Emulsion Crosslinking Polymerization of Allyl Methacrylate

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ABSTRACT

In the emulsion polymerization of allyl methacrylate (AMA), no gelation occurred, whereas gelation occurred easily at about 4% conversion in the bulk polymerization. Thus, the reactive cross-linked-polymer microspheres as microgel-like polymers with abun-dant pendant allyl groups were easily obtained in the emulsion polymerization because AMA possesses two types of vinyl groups, methacrylic and allylic double bonds, having greatly different reac-tivities. The weight-average molecular weights, the r.m.s. radii of gyration, the second virial coefficients, the intrinsic viscosities, and ^{1}H-NMR spectra of the resulting allyl-type reactive microspheres were characteristic of microgel-like polymers as compared with those of the branched-polymer-like prepolymers obtained in bulk. The precopolymers prepared from the emulsion copolymerization of AMA with methyl methacrylate and ethylene dimethacrylate in order to obtain the crosslinked-polymer microspheres having differ-ent crosslinking densities were also characterized, although the results obtained are not in conformity with our expectation.

INTRODUCTION

We have been 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, especially including

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multiallyl compounds, in order to molecularly design three-dimensional vinyl-type polymers with high performance and high functionality [1]. Thus, in the bulk polymerization of diallyl phthalate, the actual gel point was found to be 6.9 times higher than the theoretical one. In common multivinyl polymerization systems, the discrepancy was more than 10 times and sometimes more than 10^2. Moreover, the deviation became greater with increasing primary chain length, content of pendant double bonds in the prepolymer, and dilution. In order to interpret the greatly delayed gelation reasonably, intramolecular cyclization, reduced reactivity of the prepolymer, intramolecular crosslinking, and microgelation have been studied in detail. Finally, we reached the following conclusions: the primary factor is the thermodynamic excluded volume effect on the intermolecular crosslinking reaction between growing polymer radical and prepolymer, especially at high molecular weight. Beyond the theoretical gel point, a secondary factor is the intramolecular crosslinking which becomes progressively important with conversion. The latter leads to the restriction of segmental motion of the prepolymer and, moreover, imposes steric hindrance, i.e., shielding effect [2] or steric excluded volume effect, inducing reduced reactivity as a tertiary factor.

As a further discussion of this tertiary factor leading to the reduced reactivity of pendant double bonds in the prepolymer, the intramolecular crosslinking may tend to occur locally because the formation of the crosslinked unit induces the decrease of the interaction between polymer segment and solvent or the increase of the interaction between polymer chains leading to an enhanced occurrence of intra-molecular crosslinking. Thus, the locally enhanced occurrence of intramolecular crosslinking accompanied by microsyneresis could lead to the formation of a micro-gel [3, 4, 5] having a highly crosslinked microdomain which may induce microphase inversion. Here, the microgel is conceived as consisting of both core and shell parts of high and low crosslinking densities, respectively, although it is soluble due to a strong interaction of the shell part with solvent overcoming the presence of the core part, just like a microsolid, having quite a weak interaction with the solvent. That is, we will have different kinds of microgels depending on the combination of various types of core and shell parts; the microgel varies from the branched-polymer-like to rigid-sphere-like ones. Now, a more detailed understanding of microgels is significantly required not only for the elucidation of three-dimensional network formation mechanism, but also for the molecular design of vinyl-type net-work polymers with high performance and high functionality.

As an extension of our continuing work mentioned above, we are now deal-ing with the emulsion crosslinking polymerization of multivinyl compounds,

especially focusing on the formation of reactive crosslinked-polymer microspheres as models of microgels, with the intention of clarifying the correlation of the net-work structure with the reactivity of resulting microspheres which would be useful as functionalized polymeric materials. Here we report the experimental results of the emulsion crosslinking polymerization of allyl methacrylate (AMA), in which reactive crosslinked-polymer microspheres having abundant pendant allyl groups with a low crosslinking density, i.e., soft-type pseudomicrogels, would be obtain-able. That is, since AMA has two different types of double bonds, i.e., conjugated methacrylyl and unconjugated allyl groups, and the reactivity of methacrylyl group relative to allyl group is quite high, the preferential polymerization of methacrylyl group to lead to the formation of prepolymer having abundant pendant allyl groups occurs at an early stage of polymerization [6] and with the progress of polym-erization the gradually enhanced occurrence of intermolecular and intramolecular crosslinking reactions is observed, eventually to form a gel [7], although the low reactivity of the growing polymer radical toward the pendant allyl groups of pre-polymer would result in the suppressed occurrence of intramolecular crosslinking leading to the formation of crosslinked polymer having a low crosslinking density.

    In connection with the emulsion polymerization of AMA, it is noteworthy to recall that Lovell et al. [8] employed AMA for graft linking; under certain reaction conditions, the allyl groups react with other unsaturated groups to give graft linking and crosslinking. However, their reactivities are lower due to which the lower cross-linking densities are observed than would be observed with diacrylates or dimeth-acrylates.

EXPERIMENTAL

    AMA, methyl methacrylate (MMA), and ethylene dimethacrylate (EDMA), commercially available reagents, were purified by conventional methods and then, subjected to vacuum distillation under nitrogen [9]. Potassium peroxodisulfate (KPS) as initiator and sodium dodecylsulfate (SDS) as emulsifier were used as commercially available, extra pure reagents. Twice-distilled water was employed as a polymerization medium.

    Emulsion polymerizations were carried out in an ampoule at 50°C [10] according to the following recipe: typically, monomer 10 g, water 90 g, SDS 1.3 g, and KPS 0.03 g. Ultrasonification was applied to provide the fine monomer emul-sion. After a predetermined time of reaction, the polymer obtained was precipitated by pouring into a large amount of methanol.

The weight-average molecular weights $\overline{M}_w$, the r.m.s. radii of gyration $\langle S^2 \rangle^{1/2}{}_z$, and the second virial coefficients A_2 of the resulting polymers were measured by light scattering. The measurements were carried out in tetrahydrofuran (THF) at 30 $\pm$0.1°C with an Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer over the angular range between 30-150°, using unpolarized light of wavelength 632.8 nm. $\overline{M}_w$ and $\langle S^2 \rangle^{1/2}{}_z$ were also measured by size-exclusion chromatography (SEC) using a dual detector system, set in the direction of flow, consisting of a multi-angle laser light scattering (MALLS) device and a differential refractometer in sequence. SEC-MALLS measurements were performed at 40°C in THF using a Shodex GPC KF-806L x 3 and KF-807 x 2 columns, at polymer concentrations 0.1- 0.5% (w/v) and flow rate 1 mL/min. The MALLS device was a DAWN Model F (Wyatt Technology Corp.) where the laser beam, of wavelength 632.8 nm, was focused on a 67 μL flow cell. The intrinsic viscosity [η] was determined with Ubbelohde viscometer in THF at 30°C. The unreacted pendant allyl groups of the prepolymer were calculated from the iodine value obtained by the Wijs method.

RESULTS AND DISCUSSION

Cyclopolymerization and Gelation of AMA

We have investigated in detail the radical polymerization of AMA in terms of cyclopolymerization [6], especially under the specified conditions, i.e., above the ceiling temperature for a head-to-tail propagation in the polymerization of methacrylate. Thus the structure of the polymer obtained was examined by ^{1}H- and ^{13}C-NMR and IR spectroscopy; no existence of unreacted pendant methacrylyl groups was observed, which suggests that, as a cyclopolymerization mechanism of AMA, intermolecular propagation of growing radicals, followed by intramolecular cyclization or intermolecular propagation of the resulting uncyclized methacrylyl radical, occurs exclusively with methacrylyl group. Temperature dependency of cyclization constant K_C was unusual; K_C increased rapidly at elevated temperatures and no linear relationship of ln K_C vs. 1/T was observed. Five-membered ring for-mation was favored at an elevated temperature and diluted monomer concentration. These results are discussed thermodynamically in terms of controlled ring closure in cyclopolymerization.

Here, it should be noted that as a remarkable feature no pendant methacrylyl groups of polymer were detectable and the structure of poly(AMA) obtained in the early stage of polymerization, in which the presence of crosslinked units was negligible, is the following:
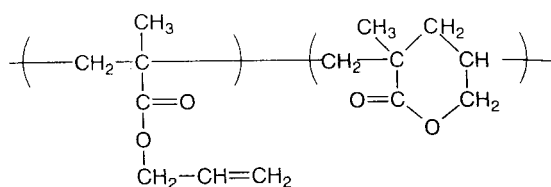
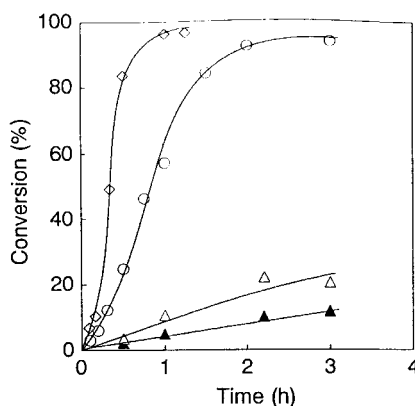**Figure 1.** Structure of poly(AMA) obtained at an early stage of polymerization.

Figure 2. Conversion-time curves for the emulsion polymerization of (O) AMA, (◇) MMA, and (△, ▲) EDMA at 50°C. Ingredients: monomer 10 g; water 90 g; SDS 1.3 g; KPS; 0.03 g. Closed marks correspond to gel polymers.

Of course, the intermolecular crosslinking reaction of growing polymer radical with the pendant double bonds of the preformed poly(AMA) will become gradually significant with the progress of polymerization, eventually forming a gel [7]. In connection with the present work, the formation of microgel as an extremely complicated prepolymer in the radical polymerization of multivinyl compounds has been investigated in detail by light scattering measurements [4, 5, 7, 11]. That is, a microgel is a highly shrunken molecule having a much lower interaction with the solvent as compared with a linear polymer of the same molecular weight. This molecular size shrinkage and lowered interaction force will be reflected as the lowering of $\langle S^2 \rangle^{1/2}{}_z$ and A_2, respectively, measured by light scattering. Thus, the solution polymerization behavior of AMA was pursued by light scattering [7] in comparison with the polymerization of EDMA in which microgelation occurs easily [4, 5]; no microgelation was observed up to the gel-point conversion as a reflection

of the low reactivity of growing methacrylyl radical toward the pendant allyl groups of prepolymer resulting in the suppressed occurrence of intramolecular crosslinking.

Emulsion Polymerization of AMA as Compared to Its Bulk Polymerization

Figure 2 shows the conversion-time curve for the emulsion polymerization of AMA along with the polymerization results of MMA and EDMA for comparison; the rate of polymerization decreased in the order MMA $\rangle$AMA$\rangle$EDMA, i.e., in proportion as the polymerization system becomes more facile to undergo crosslinking, interestingly a drastically reduced rate of polymerization being observed for EDMA polymerization. Also, no gelation was observed for the emulsion polymerization of AMA, even above 90% conversion, as compared to the case of EDMA in which gelation occurred at an early stage of polymerization, whereas in the bulk polymerization of AMA the gel point was determined as 4% [7].

The resulting poly(AMA)s as prepolymers were then characterized by comparison with the prepolymers obtained in the bulk polymerization as follows:
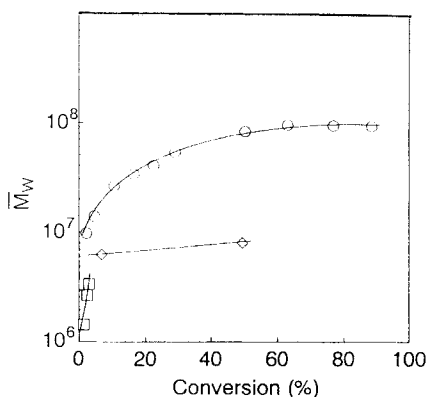

Figure 3.   Dependence of $\overline{M}_w$ on conversion for the ($\bigcirc$) emulsion and ($\square$) bulk polymerizations of AMA, along with the emulsion polymerization of ($\diamondsuit$) MMA.

Figure 3 shows the dependence of $\overline{M}_w$ on conversion along with that of MMA; in contrast to the bulk polymerization where the steep increasing tendency of $\overline{M}_w$ on conversion was observed as close to the gel point, the high-molecular-weight polymer was obtained even at an early stage of polymerization and its increasing tendency with conversion was rather gradual until leveling off above 70% conversion. Figure 4 shows the correlations of $\overline{M}_w$ versus elution volume observed by SEC-MALLS for the prepolymers obtained in emulsion at 72.8% conversion
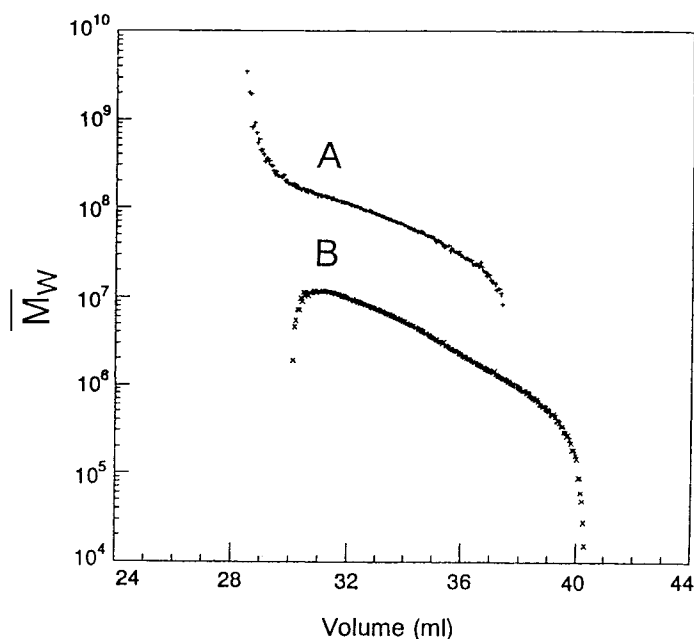
Figure 4. Correlation between $\overline{M}_w$ and elution volume for poly(AMA) obtained by the (A) emulsion and (B) bulk polymerizations.

and in bulk at 2.9% conversion, respectively; the correlation line for the emulsion prepolymer was cited above that for the bulk prepolymer, being ascribed to the difference in the occurrence of intramolecular cyclization, intermolecular crosslinking, and intramolecular crosslinking which result in the shrinkage of molecular size. This type of molecular size shrinkage was further reflected in the reduced values of $\langle S^2 \rangle^{1/2}{}_z$, A_2, and $[\eta]$, their values which were plotted against conversion as shown in Figures 5, 6, and 7, respectively; greatly lowered $\langle S^2 \rangle^{1/2}{}_z$, A_2, and $[\eta]$ values suggest the formation of microgel-like polymers. In this connection, ^{1}H-NMR spectra of the resulting prepolymers were characteristic of the microgel-like polymers. Although no peaks were detectable at 5.6 and 6.2 ppm corresponding to vinyl methylene protons of pendant methacrylyl group as was the case for the bulk polymerization of AMA [6], the absorption of the unreacted allyl groups was clearly observed at 4.7, 5.3, and 6.0 ppm corresponding to methylene, vinyl methylene, and vinyl methine protons, respectively. Here it is noteworthy that the absorption peaks at a higher magnetic field corresponding to the protons of polymer backbone were weakened as compared to those of unreacted pendant allyl
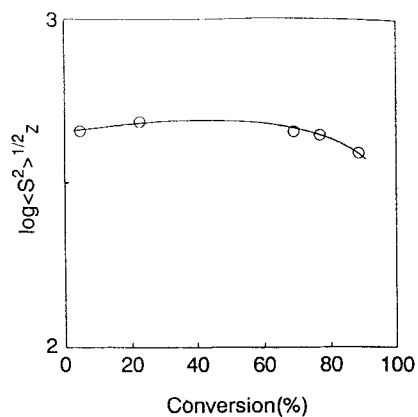
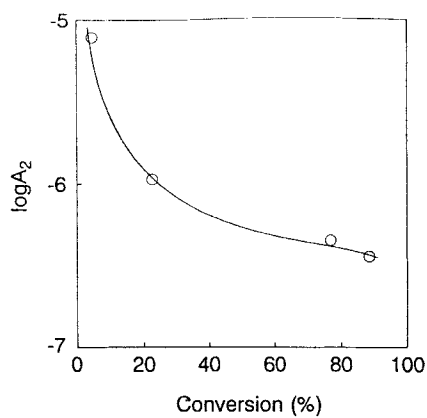**Figure 5.** Dependence of $\langle S^2 \rangle^{1/2}{}_z$ on conversion for the emulsion polymerization of AMA.

Figure 6. Dependence of A_2 on conversion for the emulsion polymerization of AMA.
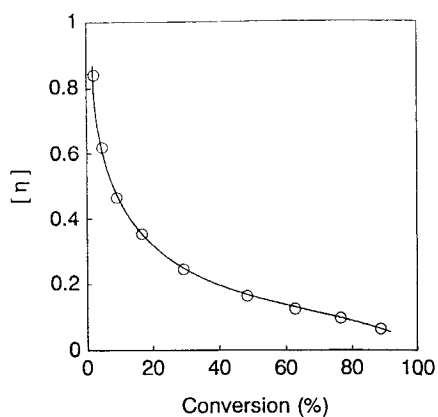

Figure 7. Dependence of $[\eta]$ on conversion for the emulsion polymerization of AMA.
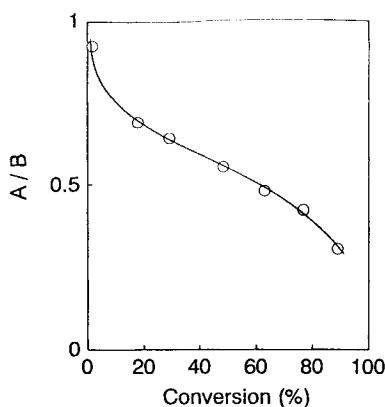
Figure 8.   Dependence of A/B on conversion for the emulsion polymerization of AMA. A and B correspond to peak areas due to polymer backbone and allyl group, respectively.
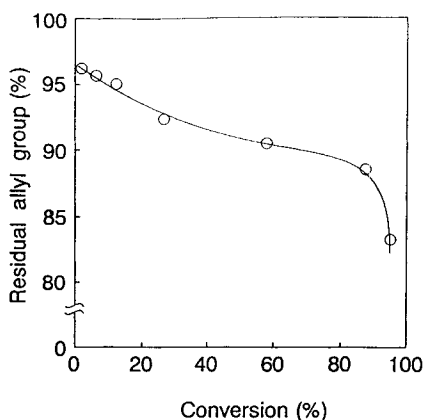
Figure 9.   Dependence of residual allyl group of poly(AMA) on conversion.

groups; the ratio A/B of the peak area of the former (A) to that of the latter (B) was plotted against conversion as shown in Figure 8. Clearly, the ratio decreased with conversion as a reflection of increased crosslinking density, although no absorption was reported for microgel due to the complete loss of segmental motion [12]. Finally, the residual unsaturation, i.e., a percentage of unreacted pendant allyl groups of the resulting prepolymer as compared to AMA monomer, was plotted against conversion as shown in Figure 9; it was found to be more than 80% even for the polymer obtained above 90% conversion, thus suggesting the formation of micro -
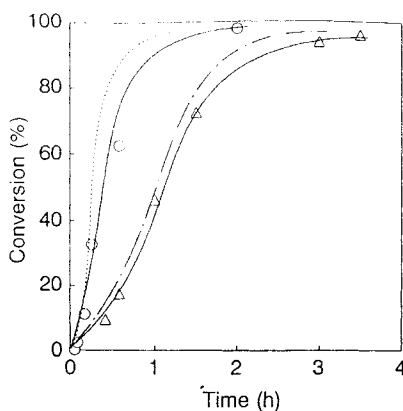
Figure 10. Conversion-time curves for the emulsion copolymerization of (O) AMA/MMA (10/90) and (Δ) AMA/EDMA(95/5), along with the results of (-------) MMA and (— • —) AMA.

spheres as pseudomicrogels having abundant pendant allyl groups by the emulsion polymerization of AMA.

Emulsion Copolymerization of AMA with MMA and EDMA for Attempt to Obtain Crosslinked-Polymer Microspheres Having Different Crosslinking Densities

As described above, the reactive crosslinked-polymer microspheres with abundant pendant allyl groups were easily obtained because AMA possesses two types of vinyl groups, methacrylic and allylic double bonds, having greatly different reactivities. However, the crosslinking density was not always low considering $\langle S^2 \rangle^{1/2}{}_z$, A_2, and $[\eta]$ values of the resulting prepolymers as opposed to our expectation. So we attempted to obtain the crosslinked-polymer microspheres having different crosslinking densities by the copolymerization of AMA with MMA and EDMA.

Thus, AMA was copolymerized with 90 mol% of MMA and 5 mol% of EDMA for the obtainment of the crosslinked-polymer microspheres having lower and higher crosslinking densities, respectively. Figure 10 shows the conversion-time curves. The rate of polymerization became slow by the change to more facile crosslinking system in conformity with our expectation. In Figure 11, the conversion dependencies of M_W of the resulting precopolymers are shown; the obtainment of resulting precopolymers of lower and higher molecular weights for AMA/MMA(10/90) and AMA/EDMA(95/5) copolymerization, respectively, was as expected. However, the correlations of $\langle S^2 \rangle^{1/2}{}_z$, A_2, and $[\eta]$ with $\overline{M}_w$ as plotted
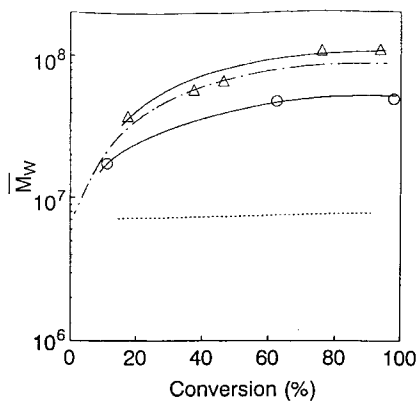
Figure 11. Dependence of $\overline{M}_w$ on conversion (see Figure 10).
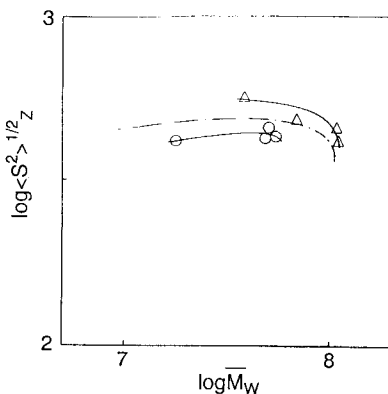

Figure 12. Double logarithmic plots of $\langle S^2 \rangle^{1/2}{}_z$ vs $\overline{M}_w$ (see Figure 10).

in Figures 12, 13, and 14, respectively, opposed to our expectation because no clear differences were observed for AMA homopolymerization and AMA/MMA(10/90) and AMA/EDMA(95/5) copolymerization. The results of our mechanistic discussion of the emulsion crosslinking polymerization of AMA may change after the obtainment of a more detailed polymerization results.

CONCLUSION

As an extension of our continuing studies concerned with the elucidation of the crosslinking reaction mechanism and the control of network formation in the
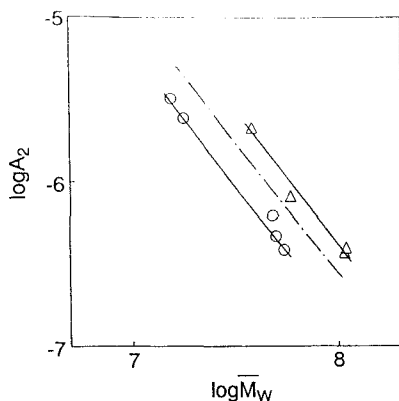
Figure 13.   Double logarithmic plots of A_2 vs $\overline{M}_w$ (see Figure 10).
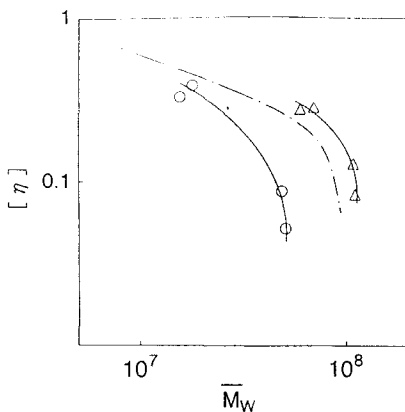

Figure 14.   Correlation between $[\eta]$ and $\overline{M}_w$ (see Figure 10).

free-radical crosslinking polymerization and copolymerization of multivinyl com-
pounds, we attempted to prepare the reactive crosslinked-polymer microspheres as
models of microgels with the intention of clarifying the correlation of the network
structure with the reactivity of resulting microspheres. Thus, the emulsion
polymerization of AMA was first taken up because we have extensively studied the
polymerization of multiallyl compounds [1]; no gelation occurred, although gelation
occurred easily at about 4% conversion in the bulk polymerization. Thus, the
reactive crosslinked-polymer microspheres as microgel-like polymers with
abundant pendant allyl groups were easily obtained because AMA possesses two
types of vinyl groups, methacrylic and allylic double bonds, having greatly different

reactivities. $\overline{M}_w$, $\langle S^2 \rangle^{1/2}{}_z$, A_2, and $[\eta]$ values and ^{1}H-NMR spectra of the resulting allyl-type reactive microspheres were characteristic of microgel-like polymers as compared with those of the branched-polymer-like prepolymers obtained in bulk. The precopolymers prepared from the emulsion copolymerization of AMA with MMA and EDMA for the obtainment of the crosslinked-polymer microspheres having different crosslinking densities were also characterized, although the results obtained are not in conformity with our expectation.

In addition to these interesting results described above, the kinetics of the emulsion crosslinking polymerization and copolymerization of AMA is now in progress in order to discuss the reaction mechanism in more detail.

ACKNOWLEDGEMENTS

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