

# Preparation of Fine Powdery Copolymer of Styrene–Maleic Anhydride–Divinylbenzene

## INTRODUCTION

It is well known that maleic anhydride (MAN) is easily copolymerized with styrene (St) and that the copolymerization is heterogeneous in aromatic or aliphatic hydrocarbon as solvent.<sup>1,2</sup> We have already reported on the preparation of a reactive fine powdery copolymer by the crosslinking precipitation–copolymerization of St–MAN–divinylbenzene (DBV),<sup>3,4</sup> but details have not yet been reported. This copolymerization system is too complicated to study in detail: the system contains many components, because commercial DVB is a mixture of *o*-, *p*-, and *m*-DVB and ethylstyrene, and the resultant copolymer is crosslinked. Therefore, this note reports on the copolymerization of St–MAN–DVB with regard to the ultimate yield and the MAN unit content of the copolymer.

## EXPERIMENTAL

### Materials

Chemical-grade St and commercial-grade DVB were washed successively with a dilute solution of sodium hydroxide and water, dried over anhydrous calcium chloride, and then distilled under reduced nitrogen pressure just before use. MAN was of chemical grade. Benzoyl peroxide (BPO) was used as a polymerization initiator (purity > 97%). Kerosene was dried over a molecular sieve and then distilled. A distillate bp 150–200°C was used as the solvent. DVB used was a mixture of *m*-DVB (40.5%), *p*-DVB (16.1%), *o*-DVB (0.2%), and ethylstyrene and others (42.6%).

### Copolymerization

A glass reaction vessel with a stirrer (1000 rpm), a thermometer, and a reflux condenser was used, shielded from light with asbestos cloth. First, kerosene (100–120 ml) was put into the reaction vessel and warmed to a definite temperature. Under nitrogen stream, a definite weight of the monomer mixture and BPO were added, and the total volume of the reaction solution was then adjusted to 150 ml by adding solvent. Reaction temperature was maintained at 61, 79, and 90°C by vapor bath, using an acetone–methanol mixture, benzene, and an ethanol–isopropanol mixture, respectively. After a certain reaction time, a small amount of *p*-benzoquinone was added to stop the copolymerization. The resultant copolymer was quickly filtered with a glass filter, washed with benzene, and dried up at 70°C under vacuum.

### Determination of the MAN Unit Content

The powdery copolymer (0.2 g), dioxane (200 ml), and a magnetic stirrer were put into a conical flask with a glass stopper. The mixture was warmed at 60°C for 1 hr with stirring and then cooled to room temperature. After adding 0.1*N* NaOH (20 ml) with stirring and standing overnight, the MAN unit quantity was determined by back-titration with 0.1*N* HCl by using phenolphthalein as indicator. The copolymerized MAN quantity was calculated as the product of the yield and the MAN unit content of the copolymer.

## RESULTS AND DISCUSSION

The resultant copolymer is fine spheroidal and of particle size less than 0.1  $\mu\text{m}$ , as shown in Figure 1. As kerosene is a poor solvent for the St–MAN copolymer, the resultant copolymer precipitates out. Also, DVB promotes the precipitation and is effective in making the copolymer fine and spheroidal.

The copolymer began to precipitate out several minutes after copolymerization had begun and it made the reaction system turbid. Thereafter, the copolymer deposited to some extent on the stirrer

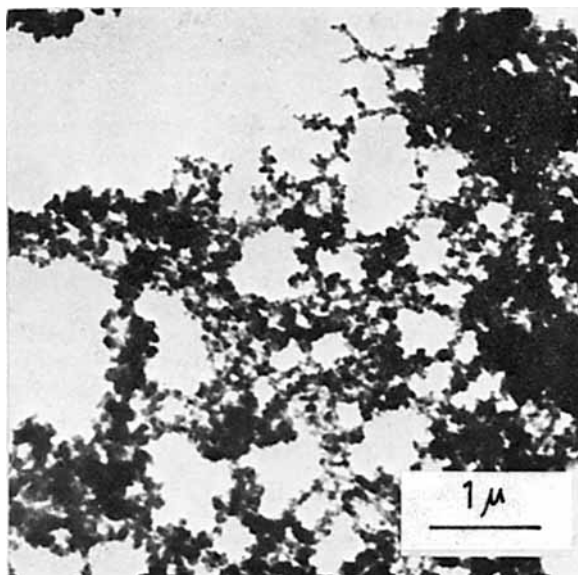


Fig. 1. Electron-microscope photograph of fine powdery copolymer. Recipe by weight ratio: MAn/TM = 0.40, DVB/TM = 0.04, BPO/TM = 0.1. TM concentration, 66.7 g/l. yield, 97%.

and the reaction vessel wall. Accordingly, this reaction system had an inevitable heterogeneity. The time-conversion curve levels off after about 1 hr, when the MAn is almost exhausted. It should be pointed out that the ultimate yield and the MAn unit content are shown as the average values of those after 2–4 hr and that the recipe is shown by weight ratio, unless otherwise noted.

Table I shows that the reaction temperature has rather little effectiveness on the ultimate yield. The appropriate BPO/TM (total monomer) ratio was about 0.05, and the increase in the BPO/TM ratio over 0.05 was rather ineffective, probably owing to the decrease in the efficacy of the radical generated from BPO. When the BPO/TM ratio was 0.005, the BPO quantity was insufficient because the radical generated from BPO should be occluded in the growing copolymer matrix without any chain transfer to the other monomers. It is also evident that the increase in the TM concentration (from 25 to 200 g/l. at 79°C) increased the ultimate yield (from 50 to 64%) and slightly decreased the MAn unit content (from 35 to 32%). The increase in the ultimate yield can be attributed to the better efficacy of the radical generated from BPO. The appropriate TM concentration was 50–100 g/l. When the TM concentration is larger (for example, 150 g/l., with an ultimate yield of 61%), the stirring of the whole reaction system becomes difficult at the later stage of the copolymerization, and the reaction temperature control also becomes difficult because of heat evolution by the rapid copolymerization.

Figure 2 shows the effect of the MAn/TM ratio on the ultimate yield and the MAn unit content of the copolymer when the DVB quantity is constant. MAn was almost exhausted. The MAn/TM ratio is an important factor: the larger the MAn/TM ratio, the larger both the ultimate yield and the MAn unit content are. Here, the change in the MAn/TM ratio by weight, from 0.05 to 0.4, corresponds to the change in the molar concentration ratio of MAn/(St + DVB), (0.032 mole/l.)/(0.553 + 0.019 mole/l.) to (0.258 mole/l.)/(0.340 + 0.019 mole/l.), and to the change in the TM molar con-

TABLE I  
Effect of Reaction Temperature on Ultimate Yield<sup>a</sup>

Reaction temp., °C	Ultimate yield, %
61	54
79	55
90	57

<sup>a</sup> Recipe by weight ratio: MAn/TM (total monomers) = 0.20; DVB/TM = 0.04; and BPO/TM = 0.094. TM concentration, 63.2 g/l.

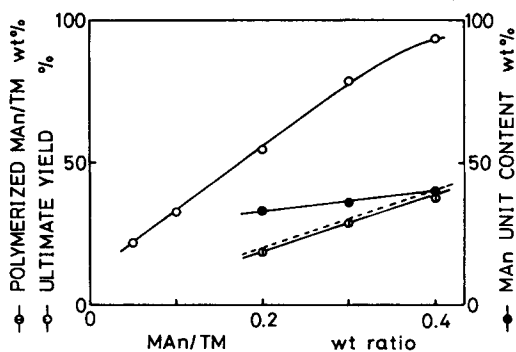


Fig. 2. MAn/TM vs. ultimate yield, MAn unit content of copolymer, and quantity of copolymerized MAn at 79°C. Recipe by weight ratio: DVB/TM = 0.04, BPO/TM = 0.094. TM concentration, 63.2 g/l. Dotted line shows the MAn/TM value of the recipe.

centration, from 0.604 mole/l. to 0.617 mole/l. The TM molar concentration is almost constant, and the DVB molar concentration is also constant. Considering that (1) MAn is rapidly copolymerizable with St, (2) MAn-St copolymer is insoluble in kerosene, and (3) the resultant copolymer is crosslinked, the result described above is reasonable. When the MAn/ ratio was  $\geq 0.3$ , the copolymerization system could hardly be stirred at the later stage of the copolymerization because of too much bulky copolymer. In these cases, all of MAn could hardly dissolve in the St-DVB mixture at room temperature. Therefore, MAn was added into the hot solvent beforehand, and then the St-DVB mixture and the BPO were added, because homopolymerization of MAn was very difficult.<sup>5</sup> Furthermore, a small amount of solid byproduct was produced.

Figure 3 shows the effect of the DVB/TM ratio on the ultimate yield and the MAn unit content of the copolymer when the MAn quantity is constant. MAn was almost exhausted. The increase in the DVB/TM ratio resulted in the larger ultimate yield and the smaller MAn unit content. Here, the increase in the DVB/TM ratio by weight, from 0.05 to 0.8, corresponds to the increase in the molar concentration ratio of MAn/(St + DVB), from (0.129 mole/l.)/(0.456 + 0.024 mol/l.) to (0.129 mole/l.)/(0 + 0.389 mole/l.), and to the change in the TM molar concentration, from 0.609 mole/l. to 0.518 mole/l. This shows the noteworthy facts that (1) the ultimate yield increases in spite of the decrease in the TM molar concentration, and (2) the MAn unit content decreases in spite of the increase in the molar concentration ratio of MAn/(St + DVB). Such tendency should be due to the characteristic behavior of DVB in promoting the formation of the crosslinked copolymer, owing to the two vinyl groups in a molecule. Since MAn, the quantity of which is constant, is almost exhausted, the increase in the ultimate yield necessarily decreases the MAn unit content. Here, the behavior of ethylstyrene contained in DVB is considered to be similar to that of St, because the behavior of the St derivatives is usually analogous to that of St.<sup>6</sup>

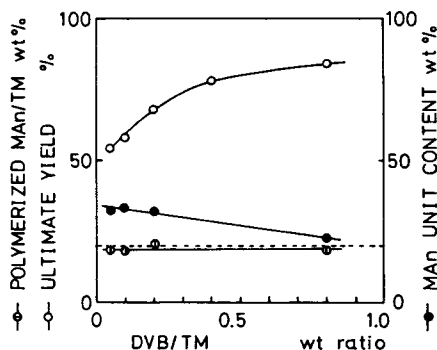


Fig. 3. DVB/TM vs. ultimate yield, MAn unit content of the copolymer, and the quantity of copolymerized MAn at 79°C. Recipe by weight ratio: MAn/TM = 0.20, BPO/TM = 0.094. TM concentration, 63.2 g/l. Dotted line shows the MAn/TM value of the recipe.

The ultimate yield can be explained as follows. MAN is exhausted within about 1 hr and DVB is more rapidly polymerizable than St,<sup>7,8</sup> which explains the preferential incorporation of MAN and DVB into the copolymer. In fact, DVB could hardly be detected in the solvent after the copolymerization by means of gas chromatography. Also, when a hot filtrate after the copolymerization was cooled to room temperature, a small amount of viscous polymer separated out of the solvent. Since MAN and DVB are exhausted, this polymer cannot be any other than polystyrene or copolymer of St-ethylstyrene, which can be easily washed away from the powdery copolymer with benzene. Thus, the ultimate yield is due to the exhaustion of MAN and DVB.

On the other hand, some investigators have reported on the charge transfer complex formation of MAN with aromatic compounds<sup>9-11</sup> and its participation in the copolymerization.<sup>11-17</sup> It can be presumed that MAN forms the charge transfer complex with St and DVB and that the complex participates in the copolymerization. However, it is not evident what role the complex plays. The mechanism must be investigated in the future in a more detailed fashion.

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Received June 25, 1980  
Accepted November 11, 1980