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Synthesis, characterization and kinetics of hydrophobically associating polyacrylamide

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Abstract: HAPAM was successfully prepared in inverse microemulsion. ^{1}H-NMR, FT-IR, DSC and TG results show that the copolymerization of acrylamide (AM) with DM16 was successful. However, the ratio of AM to DM16 is not calculated exactly due to the low percentage of hydrophobic monomer in polymer. Therein, we only proved the success of the incorporation of DM16 onto polyacrylamide backbone. According to our experiment, the conversions of monomers and molecular weight have a strong dependence on initiator concentration and aqueous phase weight fraction. But it was not completely in accordance with literature. The difference may be ascribed to the major existence of locus of DM16 (at the interface of oil/water or in droplet). Compared with literature, the influence of initiator concentration on particle size was slight due to the high surfactant weight fraction, seeming to appear independent of initiator concentration. When the surfactant weight fraction reaches a certain degree, it did not affect the conversion. For the particle size and molecular weight, it was other way around, suggesting that there was an intense chain transfer reaction to the emulsifier. In this work, we could not calculate the average number of free radical per particle n, because the part of the surfactant in excess recombines to form small micelle and the DM16 may continuously transfer from micelle to another micelle, resulting in difficulty to estimate precisely the number of the particles. This was also reflected in the difference of kinetics between our system and literature. Finally, the occurrence of nucleation at high conversion was proved indirectly.

Introduction

During the past decades, hydrophobically associating polyacrylamides (HAPAM) derived by incorporating a relatively small amount (generally less than 2 mol %) of hydrophobic groups onto a polyacrylamide backbone has been especially attractive due to their noticeable ability in controlling the viscosity at various shear rates [1-4]. Owing to its excellent viscosity building capacity, this kind of polymers has received a wide application in oilfield exploitations, including drilling, polymer-augmented water flooding, chemical flooding, etc [5-13].

Nowadays, the methods for preparing HAPAM by copolymerization could generally be categorized into two routes: micelle polymerization [14-17] and inverse emulsion polymerization [18]. However, there are some obvious disadvantages. The solid content of the resultant polymer by micelle polymerization is relatively low because of the very high viscosity of the final system [19-21], and it is well known that obtained polymers are characterized by blocky distribution of the hydrophobes, compositional inhomogeneity and strong dependence of solution properties on block length; the water-solubility of the polymer was not good [13]. The instability of the HAPAM emulsions represents the significant drawback of inverse emulsion process, which results in inconvenience during storage [18].

Today, a new trend is to adopt the inverse microemulsion polymerization (IMP) techniques to prepare HAPAMs. This technique was first reported by Candau, et al. in 1982 [22]. In their work, polyacrylamide of high molecular weight (~$3\text{x}10^6$) was obtained in inverse microemulsions without any additional cosurfactant. This kind of inverse microlatex was stable and transparent; the improvement of water-solubility of polymer was obvious [23]. But the potential of IMP in synthesizing HAPAM was not recognized until 1999, when Candau et al. successfully synthesized HAPAM with nonionic hydrophobic monomer. These polymers exhibited interesting rheological properties in aqueous solution, such as shear-shinning, shear-thickening, viscoelasticity and so on [15]. As could be seen from their work, IMP could be regarded as an effective tool in synthesizing HAPAM. Unfortunately, such a promising technology has not jet aroused extensive attention in synthesizing HAPAM. Up to now, only little literature on both theoretical and practical researches is available [15, 23].

Following our previous research [24], in this article, our attention is focused on getting further insight on to the theory of polymerization of acrylamide with cationic hydrophobic monomer in inverse microemulsion. To our best knowledge, this is the first systematic investigation on the polymerization in inverse microemulsion containing cationic hydrophobic monomer. This work is believed to be of both academic interest and practical importance. Such information could not only provide a further insight to inverse microemulsion systems for preparing HAPAM, but also could be used as guidance for future industrial process.

Results and discussion

^{1}H-NMR analysis

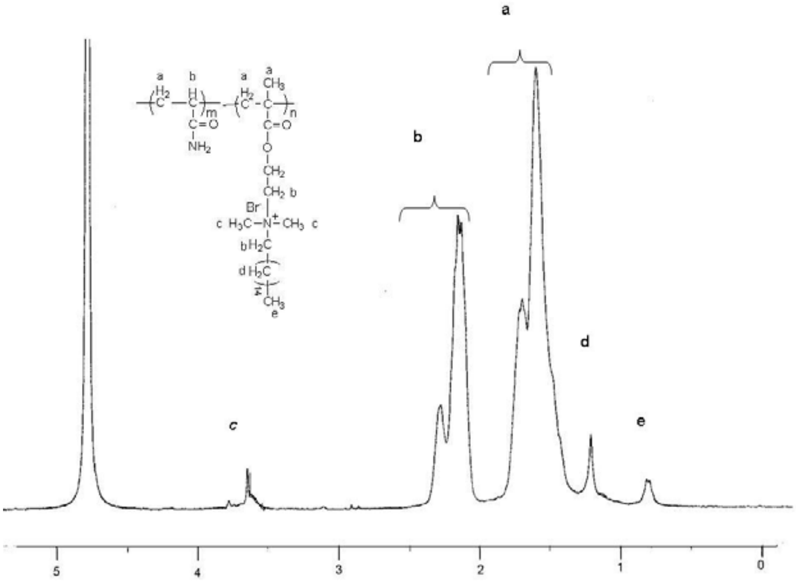

Fig. 1. ^{1}H-NMR spectra of HAPAM.

Elucidation of molecular architecture of HAPAM by traditional methods such as elemental analysis is difficult due to the low percentage of hydrophobic monomer in polymer. In this work, we confirmed it with careful ^{1}H-NMR characterization. As shown in Fig. 1, the protons in the methylene $(-CH_2-)_{14}$ in long alkyl side chains could be found at 1.3 ppm and the end methyl($-CH_3$) at 0.9 ppm. The protons in methyl ($CH_3-N^+-CH_3$) could be observed at 3.6 ppm. The other protons could also found correspondingly in the ^{1}H-NMR. It showed that the copolymerization of acrylamide with DM16 was successful.

FT-IR analysis

Fig. 2 presents the FT-IR spectrometer of PAM and HAPAM. Compared with the standard FT-IR spectrometer of PAM, there is a strong C-H stretch in 2921 cm^{-1} and 2850 cm^{-1} and a middle CH2 γ in 760 cm^{-1}(especially for $C-(CH_2)_n-C$, $n \geq 4$), indicating the existence of long chain alky group on the polymer framework. So it could be concluded that the DM16 was incorporated on the polyacrylamide backbone.

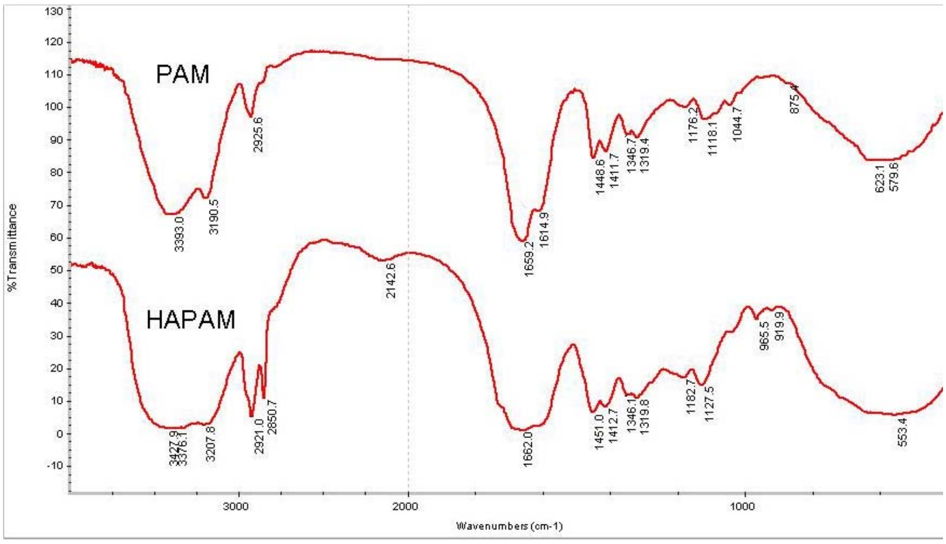

Fig. 2. FTIR spectra of PAM and HAPAM.

DSC and TGA studies

DSC thermograms of PAM were presented in Fig. 3 and Table 1. Three endothermic peaks were observed, one at 90.1 °C, which correspond to the loss of moisture(T_m) and the two others at 268 °C and 324 °C due to thermal decomposition. Similarly, for HAPAM, one at 90.9 °C, which correspond to the loss of moisture and the two others at 268 °C and 324 °C due to thermal decomposition. It show that the incorporation of hydrophobic monomer (DM16) on PAM backbone increase the stability of polymer.

Fig. 4 shows the thermal behaviour of PAM and HAPAM. Table 2 summaries the result obtained using thermogravimetry. Thermogravimetric results show the thermal behaviour of PAM and HAPAM was similar. We can note that a continuous weight loss starting at the beginning of the heating and, at last, three thermal events. The first thermal process is related to the solvent elimination. This was be proved by Silva [25].

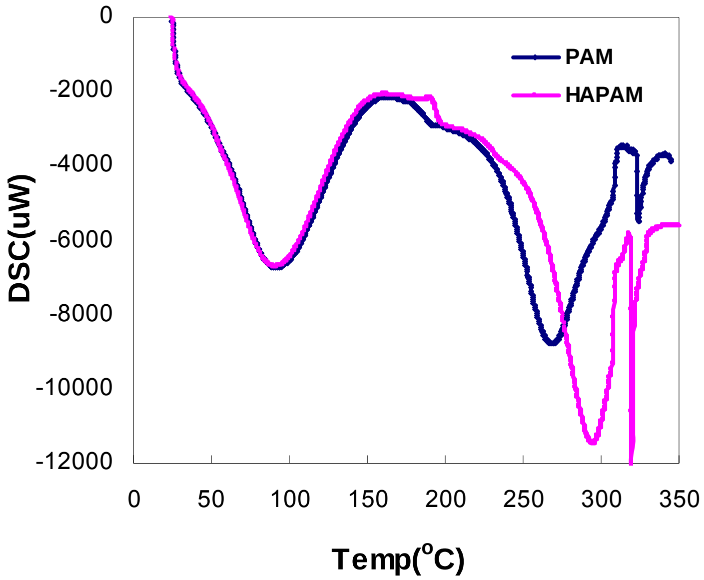

Fig. 3. DSC curves for PAM and HAPAM.

Tab. 1. Moisture loss(T_m) and degradation (T_d) temperatures determined by DSC.

Polymer	T_m(°C)	T_d(°C)
PAM	90.1	268/324
HAPAM	90.9	294/325

According to Fig. 4, the thermal degradation of PAM occurs with degradation temperature (T_d) of 269 °C and 381 °C, and weight losses of 15 and 56%, respectively. As far as HAPAM is concerned, the thermal degradation of PAM occurs with degradation temperature (T_d) of 292 °C and 402 °C, and weight losses of 17 and 52%, respectively. It indicated that the thermal stability of polymer increased due to the incorporation of long chain alky hydrophobic monomer (DM16). This result is in accordance with that observed in DSC experiments.

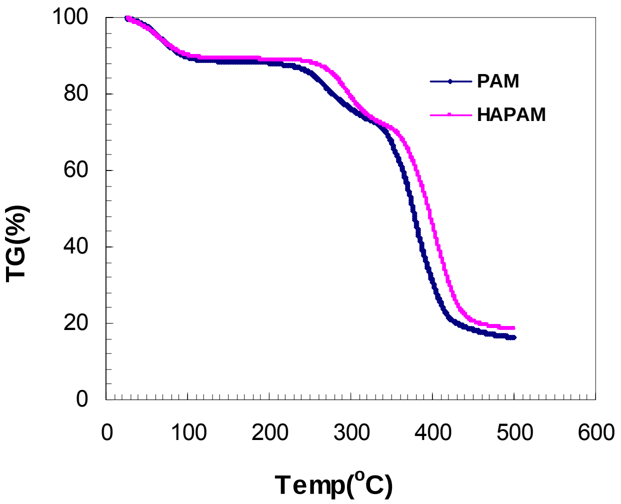

Fig. 4. TG curves for PAM and HAPAM.

Tab. 2. TG result of polymers.

Polymer	T_d(°C)	Weight loss (%)		
		Up to 200 ^{0}C	260-500 °C	Residue at 500 °C
PAM	269/381	12	15/56	16
HAPAM	292/402	11	17/52	18

All these show that the copolymerization of acrylamide with cationic hydrophobic monomer (DM16) was successful.

Reproducibility of the polymerization

In order to ensure the reliability of this method to obtain the curves of conversion, this approach requires the reproducibility of the experiment, as it is the case for runs carried out in this work. As shown in Fig. 5, the two lines were superposed except for tiny difference of some points. The basic trendline was completely con
“??”}sistent. It shows that the method is reliable to obtain conversion curves.

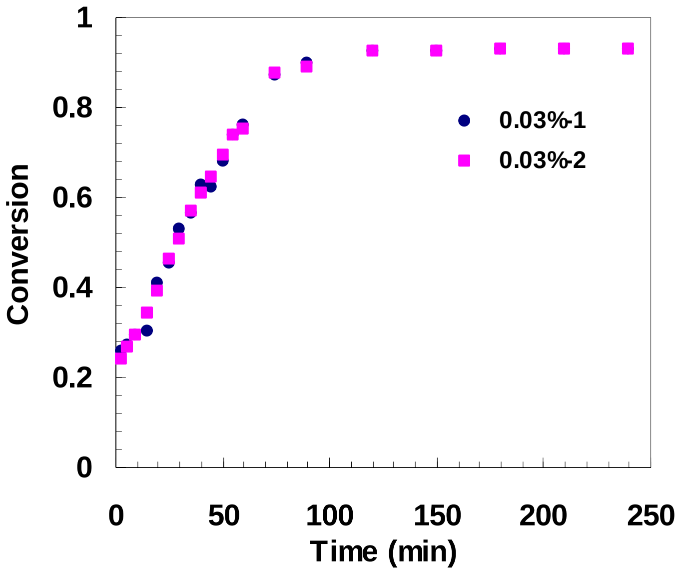

Fig. 5. Reproducibility of the polymerizations. Reaction conditions as in run 2.

Effect of concentration of initiator

Fig. 6 presents the effect of the initiator concentration on the conversion. A tendency to higher conversions appears to be the result of higher concentrations of the initiator (V50). It can be seen that the time to reach the complete conversion decrease with the increase of the initiator concentration and the rate of polymerization increased as the initiator concentration increased. This result was similar with Asua’s reported result [26], but the time to reach the highest conversion was longer than theirs. In their work, the monomer is 2-methacyloy oxyethyl trimethyl ammonium chloride with photoinitiation system. For Candau’s system with Aerosol OT, no autoacceleration phenomenon (Trommsdorf effect) was observed as is often the case in conventional inverse emulsion polymerization of acrylamide and the rate of polymerization almost ppear to be independent of initiator concentration, i.e. R_p~$[AIBN]^{0.1}$[27]. So one could speculate that different inverse microemulsion polymerization systems may exhibit different reaction kinetics.

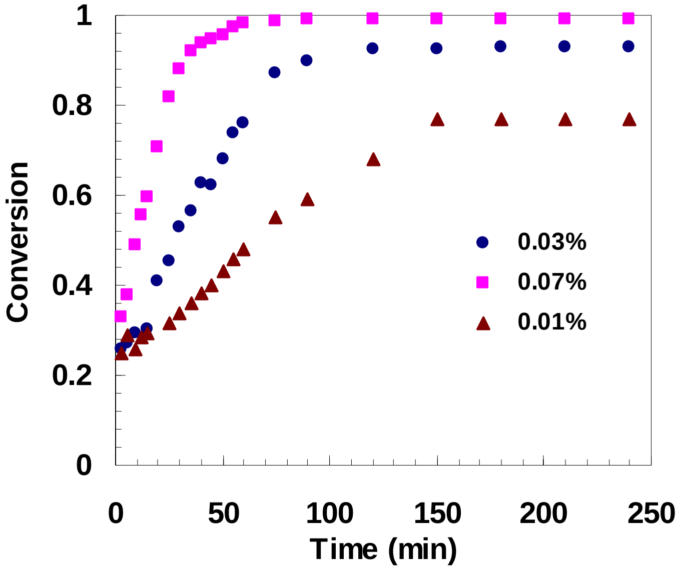

Fig. 6. Effect of the initiator concentration on the conversion. Legend: run1 (0.01 %); run 2 (0.03 %); run 4 (0.07%).

Considering the chain transfer reaction of surfactant, it will become more complicated. Based on our experiments result, the rate of polymerization must have depended on the initiator concentration. Table 3 shows that the diameter of inverse microlatex seems to appear to be independent of the concentration of the initiator. However, according to Asua's result [26], it should decrease with increase in the initiator concentration. Considering that the surfactant concentration was higher than that in their system (about 16%), these results should be reasonable.

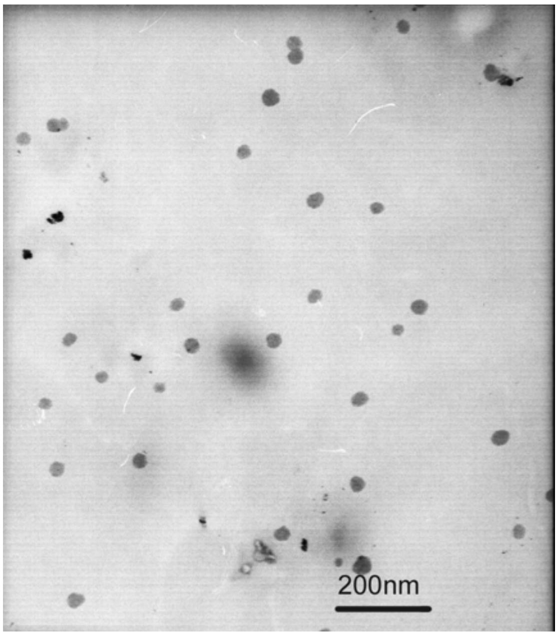

Fig. 7. TEM image of inverse microlatex (sample is run 2).

As shown in Fig. 7, the diameter of inverse microlatex is about 35 nm, which is basically in accordance with the value measured by DLS.

As indicated in Table 3, the molecular weight of HAPAM obtained was influenced much by the percentage of V50. The result obtained was almost in accordance with literature [27, 28]. The influence was more obvious than that reported [27]. The potential reason may be the existence of locus of monomers. In the literature, it was the homopolymerization of AM, but for ours, it was the copolymerization of AM and DM16. DM16 was a special polymerizable surfactant, which could mostly locate at the interface of water/oil, resulting in the difference of polymerization locus. Due to this reason, the influence of initiator concentration on molecular weight was more obvious.

Effect of weight fraction of aqueous phase

Fig. 8 presents the aqueous phase weight fraction verses monomer conversion. It can be seen that, for a given process time, as the aqueous phase fraction increase, a simultaneous increase can be observed in conversion. Similar behaviour has already been observed [28]. It could contribute to the increase of the number and size of the drops of the microemulsion that accompanies the increase of the monomer concentration. In this situation, a greater possibility of radical capture exists, and this increases the probability of the monomer reaction. Fig. 8 also indicated that the slope of the three lines was almost same, suggesting that the rate of polymerization was independent of the aqueous phase weight fraction, the difference of monomers concentration in microemulsion lead to the variance of the rate of polymerization. As far as the molecular weight of HAPAM obtained was concerned, the influence was relatively obvious. For the high weight fraction of aqueous phase, the influence was not that serious.

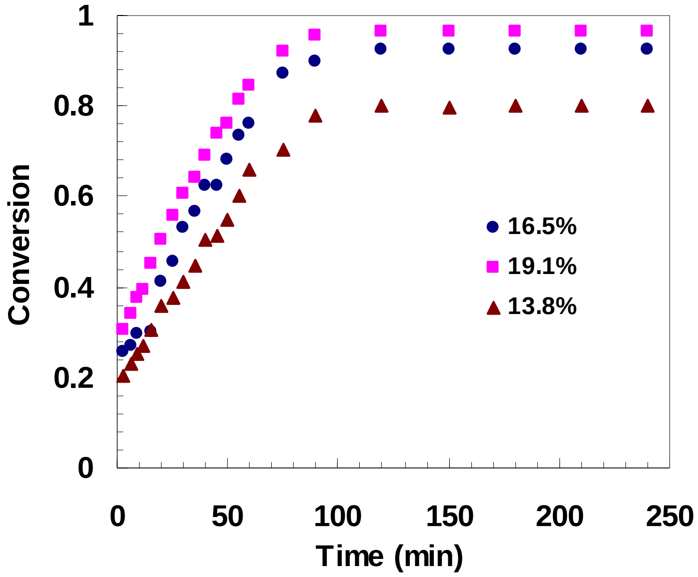

Fig. 8. Effect of the aqueous phase weight fraction on conversion. Legend: run 2 (16.5 %); run 8 (19.1 %); run 9 (13.8 %).

For the low weight fraction of aqueous phase, it was other way around. The higher the weight fraction of the aqueous phase was, the higher was the concentration of DM16 in inverse microemulsion. The concentration of DM16 may become higher in liquid droplet, which redounds in copolymerization. That is to say, the locus of DM16 at interface of oil/water did not help in copolymerization. It was in accordance with that discussed in the initiator dependence where it was more obvious than reported in literature.

As shown in Table 3, the diameter of the microlatex increase with the increase of the aqueous phase weight fraction, suggesting that the stability of the particle need a certain mass of surfactant.

Effect of weight fraction of surfactant

Fig. 9 presents the effect of surfactant weight fraction on monomer conversion. It can be seen that at low surfactant weight fraction the rate of polymerization depended strongly on surfactant weight fraction but the effect was negligible for high surfactant weight fraction. A similar phenomenon, in Table 3, was observed for the particle size that decreased with the increase of surfactant weight fraction. Zekhnini et al reported similar results: the dependence of the number of particles on [emulsifier] changed from (N_p~ $[\text{emulsifier}]^{3.2}$) at low surfactant weight fraction, to (N_p~$[\text{emulsifier}]^{0.6}$) at high surfactant weight fraction [29]. It indicates that the lowest surfactant weight fraction was too close to the stability limit for microemulsions and limited coagulation occurred. However, for this work, although the surfactant weight fraction was high, the dependence was not strong. One could ascribe it to the difference of the inverse microemulsion system. Table 3 also shows that the weight fraction of surfactant had strong increasing effect on the molecular weight, suggesting an intense chain transfer reaction to the emulsifier.

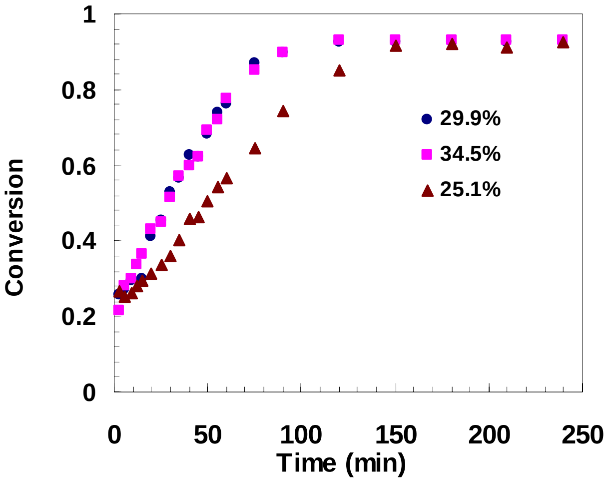

Fig. 9. Effect of the weight fraction of surfactant on conversion. Legend: run 2 (29.9%); run 11 (34.5%); run 12 (25.1%).

Effect of HLB value

As shown in Fig. 10, the curves of conversion were not influenced by HLB. According to our experiment, the final conversion and the time to reach highest conversion were basically same. In opposition, HLB has a slight influence on the molecular masses of obtained HAPAM, which ascribed to the difference of the number of chain transfer groups. Besides, the HLB has major influence on the stability of inverse microemulsion, which could be proved by the size of particles. Working at HLB = 8.8 leads to the smaller size of particle, as shown in Table 3.

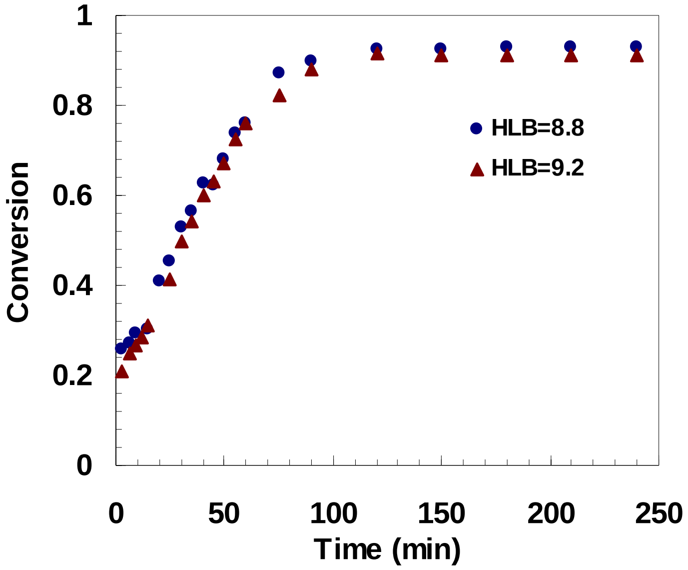

Fig. 10. Effect of HLB on conversion. Legend: run 2(HLB = 8.8); run 6 (HLB = 9.2).

Tab. 3. Summary of the polymerizations.

Run	HLB	AM (g)	DM16 (g)	Oil (g)	Surfactant (g)	Water (g)	V50 (%)	Ubbelohde (ml/g)	Diameter (nm)
1	8.8	11.64	0.72	80	45	12.28	0.01	391	26.4
2	8.8	11.64	0.72	80	45	12.28	0.03	511	32.9
3	8.8	11.4	0.72	80	45	12.28	0.05	419	32.4
4	8.8	11.64	0.72	80	45	12.28	0.07	406	36.7
5	9.2	11.64	0.72	80	45	12.28	0.03	473	32.6
6	9.6	11.64	0.72	80	45	12.28	0.03	475	41.5
7	8.4	11.64	0.72	80	45	12.28	0.03	413	46.9
8	8.8	13.52	0.84	80	45	14.28	0.03	487	51.2
9	8.8	9.76	0.60	80	45	10.28	0.03	428	31
10	8.8	11.64	0.72	70	55	12.28	0.03	397	27.4
11	8.8	11.64	0.72	90	35	12.28	0.03	519	33.2
12	8.8	11.64	0.00	80	45	12.28	0.03	481	39.7

Verification of the occurrence of nucleation at high conversion

In order to check the occurrence of nucleation at high conversion, a mixture of well-characterized microlatex and an inverse microemulsion was polymerized under the same conditions as used in run 2; the details are listed in Table 4. As shown in Table 4, after the microlatex has mixed with the original inverse microemulsion, the diameter of the microlatex was almost consistent. After second polymerization, the microlatex almost keeps consistent, except for tiny difference. In the same way, the final conversion has tiny difference. It suggested that during the polymerization the number of the microlatex increased without any change of the diameter of microlatex, which indirectly illustrates the occurrence of nucleation at high conversion.

Tab. 4. Summary of mimicking experiment.

Weight fraction of well-characterized microlatex (%)	d_m (nm)	d_p (nm)	C_m (%)	C_p (%)
100%	32.9	/	92.6	
25%	32	32.6	23.15	92.4
50%	32	33	46.3	92.9
75%	32.1	34	69.45	92.5
90%	32.2	32.3	83.34	93.0

d_m- the diameter of microlatex after mixing with the original inverse microemulsion

d_p- the diameter of microlatex of second polymerization after mixing with the original inverse microemulsion

C_m- the conversion after mixing with the original inverse microemulsion

C_m- the conversion of second polymerization after mixing with the original inverse microemulsion

Experimental part

Materials

Acrylamide (AM, Aldrich) was recrystallized twice with chloroform (m.p. 84 °C) and stored in silica gel desiccators prior to use. Isopar M, an isoparaffinic mixture with a boiling temperature range of 223-254 °C, was purchased from Exxon Mobile (TX, USA). Span80 (HLB = 4.3) and Tween80 (HLB = 15.0) were obtained from Kelong Reagent Co. Ltd (Chengdu, China). Other reagents were all analytical grade. Water (resistivity > 18 $M\Omega cm^{-1}$) prepared by distillation three times. The 2-(methacryloyloxyl) ethylheadecyldimethylammonium bromide (DM16) was self-prepared in our lab [30]. It was prepared with simple quaternization between n-headecyl bromide and 2-(dimethylamino) ethyl methacrylate. 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (V50) (97 wt.%, Aldrich) was used as received.

Polymerization

A 250-mL three-neck flask fitted with a mechanical stirrer was charged by a certain amount of Isopar M, Span80 and Tween80. The temperature was kept constant at 40 °C. The aqueous solution containing acrylamide and DM16 was added drop by drop within 20 min. The speed of stirring was 1000 rpm and the stirring time was 4 h. Then, purified nitrogen was bubbled in the microemulsion for 45 min to eliminate oxygen. Finally, the initiator (V50) solution was injected under stirring (300 rpm) and the reaction time was 4 h. The beginning stage of the polymerization was evidenced by a change from the transparency of the microemulsion to a slightly bluish coloration. The final system could remain clear and stable over months. Their viscosity was very low, usually within the range of a few centipoises. After polymerization, some samples (inverse microlatex) were poured into an excess of the mixture of ethanol and 200# solvent oil, and the precipitated copolymers were separated and washed several times. They were filtered and dried under vacuum at 60 °C.

Transmission electron microscopy

Transmission electron microscopy (TEM) was performed with a JEM-100CX electron microscope. The diluted colloidal solution was applied to a 400 mesh carbon-coated copper grid and left to dry. TEM images were obtained without any staining.

Dynamic light scattering

Particle diameters were determined by a laser light scattering spectrometer (BI200SM) equipped with a digital correlator (BI9000AT). The scattered light from an Argon laser (514.5 nm) was used for measurement at 90° at a temperature 25 °C. All the samples were prepared by filtering of 1 ml of the microlatex solution with a 0.45 µm Millipore filtered into a clean scintillation vial. The microlatex were diluted with Isopar M down to a volume fraction of the dispersed phase of around 0.5-5 % and then measured at 25 °C [31].

^{1}H-NMR spectroscopy

^{1}H-NMR spectra were obtained with a Bruker AC 200 spectrometer (Bruker Instruments, Billerica, A) and processed using software provided by the manufacturer. The solvent was D_2O. The sample was run 2 (HAPAM).

FT-IR

The samples were crushed with KBr to get pellets by applying a pressure of 600 kg/cm^2. Spectral scans were taken in the range between 4000 and 500 cm^{-1} on a Nicolet (Model Impact 410, Milwaukee, WI, USA) instrument. The samples were run 2 (HAPAM) and run 12(PAM)

Differential scanning calorimetry (DSC) and thermogravimetry (TG)

Differential scanning calorimetry (DSC) was performed on polyacrylamide (PAM) and hydrophobically associating polyacrylamide (HAPAM). DSC measurements were done on a Rheometric Scientific (DSC-SP, Surrey, UK) by heating the samples from ambient to 350 °C at the heating rate of 10 °C/min in a nitrogen atmosphere (flow rate, 20 ml/min).

The thermogravimetry (TG) was carried out under nitrogen flow (20 ml/min) using a Shimadzu TGA50 module. Samples about 4 mg were heated from 25 to 500 °C with a heating rate of 20 °C/min.

Molecular weight measurement

Ubbelohde capillary viscometer with a capillary of 0.50-0.60 mm diameter was also used to measure the molecular weight. The solvent is formamide. A stock solution of the HAPAM sample was freshly prepared by weighing and then filtered through a G5 sand filter to remove the dust. The viscosity measurements were performed at 30±0.05 °C. The density of solution was thought to be approximately the same as that of pure formamide [32, 33].

Conversion determination

The inverse microemulsion was prepared like the above mentioned polymerization experiment. After the polymerization, the 5-ml samples were withdrawn at different reaction times, that is, at different degrees of conversion. Then, it was weighted and precipitated in the cold mixture of ethanol and 200# solvent oil (2:1) with the inhibitor. It was repeatedly washed for the removal of the unreacted monomers, oil and surfactant. Then, the product was dried in a vacuum oven at 60 °C for 1 day and weighed. The conversion was calculated according to the following equation:

$$C = W_p/W_{im}C_m \qquad (1)$$

Where W_p is the weight of production, W_{im} is the weight of the sample extracted and C_m is the concentration of monomers in the inverse microemulsion system [34].

Acknowledgements

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