Formation of Irreversible Nearly Transparent Physical Polymeric Hydrogels during a Modified Microemulsion Polymerization

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Introduction. Microemulsion polymerization has been widely studied since the first studies by Stoffer[1] and Atik[2], in the early 1980s. Microemulsion polymerization is effective in producing polymer latexes in the size range of 10−50 nm.[3,4] But, two major drawbacks have limited its broad applications, i.e., (1) low monomer/surfactant weight ratios, usually <1, and (2) low polymer content, usually less than 10 wt %.[5] Hence, to make microemulsion polymerization more practical, it is desirable to minimize the surfactant amount and maximize polymer content. A number of groups have tried to overcome these drawbacks,[6−9] but some problems remain unsolved, such as the occurrence of bulk polymer,[6,7] still high surfactant amount,[8,9] and the introduction of water-soluble monomers which was undesirable in some applications.[9] These approaches did not ultimately eliminate the drawbacks of conventional microemulsion polymerization.

In our laboratories, a modified microemulsion polymerization procedure has been successfully employed to prepare high solids−content nanosize polymeric microemulsions, in which monomer was gradually added into the polymerizing microemulsion without disturbing its stability.[10,11] This method is broadly applicable for various monomers. When the system was emulsified by anionic surfactant and initiated by redox initiators at ambient temperature, a high polymer/surfactant weight ratio (7:1 or higher) and relatively concentrated polymeric microemulsions (polymer content 10−40 wt %) were achieved while maintaining the particle diameters smaller than 20 nm.[10]

However, when monomer/surfactant ratios were over a critical level or when higher initiator concentrations were employed, irreversible nearly transparent physical hydrogels for poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) would form during modified microemulsion polymerization using water-soluble redox initiators at ambient temperature. The formation conditions of these hydrogels are described in this communication, and the formation mechanism is discussed.

Experimental Section. *Materials.* All chemicals were obtained from Aldrich Chemical Co. including styrene (St), butyl acrylate (BA), ethyl methacrylate (EA), methyl acrylate (MA), butyl methacrylate (BMA), EMA, MMA, ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), sodium dodecyl sulfate (SDS), and 1-pentanol. MMA and St were distilled under reduced pressure before polymerization, and other materials were used as received. Deionized water was used for all experiments.

Polymerization. The modified microemulsion polymerization procedure is described in detail elsewhere.[10] In brief, the modified procedure can be summarized as continuous and slow addition of monomer into the polymerizing microemulsion while maintaining its stability. The initial microemulsion was composed of the entire amount of surfactant and cosurfactant if required (e.g., 1-pentanol), a very small portion of monomer, and all of the water. Most of the monomer was postadded into the polymerizing microemulsion.

A typical polymerization procedure for MMA (PMMA-970306, Table 1) is described as follows. To a 250 mL three-neck flask equipped with a reflux condenser, a thermometer, an addition funnel, nitrogen gas inlet and outlet, and a magnetic stir bar was added a transparent microemulsion composed of 2.0 g of MMA, 1.4 g of SDS, 0.2 g of 1-pentanol, and 72.4 g of water. The microemulsion was heated to 40 °C and stirred under nitrogen atmosphere. A solution of 0.0232 g of TMEDA (2 mM, based on the total reaction charge) in 5 g of water was added, and then a solution of 0.0456 g of APS (2 mM, based on the total reaction charge) in 5 g of water was added to initiate the polymerization. The appearance of the microemulsion changed from transparent to slightly bluish, but still transparent. Then 14.0 g of MMA in the addition funnel was added dropwise into the polymerizing microemulsion for 2−3 h. During addition, temperature was maintained at 40 ± 1 °C, a slow flow of nitrogen was maintained, and the reaction mixture was stirred at about 600 rpm. After addition was complete, stirring was continued for another 2−3 h at the reaction temperature to carry the reaction to >95% conversion of monomer. High solids−content nanosize polymeric microemulsions for other recipes in Table 1 could be prepared similarly. Some of them turned into nearly transparent or semitransparent hydrogels during polymerization or after a period of storage.

Results and Discussion. In Table 1 are shown polymerization recipes for various monomers, some of which resulted in polymeric hydrogels while others did not. It was found when MMA or EMA amount was increased high enough (PEMA-980217, PMMA-970306, and PMMA-980216) at a certain reaction temperature (40 or 25 °C), translucent (for PEMA) or semitransparent (for PMMA) hydrogels formed. Hydrogel formation may occur during the polymerization or after a period of storage. Reaction temperature affected the polymer content in hydrogels: at 25 °C, the polymer content in PMMA hydrogel was 27.3%, but at 40 °C, hydrogel formed as the polymer content reached 16%. On the other hand, no hydrogel resulted at higher reaction temperatures (e.g., 65 °C, PMMA-980113 in Table 1). However, for BMA, whose water solubility is much lower than MMA and EMA, no hydrogel formed even at the polymer content of 40% (PBMA-980218 in Table 1), and

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Table 1. Polymeric Hydrogel Formation by a Modified Microemulsion Polymerization

sample		composition[a] monomer[b] (wt %)	composition[a] SDS (wt %)	composition[a] water (wt %)	initiator[c] APS/TMEDA (mM)	react temp (°C)	appearance	particle size D_n (nm)	particle size D_v/D_n[d]
971218	St	15.0 (0.5 + 14.5)	1.5	83.3	2	40	bluish opaque latex	16.7	1.37
971222	BA	22.7 (0.5 + 22.2)	1.4	75.6	2	40	bluish opaque latex		
980219	EA	32.0 (2.0 + 30.0)	1.4	66.4	2	25	bluish translucent latex		
970122	MA	30.0 (5.0 + 25.0)	1.0	68.8	2	40	semitransparent latex	14.5	1.50
980302	MA	37.4 (5.0 + 32.4)	1.0	61.4	2	25	viscous bluish translucent latex		
971219	BMA	17.6 (0.5 + 17.1)	1.4	80.8	2	40	bluish translucent latex		
980218	BMA	40.0 (1.0 + 39.0)	1.4	58.4	2	25	viscous bluish translucent latex	27.8	1.33
980119	EMA	22.7 (0.8 + 21.9)	1.2	75.9	2	25	bluish translucent latex		
980217	EMA	34.5 (1.0 + 33.5)	1.2	64.1	2	25	translucent latex, then hydrogel[e]	20.8[i]	1.80
970318	MMA	14.0 (2.0 + 12.0)	1.4	84.4	2	40	nearly transparent latex	13.0	1.26
970306	MMA	16.0 (2.0 + 14.0)	1.4	82.4	2	40	semitransparent hydrogel[f]	15.3[i]	1.47
980216	MMA	27.3 (2.0 + 25.3)	1.4	71.2	2	25	semitransparent hydrogel	14.7[i]	1.50
980325	MMA	25.0 (2.0 + 23.0)	4.0	70.8	2	25	viscous semitransparent latex		
980317	MMA	12.0 (2.0 + 10.0)	1.4	86.4	10	25	nearly transparent hydrogel		
980417	MMA	7.0 (2.0 + 5.0)	1.4	91.4	10	25	nearly transparent latex		
980326	MMA	12.0 (2.0 + 10.0)	4.0	83.8	10	25	nearly transparent latex		
980318	MMA	12.0 (2.0 + 10.0)	1.4	86.4	5	25	nearly transparent hydrogel[g])		
980113	MMA	18.0 (2.0 + 16.0)	1.4	80.4	2	65	semitransparent latex		
980408	MMA	12.0 (2.0 + 10.0)	1.4	86.4	2	25	foamed hydrogel[h]		

[a] 1-Pentanol (0.2 wt % in total reaction charge) was used as cosurfactant. [b] The first part of monomer in parentheses was in the initial microemulsion and the second part was postadded. [c] Initiator concentration was based on total reaction charge. [d] D_n and D_v are number-average and volume-average diameters, respectively, determined by dynamic light scattering. [e] Translucent hydrogel formed about 1 month after polymerization. [f] Semitransparent hydrogel formed about 2 weeks after polymerization. [g] Nearly transparent hydrogel formed about 24 h after polymerization. [h] The magnetic stirring was replaced with mechanical stirring. [i] Particle size was measured before hydrogel formed.

Figure 1. A picture of nearly transparent polymeric hydrogels: left, PMMA-980317; right, PMMA-980318.

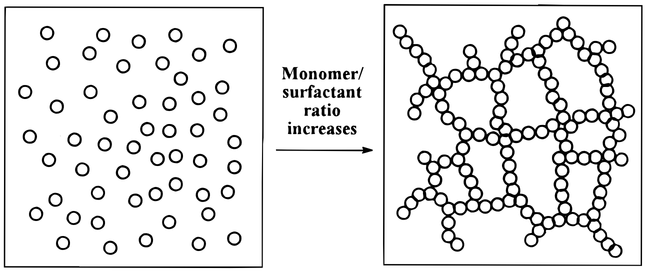
instead, a viscous translucent latex formed with a small amount of bulk polymer.

For MMA systems, increasing initiator concentration could facilitate the formation of PMMA hydrogels. As also shown in Table 1, at the MMA content of 12%, nearly transparent hydrogels could be easily formed when both APS and TMEDA concentrations were 10 and 5 mM, respectively (PMMA-980317 and PMMA-980318). Here we say “nearly transparent hydrogel” to differentiate it from “semitransparent hydrogel”, since the appearance in the former is clearer than in the latter, and it must be due to the smaller particles existing in the former. As a comparison, PMMA-970318 was a nearly transparent latex which was initiated by 2 mM APS and TMEDA. A picture of such nearly transparent hydrogels is shown in Figure 1. In such hydrogels, as high as 86.4% water could be immobilized by as low as 12% PMMA together with 1.4% SDS. However, when SDS concentration was increased to 4.0% (PMMA-980326) or MMA content was decreased to 7% (PMMA-980417), nearly transparent microlatexes were obtained. It is obvious the surfactant concentration has a major effect on the hydrogel formation.

A comparison was made with different stirring methods. In PMMA-980408, the magnetic stirrer was replaced with a mechanical stirrer. The latter could maintain the stirring even at the late stage of hydrogel formation, while the magnetic stirring would stop at the late stage of hydrogel formation due to the increased viscosity. A large amount of bubbles was brought into the hydrogel by mechanical stirring and could not escape because of high viscosity; as a result, PMMA-980408 was a foamed hydrogel with bluish tint at the bottom of the container. This suggests, to some extent, that shear stress would not inhibit the hydrogel formation.

On the other hand, for all acrylates studied (i.e., BA, EA, and MA), irrespective of their water solubilities, no hydrogels formed; even when polymer content was as high as about 35 wt %, only viscous translucent latexes formed, for example, PEA-971222 and PMA-980302 in Table 1. More investigation is needed regarding this phenomenon.

Formation of hydrogels was irreversible. For PMMA-980216, a microlatex sample was withdrawn when the microlatex was still mobile before gelation; its diameter (D_n) was 14.7 nm with a polydispersity of 1.5. Particle diameters were determined by dynamic light scattering on an L&N Microtrac 9200 series particle analyzer from Leeds & Northrup Co. There was almost no difference in the appearance to the naked eye between the final hydrogel and the above microlatex sample, suggesting small particles in final hydrogel kept their own size. A 0.4 g sample of PMMA-980216 hydrogel was added into 2.15 g of water, and vigorous magnetic stirring helped hydrogel redisperse in water uniformly, leading to a



(a) (b)

Figure 2. Schematic illustration of hydrogel formation.

translucent latex. Evaporation of the water from the redispersed microlatex was not able to recover the hydrogel. The particle diameter of the redispersed translucent latex was 47.7 nm with a polydispersity of 1.6. This could be ascribed to the agglomeration of small particles during redispersion and the redistribution of surfactant (surfactant coverage ratio of particles would increase when small particles became larger).

Our results suggest that hydrogels form when the amount of surfactant is inadequate to stabilize the microlatexes and other conditions are favorable. The situation is illustrated by the behavior of PMMA-970306. Because this latex was stable for 2 weeks before forming a semitransparent hydrogel, it is assumed to be near the critical surfactant level. In this system the weight ratio of MMA to SDS ($W_{\mathrm{MMA}}/W_{\mathrm{SDS}}$) was 11.4. Using the calculated surface area of the particles (based on particle size measurement of the ungelled latex) and a simple geometrical model,[12,13] a critical surfactant coverage ratio, C_r, is estimated. In this case C_r is about 0.25, a much lower level than is common in conventional emulsion and microemulsion polymerization. As long as the coverage ratio of surfactant is over the C_r, a stable microlatex can be obtained. But, when the monomer/surfactant ratio was over the critical $W_{\mathrm{MMA}}/W_{\mathrm{SDS}}$ ratio, a nearly transparent or semitransparent polymeric hydrogel would probably form. Besides, the formation of hydrogel depends on a combination of other factors, such as monomer type, polymerization temperature, glass transition temperature of the resultant polymer, and so on. The probable mechanism of hydrogel formation is illustrated in Figure 2. Above the C_r small particles are stabilized by surfactant (Figure 2a), but as more monomer is added, the surface coverage ratio of surfactant falls below the critical level and a physical network forms (Figure 2b). Inside the network, as much as 86.4 wt % water can be immobilized (PMMA-980317 and PMMA-980318 in Table 1). This kind of gel was mentioned in an introductory lecture by Keller.[14] Recently, Tieke et al.[15] prepared a nearly transparent polymer gel by copolymerization of styrene and a polymerizable surfactant with a polymerizable moiety near the hydrophilic headgroup in a three-component cationic microemulsion. They have shown a nearly transparent gel with a water content of about 94 wt % could be obtained with 5 wt % styrene and 1 wt % polymerizable surfactant. The single polymerized surfactant polymer chain became physically connected between polystyrene nanospheres and polymerized surfactant aggregates (from empty micelles).

DSC suggests there are two types of water in the hydrogel, bound water and free water, and the phenomenon is under investigation. Further investigation is also under way to understand the connectivity in the physical polymeric hydrogels.

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