Macromol. Symp. **2010**, 298, 167–173 DOI: 10.1002/masy.201000028

Effect of two Kinds of Imidazolium Ionic Liquids on the Microemulsion Polymerization of Methyl methylacrylate

Jingjing Lu,[1] *Yunsheng Ding,**[1,2] *Yun Yu,*[1] *Shuying Wu,*[1] *Wanggao Feng*[1]

Summary: In this paper, the microemulsion polymerization of methyl methylacrylate (MMA) was carried out with single and gemini ionic liquids as emulsifier including 1-N-tetradecyl-3-methylimidazolium bromide ($C_{14}MIM \cdot Br$) and 1, 4-Bis (3-tetradecylimidazolium-1-yl) butane bromide ($C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$) respectively, and they were all have typical microemulsion polymerization characters of MMA, but the process of polymerization directly depends on the structure of the imidazolium ionic liquids. The structure and concentration of ionic liquids have effects on the resulted latex particle sizes of PMMA, and much smaller size latexes of PMMA could be gotten with $C_{14}MIM \cdot Br$ as emulsifier than $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ in polymerization. On the other hand, the structure of emulsifier has the effects on the molecular weight (MW) and molecular weight distribution (MWD) of PMMA, so the resulting PMMA prepared from microemulsion polymerization with $C_{14}MIM \cdot Br$ as emulsifier has higher MW but narrower MWD than that of PMMA with the same dosage of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ as emulsifier.

Keywords: emulsifier; imidazolium ionic liquids; latex; methyl methylacrylate; microemulsion polymerization

Introduction

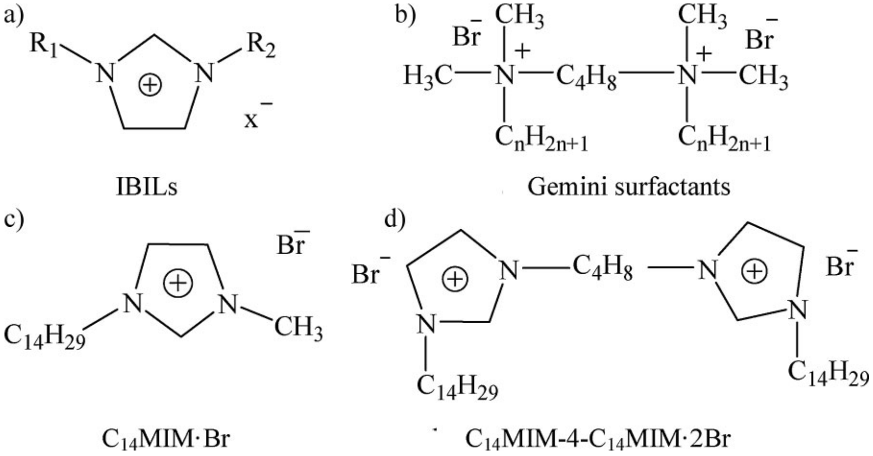
Room temperature ionic liquids (RTILs) are a class of compounds composed entirely of ions. Most of them are liquids below 373 K. In recent year, RTILs have attracted considerable attention due to their unique properties, such as negligible vapor pressure, unique physicochemical and solvation properties et al.[1–3] RTILs can provide highly polar environment for free radical polymerization,[4] atom transfer radical polymerization (ATRP),[5] reversible addition-fragmentation transfer (RAFT).[6] Some groups have investigated the incorporation of surfactants with/without RTILs in micellar solution and emulsion compositions.[7] Especially among the RTILs, imidazolium-based ionic liquids (IBILs) are used widely due to their potential applications in various areas.[8–10] The typical structure of IBILs (Figure 1(a)), which contains imidazolium and alkyl chain, is similar to the conventional cationic surfactants. Meanwhile, their usage as surfactant has gained considerable attention and investigation.[11–12]

Gemini surfactants consist of two hydrophobic side chains and two polar headgroups, which are covalently bound together through a spacer group as shown in Figure 1(b). Recently, they have drawn increased attention owing to their advanced properties compared to those of conventional single-chain surfactants.[13] The application of cationic dimeric ("gemini") surfactants as emulsifier in the microemulsion polymerization of styrene has been reported by Michael Dreja.[14] In our previous work, a geminal imidazolium ionic liquid, $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$

---

[1] Institute of Polymer Materials & Chemical Engineering, School of Chemical Engineering, Hefei University of Technology, Hefei, 230009, China
Fax: +86-551-2901545; E-mail: dingys@ustc.edu

[2] Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei, 230009, China



IBILs

Gemini surfactants

C_{14}MIM·Br

C_{14}MIM-4-C_{14}MIM·2Br

Figure 1.
Molecular structures of ionic liquids (a) imidazolium-based ionic liquids (IBILs), (b) Gemini surfactants, (c) 1-N-tetradecyl-3-methylimidazolium bromide(C_{14}MIM·Br), (d)1, 4-Bis (3-tetradecylimidazolium-1-yl) butane bromide(C_{14}MIM-4-C_{14}MIM · 2Br).

(Figure 1(d)) with two imidazolium rings and two aliphatic chains, linked by a 1,4-butanediyl group was synthesized. It shows excellent physical, chemical properties and potential application as emulsifier.[15–16]

In order to obtain nano- or micro- sized latexes containing higher polymer contents and lower surfactant dosage, the high-performance surfactant should be developed without the demand of co-surfactant. Gemini IBILs have a potential to be employed as such kind of surfactant in microemulsion polymerization since they have special structures and properties. In this paper, we investigate the microemulsion polymerization of MMA without cosurfactant in three-component system involving water, MMA and IBILs. To our knowledge, there are being increasing studies in microemulsion polymerization with ionic liquids as emulsifier, but few reports on the microemulsion polymerization stabilized only by IBILs without co-surfactant.[17]

Experimental Part

Materials and Equipment

Methyl Methylacrylate (MMA, Sinopharm Chemical Reagent Co., Ltd) was washed by 5 wt% NaOH and deionized water to eliminate the inhibitor and oligomeric impurities. Further purification was carried out by distillation at 50 °C/16.5kPa, and then the purified monomer was stored at about 0 °C. Ammonium persulfate (APS, Luzhou RheinPerChemie Co., Ltd.) was recrystallized from doubly distilled water. C_{14}MIM · 2Br and C_{14}MIM-4-C_{14}MIM ·2Br were synthesized according to the literature.[15]

Microemulsion Polymerization of MMA

Dilatometry was used to study the kinetics of microemulsion polymerization. The dilatometer consisted of a 17-mL Erlenmeyer flask and a 20 cm long capillary with diameter of 2 mm. The reactants including monomer (methyl methacrylate), initiating agent (APS) and surfactant (C_{14}MIM · Br) were charged into the flask and stirred magnetically. Then emulsion was bubbled slowly with highly pure nitrogen gas about 5 min to get rid of the dissolved oxygen. The reaction conditions were kept constant, when C_{14}MIM · Br was replaced by C_{14}MIM-4-C_{14}MIM · 2Br. All reactants were introduced directly into the dilatometer and placed in a thermostatic water bath at 60 ± 0.1 °C. The change of liquid level in the capillary of the dilatometer was monitored by a cathetometer. The polymer conversion was calculated from the volume change of liquid in the capillary as a function of time.

Characterization

Particle Size Determination

The particle sizes of microemulsion latexes were derermined used as Malvern 2000 laser granularity analyzer, and its accuracy is ± 1% with the Malvern Quality Audit Standard. Before the measurements, latexes were diluted with deionized water 100–160 times to minimize interparticle interaction.

Molecular Weight Determination

The polymerized methyl methylacrylate latexes were precipitated in 10 wt% sulfuric acid and washed by deionized water until free of surfactant, then the PMMA was dissolved in 2ml tetrahydrofuran (THF, AR) and reprecipitate in methanol (AR), the resulting white flocculent deposite was kept in oven at 50 °C for two hours to remove the solvent. The number molecular weight (M_n) and MWD of PMMA were measured on a Waters 1515 gel permeation chromatography (GPC) equipped with microstyragel columns (10^3, 10^4, 10^5 Å) and Waters RI detector at 40 °C. The columns were calibrated using monodisperse polystyrene standards (1mg/mL in THF) with a tetrahydrofuran mobile phase (Aldrich, HPLC grade) at a flow rate of 0.3 ml/min. Since some fraction of polymer has high molecular weight, the GPC results obtained are not absolute but can be compared to obtain trends in M_n and MWD.

Results and Discussion

Micromulsion Polymerization Process for MMA

The micromulsion polymerizations of methyl methylacrylate were carried out with C_{14}MIM-4-C_{14}MIM · 2Br and C_{14}MIM · Br as emulsifier and monitored with dilatometry. Figure 2(a) illustrates the conversion as a function of time for the polymerization of MMA. As shown in the corresponding polymerization rate (Rp) to time plots (Figure 2(b)), there is no incubation period, which indicates that polymerization of MMA using IBILs as emulsifier is a typical microemulsion polymerization.[18] Such polymerization consists of only acceleration and deceleration periods and shows no extended region of constant rate as often present in traditional emulsion polymerization. Besides, the maximum Rp of MMA in the polymerization with C_{14}MIM · Br as emulsifier is later than it in the polymerization with C_{14}MIM-4-C_{14}MIM · 2Br as emulsifier.

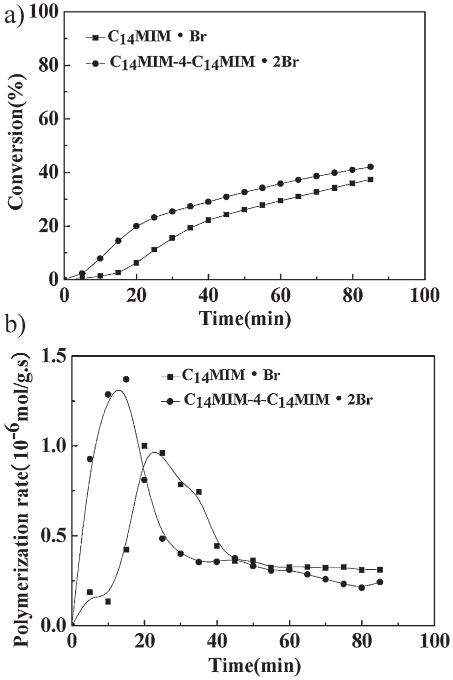


Figure 2.

Conversion versus time and Rp of MMA with C_{14}MIM · Br and C_{14}MIM-4-C_{14}MIM · 2Br as emulsifier respectively (MMA content is 10.00 wt% and the emulsifier content is 0.49 wt%).

Effects of the Dosages of C_{14}MIM · Br and C_{14}MIM-4-C_{14}MIM·2Br on the Rp of MMA

In the MMA, water and C_{14}MIM · Br ternary system, the weight ratio of water to MMA was kept constant at 9.00, and

Table 1.
Compositions for Polymerization of MMA.

system	MMA (wt%)	Ionic liquids/MMA (wt%)	Water/MMA
ST1	10.00	5	9.00
ST2	9.90	10	9.00
ST3	9.80	20	9.00
ST4	9.70	30	9.00
ST5	9.60	40	9.00

APS was 0.04 mmol in all systems. The mass ratios of C_{14}MIM · Br to MMA were chosen to be 0.05, 0.10, 0.20, 0.30 and 0.40, which meant that the dosages of surfactant were 0.49 wt%, 0.99 wt%, 1.98 wt%, 2.98 wt% and 3.99 wt% respectively (shown in the Table 1). The curves of conversion and polymerization rate as a function of time are given in Figure 3. The curve shows that the polymerization is influenced by the amounts of IBILs. can be seen that there is no latex particle generation stage; only a latex particle growing stage can be observed. Thus, time of the micelle particle formation period was short. When the dosage of C_{14}MIM · Br increased from 0.49 wt% to 3.99 wt%, only one maximum of Rp was observed in all polymerizations (Figure 3(b)), but the maximum of Rp varied with the amount of C_{14}MIM · Br. The maximum of Rp increased when the dosage of C_{14}MIM · Br changed from 0.49 wt% to 0.99 wt%, while the maximum of Rp decreased when the amount of C_{14}MIM · Br increased from1.98 wt% to 3.99 wt%. In all of microemulsion polymerizations the Rp of MMA with 0.99 wt% of C_{14}MIM · Br was higher than in other systems.

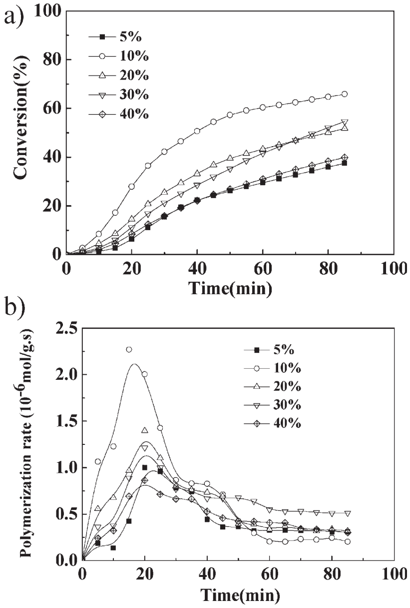


Figure 3.
The curves of conversion and Rp of MMA to time at 60 °C with different dosages of C_{14}MIM · Br.

In all polymerizations the mass ratio of water to MMA was the same but the dosages of C_{14}MIM-4-C_{14}MIM · 2Br were 0.49 wt%, 0.99 wt%, 1.98 wt%, 2.98 wt% and 3.99 wt% respectively. We found all polymerization systems could produce bluish-transparent and stable latexes regardless the variation of dosage of C_{14}MIM-4-C_{14}MIM · 2Br, but the Rp of MMA increased with the dosage of C_{14}MIM-4-C_{14}MIM · 2Br up. However, there were differences when the emulsifier varied from 0.49 wt% to 3.99 wt%, so the kinetics of microemulsion polymerization of MMA depend on the amount of IBILs in the systerm.

In microemulsion polymerization with C_{14}MIM · Br as emulsifier, considerable amounts of MMA dissolved in the aqueous phase because of its water solubility. Free radicals generated from the water-soluble APS would react with MMA solubilized in the aqueous phase to form soluble oligomeric radicals. Therefore, homogeneous nucleation could be dominant for these monomers. The soluble oligomeric radicals can absorb surfactant molecules to form particles. Then these particles swell with MMA and propagate as micelle particles. The radicals grow by competition between micellar nucleation and homogeneous nucleation. So, the combined mode of particle nucleation (monomer-swollen micelle nucleation and homogeneous nucleation) exists in the microemulsion polymerization of MMA.[19] When the dosage of C_{14}MIM · Br increase from 0.49 wt% to 0.99 wt%, the number of micelles increased, so there are more soluble oligomeric radicals in micelles, and this may be the reason for Rp of MMA to increase. When the dosage of $C_{14}MIM \cdot Br$ continues to increase, the number of micelles should remain stable but the exceeding $C_{14}MIM \cdot Br$ would cover the layer of micelles. As a result, the ability of micelles to capture oligomeric radicals decreases. This may be the main reason for a decrease of Rp of MMA with increasing amounts of $C_{14}MIM \cdot Br$.

On the other hand, cationic gemini IBILs have CMC values 1 or 2 orders of magnitude smaller than the conventional "single" IBILs, so there are large numbers of micelles in the $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ systems compared to $C_{14}MIM \cdot Br$ systems at the same concentration level.[20] As the concentrations of MMA and initiator are constant, soluble oligomeric radicals generated by APS are also the same in all systems, so there is higher Rp of the microemulsion polymerization in the $C_{14}MIM\text{-}4\text{-}C_{14}MIM{\cdot}2Br$ system. The oligomeric radicals could be captured by micelles more easily, and this may be the main reason for Rp to increase with increasing amounts of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$. There are two peaks in curves of Rp when the dosages of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ increased from 1.98 wt% to 3.99 wt% as shown in Figure 4(b), and this may be attributed to a change of the structure of micelles with increasing amounts of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$.[21]

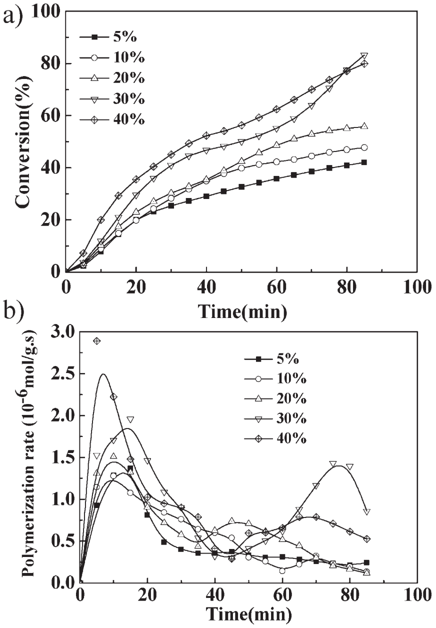


Figure 4.
Plots of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ dosages on the conversions and Rp of MMA versus time at 60 °C.

Effect of Mass Ratio of $C_{14}MIM \cdot Br$ and $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ to MMA on the Average Size of PMMA Latexes

Many references have reported that the structures of surfactants, such as the imidazole ions of IBILs and the number of alkyl chain, play a great role in the microemulsion formation.[22–23] Our study showed that the kinetics of microemulsion polymerization of MMA is affected by the structure of surfactants. The average particle size of polymethyl methylacrylate was strongly dependent both on the type and content of the IBILs. Figure 5 shows the effect of mass ratio of $C_{14}MIM{\cdot}Br$ to MMA on the particle size in microemulsion. The average particle size decreased from about 42 nm to 22 nm when the mass ratio of $C_{14}MIM{\cdot}Br$ to MMA increased from 5% to 40%. When the $C_{14}MIM{\cdot}Br$ concentration in water kept increasing and the content of solubilized MMA remained constant, the number of latex particles became larger, which further reduced the size of latex particles. With $C_{14}MIM{\cdot}Br$ further increased the additional $C_{14}MIM{\cdot}Br$ would cover the layer of micelles and any further increase of the surfactant will have no impact on the size of the micelle particles. However, when the mass ratio of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$, a kind of geminal ionic liquid, to MMA increased from 5% to 10%, the average size of PMMA latexes decreased from 82 nm to 49 nm. Furthermore, the latex size increased from 49 nm to 87 nm when the weight ratio of $C_{14}MIM\text{-}4\text{-}C_{14}MIM \cdot 2Br$ to MMA changed from 10% to 40%.

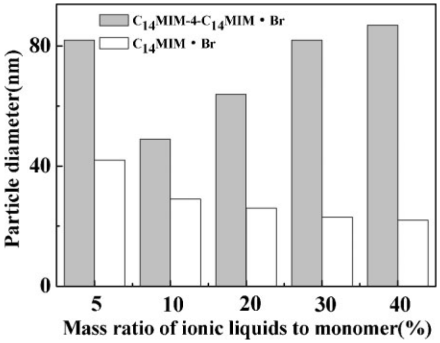


Figure 5.
Influence of mass ratio of IBILs to MMA on the average diameter of latex particle of PMMA.

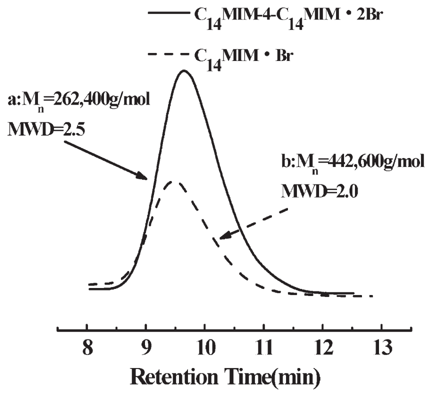


Figure 6.
GPC curves of PMMA obtained from the polymerization with C_{14}MIM-4-C_{14}MIM · 2Br (a) and C_{14}MIM · Br (b) as emulsifier respectively (MMA content is 9.60% wt% and the emulsifier content is 3.99 wt%).

Molar Mass and Dispersity of PMMA

For comparison MW and dispersity of PMMA obtained from microemulsion polymerization in both C_{14}MIM·Br and C_{14}MIM-4-C_{14}MIM · 2Br as emulsifier are shown in Figure 6. The results of GPC measurement showed that the M_n of PMMA obtained from the microemulsion polymerisation in the presence of C_{14}MIM-4-C_{14}MIM · 2Br and C_{14}MIM·Br were 262.400 g/mol and 442.600 g/mol respectively. In addition, it can be seen that both GPC curves of PMMA have a single peak; narrower molecular weight distribution was observed for the system with C_{14}MIM·Br.

Conclusion

In our work, a series of microemulsions consisting of MMA, water, two different IBILs was polymerised with APS to produce stable and transparent microlatexes. The different structures of IBILs have a different impact on the forming of micelle, the kinetics of microemulsion polymerization of MMA and the size of latex particles. In systems with C_{14}MIM-4-C_{14}MIM · 2Br, the particle size of microlatex decreased from 82 nm to 49 nm at first, and then it increased to 87 nm when the mass ratio of C_{14}MIM-4-C_{14}MIM · 2Br to MMA increased, while the latex particle sizes of PMMA microlatex decreased from about 42 nm to 22 nm when the mass ratio of C_{14}MIM·Br to MMA increased from 5% to 40%. The number average molar mass of PMMA from the microemulsion polymerization in the presence of C_{14}MIM·Br is 4.4×10^5g/mol, which is higher than that from the microemulsion polymerisation in the presence of the same dosage of C_{14}MIM-4-C_{14}MIM · 2Br. The dispersity of MMA stabilized by C_{14}MIM·Br is 2.0, which is narrower than that of the C_{14}MIM-4-C_{14}MIM · 2Br system.

Acknowledgements: We thank Prof. Jun Zhang at Institute of Chemistry Chinese Academy of Sciences (ICCAS) for insightful discussions on the synthesis of Ionic Liquid and its application, and also thank people from University of Science and Technology (USTC) for their kind help on the characterization. This research is financially supported by Nature Science Foundation of Anhui Province (090414180), Natural Science Foundation of China (50973025), Important Scientific Research Items of University from Anhui Province (KJ2009A019), Innovation Foundation for Students of Hefei University and Technology (XS08036), and Innovation items of Experiment of Hefei University and Technology (2009CXSY119, 2009CXSY114).

[1] P. Wasserscheid, W. Keim, *Angew chemie International Edition* **2000**, *39*, 3772.
[2] K. R. Seddon, *J. Chem. Technol. Biotechnol* **1997**, *68*, 351.

[3] T. Welton, *Chemical Review*, **1999**, *99*, 2071.

[4] H. W. Zhang, K. L. Hong, W. Jimmy, *J.Am.Chem.Soc.* **2005**, *193*.

[5] J. C. Adrian, D. M. Haddleton, A. F. Stefan, *Chem. Commun* **2000**, *14*, 1237.

[6] S. Perrier, T. P. Davis, A. J. Carmichael, D. M. Haddleton, *Eur. Polym. J* **2003**, *39*, 417.

[7] J. L. Anderson, V. Pino, E. C. Hagberg, V. V. Sheares, D. W. Armstrong, *Chem. Commun* **2003**, 2444.

[8] T. Singh, A. Kumar, *J. Phys. Chem. B* **2007**, *111*, 7843.

[9] L. George, R. Philip, *Langmuir.* **2001**, *17*, 6138.

[10] T. Iimori, T. Iwahashi, K. Kanai, *J. Phys. Chem. B* **2007**, *111*, 4860.

[11] A. Beyaz, S. O. Woon, V. Prakash Reddy, *Colloids Surf., B* **2004**, *36*, 71.

[12] Y. S. Ding, H. O. Tang, X. M. Zhang, S. Y. Wu, R. Y. Xiong, *J. Appl. Polym. Sci.* **2008**, *109*, 1138.

[13] F. M. Menger, C. A. Littau, *J. Am. Chem. Soc.* **1993**, *115*, 10083.

[14] M. Dreja, B. Tieke, *Langmuir* **1998**, *14*, 800.

[15] Y. S. Ding, M. Zha, J. Zhang, S. S. Wang, *Colloids Surf., A* **2008**, *298*, 201.

[16] L. Jared, R. D. Anderson, E. Arkady, W. A. Daniel, *J. Am. Chem. Soc* **2005**, *127*, 593.

[17] Z. Qiu, J. Texter, *Curr. Opin, Colloid Interface Sci.* **2008**, *13*, 252.

[18] C. H. Zhang, Q. Wang, H. S. Xia, G. H. Qiu, *Eur. Polym. J.* **2002**, *38*, 1769.

[19] J. Chen, Z. C. Zhang, *Eur. Polym. J.* **2007**, *43*, 1188.

[20] F. Li, M. J. Rosen, S. B. Sulthana, *Langmuir.* **2001**, *17*, 1037.

[21] S. Magdassi, M. B. Moshe, Y. Talmon, D. Danino, *Colloids Surf., A* **2003**, *212*, 1.

[22] T. Singh, A. Kumar, *J. Phys. Chem. B.* **2007**, *111*, 7843.

[23] D. Seth, A. Chakraborty, P. Setua, N. Sarkar, *Langmuir.* **2006**, *22* 18, 7768.