

EFFECT OF MOLECULAR WEIGHT OF PEO ON THE STRUCTURE AND PROPERTIES OF PDMAEMA/PEO HYDROGELS

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Abstract A new kind of binary hydrogels composed of poly(dimethylaminoethylmethacrylate) (PDMAEMA) and poly(ethylene oxide) (PEO) with varying weight average molecular weights ($\bar{M}_w = 5 \times 10^4$, 1×10^5 and 2.5×10^6) were prepared by γ -irradiation technology. The properties of PDMAEMA/PEO hydrogels obtained were evaluated in terms of gel fraction, gel strength, thermal characterization and swelling behavior. The gel strength and swelling degree of the hydrogels could be improved obviously after adding PEO into the PDMAEMA system, while the degree of improvement decreased with increasing $\bar{M}_w$ of PEO. The temperature sensitivity of PDMAEMA/PEO was retained only in the sample with PEO of $\bar{M}_w = 5 \times 10^4$, and the pH sensitivity was retained in samples with PEO of $\bar{M}_w = 5 \times 10^4$ and 1×10^5 . When DMAEMA/PEO mixtures containing PEO of $\bar{M}_w = 5 \times 10^4$ were irradiated, the main reaction could be the cross-linking of DMAEMA, and the linear PEO molecular chains could penetrate into the cross-linked network of PDMAEMA. With increasing $\bar{M}_w$ of PEO, some side reactions were induced, such as grafting of DMAEMA onto PEO molecules, the scission or cross-linking of PEO.

Keywords: Poly(dimethylaminoethylmethacrylate); Poly(ethylene oxide); Molecular weight; Binary hydrogels; Irradiation.

INTRODUCTION

The environmental stimuli-sensitive hydrogels have attracted obvious attention because of their applications in biomedical and biotechnology^[1, 2]. DMAEMA has aliphatic tertiary amino groups, and after polymerization and cross-linking DMAEMA forms a kind of typical stimuli-responsive hydrogels exhibiting a combined temperature and pH sensitivity, but their mechanical and swelling properties need to be improved further^[3, 4]. Modification of the hydrogels by blending, forming IPNs or semi-IPNs has been a subject of fundamental and practical importance^[5].

In a previous work, three semi-IPNs hydrogels composed of 80:20, 90:10 and 95:5 weight ratios of DMAEMA to PEO ($\bar{M}_w = 5 \times 10^4$) were synthesized by γ -irradiation and their environmental responsiveness were investigated^[6]. The results showed that the temperature and pH sensitivity of the semi-IPNs hydrogels were retained only in the samples with 95:5 weight ratio of DMAEMA to PEO.

In this study, PEO with different $\bar{M}_w$ was incorporated into PDMAEMA hydrogels by radiation technique. The influence of $\bar{M}_w$ of PEO on the structure and properties of the prepared hydrogels were investigated.

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EXPERIMENTAL

Materials

DMAEMA was purchased from Acros and purified by vacuum distillation prior to use. The sample PEO5 ($\bar{M}_w = 5 \times 10^4$) was synthesized by anionic polymerization in this lab^[6]. Anhydrous dimethylsulphoxide (DMSO) was used as the solvent and potassium tert-butoxide as the initiator. Samples PEO10 ($\bar{M}_w = 1 \times 10^5$) and PEO250 ($\bar{M}_w = 2.5 \times 10^6$) were purchased from Acros and Shanghai Liansheng Chemical Plant. The $\bar{M}_w$ of PEO obtained was measured by gel permeation chromatography (GPC) using Stryragel columns (Waters), with tetrahydrofuran as the eluent and polystyrene as standard sample, respectively. The other reagents were used without further purification.

Preparation of PDMAEMA/PEO Hydrogels

DMAEMA and PEO were dissolved in distilled water by gentle stirring for about 20 h to form homogeneous solutions. The total content of DMAEMA and PEO in aqueous solutions was 30 wt%, and the weight ratio of DMAEMA to PEO was 95:5. The content of cross-linking agent, *N,N'*-methylene-bisacrylamide (Bis) was 1 wt% of the total weight of DMAEMA and PEO in feed solutions. Three kinds of hydrogel, PDMAEMA/PEO250, PDMAEMA/PEO10 and PDMAEMA/PEO5 were denoted as A, B and C, respectively.

Oxygen in the feed solutions prepared was removed by bubbling high purity nitrogen for 15 min. Then the samples were sealed and irradiated by γ -rays from a ^{60}Co source (7.4×10^{13} Bq) in Peking University at room temperature with a dose rate of 100 Gy/min. The dose rate was determined by Fricke dosimetry ($G_{\text{Fe}^{3+}} = 15.5$ molecules per 100 eV). After irradiation the gels obtained were taken out of the irradiation field and washed with distilled water for 16 h and then were dried in a vacuum oven at about 40°C to constant weight.

This method is a typical way to prepare semi-IPNs. In above conditions DMAEMA in aqueous solutions was polymerized and cross-linked by 20 kGy γ -irradiation, while PEO still remains in the linear structure which penetrates into the cross-linked network of PDMAEMA to form semi-IPN^[6]. When the M_w of PEO was high enough, some new phenomena appeared. So the products obtained by this way are generally called as the binary hydrogels here.

Gel Fraction

The gel fraction was determined gravimetrically and calculated by the ratio of the dried gel weights after and before extraction.

Compression Strength Test

The gel strength was measured by compressing the samples between two parallel plates with constant compressive stress (a weight of 50 g on the upper plate). This simple equipment was made in our lab^[7]. The gel was cut into cylindrical test piece with 10 mm diameter and 5 mm height. The compression ratio (*CR*) of the hydrogel was calculated as

$$CR (\%) = h_2/h_1 \times 100 \quad (1)$$

where h_1 and h_2 are the height of hydrogels before and after compression, respectively.

Swelling Behavior

The dried cylindrical gels were weighed and immersed in distilled water. The samples were swollen to equilibration at different temperature. The equilibration degree of swelling (*EDS*) was calculated from the following equation

$$EDS = m_t/m_o \quad (2)$$

where m_o is the weight of dry gel and m_t is the weight of swollen gel at equilibration.

Thermal Analyses

The melting points and melting enthalpies of PEO and binary PDMAEMA/PEO dry gels were determined by a differential scanning calorimeter (DSC131, SETARAM, France), equipped with a refrigerator cooling system under nitrogen atmosphere at a heating rate of 1 K/min. Thermal stability of the samples was carried out with a thermogravimetric analyzer (Universal V2.6D TA Instrument) by heating the samples from room temperature to 600°C at a heating rate of 10 K/min under a nitrogen flow.

RESULTS AND DISCUSSION

Gel Fraction

The relation between gel fraction and absorbed dose of the feed solution is presented in Fig. 1. The results show that the gel fraction of all the three kinds of PDMAEMA/PEO hydrogels increases with the absorbed dose, but the gelation dose (the estimated values are 1.0, 2.5 and 4.0 kGy) is different, the higher the M_w of PEO, the lower is the gelation dose. The gel fraction levels off at approximately the same value (75%) for these three hydrogels.

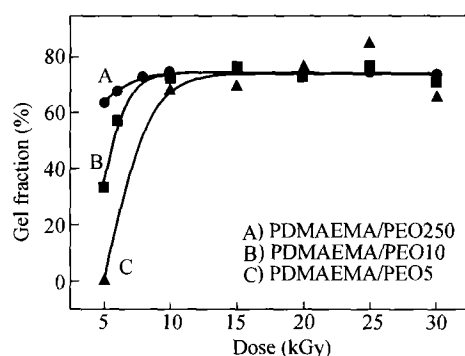


Fig. 1 Gel fraction of PDMAEMA/PEO hydrogels as a function of absorbed dose

Gel Strength

The gel strength of PDMAEMA/PEO hydrogels was measured by compression method. Figure 2 shows the effect of absorbed dose on the compression strength of the samples. PDMAEMA/PEO hydrogels have quite good elasticity, which shrink under the compressive stress and recover to original shape after removing the stress, while PDMAEMA gels obtained by using the same synthesized conditions can not recover after the same operation. The compression strengths of all the three kinds of PDMAEMA/PEO hydrogels have been improved obviously and attain their maxima at about 15 kGy. Figure 2 also shows that compression strength decreases with increasing the M_w of PEO. This result indicates that M_w of PEO has obvious influence on the gel strength of PDMAEMA/PEO hydrogels.

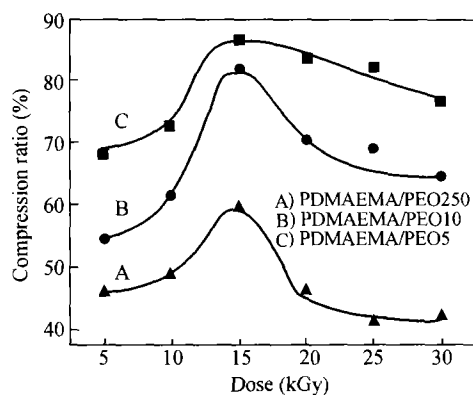


Fig. 2 Compression strength of PDMAEMA/PEO hydrogels as a function of absorbed dose

Thermal Characterization

Table 1 shows the results of DSC measurements for pure PEO and PDMAEMA/PEO hydrogels with different $\overline{M}_w$ of PEO. It can be seen that there are no apparent differences in melting point (T_m) and enthalpy (ΔH_m) of PEO with different $\overline{M}_w$; the former is to 60°C and the latter is close to 186 J/g, respectively. The T_m for these binary hydrogels are nearly the same (~60°C) while the ΔH_m of the obtained binary samples decrease obviously with the increase of the $\overline{M}_w$ of PEO. This result indicates that PEO with higher $\overline{M}_w$ influences the thermal behavior of PDMAEMA/PEO dry gel more obviously.

Table 1. Melting point (T_m) and enthalpy (ΔH_m) of PEO and PDMAEMA/PEO dry gels

Sample	PEO5	PEO10	PEO250	PDMAEMA/PEO5	PDMAEMA/PEO10	PDMAEMA/PEO250
PEO $\overline{M}_w$	5×10^4	1×10^5	2.5×10^6	5×10^4	1×10^5	2.5×10^6
T_m (°C)	60.8	60.34	59.1	60.2	59.8	59.2
ΔH_m (J/g)	189.83	182.6	185.42	14.52	13.16	4.40

The thermal stability of PEO, PDMAEMA and the binary gels were measured by using TGA (Fig. 3). PDMAEMA and the binary gels show mainly two-step thermograms after omitting the peak of bound water. The onset decomposition temperature of the binary gels is lower than that of pure PDMAEMA and PEO, and decreases with increasing the $\overline{M}_w$ of PEO. The activation energies (kJ/mol) calculated from curves of the first-step thermogram are 86.6 (PDMAEMA), 31.49(C), 5.86(B) and 5.32(A), respectively. The result indicates that the thermal stability of binary gels is not good compared with PDMAEMA or PEO, but the small decrease will not affect their practical applications in biotechnology. The inset in Fig. 3 shows that the $\overline{M}_w$ of PEO has a little effect on the thermal stability of pure PEO.

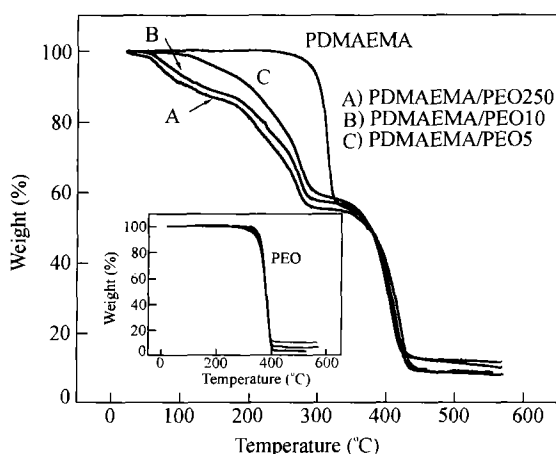


Fig. 3 TGA thermograms of PDMAEMA/PEO and PDMAEMA dry gels

Inset is TGA results of PEO with different $\overline{M}_w$ (from top to bottom: PEO250, PEO10, PEO5).

Temperature Sensitivity

The equilibrium degree of swelling (EDS) of PDMAEMA/PEO hydrogels in aqueous solutions at different temperatures measured by gravimetric method is shown in Fig. 4(a). It can be seen that the EDS decreases with increasing the $\overline{M}_w$ of PEO in the experimental temperature range. However only the PDMAEMA/PEO5 hydrogel (curve C) shows obviously temperature sensitivity, and the lower critical solution temperature (LCST) is about 30°C while the temperature sensitivity of PDMAEMA/PEO10 (curve B) and PDMAEMA/PEO250 (curve A) hydrogels disappear. Similar results are exhibited in DSC measurements (Fig. 4b). The LCST of PDMAEMA/PEO5 hydrogels measured by DSC is slightly higher.

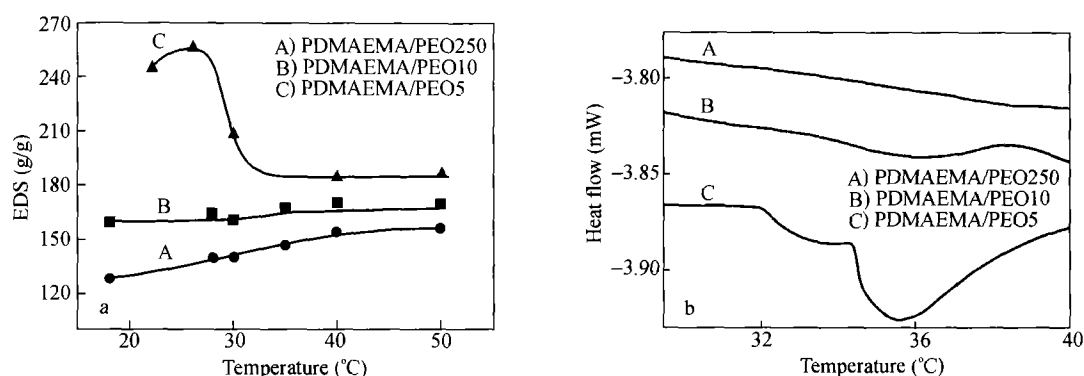


Fig. 4 (a) Change of EDS of PDMAEMA/PEO hydrogels with temperature; (b) DSC curves of PDMAEMA/PEO hydrogels

pH Sensitivity

The variation of EDS of PDMAEMA/PEO hydrogels in buffer solutions with pH at a fixed ionic strength (1.96×10^{-2} mol/L) is shown in Fig. 5, from which it can be seen that PDMAEMA/PEO5 and PDMAEMA/PEO10 hydrogels have pH sensitivity while PDMAEMA/PEO250 hydrogel is less sensitive to pH. Conversely, the EDS of PDMAEMA/PEO250 hydrogel has the tendency of increasing with pH.

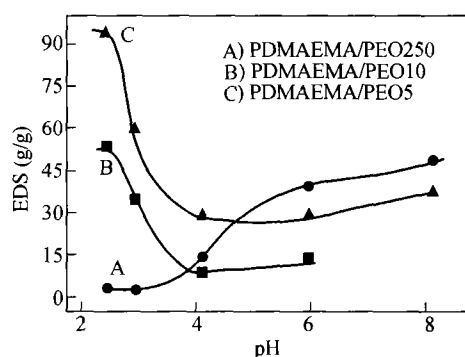


Fig. 5 Effect of pH on the EDS of PDMAEMA/PEO hydrogels (Ionic strength: 1.96×10^{-2} mol/L)

In the process of forming PDMAEMA/PEO hydrogels, some side reactions might be induced by irradiation^[8].

(1) Grafting: DMAEMA monomers may graft on PEO molecules to form branched PEO-g-PDMAEMA molecules.

(2) Degradation: PEO molecules may degrade by γ -irradiation, and carbonyl groups are the main products of the chain scission of PEO^[9].

(3) Cross-linking: PEO molecules may be crosslinked by γ -irradiation. The higher the molecular weight of PEO, the easier is the cross-linking of PEO molecules^[10].

So when DMAEMA/PEO mixture containing PEO of low $\overline{M}_w$ (5×10^4) was irradiated, the main reaction is the cross-linking of DMAEMA, and the linear PEO molecular chains penetrate into the cross-linked network of PDMAEMA. With increasing $\overline{M}_w$ of PEO, the above side reactions could be induced inevitably in addition to the cross-linking reaction of DMAEMA.

CONCLUSION

A new kind of binary hydrogels composed of 95:5 weight ratio of DMAEMA to PEO ($\overline{M}_w = 5 \times 10^4$, 1×10^5 , 2.5×10^6) in feed solutions were synthesized separately by γ -irradiation. The $\overline{M}_w$ of PEO has obvious influence on the formation, properties and structure of PDMAEMA/PEO binary hydrogels. When DMAEMA/PEO ($\overline{M}_w = 5 \times 10^4$) mixture was irradiated, the main reaction is the cross-linking of DMAEMA, and the linear PEO molecular chains could penetrate into the cross-linked network of PDMAEMA, then PDMAEMA/PEO binary hydrogels with high strength, temperature and pH sensitivity could be prepared. With high $\overline{M}_w$ of PEO (2.5×10^6), some side reactions are induced, such as grafting of DMAEMA on PEO molecules, the scission or cross-linking of PEO, then the gel strength of prepared PDMAEMA/PEO binary hydrogels decreases, and temperature and pH sensitivity disappear.

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