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Swelling behaviour of amphiphilic poly(methacryloxyethyl dimethylalkane ammonium bromide) gels in alcohol/water solvent systems*

LI Can-Can (李灿灿),[1,2] ZHAI Mao-Lin (翟茂林),[2,1,†] PENG Jing (彭静),[2] and LI Jiu-Qiang (李久强)[2]

[1]*School of Materials and Engineering, University of Science and Technology Beijing, Beijing 100083, China*
[2]*Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

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Three kinds of amphiphilic PMADAB gels were prepared through radiation-induced polymerization and crosslinking of methacryloxyethyl dimethylalkane ammonium bromide (MADAB) with different alkyl side chains (butyl, octyl and dodecyl). The length of alkyl side chains had significant influence on swelling behavior of the PMADAB gels in alcohol/water solvent. Equilibrium swelling degree (EDS) of PMBDAB (butyl) gel in water was ca. 160 and decreased with increasing alcohol content (x), whereas EDS of PMODAB (octyl) and PMDDDAB (dodecyl) gels showed a convex-upward function of x, i.e., these two gels barely swelled in pure water and swelled with increasing x and then shrank gradually. This phenomenon was explained by the hydrophobic association of long alkyl chains and a cosolvency effect of PMADAB in alcohol and water. The swelling behavior of PMADAB gels in methanol, ethanol and isopropanol were similar, and their EDS are related with the dielectric constant of alcohol solvents. The results suggest that PMADAB gels may be potential absorbents for various kinds of alcohols.

Keywords: Dimethylaminoethyl methacrylate, Amphiphilic gels, Alcohol/water mixed solvents, Swelling behavior

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I. INTRODUCTION

A noteworthy property of gels is their stimuli or environmental response. Gels could swell and shrink depending on solvents, temperature, pH, light, ionic strength and so on, making them useful in many fields, such as sanitary, drug delivery system, separation, micro-actuator, and so on [1–3].

In the mixed solvents, gels generally show continuous volume change upon variation of solvent ratio. However, Tanaka *et al.* [4] found discontinuous volume change, termed as phase transition, for hydrolyzed polyacrylamide gel. Thereafter, reentrant gels were reported, which have two-phase transition from swelling to swelling via shrinking upon changes in methanol concent in water [5]. Poly(N-isopropylacrylamide) gel is a good example of reentrant gel.

On the opposite, gels having the swelling property in aqueous organic solvent were also reported. Hiroki *et al.* [6] found poly(acryloyl-L-proline methyl ester) gel with two swelling phases and two shrinking phases in alcohol/water mixture; the swollen gel undergoes first shrinking, then reswelling and finally a second shrinking on increasing alcohol concentration. Amphiphilic lignin gels [7] were also found to swell in aqueous ethanol solution, in particular 50% (v/v) solution. Similar phenomenon was found by Ikkai *et al.* [8, 9] in poly(acrylic acid) (AA) homopolymer and poly(12-acryloyloxydodecanoic acid-co-acrylic acid) copolymer gels. Equilibrium swelling degree (EDS) of these gels showed a convex-upward function of x (x = vol% of ethanol). That is, the gels swelled with increasing x and then shrank gradually. This phenomenon was explained by hydrophobic association of long alkyl chains of 12-acryloyloxydodecanoic acid (ADA) and a cosolvency effect of PAA in ethanol and water. All these work indicate that it is possible to use gels as absorbent to selectively absorb leaks comprised of water and solvents.

Our group has been focused on studying stimuli-responsive hydrogels for decades by radiation technique [10–20]. Recently [16, 17], we synthesized a series of hydrophobicly modified poly(dimethylaminoethyl methacrylate) (PDMAEMA) gels, i.e., poly(methacryloxyethyl dimethylalkyl ammonium bromide) (PMADAB) gels. The length of alkyl side chains had significant influence on swelling behavior of PMADAB gels. The PMADAB gels with longer alkyl side chains, such as octyl and dodecyl, can hardly swell in water. However, preliminary work found that these gels could absorb organic solvents, especially alcohols. In this article, we report swelling behavior of the gels in water/alcohol solvents system. It is expected that the PMADAB gels can be used to selectively absorb leaks comprised of water and alcohols.

II. EXPERIMENTS

A. Materials

Dimethylaminoethyl methacrylate (DMAEMA, 99% purity), 1-bromobutane (BB, 98% purity), 1-bromooctane (BO, 99% purity) and 1-bromododecane (BD, 98% purity) were provided by Acros and used as supplied. Poly (ethyleneglycol

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† Corresponding author, mlzhai@pku.edu.cn

col dimethacrylate) (PEGDMA, $M_n = 875$) was purchased from Aldrich. Other chemicals for this study were analytic reagents obtained from Beijing Chemicals Company and used as-received.

B. Synthesis of amphiphilic PMADAB gels

Amphiphilic electrolytes, methacryloxyethyl dimethylbutane ammonium bromide ((MBDAB), methacryloxyethyl dimethyloctane ammonium bromide (MODAB) and methacryloxyethyl dimethyldodecane ammonium bromide (MDDAB) were synthesized by quaternization of DMAEMA with BB, BO and BD, respectively, using the same method reported in our previous work [15, 16]. Synthesis route of amphiphilic PMADAB gels (for simplification, n ($= 4, 8$ and 12) is used instead of butyl, octyl and dodecyl in the text) is shown in Fig. 1. The concentrations of monomer and PEGDMA (cross-linker) are 1.0 mol/L and 1.2×10^{-4} mol/L, respectively. The monomer/PEGDMA aqueous solution was poured into glass tube of Φ10 mm, and bubbled with nitrogen for 15 min. The tube was sealed and irradiated to 5 kGy to form the gels at a dose rate of 20 Gy/min at room temperature. The gels were cut into cylinders of ca. 5 mm length and dried in vacuum at 25 °C to constant weight.

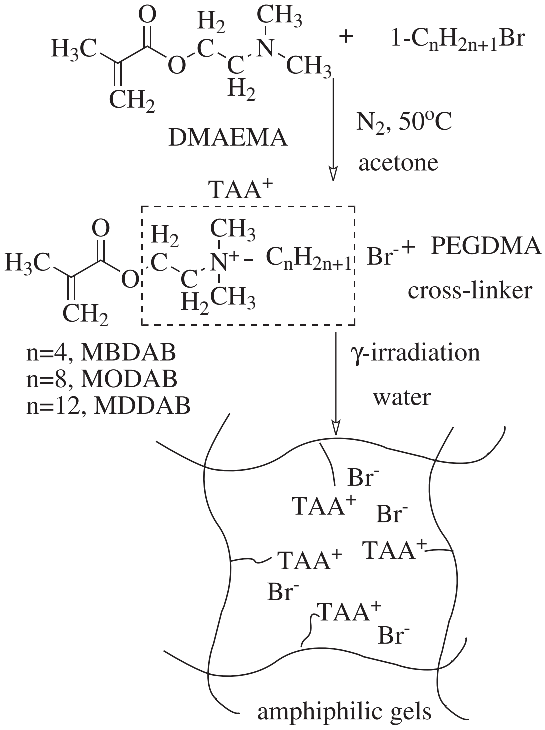

Fig. 1. Synthesis route of amphiphilic gels: PMBDAB (n = 4); PMODAB (n = 8); PMDDAB (n = 12).

TABLE 1. Properties of amphiphilic PMADAB gels synthesized with an absorbed dose of 5 kGy at 20 Gy/min.

Gels	Hydrophobic side chain	G_f (%)	EDS (in water)
PMBDAB (n = 4)	butyl	89.7	160.5
PMODAB (n = 8)	octyl	90.2	2.4
PMDDAB (n = 12)	dodecyl	91.6	0.7

C. Gel fraction

The sol part of the samples was extracted by deionized water (for gels $n \leq 8$) or acetone (for gel $n = 12$) and then dried in vacuum oven at 25 °C to constant weight. Gel fraction (G_f) of the gel was defined as

$$G_f(\%) = W_g/W_0 \times 100, \tag{1}$$

where W_0 and W_g were the weights of dried gel before and after removing sol, respectively.

D. Morphology of amphiphilic PMADAB gels

To maintain the network structure of amphiphilic gels, the swollen gels in water were lyophilized. The cross-sectional morphology of amphiphilic gels in swollen state was observed using Scanning Electron Microscope (SEM) (FEI Quanta 200F).

E. Swelling behavior of amphiphilic PMADAB gels

The dried gels were immersed in alcohol/water solution until swelling equilibrium was reached (7 days). The swollen gels were weighed after the removal of excess surface water with filter paper. Equilibrium swelling degree (EDS) was obtained with the following equation:

$$EDS = (W - W_0)/W_0, \tag{2}$$

where W is the weight of the gel at the equilibrium and W_0 is the weight of the dried gel.

III. RESULTS AND DISCUSSION

A. Properties of amphiphilic PMADAB gels

The radiation condition and its influence on gel swelling properties have been discussed in our previous work and will not be described further [16]. In this work, three kinds of amphiphilic PMADAB gels were prepared under the same condition. G_f of the PMADAB gels are almost the same, ca. 90%, however, water uptake capabilities of these gels are quite different (Table 1). EDS of PMBDAB (n = 4) gel in water is high, ca. 160.5. On the other hand, PMODAB (n =

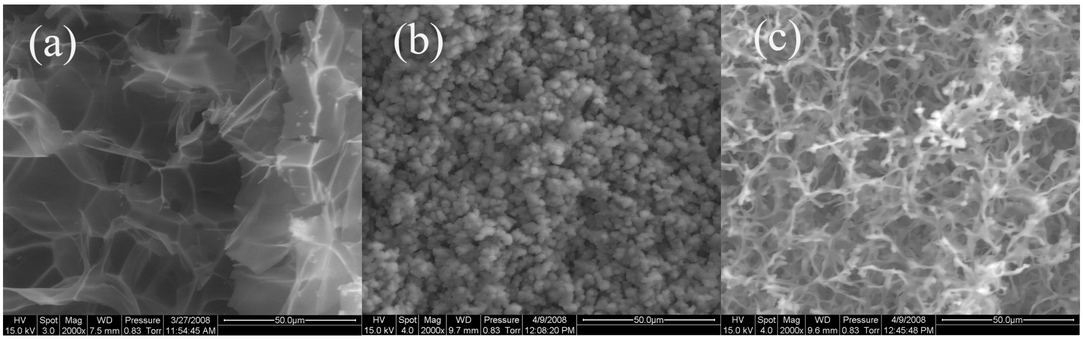

Fig. 2. SEM images of the swollen gels (scale bar: 50 μm): (a) PMBDAB (n = 4); (b) PMODAB (n = 8); (c) PMDDAB (n = 12).

8) and PMDDAB (n = 12) gels can hardly swell in water ($EDS = 2.4$ and 0.7, respectively). With the naked eye, swollen PMBDAB gels in water are transparent, while the swollen PMODAB and PMDDAB gels in water are milk-white and opaque, and PMODAB gel is soft, while PMDDAB gel is not so elastic.

In order to elucidate their difference on microstructure, morphology of the gels in different swelling media was observed by SEM (Fig. 2). The microstructure of amphiphilic gel with shorter side chains (PMBDAB) (Fig. 2(a)) is similar to that of PDMAEMA gel [16], being of cellular structure of normal gels, while the PMODAB and PMDDAB gels are composed by aggregations. The aggregations are of different appearances (Fig. 2(b) and 2(c)), and the different microstructures lead to different swelling behaviors of the gels in aqueous medium [15, 16] and probable interesting swelling behaviors in alcohol/water systems.

B. Swelling behavior of amphiphilic PMADAB gels in ethanol/water solutions

Figure 3 shows the swelling behavior of PMADAB gels (i.e., PMBDAB, PMODAB, or PMDDAB) in ethanol/water solutions as a function of ethanol content (x). The swelling ratio of PMADAB gels depends on ethanol concentration. The length of hydrophobic alkyl chains exerts big influence on the swelling curves of PMADAB gels. For PMBDAB (n = 4) gels with shorter hydrophobic chains, the EDS decreases with increasing x. The EDS is ca. 160.5 in water but 55.2 in pure ethanol. On the other hand, the PMODAB (n = 8) and PMDDAB (n = 12) gels with longer hydrophobic chains show a bell-shaped swelling curve as a function of x. Due to their strong hydrophobicity, both the gels can hardly swell in water ($EDS = 2.4$ and 0.7, respectively). Adding ethanol into water causes a drastic increase in EDS of the gels, swelling up to 76.1 and 147.6 times at $x = 40\%$ for PMODAB gel and $x = 90\%$ for PMDDAB gel.This is mainly due to intercalation of the organic solvent between the alkyl chains and disorganization of hydrophobic domains [8, 9]. Because hydrophobicity of the PMDDAB gel is stronger than that of the PMODAB gel, the PMDDAB gel start to swell at a higher x and its EDS_{max} appeared at a higher x in ethanol/water. The subsequent decrease of EDS at even higher x can be explained as a result of the non-solvency of ethanol to the hydrophilic component of the gels [8, 9]. Similarly, because hydrophobicity of the PMDDAB gel is stronger than that of PMODAB gel, EDS of PMDDAB gel (100.8) is larger than that of PMODAB gel (39.9).

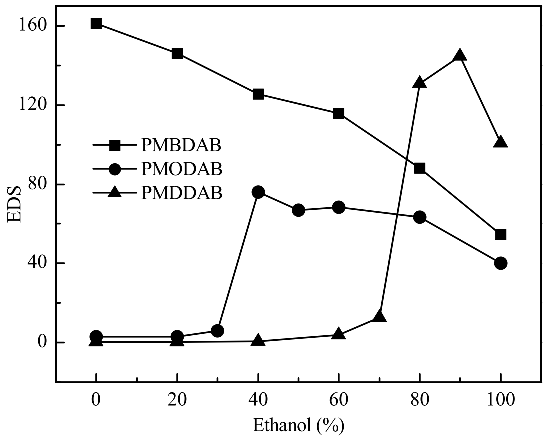

Fig. 3. Swelling curves of amphiphilic PMADAB gels in ethanol/water system (25 °C).

The dimensions of network chains in mixed-solvent medium are not only dependent on polymer segments-solvents molecules interactions but also influenced by the interactions between the solvents themselves [8, 18, 20]. For PMADAB gels, the MADAB monomer consists of two parts, i.e., the hydrophilic carbonyl group, quaternary ammonium group and hydrophobic alkyl backbone. The former part is more familiar with water than alcohols, while the latter part has a higher solubility in alcohols than water. Therefore, the solubility of PMBDAB chains is high in water, hence its high EDS in water. With increasing x, the interaction between the hydrophilic group and solvents decreases, whereas the interaction between hydrophobic group and solvents increases. Because of its more hydrophilic nature of PMBDAB gel, and the decrease of interaction between the hydrophilic group and solvents, the EDS of PMBDAB gel decreases with increasing x. In another word, the "non-solvency" effect is expected when a mixed solvent is used as a swelling medium for PMBDAB gel [8, 9]. Unlike PMBDAB gel (n $= 4$), more hydrophobic PMODAB (n $= 8$) and PMDDAB (n $= 12$) gels can hardly swell in water. Differing from the porous structure of PMBDAB gel (Fig. 2(a)), the two gels are composed by aggregated particles (Fig. 2(b) and 2(c)). These are clear evidences of hydrophobic association of the long-alkyl side chains of these gels. This is probably due to the cooperative effects of hydrophobic association of the long-alkyl side chains, in which the hydrogen bonding of the carboxyl groups takes a part, too. Adding ethanol into water probably leads to intercalation of the organic solvent between the alkyl chains and disorganization of hydrophobic domains, hence a drastic increase in EDS of the gels. Because the hydrophobicity of PMDDAB gel is stronger than that of PMODAB gel, the PMDDAB gel tends to swell at a higher x , hence the $EDS_{\max}$ at a higher x in ethanol/water. The subsequent decrease of EDS at even higher x can be explained as a result of the non-solvency of ethanol to the hydrophilic component of the gels [23].

C. Swelling behaviour of PMADAB gels in different alcohol/water systems

The swelling behaviours of the PMADAB (n $= 4, 8, 12$) gels in different alcohol/water (methanol, ethanol, isopropanol) systems were shown in Fig. 4. The swelling curves are similar, i.e., EDS of the gel deceases with increasing x, and with increasing carbon numbers in alcohol. This can be explained by increased hydrophobic interaction between alkyl side chains of gel and alcohol.

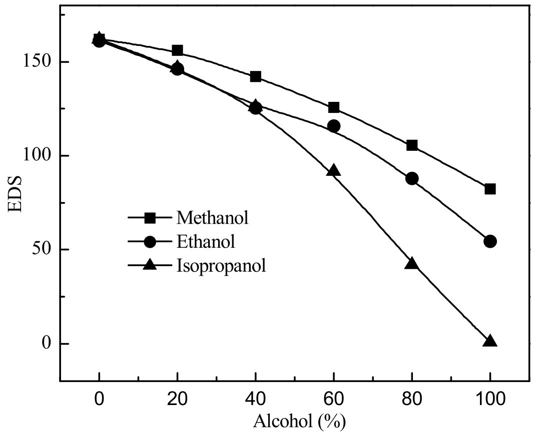

Fig. 4. Swelling curves of amphiphilic PMBDAB gel (n $=$ 4) in different alcohol/water systems (25 °C).

As shown in Fig. 5, the PMODAB (n $= 8$) gels have similar swelling curves irrespective of the type of alcohol used, except that the threshold of gel swelling appears at higher x region and the $EDS_{\max}$ moves to higher x region at higher number of carbon in the alcohol. As discussed in previous text, the upturn of EDS by adding alcohol is caused by intercalation of the organic solvent between the alkyl chains and disorganization of hydrophobic domains. Considering its more hydrophobicity, the isopropanol shall be more difficult to intercalate into hydrophobic domains between the alkyl chains. However, once the disorganization of hydrophobic domains is initiated, the interaction between the alcohol and alkyl chains in gel shall dominate. As a result, the $EDS_{\max}$ is higher in isopropanol/water system. Cheng *et al.* [23, 24] indicated that alcohol uptake of alcohol absorption resin related with its dielectric constant and generally decreased with the dielectric constant. The alcohol uptake of the PMADAB gels will be further discussed in Sec.III.

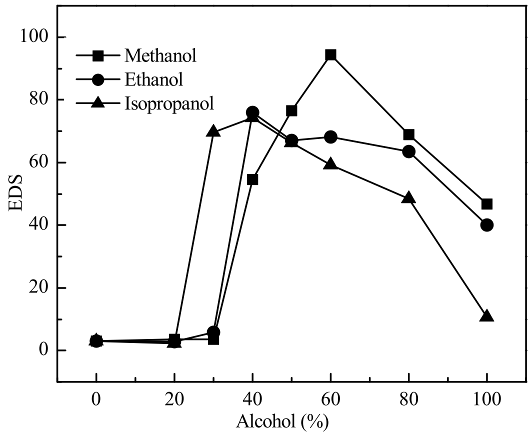

Fig. 5. Swelling curves of amphiphilic PMODAB gel (n $=$ 8) in different alcohol/water systems (25 °C).

Swelling curves of PMDDAB gel (n $=$ 12) in different alcohol/water systems (Fig. 6) are similar with that of PMODAB gel (n $=$ 8). The difference is that the threshold of gel swelling appears at higher x region and the $EDS_{\max}$ moves to higher x region.

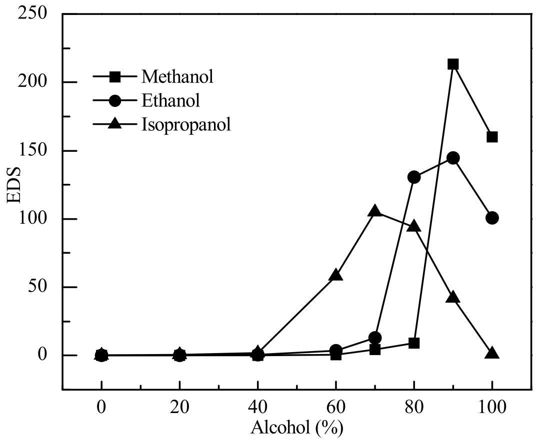

Fig. 6. Swelling curves of amphiphilic PMDDAB gel (n $=$ 12) in different alcohol/water systems (25 °C).

TABLE 2. EDS of PMADAB gels in solvents of different dielectric constants

	H_2O	Methanol	Ethanol	Isopropanol
ε at 25 °C	80	33	24.3	20.1
PMBDAB	160.5	82.2	55.2	0.7
PMODAB	2.4	47.6	39.9	10.6
PMDDAB	0.7	160.1	100.8	0.9

D. *EDS* of PMADAB gels in solvents of different dielectric constants

The EDS of PMADAB gels in solvents of different dielectric constants (ε) are given in Table 2. The EDS decreases with the dielectric constant. PMADAB gels are polyelectrolyte, so the electrostatic repulsion between polymer chains is the driving force for gel swelling. For polyelectrolyte gels, coulombic interactions between polymer chains in organic solvents are stronger than that in water [23]. Lin *et al.* [25, 26] prepared a series of copolymer sulfonic acid gels and studied their volume phase transition in mixed organic solvents. It was found that the sulfonic groups could be fully ionized in solvent of larger dielectric constant (such as DMSO, $\varepsilon = 48.9$). With the polymer chains negatively charged, the electrostatic repulsion between polymer chains promotes chain stretching.

Osmotic pressure of counter-ions is a driving force, too, for gel swelling, but sulfonic groups cannot be ionized in solvent with small dielectric constant (such as THF, $\varepsilon = 7.52$). Dipole-dipole interaction is formed between sulfonic groups and its counter-ions, which results in the contraction of polymer chains and the gels cannot swell in the solvents. In our previous work [17, 18], it was found that ion-clusters were formed between the tetra-alkyl ammonium cation and Br^-, causing particulate aggregation of PMADAB gels. It is possible that in methanol ($\varepsilon = 33$), ion-clusters in PMADAB gels are disassociated and the electrostatic repulsion between polymer chains is more remarkable than that in isopropanol ($\varepsilon = 20.1$). As a result, the EDS of the PMADAB gels decreased with increasing carbon number in alcohols.

IV. CONCLUSION

The alcohol-stimuli responsive swelling behavior of three kinds of amphiphilic PMADAB gels were studied. It was found that the length of alkyl side chains had significant influence on the swelling behavior of the gels in alcohol/water solvent. EDS of more hydrophilic PMBDAB gel in water was quite high, ca. 160 and decreased with increasing alcohol content x, whereas EDS of more hydrophobic PMODAB and PMDDDAB gels showed a convex-upward function of x. It can be explained by the amphiphilicity of PMADAB gels and a cosolvency effect of its long alkyl chains in alcohol/water. Swelling behavior of the PMADAB gels in methanol, ethanol and isopropanol were similar. EDS of PMADAB gels decreases with the dielectric constant of alcohol solvents. EDS of PMADAB gels in certain alcohol/water solvent can be 80 or even 200. It is possible that PMADAB gels can be potentially used as superabsorbent of alcohols and to selectively absorb leaks comprised water and alcohols.

[1] Stuart M A C, Huck W T S, Genzer J, *et al.* Nat Mater, 2010, **9**: 101–103.

[2] Reynolds J G, Coronado Paul R, Hrubesh L W. J Non-Cryst Solids, 2001, **292**: 127–137.

[3] Wang G Q, Kuroda K, Enoki T, *et al.* P Natl Acad Sci USA, 2000, **97**: 9861–9864.

[4] Tanaka T, Fillmore D, Sun S T, *et al.* Phys Rev Lett, 1980, **45**: 1636–1639.

[5] Amiya T, Hirokawa Y, Hirose Y, *et al.* J Chem Phys, 1987, **86**: 2375–2379.

[6] Hiroki A, Maekawa Y, Yoshida M, *et al.* Polymer, 2001, **42**: 1863–1867.

[7] Nishida M, Uraki Y, Sano Y. Bioresource Technol, 2003, **88**: 81–83.

[8] Ikkai F, Masui N, Karino T, *et al.* Langmuir, 2003, **19**: 2568–2574.

[9] Masui N, Ikkai F, Karino T, Naito S, *et al.* Langmuir, 2002, **18**: 5092–5098.

[10] Chen Y F and Yi M. Radiat Phys Chem, 2001, **61**: 65–68.

[11] Liu N, Yi M, Zhai M L, *et al.* Radiat Phys Chem, 2001, **61**: 69–73.

[12] Zhai M L, Chen Y F, Yi M, *et al.* Polym Int, 2004, **53**: 33–36.

[13] Yan Y, Yi M, Zhai M L, *et al.* React Funct Polym, 2004, **59**: 149–154.

[14] Liu Z G, Yi M, Zhai M L, *et al.* J Appl Polym Sci, 2004, **92**: 2995–3001.

[15] Zhang Y L, Xu L, Yi M, *et al.* Eur Polym J, 2006, **42**: 2959–2967.

[16] Li C C, Xu L, Zhai M L, *et al.* Polymer, 2009, **50**: 4888–4894.

[17] Xu L, Zhai M L, Huang L, *et al.* J Polym Sci A1, 2008, **46**: 473–480.

[18] Cheng Q, Li C C, Xu L, *et al.* Chem Eng J, 2011, **173**: 42–48.

[19] Li C C, Xu L, Zhai M L, *et al.* J Appl Polym Sci, 2011, **120**: 2027–2033.

[20] Li C C, Zhang Y W, Peng J, *et al.* Radiat Phys Chem, 2012, **81**: 967–970.

[21] Alenichev I, Sedlakova Z, Ilavsky M. Polym Bull, 2007, **58**: 191–199.

[22] Bhardwaj Y K, Kumar V, Sabharwal S. J Appl Polym Sci, 2003, **88**: 730–742.

[23] Cheng Z P, Lu J M, Zhu J, *et al.* Petrochemical Technology, 2000, **29**: 571–574. (In Chinese)

[24] Cheng Z P, Lu J M, Zhu J, *et al.* Journal of Chemical Engineering of Chinese Universities, 2000, **14**: 497–500. (In Chinese)

[25] Liu X X, Yi Y H, Zeng F, *et al.* Polymeric Materials Science and Engineering, 1997, **13**: 73–76. (In Chinese)

[26] Liu X X, Hu O, Tong Z, *et al.* Chemical Journal of Chinese Universities, 1998, **19**: 460–463. (In Chinese)