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SHORT COMMUNICATION

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Emulsifier for microemulsion polymerization

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Abstract By introducing an hydroxyl group and a lipophilic branch into the middle of lipophilic head of emulsifier 12-oxy-9-octadecenoic acid, a new emulsifier was synthesized and applied in microemulsion polymerization. When the emulsifier content in the microemulsion was kept to about 12%, the highest monomer content in microemulsion could achieve 35% for BA, 20% for St and MMA. The microemulsion with high monomer content remained clear after polymerization, and the average diameters of polymer particles were 38.9 nm for St microemulsion, 47.4 nm for BA, and 50.7 nm for MMA.

Key words Emulsifier – microemulsion – composition – microemulsion polymerization

Introduction

Since Stoffer and Bone [1] published their first paper on microemulsion polymerization in 1980, great developments had been made in this new branch of emulsion polymerization. The speciality of microemulsion polymerization had been reviewed by several papers [2–5].

In comparison with emulsion polymerization, the main disadvantage of microemulsion polymerization is that the emulsifier was very high and the monomer content very low. In the past, the microemulsion polymerization system had been optimized to some degree [6, 7]. For polymerization of water-soluble monomers in W/O microemulsion, Candau [6] adapted the CER (cohesive energy ratio) concept for optimizing the polymerization system. By using an emulsifier mixture, the emulsifier efficiency and the monomer content in the system were both greatly enhanced. For polymerization of oil monomers in W/O microemulsion, Gan et al. [7, 8] synthesized some polymerizable emulsifier to stabilize the polymerization system. They successfully produced transparent porous materials with high water content.

However, the emulsifiers used for oil monomer in O/W microemulsion polymerization were all common ones that were widely applied in emulsion polymerization.

Anionic emulsifier SDS (sodium dodecyl sulfate) was the first emulsifier used in microemulsion polymerization, and widely adapted in O/W microemulsion polymerization of styrene [9] (St), methyl methacrylate [10] (MMA) and butyl acrylate [11] (BA). Only with the help of coemulsifier, such as *n*-pentanol, can SDS form transparent microemulsion. For example, the typical formulation for St microemulsion polymerization was 5% St, 9% SDS, 4% pentanol and 72% H_2O.

Cationic emulsifiers, such as dodecyltrimethylammonium bromide (DTAB) [12], tetradecyltrimethylammonium bromide [13] (TTAB), and octadecyltrimethylammonium chloride [14] (OTAC), were also often used in O/W microemulsion polymerization. In contrast to SDS, these cationic emulsifiers could stabilize monomer microemulsion in the absence of a coemulsifier. It makes the investigation of polymerization kinetics simpler, since the coemulsifier always changes the phase partition of the monomer and affects the polymerization kinetics. A mixture of nonionic emulsifier, octylphenol with different moles of ethyl oxide [15] (OP), was also applied in

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microemulsion polymerization. In order to keep the microemulsion stable during the whole polymerization process, the cationic or nonionic emulsifier was always about 10%, while the monomer content was always below 7%. Otherwise, the final latex would turn opaque.

In order to improve the system stability during O/W microemulsion polymerization, some efforts were made, e.g., applying the mixture of anionic and cationic emulsifier [16], or anionic and nonionic emulsifier [17] to stabilize the microemulsion. In this way, the polymer particles produced were obviously reduced. However, the monomer content was only slightly improved.

The work of Full should be emphasized [18]. Emulsifier Aerosol OT (AOT) was adapted to stabilize the microemulsion of THFM (tetrehydrofurfuryl methacrylate), without the help of coemulsifier. The monomer microemulsion was composed of 5% AOT, THFM 8%, and 87% H_2O. Though the monomer content was still very small, the emulsifier content was the lowest in all the O/W microemulsion polymerization systems reported previously, and the monomer to emulsifier ratio (1.6) was the highest.

In order to improve the monomer content in O/W microemulsion polymerization system, in this paper, a new emulsifier was designed to stabilize monomer microemulsion for polymerization. The monomer content could be enhanced above 20% while the microemulsion remained clear after polymerization.

Experimental section

Chemicals

Castor oil was hydrolyzed in NaOH solution at 100 °C for about 1 h and then be neutralized with H_3PO_4 to give OOA (12-oxy-9-octadecenoic acid). It is shown in Fig. 1 that the peak c at 4.1 disappeared after hydrolyze which is attributed to the hydrogen of the glycerol group in castor oil. BOA (12-butinyoloxy-9-octadecenoic acid) was synthesized by direct esterfication of OOA with excessive butyric acid, at 130 °C with H_2SO_4 as catalysis. It was clear that the peak d at 3.4 which is due to hydroxyl group diminished.

Preparation and polymerization of monomer microemulsion

Monomer microemulsion could be produced as follows: The monomer, emulsifier and distilled water were firstly mixed together, then NaOH solution was dropped into the mixture under stirring, till the system suddenly turns clear.

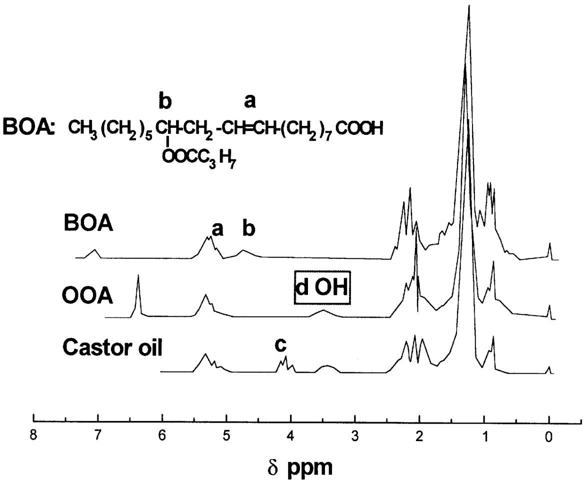

Fig. 1 The NMR spectrum of castor oil, OOA and BOA

Polymerization of monomer microemulsion was initiated with γ ray at 30 °C while does rate is 28.5 Gy/min.

Particle size and its distribution

The size and its distribution of polymer particles were measured with photo correlation spectroscopy (PCS) using Brookhaven BI-200SM instrument [19].

Results and discussion

Introducing hydroxyl group to the middle of lipophile head of emulsifier

It was noticed that when SDS was selected as the emulsifier for styrene microemulsion, the emulsifier content could be much reduced if suitable cosurfactant was added to the microemulsion simultaneously. The cosurfactant was usually an alcohol with middle carbon length (C4–C7). The efficiency of cosurfactant was the highest if the carbon number in alcohol was near to half of the emulsifier SDS. This fact leads us to consider the following question: if a hydroxyl group was introduced to the middle of the emulsifier, what will happen?

In this way, OOA was synthesized and the efficiency of OOA in microemulsion polymerization of St was examined.

Monomer microemulsions with different OOA and St content were produced and initialized with γ ray. The samples that remained clear after polymerization were recorded and shown by the enclosed area in Fig. 2. The maximum monomer content at certain OOA content is shown in Fig. 3.

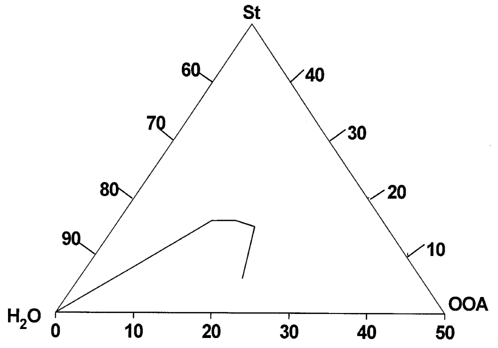

Fig. 2 The phase diagram of styrene microemulsion stabilized with OOA at 25 °C. The enclosed area is that which remained clear after polymerization

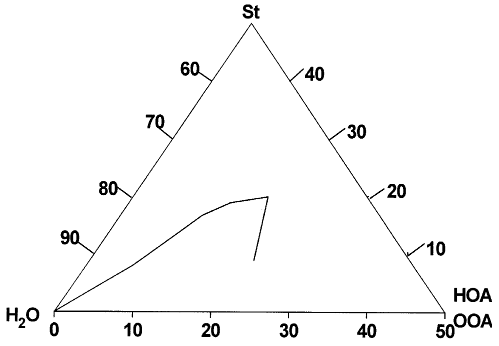

Fig. 4 The phase diagram of styrene microemulsion stabilized with OOA/BOA at 25 °C. The enclosed area is that which remained clear after polymerization

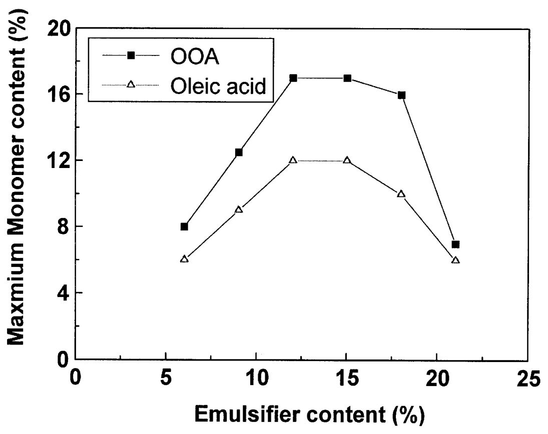

Fig. 3 The relationship between the maximum St content and the emulsifier content in microemulsion stabilized with OOA

It is clear that the microemulsion region after polymerization is much wider than when SDS or CTAB was used to stabilize St microemulsion [9, 14]. It is also true for BA and MMA microemulsion. The maximum monomer content could be increased up to 25% for BA and 20% for MMA, when OOA was used to stabilize microemulsion.

It seems that the hydroxyl group in the middle of lipophile head of OOA plays an important role. It makes OOA to act as emulsifier and cosurfactant simultaneously. In this way, the efficiency of emulsifier is enhanced. In fact, oleic acid had almost the same structure as OOA, except that there is no –OH in the middle of lipophile head. The maximum content of St in microemulsion stabilized with oleic acid is much lower than the stabilized with OOA (Fig. 3).

Now, it is easy to understand the superiority of the microemulsion polymerization system adapted by Full [18]. The hydrophilic group $-SO_3Na$ is just in the middle of AOT. Therefore, in this system, no other coemulsifier is needed to form the THFM microemulsion, and the emulsifier content needed to form the microemulsion is very low.

Introducing a branch into the middle of lipophile head of the emulsifier

In microemulsion, the surfactant content was more than the amount needed to form a thick monolayer around all particles (monomer microdroplets) and monomer-swollen polymer particles). If the average area occupied per surfactant molecules were increased, then the emulsifier content in the microemulsion polymerization system could be reduced further. In order to increase the average area occupied by the surfactant, introducing a branch in the lipophile head of the surfactant seems to be a good procedure.

Following the above idea, OOA was esterified with butyric acid to give BOA. In this way, a new emulsifier with a branch in the lipophile head (Y type emulsifier) was synthesized. When BOA was mixed with OOA (1 : 1 by weight), the stable region of St microemulsion after polymerization was as shown in Fig. 4. The maximum St content at different emulsifier content was depicted in Fig. 5. By comparing with Figs. 2 and 3, it could be seen that the clear region after polymerization was a little wider, and the maximum monomer content was increased up to 20%. The above facts suggest that by introducing a branch into the middle of the surfactant, the efficiency of surfactant was indeed enhanced, and the monomer content was further increased. The size and the distribution of polystyrene particles after polymerization are shown in Fig. 6. The average hydrodynamic diameter of the final polymer particles was 38.9 nm.

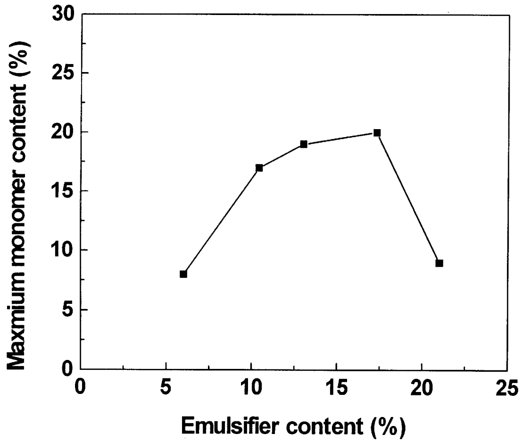

Fig. 5 The relationship between the maximum St content and the emulsifier content in the microemulsion stabilized with OOA/BOA

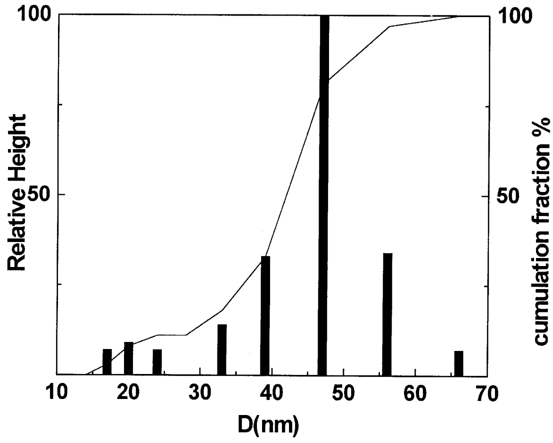

Fig. 6 The size and the distribution of polystyrene particles. The monomer microemulsion was composed of 6% BOA, 6% OOA, 20% St, and 68% H_2O. The polymerization was initiated with γ ray at 28.5 Gy/min at 33 °C

When a mixture of BOA and OOA (1 : 1 by weight) was used to stabilize BA and MMA microemulsions, the maximum monomer contents were raised to 30% and 20%, respectively. The average hydrodynamic diameters of polymer particles were measured to be 47.4 nm for BA and 50.7 nm for MMA.

Cooperation of OOA with BOA

In order to find the appropriate fraction of BOA in the emulsifier mixture, the emulsifier mixture with different BOA fractions was used to stabilize microemulsion with different monomer content. The sample with highest monomer content and remaining transparent after polymerization was recognized as the best composition. In this way, the best BOA fraction in the emulsifier mixture and the highest monomer content for St, BA and MMA microemulsions, were derived. The results are shown in Table 1.

Table 1 Matching between the monomer and the lipophilic head

Monomer	$[M]_{\text{highest}}$[a]	BOA%[b]	δ_M[c]	δ_L[c]
MMA	20	50	9.1	8.9
BA	30	50	8.8	8.9
St	20	35	9.2	9.2

[a] $[M]_{\text{highest}}$, the highest monomer content in microemulsion stabilized with BOA/OOA mixture.

[b] BOA%, the appropriate weight fraction of BOA in the emulsifier mixture.

[c] δ_M, δ_L, the solubility parameters of the monomer and the lipophilic head of the appropriate mixed emulsifier, estimated with Hoy method [20].

Candau et al. [6] applied the concept of cohesive energy ratio (CER) for choosing the emulsifier mixture of W/O microemulsion polymerization. The formation of ideal microemulsion requires perfect chemical matching between the lipophilic moiety of the emulsifier and oil phase. In other words, the solubility parameter of the lipophile head should equal that of the oil phase. Therefore the solubility parameters of the lipophilic moiety of the appropriate emulsifier mixture, estimated by Hoy method [20], are shown in Table 1. For all the above three monomers, the appropriate fraction is in good agreement with the chemical matching requirement. It can be concluded that the chemical matching is also necessary for the formation of O/W microemulsion.

Conclusion

By introducing an hydroxyl group and a lipophilic branch in the middle of the lipophilic head of the emulsifier, a new emulsifier BOA was synthesized and applied to stabilize monomer microemulsion for polymerization. The hydroxyl group in the middle of lipophilic head makes the emulsifier to act as emulsifier and coemulsifier simultaneously, while the lipophilic branch enhances the average area per emulsifier molecule occupied. Therefore, the efficiency of the emulsifier was greatly enhanced, in comparison with the usually adapted emulsifier SDS and CTAB. It further led to the high monomer content and to a high monomer to emulsifier ratio in the microemulsion polymerization system.

It was also demonstrated that the appropriate emulsifier mixture of BOA/OOA for all three monomers, is in good chemical matching with the monomer phase.

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