Polytetrahydrofuran amphiphilic networks
II. Swelling behavior of polyacrylamide-*l*-polytetrahydrofuran networks

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Received (in Montpellier, France) 12th March 2002, Accepted 17th June 2002
First published as an Advance Article on the web 2nd October 2002

The swelling behavior of polyacrylamide-*l*-polytetrahydrofuran (PAm-*l*-PTHF) amphiphilic networks was studied in detail. Four solubility parameters δ [= 16.7, 23.3, 30.2 and 47.3 $(\mathrm{MPa})^{1/2}$] were obtained. The values of 16.7 and 47.3 $(\mathrm{MPa})^{1/2}$ correspond to the interaction of the PTHF and PAm segments with solvent, respectively, while the other two reflect the synergistic effect of the two phases during swelling. In acetone–water mixture no "volume phase transition" occurs, but the same synergistic effect renders a maximum swelling at certain mixture compositions. In aqueous solution the networks are sensitive to ionic strength when the ionic strength is low. A dynamic study reveals that the swelling of the networks in both water and cyclohexane is a non-Fickian diffusion process. The swelling behavior is entirely due to the microphase-separated and bicontinuous structure of the amphiphilic networks.

Amphiphilic networks are cross-linked random assemblages of hydrophilic and hydrophobic polymer segments. Because the two segments are immiscible, they usually form a microphase-seperated structure. They are able to swell in both water and organic solvents. Due to their special characteristics[1–6] and potential applications,[7–10] such as blood- and biocompatibility materials, and drug release carriers, they have received increasing attention.

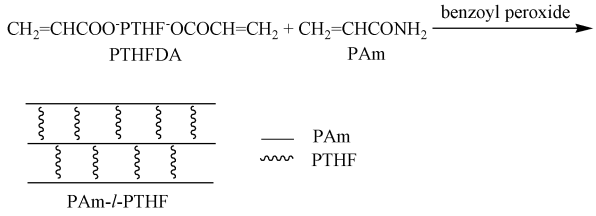
Up to now, most reported works used polybutadiene or polyisobutylene as the hydrophobic segments to build an amphiphilic network. In the first paper[11] of this series, we reported the synthesis of a series of novel polyacrylamide-*l*-polytetrahydrofuran (PAm-*l*-PTHF) amphiphilic networks using polyacrylamide and polytetrahydrofuran for the hydrophilic and hydrophobic segments, respectively. The composition and structure of the networks were studied using elemental analysis, FTIR, DSC, and SEM. Some preliminary results on the swelling behavior of networks were also reported. Like common amphiphilic networks, the PAm-*l*-PTHF networks can also swell in both water and organic solvents.

Swelling behavior is the most important property for amphiphilic networks. It not only reflects the structure of the networks, but also determines their potential applications. In this paper, a systematic study on the swelling behavior of these networks was carried out.

Experimental

Materials

Polyacrylamide-*l*-polytetrahydrofuran (PAm-*l*-PTHF) networks were prepared by free radical copolymerization of acrylamide (Am) with macromolecular crosslinker polytetrahydrofuran diacrylates (PTHFDA) as before.[11] The synthesis process is outlined in Scheme 1 and the composition of the resulting networks is summarized in Table 1. All solvents were of analytical grade and used without further treatment.



Scheme 1 Synthesis of of PAm-*l*-PTHF networks.

Swelling measurements

Swelling measurements were performed at 37 °C. Preweighed strips of the samples (about 100 mg) were immersed in a large

Table 1 Amphiphilic network compositions

Network[a]	% Yield	PTHF/wt %	F_{Am}[b]	$M_{\mathrm{c,PAm}}$[c]
Am-2-50	34.5	50.2	0.501	1133
Am-2-53	64.5	53.1	0.463	1005
Am-2-57	72.4	56.9	0.425	855
Am-2-73	73.4	73.4	0.265	419
Am-2-80	68.4	80.3	0.198	283

[a] Am stands for Am monomer; 2 gives the $\bar{M}_n$ of the PTHFDA ditelechelic in thousands; the last number shows the wt % of PTHF in the network. [b] F_{Am}, mole fraction of Am in the networks, is calculated based on nitrogen analysis. [c] $M_{\mathrm{c,PAm}}$, the average molecular weight of PAm between two crosslinks, is calculated as in ref. 11.

DOI: 10.1039/b202554j

excess of solvent. They were periodically removed from the solution and weighed after the excess liquid was blotted out with laboratory tissue paper.

The swelling ratio (SR) was measured as the ratio of the weights of the absorbed solvent and the dried amphiphilic network:[12]

$$\mathrm{SR} = (W_s - W_o)/W_o \tag{1}$$

where W_s is the weight of the swollen sample and W_o the weight of the original dried sample. The equilibrium swelling ratio (SRe) was obtained when the weight of swollen samples remained unchanged.

A serious of solvents with different solubility parameters (δ) were obtained by mixing two solvents in varying ratios. Their solubility parameters were referred to ref. 13. The ionic strength of the aqueous solutions was controlled by changing the potassium chloride concentration.

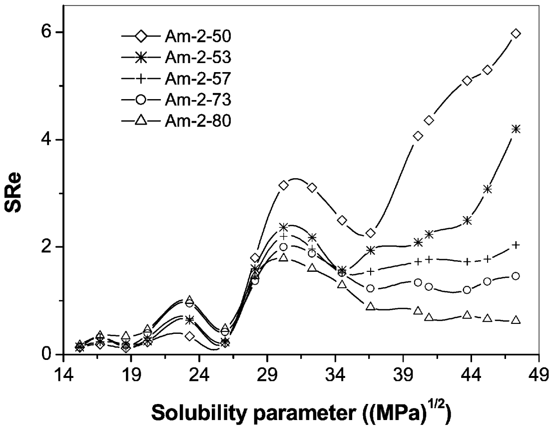


Fig. 1 Swelling behavior of PAm-*l*-PTHF networks in different solvents.

Results and discussion

Solubility parameters of the PAm-*l*-PTHF networks

The solubility parameter (δ) is the most widely used parameter to study the swelling of polymer networks. Other methods, for example, phase diagram based on cloud point determination, also provide information about the swelling behavior of polymers, but they are not as direct as the solubility parameter. In theory, the solubility parameter of a polymer is defined by the following fomula:[13]

$$\delta^2 = U/V \tag{2}$$

where U is the cohesive energy and V the molar volume. It can be assumed that the cohesive energy of polymers are additive; namely, the interaction of a pair of groups is not influenced by the presence of other groups.[14] According to this rule, we calculated the solubility parameters for the homopolymers PTHF and PAm, which are 17.6 $(\mathrm{MPa})^{1/2}$ for PTHF and 38.4 $(\mathrm{MPa})^{1/2}$ for PAm. The calculated value of δ for PTHF is very close to the average value measured by Huglin and Pass *via* several methods [17.4 $(\mathrm{MPa})^{1/2}$ when converted to modern units].[15] Because the rule is intended for nonpolar and disassociated systems, the calculated solubility parameter of PAm may show some deviation. Swelling experiments are the usual method to determine the solubility parameter of a polymer. Polymer networks cannot dissolve in any solvents because of their covalent crosslinked structure but can swell in certain solvents. When the solubility parameter of the solvent approaches that of the polymer network, a maximum equilibrium swelling ratio will be obtained and a peak appears in the plot of SRe *versus* δ. The solubility parameter corresponding to this peak is considered as the solubility parameter of the network.[16] In the case of a homopolymer network, there will be only one peak at the SRe–δ plot. Because amphiphilic networks contain 2 different segments, their swelling behavior could differ from networks containing only one segment.

The SRe of the PAm-*l*-PTHF networks in a serious of solvents with different solubility parameters are shown in Fig. 1. In accord with our previous results,[11] the swelling of the networks is composition-dependent, that is, in solvents with a lower solubility parameter, SRe increases with increasing PTHF content in the networks, while in solvents with a higher solubility parameter, SRe decreases with increasing PTHF content in the networks. Despite their different compositions, all samples give a maximum swelling ratio at four solubility parameters. In order to facilitate comparison, swelling ratios at the 4 solubility parameters are summarized in Fig. 2.

The results indicate that the PAm-*l*-PTHF networks have four solubility parameters: 16.7, 23.3, 30.2 and 47.3 $(\mathrm{MPa})^{1/2}$. The lowest one, 16.7 $(\mathrm{MPa})^{1/2}$, approaches the solubility parameter of the homopolymer PTHF, 17.6 $(\mathrm{MPa})^{1/2}$, and the highest one, 47.3 $(\mathrm{MPa})^{1/2}$, approaches that of PAm, 38.4 $(\mathrm{MPa})^{1/2}$. In the previous paper,[11] we have shown that the PAm-*l*-PTHF networks possess a microphase-seperated and bicontinuous structure because the PAm and PTHF segments are immiscible. Obviously these two solubility parameters indicate the interaction of the PTHF and PAm phases with solvents, respectively. In solvents with a solubility parameter of 16.7 $(\mathrm{MPa})^{1/2}$, the SRe of the networks increases with increasing PTHF content in the networks, while in solvents with a solubility parameter of 47.3 $(\mathrm{MPa})^{1/2}$, the SRe decreases with increasing PTHF content in the networks (Fig. 2). This fact confirms further that $\delta = 16.7$ and $\delta = 47.3$ correspond to the PTHF and PAm phases, respectively.

The appearance of other two solubility parameters, $\delta = 23.3$ and $\delta = 30.2$, is very interesting. They should be due to the special microphase-seperated and bicontinuous structure of the PAm-*l*-PTHF networks too, in which swelling of one phase will influence of the swelling of another phase. Maximum swelling at $\delta = 23.3$ can be explained as the result of two opposite effects of increasing solvent solubility parameter on the swelling of the PTHF phase. First, increasing solvent solubility parameter decreases the swelling of the PTHF phase, but it increases the swelling of the PAm phase at the same time. Although the increase in the swelling of the PAm phase may be small, it decreases the restriction of the PAm phase on the PTHF phase, and so increases the swelling of the PTHF phase to a certain extent. Maximum swelling at $\delta = 30.2$ can be explained in the same way. These results indicate that the

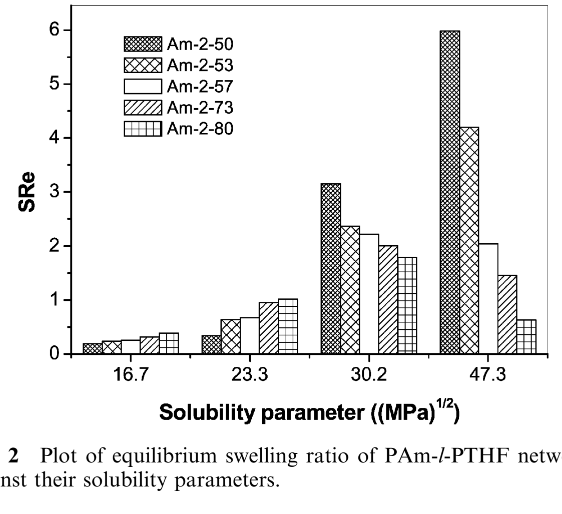


Fig. 2 Plot of equilibrium swelling ratio of PAm-*l*-PTHF networks against their solubility parameters.

PAm-*l*-PTHF networks exhibit not only properties of both segments but also the combined properties of the two segments, which cannot show up when only one segment is present.

Careful examination reveals a crossover point appears in Fig. 1 when δ is about 27.1 $(\mathrm{MPa})^{1/2}$, indicating that the SRe of all the PAm-*l*-PTHF networks in a solvent with $\delta = 27.1\ (\mathrm{MPa})^{1/2}$ is the same, that is, it is independent of the composition of the network. The occurrence of a crossover point indicates that the two segments have the same SRe at this point.

Swelling behavior in acetone–water mixture

Tanaka *et al.* reported the swelling behavior of polyacrylamide gels in acetone–water mixtures. With increasing acetone content in the mixture, the swelling ratio of PAm gels decreases. At a certain acetone–water mixture composition, the PAm gel collapses discontinuously,[17,18] which is called a "volume phase transition". The PAm-*l*-PTHF networks can be regarded as a special PAm gel modified with PTHF, they may also response to the composition variation of an acetone–water mixture.

The swelling behavior of the PAm-*l*-PTHF networks in acetone–water mixtures with different compositions is shown in Fig. 3.The SRe of the networks changes continuously when varying the mixture composition. No discontinuous change was observed for any of the samples, which is different from the homopolymer PAm gel. This result indicates that the presence of PTHF decreases the sensitivity of PAm towards the acetone–water mixture composition. Apparently, this difference could be attributed to the microphase-separated structure of the PAm-*l*-PTHF networks,[11] in which the PAm phase is separated into different size domains and the mobility of PAm is restricted. As a result, volume collapse of the PAm-*l*-PTHF networks does not occur sharply but over a wide range of mixture compositions.

For networks with a low PAm content, SRe decreases almost monotonously with increasing acetone content in the mixture. But in the case of networks with a larger PAm content, such as PAm-2-50 and PAm-2-53, SRe increases first and then drops, and a peak appears in the plot of SRe *vs.* acetone–water mixture composition. This result can also be attributed to the synergistic effect of the PAm and PTHF phases. The expansion of PAm and PTHF chains in solvents is restricted by each other because of the microphase-separated and bicontinuous structure. Increasing acetone content in the mixture will decrease the swelling of PAm phase, but the swelling of the PTHF phase will increase and reduce its restriction on the PAm phase, so the PAm chains can swell more completely. As the result of the two opposite effects of increasing acetone content on the swelling of the PAm phase, a maximum SRe appears at a certain mixture composition.

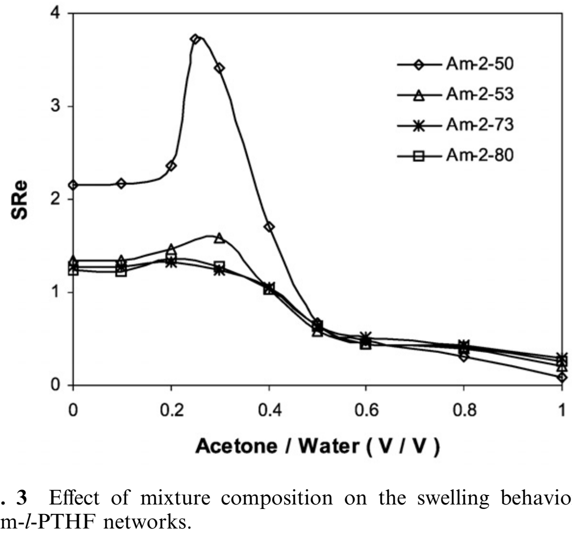


Fig. 3 Effect of mixture composition on the swelling behavior of PAm-*l*-PTHF networks.

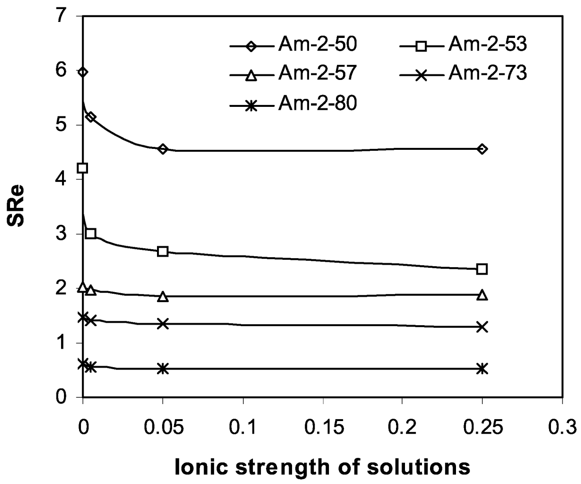


Fig. 4 Effect of the ionic strength of solutions on the swelling behavior of PAm-*l*-PTHF networks.

Swelling behavior in different ionic strength aqueous solutions

For its application as biomaterials, we need to know the effect of ionic strength on the swelling of PAm-*l*-PTHF networks in aqueous solution. Fig. 4 shows the SRe of PAm-*l*-PTHF networks in aqueous solutions with different ionic strengths. For all samples the swelling of the networks decreases with increasing ionic strength, but when the ionic strength is larger than 0.05, it has little effect on the SRe of the networks and a plateau forms in the plot of SRe against ionic strength. This indicates that the PAm-*l*-PTHF networks are sensitive to salt in the aqueous solution when the ionic strength is low. Fig. 4 also shows that networks with higher PAm content are more sensitive to the change of ionic strength. The effect of ionic strength reflects the interaction between the PAm phase in the networks and small electrolytes in the solution. The presence of small electrolytes reduces the affinity of the PAm chains for water, therefore, the swelling of the networks decreases. The interaction between PAm chains and electrolytes will reach a balance at a certain electrolyte concentration, so further increasing ionic strength will not influence the swelling of the networks.

Swelling dynamics of networks in different solvents

The dynamic swelling kinetics of the networks in water ($\delta = 47.3$) and an organic solvent, cyclohexane ($\delta = 16.7^{12}$), were also studied. Swelling curves in the two solvents are shown in Fig. 5. The swelling is composition dependent in both solvents. With increasing PTHF content, the swelling in cyclohexane increases. On the contrary, the swelling in water decreases with increasing PTHF content. For the same sample, the SRe in water is much larger than that in organic solvents. For example, the SRe of Am-2-50 in water is 598%, while it is only 19% in cyclohexane. This may be due to the high hydrophilicity of the PAm segment and the relatively low hydrophobicity of the PTHF segment.

The following well-known relationship was used to study the swelling dynamics of the networks:[15]

$$\mathrm{SR}(t) = kt^n \qquad (3)$$

where SR(t) is the swelling ratio at time t, k is a constant and n the kinetic exponent. In this phenomenological rate law the

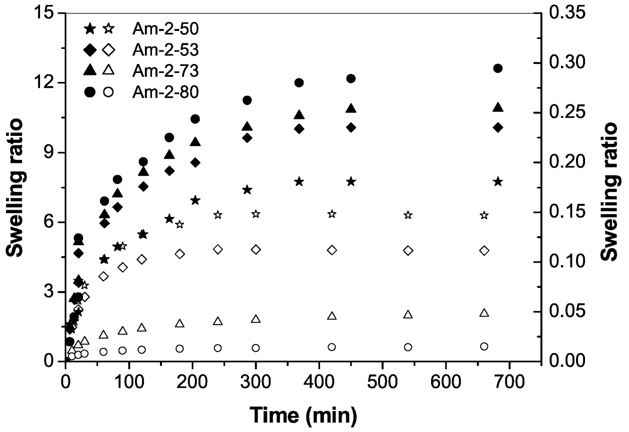


Fig. 5 Swelling curves of PAm-*l*-PTHF networks in cyclohexane and water at 37 °C.

kinetic exponent *n* provides insight into the sorption mechanism.[19] For a Fickian rate-limiting diffusion process, *n* is 0.5, whereas when *n* is between 0.5 and 1 or lower than 0.5, it indicates a non-Fickian process. The *n* values of the PAm-*l*-PTHF networks were obtained from the slope of a log–log plot of swelling ratio *versus* time and are summarized in Table 2.

As shown in Table 2, the *n* values for all samples are less than 0.5, indicating a non-Fickian process in which the diffusion of solvent molecule prevails, but the swelling is limited by network chain relaxation. When the networks swell in water or cyclohexane, the relaxation of the PAm and PTHF segments is always different. Water is a good solvent for the PAm segment but a poor solvent for the PTHF segment, while cyclohexane is a good solvent for the PTHF segment but a poor solvent for the PAm segment. Therefore, the PAm segment will expand in water and contract in cyclohexane, while the PTHF segment will expand in cyclohexane and contract in water. Hence, the diffusion of both solvents is restricted by network chain relaxation.

Conclusions

Because of the microphase-separated and bicontinuous structure of the amphiphlic PAm-*l*-PTHF networks, they present swelling behavior different from that of homopolymer networks. They can swell in both water and organic solvents and their swelling is composition-dependent. In addition, they present four solubility parameters: 16.7, 23.3, 30.2 and 47.3. $\delta = 16.7$ and $\delta = 47.3$ correspond to the interaction of PTHF and PAm with solvent, respectively, while the other two parameters reflect the synergistic effect of the two phases during swelling. The same effect was observed when the networks swell in acetone–water mixture and no "volume phase transition" was observed. The networks also present sensitivity toward ionic strength when swelling in aqueous solution. A dynamic study shows the swelling of the amphiphilic networks in both water and cyclohexane is a non-Fickian diffusion process.

The synergistic effect shown here renders an amphiphilic network possessing not only the properties of the single components, but also the combined properties of the two components. This is important for the design and application of an amphiphilic network. For example, the swelling behavior of an amphiphilic network can be adjusted finely by carefully choosing components with suitable solubility parameters. On the other hand, four solubility parameters make it easy to find a suitable solvent for a given amphiphilic network to get maximum swelling. When used as drug release system, the synergistic effect will provide the amphiphilic network with more freedom than homopolymer networks for drug loading and release control.

Table 2 The swelling exponent (*n*) of PAm-*l*-PTHF amphiphilic networks in cyclohexane and water

	Swelling exponent *n*	
Sample	Cyclohexane	Water
Am-2-50	0.424	0.320
Am-2-53	0.446	0.255
Am-2-57	0.321	0.340
Am-2-73	0.445	0.328
Am-2-80	0.492	0.250

Acknowledgements

The National Natural Science Foundation of China is gratefully acknowledged for financial support (Grant No. 59773019).

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