water in the hydrogels

As water inclusion is a basic phenomenon in hydrogels, a study of the physical state of the water in hydrogels will provide useful information on the swelling/deswelling behavior and the nature of the physical interactions between the polymer chains and the swelling medium [22,23]. Moreover, DSC is also used study relate the high heat of fusion to the higher free water content caused by the hydrophilicity of the network and porous morphology of the hydrogels [27]. Therefore, the characterization of the amount of imbibed water in the swollen hydrogel seems to be interesting and vital. In general, the state of water in the hydrogels can be divided into free water, freezing bound water and non-freezing bound water [28,29]. Free water dose not take part in hydrogen bonding with polymer molecules, and has a similar transition temperature, enthalpy and DSC curves as pure water. Freezing bound water interacts weakly with polymer molecules. Non-freezing water is combined with the polymer network chains through hydrogen bonds. The total content of freezing water ($W_{\mathrm{freezing}}$) can be calculated by DSC from the areas under the endothermic curves, and the content of non-freezing bound water ($W_{\mathrm{nfb}}$) can be indirectly determined by subtracting $W_{\mathrm{freezing}}$ from the equilibrium water content.

$$\mathrm{EWC}\,(\%) = \frac{W_{\mathrm{e}} - W_{\mathrm{d}}}{W_{\mathrm{e}}} \times 100 \tag{6}$$

$$W_{\mathrm{freezing}}\ (\%) = W_{\mathrm{f}} + W_{\mathrm{fb}} = \frac{Q_{\mathrm{endo}}}{Q_{\mathrm{pw}}} \tag{7}$$

$$W_{\mathrm{nfb}}\,(\%) = \mathrm{EWC} - W_{\mathrm{freezing}} \tag{8}$$

where $W_{\mathrm{f}}$, $W_{\mathrm{fb}}$, $W_{\mathrm{nfb}}$, and $W_{\mathrm{freezing}}$ are the fractions of free water, freezing bound water, non-freezing bound water and total content of freezing water (%), respectively. $Q_{\mathrm{endo}}$ and $Q_{\mathrm{pw}}$ are the heat fusion of free water in samples and pure water (333.3 J g$^{-1}$) [28,30].

DSC studies by Baumgartner et al. relate the high heat of fusion to the higher free water content caused by the hydrophilicity of the network and porous morphology of the hydrogels [17,27]. The results obtained from the DSC melting endotherms of the frozen water in the hydrogels are given in Fig. 3 and Table 2. From Fig. 3, it is noticed that water melting for all samples happens at a temperature greater than 0 °C. It is likely that a strong hydrogen bonding or some weak interaction between water molecules and hydrophilic groups on polymeric hydrogel bones may have impact on the melting temperature change [27]. In Table 2, the freezing water content is found to accumulate with the increasing concentration in PDADMAC, which means a raise in hydrogen bond formation between the hydrophilic chains and the water molecules. In addition, The bound water content is found to increase with the increase in PDADMAC concentration, which means an increase in hydrogen bond for-

**Table 2**
States of water in the hydrogels.

| Sample | Change in enthalpy (mJ/mg) | EWC (%) | Freezing water (%) | Non-freezing bound water (%) |
|---|---|---|---|---|
| PDEA | 181 | 92.42 | 54.31 | 38.11 |
| Semi-INP1 | 194 | 97.57 | 58.21 | 39.21 |
| Semi-INP2 | 195 | 98.06 | 58.51 | 39.45 |
| Semi-INP3 | 208 | 98.56 | 62.41 | 36.45 |
| Semi-INP4 | 211 | 98.75 | 63.31 | 35.44 |

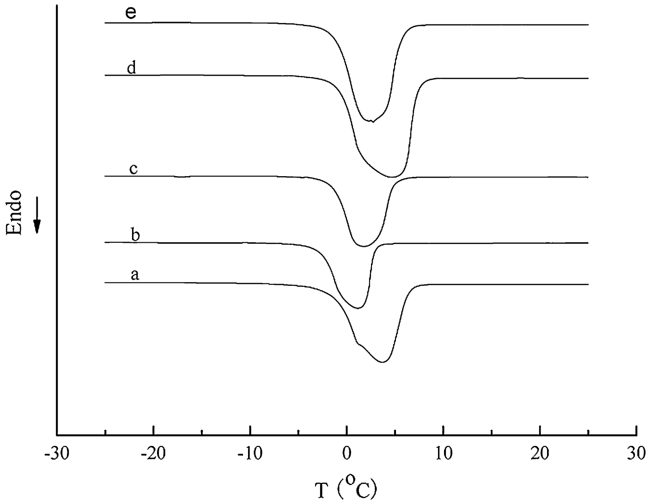


**Fig. 3.** DSC thermograms of the hydrogels at an equilibrium swollen state: (a) PDEA hydrogel; (b) semi-IPN1 hydrogel; (c) semi-IPN2 hydrogel; (d) semi-IPN3 hydrogel and (e) semi-IPN4 hydrogel.

mation between the hydrophilic chains and the water molecules. However, as the content of PDADMAC increase to some extent, the bound water content followed by a gradual decrease, indicating that the increase in the ESR is attributable mainly to the free water content of the semi-IPN hydrogels since the interconnected and large pore in the hydrogel network may be able to provide enough space for the loading free water, as mentioned above.

### *3.5. Temperature dependence of the equilibrium swelling ratio*

The equilibrium swelling ratio is one of the most important parameters for evaluating hydrogels because it illustrates their LCST behavior. The swelling behavior of these hydrogels in water at different temperatures was studied and the results are shown in Fig. 4. As clearly seen, at the same temperature (below the $T_{tr}$), the ESR of the hydrogels increases with the increase of the PDADMAC content in the corresponding hydrogel. For example, semi-IPN4 has the highest ESR (75.88) at 20 °C, while the ESR of semi-IPN3, semi-IPN2, semi-IPN1 and PDEA is 60.03, 47.44, 39.13, 13.30, respectively. The ESR of the hydrogels is attributed to the following two reasons. One is due to the hydrophilicity, and the other reason is due to the pore size of the hydrogel. It is known that there are hydrophilic groups (–$CONR_2$) and hydrophobic groups (–$CH_2CH_3$) in the monomer DEA, corresponding to hydrophilic and hydrophobic regions in the PDEA network [9,10,26]. In the PDEA hydrogel network, there exists a hydrophilic/hydrophobic balance and many interactions, such as hydrogen bonds and polymer–polymer hydrophobic interactions, which results in a remarkable hydration–dehydration change in response to temperature. At temperature below its $T_{tr}$, the hydrophilic groups of the PDEA hydrogel bond to water molecules through hydrogen bonds, and these hydrogen bonds behave cooperatively to form a stable shell around the hydrophobic groups. Therefore, the PDEA hydrogel exhibits a great water uptake. Moreover, the hydrophilic and ionic groups in polymer network have significant impact on the swelling behavior, and play an important role on the swelling ratios [10,31]. When PDADMAC is incorporated into the hydrogel network, the hydrophilicity of the semi-IPN hydrogels would increase. Moreover, PDADMAC is attributed to the expanded network structure during the polymerization process as discussed earlier. The SEM data (Fig. 2) described previously also support this relationship. Therefore, the higher the PDADMAC content, the more water is contained in the hydrogel below $T_{tr}$.

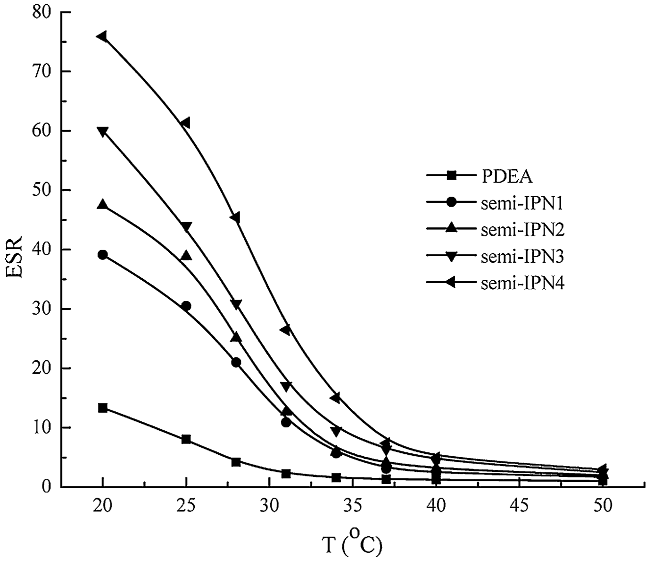


**Fig. 4.** Temperature dependence of the ESR of PDEA and semi-IPN hydrogels in double distilled water over the temperature range from 20 to 50 °C.

By increasing the temperature, the hydrogels change their appearances from transparent to translucent, even opaque, and all hydrogels exhibited volume phase transition from swelling states to deswelling states, indicating all hydrogels are thermosensitive. The data in Fig. 4 also exhibit that the semi-IPN hydrogel have similar temperature dependence as the PDEA hydrogel, i.e., the ESR of the hydrogels decreases gradually as the temperature increases from 20 to 50 °C. The thermosensitivity of the PDEA hydrogel is attributed to the alteration of hydrophilicity of the network. At temperature increase, a part of hydrogen bonds will be destroyed, and the hydrophobic interactions among the hydrophobic groups in the PDEA become dominant and consequently the PDEA hydrogels become much less hydrophilic. As a result, the water molecules entrapped in the network are released out, causing the hydrogel to collapse of polymer network. The ESR of the hydrogels decreases dramatically as the temperature increases to above 31 °C, and the phase separation of the hydrogel occurs. In generally, based on the swelling ratio experiments, the $T_{tr}$ or LCST of a thermosensitive hydrogel is regarded as the temperature at which the phase separation degree (changes in the swelling ratio vs. temperature changes) is the largest or the swelling ratio of the hydrogel decreases most dramatically. According to this definition, from Fig. 4, it can be found that the $T_{tr}$ of the PDEA and the semi-IPN hydrogels is in the region of 31 °C [10,12]. Regardless of the PDADMAC content of the semi-IPN hydrogels, the linear PDADMAC chains are uncrosslinked and hydrophilic in the hydrogel network, which are interpenetrated into the PDEA network. No chemical bonding exists between the two components, and each component may keep its own property. The phase behavior is controlled by the thermosensitive component as that of PDEA. Therefore, the hydrophilic/hydrophobic balance in the PDEA chains determines the LCST of the semi-IPN hydrogels.

However, during the process of temperature increasing, the value of reduction in the ESR of the hydrogels is different. When the external temperature is increased from 20 to 40 °C, semi-IPN4 has the largest change in the ESR ($\Delta ESR = ESR_{20\,^\circ C} - ESR_{40\,^\circ C}$) which is about 70.98, while the corresponding changes in the ESR of semi-IPN3, semi-IPN2, semi-IPN1 and PDEA are around 63.60, 44.37, 36.73, 12.08, respectively. It suggests that the capability of the temperature of stimulating hydrogels is enhanced when the content of PDADMAC in the hydrogels increases. The phenomena result from two factors. Firstly, the pores tend to larger with the increasing con-

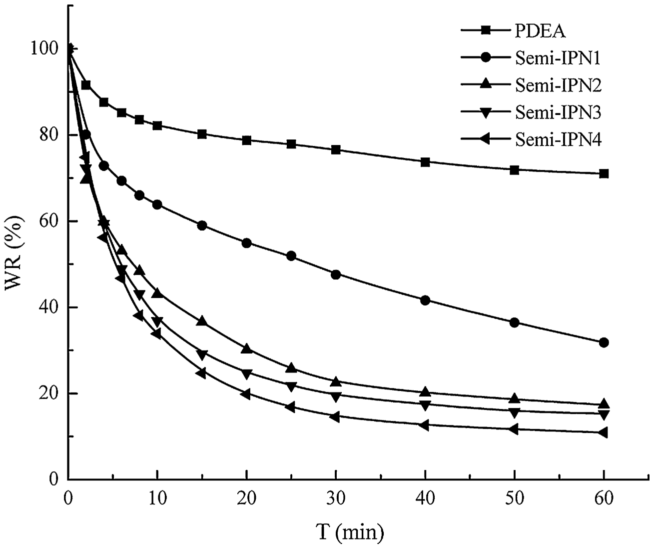


**Fig. 5.** Deswelling kinetics of the hydrogels in double distilled water at 50 °C as measured from an equilibrium swelling state at 20 °C.

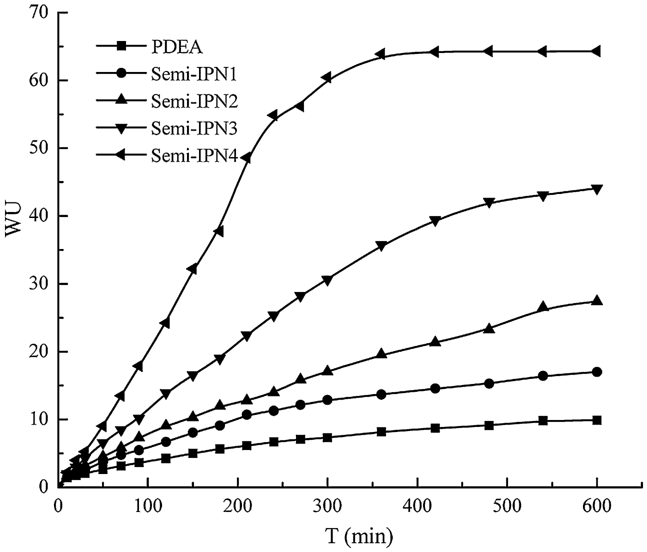


**Fig. 6.** Swelling kinetics of the hydrogels in double distilled water at 20 °C.

tent of PDADMAC. Secondly, the quaternary ammonium groups in the side chains of PDADMAC improve the hydrophilicity of the network. So the introduced PDADMAC chains within PDEA network would enhance the temperature-induced deswelling capability. The large change of the ESR is especially beneficial to improve the efficiencies of applications in drug delivery, concentration and separation process.

### 3.6. Deswelling kinetics of the hydrogels

The response rate of the thermosensitive hydrogel is one of the most important factors and in particular, high rate is needed in many applications. The deswelling kinetics of the hydrogels from the equilibrated swollen state at 20 °C (below $T_{tr}$) to 50 °C (above $T_{tr}$) is shown in Fig. 5. The data illustrate that the deswelling rate of the hydrogel samples is obviously dependent on the feed ratio, and the semi-IPN hydrogels have a faster deswelling rate and lose more water to the external temperature change than PDEA hydrogel within the same time. PDEA hydrogel loses only 21.29% water within 20 min, while semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 lose about 36.18%, 56.99%, 63.12% and 66.16% water within 10 min, respectively.

The deswelling process is complicated because many factors influence and control the deswelling rate. When the PDEA hydrogel is immersed into hot water at 50 °C, the surface region of the hydrogel would be affected firstly and the hydrophobic interactions among the hydrophobic groups in the surface region become stronger, which results in a rapid shrinkage of the surface and a dense skin layer. Once this skin layer is formed, the free water molecules in the hydrogel are prevented from diffusing out, which results in the slow response rate [9,26]. However, the introduction of the hydrophilic chains, PDADMAC, could inhibit the formation of the dense skin layer, and the hydrophilic chains act as releasing channels for water molecules when the collapse occurred [12,13]. The more PDADMAC introduced into the hydrogel network, the more water-releasing channels formed, so the water molecules can be diffused out easily. Moreover, the pore of the hydrogel network would also affect the response rate, and the existence of the large and interconnected pore structures would lead to faster response rate [10]. During the deswelling process, heat transfers from the hot water to innermost hydrogel occur rapidly due to existence of the pores, which results in a rapid phase separation throughout the network, and a large amount of the free water can diffuse out quickly. As observed by SEM, the interconnected porous structure is generated in the semi-IPN hydrogel owing to the presence of PDADMAC, and the pore size of the hydrogel networks increases with the increase of PDADMAC content. Therefore, the deswelling rate increases with the increase of the PDADMAC content from PDEA to semi-IPN4. This characteristic could be advantageously used to adjust the desired rate sensitivity of the thermosensitive hydrogel.

### 3.7. Swelling kinetics at 20 °C

Fig. 6 shows the swelling behavior of the dried gels with different composition ratios at 20 °C. The data show that the semi-IPN hydrogels exhibit faster swelling rate than the PDEA hydrogel, and as the content of PDADMAC in the semi-IPN hydrogel increases, the swelling rate of the semi-IPN hydrogels increases. The WU of PDEA hydrogel is about 5.67 within 180 min, about 8.16 within 360 min, while the WU of semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 is about 9.09, 11.95, 19.03 and 37.77 within 180 min, and about 13.69, 19.56, 35.57 and 63.89 within 360 min, respectively. For the semi-IPN hydrogels, due to the existence of PDADMAC, which acts as water-moving channels, water molecules may easily diffuse into the hydrogel network, and the expansion of the polymer chains may easily occur [12]. Moreover, the large and interconnected pore structure of the hydrogel also plays an important role and leads to a faster swelling rate, because they could make the water molecules transfer easily between the hydrogel network and the external aqueous phase. During the swelling process, the interconnected and large pore structure of the semi-IPN hydrogel begins to recover gradually, which could bring about the acceleration of water absorption. As mentioned above, the freezing water of the hydrogels increases from PDEA to semi-IPN4 hydrogel. Because the diffusion of the freezing water is easy, the swelling rate would be affected, which is in agree with DSC measurement [27]. Therefore, the swelling rate is improved with the increase of PDADMAC content due to excellent hydrophilicity and highly porous network. The ESRs of PDEA, semi-IPN1, semi-IPN2, semi-IPN3 and semi-IPN4 are 12.63, 22.10, 30.17, 45.51 and 64.31, respectively. It is also noticed that the ESRs of different compositions in Fig. 6 were lower and not accordance with the ESRs of the same hydrogels immersed in water directly after their preparations in Fig. 4. It may be probably due to the increased physical entanglements which restricted the swelling process after the vacuum desiccation [2].

**Table 3**
Kinetic exponents, *n*, and characteristic constant, *k*, of the hydrogels.

| | Sample | | | | |
|---|---|---|---|---|---|
| | PDEA | Semi-IPN1 | Semi-IPN2 | Semi-IPN3 | Semi-IPN4 |
| $n$ | 0.515 | 0.668 | 0.704 | 0.821 | 1.010 |
| $k \times 10^2$ | 2.991 | 1.281 | 1.000 | 0.592 | 0.296 |
| $R^2$ | 0.995 | 0.996 | 0.998 | 0.998 | 0.997 |

The following three steps are proposed to occur in succession during swelling of a dried gel in water [32]: (1) water molecules diffuse into the polymer network; (2) the hydrated polymer chains relax and (3) the polymer network expands into the surrounding liquid.

To obtain a more quantitative understanding of the nature of the transport kinetic in the hydrogels, the swelling ratio is analyzed as a function of the time for $0 \leq M_t/M_\infty \leq 0.6$ [33]. The data were fitted to the following equation:

$$\frac{M_t}{M_\infty} = kt^n \tag{9}$$

where $M_t$ and $M_\infty$ are the weight of water absorbed by the hydrogel at time $t$ and at the equilibrium swollen state, respectively. $k$ is a characteristic constant related to the structure of the hydrogel network, and n is a swelling exponent. The $n$ and $k$ would be calculated from the slope and intercept of the plot of $\ln(M_t/M_\infty)$ against $\ln t$, respectively. The value of n can indicate the rate determining step of the swelling mechanism. There are three models, which describe the diverse range of responses of hydrophilic polymer networks to the presence of water. These models are based on the relative rates of penetrant diffusion and polymer chain relaxation [34]: (a) Fickian diffusion ($n = 0.5$), also known as Case I diffusion, occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains. (b) Case II transport ($n = 1$) arises when the rate of diffusion is greater than the rate of the relaxation of the polymer chains. The main feature of this second limiting model is the establishment of a sharp boundary between the glassy core and the swollen shell, which advances at a constant velocity. (c) Non-Fickian or anomalous diffusion ($0.5 < n < 1$) occurs when the rates of diffusion and polymer relaxation are comparable and is connected with the transition region between the two limiting cases of Case I and Case II. The corresponding values for $k$ and $n$ of the hydrogel are listed in Table 3. It could be found the swelling exponent, n, for the hydrogels are between 0.515 and 1.010. These results show that the swelling mechanism would be transformed from Fickian diffusion to Case II transport. In other words, the PDADMAC segment in the semi-IPN hydrogels affects the transport model. It is also evident from Table 3 that all the correlation coefficient values are greater than 0.99, and indicating a small estimated standard error and a high precise linear regression equation, and suggesting a best fit to the Fickian model.

### 3.8. Oscillating deswelling–swelling kinetics of the hydrogels

The above results of the deswelling and swelling kinetics studies have shown that the semi-IPN hydrogels exhibit faster deswelling kinetics and better permeability due to the PDADMAC chain incorporated on the PDEA hydrogels. From the point of applications, the oscillating deswelling–swelling properties over a shorter time intervals with the small temperature cycles (e.g. cycled around the physiologic temperature) of the hydrogel are important, which would be stable for potential applicants. So it is necessary to investigate the oscillating deswelling–swelling kinetics in response to the temperature changes around the body temperature [16,35]. Fig. 7 gives the SR changes of the hydrogels equilibrated at 25 °C in predetermined period cycles between 25 and 40 °C. The data show that all the hydrogels exhibit a consecutive reduction in the magnitude of SR due to their relatively slow swelling rate when compared with their shrinking rate. Compared to PDEA, the semi-IPN hydrogels exhibit much rapid, sharper and larger magnitude deswelling–swelling changes. The magnitude of the oscillating deswelling–swelling increases with the increase of PDADMAC content, and the most rapid and largest magnitude of the oscillating deswelling–swelling is achieved with semi-IPN4 hydrogels. These reasons are that the hydrophilicity of hydrogel could be improved, and the interconnected and large pores could also be enlarged because of the presence of the PDADMAC segment. Therefore, the more the difference of swelling ratios between deswelling and swelling of the semi-IPN hydrogel, the better thermosensitivity is.

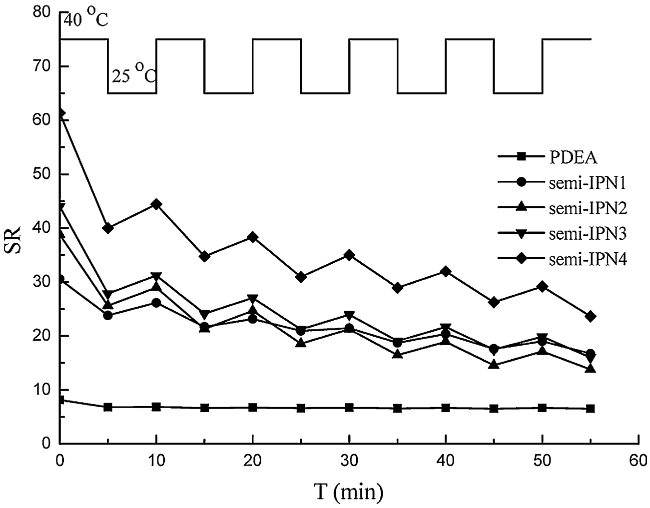


**Fig. 7.** Oscillatory deswelling–swelling kinetics of the PDEA and semi-IPN hydrogels over 10 min temperature cycles in distilled water between 25 and 40 °C.

The slower and smaller magnitude of the oscillatory action of PDEA would limit its potential applications in such areas like the on–off switches for controlled drug release [16]. This faster and larger magnitude of oscillating responses from semi-IPN hydrogels may be advantageous for practical applications in many fields such as bioengineering and biotechnology because faster response kinetics of the oscillating deswelling–swelling property of hydrogels to small temperature cycles (e.g. cycled around the physiological temperature) should be useful.

### 3.9. pH dependence of the semi-IPN hydrogels

It is known that polyampholytes contain both anionic and cationic groups. When polyampholytes are anion-rich or cation-rich, they behave like polyelectrolytes. PDADMAC is a kind of natural polyampholyte, which has many tetra-ammonium groups in its molecular chain. The dissociation degree of tetra-ammonium group is closely related to the pH value of the medium. To investigate the influence of pH value of the medium on the swelling ratios of the hydrogels, the pH range was selected from 2.2 to 9.2 in this study, and the ionic strong was fixed to 0.1 M to diminish the influence of ionic strength on the swelling. As shown in Fig. 8, it can be found that these swelling curves exhibited a sharp transition at certain pH value. As pH exceeded this value, the ESR increases and then levels off. A physical adsorption of $OH^-$ at a water/hydrophobic interface is likely to occur in semi-IPN hydrogel in the high pH media [36,37]. The semi-IPN hydrogel collapse occurred in strong acidic solution via the hydrophobic interaction. However, the aggregation because of the hydrophobic interaction may be disassembled upon the $OH^-$ binding to the hydrophobic chains when the pH of solution increases. So the semi-IPN hydro-

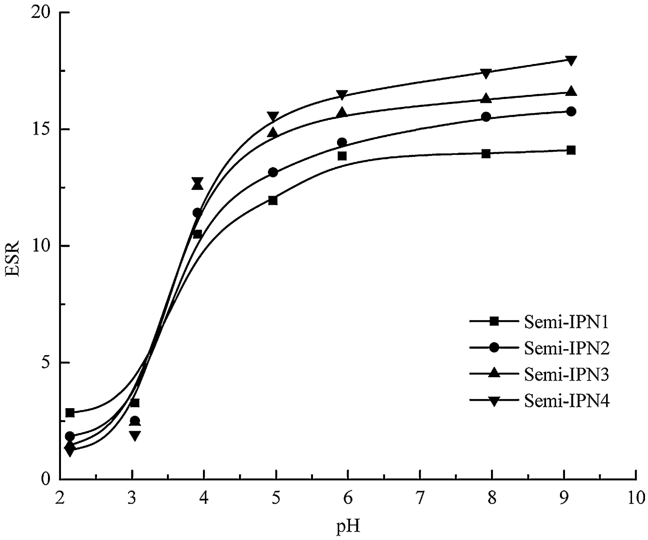


**Fig. 8.** pH dependence of the ESR of the semi-IPN hydrogels ($T = 18\,^{\circ}\mathrm{C}$, $I = 0.1$ M).

gels exhibit the lowest swelling ratio in an acidic medium, and the ESR increases with the increasing pH of the solution.

Moreover, the ESR of the semi-IPN hydrogels in pH solutions decreases compared with the values measured in water. This well-known phenomenon commonly observed in the swelling of ionizable hydrogels is often attributed to the charge screening effect of the addition ions.

## 4. Conclusions

A series of thermo- and pH-sensitive semi-IPN hydrogels composed of PDADMAC and PDEA were synthesized from DEA via free-radical polymerization in the presence of crosslinker in PDADMAC aqueous solution. Owing to the introduction of PDADMAC component, the interconnected porous structure is generated, and the state of water and the $T_{\mathrm{tr}}$ for the hydrogels are also affected. The larger ESR of the PDADMAC/PDEA semi-IPN hydrogels was attributed to the synergistic effect of the hydrophilicity of the PDADMAC chains and the interconnected porous morphology at temperatures below LCST. Moreover, the synergistic effect would also influence the deswelling and swelling kinetics, namely, the different temperature response rates of the semi-IPN hydrogels can be prepared by modifying the proportion of PDADMAC to DEA. The oscillating deswelling–swelling behavior of the semi-IPN hydrogels upon temperature changes around $T_{\mathrm{tr}}$ depends on the PDADMAC content. In addition, due to the existence of ionic groups in the chains of PDADMAC, the semi-IPN hydrogels also possess pH-sensitivity. Therefore, the introduction of PDADMAC component with IPN technology could improve the thermo- and pH-sensitive behavior of the semi-IPN hydrogels, which could be expected to be useful for biomedical and biotechnology fields.

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