Emulsion polymerization of lauryl methacrylate and its copolymerization with trimethylolpropane trimethacrylate

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Abstract

The emulsion polymerization of lauryl methacrylate and its copolymerization with trimethylolpropane trimethacrylate (TMPTMA) were investigated. The induction period (IP) for LMA polymerization was observed to be very long as compared to substantially no IP for methyl methacrylate polymerization. The addition of TMPTMA as a crosslinker clearly prolonged IP, owing to the reduced radical entry of oligomeric growing radical having rather hydrophilic and crosslinkable TMPTMA units into the polymer particle surface. Besides, no gelation was observed even above 90% conversion for LMA/TMPTMA(80/20) copolymerization. The initial abrupt increase in the conversion dependencies of weight-average molecular weight results from the compartmentalization of reaction loci and the gel effect. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We were concerned with the elucidation of the crosslinking reaction mechanism and the control of network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds as a long-term controversial problem because of the complexity of the reaction involved [1]. As part of our continuing studies, we attempted to control network formation with the intention of collecting the basic data for the molecular design of three-dimensional vinyl-type polymers with high performance and high functionality. First, the steric effects of long-chain alkyl groups on free-radical vinyl polymerization including a multivinyl compound were discussed in terms of the control of gelation; [2] the occurrence of intermolecular crosslinking leading to gelation was obviously suppressed by the steric effect of the long-chain alkyl group, providing a new way for the preparation of novel self-crosslinkable prepolymers having pendant vinyl groups. This was further extended to the copolymerizations of alkyl methacrylates (RMA) with trimethylolpropane trimethacrylate (TMPTMA), [3] in which trivinyl monomer was employed in place of the divinyl monomer as a crosslinker because, more than one methacryloyl groups, i.e., uncyclized structure unit having two methacryloyl groups or monocyclic structure unit having one methacryloyl group, will be introduced by the incorporation of one TMPTMA unit into the polymer chain: [4]. The primary chain length increased with an increase in the size of the alkyl group in RMA and concurrently, the deviation of the actual gel point from the theoretical one became greater because of the reduced occurrence of bimolecular termination and intermolecular crosslinking caused by the steric effect of a long-chain alkyl group. The effects of primary chain length, dilution, TMPTMA content, and solvent on the gelation were also investigated [5].

As an extension of our previous works mentioned earlier, we attempted to study the emulsion copolymerization of lauryl methacrylate (LMA) having long-chain alkyl group with TMPTMA, especially focusing on the preparation of self-crosslinkable prepolymers having pendant vinyl groups. In this connection, it should be noted that reactive microgels as intramolecularly crosslinked macromolecules, having substantial amounts of reactive groups remaining in their interior and at their surface, were prepared by the emulsion polymerization of multivinyl compounds accompanied by crosslinking [6].

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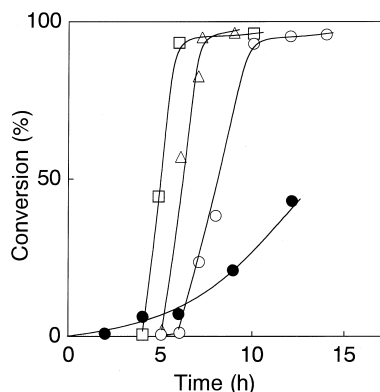*E-mail address:* amatsu@ipcku.kansai-u.ac.jp (A. Matsumoto)

Fig. 1. Conversion-time curves for the emulsion copolymerizations of LMA with (□) 5, (△) 10, (○) 20 and (●) 50 mol% of TMPTMA at 50°C. Ingredients: monomer/water = 10/90 (w/w); [KPS] = 0.01 mol/L; [SDS] = 0.05 mol/L. Concentrations of KPS and SDS are related to the aqueous phase.

2. Experimental

Commercially available methyl methacrylate (MMA), hexyl methacrylate (HMA), bornyl methacrylate (BoMA), LMA, and TMPTMA monomers (kyoeisha Chemical Co., Ltd.) were purified by the conventional method. Initiator potassium peroxodisulfate (KPS) and emulsifiers sodium dodecylsulfate (SDS), potassium laurate (PL), and polyethylene glycol monolauryl ether $HO(CH_2CH_2O)_n(CH_2)_{11}CH_3$ ($n = 23$) (PEG23LE) (Tokyo Chemical Industry Co., Ltd.) were used as supplied. Twice-distilled water was used as a polymerization medium.

Emulsion polymerizations were carried out in an ampoule at 50°C [7,8]. Ultrasonification was applied to provide the fine monomer emulsion. After a predetermined time of reaction, the polymer obtained was precipitated by pouring into a large amount of methanol.

The weight-average molecular weight $\bar{M}_w$ was measured by light scattering (LS). LS measurements were carried out in tetrahydrofuran at 30°C with an Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer over the
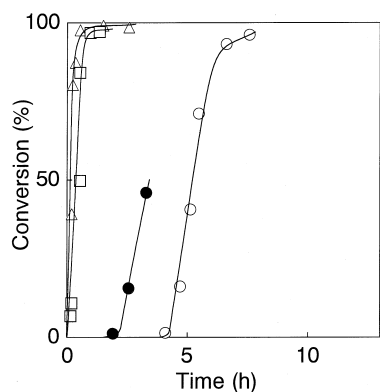

Fig. 2. Conversion-time curves for the emulsion polymerizations of (□) MMA, (△) HMA, (●) BoMA and (○) LMA at 50°C (see Fig. 1).
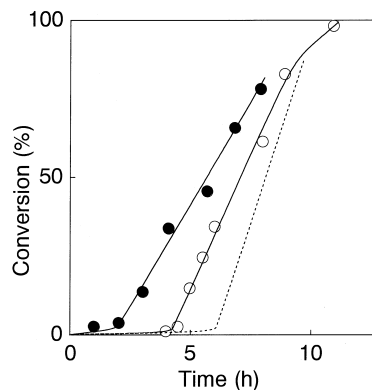

Fig. 3. Conversion-time curves for the emulsion copolymerizations of (●) MMA, (○) HMA and (–-) LMA with 20 mol% of TMPTMA at 50°C (see Fig. 1).

angular range between 30–150°, using unpolarized light of wavelength 632.8 nm.

3. Results

During the progress of this investigation with the above mentioned aim, we found by chance that the emulsion copolymerization of LMA with TMPTMA showed the following specific features: Thus, Fig. 1 shows the conversion-time curves for the radical emulsion copolymerizations of LMA with different amounts of TMPTMA as a crosslinker in the presence of SDS as an emulsifier initiated by KPS at 50°C. Interestingly, the induction period (IP) was very long and it prolonged with increased TMPTMA feed. Moreover, the rate of polymerization (R_p) tended to decrease with an increase in the TMPTMA content in the feed as opposed to the cases of the solution copolymerizations [3,5]. Also, no gelation was observed even above 90% conversion for LMA/TMPTMA(80/20) copolymerization, although gelation occurred for MMA/TMPTMA and HMA/TMPTMA copolymerizations.

These specific features may have arisen from mainly two factors, including a hydrophobic, long-chain alkyl group belonging to LMA and a crosslinking nature of TMPTMA units incorporated into the copolymer. First, we checked the significance of hydrophobicity of LMA in comparison with the emulsion polymerizations of various RMAs: Fig. 2 shows the conversion-time curves for the polymerizations of MMA, HMA, BoMA, and LMA. Emulsion polymerization of hydrophilic MMA monomer clearly reached a conversion close to 100% in a short time. On the contrary, the very long IPs were observed for the polymerizations of hydrophobic BoMA and LMA monomers.

Second check was done for the significance of crosslinking nature of TMPTMA units incorporated into the copolymer by comparing LMA/TPMTMA(80/20) emulsion copolymerization with MMA/TMPTMA(80/20) and HMA/TMPTMA(80/20) ones as shown in Fig. 3. IP became
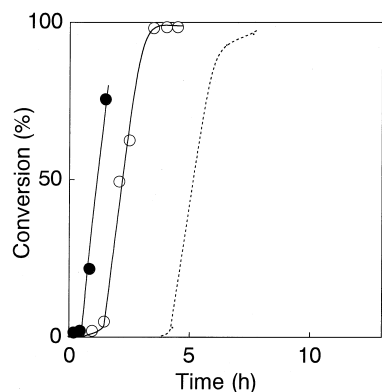
Fig. 4. Conversion-time curves for the emulsion polymerizations of LMA using (––) SDS, (○) PL, or (●) PEG23LE as emulsifier at 50°C (see Figs. 1 and 2).

shorter with an increase in the hydrophilicity of mono-mer from LMA to MMA, while the R_p tended to decrease.

In addition, we examined the effect of emulsifier types on the rate feature of LMA polymerization as shown in Fig. 4; thus, IP was shortened in the order: strongly anionic SDS > weakly anionic PL > non-ionic PEG23LE.

Finally, the dependence of $\bar{M}_w$ on conversion was exam-ined for the copolymerizations of LMA with different amounts of TMPTMA as shown in Fig. 5; interestingly, the molecular weights of resulting copolymers increased with an increase in the TMPTMA content from 5–10 mol% and then, decreased from 10–20 mol% Also, the $\bar{M}_w$ values were observed to increase with conversion and its increasing tendency was much more pronounced at a lower conversion.

4. Discussion

4.1. Prolonged IP for the emulsion polymerization of LMA

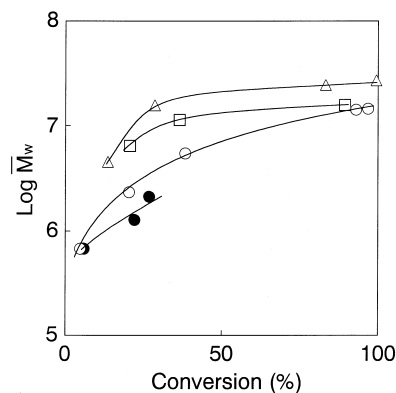In the emulsion polymerization of LMA and its copoly-

Fig. 5. Dependence of $\bar{M}_w$ on conversion for the emulsion copolymeriza-tions of LMA with (□) 5, (△) 10, (○) 20 and (●) 50 mol% of TMPTMA at 50°C (see Fig. 1).

merization with TMPTMA, the specific features were observed as described earlier. That is, as shown in Fig. 2, the IP increased with decreasing water solubility (WS) of RMA as follows:

$$RMA/IP(h) : MMA, HMA/0 < BoMA/2.3 < LMA/4.2 \quad (1)$$

and

$$RMA/WS(g/100gwater) : MMA/1.5 > HMA/0.011$$
$$> BoMA/0.0060 > LMA/0.00077 \quad (2)$$

It is generally expected that primary radicals, i.e., sulfate-radical anions, do not enter directly into a hydrophobic polymer particle but instead must add a few monomer units to become more hydrophobic, oligomeric growing radicals with amphiphilic or surface active nature. Particle nucleation takes place when primary or hydrophilic radicals in the aqueous phase grow via propagation to become hydrophobic or amphiphilic ones to enter into hydrophobic monomer-swollen micelles or precipitate from water to form primary particles. This is the case with the hydrophilic monomer such as MMA where the monomer-saturated aqueous phase favors the formation of such surface active or hydrophobic oligomeric growing radicals able to enter into the monomer-swollen micelles or precipitate from water. The sparingly water-soluble monomers such as BoMA and LMA do not exist enough in an aqueous phase to promote the growth of primary radicals to form oligo-meric growing radicals. Under such conditions, the primary and/or oligomeric growing radical recombination or termi-nation is supposed to be very efficient. This is one of the reasons why the radical entry rate coefficient decreases from MMA to LMA.

Also, the emulsion polymerization of LMA depended on the type of emulsifier as shown in Fig. 4. The IP was found to vary with the emulsifier type as follows:

$$IPin\ h/emulsifier :\ 0.4/PEG23LE < 1.3/PL < 4.2/SDS \quad (3)$$

The successful capture of radicals by monomer-swollen micelles occurs in the runs with weakly anionic PL and remarkably, with non-ionic PEG23LE. As a reason of mark-edly prolonged IP for the LMA polymerization using strongly anionic SDS as an emulsifier, it may, in addition, be noteworthy to consider that the molecular structure of the primary radical, i.e., sulfate radical anion is very similar to that of SDS.

4.2. Addition effect of TMPTMA as crosslinker

The addition of crosslinker such as TMPTMA was found to vary both IP and R_p as shown in Figs. 1 and 3, both of

which were observed in the following order:

IP in h (monomer type) : 0 (MMA, HMA)

   $<$ 1.8 (MMA/TMPTMA(80/20))

   $<$ 4.0 (HMA/TMPTMA(80/20)) $<$ 4.2 (LMA)

   $<$ 6.0 (LMA/TMPTMA(80/20))   (4)

and

R_p in %/h (monomer type) : 250 (HMA) $>$ 125 (MMA)

   $>$ 50 (LMA) $>$ 25 (LMA/TMPTMA(80/20))

   $>$ 17 (HMA/TMPTMA(80/20))

   $>$ 14(MMA/TMPTMA(80/20))   (5)

The water solubility of TMPTMA(0.017 g/100 g water) is high, enough not only to initiate polymerization, but also to aid the growth of oligomeric growing radicals in a water phase. However, the prolonged induction period with TMPTMA indicates that the polymer growth in water and the radical entry events are restricted. That is, the rigidity of oligomeric radicals having TMPTMA units and its lower reactivity caused by a steric effect disfavors the growth of radicals and their entry into the monomer-swollen micelles.

The addition of TMPTMA was found to decrease remarkably the rate of copolymerization and its decreasing tendency is more pronounced in the runs with more hydrophilic comonomers. Thus, the stronger decrease was observed in MMA/TMPTMA(80/20) copolymerization. It is reasonable to suppose that the reactivity of methacryloyl groups of TMPTMA monomer is much more reactive than the ones belonging to TMPTMA units incorporated into the high-molecular-weight polymer chain. Moreover, the reduced extent of reactivity of pendant double bonds in the copolymer depends on the comonomer from MMA to LMA. In the copolymerization with MMA, the less steric effect would be reflected as the formation of polymer network with high crosslinking density. Under such conditions, the polymerization proceeds on the particle surface and, therefore, the rate is slow. In the case of the copolymerization with LMA, the rather branched copolymers are formed as a reflection of reduced intramolecular crosslinking [5]. The high alkyl chain density at the reaction loci and the bulky, rigid structure of TMPTMA promote the effect of steric factor on the polymerization process; this reduces the reactivity of pendant double bonds for intermolecular and/or intramolecular crosslinking [1].

4.3. Conversion dependencies of molecular weight

The weight-average molecular weights $\bar{M}_w$ of LMA/TMPTMA copolymers were observed to increase with conversion and its increasing tendency was much more pronounced at a lower conversion as shown in Fig. 5. The initial abrupt increase in $\bar{M}_w$ results from the compartmentalization of reaction loci and the gel effect. At medium or high conversions, $\bar{M}_w$ increases slightly or reaches the plateau. This behavior may be attributed to a decrease in the monomer concentration at the reaction loci, the low monomer swellability of polymer particles, and the polymerization at the particle surface. The high conversion polymerization behavior in the particle is rather sophisticated because more reactive TMPTMA would be consumed earlier as compared to LMA, resulting in the less crosslinked polymerization at a later stage of polymerization and, moreover, the gel effect is more operative.

Interestingly, the dependence of $\bar{M}_w$ on TMPTMA content shows a maximum at ca.10 mol% in feed. The increase of TMPTMA feed of above 20 mol% disfavors the growth events. The steric effect and the lower reactivity of propagating chains having dense crosslinking densities are responsible for the formation of polymers of lower-molecular weights.

5. Conclusion

From the foregoing discussion, it appears that the IP increases with increasing the hydrophobicity of RMA. The more hydrophilic MMA monomer favors the formation of more active oligomeric growing radicals for entry and growth events than the sparingly water-soluble monomer such as LMA. No gelation was observed even above 90% conversion for LMA/TMPTMA copolymerization. The presence of a rigid TMPTMA crosslinker decreases the rate of polymerization owing to lower reactivity of growing radicals caused by the steric effect.

The initial abrupt increase in $\bar{M}_W$ results from the compartmentalization of reaction loci and the gel effect. The addition of TMPTMA of more than 20 mol% decreases the reactivity of growing polymer radicals by the steric effect owing to the dense crosslinking densities.

The experimental work for a detailed mechanistic discussion is now in progress.

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