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

\[
\begin{align*}
\text{CH}_3 \\
\text{C}_{12}H_{25}O(CH_2CH_2O)_n\text{C}=\text{CH}_2 \\
\text{O} \\
\text{C}_{12}-\text{PEO-MA-n}
\end{align*}
\]

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
C_{12}-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-cyanovaleric acid) (AVA) was used as supplied commercially (Aldrich).

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. C_{12}-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, \( r_1 = \frac{k_1}{k_2} \), was estimated by the approximate composition equation (3-5) which hold under the condition of \([M_1]/[M_2] \approx 1\),

\[
\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}
\]

where \(d[M_1]/d[M_2] \) is the molar ratio of \( M_1 \) (BzMA) to \( M_2 \) (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-