Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Polymer 46 (2005) 3936–3941

polymer

www.elsevier.com/locate/polymer

Effect of PEO–PPO–PEO structure on the compressed ethylene-induced reverse micelle formation and water solubilization

Rui Zhang, Jun Liu, Buxing Han*, Bo Wang, Donghai Sun, Jun He

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 21 October 2004; received in revised form 25 February 2005; accepted 27 February 2005
Available online 2 April 2005

Abstract

Some of the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) tri-block copolymers aggregate in *p*-xylene upon addition of ethylene and form reverse micelles at higher temperature at which the reverse micelles cannot be formed without addition of compressed ethylene. An abrupt increase of water solubilization is observed at a certain ethylene pressure. The effects of surfactant structure, such as the ratio of EO (EO weight percent) and the molecular mass, on the copolymer micellization and the solubilization of water in such systems are studied. For the copolymers with the same length of PO block, higher EO ratios facilitate the reverse micelle formation. However, as the EO ratio reaches 70%, it cannot form reverse micelles because the hydrophilicity is too high. For the copolymers with same composition, higher molecular weight is favorable to forming the reverse micelle due to the hydrophilic and folding effects, respectively. The reverse micelle solution can solubilize water with W_0 (molar ratio of water to EO segment) up to 4.1.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Reverse micelle; Surfactant structure; PEO–PPO–PEO

1. Introduction

Reverse micelle solutions or w/o microemulsions are surfactant solutions in which the surfactants are self-assembled and dispersed in the organic continuous phase with nano-scaled size [1]. They have attracted a great deal of attention over the past decades because of their potential applications in many fields, such as catalysis, separations, cosmetics, and nanoparticles synthesis [2–6].

Tri-block copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) are commercially available non-ionic macromolecular surfactants. Variation of the copolymer composition (PPO/PEO ratio) and molecular weight (PEO and PPO block length) leads to the production of molecules with different properties that meet the specific requirements in various areas, including dispersion stabilization [7], formulation of cosmetics [8], pharmaceuticals [9], separations [10], etc. Because of wider variations in the molecular architecture [11], the polymer colloids offer great potential in creating tailor-made supra-molecules.

Reverse micelle formation by a number of PEO–PPO–PEO copolymers in organic solvents has been reported [12, 13]. The solvent property has a pronounced effect on the formation of the micelles. An increase in temperature or the presence of added salts has shown considerable influence on critical micelle concentrations (CMC), micelle structures and micellar parameters of PEO–PPO–PEO copolymer surfactants both in aqueous and organic solvents [13–15]. The effect of the copolymer composition and molecular weight on micelle formation was experimentally studied in aqueous solution [16,17]. Recently, the effect of block composition on the micellization of ABA and BAB type tri-block copolymers in different solvents was theoretically simulated [18].

Compressed gases (e.g. CO_2 and ethylene) are poor solvents for many solutes. Meanwhile, they can dissolve in many organic solvents and decrease the solvent strength of the solvents [19]. Therefore, they can act as anti-solvents. Gas anti-solvent techniques have been used in recrystallization [20], fractionation [21–23] and particle generation [24–27]. It is well known that the solvent characteristic is

---

* Corresponding author. Tel./fax: +86 10 62562821.
E-mail address: hanbx@iccas.ac.cn (B. Han).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.105

very important to the micellization. Our studies showed that $EO_{27}PO_{61}EO_{27}$ (P104) copolymer in *p*-xylene could not form reverse micelles at 40 °C, while reverse micelles were formed in the presence of compressed CO_2 or ethylene at suitable pressures [28,29]. This can be ascribed to the fact that *p*-xylene is such a good solvent for both PEO and PPO blocks at high temperature that the copolymer cannot assemble to form micelles [13]. The compressed gases tuned the solvent power of the solvent and made it possible to form the reverse micelles.

In previous work, we studied the effect of surfactant structure and molecular mass on reverse micelle formation induced by compressed CO_2 [30]. In this work, we study the effects of the polymer chemical composition and molecular mass on the micellization of PEO–PPO–PEO copolymers in *p*-xylene induced by compressed ethylene, and the solubilization of water in these systems is also studied.

2. Experimental

2.1. Materials

Nine different PEO–PPO–PEO copolymers were examined. Copolymers used in this work were provided by BASF Corporation and used as received. *p*-Xylene were produced by Beijing chemical reagent factory (A.R. Grade). Ethylene (99.9% purity) was supplied by Beijing analytical instrument factory. Double distilled water was used.

2.2. Apparatus and procedures to determine water solubilization

The experiments were based on the fact that the solution was clear and transparent only if the water was all solubilized [12,13]. The apparatus to study water solubilization of H_2O/P104/*p*-xylene/ethylene quaternary system was same as that used previously [28,29]. The apparatus consisted mainly of a high-pressure view cell of 40 cm^3, a constant temperature water bath, a high-pressure syringe pump (DB-80), a pressure gauge, a magnetic stirrer, and a gas cylinder. The experimental temperature of the water bath was controlled by a HAAKE D8 temperature controller. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, Model 93) and an indicator, which was accurate to ±0.025 MPa in the pressure range of 0–20 MPa.

In a typical experiment, the air in the view cell was replaced by ethylene, 5 g solution of copolymer surfactant in *p*-xylene and the desired amount of double distilled water was loaded into the high-pressure view cell. The cell was placed into the constant temperature water bath. After thermal equilibrium had been reached, the stirrer was started and the solution was hazy and milky. Gaseous ethylene was charged into the cell slowly until the hazy and milky solution became transparent and completely clear, indicating the complete solubilization of the water [12,13].

3. Results and discussions

3.1. Copolymers used

The commercial notations of the copolymers, together with their nominal molecular masses, polyoxyethylene contents, and the chemical formulas (calculated from the molecular masses and PEO contents), are listed in Table 1. The hydrophilic–lipophilic balance (HLB) numbers and the cloud point (CP) temperatures of the copolymers in aqueous solutions are also tabulated in Table 1. Both HLB and CP are measures of the relative hydrophobicity of the amphiphilic polymers and depend on the copolymer PEO content, architecture and molecular mass.

3.2. Volume expansion coefficient

The solution is expanded after adding ethylene. Our experimental results indicate that the difference in volume expansion coefficient, $(V-V_0)/V_0$ (V_0 and V are the volumes of the solution before and after dissolving ethylene, respectively), of different copolymer solutions is not considerable provided that the concentration and pressure are the same. As examples, Fig. 1 shows the volume expansion coefficients of some solutions. As expected, the volume expansion coefficient or the concentration of ethylene in the solutions increases with increasing pressure, which reduce the solvent power of the solvent, as has been discussed by other researchers [19]. The volume fraction of ethylene in the solution at different conditions can be estimated from the volume expansion coefficient. As shown in Fig. 1, in the pressure range of 3–4.5 MPa, the volume of the solution (copolymer/*p*-xylene) is expanded by 20–40%, i.e. the ethylene has a volume fraction of about 17–30% [29].

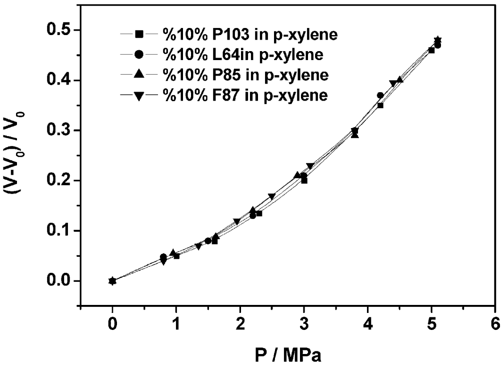

Fig. 1. The dependence of volume expansion coefficient of some copolymer in *p*-xylene solutions on ethylene pressure at 40 °C (the concentration of copolymers is 10 wt%).

Table 1
Properties of the PEO–PPO–PEO block copolymers

Notation	Mol. mass	EO wt%	Chemical formula[a]	HLB[b]	CP/°C[c]
P103	4950	30	$EO_{17}PO_{60}EO_{17}$	9	52
P104	5900	40	$EO_{27}PO_{61}EO_{27}$	13	78
L64	2900	40	$EO_{13}PO_{30}EO_{13}$	15	60
L44	2200	40	$EO_{10}PO_{23}EO_{10}$	16	73
P105	6500	50	$EO_{37}PO_{56}EO_{37}$	15	94
P85	4600	50	$EO_{26}PO_{40}EO_{26}$	16	86
F87	7700	70	$EO_{61}PO_{40}EO_{61}$	24	>100
F88	11,400	80	$EO_{104}PO_{39}EO_{104}$	28	>100
F77	6600	70	$EO_{52}PO_{34}EO_{52}$	25	>100

The data of molecular mass, HLB and cloud point derive from the webpage of BASF [31].

[a] The chemical formulas were calculated from the molecular masses and PEO contents.

[b] Hydrophilic–lipophilic balance.

[c] Cloud point determined in 10% aqueous solution.

3.3. Formation of reverse micelles

W_0 (molar ratio of water to EO segments in the polymer) is often used to characterize the amount of water solubilization of the different copolymer/*p*-xylene solutions. In this work, the trace amount of water dissolved in the solvent (*p*-xylene/ethylene) has been corrected using a commonly used method [32], although it is less than 2% of the solubilized water. The W_0 is calculated from the following equation.

$$W_0 = \frac{(m_w - m_{w,0})M_p}{18nm_p} \tag{1}$$

where m_w is the total mass of water, $m_{w,0}$ stands for the mass of water dissolved in the solvent at the experimental temperature and pressure, Mp is the molecular weight of polymer, n is the number of EO segments in a polymer, m_p denotes the mass of the surfactant.

We define the pressure at which W_0 begin to increase sharply as a critical micelle pressure (CMP) [28,29]. Fig. 2 shows the critical micellization pressure (CMP) of the 10 wt% copolymer solutions. Six copolymers, P103, P104, P105, L64, L44 and P85 can form reverse micelle under suitable pressure of ethylene, while F87, F77 and F88 cannot form reverse micelle. Both the length of PPO block and PEO block are important for reverse the micelle formation.

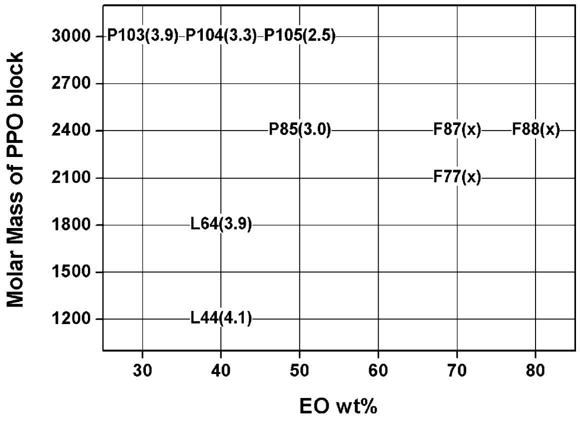

Fig. 2. The critical micelle pressure of 10 wt% polymer solution in *p*-xylene at 40 °C. (The values in parentheses stand for the CMPs in MPa; x denotes that the copolymer cannot form reverse micelle; F87, F77 and F88 were measured at 50 °C because their solubility is too low at 40 °C).

3.4. Effect of the ratio of EO block on the reverse micelle formation

P103, P104 and P105 are copolymer surfactants in which the length of PO block is almost same, but the number of EO segments increase from 17 to 37. At 40 °C, all the three copolymers can dissolve in *p*-xylene and their solutions cannot solubilize water in the absence of the gas. However, with the addition of ethylene of suitable pressure, the solutions can solubilize large amount of water, which indicates formation of the reverse micelles.

Fig. 3 shows the effect of ethylene pressure on maximum W_0 (maximum solubilization capacity) of copolymer solutions with different concentrations. It can be seen from Fig. 3 that the maximum W_0 is very small as ethylene pressure is low. This shows that reverse micelles are not formed without ethylene or at the lower pressures. However, in each curve there is a pressure where maximum W_0 increases sharply with increasing pressure, indicating the reverse micelles begin to form [28,29]. This pressure was defined as a critical micelle pressure (CMP), as discussed above.

From Fig. 3, we can see that the CMP decreases from P103 to P105. It is known that the hydrophilicity of the surfactants increases with increasing number of EO segments as the quantity of PO is constant. For example, the HLB value of P103, P104 to P105 increases from 9, 13 to 15. It means that the interaction between water and P105 is stronger than that between water and P104 or P103. So P105 can solubilize water at lower pressure of ethylene. On the other hand, the existence of ethylene not only decreases the solvent power of the solvent, but also makes the solvent to be more selective to the PPO block [29]. Therefore, the EO block have to assemble together to decrease the energy

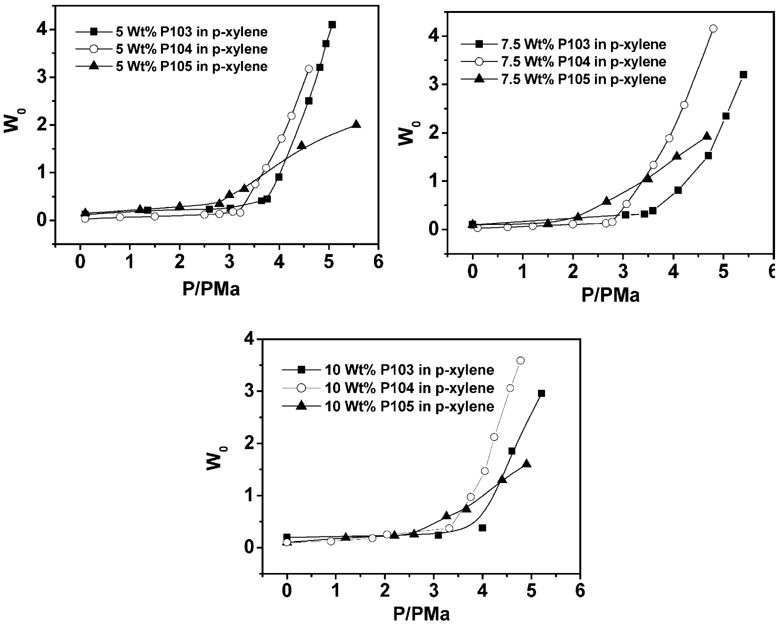

Fig. 3. Dependence of maximum W_0 on pressure of ethylene and initial concentration (*p*-xylene-basis) of different PEO–PPO–PEO copolymers.

of the system. Then the copolymers associate to form reverse micelles with a core of PEO coils and a PPO corona at a sufficient concentration of ethylene in the solution. Therefore, for these copolymers, the longer length of PEO block is favorable to forming reverse micelle and the CMP is lower. The effect of the EO ratio, or hydrophilicity, on the reverse micellization is opposite to that of the micellization in aqueous solution in which higher EO ratio is not favorable to the formation of the micelles [16,17].

The maximum W_0 of P105 is lower than those of the P104 and P103 at higher pressure of ethylene. One of the reasons is that the EO segments in different positions, i.e. near the chain-end or near the PO segments, must have different capacity of water solubilization. The EO segments near the chain-end, especially the hydroxyl-ended EO segment, should be more hydrophilic than other EO segments. Because P105 has the longest PEO chain, the ratio of EO segments near the chain-end is lower than that of P103 and P104. So the water solubilization capacity based on all the EO segments is lower.

F87 and F88 are quite hydrophilic because they both have a high ratio of EO block and their quantity of PO block is same. The water solubilization capacity of F88 and F87 solution of *p*-xylene under pressure of ethylene was also studied. The experiment was done at 50 °C because their solubility is too low at 40 °C. The result shows that both F88 and F87 cannot form reverse micelle in even in the presence of ethylene.

The above results indicate that suitable ratio of EO is very important to the formation of the reverse micelles. Too high or too low ratio of EO is not favorable to forming the reverse micelles.

3.5. *Effect of molecular mass on the reverse micelle formation*

P104, L64 and L44 are copolymer surfactants with EO block ratio of 40%. But the length of both PPO and PEO blocks decreases from P104 to L64. The molecular mass of P104, L64 and L44 are 5900, 2900 and 2200, respectively, and their HLB is similar.

Fig. 4 shows the effects of ethylene and initial concentration of L44, L64 and P104 on maximum W_0 at 40 °C. The CMP of P104 is smaller than that of L64 and L44 at the same concentration. The reason may be that L64 and L44 have small molecular mass. Although they have larger HLB than P104, the cloud point temperature (CP) of their aqueous solution is lower (Table 1). Therefore, L64 and L44 should be less hydrophilic, which disfavors solubilization of water. On the other hand, for a PEO–PPO–PEO block copolymer, the PPO block must be folded to make the two PEO blocks come into the core of the reverse micelles [29, 30]. Therefore, it is easy for a larger copolymer to form reverse micelles, so the CMP of P104 is smaller than L64 and L44. Similarly, P105 and P85 have same ratio of PEO, but molar mass P105 is larger, and the P105 has smaller CMP than P85, as shown in Fig. 5.

3.6. *Comparison of the results of CO_2 and ethylene as anti-solvents*

In previous work [30], we studied the effects of the polymer chemical composition and molecular mass on the micellization of PEO–PPO–PEO copolymers in *p*-xylene induced by compressed CO_2 and the solubilization of water

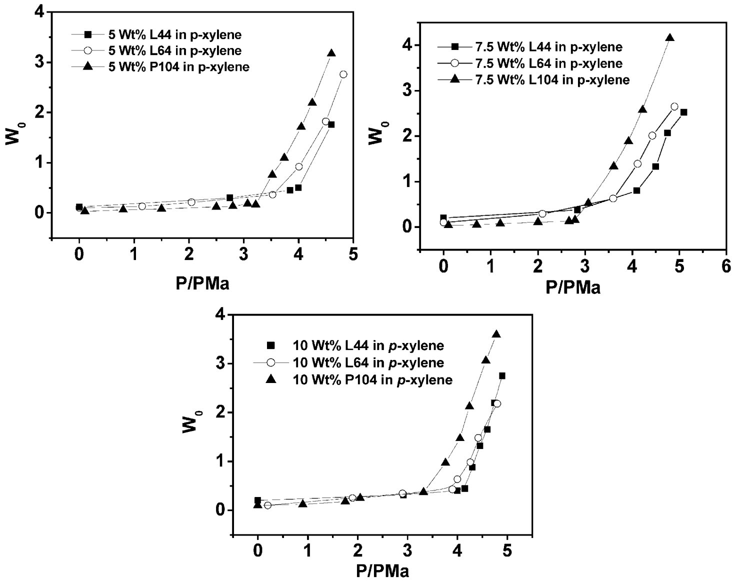

Fig. 4. Dependence of maximum W_0 on pressure of ethylene and initial concentration (*p*-xylene-basis) of the copolymers at 40 °C.

in these systems. Comparing the results of this work and previous work, we conclude that both CO_2 and ethylene can induce formation of reverse micelles of P103, P104 and P105 at suitable pressures. F88 and F77 can form reverse micelles induced by CO_2 as anti-solvent, while they cannot form reverse micelles induced by ethylene. On the contrary, CO_2 cannot induce formation of reverse micelles of L44, L64 and P85, while they can form reverse micelles in the presence of ethylene at suitable pressure. It indicates that the effects of CO_2 and ethylene on the formation of PEO–PPO–PEO copolymer reverse micelles are different because of their different properties. How to explain this phnomenon is an interesting topic and needs to be studied further.

4. Conclusion

The effects of structure and composition of PEO–PPO–PEO copolymers and ethylene pressure on the micellization in *p*-xylene have been studied in this work. For the copolymers with the same length of PO block, increasing EO ratio is favorable to the formation of reverse micelle in low EO ratio range. However, as the EO ratio reaches 70%, it cannot form reverse micelles because the hydrophilicity is too high. For the copolymers with same composition, increasing the molecular weights enhances the ability to form reverse micelles. The surfactant structure and composition also affect the efficiency of the ethylene and CO_2 to induce the formation of the reverse micelles.

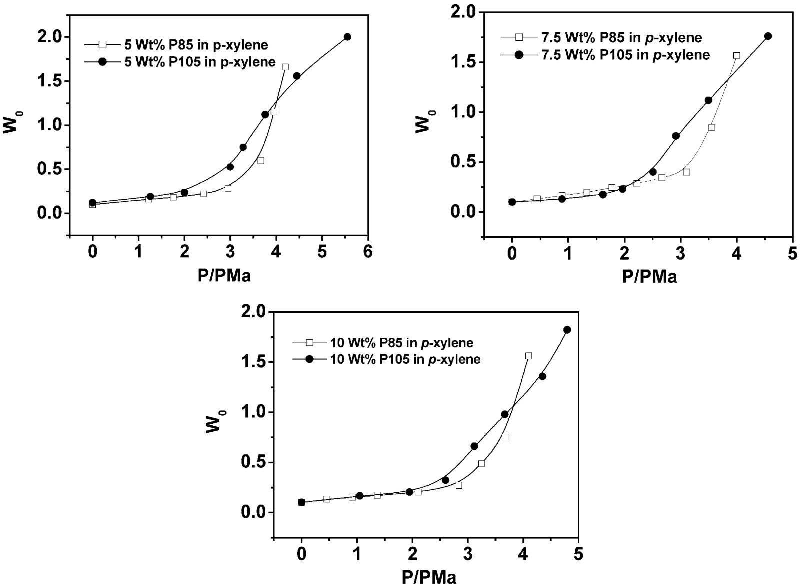

Fig. 5. Dependence of maximum W_0 on pressure of ethylene and initial concentration (*p*-xylene-basis) of P85 and P105 in *p*-xylene 40 °C.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (20133030, 20374057).

References

[1] Luisi PL, Straub BE. Reverse micelles. New York: Plenum Press; 1984.
[2] Phelps DK. Abstracts of papers of the American chemical society. Part 2; 2002. p. 224.
[3] Biswas R, Pal SK. Chem Phys Lett 2004;387:221.
[4] Sugimoto T, Kimijima K. J Phys Chem B 2004;107:10753.
[5] Zhong Q, Baronavski AP, Owrutsky JC. J Chem Phys 2003;119:9171.
[6] Hambardzumyan A, Aguie-beghin V, Daoud M, Douillard R. Langmuir 2004;20:756.
[7] Sosnik A, Cohn D. Biomaterials 2004;25:2851.
[8] Bohner M, Ring TA, Rapoport N, Caldwell KD. J Biomater Sci, Polym Ed 2002;13:733.
[9] Sosnik A, Cohn D, San Roman JS, Abraham GA. J Biomater Sci, Polym Ed 2003;14:227.
[10] Rabelo APB, Tambourgi EB, Pessoa A. J Chromatogr B 2004;807:61.
[11] Mays H, Almgren M. J Chem Phys 1999;103:9432.
[12] Alexandridis P, Andersson K. J Phys Chem B 1997;101:8103.
[13] Alexandridis P, Andersson K. J Colloid Interface Sci 1997;194:166.
[14] Jain NJ, Aswal VK, Goyal PS, Bahadur P. Colloids Surf A 2000;173:85.
[15] Wanka G, Hoffmann H, Ulbricht W. Macromolecules 1994;27:4145.
[16] Booth C, Attwood D. Macromol Rapid Commun 2000;21:501.
[17] Alexandridis P, Hatton TA. Colloids Surf A 1995;96:1.
[18] Kim SH, Jo WH. J Chem Phys 2002;117:8565.
[19] McHugh MA, Krukonis VJ. Supercritical fluids extraction: principles and practice. Stoneham MA: Butterworth-Heinemann; 1994.
[20] De Gioannis B, Jestin P, Subra P. J Cryst Growth 2004;262:519.
[21] Catchpole OJ, Grey JB, Mitchell KA, Lan JS. J Supercrit Fluids 2004;29:97.
[22] Kaneko S, Yamagami Y, Tochihara H, Hirasawa I. J Chem Eng Jpn 2002;35:1219.
[23] Zhang HF, Lu J, Han BX. J Supercrit Fluids 2001;20:65.
[24] Jarmer DJ, Lengsfeld CS, Randolph TW. J Supercrit Fluids 2003;27:317.
[25] Muhrer G, Mazzotti M, Muller M. J Supercrit Fluids 2003;27:195.
[26] Owens JL, Anseth KS, Randolph TW. Langmuir 2003;19:3926.
[27] Muhrer G, Mazzotti M. Biotechn Progr 2003;19:549.
[28] Zhang R, Liu J, He J, Han BX, Zhang XG, Liu ZM, et al. Macromolecules 2002;35:7869.
[29] Zhang R, Liu J, He J, Han BX, Liu ZM, Jiang T, et al. Macromolecules 2003;36:1289.
[30] Zhang R, Liu J, He J, Han BX, Wang B, Sun DH. J Colloid Interface Sci 2004;276:414.
[31] The data of HLB and cloud point derive from the webpage of BASF. The URL is: http://www.basf.com/static/OpenMarket/Xcelerate/Preview_cid-982931199931_pubid-974236729499_c-Article.html
[32] Heitz MP, Carlier C, deGrazia J, Harrison KL, Johnston KP, Randolph TW, et al. Phys Chem B 1997;101:6707.