

Preparation of Nanometer-Sized Poly(methacrylic acid) Particles in Water-in-Oil Microemulsions

Qiuyu Zhang,¹ Xujin Bao,² Mian Lin,² Douglas J. Hourston²

¹Department of Applied Chemistry, Northwestern Polytechnical University, Xian, 710072, China

²Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom

Received 9 February 2005; accepted 22 August 2005

DOI 10.1002/app.23619

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A water-in-oil microemulsion, water-in-cyclohexane stabilized by poly(ethylene glycol) *tert*-octylphenyl, was developed to prepare poly(methacrylic acid) (PMAA) particles. Up to 100% conversion of the amphiphilic monomer, methacrylic acid (MAA), which could not be converted to the polymer efficiently in a dioctylsulfosuccinate sodium salt/toluene microemulsion, was achieved. The viscosity-average molecular weight of the PMAA prepared was 1.45×10^5 g/mol. The effects of some polymerization parameters, including the reaction temperature and the concentrations of the initiator and the monomer, on the polymerization of MAA were investigated. The results showed that the polymerization rate of MAA was slower than that of

acrylamide in the microemulsions reported in the literature. The degree of conversion increased with the initiator concentration, reaction temperature, and monomer concentration. However, the stable microemulsions became turbid during the polymerization when the reaction temperature was at 70°C or at a high monomer concentration (40 wt %). The synthesized PMAA particles were spherical and had diameters in the range of ~50 nm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2497–2503, 2006

Key words: poly(methacrylic acid); microemulsion polymerisation; nanoparticles

INTRODUCTION

A microemulsion may be defined as a thermodynamically stable isotropic dispersion of two immiscible liquids consisting of nanometer-sized domains of one or both liquids in the other, stabilized by an interfacial film of surface-active molecules. They can be classified as oil-in-water and water-in-oil (w/o) according to the dispersed and continuous phases. In both cases, the dispersed phase consists of monodispersed droplets in the size range of 10–100 nm.^{1,2}

Recently, w/o (inverse) microemulsions have attracted much more attention as a route for preparing inorganic nanomaterials^{3–5} and high-molecular-weight water-soluble polymers.^{1,6} This route offers a novel and versatile technique for the synthesis of a wide variety of nanophase materials with the ability to control precisely the size of the particles formed and to yield polymer particles with a narrow particle size distribution and excellent latex stability. It also offers a unique method for controlling the kinetics of particle formation and growth by varying the physicochemical characteristics of the microemulsion system.⁴

Most studies on the polymerization of water-soluble monomers via inverse microemulsions have mainly focused on acrylamide (AM).^{7–11} The use of the microemulsion approach has led to stable and clear micro-latexes with uniform diameters of about 50 nm. Each of the final latex particles contains only about one high-molecular-weight macromolecule in a collapsed state.¹ More recently, polymerizations in inverse microemulsions of other water-soluble monomers, including 2-methacryloyl oxyethyl trimethyl ammonium chloride, have also been reported.^{12–15}

Poly(methacrylic acid) (PMAA) possesses a wide range of physical and chemical properties, such as good variations in the hydrophilicity, hardness, toughness, adhesion, complex formation, a special pH-responsive ability, and electrolyzable properties, and this makes it a good candidate for many applications.^{16,17} In some cases, nanometer-sized PMAA particles are preferred, such as controlled drug delivery^{18,19} and self-assembly processes.²⁰ Obviously, the inverse microemulsion route offers a possible way of preparing nanometer-sized PMAA particles as the polymerization is carried out in restricted small droplets in the microemulsion system. However, so far, no results have been reported on the polymerization of methacrylic acid (MAA) with an inverse microemulsion method.

In this work, w/o microemulsion systems were used to prepare nanometer-sized PMAA particles. The effects of the reaction parameters, including the temperature and the initiator and monomer concentrations, on the

Correspondence to: X. Bao (x.bao@lboro.ac.uk).

Contract grant sponsor: Royal Society.

Contract grant sponsor: Loughborough University.

polymerization were investigated. The mechanism of the formation of the PMAA nanoparticles is discussed and compared with the ionic surfactant sodium bis(2-ethylhexylsulfosuccinate) (AOT) system.

EXPERIMENTAL

Materials

The surfactants polyoxyethylene(5)nonylphenylether (Igepal-CO-520), poly(ethylene glycol) *tert*-octylphenyl (Triton-114), AOT, and sorbitan trioleate (Tween-85) were purchased from Sigma–Aldrich (Gillingham, United Kingdom), were analytical-grade, and were used without further purification. Toluene, cyclohexane, and 2,2,4-trimethylpentane (analytical-grade) were purchased from Fisher Scientific (Loughborough, United Kingdom) and used as the oil phase. MAA, purchased from Sigma–Aldrich, was vacuum-distilled at 60°C just before the reaction. *N,N*-Methylenebis(acrylamide), purchased from Fisher Scientific, was recrystallized before use. Analytical-grade potassium persulfate (KPS) was used as the initiator without further purifying treatment. Acetone and ethanol were used as supplied. Distilled water was used throughout the experiments.

Loading and partitioning of the monomer solution

The loadings of the monomer and its salt solution in the microemulsions were measured. The monomer, or its ammonium salt solution, was added dropwise into the prepared oil/surfactant solution, which was stirred continuously. The next drop of monomer was not added until the system had turned transparent. If the system did not turn back to the transparent state after 30 min, this point was taken as the loading of the monomer in the microemulsion. The transparency of the system was judged by visual observation, and the experiments were conducted at 20°C.

The partitioning of the monomer solution in the microemulsion systems was measured with the following procedure. The MAA monomer (2 g) was added to a mixture of 10 g of distilled water and 10 g of oil. The resulting mixture was well shaken to allow the monomer to dissolve into the water and oil phases. Then, the mixture was poured into a separating funnel. The funnel was kept still for 4 h to allow the oil and water phases to separate fully. The final weight of MAA in the two phases (water and oil) was determined, and the partitioning percentage of the monomer in the oil and water was calculated. The experiments were carried out at 20°C.

Polymerization

MAA solutions were prepared with, or without, a crosslinking agent, *N,N'*-methylenebisacrylamide (cross-

TABLE I
Loadings of MAA Aqueous Solutions in Microemulsion Systems (Surfactant/Oil = 3/7 w/w) at 20°C

Microemulsion system	Loading [aqueous MAA solution/surfactant (g/g)]
AOT/toluene	0.51
Igepal-CO-520/cyclohexane	0.77
Triton-114/cyclohexane	1.54

linker/monomer = 0.01 mol %). The monomer solution and the initiator were added to the oil/surfactant solution. The amount of KPS was varied and quoted as the weight percentage of the total weight of the monomer in the microemulsion. Oxygen was removed via the bubbling of nitrogen through the microemulsion reaction medium for about 30 min at the ambient temperature. The polymerizations were carried out at 40–70°C for a certain time. The polymer was precipitated out by the addition of acetone and then washed with acetone five times to remove the surfactant and any monomer residues. The polymers were vacuum-dried at 40°C for 48 h before characterization.

Characterization

The size and morphology of the polymer particles were investigated with transmission electron microscopy (TEM) (JEM 100CX, JEOL Ltd., Tokyo, Japan). The polymer samples were diluted with acetone. A copper grid coated with carbon film was covered with a hemispherical drop of the aforementioned diluted latex. The molecular weights of PMAA were determined by their relative viscosities in 0.002M HCl aqueous solutions with an Ostwald viscometer. The molecular weights of the polymers were calculated with the following equation:²¹

$$[\eta] = 66 \times 10^{-3} M^{0.5} (\text{cm}^3/\text{g}) \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and M is the viscosity average molecular weight.

RESULTS AND DISCUSSION

Selection of the microemulsion systems

It is desirable for selected microemulsion systems to have a high loading of the aqueous monomer solutions and a relatively high stability with temperature, which is particularly important for thermally induced radical polymerization. Based on our previous work in optimizing components of microemulsion systems that have relatively high water loadings, three w/o microemulsion systems—AOT/toluene/aqueous MAA solution, Triton-114/cyclohexane/aqueous MAA solution, and Igepal-CO-520/cyclohexane/aqueous MAA solution—were employed in this research. The loadings of the

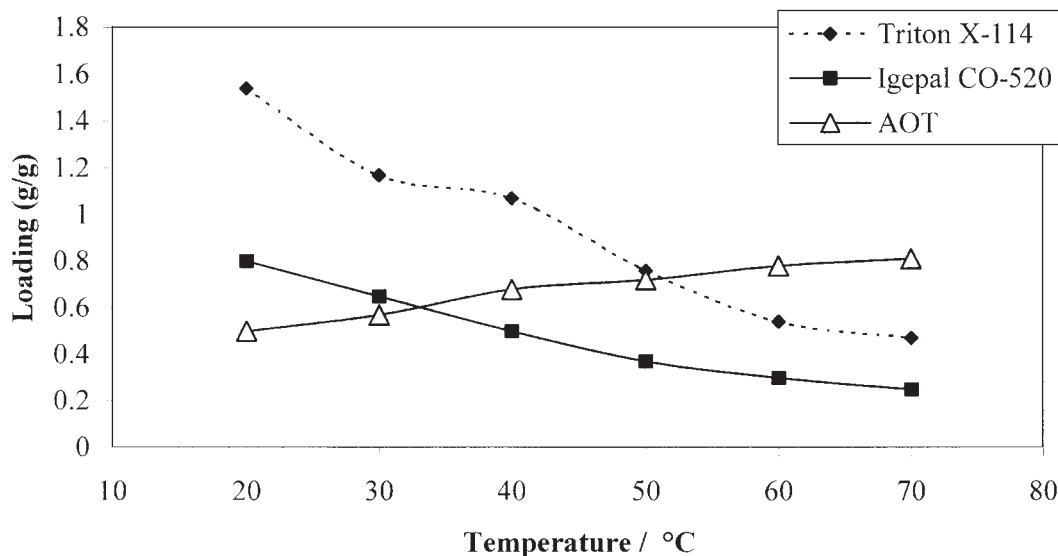


Figure 1 Effect of temperature on the loading of aqueous MAA solutions in microemulsion systems [MAA solution/surfactant (g/g)].

aqueous MAA solution (25 wt %) in these three microemulsion systems at 20°C are listed in Table I. Among the three microemulsion systems, the highest loading of the MAA solution was obtained with the Triton-114 system.

The effect of temperature on the loading of the aqueous MAA solution was also investigated and is shown in Figure 1. Both the Igepal-CO-520 and Triton-114 systems were rather sensitive to changes in the temperature. The loading of the aqueous MAA solution in these two systems decreased with increasing temperature. On the contrary, the AOT system was more stable with a change in the temperature, and the loading even increased with the temperature increasing. As the radical polymerization normally is carried out at a temperature greater than 60°C and the Igepal-CO-520 system had a very low loading at that temperature, the Triton-114 and AOT systems were chosen for the preparation of PMAA.

The polymerizations were carried out at 60°C, and KPS was used as the initiator. The degrees of conversion of MAA in these two microemulsion systems are given in Table II. A very limited conversion of about 3.4% was obtained in the AOT/toluene system. This is quite different from the polymerization of AM in the

AOT/toluene/water system, which has been studied extensively,^{1,7-9} and 100% conversion of the monomer to the polymer was achieved in a few minutes. A better degree of MAA conversion of nearly 15% was observed in the AOT/cyclohexane system. However, a complete MAA monomer conversion (100%) was achieved in the Triton-114/cyclohexane system.

The low degree of conversion of MAA in the AOT system may be related to the partitioning of the monomer in the water and oil phases. The partitioning of aqueous MAA in water and different oil phases is shown in Table III. The partition of MAA in the water phase was generally very low. Only 0.7% MAA stayed in the water phase in the water/toluene mixture, but 14% MAA dissolved in the water phase in the water/cyclohexane system. Therefore, it can be assumed that the majority of the MAA monomer was partitioned into the oil phase in the AOT/toluene/monomer microemulsion system.

Moreover, the polymerization of MAA generally took place in the water phase in the microemulsion system when the water-soluble initiator, KPS, was used, as the initiating radicals formed in a dispersed water phase and were, at any time, preferentially captured by un-nucleated micelles containing MAA monomer.¹ That led to the very low conversion of MAA in the AOT/toluene system, which indicated

TABLE II
Degree of Conversion of MAA Polymerized
in Three Microemulsion Systems (Surfactant/Oil
= 3/7 wt/wt) at 60°C for 6 h

Microemulsion system	Triton-114/cyclohexane	AOT/toluene	AOT/cyclohexane
Degree of conversion (wt %)	100	3.4	14.9

TABLE III
Percentage of MAA in the Oil and Water Phases
(Water/Oil = 50/50 wt/wt)

	Water phase (wt %)	Oil phase (wt %)
Water/cyclohexane	14.0	86.0
Water/toluene	0.7	99.3

TABLE IV
Effect of Temperature and Reaction Time on the Degree of Conversion (wt %) of MAA^a

Temperature (°C)	Reaction time (h)					
	0.25	0.5	1.0	2.0	4.0	6.0
50	—	—	—	—	—	—
60	7	35	61	92	97	99
70	20	39	69	94	99	100

^a Monomer solution (4.7 wt % in the 3/7 wt/wt Triton-114/cyclohexane microemulsion).

that the partitioning of the monomer in the water and oil phases played an important role in the conversion of the monomer to the polymer in these w/o microemulsions. This was further supported by the increase in the degree of conversion of MMA to 14.9% in the AOT/cyclohexane/MAA microemulsion due to the greater partitioning of MAA in the water phase.

However, the conversion of MAA to PMAA in the AOT/cyclohexane system was much less than that in the Triton-114/cyclohexane system, although the oil phase was the same in both systems; this implied that the surfactants used in these systems may also play an important role. The anionic surfactant, AOT, had a more hydrophilic head than the nonionic surfactant, Triton-114. Hence, a bigger cagelike effect may have been produced by the strong hydrophilic interactions between the polar head groups of AOT, which could lead to lower transfer of the MAA monomer from the oil phase to the water phase during polymerization in the AOT system. As MAA showed only a small partition in the water phase and the monomer in the water phase was used up rapidly, the propagation of the polymer chains needed more monomer, which was transferred from the monomer-rich oil phase to the water phase through the surfactant layer. The stronger cagelike effect caused by the close packing of the AOT molecules restricted this transfer, resulting in a lower degree of conversion. On the other hand, the barrier formed by the nonionic surfactant, Triton-114, at the oil/water interface was electrically neutral and small, so it had lower steric hindrance to the transfer of the monomer from the oil phase to the water phase during polymerization, leading to a complete conversion of MAA in the Triton-114 system.

Effects of the temperature and reaction time on the polymerization of MAA

As the loading of the MAA aqueous solution in the Triton-114/cyclohexane microemulsion system was sensitive to the temperature (see Fig. 1), a lower temperature was preferred to obtain a higher loading of the aqueous monomer solution in the microemulsion system, which resulted in a higher polymer yield. However, as shown in Table IV, no polymer was

precipitated out in the microemulsion systems until the polymerization temperature reached 60°C, and this could be attributed to the low initiation efficiency of KPS at low temperatures in the microemulsion system containing large amounts of the surfactant. It was also observed that the polymerization rate of MAA was not as rapid as that of AM. The latter only needed a few minutes to achieve a total conversion of the monomer to the polymer in a microemulsion.⁷ The polymerization of MAA was slow at the beginning of the reaction, and over a 90% conversion of MAA to PMAA was obtained after 2 h of reaction in our systems (Table IV). It was also observed, from Table IV, that the polymerization rate of MAA increased with the reaction temperature. However, the microemulsions were not stable during polymerization at 70°C as they became slightly opaque.

Effects of the concentrations of the initiator and monomer on the polymerization

The effect of the initiator concentration on the degree of conversion of PMAA was investigated, and the results are summarized in Table V. There was only a 23% conversion obtained when the KPS concentration was 0.56 wt % of the monomer. However, nearly complete conversions were reached when the initiator concentration was larger than 1.01 wt %. There was an initial increase in the molecular weight of the polymers with an increase in the initiator concentration up to 1.01 wt %, and it then decreased with a further increase in the KPS concentration. On the basis of the study of the polymerization of the water-soluble monomer AM in an inverse microemulsion,¹ it is believed that the initiation of the water-soluble monomers occurred in the water pools of the inverse micelles by the free radicals generated from the dissolved initiator in these pools. Hence, the higher the initiator concentration was, the more radicals were produced and the higher the polymerization rate and the degree of conversion were.

The phenomenon of a molecular weight decrease with an increase in the initiator concentration is often the case in conventional inverse emulsion polymerizations of certain acrylic compounds.²² When more initiator was used, more radicals were captured as the

TABLE V
Effects of KPS on the Degree of Conversion and Molecular Weight of PMAA^a

	KPS/monomer (wt %)			
	0.56	1.01	2.16	3.19
Degree of conversion (wt %)	22.6	95.9	98.9	100
Molecular weight × 10 ⁻⁵ (g/mol)	1.67	2.97	1.45	1.44

^a MAA (4.7%) aqueous solution reacted at 60°C for 6 h in the 3/7 w/w Triton-114/cyclohexane microemulsion.

TABLE VI
Effect of the Monomer Concentration on the Conversion and Molecular Weight of MAA^a

	MAA concentration (wt %)		
	12.5	25	40
Degree of conversion (wt%)	95	100	100
Molecular weight $\times 10^{-5}$ (g/mol)	0.43	1.45	0.74

^a Polymerization at 60°C for 6 h in the 3/7 w/w Triton-114/cyclohexane microemulsion.

amount of the surfactant was greatly augmented with respect to that in conventional emulsions, and more nucleated particles were produced, resulting in a lowering of the molecular weights of the polymers. However, the lower molecular weight of the polymer made with 0.56 wt % KPS compared with that made with 1.01 wt % was probably due to chain-transfer reactions caused by the large amount of the surfactant, so the growing chains had more chance to terminate the propagation reactions in the microemulsion systems.

The effect of the monomer concentration on the polymerization was also investigated in terms of the molecular weights and the degrees of conversion of the polymers formed in the Triton-114/cyclohexane microemulsion system (Table VI). The polymerization rate increased with the monomer concentration (Fig. 2), and a complete conversion of the monomer to the polymer was observed after polymerization for 4 h for a monomer concentration of 25 wt % and for 8 h for a monomer concentration of 12.5%; this was much slower in comparison with the polymerization of AM in the AOT/toluene microemulsion system. There was an increase in the molecular weights of the polymers with an increase in the monomer concentration, as

there was more monomer to take part in the propagation reaction.¹ The molecular weights of the polymer decreased when the monomer concentration increased to 40%, and this was accompanied by an observed phase separation.

The molecular weight of PMAA prepared in the Triton-114 system was rather low compared to that of polyacrylamide (PAM) prepared in a microemulsion with AOT as the surfactant [weight-average molecular weight (M_w) $> 1.0 \times 10^6$ g/mol].¹ The surfactant, Triton-114, probably was the reason for this result. Triton-114 has hydroxyl groups that may act as chain-transfer sites to terminate chain growth, leading to the observed low molecular weights. This assumption was supported by the result obtained when we used another surfactant, Tween-85, in which the molecular weight of the synthesized PMAA was larger than 4.1×10^5 g/mol. Tween-85 does not have hydroxyl groups in its molecular structure.

The low polymerization rate of the PMAA synthesized in our microemulsion systems was probably related to the very low partitioning of the MAA monomer in the water phase, as discussed previously. Most of the MAA monomer dissolved in the oil phase, and the concentration of the monomer in the water phase was low at the beginning of the polymerization. As a water-soluble initiator, KPS was used in the polymerization; the initiation occurred in the water phase. Then, these radicals propagated by the addition of the monomer in the water phase to form oligomers that were water-soluble. Because acetone was used as the solvent to wash the product, these oligomers were able to dissolve in this polar solvent, and so no product was found after washing for the polymers synthesized for short reaction times. Growing (nucleated) inverse micelles, for further propagation, collected the

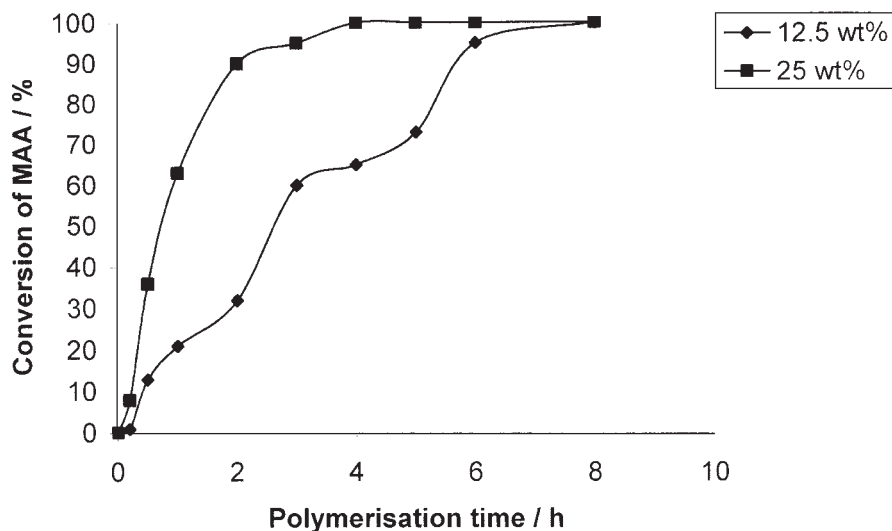


Figure 2 Effect of the monomer concentration on the polymerization rate of MAA in the Triton-114/cyclohexane microemulsion system.

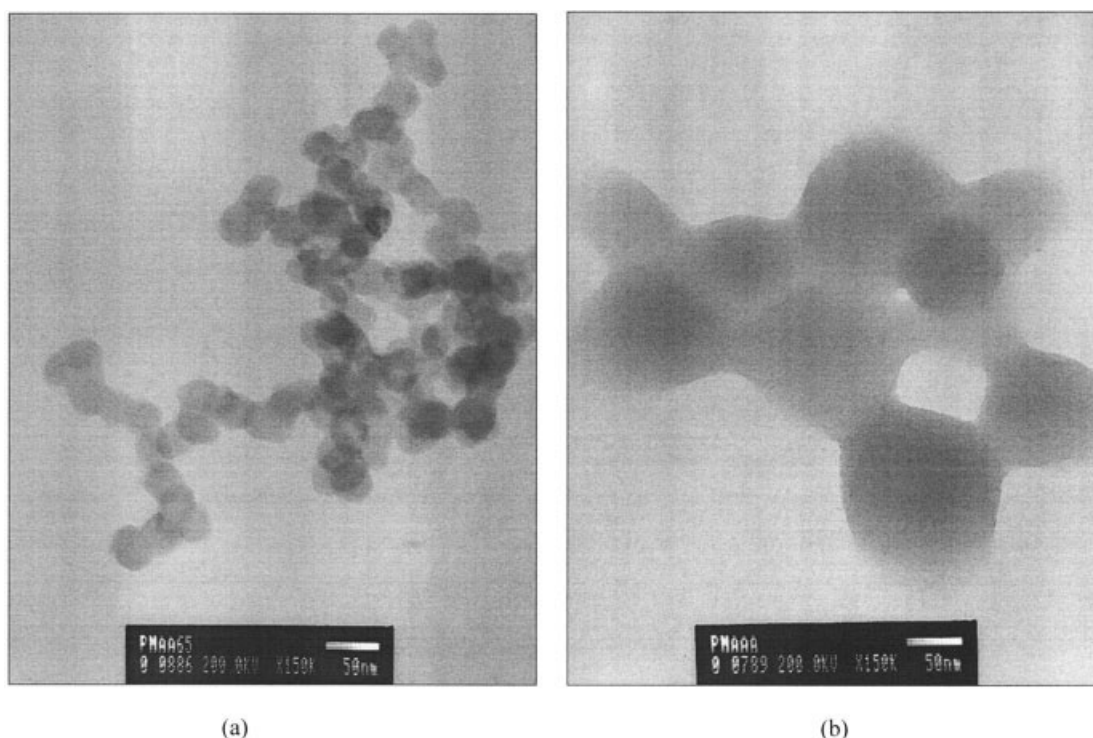


Figure 3 PMAA nanoparticles prepared via polymerization in the Triton-114/cyclohexane microemulsion with monomer concentrations of (a) 25 and (b) 40 wt %.

monomer from the unnucleated inverse micelles via a micelle collision mechanism or by the diffusion of the monomer through the continuous oil phase to the water phase. However, this monomer feeding rate seemed likely to be slow because of the small partitioning of MAA in the water phase and the cage-like effect of the large amount of the surfactant on the transfer of the monomer. That was why the MAA polymerization rate was lower than that of AM.⁷ The dispersability of the monomer from the continuous phase to the disperse phase played a very important role in controlling the polymerization rate.

Morphology of the PMAA particles

Figure 3 shows TEM micrographs of the PMAA synthesized under different reaction conditions. The particles were, in general, spherical and easily aggregated because of the attractions between polar groups. The sizes of the polymer particles were about 30–50 nm [Fig. 3(a)] with a very narrow size distribution when a low monomer concentration (<25 wt %) was used. However, the particle size increased to over 100 nm with a polydisperse size distribution when the polymerization took place at a high monomer concentration [40 wt %; Fig. 3(b)].

CONCLUSIONS

A water-in-cyclohexane microemulsion stabilized by Triton-114 was developed to produce amphiphilic

PMAA, which could not be prepared efficiently in an AOT/toluene microemulsion, probably because of a very low partitioning of the MAA monomer in the oil phase and a larger cage-like effect formed by the strong hydrophilic interactions between the polar head groups of AOT. The polymerization rate of the monomer (MAA) in the Triton-114 microemulsion system was slower than that reported⁷ for AM in the AOT microemulsion. The polymerization rate and the degree of conversion of the monomer increased with the concentrations of the initiator (KPS) and monomer. The viscosity-average molecular weight of the prepared PMAA was about 1.45×10^5 g/mol, which was rather low compared with that of PAM prepared via an AOT-microemulsion ($M_w > 1.0 \times 10^6$ g/mol). This is probably caused by chain transfer between the surfactant hydroxyl groups and the propagating chains. The PMAA particles were spherical, in general. About 30–50-nm PMAA particles were obtained when low monomer concentrations were used, but the particle sizes increased to over 100 nm at high monomer concentrations.

The authors give special thanks to J. Bates for his help and advice with transmission electron microscopy.

References

1. Polymerization in Organized Media; Paleos, C. M., Ed.; Gordon & Breach: New York, 1992; p 215.

2. Boutonnet, M.; Kizling, J.; Stenius, P.; Marie G. *Colloids and Surfaces* 1982, 5, 209.
3. Adair, J. H.; Li, T.; Kido, T.; Havey, K.; Moon, J.; Mecholsky, J.; Morrone, A.; Talham, D. R.; Ludwig, M. H.; Wang, L. *Mater Sci Eng* 1998, 23, 139.
4. Klier, J.; Tucker, C. J.; Kalantar, T. H.; Green, D. P. *Adv Mater* 2000, 12, 1751.
5. Santra, S.; Tapeç, R.; Dobson, N. T.; Hebard, A.; Tan, W. *Langmuir* 2001, 17, 2900.
6. Barton, J. *Prog Polym Sci* 1996, 21, 399.
7. Candau, F.; Leong, Y. S. *J Polym Sci Polym Chem Ed* 1985, 23, 193.
8. Leong, Y. S.; Candau, F. *J Phys Chem* 1982, 86, 2269.
9. Candau, F.; Leong, Y. S.; Pouyet, G.; Candau, S. J. *J Colloid Interface Sci* 1984, 101, 167.
10. Carver, M. T.; Dreyer, U.; Knoesel, R.; Candau, F.; Fitch, R. M. *J Polym Sci Part A: Polym Chem* 1989, 27, 2161.
11. Carver, M. T.; Candau, F.; Fitch, R. M. *J Polym Sci Part A: Polym Chem* 1989, 27, 2179.
12. Moumen, N.; Pileni, M. P.; Mackay, R. A. *Colloids Surf A* 1999, 151, 409.
13. Robon, M.; Corpart, J. M.; Selb, J.; Candau, F. *J Appl Polym Sci* 2002, 84, 1418.
14. Braun, O.; Selb, J.; Candau, F. *Polymer* 2001, 42, 8499.
15. de Saenz, A.; Buruaga de la Cal, J. C.; Asua, J. M. *Polymer* 2000, 41, 1260.
16. Glass, J. E. *Advances in Chemistry Series 223*; American Chemical Society: Washington, DC, 1989; p 113.
17. Meltzer, Y. L. *Water-soluble polymers: Developments Since 1978*. Noyes Data Corp.: Park Ridge, NJ, 1981; p 41.
18. Victor, S. P.; Sharma, C. P. *J Biomater Appl* 2002, 17, 125.
19. Lippi, B.; Cerchiara, T.; Bigucci, F.; Orienti, I.; Zecchi, V. *Eur J Pharm Biopharm* 2003, 55, 199.
20. Schonhoff, M. *Curr Opin Colloid Interface Sci* 2003, 8, 86.
21. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Abe, A.; Bloch, D. R., Ed.; *Polymer Handbook*, John Wiley & Sons Inc., New York, 1999.
22. Liu, Z. Ph.D. Thesis, Loughborough University, 1997.