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POPCORN POLYMERIZATION OF 3,5-DIMETHYLSTYRENE

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Occurrence of popcorn polymerization in 3,5-dimethylstyrene (DMS) without any seed was found. Methyl methacrylate (MMA) and methyl acrylate (MA), in which small amounts of DMS popcorn polymer were employed as a seed, caused popcorn polymerization.

It has well been known that the popcorn polymerization of butadiene[1], chloroprene[2] and styrene[3] is observed. With styrene, popcorn polymerization requires small amounts of divinylbenzene[3]. However, we have obtained the popcorn polymer of DMS[4] without divinyl compound. On standing or shaking 5ml of DMS in sealed tube under nitrogen at 25°C in the dark place for 10 days, a small polymer appeared in monomer solution. Further, polymer grew gradually and reached the monomer solution surface. Finally, all of monomer apparently propagated into the popcorn polymer. It took about one day from the appearance of a small polymer to the popcorn polymer. Such spontaneous polymerization of styrene has not been found in the literature.

The popcorn polymer obtained was insoluble in all solvents. The popcorn polymerization did not occur in the presence of air. On being degassed with nitrogen and in vacuo, the polymerization was reproduced with an error of about ±1 day for different samples. Because of experimental error, the correct time-conversion curve was not drawn. A case is shown in Fig. 1. The polymer obtained was extracted

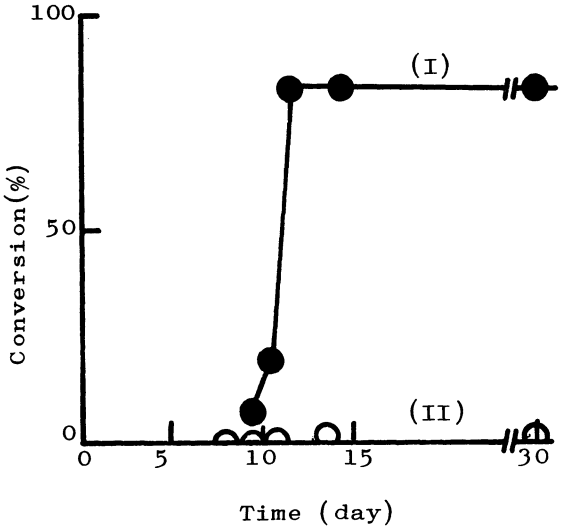


Fig. 1 Popcorn polymerization of DMS at 25°C; I, Popcorn polymer, II, Soluble polymer in benzene.

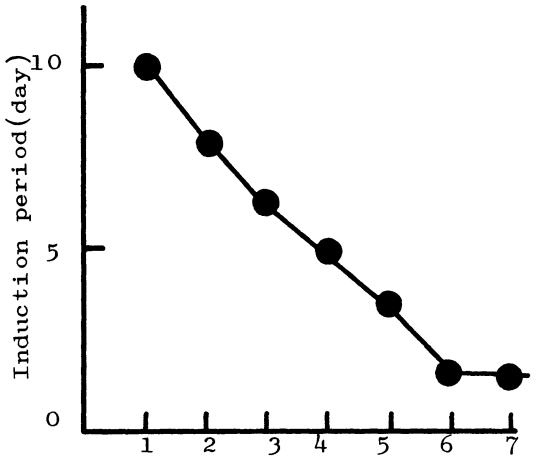
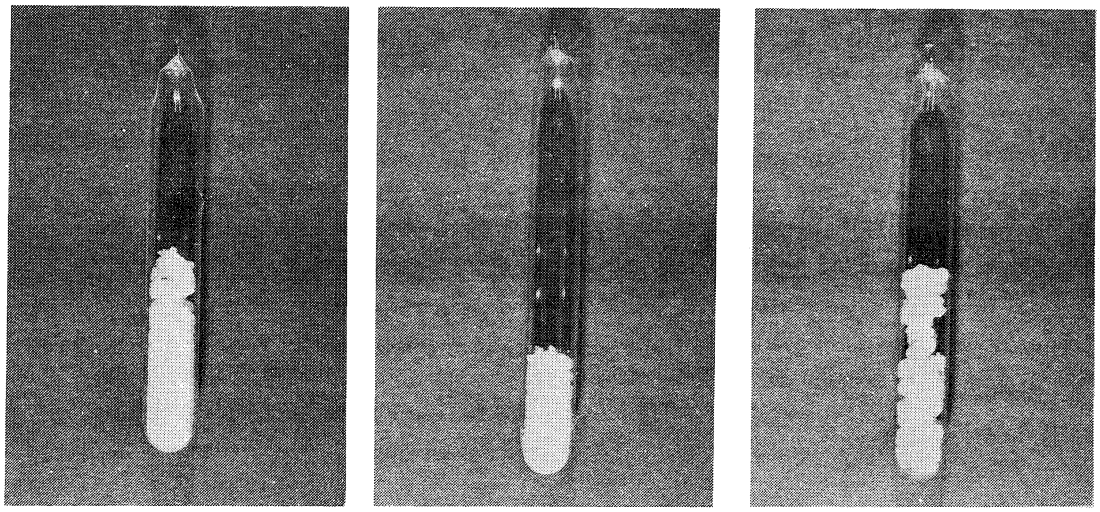


Fig. 2 Relation between the induction period and the generation in the popcorn polymerization of DMS at 25°C.

with methanol and benzene. The polymer which was soluble in benzene was not more than 2% in spite of the high conversion of popcorn polymer.

When the polymerization of 5ml of DMS was carried out by adding 0.2g of the popcorn polymer without extraction with benzene as the first seed, the popcorn polymerization began about 2 days earlier than in the absence of the seed. However, if the first seed was extracted with benzene, the growing curve of the popcorn was almost the same as in Fig. 1. The popcorn polymer obtained adding the first seed was employed as the second seed. When 0.2g of the second seed was added to 5ml of DMS, the popcorn grew up in about 7 days. Such acceleration continues endlessly. As shown in Fig. 2, the induction periods can be reduced, but not eliminated, by adding a seed of preformed popcorn to the monomer.

Also, it was found that the use of the popcorn of DMS as a seed made the popcorn polymerization of MMA and MA possible. The popcorn polymers of MMA and MA are shown in Fig. 3. The periods for MMA and MA to become the popcorn polymer were about 1 day and 15-20 days, respectively.



(I) (II) (III)

Fig. 3 Popcorn polymer of DMS(I), MMA(II) and MA(III)

References and Notes

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2) A. K. Banbrook, R. S. Lehrle, J. C. Robb, J. Polymer Sci., C4, 1161 (1966).
3) J. Breitenbach, A. Eally, Monatch. Chem., 82, 1118 (1951).
4) DMS is contaminated with less than 1% of 3,5-dimethyl ethylbenzene. Gas chromatographic analysis showed that there was no detectable amount of the divinyl compounds.

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