

## **Effect of Additives on the Initial Stage of Emulsion Polymerization of Methyl Methacrylate Using Polyvinyl Alcohol as a Protective Colloid**

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**SUMMARY:** Model experiment of emulsion polymerization of methyl methacrylate was carried out at a diluted monomer concentration of 1 %, in the presence of 1 % polyvinyl alcohol based on water as a protective colloid using ammonium persulfate as an initiator. The polymerization proceeded smoothly yielding stable emulsion with about 80 nm particle size. Fractionation of the polymers in the emulsion revealed that 90 % of polymethyl methacrylate and 60% of polyvinyl alcohol were grafted. Addition of alcohols such as isopropyl alcohol to the system decreased the grafting to a great extent, resulting in the increase in the particle size. This was attributed to the decrease in hydrogen abstraction reaction from polyvinyl alcohol with sulfate radical, due to the competing hydrogen abstraction reaction from low molecular weight alcohol.

### **Introduction**

In the emulsion polymerization using polyvinyl alcohol (PVA) as a protective colloid, grafting of the monomers onto PVA has been believed to be of importance to yield stable emulsions. In fact, in the presence of reactive PVA having a thiol end group, stable emulsions of polystyrene and of copolymers of acrylates were obtained, whereas in the presence of ordinary PVA, the emulsion polymerization of the monomers did not proceed smoothly<sup>1,2)</sup>. In relation to this point, we have been studying the capability of grafting of these monomers. To clarify the initial stage of emulsion polymerization, 1 % aqueous solution of methyl methacrylate (MMA) containing 1 % PVA was polymerized using ammonium persulfate (APS) or azobisisobutyronitrile as an initiator. In both cases, unexpected high grafting was observed<sup>3,4)</sup>. To realize the grafting phenomenon more precisely in the model experiment, we studied the effect of additives on the emulsion polymerization, especially on grafting.

## Experimental

MMA was purified by vacuum distillation. Water was distilled after ion-exchanged. APS and low molecular weight alcohols were of reagent grade and used as received. Emulsion polymerization was carried out using mainly the following recipe: MMA/PVA (DP 580, DH 88 %)/water = 0.93/1/103(wt. ratio), 7080, 2 hrs. Polymers in emulsion were fractionated into acetone-soluble, water-soluble and insoluble parts. The last fraction was regarded as the graft polymer. Particle diameter was measured with a dynamic light scattering apparatus (Otsuka).

## Results and discussion

In Figure 1 are shown the time-conversion curves of polymerization of MMA in 1 % aqueous solution in the presence and absence of PVA. The same figure also shows the effect of isopropyl (i-PrOH) in the presence of PVA on time-conversion curve.

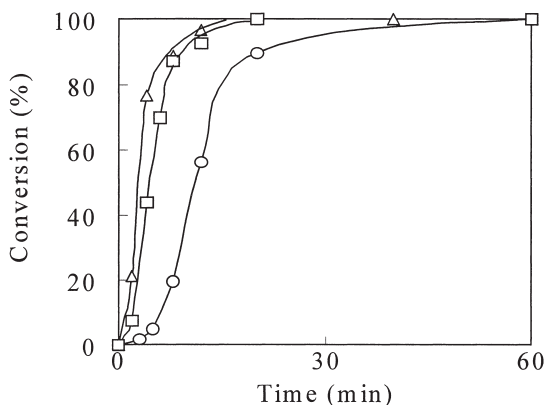


Figure 1. Time-conversion curves of emulsion polymerization of MMA  
MMA 0.9g, water 103g, APS 0.05g PVA: ○ 0g, △ 1g, □ 1g (i-PrOH 5g).

In all cases, emulsions were obtained without flocculation. In the absence of PVA, the time-conversion curve reveals s-letter type, which is seen in common emulsion polymerization. In the presence of PVA, rate of polymerization became higher. Addition of isopropyl alcohol to this did not affect the rate.

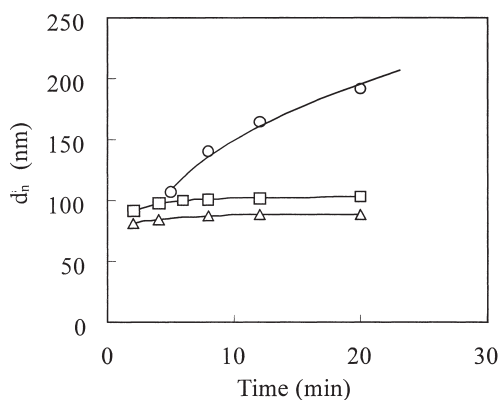


Figure 2. Particle diameter ( $d_n$ ) during the course of polymerization.

MMA 0.9g, water 103g, APS 0.05g, PVA: ○ 0g, △ 1g, □ 1g (i-PrOH 5g).

Figure 2 shows the change in particle diameter ( $d_n$ ) during the course of polymerization.

In the absence of PVA, particle size became larger with polymerization time, which is well-known phenomenon in soap-free emulsion polymerization. In the presence of PVA, increase in particle size was not remarkable.

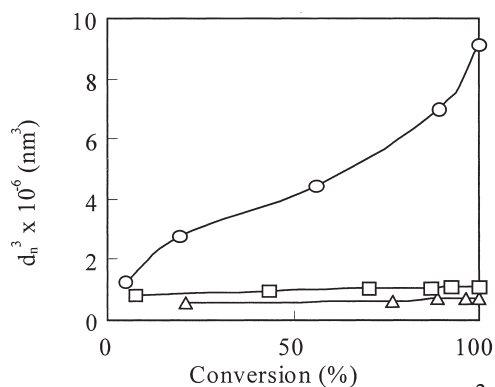


Figure 3. Relation between conversion and  $d_n^3$

MMA 0.9g, water 103g, APS 0.05g, PVA: ○ 0g, △ 1g, □ 1g (i-PrOH 5g).

Figure 3 shows the relation between conversion and volume of a particle (expressed by  $d_n^3$ ).

In the absence of PVA, particles formed at very early stage of the polymerization seemed to grow up without forming new particles until almost the final stage. At the final stage, particle volume became larger due to the agglomeration of unstable particles. In the presence of PVA, particle volume did not increase with conversion. This means that new particle formation takes place frequently during the polymerization in the presence of PVA, while it does not in the absence of PVA .

Polymers in the emulsion from PVA system were fractionated to investigate the grafting. Figure 4 shows the results of both emulsions, in the absence (A) and presence (B) of n-propyl alcohol (n-PrOH).

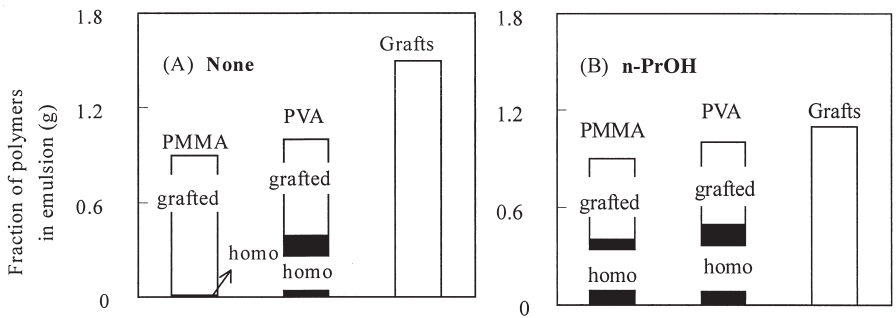


Figure 4. Fractionation of polymers in emulsion in the absence (A) and presence (B) of additives.

As is clear in Figure 4(A), more than 90 % MMA was grafted, and 62% PVA was associated with grafting in this model experiment. Addition of n-propyl alcohol to the system decreases the grafting to a great extent, shown in Figure 4(B): decrease in grafting being 40 % in PMMA, 10 % in PVA.

Effect of other alcohols was also investigated. The results are listed in Table 1.

Table 1. Effect of alcohols on grafting of MMA onto PVA in the emulsion polymerization.  
Alcohol: 0.75mol/L, MMA: 0.93g, PVA: 1g, water: 103mL

Alcohol	Grafted PMMA(%)	Grafted PVA(%)	Remarks
None	98	62	
n-Propyl alcohol	60	51	
Isopropyl alcohol	75	36	
Isobutyl alcohol	75	53	Flocculation observed
t-Butyl alcohol	95	59	

Alcohols in Table 1 affected the grafting of PMMA and PVA, except t-butyl alcohol which showed almost no effect. Figure 5 shows the effect of amounts of alcohols on grafting.

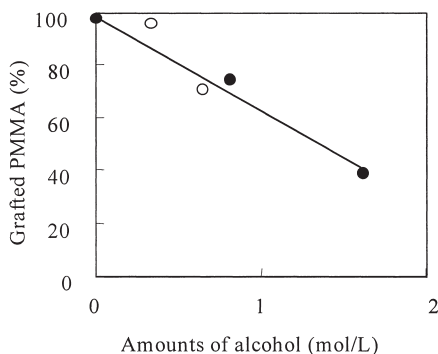


Figure 5. Change in grafted PMMA vs. amounts of alcohol: ● i-PrOH, ○ i-BuOH

Figure 5 shows that with increase in the amounts of isopropyl and isobutyl alcohol (i-BuOH), grafted PMMA decreased markedly. Particle size became larger, although the data are not shown.

The phenomenon is thought to be arisen from the competitive reactions of sulfate radical with PVA and with alcohols. PVA radicals formed from the former reaction add MMA, yielding grafts which may form particles stabilized with PVA. Low molecular weight alcohol radicals formed from the latter reaction may also add MMA, yielding homo-PMMA. Consequently, grafting may be retarded by added alcohols. Particle size may become larger, because there is no stabilization effect with low molecular weight alcohol residue at an end of PMMA.

There have been many papers dealing with the hydrogen abstraction rate constants of alcohols with sulfate radicals. In Table 2 are listed one of them<sup>5)</sup>.

Table 2. Rate constants of hydrogen abstraction from alcohols with sulfate radical<sup>5)</sup>.

Alcohol	Rate constant of hydrogen abstraction with $\text{SO}_4^{\cdot-}$ ( $10^8, \text{L mol}^{-1} \text{s}^{-1}$ )
n-Propyl alcohol	0.59
Isopropyl alcohol	0.86
Isobutyl alcohol	1.3
t-Butyl alcohol	0.084

As shown in Table 2, the rate constants of hydrogen abstraction with sulfate radical were

reported to be very large. Since there have been no data available in literature with respect to PVA, we estimated it as  $12\text{--}29 \times 10^8 (\text{L mol}^{-1} \text{ s}^{-1})^{(4)}$ , on the basis of a rate constant of addition of sulfate radical to MMA monomer<sup>(6)</sup>, and ratio of grafted MMA to total MMA polymerized. The value seems to be overestimated due to uncertainty of the addition constant. Taking this into account, and considering the mole ratio of alcohol to PVA being about five, we assume that there are three main reactions associated with sulfate radical. The first is addition to MMA monomer, the second is abstraction of hydrogen from PVA, and the third is that from added alcohol. The rate constant of the second reaction may be more than five times larger than that of the third reaction. In the case of addition of t-butyl alcohol, the rate constant of hydrogen abstraction with sulfate radicals is much smaller (one tenth, compared with isopropyl alcohol). Accordingly, addition of such a low reactive compound as t-butyl alcohol did not affect the grafting substantially.

## Conclusion

As a model experiment of emulsion polymerization of MMA using PVA as a protective colloid, 1% MMA aqueous solution was polymerized with APS. Almost all of MMA was grafted onto PVA. To the same medium, low molecular weight alcohols were added. Grafting was retarded markedly. This might arise from the decrease in hydrogen abstraction reaction from PVA with sulfate radicals, owing to the competing hydrogen abstraction reaction from the alcohols.

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