

Poly(ethylene oxide) macromonomers

5. Dodecyloxy poly(ethylene glycol) methacrylate as an amphiphilic macromonomer for dispersion polymerization

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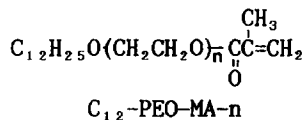
Summary

Dodecyloxy poly(ethylene glycol) methacrylates with a degree of polymerization from 9 to 20 were used as comonomers in the dispersion polymerization of benzyl methacrylate (BzMA) and styrene (St) to obtain soapless emulsions stabilized by the resulting graft copolymers. In the aqueous dispersion with BzMA, the apparent reactivities of the macromonomers were essentially the same as those observed in the benzene solution, while in heptane they increased as also found in the case of the aqueous dispersion with St. The latter fact suggests a preferential polymerization near on the surface of the micellar particles where the macromonomers are enriched.

Introduction

In the first report of macromonomers by ICI group (1), the glycidyl methacrylate adducts of poly(12-hydroxystearic acid) or ω -carboxylated poly(dodecyl methacrylate) were used as the soluble components in the dispersion polymerization in organic media (petroleum). The macromonomers also functioned as the comonomers during polymerization of the major-component monomers such as methyl methacrylate to produce the graft copolymers which served in turn to make a stable high-solid dispersion system.

In a preceeding paper (2), we described the radical copolymerizations of dodecyloxy poly(ethylene glycol) methacrylate with St and BzMA in benzene solution.



This macromonomer is interesting in that it is by itself an amphiphilic monomer carrying hydrophilic (poly(ethylene glycol)) and hydrophobic (dodecyl) segments so that it will also be able to function as a surface-active dispersant in both oil-in-water and water-in-oil systems. Thus it will be expected to be a useful macromonomer for preparing soapless

emulsions via simple copolymerizations with a variety of conventional monomers in both aqueous and organic media. This paper describes the apparent reactivities of these macromonomers in dispersion copolymerization with St and BzMA in comparison with those obtained in benzene solution.

Experimental

C₁₂-PEO-MA was prepared and characterized as described before (2). 2,2'-Azobisisobutyronitrile (AIBN) and potassium persulfate (KPS) were recrystallized from methanol and water, respectively. 4,4'-Azobis(4-cyanovaleic acid) (AVA) was used as supplied commercially (Aldorich).

Dispersion copolymerization was typically conducted as follows. A mixture of monomers (total 2 g) and water (200 ml) was magnetically stirred (around 900 rpm) at 60°C under Argon atmosphere to give an emulsion. After addition of the initiator, stirring was continued for a desired time to give 10 to 20 wt% conversion. The product was precipitated out by pouring into methanol (sometimes containing a small amount of calcium nitrate to help rapid coagulation), washed repeatedly with methanol, and dried in vacuo. The polymers obtained were confirmed by GPC to be free of the unreacted monomers and analyzed for the composition by ¹H NMR as described before (2).

Results and Discussion

Dispersion Copolymerization with BzMA. C₁₂-PEO-MA-9 was found to be an effective emulsifier for BzMA in water even in a concentration less than 5 wt%, to give a stable milky emulsion. Upon addition of either water-soluble (KPS, AVA) or oil-soluble initiator (AIBN), the polymerization proceeded to give also a stable emulsion including polymers at least before about 30 wt% conversion. The "apparent" monomer reactivity ratio, $r_1 = k_{11}/k_{12}$, was estimated by the approximate composition equation (3-5) which hold under the condition of $[M_1]/[M_2] \gg 1$,

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (1)$$

where $d[M_1]/d[M_2]$ is the molar ratio of M₁ (BzMA) to M₂ (macromonomer) in the polymer obtained and $[M_1]/[M_2]$ is that in the monomer feed as charged.

The results given in Table 1 clearly show that the r_1 thus determined is constant, irrespective of the composition, supporting the above approximation. Table 2 summarized the r_1 data. In aqueous dispersion, r_1 is independent of the nature of the initiator and also very close to that obtained in the benzene solution previously (2). This fact suggests that not only the monomer composition at the polymerization site (active center) but also the reactivity ratio are the same as those of the solution (homogeneous) polymerization. This may be expected because the macromonomer here is compatible with poly-

Table 1. Dispersion Copolymerization of BzMA (M_1) and C_{12} -PEO-MA-9

| Medium | Initiator | $\frac{[M_1]}{[M_2]}$ | Time min | Conv. wt% | $\frac{d[M_1]}{d[M_2]}$ | r_1 |
|----------------------|-----------------|-----------------------|-------------|--------------|-------------------------|-------|
| | | | | | | |
| Water ¹ | KPS 0.3 mol% | 48.1 | 30 | 10 | 65.7 | 1.37 |
| | | 19.1 | 35 | 11 | 26.8 | 1.40 |
| | | 13.3 | 40 | 30 | 18.2 | 1.37 |
| | | 9.1 | 20 | 8 | 13.5 | 1.48 |
| Water ¹ | AVA 1 mol% | 94.7 | 120 | 25 | 124 | 1.31 |
| | | 31.2 | 120 | 20 | 44.5 | 1.43 |
| | | 18.4 | 90 | 15 | 25.3 | 1.38 |
| | | 13.2 | 120 | 25 | 18.2 | 1.38 |
| Water ¹ | AIBN 1 mol% | 92.9 | 30 | 9 | 124 | 1.34 |
| | | 32.0 | 30 | 20 | 44.5 | 1.39 |
| Heptane ² | AIBN 1 mol% | 98.8 | 120 | 8 | 40.7 | 0.41 |
| | | 49.9 | 120 | 5 | 19.0 | 0.38 |
| | | 31.1 | 120 | 5 | 13.1 | 0.42 |

¹ Total monomers 2 g, water 200 ml, 60°C.

² Total monomers 4 g, heptane 40 ml, 60°C.

Table 2. Copolymerization of BzMA (M_1) and C_{12} -PEO-MA-9 (M_2)

| Initiator | Medium | Appearance | | r_1 |
|-----------|---------|------------|----------------------|-------------------|
| | | Monomer | Polymer ¹ | |
| AIBN | Benzene | Solution | Solution | 1.23 ± 0.09^2 |
| KPS | Water | Emulsion | Emulsion | 1.41 ± 0.07 |
| AVA | Water | Emulsion | Emulsion | 1.38 ± 0.07 |
| AIBN | Water | Emulsion | Emulsion | 1.37 ± 0.03 |
| AIBN | Heptane | Solution | Suspension | 0.40 ± 0.02 |

¹ Stopped before about 20 wt% conversion.

² Ref. 2.

BzMA (2) and the reactivity ratio in the radical copolymerization will not change so much with the medium.

In contrast, however, the reversed "apparent" reactivity was observed in heptane in which the monomer clear solution turned into a polymer suspension upon polymerization. Since BzMA is soluble in the medium, the result suggests that the polymerization occurred preferentially near on the (inversed) micelle surface where the macromonomers should be enriched.

Thus the observed change in the "apparent" monomer reactivity ratio in these dispersion systems appears only to reflect the corresponding change in the monomer composition near the polymerization site ("effective" monomer composition), $([M_1]/[M_2])_{\text{eff}}$, since the approximate composition equation should be then

$$\frac{d[M_1]}{d[M_2]} = (r_1)_{\text{true}} \cdot \left(\frac{[M_1]}{[M_2]} \right)_{\text{eff}} \quad (2)$$

with $(r_1)_{\text{true}}$ being the true monomer reactivity ratio. From eqs (1) and (2), it follows that

$$\frac{r_1}{(r_1)_{\text{true}}} = \frac{([M_1]/[M_2])_{\text{eff}}}{[M_1]/[M_2]} \quad (3)$$

Therefore, under a reasonable assumption that the $(r_1)_{\text{true}}$ should not change with the polymerization medium, i. e., $(r_1)_{\text{true}} = (r_1)_{\text{solution}}$, the change in the "apparent" reactivity ratio, r_1 , should merely correspond to the change in $([M_1]/[M_2])_{\text{eff}}$ from the feed composition $[M_1]/[M_2]$.

Dispersion Copolymerization with St. In the aqueous dispersion system with C_{12} -PEO-MA-9, which is the least hydrophilic macromonomer presently studied, some polymers precipitated out during polymerization, in contrast to the stable emulsion as found with BzMA above. This is expected because St is more hydrophobic than BzMA and poly-St is incompatible with the macromonomer (2). The "apparent" r_1 in Table 3 showed a composition dependence, increasing at higher St composition. C_{12} -PEO-MA-20 appears to have the most suitable hydrophilic-hydrophobic balance to make stable emulsions for both monomers and polymers, and the "apparent" r_1 is constant, independent of the composition. The most hydrophilic macromonomer with ω -methyl terminal, C_1 -PEO-MA-39, could not disperse the monomer so that the St droplets coexisted during polymerization. Table 4 summarized the "apparent" r_1 's together with those obtained for the solution copolymerization (2).

In contrast to the results of the aqueous dispersion system with BzMA, the "apparent" r_1 's of St were always significantly lower than those of the solution system, meaning the lower St composition or the higher macromonomer composition in the produced polymers. This result, coupled with the consideration given above for the copolymerization with BzMA in heptane, appears most reasonably to indicate that the polymerization proceeded preferentially near on the surface of the micelle or the particles which had solubilized or emulsified St monomers in the interior, surrounded by the PEO macromonomers on the periphery. This model can explain the higher incorporation of the macromonomers, particularly of the less hydrophilic macromonomer which would aggregate more extensively to form the micelle.

In view of the above results, the dispersion polymerization using the amphiphilic PEO macromonomer appears to be promising for organized (morphology-controlled) polymerization by choice of appropriate macromonomer and medium. Unfortunately, however, the reported system was found to give gelled polymers at increased conversions, for some reason not clearly understood at present, while the solution system gave the soluble polymers up to nearly complete conversions under the similar condition.

Table 3. Aqueous Dispersion Copolymerization of St (M_1) and PEO Macromonomers (M_2)¹

| M_2 | $\frac{[M_1]}{[M_2]}$ | Time h | Conv. wt% | $\frac{d[M_1]}{d[M_2]}$ | r_1 |
|--|-----------------------|-----------|--------------|-------------------------|-------|
| C _{1,2} -PEO-MA-9 | 93 | 5 | 20 | 39 | 0.42 |
| | 48 | 6 | 15 | 14 | 0.30 |
| | 32 | 6 | 13 | 5 | 0.15 |
| C _{1,2} -PEO-MA-20 | 329 | 2 | 5 | 142 | 0.43 |
| | 241 | 2 | 5 | 110 | 0.46 |
| | 204 | 4 | 10 | 82 | 0.40 |
| C ₁ -PEO-MA-39 ² | 501 | 4 | 6 | 332 | 0.66 |
| | 330 | 3 | 9 | 249 | 0.75 |

¹ Total monomers 2 g, AVA 1 mol%, water 200 ml, 60°C.

² $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{39}\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}\text{C}=\text{CH}_2$; Mw/Mn = 1.1, see ref. 2 for preparation.

 Table 4. Copolymerization of St (M_1) and PEO Macromonomers (M_2)

| M_2 | Aqueous dispersion | | r_1 | Solution |
|-----------------------------|--------------------|------------------------|-----------|--|
| | Monomer | Polymer ¹ | | r_1 |
| C _{1,2} -PEO-MA-9 | Emulsion | Emulsion (+ppt) | 0.15~0.42 | 0.79±0.05 (in benzene) ² |
| C _{1,2} -PEO-MA-20 | Emulsion | Emulsion | 0.43±0.03 | 0.82±0.02 (in benzene) ² |
| C ₁ -PEO-MA-39 | Droplet | Emulsion (+droplet) | 0.71±0.05 | 1.02±0.02 (in THF) ³ |

¹ Stopped before about 20 wt% conversion.

² Ref. 2.

³ The value with tert-butoxy-PEO-MA-35, see ref. 5.

References

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