

# Vinyl Polymerization. 205.\*<sup>1</sup> Polymerization of Methyl Methacrylate in the Presence of Cellulose Triacetate and Water

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In the series of our papers, we have shown that some sorts of macromolecule could initiate the polymerization of methyl methacrylate (hereafter abridged as MMA) by radical mechanism in the presence of water. It was concluded that the effective macromolecules contained  $-OH$  or  $-NHCO-$  groups.<sup>1-7</sup> In the present communication, the polymerization of MMA was carried out with the system of the partially or completely acetylated cellulose and water. The polymerization was found to be able to be initiated even with cellulose triacetate in which no  $-OH$  groups were contained.

Partially and completely acetylated cellulose fibers with different grade of acetylation were prepared by the reaction of commercial tissue paper (99.0%  $\alpha$ -cellulose) in benzene with a mixture of acetic acid, acetic anhydride and sulfuric acid.

The reaction was carried out under stirring at 40°C in the range of 2–48 hr. Degree of acetylation was measured by alkaline hydrolysis.<sup>8)</sup>

Polymerization was carried out in sealed tubes in dark, in the same manner as described earlier.<sup>1)</sup> 0.2 g of acetylated cellulose, 10.0 ml of water and 4.68 g of MMA were charged in each tube, and the reaction was carried out for 5 hr at 85°C.

Figure 1 shows the results of the polymerization of MMA initiated with this system. It can be seen from the figure that the polymerization could proceed even in the case where cellulose triacetate

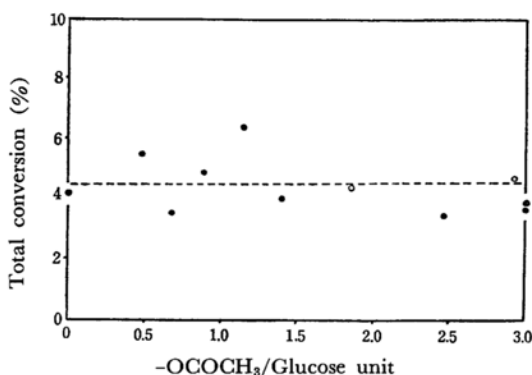


Fig. 1. Polymerization of MMA in the presence of acetylated cellulose fiber and water: Relationship between total conversion and the degree of acetylation of cellulose (85°C, 5 hr).

● Averaged value in two measurements,  
○ Value in one measurement,  
⊙ Acetylation was repeated twice.

having no hydroxy groups was chosen as a macromolecule, and that the total conversion resulted in almost the same amount as these by partially acetylated cellulose. These results differed from the case of polymerization initiated with water and partially hydrolyzed polyvinyl acetate system, where the completely acetylated polyvinyl acetate and completely hydrolyzed polyvinyl alcohol showed no initiating abilities.<sup>9)</sup>

In 1961, Ceresa carried out a block copolymerization based on the vapor phase swelling of cellulose acetate (degree of acetylation 1.35 per glucose unit) with acrylonitrile.<sup>10)</sup> Differed from his experiment, a large amount of water was present in our reaction system. Although the initiation mechanism by the system of cellulose or cellulose triacetate and water is not yet clear, it may be sure that the Ceresa's mechanism could not be applied to the present experiment from the formerly mentioned considerations<sup>1-7)</sup> which include the homogeneous initiation of MMA in the presence of water and low molecular polyvinyl alcohol or soluble starch.

\*1 Part 204 of the series: H. Yano, K. Takemoto and M. Imoto, *J. Macromolecular Chem.*, in press.

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