Radical-Induced Ionic Polymerization in the Presence of Maleic Anhydride.   II.   Cationic Polymerization of 1,2-Butylene Oxide by Benzoyl Peroxide and α,α'-Azobisisobutyronitrile in the Presence of Maleic Anhydride

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Synopsis

The cationic polymerization of 1,2-butylene oxide initiated by radical catalysts has been investigated in detail in the presence of maleic anhydride.   The active species of this ionic polymerization was thought to be a conjugated radical of poly(maleic anhydride).

INTRODUCTION

It was reported that cationic polymerizations of cyclic ethers is initiated by radical catalysts in the presence of maleic anhydride (MAH).[1,2]   The authors have also reported in the previous paper[3] that poly(maleic anhydride) formed by radical catalyst initiates the ionic polymerization of isobutyl vinyl ether (IBVE).   In this paper, the cationic polymerization of 1,2-butylene oxide (BO) initiated by radical catalysts has been investigated in the presence of MAH.

EXPERIMENTAL

Benzoyl peroxide (BPO) and α,α'-azobisisobutylonitrile (AIBN) were purified by the usual method.   BO was distilled in the presence of calcium hydride.   The polymerization rates were measured dilatometrically at 60°C and stopped by pouring the reaction mixture into water; unreacted butylene oxide was then eliminated by evaporation.   Crude poly(butylene

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oxide) obtained was purified by reprecipitation in water from methanol solution.

RESULTS AND DISCUSSION

The result of the polymerization in vacuo initiated by BPO is shown in Figure 1. Oily, colored products were obtained by this polymerization. The structure of these polymers was determined from the carbon content in elemental analysis and by infrared spectroscopy, by supposing that poly-BO involves 10–15 mole-% MAH unit. The volume contraction due to the progress of polymerization was estimated using an oily polymer formed by BF_3 esterate catalyst.

Figure 2 shows the relationship between the rate of polymerization and the concentration of initiator BPO, in which a first-order relationship is obtained. On the other hand, a half-order relationship is maintained in the polymerization initiated by AIBN, as shown in Figure 3. The rate of decomposition of AIBN is much faster than that of BPO at 60°C, and so a large difference could be expected in the rate of polymerization of the usual monomers initiated by these catalysts. In Figures 1 and 2, however, similar rates of polymerization are indicated.

The influence of BO on the decomposition of BPO was examined from the results of the polymerization of styrene in dichloroethane, benzene, and BO. The rate of polymerization of styrene initiated by BPO in BO is 15% less than that in the two other solvents, but the polymerization rates were much smaller than that of AIBN. It was also shown that MAH has no influence on the decomposition of BPO. The observed low efficiency of AIBN should be explained by the lower reactivity of primary radical formed from AIBN toward MAH, as shown in the previous report.[3] In the case of BPO, however, the primary radical of BPO could easily produce
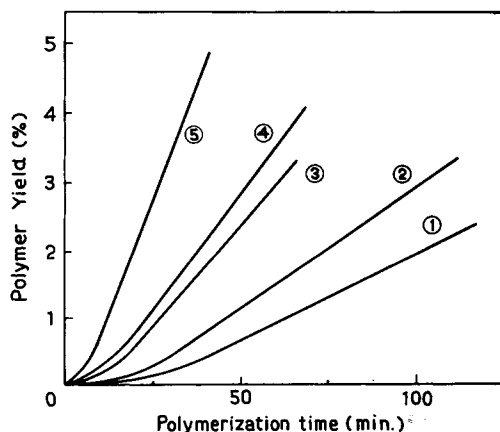

Fig. 1. Polymerization of 1,2-butylene oxide in the presence of MAH using BPO as initiator at 60°C in vacuo: MAH, 2.1 moles/l.; BPO, ① 0.0057 mole/l.; ② 0.0086 mole/l.; ③ 0.0114 mole/l.; ④ 0.0171 mole/l.; ⑤ 0.0285 mole/l.
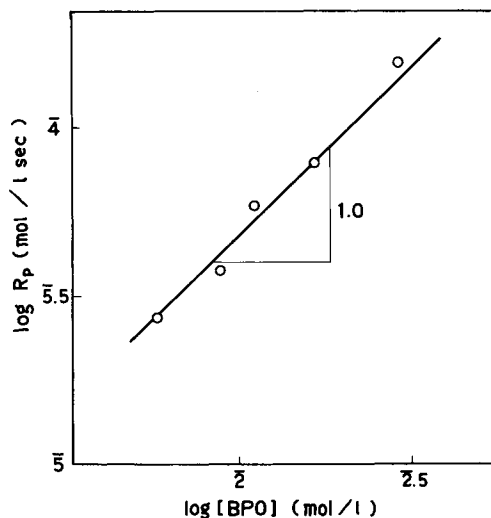
Fig. 2. Dependence of rate of polymerization on BPO concentration in the presence of MAH at 60°C, in vacuo: MAH, 2.1 moles/l.; BPO, 0.0057–0.0285 mole/l.
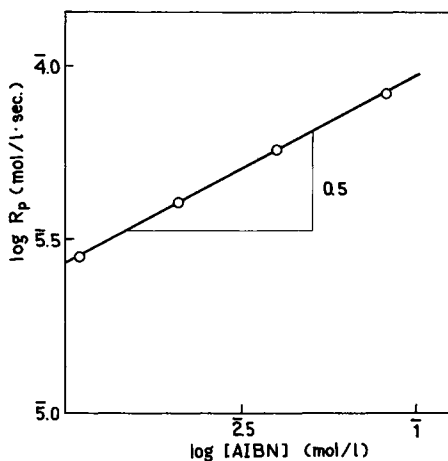

Fig. 3. Dependence of rate of polymerization on AIBN concentration in the presence of MAH at 60°C in vacuo: MAH, 2.1 moles/l.

a BO radical by hydrogen abstraction, since the benzoyloxy radical has a strong ability for hydrogen abstraction. This BO radical has the favorable property for attacking MAH molecule and easily produces an MAH radical which may be converted to active species of cationic polymerization.

The polymerization of BO certainly occurred by an ionic mechanism, and a first-order dependence on initiator concentration is given for overall polymerization. On the other hand, primary radicals of AIBN (2-cyano-isopropyl radical) cannot attack MAH effectively, and also have little ability to abstract hydrogen from BO. Most primary radicals decay by
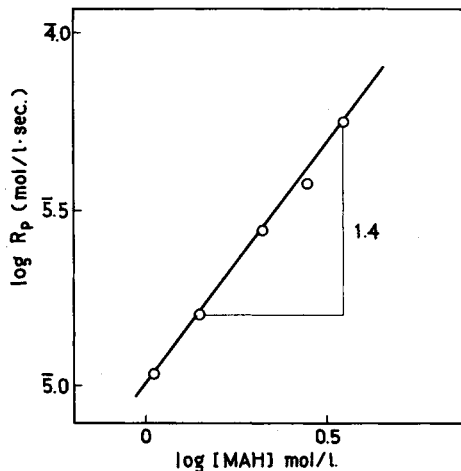
Fig. 4. Dependence of rate of polymerization on MAH concentration using BPO as initiator at 60°C in vacuo: BPO, 0.0057 mole/l.
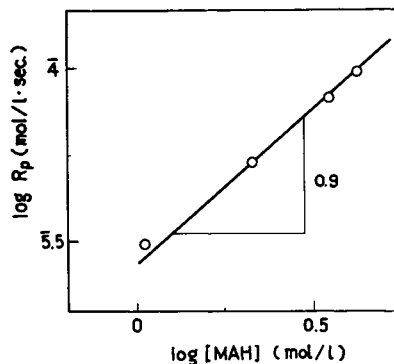

Fig. 5. Dependence of rate of polymerization on MAH concentration using AIBN as initiator at 60°C in vacuo: AIBN, 0.036 mole/l.

mutual recombination of two primary radicals. The probability of conversion from the primary radical to MAH radical is proportional to the concentration of primary radical. In such a case, half-order dependence on initiator concentration for total rate of polymerization should apparently be obtained.

Figures 4 and 5 show the rates of polymerization as a function of MAH concentration using AIBN and BPO as initiator, respectively. An order of 0.9 and 1.4 with respect to MAH concentration is estimated for AIBN and BPO, respectively. In the previous paper,[3] the authors reported that the decomposition rate of BPO is not dependent upon MAH concentration. It was also demonstrated that the highly effective conversion of primary BPO radical to MAH radical is carried out through the BO radical as intermediate. As a consequence, the observed difference between the two initiators should be due to the smaller efficiency of AIBN for this polymerization. In the case of AIBN, the formation of MAH radical via the

BO radical as intermediate is also possible, because addition of a small amount of ether in the polymerization of MAH initiated by AIBN shows an acceleration based on hydrogen transfer from ethers to the AIBN radical. The increase in the concentration of MAH accompanies the decrease in BO concentration. This causes the decrease dependence on MAH concentration of the rate of polymerization in the case of AIBN. By the same reason, the low apparent rates of polymerization by both initiators could be explained. These orders (0.9 and 1.4) should be considered as lower limits in the case of polymerization in which the concentration of BO monomer is kept at constant.

A similarly great dependence on MAH concentration was observed in the polymerization of IBVE initiated by MAH–dioxane using UV irradiation. Such a phenomenon was also reported for the polymerization of trioxane using UV or γ-ray irradiation in the presence of MAH.[1] A discussion on the oligomer radical,[3] which is thought to be the active species of ionic polymerization, is appropriately quoted here in order to explain this high dependence of the polymerization rate on MAH concentration. The conjugated radical involved in Poly-MAH[3] also becomes the active species in cationic polymerization of BO as reported for IBVE in part III.[4] We could not detect these radicals in this system by ESR, but the absorption at 450 nm, attributed to the conjugated system included in Poly-MAH, was observed for the polymerization system.[3] The polymerization system initiated by UV irradiation instead of AIBN also showed the same absorption, and this solution possibly initiates the radical copolymerization of styrene and MAH for long enough periods after irradiation.

All these phenomena indicate the existence of a stable conjugated radical included in Poly-MAH as shown in part I.[3] Therefore, a high concentration of MAH is necessary for the formation of Poly-MAH, and this is the reason for the high dependence on MAH concentration. In fact, the cationic active species in the MAH–dioxane system irradiated by UV light still remained after removing dioxane and MAH from the system by distillation.

Figure 6 shows the results of polymerizations in air by AIBN. The long induction period is due to air dissolved in the solution, because the induction period is inversely proportional to the concentration of initiator, and the introduction of air during the course of polymerization brought about inhibition. It should be noted that a small amount of polymer is formed in the earlier stage of the induction period. The rates of subsequent polymerization are much accelerated as compared with the polymerization initiated by the same concentration of AIBN in vacuo. This phenomenon shows that oxygen itself does not inhibit directly the polymerization of BO, but the product obtained by reaction between oxygen and AIBN radical may behave as inhibitor and, after the consumption of all oxygen, the product obtained by the inhibiting reaction becomes a more effective initiator than AIBN.

In the earlier stage of the induction period, there are two possible reactions of AIBN radicals which are in coexistence because of the low reactivity
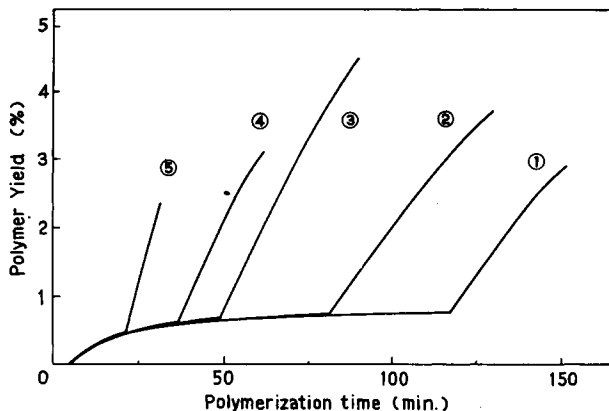
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Fig. 6. Polymerization of 1,2-butylene oxide in the presence of MAH using AIBN as initiator at 60°C in air: AIBN, ① 0.0045 mole/l.; ② 0.0089 mole/l.; ③ 0.018 mole/l.; ④ 0.036 mole/l.; ⑤ 0.045 mole/l.
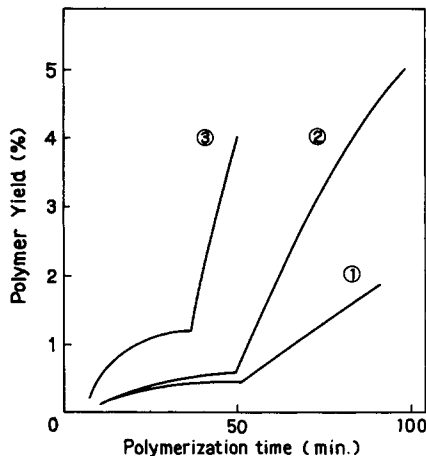

Fig. 7. Polymerization of 1,2-butylene oxide in the presence of various MAH concentration using AIBN as initiator at 60°C in air: AIBN, 0.036 mole/l.; MAH ① 1.5 mole/l.; ② 2.1 mole/l.; ③ 4.2 mole/l.

of AIBN radical to attack on MAH: (1) reaction with MAH to form MAH radical, which is thought to be the cationic active species, (2) reactions with oxygen, which produces stable peroxide radical. This stable peroxide radical produced by the latter reaction yields a peroxide by the reaction with MAH radical which is formed in the former reaction, and then the accumulation of this peroxide radical results in the inhibition of the polymerization of this system. At the same time, this peroxide decomposes to form oxide radical, which effectively reacts with MAH, and a large rate of polymerization after the induction period is initiated by this oxide radical instead of the AIBN radical. By assuming that decomposition of peroxide would not occur during the inhibition period, the rates of polymerization after this period should be proportional to the oxygen con-

tent in the system and independent of initial AIBN concentration. However, the decomposition occurs in this period and the polymerization initiated directly by AIBN is not negligible, so the rate is not independent of initial concentration of AIBN. A relatively low value of 0.4 was obtained as the order of dependence on AIBN concentration. These mechanisms are represented by the following reaction scheme:
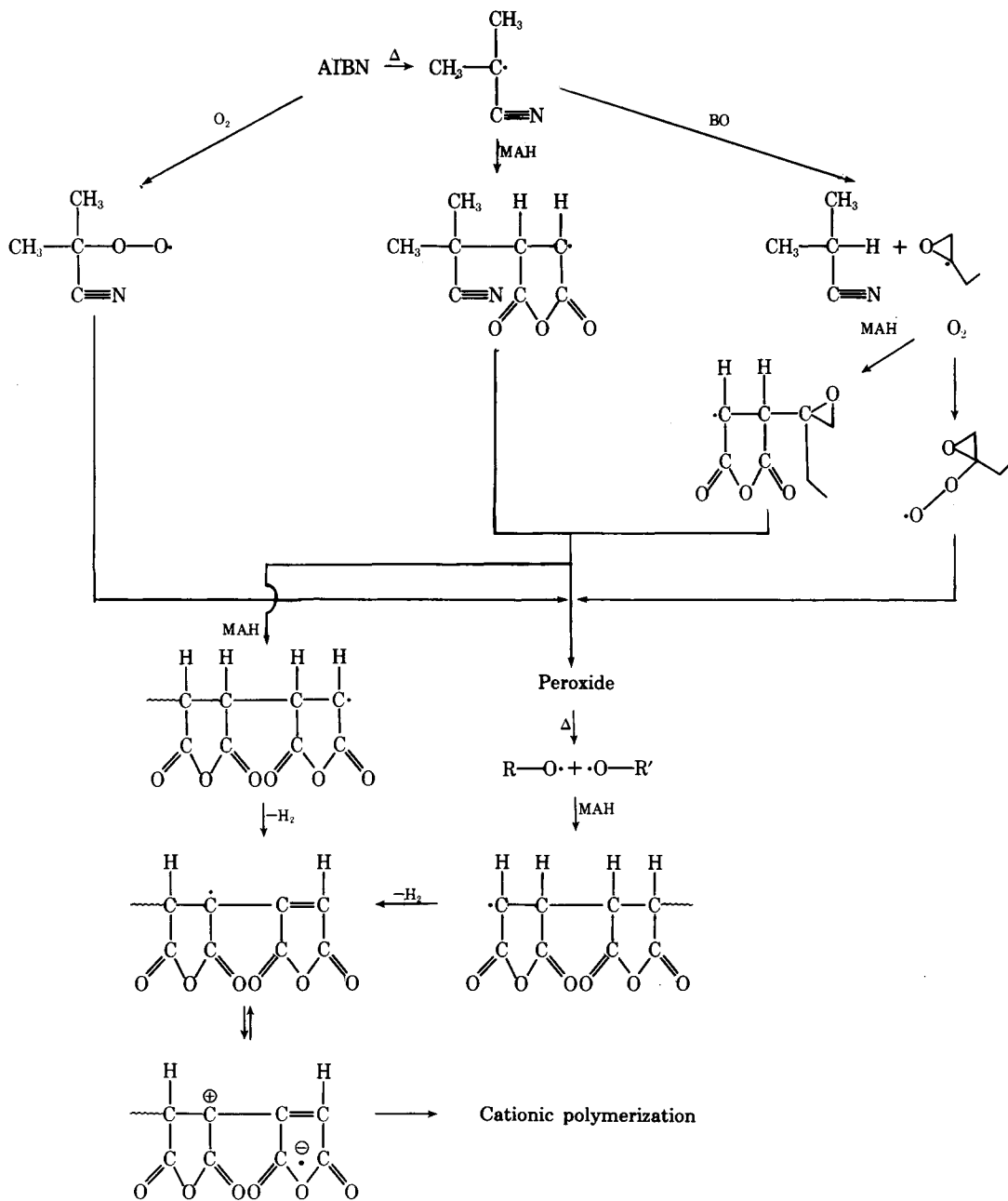
Figure 7 shows the influence of MAH concentration on the polymerization in air; the induction periods are almost independent of MAH concentration. The dependence of the rate of polymerization on MAH concentration after the induction period is found to be of the order of 1.3 from these data. This value is very similar to the order of 1.4 which is obtained for effective polymerization by BPO in vacuo, and the difference between polymerization initiated by same initiator in air and in vacuo is very much pronounced. This indicates that the major initiator after the induction period is not AIBN, but a very effective one in order to form MAH radical, such as BPO, could initiate the polymerization of BO.

The polymerization by BPO in air starts after a very long induction period because of slow decomposition of BPO; but the subsequent polymerization rate is not accelerated in comparison with the rate in vacuo.

In conclusion, Poly-MAH is found to be the active species which initiates the cationic polymerization of BO in this system.

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