

## Emulsion Crosslinking Polymerization of Vinyl Methacrylate as Compared with Allyl Methacrylate

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**ABSTRACT:** The emulsion crosslinking polymerization behavior of vinyl methacrylate (VMA) bearing two types of carbon-carbon double bonds, methacryloyl and vinyloxycarbonyl groups, of greatly different reactivities was explored in detail as compared with allyl methacrylate. No gelation occurred even above 90% conversion, whereas the reactive crosslinked-polymer microspheres with abundant pendant vinyloxycarbonyl groups were easily obtained. The weight-average molecular weights, the r.m.s. radii of gyration, the second virial coefficients, the intrinsic viscosities and <sup>1</sup>H NMR spectra of the resulting vinyl-type reactive microspheres were characteristic of microgel-like polymers.

**KEY WORDS** Vinyl Methacrylate / Emulsion Polymerization / Crosslinking / Gelation / Microsphere / Microgel /

As an extension of our continuing studies 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,<sup>1</sup> we are dealing with the emulsion crosslinking polymerization of multivinyl compounds, especially focusing on the formation of reactive crosslinked-polymer microspheres as models of microgels.<sup>2</sup> The aim of these studies is to clarify the correlation of the network structure with the reactivity of resulting microspheres which would be useful as functionalized polymeric materials. In our previous articles,<sup>3,4</sup> we have reported the emulsion crosslinking polymerization of allyl methacrylate (AMA), in which reactive crosslinked-polymer microspheres having abundant pendant allyl groups with a low crosslink density, *i.e.*, soft-type pseudomicrogels, are obtained. That is, since AMA has two different types of double bonds, *i.e.*, conjugated methacryloyl and unconjugated allyl groups, and the reactivity of methacryloyl group relative to allyl group is quite high, the preferential polymerization of methacryloyl group to lead to the formation of prepolymer having abundant pendant allyl groups occurs at an early stage of polymerization.<sup>5</sup> With the progress of polymerization, the intermolecular and intramolecular crosslinking reactions occur gradually, eventually to form a gel.<sup>6</sup> Here it should be noted that the low reactivity of the growing methacryloyl radical toward the pendant allyl groups of prepolymer would result in the suppressed occurrence of intramolecular crosslinking leading to the formation of crosslinked polymer having a low crosslink density.

This article deals with the comparison of the emulsion crosslinking polymerization behavior of vinyl methacrylate (VMA), having conjugated methacryloyl and unconjugated vinyloxycarbonyl groups, with that of AMA. Here the reactive crosslinked-polymer microspheres with abundant pendant vinyloxycarbonyl groups would be obtainable in the emulsion polymerization of VMA,

similar to AMA polymerization,<sup>3,4</sup> since the similar reactivity of both vinyloxycarbonyl and allyl groups has been verified by the copolymerization of vinyl acetate with various allyl esters.<sup>7-10</sup>

### EXPERIMENTAL

VMA, supplied by Shin-Etsu Vinyl Acetate Co., Ltd., AMA, methyl methacrylate (MMA) and ethylene dimethacrylate (EDMA), commercially available reagents, were purified by conventional methods and then, subjected to vacuum distillation under nitrogen.<sup>11</sup> Potassium peroxydisulfate (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<sup>12</sup> 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 emulsion. 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°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. The intrinsic viscosity  $[\eta]$  was determined with Ubbelohde viscometer in THF at 30°C. The unreacted pendant vinyloxycarbonyl groups of the prepolymer were calculated from the iodine value obtained by the Wijs method.<sup>13</sup>

### RESULTS AND DISCUSSION

*No Observation of Microgelation in the Solution Polymerization of VMA*

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**Table I.** Solution polymerization results of VMA, AMA, and EDMA<sup>a</sup>

Monomer	$\bar{P}_{w,0}^c \times 10^{-2}$	Gel point/%
VMA	71	15.9
AMA <sup>b</sup>	7.9	52.5
EDMA <sup>b</sup>	76	22.0

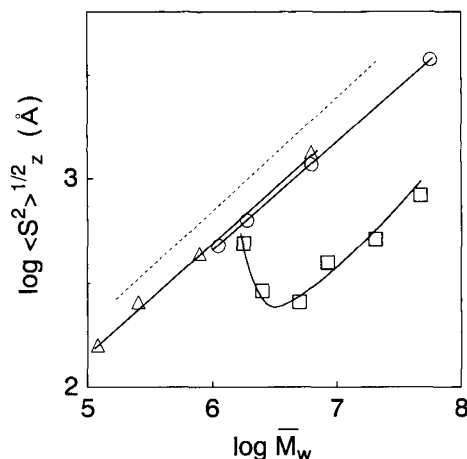
<sup>a</sup> Solvent: 1,4-dioxane; [monomer]/[solvent] = 1/9 (v/v); 50°C.  
<sup>b</sup> AMA and EDMA polymerizations were carried out using 0.04 and 0.002 mol L<sup>-1</sup> of 2,2'-azobisisobutyronitrile, respectively, in place of 0.02 mol L<sup>-1</sup> of 1,1'-azobiscyclohexane-1-carbonitrile for VMA polymerization. <sup>c</sup> The primary chain length  $\bar{P}_{w,0}$  is defined as the weight-average degree of polymerization of the primary chains which would result if all crosslinks in the network at the gel point were cut. Here  $\bar{P}_{w,0}$  was estimated by the extrapolation of the conversion dependence of weight-average molecular weight of the prepolymer determined by light scattering to zero conversion.<sup>19</sup>

In our previous article,<sup>6</sup> the solution polymerization behavior of AMA was pursued by light scattering in comparison with the polymerization of EDMA in which microgelation occurs easily;<sup>14-16</sup> 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. Here it should be recalled that 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, the molecular size shrinkage and lowered interaction force being reflected as the lowering of  $\langle S^2 \rangle^{1/2}_z$  and  $A_2$ , respectively.

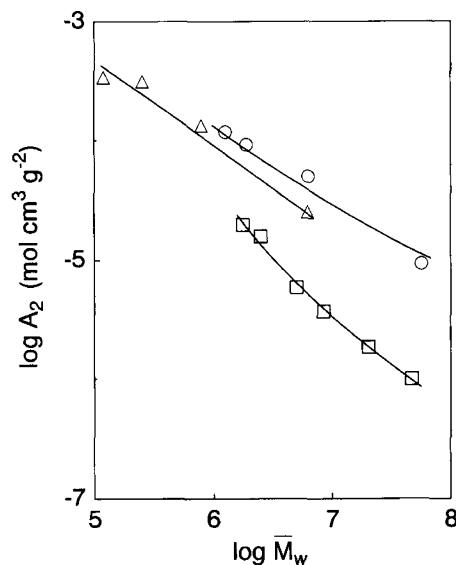
In this connection, the solution polymerization behavior of VMA was pursued by light scattering in comparison with the polymerizations of AMA and EDMA. Here no observation of microgelation up to the gel-point conversion is expected as a reflection of the low reactivity of growing methacrylyl radical toward the pendant vinyl oxycarbonyl groups of prepolymer as was the case of AMA polymerization.<sup>6</sup> Thus, VMA was polymerized in 1,4-dioxane at a dilution of 1/10 using 0.02 mol L<sup>-1</sup> of 1,1'-azobiscyclohexane-1-carbonitrile at 50°C. Table I summarizes the results of primary chain length  $\bar{P}_{w,0}$  and gel point, along with those of AMA and EDMA polymerizations.<sup>6,16</sup> Figure 1 shows the double logarithmic plots of  $\langle S^2 \rangle^{1/2}_z$  vs.  $\bar{M}_w$  for the solution polymerizations of VMA, AMA, and EDMA. In the polymerization of EDMA where microgelation occurred easily,<sup>14-16</sup> the plot had the minimum point, corresponding to the turbid point, and, moreover, the solution became white. On the other hand, the plots of VMA and AMA polymerizations were close to the linear poly(MMA)<sup>6</sup> and only transparent solutions were obtained, demonstrating no occurrence of microgelation up to the gel point. Also, the second virial coefficient  $A_2$  supports no microgelation in the polymerizations of VMA and AMA as is shown in Figure 2, although microgelation was demonstrated in EDMA polymerization as a small  $A_2$  value of less than 10<sup>-5</sup> mol cm<sup>3</sup> g<sup>-2</sup>.<sup>14,16</sup>

#### Comparison of Emulsion Polymerization Behaviors of VMA and AMA, and Characterization of Resulting Crosslinked-Polymer Microspheres

Figure 3 shows the conversion-time curve for the emulsion polymerization of VMA along with those of AMA, EDMA, and MMA polymerizations<sup>3</sup> for compari-



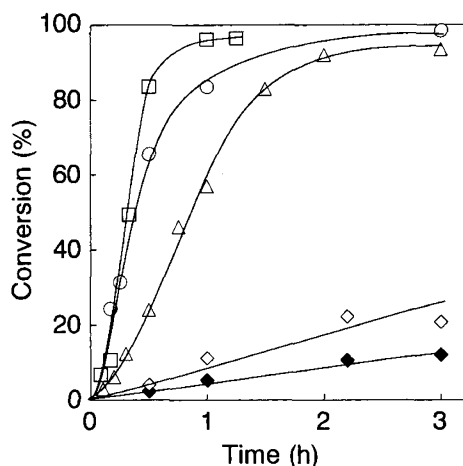
**Figure 1.** Double logarithmic plots of  $\langle S^2 \rangle^{1/2}_z$  vs.  $\bar{M}_w$  for the solution polymerizations of (○) VMA, (△) AMA, and (□) EDMA in 1,4-dioxane at a dilution of 1/10 at 50°C. Dotted line corresponds to poly(MMA) for comparison.



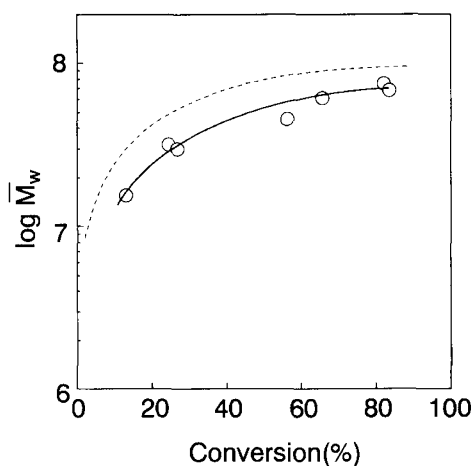
**Figure 2.** Double logarithmic plots of  $A_2$  vs.  $\bar{M}_w$  (see Figure 1).

son. The rate of polymerization decreased in the order: MMA > VMA > AMA > EDMA. In particular, the rate of polymerization for EDMA was reduced drastically. Also, no gelation was observed for the emulsion polymerizations of VMA and AMA, even above 90% conversion, although in EDMA polymerization, gelation occurred at an early stage of polymerization.<sup>3</sup>

The resulting poly(VMA) prepolymers as crosslinked-polymer microspheres were then characterized in comparison with poly(AMA). Figure 4 shows the dependence of  $\bar{M}_w$  on conversion. The lower molecular weight prepolymers were obtained for VMA polymerization as compared with AMA, although both polymerizations provided the high-molecular-weight polymers even at an early stage of polymerization as the characteristic of emulsion crosslinking polymerization.<sup>3</sup> The increasing tendency of  $\bar{M}_w$  with conversion was gradual until leveling off above 70% conversion. This is opposed to the cases of bulk and/or solution polymerizations accompa-



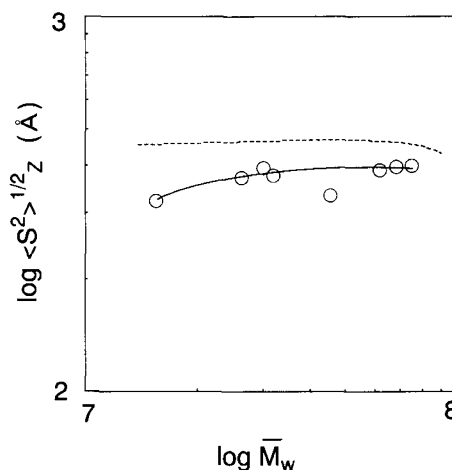
**Figure 3.** Conversion-time curves for the emulsion polymerization of (○) VMA, (△) AMA, (□) MMA, and (◇,◆) EDMA at 50°C. Ingredients: monomer 10 g; water 90 g; SDS 1.3 g; KPS; 0.03 g. Full symbol denotes gel polymer.



**Figure 4.** Dependence of  $\bar{M}_w$  on conversion for the emulsion polymerization of VMA (see Figure 3). Dotted line corresponds to AMA polymerization for comparison.

nied by gelation where the steep increasing tendency of  $\bar{M}_w$  on conversion was observed as close to the gel point.<sup>6</sup>

As a characteristic feature of VMA polymerization compared with AMA, a high rate of polymerization and a formation of lower molecular weight prepolymer were observed; this may be related to somewhat higher hydrophilicity of VMA than AMA. Here it should be recalled that the emulsion polymerization behavior of AMA accompanied by crosslinking is complicated as follows:<sup>4</sup> The formation of primary particles is supposed to proceed preferentially through the formation of precipitated oligomeric growing radicals and their interaction or absorption with emulsifier and monomer. The distinct feature of these small particles having non-spherical surface is that they contain reactive pendant double bonds which promote irreversible agglomeration during the polymerization. Thus, the increased number of polymer particle as reactive crosslinked-polymer microspheres, the polymerization in the polymer particle surface area, the small monomer/polymer weight ratio and the gel effect are assumed to be operative. The non-uniform parti-



**Figure 5.** Double logarithmic plot of  $\langle S^2 \rangle_z^{1/2}$  vs.  $\bar{M}_w$  (see Figure 4).

cle morphology may result from the agglomeration of microgels between themselves and with large stable particles. The polymerization accompanied by crosslinking mainly would occur in the surface area of the particle because of the restricted penetration of radicals into crosslinked particle cores. As a result of higher hydrophilicity of VMA than AMA, the stability of poly(VMA) particle as reactive crosslinked-polymer microsphere may be enhanced, leading to a reduced occurrence of agglomeration as compared with AMA polymerization. This would result in the high rate of polymerization and the formation of lower molecular weight prepolymer for VMA polymerization, although the low rate for AMA polymerization may be partly related to the degradative chain transfer characteristic of allyl polymerization.<sup>17</sup>

The above discussion is supported by the correlation of  $\langle S^2 \rangle_z^{1/2}$  vs.  $\bar{M}_w$  as is shown in Figure 5; the occurrence of crosslinking in the surface area of the particle would be more favorable for hydrophilic VMA polymerization than AMA. The dependence of intrinsic viscosity  $[\eta]$  of resulting prepolymers on conversion as shown in Figure 6 is also in line with the above discussion; the lower  $[\eta]$  values were observed for VMA polymerization as compared with AMA.

Finally, the residual unsaturation, *i.e.*, a percentage of unreacted pendant vinyloxycarbonyl groups of the resulting prepolymer as compared to VMA monomer, was plotted against conversion as shown in Figure 7. More than 80% of unreacted vinyloxycarbonyl groups were remained even for the polymer obtained above 90% conversion, leading to the formation of microspheres as pseudomicrogels having abundant pendant vinyloxycarbonyl groups.

#### Variation of $^1\text{H}$ NMR Spectra of Resulting Crosslinked-Polymer Microspheres with Conversion

As is discussed in our previous articles,<sup>3,4</sup>  $^1\text{H}$  NMR spectra of the crosslinked-polymer microspheres obtained at high conversions in the emulsion crosslinking polymerization of AMA were characteristic of the microgel-like polymers. That is, the absorption of the unreacted allyl groups was clearly observed at 4.7, 5.3, and

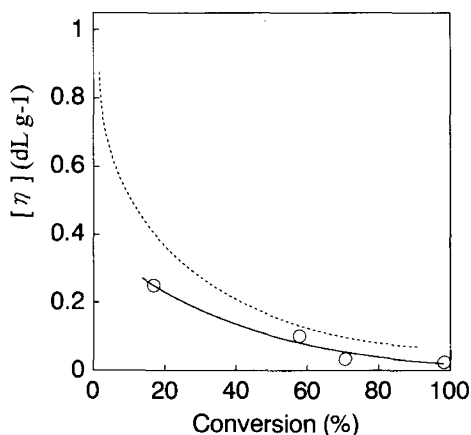


Figure 6. Dependence of  $[\eta]$  on conversion (see Figure 4).

6.0 ppm corresponding to methylene, vinyl methylene and vinyl methine protons, respectively, whereas the absorption peaks at a higher magnetic field corresponding to the protons of polymer backbone were weakened as compared with those of unreacted pendant allyl groups. The ratio of the peak area of polymer backbone protons to that of allyl group protons decreased clearly with conversion as a reflection of increased crosslink density. Here it should be recalled that no absorption was reported for microgel due to the complete loss of segmental motion.<sup>18</sup>

In the polymerization of VMA, the absorption of the unreacted pendant vinyloxycarbonyl groups of the resulting prepolymer was observed at 4.6 and 4.9 ppm corresponding to vinyl methylene protons and at 7.1 ppm to vinyl methine ones, but their absorption peaks were markedly weakened with an increase in conversion as well as those at a higher magnetic field corresponding to the protons of polymer backbone. Figure 8 shows the rapidly weakened change of absorptions of <sup>1</sup>H NMR spectra of resulting crosslinked-polymer microspheres with conversion for the emulsion crosslinking polymerizations of VMA. Here both polymer backbone methyl protons and vinyl methylene protons of unreacted pendant vinyloxycarbonyl groups were determined by using poly(vinyl benzoate) as an internal standard. This result is in line with the formation of the microgel-like polymers.

## 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 free-radical crosslinking polymerization and copolymerization of multivinyl compounds, we are dealing with the preparation of 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 crosslinking polymerization of VMA bearing two types of carbon-carbon double bonds, conjugated methacryloyl and unconjugated vinyloxycarbonyl groups, of

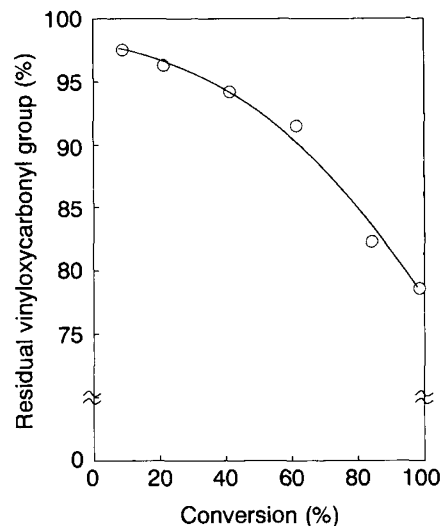


Figure 7. Dependence of residual vinyloxycarbonyl group of poly(VMA) on conversion (see Figure 3).

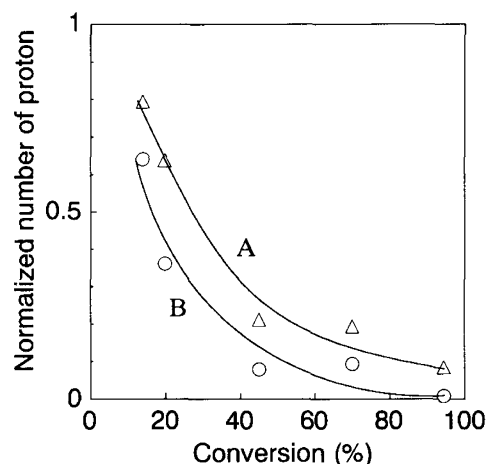


Figure 8. Weakened absorption of <sup>1</sup>H NMR spectra, corresponding to (A) polymer backbone methyl protons and (B) vinyl methylene protons of unreacted pendant vinyloxycarbonyl groups of resulting VMA microspheres, with conversion (see Figure 3).

greatly different reactivities was investigated in comparison with the previous work of AMA polymerization.<sup>3,4</sup> No gelation occurred even above 90% conversion, whereas the reactive crosslinked-polymer microspheres with abundant pendant vinyloxycarbonyl groups were easily obtained. The weight-average molecular weights, the r.m.s. radii of gyration, the second virial coefficients, the intrinsic viscosities and <sup>1</sup>H NMR spectra of the resulting vinyl-type reactive microspheres were characteristic of microgel-like polymers.

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