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LETTER TO THE EDITOR

Radical Copolymerization of Maleic Anhydride and Acetone Dimethylacetal

In recent years, investigations of maleic anhydride have been carried out on radical copolymerization with other monomers which are unable to homopolymerize in radical mechanism, such as olefins [1-4], vinyl ether [5-8], furan [9], or phenanthrene [10].

This paper reports a radical copolymerization of maleic anhydride with acetone dimethylacetal, having no double bond. This copolymerization was initiated by α, α' -azobisisobutyronitrile (AIBN) at 60°C in various solvents. However this system gave a white powdery polymeric product which is dissolved in benzene, even in the absence of initiator, and the polymer yield was very low in comparison with the case by AIBN.

The composition of polymer determined by elemental analysis was found to be a fixed value (Table 1). The molecular weight of this polymer was measured by viscosity method at 30°C ($[\eta]$: 0.05-0.1, Table 1). These results indicate that the product is a high molecular weight polymer, and the structure of polymer is explained as a 1:1 alternative copolymer of maleic anhydride and α -methyl vinyl ether. It is already reported that acetal [11] or ketal [RC(OCH₃)₂CH₃] [12] are decomposed to form vinyl ether and alcohol in the presence of an acid-type catalyst. On the other hand, the usual radical has an electron-accepting property [13]. The radical of maleic anhydride has a very strong electron affinity, owing to the two side carbonyl groups. In this system, maleic anhydride radical is a catalyst on the decomposition of acetone dimethylacetal. This reaction is expressed by the following reaction scheme;

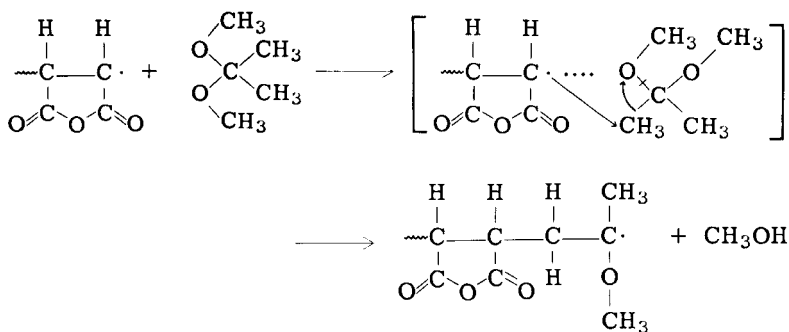


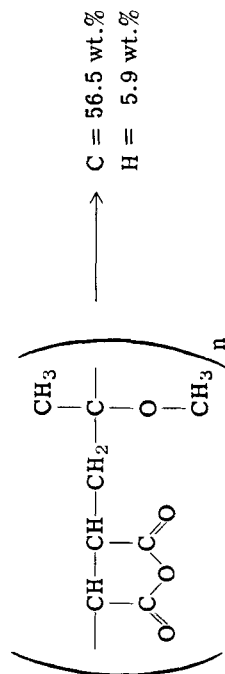
Table 1. Composition of Copolymer

| No. | Maleic anhydride, g | Acetone dimethylacetal, g | AIBN, mg | Time, hr | Yield, g | Copolymer | | | | |
|------|---------------------|---------------------------|----------|----------|----------|------------|------------|------------|----------------------|--|
| | | | | | | C, (wt. %) | H, (wt. %) | N, (wt. %) | $[\eta]_{30}$ in THF | |
| 284a | 0.5 | 3.9 | 100 | 20 | 0.61 | 53.4 | 5.4 | — | 0.05 | |
| 290a | 0.5 | 3.9 | 20 | 20 | 0.50 | 55.7 | 4.4 | — | 0.09 | |
| 291a | 1.0 | 3.51 | 20 | 20 | 0.40 | 56.0 | 5.6 | — | — | |
| 292a | 1.5 | 3.20 | 20 | 20 | 0.38 | 56.8 | 5.9 | — | 0.07 | |
| 293a | 2.0 | 2.81 | 20 | 20 | 0.15 | 56.3 | 6.0 | — | — | |
| 378b | 0.25 | 0.65 | 50 | 8 | 0.12 | 55.6 | 5.5 | 0.62 | — | |
| 379b | 0.38 | 0.54 | 50 | 8 | 0.14 | 57.2 | 5.7 | 0.65 | — | |
| 380b | 0.50 | 0.43 | 50 | 8 | 0.15 | 58.2 | 5.7 | 0.64 | — | |
| 381b | 0.63 | 0.32 | 50 | 8 | 0.14 | 57.3 | 5.5 | 0.59 | — | |
| 382b | 0.75 | 0.22 | 50 | 8 | 0.13 | 55.4 | 5.4 | 0.69 | — | |

^aTotal volume, 5 ml; temp., 60°C.

^bIn benzene; total volume, 5 ml; temp., 60°C.

After drying for 20 hr in vacuum at 60°C:



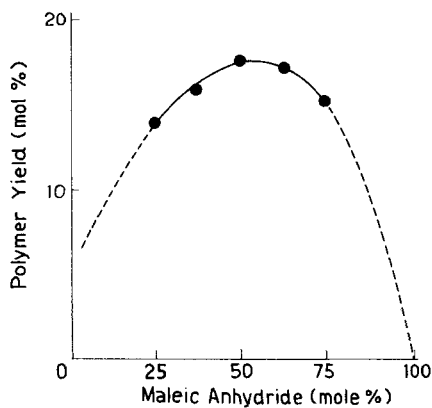


Fig. 1. Copolymerization of maleic anhydride and acetone dimethylacetal. Total concentration of two monomers; 2 moles/liter in benzene; polymerization time, 8 hr; polymerization temp., 60°C; AIBN, 0.12 mole/liter, in vacuo.

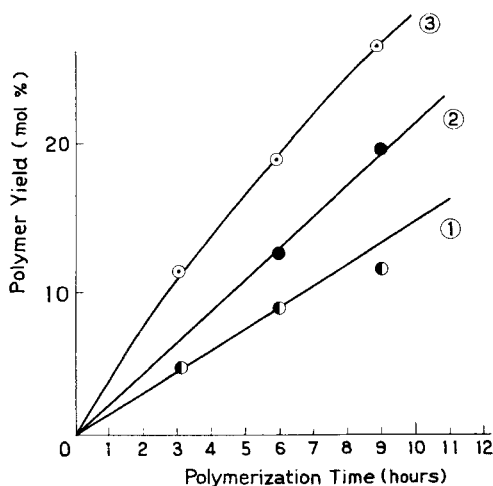


Fig. 2. Copolymerization of maleic anhydride and acetone dimethylacetal in benzene solution as a function of initiation concentration. Concentration of each monomer, 1 mole/liter; total volume; 5 ml; polymerization temp., 60°C. AIBN: 1, 20 mg; 2, 40 mg; 3, 80 mg in vacuo.

Here the copolymerization takes place at the same time as the decomposition reaction.

Figure 1 shows that the maximum conversion appears at the composition of 1 : 1 mole ratio of two monomers. These polymerization rates are obeyed with the square-root rule of initiator concentration as shown in Fig. 2.

It was observed that this copolymerization was made also between maleic anhydride and acetal such as diethylacetal, but the polymerization rate is much smaller than with acetone dimethylacetal.

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