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Copolymerization of styrene with acrylates in emulsion and microemulsion

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Based on the copolymerization data of St/MA and St/BA in emulsion and microemulsion polymerization, the mechanism of microemulsion polymerization was discussed. The different copolymerization behaviours between these two systems were attributed to the different monomer ratios in polymerization loci. It was found that for both monomer pairs, the copolymerization behaviour in emulsion system can be well described with the semiempirical equations presented by Maxwell. Due to the much higher content of emulsifier in microemulsion polymerization, copolymerization behaviour in microemulsion is obviously different from that in emulsion copolymerization. The result of St/BA copolymerization strongly hints that the real copolymerization locus in microemulsion polymerization is the interside of the emulsifier layer. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: microemulsion copolymerization; emulsion copolymerization; reactivity ratios)

INTRODUCTION

Copolymerization of styrene with acrylates in emulsion has been extensively studied. Based on the Morton thermodynamic equations which provide a complete description of the swelling of polymer particles, Maxwell[1–4] presented a semiempirical approach to predict the monomer fraction ratios in copolymerization loci. Besides the Maxwell approach, the approach based on constant partition coefficients was also often adapted[5].

Microemulsion is quite different from emulsion. For example, it is thermodynamically stable, the monomer droplets are much smaller and the surface tension is much lower. Also, the emulsifier content in microemulsion is always much higher than that in emulsion. Thus, copolymerization in microemulsion is greatly different from that in emulsion.

Candau[6] showed that the reactivity ratios of acrylamide (M1) and sodium acrylate (M2) in inverse microemulsion polymerization were close to unity. When the copolymer of sodium 2-acrylamido-2-ethylpropanesulfonate (NaAMPS, M1) and 2-methyl acryloyethyltrimethyl ammonium chloride (MADQUAT, M2) was prepared through microemulsion copolymerization[7], $r_1 = 0.81$ and $r_2 = 1.97$. When acrylamide (M1) is copolymerized with MADQUAT (M2)[8], the reactivity becomes 0.53 (r_1) and 1.11 (r_2).

Taking the above facts into account, Candau[9] proposed a mechanism for copolymerization in inverse microemulsion, based on interparticular collisions followed by complete mixing of the particle content. The monomer proportions at the reaction sites would be maintained throughout the polymerization at their initial values, thus generating a homogeneous microstructure.

In contrast to copolymerization in inverse microemulsion, there are only a few reports on copolymerization in O/W microemulsion. Gan *et al.*[10] studied the copolymerization of styrene (St) and methyl methacrylate (MMA) in ternary o/w microemulsion. The reactivity ratios for St and MMA are 0.74 and 0.38, and differ from those for homogeneous polymerization ($r_{\mathrm{St}} = 0.5$, $r_{\mathrm{MMA}} = 0.45$). Copolymerization of St with acrylonitrile (AN) in microemulsion polymerization[11] is also different from that in solution copolymerization. It was proposed that the difference was due to the fact that some of the MMA or the AN was dissolved in the aqueous phase. It was suggested that the copolymerization was carried out inside the microemulsion droplets.

In this article, styrene was copolymerized with BA (sparingly soluble in water) and MA (rather soluble in water) in both emulsion and microemulsion. The reactivity ratios were determined by n.m.r. according to Gan *et al.*[10] The differences between reactive ratios were discussed, and the copolymerization loci in microemulsion polymerization were investigated.

EXPERIMENTAL

Materials

Styrene (St), butyl acrylate (BA) and methyl acrylate (MA) were purified by vacuum distillation and stored at −10°C until use. SDS was recrystallized from methanol. 12-butinoyloxy-9-octadecenoic acid (BOA) was synthesized at 130°C by direct esterification of butanoic acid with 12-oxy-9-octadecenoic acid (OOA) with H_2SO_4 as catalyst. BOA was further neutralized with NaOH to give sodium 12-hexinoyloxy-9-octadecenate (SBOA).

Bulk copolymerization

The mixed monomers were first degassed twice under water pump to remove oxygen, then they were irradiated with gamma ray at a dose rate of about 20 Gy/min at 25°C. The copolymerizations were stopped at low conversion (below 10%). Then the resulted copolymers were precipitated by a large quantity of methanol.

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Emulsion copolymerization

The mixed monomers (25 g) were emulsified with 75 g aqueous solution of SDS (3 wt% based on water) for about 10 min. After being degassed, the emulsions were irradiated with gamma ray (dose rate 20 Gy/min) at 25°C. The total conversion was controlled below 10%. Then the copolymer was precipitated immediately with methanol. In order to remove the emulsifier completely, the copolymer was redissolved in toluene, and reprecipitated with methanol again.

Microemulsion copolymerization

The mixed monomers (15 g) were charged into the 85 g aqueous solution of SHOA (15 wt% based on water). The microemulsions were formed automatically. Then microemulsions were polymerized and processed in the same way as depicted in emulsion copolymerization.

Copolymer characterization

The compositions of the copolymers were determined by n.m.r. n.m.r. spectra were recorded with CCl_4 as solvent at a sample concentration of about 2% w/v and with TMS as an internal reference.

RESULTS

Copolymerization of St with MA

St was sparingly soluble in aqueous phase (0.06 g/100 g of water, 25°C), while MA is rather soluble (5 g/100 g water, 25°C). They have different reactivity ratios. Therefore, copolymerization of MA and St in bulk, emulsion and microemulsion were studied to find the difference between the emulsion and microemulsion copolymerization.

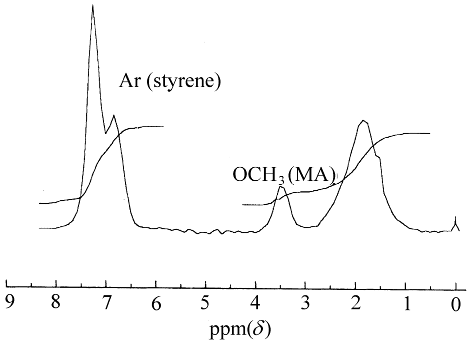

Figure 1 A typical n.m.r. spectrum of a St–MA copolymer produced by microemulsion copolymerization. The molar fraction of St in monomer feed is 0.480, and that in copolymer is 0.684

Figure 1 showed the typical n.m.r. spectrum of a St/MA copolymer. The chemical shift of the phenyl protons appeared around 7.2 ppm and that of protons in OCH_3 of MA unit was around 3.5 ppm. The styrene molar fraction (F_{St}) in copolymer was calculated from the peak area of the protons due to the phenyl group (A_p) and the peak area of methyl in MA (A_m). $F_{St}=3\times A_p/(3\times A_p+5\times A_m)$.

The St molar fraction (F_{St}) in copolymers produced under the same monomer composition by bulk, emulsion and microemulsion copolymerization are summarized in *Table 1*. The Fineman–Ross, Kelen–Tudos, YBR and Tidwell–Mortimer methods were used to evaluated the monomer reactivity ratios. The results of the three latter systems are shown in *Table 2*.

It is noted that the monomer reactivity ratios for bulk copolymerization are consistent with the result given in Ref. [15]. It implies that the monomer reactivity ratios obtained in this way are reliable and there are no obvious differences between chemical initiation and radiation initiation.

Tables 1 and *2* show that there are large differences between bulk, emulsion and microemulsion copolymerization. When the monomer composition of feed is the same, the F_{St} in copolymer from bulk copolymerization is the lowest, and that from microemulsion copolymerization is the highest.

Copolymerization of St with BA

To understand more clearly the difference between emulsion and microemulsion copolymerization, St and BA were chosen as the monomer pairs as they are both sparingly soluble in aqueous phase.

Table 3 shows the copolymerization results from bulk, emulsion and microemulsion copolymerization. In contrast to the St/MA pair, in this case the copolymer from bulk copolymerization has the largest F_{St} under the same conditions, and that from microemulsion polymerization the smallest F_{St}.

The reactivity ratios of St and BA derived by three methods for three systems are shown in *Table 4*. The reactivity for bulk is in good agreement with the data given in the Polymer Handbook[15].

Table 1 Copolymerization of St with MA in different systems

f_{St} in monomer feed	0.282	0.331	0.371	0.404	0.447	0.480	0.523	0.560	0.623	0.667	0.772
F_{St} in polymer from bulk copolymerization	0.458	0.507	0.523	0.545	0.582	0.588	0.603	0.619	0.674	0.727	0.744
F_{St} in polymer from emulsion copolymerization		0.519	0.541	0.563	0.595		0.611	0.643	0.670	0.726	0.766
F_{St} in polymer from microemulsion copolymerization	0.558	0.578		0.637		0.684	0.712		0.755	0.791	0.812

Table 2 Reactivity ratio of St (r_1) and MA (r_2) calculated using different methods

Method	Bulk copolymerization		Emulsion copolymerization		Microemulsion copolymerization	
	r_1	r_2	r_1	r_2	r_1	r_2
YBR[12]	0.85 ± 0.09	0.21 ± 0.05	0.83 ± 0.10	0.17 ± 0.08	1.45 ± 0.09	0.09 ± 0.04
Kelen–Tudos[13]	0.84 ± 0.08	0.21 ± 0.05	0.82 ± 0.09	0.17 ± 0.07	1.46 ± 0.09	0.09 ± 0.04
Tidwell–Mortimer[14]	0.84	0.21	0.80	0.17	1.53	0.11

Table 3 Copolymerization of St with BA in different systems

F_{St} in monomer feed	0.256	0.338	0.386	0.448	0.495	0.561	0.591	0.652	0.700	0.742	0.783	0.827
F_{St} in copolymer from bulk copolymerization	0.485	0.510	0.544	0.575	0.600	0.647	0.659	0.705	0.737	0.758	0.774	
F_{St} in copolymer from emulsion copolymerization		0.521		0.575		0.609		0.694	0.711	0.747	0.775	0.777
F_{St} in copolymer from microemulsion copolymerization	0.453	0.478	0.490	0.523	0.550	0.587	0.619	0.653	0.693		0.751	0.775

Table 4 Reactivity ratio of St (r_1) and BA (r_2) calculated using different methods

Method	Bulk copolymerization		Emulsion copolymerization		Microemulsion copolymerization	
	r_1	r_2	r_1	r_2	r_1	r_2
YBR[12]	0.77 ± 0.04	0.14 ± 0.04	0.64 ± 0.04	0.10 ± 0.06	0.57 ± 0.04	0.21 ± 0.04
Kelen–Tudos[13]	0.79 ± 0.05	0.15 ± 0.04	0.65 ± 0.05	0.10 ± 0.05	0.58 ± 0.04	0.22 ± 0.04
Tidwell–Mortimer[14]	0.79	0.15	0.66	0.12	0.57	0.21

Table 5 Parameters used in the Maxwell approach[5]

Monomer	Saturation concern in aqueous phase (mol/l)	Saturation concern in polymer (mol/l)	Density of monomer (g/l)	Density of homopolymer (g/l)
St	0.0037	5.13	0.906	1.05
BA	0.0079	4.60	0.889	1.16
MA	0.6	7.1	0.953	1.20

DISCUSSION

There is only one possible reason for the difference between the reactivity ratios of the bulk, emulsion and microemulsion systems. This is that the monomer fraction in polymerization loci is different although the feed composition is identical.

For emulsion copolymerization, there are two approaches to predict the monomer ratios in the polymerization loci. One is the semiempirical approach presented by Maxwell, and the other is through partition coefficients that are considered to be constant throughout the reaction.

Based on the Morton equation which provides the complete description of swelling of polymer particles, Maxwell *et al*. suggested a semiempirical approach, valid for monomers of limited solubility in water[4]. At first, this approach is used to simulate the copolymerization in emulsion. As an approximation, styrene is considered as a monomer completely insoluble in aqueous phase and is partitioned into monomer droplets or polymer particles. In simulation, the reactivity ratios for St (0.84) and MA (0.21) from the bulk system were adapted. The other parameters used for the calculation are listed in *Table 5*. The simulated results are shown in *Table 6*. Apparently the results predicted by the Maxwell equation are consistent with the actual results obtained in emulsion copolymerization.

On the other hand, the monomer reactivity ratios r_1 and r_2 from the emulsion and microemulsion copolymerization can be related to those from bulk copolymerization as follows[16]:

$$r_1 = r_1'^{*}k \tag{1}$$

$$r_2 = r_2'/k \tag{2}$$

$$f_1'/f_2' = k(f_1/f_2) \tag{3}$$

where r_1' and r_2' are those from bulk copolymerization (see *Table 2*), f_1/f_2 and f_1'/f_2' are the styrene molar ratio in the feed and in polymerization loci, respectively; k is the distribution coefficient.

When St is copolymerized with MA in emulsion, the distribution coefficient k from equation (1) is 0.95, and that from equation (2) is 1.23. Taking into account that MA has much higher solubility in aqueous phase, k is assumed to be 1.23. The St fraction in polymerization loci and in the resulting copolymer, and the MA in aqueous phase are calculated and shown in *Table 6*. In the calculation, St was regarded as insoluble in aqueous phase, therefore $f_1' = f_1$.

When St is copolymerized with MA in microemulsion, the distribution coefficient k from equation (1) is 1.82, that from equation (2) is 1.91, and the average is 1.86. As depicted above, the St fraction in polymerization loci and in the resulting copolymer, and the MA concentration in aqueous phase were also calculated for $k = 1.86$. The result is shown in *Table 6*.

It is clearly shown in *Table 6* that there is no obvious difference between the Maxwell approach and the partition coefficient approach ($k = 1.23$) for emulsion copolymerization. This has also been observed by Asua[5]. For microemulsion copolymerization, only 54% of added MA was presented in the polymerization loci. It was surprising to note that the highest solubility of MA (7.2 wt%, see *Table 6*) is in the same order of the maximum solubility (5.2 wt%) of MA in water[5]. This phenomenon has also been observed for copolymerization of St with MMA in microemulsion stabilized with cationic emulsifier[10].

What is the situation when MA is changed to BA which is sparingly soluble in the aqueous phase?

As in shown above, the Maxwell approach is also applied to predict the St fraction in polymerization loci and in the copolymer. In calculation, reactivity ratios of St and BA are those from bulk copolymerization shown in *Table 4*; the other physical values are listed in *Table 5*. The results obtained from the calculation are shown in *Table 7*. As expected, the predicted St fraction in the copolymer is in good agreement with the actual value for emulsion

Table 6 Copolymerization of St with MA

f_{St} in feed	0.282	0.331	0.372	0.404	0.447	0.480	0.523	0.560	0.603	0.668	0.722
Calculated using Maxwell approach[a]											
f_{St} in polymerization loci	0.338	0.384	0.427	0.461	0.506	0.539	0.580	0.616	0.655	0.717	0.765
F_{St} in copolymer	0.499	0.533	0.559	0.580	0.607	0.627	0.652	0.675	0.701	0.743	0.778
MA in aqueous phase (wt%)	3.45	3.18	2.96	2.78	2.55	2.38	2.17	1.98	1.70	1.46	1.21
Calculated using partition coefficient, $k = 1.23$[b]											
f_{St} in polymerization loci	0.326	0.379	0.422	0.456	0.499	0.533	0.575	0.611	0.652	0.713	0.762
F_{St} in copolymer	0.495	0.529	0.556	0.577	0.603	0.623	0.649	0.672	0.698	0.740	0.777
MA in aqueous phase (wt%)	3.21	2.89	2.70	2.55	2.35	2.20	2.01	1.84	1.65	1.37	1.14
Calculated using partition coefficient, $k = 1.86$[c]											
f_{St} in polymerization loci	0.422	0.479	0.524	0.558	0.601	0.632	0.671	0.702	0.738	0.789	0.828
F_{St} in copolymer	0.556	0.590	0.617	0.638	0.665	0.685	0.711	0.733	0.758	0.797	0.829
MA in aqueous phase (wt%)	7.27	6.75	6.32	5.97	5.52	5.17	4.74	4.35	3.92	3.26	2.72

[a] For emulsion copolymerization
[b] For emulsion copolymerization
[c] For microemulsion copolymerization

Table 7 Copolymerization of St with BA

f_{St} in feed	0.256	0.338	0.386	0.448	0.495	0.561	0.591	0.652	0.700	0.742	0.783	0.827
Calculated using Maxwell approach[a]												
f_{St} in polymerization loci	0.250	0.333	0.381	0.444	0.492	0.559	0.589	0.651	0.699	0.742	0.783	0.827
F_{St} in copolymer	0.468	0.519	0.546	0.580	0.605	0.642	0.659	0.696	0.728	0.757	0.787	0.823
Calculated through partition coefficient, $k = 0.72$[b]												
f_{St} in polymerization loci	0.199	0.269	0.312	0.369	0.414	0.479	0.510	0.574	0.627	0.674	0.722	0.775
F_{St} in copolymer	0.427	0.478	0.505	0.538	0.563	0.598	0.614	0.650	0.681	0.711	0.743	0.781

[a] For emulsion copolymerization
[b] For microemulsion copolymerization

copolymerization, although it deviates completely from the value resulting from microemulsion copolymerization.

Unexpectedly, in this case the reactivity ratios for microemulsion copolymerization can also be related to those from bulk copolymerization. The partition coefficient is 0.72 from equation (1), 0.71 from equation (2) and the average is 0.72. The styrene fraction in polymerization loci is shown in *Table 7*. It implies that only a part of added monomer was partitioned in the polymerization loci. The remaining monomer is not in the aqueous phase, because both St and BA are almost insoluble in the aqueous phase. Now the following question arises: where is the remaining monomer and the copolymerization locus?

On account of the fact that the emulsifier contents in microemulsion are always much higher than in emulsion, we assume that the thick emulsifier layer around the monomer droplets and polymer particles plays an important role in microemulsion polymerization. The interside of the emulsifier layer phase may be polymerization loci. This assumption was supported by the following facts.

At first, the simulated results for microemulsion copolymerization of St with MA shown in *Table 6*, indicate that polymerization does not take place in the aqueous phase. It is also noted that the calculated MA amounts in the aqueous phase for microemulsion copolymerization are always almost twice those of the calculated values for emulsion copolymerization using the Maxwell approach or partition coefficient (1.23). Especially when the St fraction in feed is low, the calculated MA in aqueous phase for microemulsion polymerization is higher than the maximum solubility of MA in water (5.2 wt%) given in Ref. [5]. The above two facts suggest that MA is not only located in aqueous phase and the core of monomer droplets, but also located in the emulsifier layer. It could be concluded that some of MA or MMA is located in the outside of the emulsifier layer and acts as cosurfactant due their high hydrophilicity. So the role of emulsifier in microemulsion polymerization is much more important than in emulsion polymerization.

Furthermore, when St is copolymerized with BA in microemulsion, as shown in *Table 7*, the St fraction in polymerization loci is lower than that in feed. Both St and BA are almost insoluble in water, so the partition of St can only take place in the microdroplets or polymer particles. Taking account of the fact that all the microdroplets and polymer particles are surrounded by a thick emulsifier layer, we assume that monomer composition in the interside of the emulsifier layer and the centre of particles may be different. It was reported that when microemulsion is stabilized with SBOA, the highest content of BA in microemulsion is about 30%[17] and that for St is only about 20%[18]. It hints that BA may have higher saturation concentration in emulsifier layer than St, because there is an ester group in the lipophilic head of SBOA. Therefore, when St is copolymerized with BA in this microemulsion, St fraction in emulsifier layer may be lower than that in the centre of the particle. It can be concluded that the polymerization locus is the interside of the emulsifier layer, not the centre of microdroplets, because F_{St} in the copolymer from microemulsion copolymerization is lower than that from bulk copolymerization when the feed is identical.

Moreover, it was reported that the homopolymerization rates of St and BA in microemulsion polymerization both decreased with the increase of emulsifier content[17,18]. It was consistent with the assumption, because the increase of emulsifier content dilutes the monomer content in polymerization loci (interside of emulsifier lay around particles).

In summary, although there is still much work to do, it can be concluded that the real polymerization locus in microemulsion polymerization is the interside of the emulsifier layer around particles.

CONCLUSION

Copolymerizations of St/MA and St/BA in bulk, emulsion and microemulsion were studied with n.m.r. It was demonstrated that there are great differences among these three systems for both monomer pairs.

For both monomer pairs, the copolymerization behaviour of emulsion copolymerization can be well described with the semiempirical approach presented by Maxwell.

In contrast to emulsion copolymerization, microemulsion copolymerization cannot be processed with the Maxwell approach, and it can be well predicted with the partition coefficient approach for both monomer pairs. The result of St/BA copolymerization in microemulsion strongly hints that the real copolymerization locus in microemulsion polymerization is the interside of the emulsifier layer, not the centre of particles.

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