

Radiation Synthesis and Environmental Responsiveness of Semi-Interpenetrating Polymer Networks Composed of Poly(dimethyl-aminoethyl methacrylate) and Poly(ethylene oxide)

Zhugen Liu,¹ Min Yi,¹ Maolin Zhai,¹ Hongfei Ha,¹ Zhifu Luo,² Xueqing Xiang²

¹College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

²Institute of Chinese Atomic Energy, Beijing 102413, China

Received 24 April 2003; accepted 12 November 2003

ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs) composed of poly(dimethyl-aminoethyl methacrylate) (PDMAEMA) and poly(ethylene oxide) (PEO) were synthesized by γ -radiation; three semi-IPNs with 80 : 20, 90 : 10, and 95 : 5 weight ratios of DMAEMA/PEO were obtained by use of this technique. The gel-dose curves showed that the hydrogels were characterized by a structure typical of semi-IPNs and the results of elemental analysis supported this point. The temperature-induced phase transition of semi-IPNs with the composition of 95 : 5 was still retained, with the lower critical solution temperature of

PDMAEMA shifting from 40 to 27°C. The temperature sensitivity of the other two semi-IPNs gradually disappeared. The pH sensitivity of three semi-IPNs was still retained but the pH shifted slightly to lower values with increasing PEO content in the semi-IPNs. The effect of PEO content in semi-IPNs on their environmental responsiveness was discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2995–3001, 2004

Key words: radiation; semi-interpenetrating polymer networks (semi-IPN); hydrogels; swelling; thermal properties

INTRODUCTION

Some hydrogels may undergo reversible and discontinuous volume changes in response to changes in environmental conditions, such as temperature, pH, salt concentration, or solvent composition. This kind of hydrogels has attracted much attention because of their applications in biomedicine and biotechnology.^{1–3}

The radiation method of synthesizing hydrogels has been determined to be very useful in preparing hydrogels for medical application where even a small contamination is undesirable. The radiation polymerization and crosslinking can be carried out at room temperature (or even lower) and do not require the addition of any extra materials.⁴

Poly(dimethyl-aminoethyl methacrylate) (PDMAEMA), which has aliphatic tertiary amino groups, is a typical stimuli-responsive hydrogel that exhibits a combined temperature and pH sensitivity. Synthesis and characteristics of PDMAEMA were previously investigated,^{5,6} although its mechanical and swelling properties need further modification. Modification of hydrogels in the form of interpenetrating polymer

networks (IPNs) or semi-IPNs has been a subject of fundamental and practical importance.^{7–9}

In this study semi-IPNs composed of DMAEMA and PEO were synthesized, in the presence of a crosslinker, by radiation technology. PEO was chosen as the linear polymer in the semi-IPNs mainly because of its excellent biocompatibility, good swelling characteristics in aqueous solution, and cheaper cost compared with those of DMAEMA.¹⁰ The effect of PEO content in semi-IPNs on their stimuli responsiveness was investigated.

EXPERIMENTAL

Materials

DMAEMA was purchased from Acros Organics (Morris Plains, NJ) and purified by vacuum distillation before use. In this study, PEO was synthesized by the anionic polymerization method,¹¹ in which anhydrous dimethylsulfoxide (DMSO) was used as solvent and potassium *tert*-butoxide as initiator. The number- and weight-average molecular weights and polydispersity of PEO, measured by gel permeation chromatography (GPC) using Waters Styragel columns (Waters Chromatography Division/Millipore, Milford, MA) and tetrahydrofuran as the solvent, were $\bar{M}_n = 1.64 \times 10^4$, $\bar{M}_w = 2.60 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.58$, respectively. The other reagents were used without further purification.

Correspondence to: M.-L. Zhai (mlzhai@chem.pku.edu.cn).

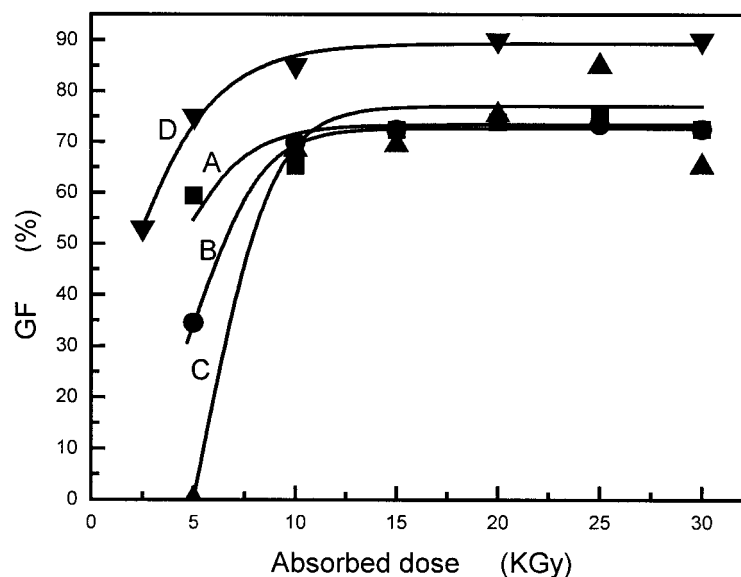


Figure 1 Gel fraction as a function of absorbed dose for samples A, B, C, and D (PDMAEMA). Dose rate: 100 Gy/min; Bis content: 1 wt %.

Preparation of semi-IPNs

Aqueous solutions of DMAEMA monomer and PEO were prepared in distilled water by gently stirring. The dissolution at room temperature took about 20 h to obtain homogeneous solution. The total content of DMAEMA and PEO in aqueous solution was maintained at 30 wt %. The content of the crosslinking agent *N,N'*-methylene-bisacrylamide (Bis) was 1 wt % of the total weight of DMAEMA and PEO in the feed solution. Three samples were prepared with 80 : 20, 90 : 10, and 95 : 5 weight ratios of DMAEMA : PEO, denoted as A, B, and C, respectively.

The prepared feed solutions were degassed by bubbling high-purity nitrogen for 15 min and sealed in glass tubes. The samples were irradiated by γ -rays from a ^{60}Co source (Peking University) at room temperature at a dose rate of 100 Gy/min. After irradiation the gels obtained were removed from the irradiation field and washed with distilled water for 16 h, after which they were dried in a vacuum oven at about 40°C to a constant weight.

Gel fraction

Gel fractions of semi-IPNs were determined gravimetrically and calculated by the ratio of the dried gel mass after and before extraction.

Swelling ratio measurement

The dried cylindrical gels were weighed and immersed in distilled water. The samples were swollen to equilibration at different temperatures. The equilibration swelling ratio (ESR) was calculated from the following equation:

$$\text{ESR} = m_t/m_0$$

where m_0 is the initial mass of the dry gel and m_t is the mass of the swollen gel at time t .

Elemental analysis

The obtained semi-IPNs samples were washed in distilled water by gently stirring at room temperature for

TABLE I
Elemental Analysis of Obtained Hydrogels

Sample designation	Content of elements (%)					
	Calculated values			Experimental values		
	N	C	H	N	C	H
PDMAEMA	8.66	59.38	9.90	7.72	52.66	10.24
A	7.12	59.83	9.40	6.22	58.21	9.06
B	8.01	60.48	9.51	6.39	56.26	9.30
C	8.46	60.82	9.53	6.78	56.45	9.27

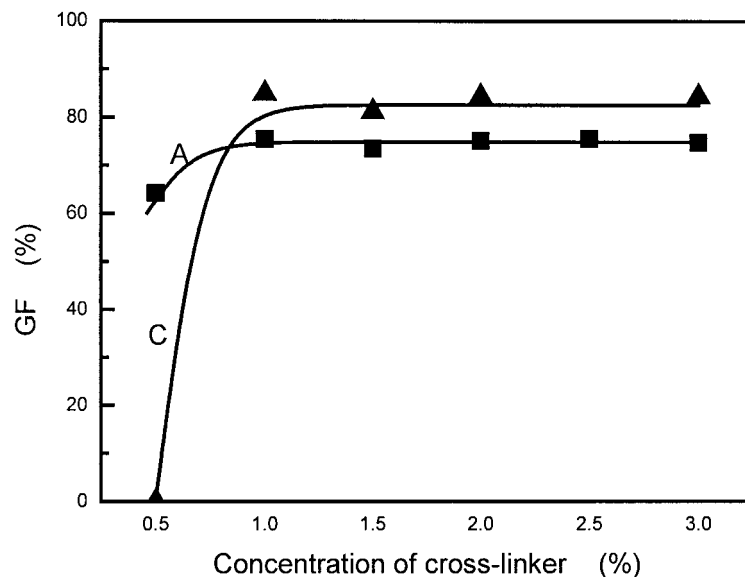


Figure 2 Gel fraction as a function of crosslinker content. Total dose: 25 kGy; dose rate: 100 Gy/min.

48 h to remove the unreacted monomers and homopolymers. The samples were dried completely, kept in liquid nitrogen, and ground immediately.

Compositions of semi-IPNs were measured by elemental analysis (Elementar Vario EL, Germany).

Thermal properties

The thermal properties of semi-IPNs were determined by differential scanning calorimetry (DSC131, Setaram, France) in a refrigerator cooling system under

nitrogen atmosphere at an increasing temperature rate of 1°C/min.

RESULTS AND DISCUSSION

Radiation synthesis of the semi-IPNs

The effect of dose on the gel fraction of DMAEMA/PEO semi-IPNs is shown in Figure 1, from which it can be seen that the gel fraction rapidly increased to 70–80% by irradiation to a dose of 10 kGy, after which it then leveled off.

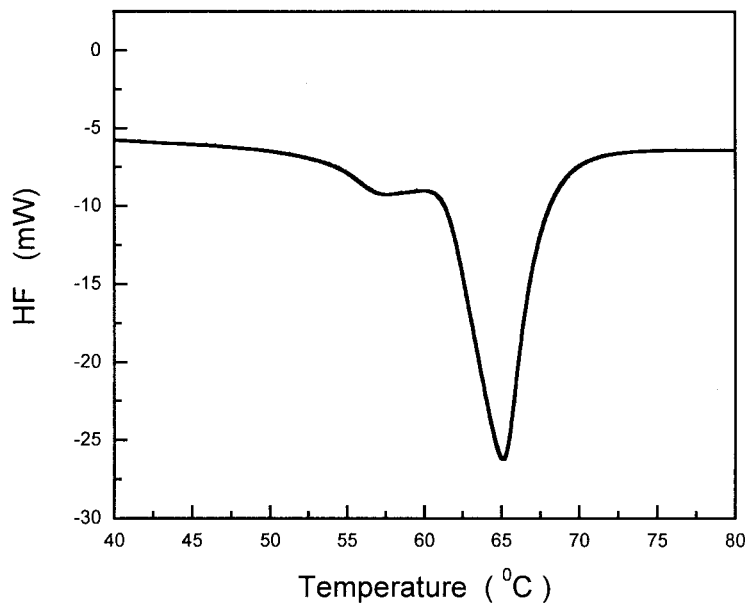


Figure 3 DSC melting endotherm of PEO.

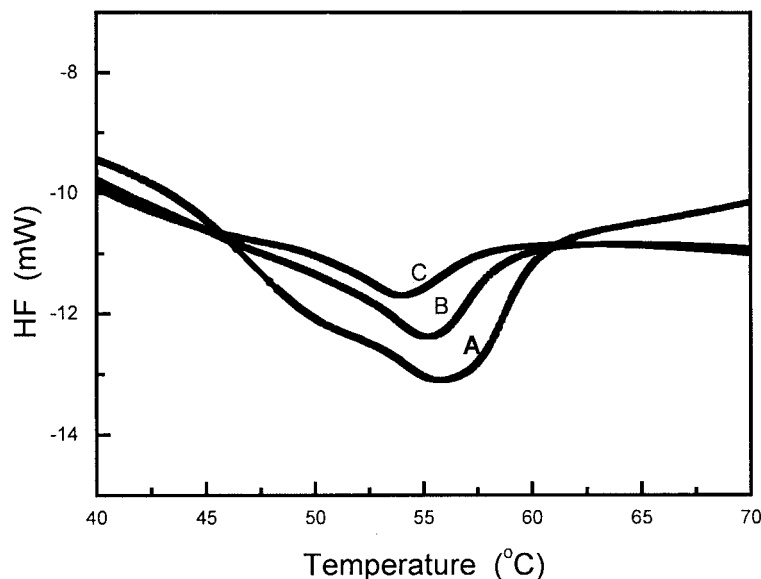


Figure 4 DSC melting endotherms of semi-IPNs.

It was also found that the values of maximum level of gel fraction for the three semi-IPNs were 15–20% lower than that of pure PDMAEMA. This result was consistent with nitrogen content analysis in semi-IPNs (see Table I).

Elemental analysis of three synthesized hydrogels showed that the nitrogen contents of obtained hydrogels were about 20% lower than calculated values. Decrease of the nitrogen content in semi-IPNs after water washing released part of the linear PDMAEMA molecules, and/or the residual monomer was washed out from semi-IPNs because the linear PEO molecules inhibited by steric effect formation of crosslinking structure of PDMAEMA, so it is reasonable to obtain a similar lower gel fraction of semi-IPNs.

It was also found that the change of dose rate within 150 Gy/min had no influence on the gel fraction.

Figure 2 shows that 1 wt % crosslinker of total DMAEMA/PEO weight in feed solution was sufficient to induce polymerization and crosslinking of DMAEMA.

In summary, 25 kGy dose, 100 Gy/min dose rate, and 1 wt % crosslinkers in 30 wt % aqueous solution of PEO and DMAEMA with different ratios constitute the optimum conditions for preparing transparent and elastic hydrogel semi-IPNs.

Structure of synthesized hydrogels

From the gel–dose curves in Figure 1 it can be seen that the crosslinking structure of PDMAEMA was formed at a dose of 25 kGy, although at this dose the molecules of PEO still retained their linear state, and formation of the crosslinking structure for PEO needs

at least 50 kGy, as reported in our study and the study by Yoshii et al.¹²

From the above discussion it can be concluded that the hydrogels synthesized here are typical semi-IPNs, by definition. The nitrogen content analysis suggested this point of view as well.

Thermal characterization

DSC measurements gave the melting thermograms of PEO and semi-IPNs. The thermogram of pure PEO revealed a sharp melting endothermic peak at 65°C (Fig. 3), whereas broader and smaller melting peaks of the semi-IPNs were observed at lower temperatures with decreasing PEO contents (Fig. 4). The same tendency appeared in the values of T_m and ΔH_f (see Table II).

The reason may be that the reorientation of PEO segments in the structure of semi-IPNs was limited and DMAEMA was grafted onto PEO chains, resulting in a further decrease in the crystallinity of the semi-IPNs compared to that of the linear PEO chains. Subsequently, the T_m of PEO in the semi-IPNs was obviously lower than that of the linear PEO. The depression of the melting peak indicated that the or-

TABLE II
 T_m and ΔH_f of PEO Part of Semi-IPNs

Sample	T_m (°C)	ΔH_f (J/g)
A	56.17	10.05
B	55.37	3.84
C	54.0	2.52

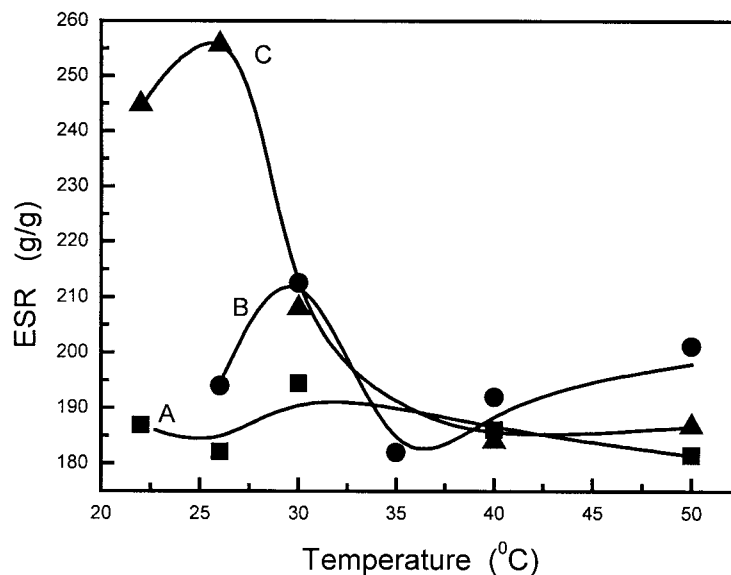


Figure 5 Equilibrium swelling ratios (ESR) of semi-IPNs as a function of temperature. Total dose :25 kGy; dose rate: 100 Gy/min; pH = 5.5.

dered association of linear PEO molecules interpenetrating among the crosslinking networks of PDMAEMA was decreased. These results were in agreement with results reported in some other studies.^{13,14}

Effect of semi-IPN composition on swelling ratio

The effect of PEO content in semi-IPNs on equilibrium swelling ratios (ESR) was studied. From Figure 5 it can be seen that a small amount of PEO (5 wt %) in

semi-IPNs could obviously increase the ESR before the sample’s lower critical solution temperature (LCST; ~ 30°C),¹⁵ but the ESR of semi-IPNs decreased with increasing PEO content in the gel network. Because the PEO linear molecules have high water absorability, when the semi-IPNs contained less PEO the ESR rapidly increased; with increasing PEO content, the cavities among the crosslinking networks of PDMAEMA would be gradually filled by PEO molecules, so the swelling of water molecules into semi-IPNs became difficult.

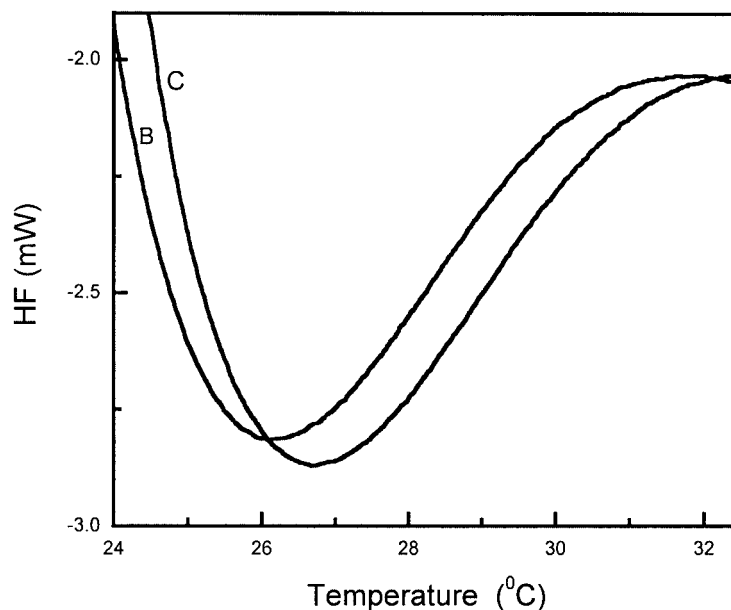


Figure 6 HF as a function of temperature in melting endotherms of wet samples B and C.

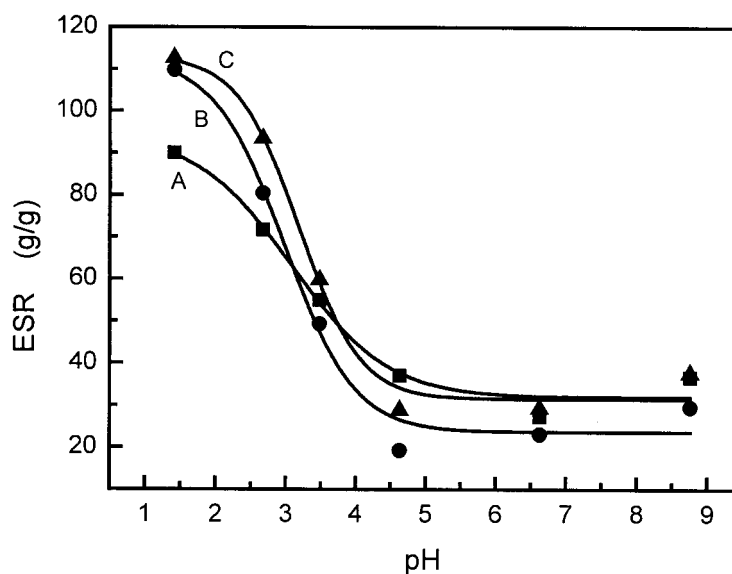


Figure 7 ESR of semi-IPNs as a function of pH at 25°C. Ionic strength: 0.02 mol/L NaCl.

Figure 5 provides additional important information: the temperature-induced phase transition of semi-IPNs with the composition of 95 : 5 was still retained, with the LCST of PDMAEMA shifting to a lower value, from 40 to 27°C.

The temperature sensitivity of the other two samples gradually disappeared. The reason may be attributed to the electronegativity of oxygen atoms in PEO, and the abundance of hydrogen bonds caused the semi-IPNs to lose their thermal reversibility.

DSC measurements for the wet semi-IPN samples A and B provided the respective LCST values (see Fig.

6). These results were consistent with those measured by the swelling method (Fig. 5).

Effect of pH on ESR

ESRs of semi-IPNs in buffer solution, with varying pH values at fixed ionic strength (1.96 E-2 mol/L), are shown in Figure 7, from which it can be observed that all three semi-IPNs have still retained their pH sensitivity.

The PDMAEMA with tertiary amine basic functional groups is a typical pH-sensitive hydrogel. PEO

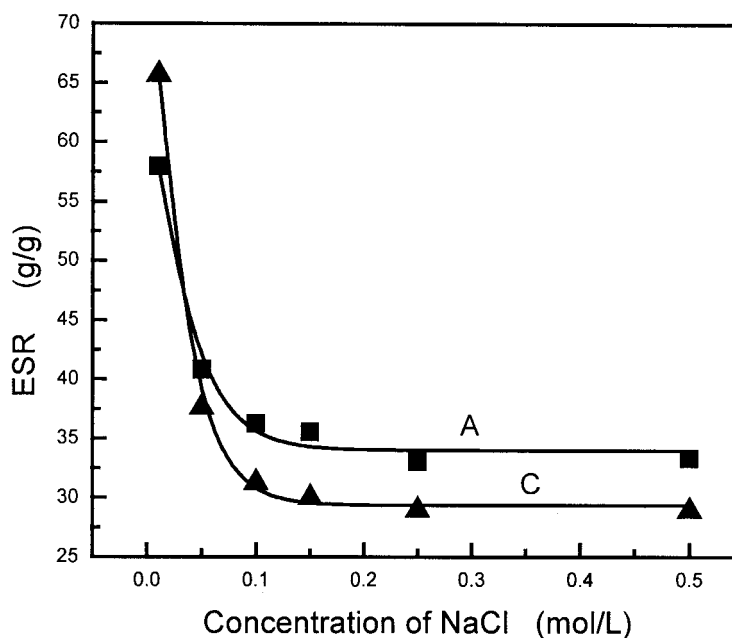


Figure 8 ESR of semi-IPNs as a function of NaCl concentration at pH 5.5.

is a neutral polymer that has no obvious influence on pH sensitivity of semi-IPNs.

Effect of NaCl concentration on swelling behavior

In the swelling experiments the ionic strength of the buffer solution was changed at pH = 5.5. The variation of ESR with NaCl concentration is given in Figure 8.

The results in Figure 8 show that the ESR of the two semi-IPNs decreased sharply with increasing NaCl concentration before the NaCl concentration was 0.1 mol/L. This is because the osmotic pressure inside decreased when the semi-IPNs were in a swollen state, which decreased the degree of swelling of the hydrogels. When the NaCl concentration exceeded 0.2 mol/L, the osmotic pressure would not change.

CONCLUSIONS

Three semi-IPNs, composed of 80 : 20, 90 : 10, and 95 : 5 weight ratios of PDMAEMA : PEO, were synthesized by γ -radiation technology. The optimum preparation conditions, including total dose (25 kGy), dose rate (100 Gy/min), and content of crosslinking agent (1 wt %), were given. Water uptake increased sharply with a small content of PEO (5 wt %) in the semi-IPNs, but the water absorption of the semi-IPNs decreased with increasing ratio of PEO. The temperature-induced phase transition of semi-IPNs with the composition of 95 : 5 was still retained, with the LCST of

PDMAEMA shifting to a lower value, from 40 to 27°C. The temperature sensitivity of other two semi-IPNs disappeared gradually. The pH sensitivity of three semi-IPNs were still retained but the pH shifted slightly to lower with increasing of PEO content in semi-IPNs. The structure of semi-IPNs and effect of PEO on their environmental responsiveness were discussed.

References

- Gehrke, H. S. *Adv Polym Sci* 1993, 110, 80.
- Shibayama, M.; Tanaka, T. *Adv Polym Sci* 1993, 109, 1.
- He, Q.; Sheng, J. *J Funct Polym* 1997, 10, 118.
- Ha, H.-F.; Wu, J.-L. *Radiation Chemistry of Polymer Systems: Principle and Application*; Peking University Press: Beijing, 2002; pp. 124–143.
- Hang, C.; Shik, S.; Jhon, M. *J Polym Sci Part B: Polym Phys* 1997, 35, 595.
- Lu, J.; Yi, M.; Li, J.-Q.; Ha, H.-F. *J Appl Polym Sci* 2001, 80, 3578.
- Bhalerao, V. S.; Varghese, S.; Lete, A. K.; Badiger, V. *Polymer* 1998, 39, 2255.
- Ren, J.; Ha, H.-F. *Eur Polym Mater* 2001, 37, 2413.
- Shin, B. C.; Jhon, M. S.; Lee, H. B.; Yuk, S. H. *Eur Polym Mater* 1998, 34, 171.
- Savas, H.; Güven, O. *Radiat Phys Chem* 2002, 64, 35.
- Bawn, C. E. H.; Ledwith, A.; McFarlane, N. *Polymer* 1969, 10, 653.
- Yoshii, F.; Zhanshan, Y.; Isobe, K.; Shinozaki, K.; Makuuchi, K. *Radiat Phys Chem* 1999, 55, 133.
- Lee, S. J.; Kim, S. S.; Lee, Y. M. *Carbohydr Polym* 2000, 41, 197.
- Ozeki, T.; Yuasa, H.; Kanaya, Y. *J Controlled Release* 1999, 58, 87.
- Lin, N.; Li, J.; Yi, M.; Zhai, M.-L.; Li, J.-Q.; Ha, H.-F. *Radiat Phys Chem* 2001, 61, 69.