Conformational changes and swelling behavior of poly[(methacrylic acid)-*co*-(methyl methacrylate)] gel in solution of linear poly(ethylene glycol)

Yiping Cao,[a] Guoqin Liu,[a] Xueyong Liu,[a] Xiaobin Ding,*[a] Yuxing Peng*[a] and Albert S. C. Chan*[b]

[a] *Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, P. R. China*
[b] *Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P. R. China*

Received (in Montpellier, France) 29th November 2002, Accepted 26th February 2003
First published as an Advance Article on the web 29th May 2003

The contraction of poly[(methacrylic acid)-*co*-(methyl methacrylate)] [P(MAA-*co*-MMA)] gel induced by complexation with linear poly(ethylene glycol) (PEG) is quite different from that of poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA) gels. The effects of molecular weight and concentration of PEG, cross-linking density and composition of the gel, and the pH of the external solution on the conformational transitions of P(MAA-*co*-MMA) gels were investigated. A special feature of the conformational transitions for the P(MAA-*co*-MMA) gel/PEG system is the absence of a certain range of PEG concentrations where a reswelling of the collapsed gel is observed. The strong hydrophobicity of PMMA units will improve the PEG/network hydrophobic interactions and thereby stabilize the formed complex inside the gel network.

Introduction

Interpolymer complexation is the non-covalent association between groups on different polymer chains.[1] These macromolecular complexes form under conditions in which the polymers are thermodynamically compatible. The gels of poly(methacrylic acid) (PMAA) can form stable interpolymers with linear poly(ethylene glycol) (PEG) due to hydrogen bonding between carboxy groups of PMAA and ether oxygens of PEG.[2–4]

In three-dimensional polymer networks, complexation can significantly affect the network structure. As a result, the swelling behavior, mechanic properties and solute transport characteristics will vary dramatically between complexed and uncomplexed networks.[5–8] This behavior can be of pronounced practical interest, including applications in areas such as desalination and ultra-filtration membranes, chemo-mechanical systems, biosensors, molecular imprinting and drug delivery devices.[9–13]

In our laboratory we recently observed[14] shape memory behavior exhibited by poly[(acrylic acid)-*co*-(methyl methacrylate)]/cetyltrimethylammonium bromide [P(AA-*co*-MMA)/C_{16}TAB] complexes. The principle of shape memory behavior in this type of complex is based on a reversible order-disorder transition due to the formation of crystalline aggregates among the long alkyl chains of C_{16}TAB in the complexes. In our previous paper,[15] we synthesized complexes of poly[(methacrylic acid)-*co*-(methyl methacrylate)] [P(MAA-*co*-MMA)] networks with poly(ethylene glycol) (PEG) stabilized by hydrogen bonds and found that this complex shows shape memory behavior due to a large difference in storage modulus below and above the glass transition temperature.

The swelling behavior of PMAA gels in PEG solution was thoroughly reported in previous papers.[3,4,16] However, there are no reports on the formation of complexes between copolymer networks and PEG because of the complexity of such systems. In this paper, we present the conformational transitions and swelling behavior of P(MAA-*co*-MMA) gels in solution of linear PEG. Investigation of the specific features of the P(MAA-*co*-MMA) gel/PEG complexes is of substantial practical interest because of their potential applications as shape memory materials as evoked above.

Experimental

Materials

Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2′-azobis(isobutyronitrile) (AIBN) and *N*,*N*′-methylenebis(acrylamide) (MBAA) were analytical grade from Chengdu Reagent Factory. Poly(ethylene glycol) (PEG) with catalog number average molecular weights of 400, 800, 1000, 2000, 4000, 8000, 10 000 and 20 000 (Aldrich) was used as received. MAA monomer and MMA monomer were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. MBAA, a cross-linker, was used without further purification.

Preparation of gels

P(MAA-*co*-MMA) gels were prepared by radical copolymerization. An 18 wt·% dimethyl sulfoxide solution (100 mL) of the reaction mixture with the desired comonomer molar ratio and cross-linking density was bubbled with nitrogen for 15 min to remove oxygen in the reaction mixture. The cross-linking density of the networks in this study uses only the initial crosslinker concentration in the feed and was simply calculated as the molar ratio of cross-linking agent to the total monomer. A 1 mL amount of 10 wt·% AIBN solution was added to the mixture. The final solutions were injected into the space between two glass plates separated by polyethylene spacers (3 mm thick) or into a cylindrical glass tube

of 7 mm diameter. Gelation was carried out at 60 °C for 24 h. After polymerization, the crosslinked P(MAA-*co*-MMA) was immersed in 2000 mL of an ethanol–water mixture (50/50 wt·%) for 1 week to remove the monomers and uncrosslinked polymers, then in a large amount water for 3 weeks, until equilibrium was reached. The sample was divided into two parts. One represented as P(MAA-*co*-MMA) network was left immersed in water. The other part was put in PEG solution (3 mL of the solution per 1 mg of swollen network). The pH of the initial PEG solution was regulated by dropping 35.0 wt·% HCl solution. The samples were thermostated at 25 °C for 1 week, then immersed in water to remove PEG absorbed on the surface of the P(MAA-*co*-MMA)/PEG complex. All specimens were dried under vacuum at room temperature for 7 days.

Composition of complexes

To obtain information on copolymer composition and polymer yield, a sample of the prepared gels was quenched, then dried under vacuum at room temperature for 10 days and at 80 °C for another 10 days to remove solvent and unreacted monomers. The weight loss, except for the solvent, during the drying process was negligible, indicating that monomer-to-polymer conversion was nearly 100% and that the molar ratio of PMAA to PMMA in the copolymer was close to the comonomer molar ratio. The composition of the complexes was characterized as follows: by knowing the weight of the dried gel before complexation, the weight of the complexes equilibrated with water (the water on the surface of the complex disks was adsorbed before weighing) and the weight of the dried complexes, we could calculate the ratio μ (the binding degree) of the PEG/PMAA repeating units in the gel. The relative mass of the sample was characterized by the m/m_0 ratio, where m is the mass of the complex at the equilibrium state and m_0 is the mass of the gel equilibrated with water.

Differential scanning calorimetry (DSC)

The thermal analyses were carried out with a differential scanning calorimeter (Du Pont 9900) over a temperature range from −40 °C to 160 °C at a heating rate of 10 °C·min^{-1}, purged with nitrogen gas (N_2 purge rate = 50 mL·min^{-1}), and quenched with liquid nitrogen. The cell was calibrated using an indium standard. About 5–10 mg of the sample was placed in a hermetic aluminum pan and tested immediately after sealing. From repeated measurements, the data reported has a standard deviation of ±0.05 °C.

Results and discussion

Four series of P(MAA-*co*-MMA) gel/PEG complexes were processed and compared to a standard P(MAA-*co*-MMA) gel system without complexation. First, the effect of pH of the PEG solution on the conformational changes and swelling behavior of P(MAA-*co*-MMA) gels was investigated. In the second and third series, P(MAA-*co*-MMA) gels were immersed in the PEG solutions having various concentrations and molecular weights, respectively, and the fourth series combined the use of a MBAA cross-linker with increasing cross-linking density. In all the above systems the comonomer molar ratio was 1:1. The Influence of the composition of copolymer on the conformational changes and swelling behavior of P(MAA-*co*-MMA) gels was studied in the final series. The samples and their characteristics are presented in Tables 1 and 2 for the five series.

Table 1 Sample identification and compositions of P(MAA-*co*-MMA)/PEG complexes with an equimolar MAA:MMA ratio

Sample	Cross-linking density (%)	Formulation of initial PEG solution		
		MW	C_P[a] (%)	pH
A1	1	4000	8	1
A2	1	4000	8	2
A3	1	4000	8	3
A4	1	4000	8	4
A5	1	4000	8	5
B1	1	4000	1	2
B2	1	4000	3	2
B3	1	4000	5	2
B4	1	4000	7	2
B5	1	4000	9	2
B6	1	4000	11	2
B7	1	4000	13	2
B8	1	4000	20	2
B9	1	4000	30	2
B10	1	4000	40	2
C1	1	2000	8	2
C2	1	4000	8	2
C3	1	6000	8	2
C4	1	8000	8	2
C5	1	10 000	8	2
C6	1	15 000	8	2
C7	1	20 000	8	2
D1	0.5	4000	8	2
D2	1	4000	8	2
D3	3	4000	8	2
D4	5	4000	8	2
D5	7	4000	8	2
D6	10	4000	8	2

[a] The initial concentration of PEG.

Influence of pH of PEG solution

When PAA or PMAA gel is put in an aqueous solution of PEG, it can drastically change its dimensions with infinitesimal variation of external parameters such as temperature, pH and the concentration of the PEG solution. This phenomenon is called polymer gel collapse, which may be the reason why research work concerning the mechanical properties of complexes has not been presented previously. Starodubtzev *et al.*[5,17] showed that the absorption of PEG leads to the contraction of the PMAA or PAA gel, and a small change of pH induces a drastic jumplike conformational transition accompanied by a 30-fold shrinking of the network. However, only a slight contraction is observed for the P(MAA-*co*-MMA) gel. Fig. 1 (curve 1) illustrates the dependence on pH of the relative mass of the P(MAA-*co*-MMA)/PEG complexes, series A, in initial PEG solution. The obtained results show that the relative mass slightly increases with increasing pH value, while a

Table 2 Sample identification and compositions of P(MAA-*co*-MMA)/PEG complexes with various comonomer molar ratios

Sample	Cross-linking density (%)	MAA: MMA	Formulation of initial PEG solution		
			MW	C_P[a] (%)	pH
E1	1	1:3	4000	8	2
E2	1	1:2	4000	8	2
E3	1	1:1	4000	8	2
E4	1	2:1	4000	8	2
E5	1	3:1	4000	8	2

[a] The initial concentration of PEG.

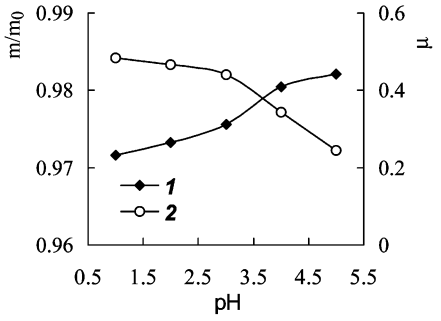

Fig. 1 Dependence on pH of the relative mass m/m_0 (1) and binding degree μ (2) of the P(MAA-*co*-MMA)/PEG complexes, series A, in initial PEG solution.

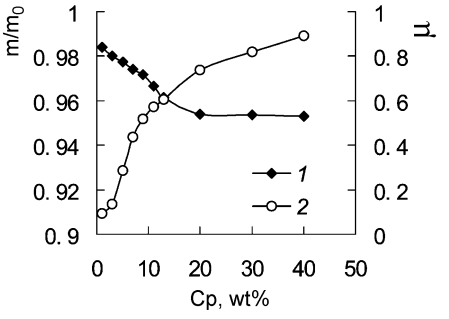

Fig. 2 Dependence of the relative mass m/m_0 (1) and binding degree μ (2) of the P(MAA-*co*-MMA)/PEG complexes, series B, on the initial concentration of PEG (C_P).

critical pH value at which a drastic jumplike conformational transition takes place does not exist. Apparently, this appears to be due to the difference in hydrophobic character of the network. P(MAA-*co*-MMA) is highly hydrophobic compared with PAA or PMAA because it has the MMA component in its backbone chain, thus it contains less water in the polymer network. At pH 4, a small amount of H^+ ions arising from the dissociation of the COOH groups of PMAA produces the osmotic pressure in the swollen network, which leads to a lowering of the amplitude of the P(MAA-*co*-MMA) gel contraction.

It is to be noted that the contraction of the gel in the solution of the linear polymer takes place as a result of the formation of an intermacromolecular gel/polymer complex on the basis of hydrogen bonding.[17,18] Fig. 1 (curve 2) illustrates the dependence of the binding degree (μ) on pH in initial PEG solution. The μ value decreases with increasing pH. This gives an explanation for the conformational changes of series A gels as mentioned above. It has been suggested[15,19] that the driving forces of the aggregation of the complexes are partly due to hydrophobic interactions, and that these hydrophobic interactions between the CH_2 groups of PEG and the CH_3 groups of PMAA stabilize the complex. For P(MAA-*co*-MMA)/PEG complexes, MMA units are able to participate in interactions between their hydrophobic group and the main chain of PEG as well as participating in hydrogen bonding, which is the main interacting force. The resulting complexes are more stable and the cooperativity on complexation is larger. The influence of hydrophobic interactions on complexation is discussed in detail later in this paper. Meanwhile, it is found that the relative mass and binding degree undergo a significant change at pH 3 as shown in Fig. 1. This phenomenon may be associated with the dissociation of the COOH groups of PMAA. In the region of pH > 3, more carboxylic groups on the polymer chain dissociate and the complexation between PEG and PMAA is suppressed.

Influence of PEG concentrations

It has been shown that PMAA gel can undergo two conformational transitions in PEG solution.[5,6] The first transition of PMAA gel from the swollen to a collapsed state is observed at very low PEG concentrations (< 5 wt·%). The second transition—the reswelling of the collapsed network—proceeds at relatively high concentrations of PEG in the external solution (5–< 10 wt·%). The reswelling of PAA or PMAA gels in PEG solution is accompanied by a jump-like penetration of PEG in the gel, leading to an equalization of the PEG concentrations inside and outside the gel.[5] It is then interesting to investigate the P(MAA-*co*-MMA)/PEG system. Fig. 2 (curve 1) illustrates the dependence of the relative mass of the series B P(MAA-*co*-MMA)/PEG complexes on the initial concentration of PEG 4000 (C_P). We see that the increase of C_P up to 20 wt·% leads to a further contraction of the P(MAA-*co*-MMA) gel. Then, in a broad range of PEG concentrations (20–40 wt·%), the relative mass of the gel changes insignificantly. For the P(MAA-*co*-MMA) gel system, reswelling of the slightly contracted network does not take place, which is explained by the absence of excess PEG in the network as discussed later.

When the concentration of PEG increases to 13 wt·%, there is a fair amount of PEG that is not complexed with PMAA or PAA in the gel.[6] It would be of interest to study the P(MAA-*co*-MMA)/PEG system. Differential scanning calorimetry (DSC) is extensively used to investigate miscibility in polymer blends or complexes. A single compositionally dependent glass transition is an indication of full miscibility on a dimensional scale between 20 and 40 nm.[15,20] DSC results in Table 3 suggest that no excess PEG is present and that there is only the PEG/PMAA complex phase, even in complex B10 formed in a solution having $C_P = 40$ wt·%. Fig. 2 (curve 2) illustrates the dependence of $\mu$of the series B complexes on initial concentration of PEG 4000. With increasing C_P of the PEG solution, the μ value increases simultaneously.

Influence of PEG molecular weight

It is known that complexation is subject to a dramatic chain-length dependence, which suggests that complexation proceeds by "cooperative interaction" between two macromolecules.[21] In Fig. 3, we can distinguish two types of m/m_0 *vs.* C_P dependence. The swelling curves of P(MAA-*co*-MMA) gel in the solutions of PEG having molecular weights of 400, 800 and 1000 belong to the first group. The common feature of these curves is a slight increase in m/m_0 value with increasing initial concentration of PEG. We suppose that PEG with low molecular weight does not interact with the P(MAA-*co*-MMA) network as evidenced by the previous DSC results.[15] A slight increase of the relative mass of the gel can be explained by a penetration of PEG molecular into the network. In the second group of swelling curves (PEG with molecular weights of 2000, 6000 and 10 000) a gradual decrease in the gel dimensional is observed with an increase of PEG concentration.

Table 3 DSC data of P(MAA-*co*-MMA)/PEG complexes, series B[a]

Sample	T_g[b]/°C	Sample	T_g/°C
B1	83.6	B6	72.6
B2	86.9	B7	70.5
B3	78.8	B8	71.8
B4	76.3	B9	68.8
B5	78.1	B10	70.3

[a] Endothermic peaks due to the melting of PEG crystallites cannot be observed for all complexes. [b] Glass transition temperature.

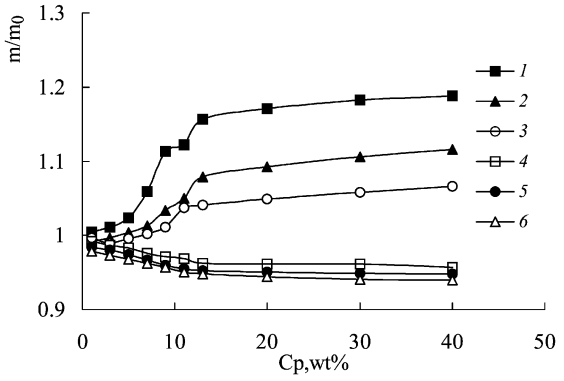

Fig. 3 Variation of the relative mass $m/m_0$of the P(MAA-*co*-MMA)/PEG complexes on the initial concentration of PEG (C_P). Molecular weight of PEG: 400 (1), 800 (2), 1000 (3), 2000 (4), 6000 (5)and 10 000 (6). The compositions of the P(MAA-*co*-MMA) gel and the pH of the initial PEG solution are the same as in Fig. 2.

Fig. 4 shows the dependence of the binding degree μ of series C complexes on the molecular weight of PEG. It can be seen that up to a molecular weight of 8000, the μ value gradually increases with the increase of PEG molecular weight. A further increase of the molecular weight results in a decrease of the binding degree. There is a defined range of PEG molecular weights where the stable complexes exist, below and above which the conditions of complete complexation will be disrupted. When the molecular weight is increased above 8000, the decreasing μ values can be attributed to steric hindrance in the interaction of the long PEG chain with PMAA, arising from the relatively small mesh size of the polymer network, as evidenced by experiments showing that higher cross-linking density (corresponding to smaller mesh size) of P(MAA-*co*-MMA) networks hinder PMAA complex formation with PEG.

Influence of gel cross-linking density

It is common knowledge that the degree of cross-linking density is one of the principal factors influencing the conformational lability of a complex.[18,22] Fig. 5 (curve 1) shows the swelling behaviors of P(MAA-*co*-MMA) gels with various cross-linking densities, which is a function of PEG concentration in the external solution. It can be seen that the conformational changes decreased with increasing cross-linking density of network. The complex is formed by the interaction between PMAA and PEG inside the three-dimensional (3D) gel network. An increase in the cross-linking density of the network for PEG with a fixed chain length or in the PEG chain length for a network with a fixed mesh size could prevent PEG molecules from

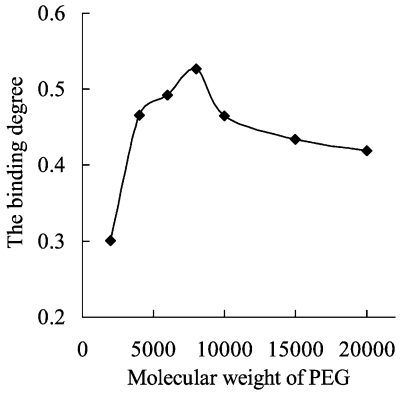

Fig. 4 Dependence of the binding degree μ of the P(MAA-*co*-MMA)/PEG complexes, series C, on the molecular weight of PEG.

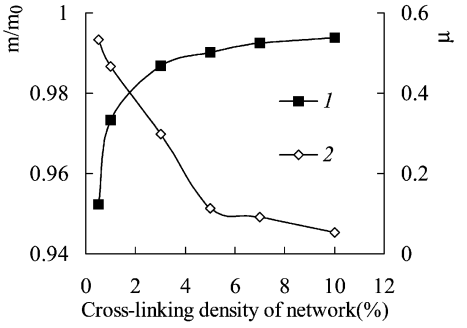

Fig. 5 Dependence of the relative mass m/m_0 (1) and binding degree μ (2) of the P(MAA-*co*-MMA)/PEG complexes, series D, on the cross-linking density of the network.

forming complexes inside the 3D gel network. Meanwhile, the interpolymer complex formed by a network with a small mesh size must have first developed on the surface layer.[2,23] This will prevent further interactions of the segments not involved in the complexation process. The above reasons explain that the μ value sharply decreases with increasing cross-linking density of the network as shown in Fig. 5 (curve 2).

Influence of copolymer composition

Iliopoulos and coworkders[24,25] studied the complexation of linear PAA at varying degrees of ionization with PEG. The copolymer is a partially neutralized PAA. The neutralized groups of PAA cannot form hydrogen bonds and so behave like structure defects. It was found that the presence of structure defects, even in a small amount, largely influence the formation and the stoichiometry of the complex.[24] It is then interesting to investigate the P(MAA-*co*-MMA) network. Fig. 6 (curve 1) shows the swelling behavior of the P(MAA-*co*-MMA) gels as a function of the comonomer molar ratio p of MAA to MMA. The contraction degree of the gels increases with increasing molar ratio p. Obviously, the hydrophobic character of PMMA is responsible for this effect. From Fig. 6 (curve 2), we see that P(MAA-*co*-MMA) network E1 can also form complexes with linear PEG even though its comonomer ratio is 1:3. We assume that the different complexation phenomena of P(MAA-*co*-MMA) and the copolymer of partially neutralized PAA studied by Iliopoulos and Audebert[24] could be associated with the difference in the hydrophobic character of the inactive groups (structural defects). In the case of the crosslinked P(MAA-*co*-MMA), the MAA units are not miscible with MMA units due to their hydrophilicity, which brings about a loss in interfacial energy. Meanwhile, the strong hydrophobicity of the MMA units will improve the PEG/network hydrophobic interaction and thereby stabilize the formed

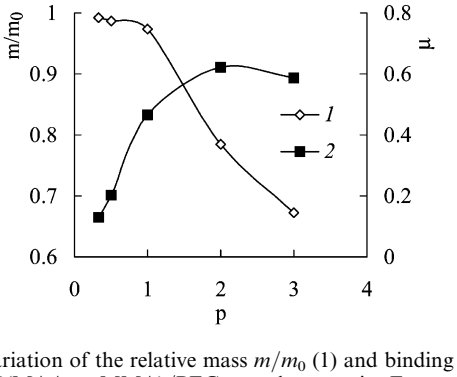

Fig. 6 Variation of the relative mass m/m_0 (1) and binding degree μ (2) of the P(MAA-*co*-MMA)/PEG complexes, series E, as a function of the comonomer molar ratio p of MAA to MMA.

complex inside the 3D gel network. In contrast, the acrylate groups on the copolymer of partially neutralized PAA are hydrophilic and cannot be complexed; thus, the presence of the inactive groups takes on a great importance in the complexation reaction. The above results allow us to make the assumption that the hydrophobicity of network gels also plays an important role in driving the formation of complex inside the gel network. This is evidenced by the fact that E4 shows a higher μ value than E5, as shown in Fig. 6 (curve 2), though it contains many more PMMA units. In addition, we believe that there are other two possible reasons for the big difference in binding degree μ between P(MAA-*co*-MMA) and the copolymer of partially neutralized PAA: (1) the decrease in apparent dissociation constant of PAA by crosslinking and (2) the local concentration effect of PEG near the P(MAA-*co*-MMA) network.

Conclusion

The contraction of P(MAA-*co*-MMA) gel immersed in PEG solution occurs in a different way from that of PAA or PMAA gels. The obtained results show that the relative mass of P(MAA-*co*-MMA)/PEG complex slightly increased with increasing pH value. With increasing C_P of PEG solution, the μ value increases simultaneously. However, no excess PEG is observed in the P(MAA-*co*-MMA)/PEG complex, even when C_P reaches 40 wt·%. The μ value is the highest at MW = 8000 and gradually decreases with increasing molecular weight of PEG. The hydrophobicity of network gels also plays an important role in driving the formation of complex inside the gel network.

Acknowledgements

We thank the Hong Kong Polytechnic University ASD Fund for financial support.

References

1 A. M. Lowman and N. A. Peppas, *Polymer*, 2000, **41**, 73.
2 E. A. Bekturov and L. A. Bimendina, *Adv. Polym. Sci.*, 1981, **43**, 100.
3 Y. Osada and M. Sato, *Polymer*, 1980, **21**, 1057.
4 Y. Osada, *Adv. Polym. Sci.*, 1987, **82**, 1.
5 O. E. Philippova, N. S. Karybiants and S. G. Starodubtzev, *Macromolecules*, 1994, **27**, 2398.
6 V. D. Skirda, I. Y. Aslanyan, O. E. Philippova, N. S. Karybiants and A. R. Khokhov, *Macromol. Chem. Phys.*, 1999, **200**, 2152.
7 J. Klier, A. B. Scranton and N. A. Peppas, *Macromolecules*, 1990, **23**, 4944.
8 C. L. Bell and N. A. Peppas, *J. Biomater. Sci., Polym. Ed.*, 1996, **7**, 671.
9 S. Nishi and T. Kotaka, *Macromolecules*, 1986, **19**, 1978.
10 C. L. Bell and N. A. Peppas, *J. Controlled Release*, 1997, **39**, 201.
11 A. M. Lowman and N. A. Peppas, *Macromolecules*, 1997, **30**, 4959.
12 I. M. Papisov and A. A. Litmanovich, *Adv. Polym. Sci.*, 1988, **90**, 139.
13 Y. Osada, K. Honda and M. Ohta, *J. Membr. Sci.*, 1986, **27**, 339.
14 Y. Guan, Y. P. Cao, Y. X. Peng and A. S. C. Chen, *Chem. Commun.*, 2001, **17**, 1694.
15 Y. P. Cao, Y. Guan, Y. X. Peng and A. S. C. Chan, *J. Mater. Chem.*, 2002, **12**, 2957.
16 X. Yu, A. Tanaka, K. Tanaka and T. Tanaka, *J. Chem. Phys.*, 1992, **97**, 7805.
17 S. G. Starodubtzev and O. E. Philippova, *Vysokomol. Soedin., Ser. B*, 1992, **34**, 72.
18 N. S. Karybiants, O. E. Philippova, S. G. Starodubtzev and A. R. Khokhlov, *Macromol. Chem. Phys.*, 1996, **197**, 2373.
19 E. Tsuchida and K. Abe, *Adv. Polym. Sci.*, 1982, **45**, 1.
20 S. W. Kuo and F. C. Chang, *Macromolecules*, 2001, **34**, 4089.
21 Y. Osada, *J. Polym. Sci., Part A: Polym. Chem. Ed.*, 1979, **17**, 3485.
22 S. Q. Zhou, C. Burger, F. Yeh and B. Chu, *Macromolecules*, 1998, **31**, 8157.
23 E. A. Bekturov, V. A. Frolova and L. A. Bimendina, *Macromol. Chem. Phys.*, 1999, **200**, 431.
24 I. Iliopoulos and R. Audebert, *Eur. Polym. J.*, 1988, **24**, 171.
25 I. Iliopoulos, J. L. Halary and R. Audebert, *J. Polym. Sci., Part A: Polym. Chem. Ed.*, 1988, **26**, 275.