

Radical-Induced Ionic Polymerization in the Presence of Maleic Anhydride. III. Polymerization of Isobutyl Vinyl Ether Initiated by Trapped Radicals in Poly(Maleic Anhydride)

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Synopsis

In a previous paper¹ it was mentioned that trapped radicals in poly(maleic anhydride) (Poly-MAH) have the ability to initiate cationic polymerization. In this paper, the cationic polymerization of isobutyl vinyl ether (IBVE) is described using Poly-MAH as the initiator. These radicals show different behavior during polymerization depending upon their structure. In particular, large conjugated radicals initiate ionic polymerizations.

INTRODUCTION

It was reported in a previous paper¹ that poly(maleic anhydride) (Poly-MAH) prepared by radical catalyst occludes three different types of radicals which could initiate the ionic polymerization of isobutyl vinyl ether (IBVE).

In this paper, the authors studied the detailed mechanism of initiation reaction from the viewpoint of kinetic studies using different types of Poly-MAH. These polymerizations show different behavior depending upon each active species and also indicate the characteristics which could not be found in cationic polymerization by conventional catalysts.

EXPERIMENTAL

Preparation of Poly-MAH

MAH purified by recrystallization from absolute chloroform was polymerized at 60°C in bulk, benzene, dichloroethane, and dioxane solutions (Table I). Poly-MAH was dried in vacuo at room temperature after washing with a large amount of benzene.

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TABLE I
Properties of Poly-MAH Produced Under Various Polymerization Conditions (60°C, 20 Hr)

Sample no.	MAH, moles/l.	Initiator, moles/l.	Solvents	Condition	Yield, %	Electronic spectra			Trapped radical, ^a no./gr			Rate of polymerization [IBVE] = 2.29 mol/l. [PMAH] = 1.0 g/l. 20°C in vac., mole/sec ⁻¹
						λ_e max, nm	ϵ_0 , cc/g	ϵ_0 , cc/g	3.5 gauss	14.7 gauss	18.3 gauss	
1	1	AIBN 0.13	benzene	heterogeneous	13	460	1.3×10^3	1.2×10^{16}	1.0×10^{16}	~ 0	4.8×10^{-4}	
2	bulk	AIBN 1.7	none	homogeneous	14	450	1.5×10^3	2.0×10^{15}	2.6×10^{15}	~ 0	1.0×10^{-5}	
3	1	AIBN 0.13	dioxane	homogeneous	20	450	1.8×10^2	4.0×10^{14}	6.5×10^{14}	~ 0	1.6×10^{-6}	
4	1	AIBN 0.13	dichloroethane	heterogeneous	5.0	465	3.1×10^3	5.0×10^{15}	5.3×10^{15}	~ 0	1.8×10^{-4}	
5	1	AIBN 0.013	benzene	heterogeneous	7.4	450	5.3×10^2	2.0×10^{15}	3.5×10^{15}	~ 0	3.6×10^{-5}	
6	4	AIBN 0.26	benzene	homogeneous	7.5	450	8.3×10^2	1.0×10^{16}	1.3×10^{15}	~ 0	2.5×10^{-6}	
7	1	AIBN 0.13	{benzene = 9 THF = 1}	heterogeneous	34	455	2.7×10	7.0×10^{14}	6.3×10^{14}	~ 0	5.3×10^{-6}	
8	1	BPO 0.081	benzene	heterogeneous	10.4	445	4.1×10	~ 0	~ 0	4.0×10^{15}	2.2×10^{-4}	

^a Peak-to-peak distance (separation).

Polymerization of IBVE

Cyclohexanone was purified twice by repeated distillation in the presence of Na_2SO_4 anhydride. Purification of IBVE was performed by washing with dilute NaOH aqueous solution and then distilling twice in the presence of calcium hydride after standing over KOH . These distillations were carried out immediately before the polymerization. Poly-MAH was added as initiator in a mixed solution of cyclohexanone and IBVE.

The efficiency of the initiator was influenced by the preservation time of Poly-MAH and by contact with the water in air. In the case of the Poly-MAH obtained by BPO, the reproducibility of the polymerization rate of IBVE was satisfactory. On the other hand, Poly-MAH obtained by AIBN gave a different polymerization rate depending on its history (maximum $\pm 50\%$), but the exactly identical result was obtained when the same Poly-MAH was used.

The polymerization was also examined in air, but reproducible results were not obtained.

RESULTS AND DISCUSSION

Table I shows the absorption at about 450 nm, the number of trapped radicals, and the polymerization rates of IBVE, for Poly-MAH obtained under various conditions. Any relationship between optical absorptions at about 450 nm and rate of polymerization was not observed. The efficiency of Poly-MAH samples to initiate the polymerization decreases with preservation time, but the absorptions were not changed. On the other hand, the amounts of these radicals are roughly correlated with rate of polymerization (except samples 6 and 7). In this polymerization, it is necessary to use large amounts of Poly-MAH, because of the weakness of this polymer initiator. The values in Table I were calculated on the assumption of first-order dependence of the rate on the initiator concentration. Polymer 6 hardly dissolved in the solution. This may be one of the reasons for the lower yield of polymer in proportion to the amount of trapped radical. Another reason is that the number of active species occluded in Poly-MAH is dependent on the preparation made in a homogeneous or heterogeneous system. As shown in experiments 2, 3, and 6 of Table I, Poly-MAH obtained from a homogeneous system has poor ability to initiate the polymerization of IBVE in proportion to the amount of trapped radical. Poly-MAH recovered by reprecipitation into benzene from cyclohexanone solution of polymer 1 could hardly polymerize IBVE in spite of the existence of a sufficient amount of trapped radical. Of course, it is not possible to recover perfectly Poly-MAH in this procedure. This Poly-MAH recovered has a relatively high molecular weight, and the radicals trapped in this Poly-MAH experience a large steric hindrance which reduces their initiation ability. For the same reason, the radicals which remained after homogeneous polymerization are stable.

The decay in trapped radicals and the rates of polymerization after one week of preservation in vacuo at room temperature indicate relatively good agreement, as shown in Table III of part I. In the case of polymer 1,

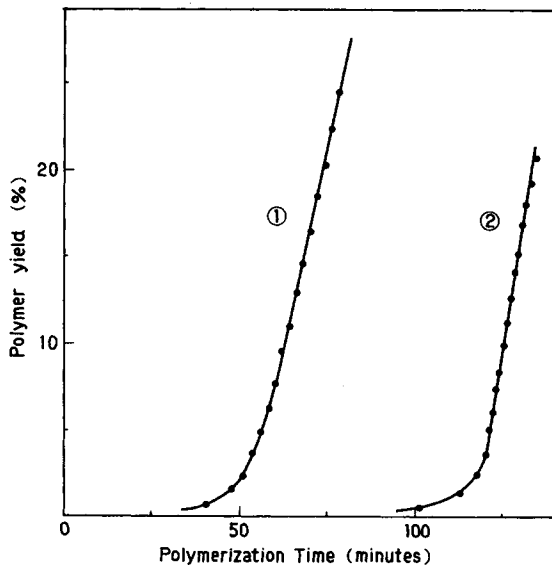


Fig. 1. Polymerization of IBVE in cyclohexanone initiated by Poly-MAH at 20°C in vacuo: IBVE, 2.29 mole/l.; ① Poly-MAH no. 8 in Table I, 1.9 g/l.; ② Poly-MAH no. 1 in table I, 1.0 g/l.

the reduction in polymerization rate was placed between two values of the decrease in trapped radicals. This result suggests the contribution of both radicals for this polymerization.

Figure 1 shows a typical result of time conversion curves of IBVE polymerization initiated by Poly-MAH. Here, detailed studies of samples 1 and 8 in Table I corresponding to large and small conjugated radicals are introduced.¹

At first, the polymerization of IBVE using sample 8 was examined, which contains only one kind of small conjugated radical. The proportional relationship between rate of polymerization and concentration of sample 8 is observed in Figure 2. Figure 3 shows the influence of monomer concentration on the polymerization rate, that is, the high monomer concentration decreases the rate of polymerization. This phenomenon is explained by the strong interaction between propagating cation and counter anion according to the decrease in polarity of the solution, because cyclohexanone has a much larger polarity than IBVE.

The apparent activation energy is calculated as 16.2 kcal/mole from Figure 4. It is considered that this energy is too large for the usual cationic polymerization, and some energy is caused to produce cationic active species in the reaction between IBVE and trapped radicals. In case of the polymerization under the conditions of sample 8, which was dissolved in cyclohexanone at first and 10 min after IBVE was added at 20°C, the rate of polymerization was 1/3 times slower than usual. This decrease is attributed to the recombination of active species in the absence of monomer. Considering the long induction period after dissolution of sample 8 in the

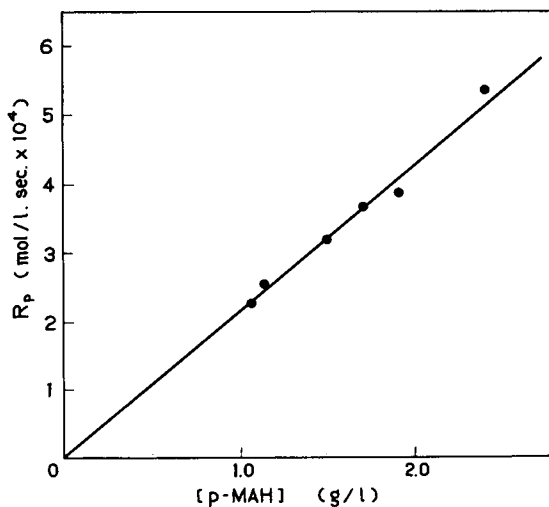


Fig. 2. Polymerization of IBVE in cyclohexanone at 20°C, initiated by Poly-MAH formed by BPO. Influence of initiator concentration: IBVE, 2.29 moles/l.

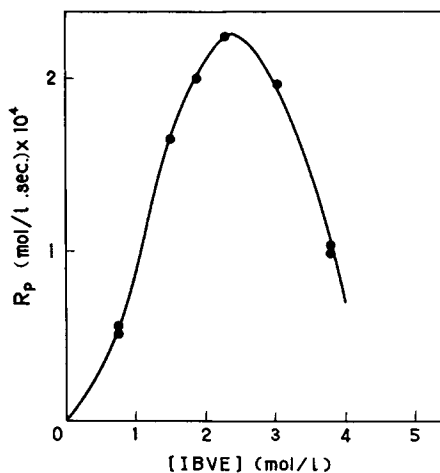
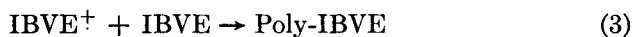
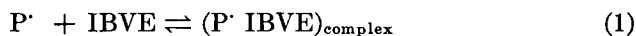


Fig. 3. Polymerization of IBVE in cyclohexanone at 20°C, initiated by poly-MAH formed by BPO. Influence of monomer concentration: P-MAH, 1.0 g/l.

solution (Fig. 1), the first reaction between IBVE and radical should be expected. If these two species do not interact during the induction period, most radicals should disappear by mutual recombination. The process for the formation of the cationic active species is postulated as follows:



P' = Poly-MAH radical

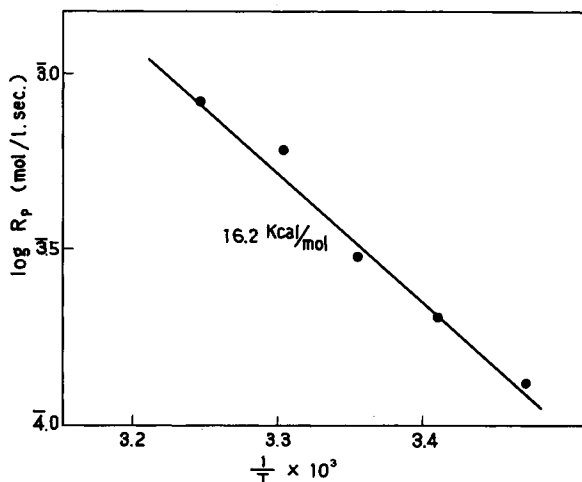


Fig. 4. Polymerization of IBVE in cyclohexanone initiated by Poly-MAH formed by BPO. Influence of polymerization temperature: P-MAH, 1.0 g/l.; IBVE, 2.29 moles/l.

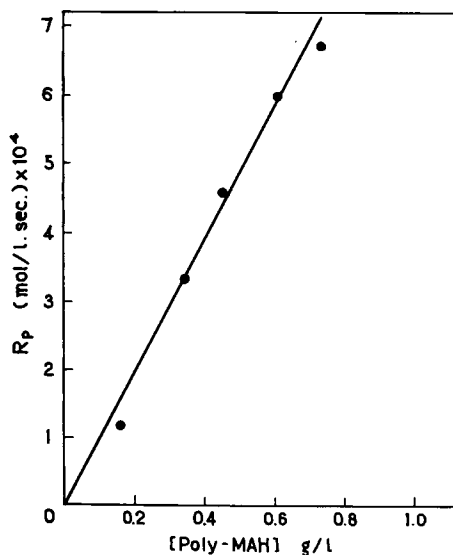


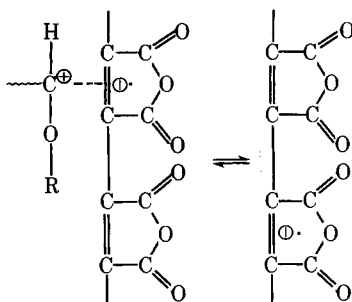
Fig. 5. Polymerization of IBVE in cyclohexanone at 20°C, initiated by Poly-MAH formed by AIBN. Influence of initiator concentration: IBVE, 2.29 moles/l.

The first step of the formation of the complex is expected to occur immediately with low activation energy and to hinder the recombination of radicals. This complex is then converted to ionic active species with higher activation energy.

Poly-MAH sample 1 contains two kinds of radicals; one is a short conjugated radical as observed for sample 8, and the other is a radical of long conjugation. Figure 5 shows that the rate of polymerization is proportional to the concentration of sample 1 just as sample 8, but the rate dependence of monomer concentration indicates a large difference in the na-

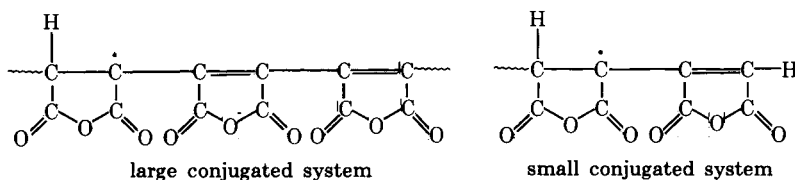
ture of the two samples (1 and 8). The rate of polymerization initiated by sample 1 is increased as a function of monomer concentration without saturation (Fig. 6). This is represented more clear in Figure 7, in which sample 1 was preserved for eight days before use. In this case, the radical (14.7 gauss) of the small conjugation disappeared and the amount of the large conjugated radical is relatively increased. It was found that the order (1.6) for monomer concentration in Figure 7 is higher than that in Figure 6 (1.1). Moreover, the authors observed an approximately second order for monomer concentration in the polymerization initiated by sample 1 preserved for a very long time. Consequently, it is concluded that the polymerization initiated by large conjugated radicals have a second-order dependence on monomer concentration, and small conjugated radicals show the same behavior of a decrease in rate at high monomer concentration as we have seen with sample 8. The coexistence of the two radicals gives the variable apparent order as shown in Figures 6 and 7.

In the case of large conjugate of radicals, the negative charge of the counter anion is extensively delocalized through the conjugated system, as follows:



In this mechanism, the coupling between propagating cation and the counter anion is very weak, and this active species seems to be the nature of solvated ion pair or free ion.

The different behavior of these two radicals is also observed in the estimation of activation energy. Figure 8 shows an activation energy of 19 kcal/mole for fresh sample 1. However, after five days of preservation of this sample, the value increased to 23 kcal/mole, and after nine days, to 30 kcal/mole, as shown in Figure 9. This suggests that the radical having a large conjugated system shows a very high activation energy. One reason for this high activation energy for a large conjugated system may be steric hindrance, because the active site of a large conjugated system is incoordinately settled inner place of polymer, as follows;



The second order for monomer concentration indicates the necessity of the reaction between radical and IBVE in the formation of cationic active

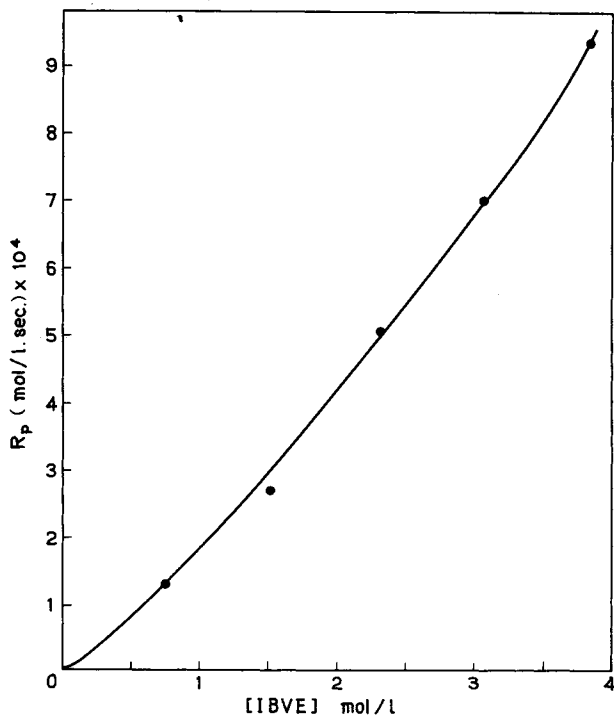


Fig. 6. Polymerization of IBVE in cyclohexanone at 20°C, initiated by Poly-MAH formed by AIBN. Influence of the monomer concentration: P-MAH, 1.0 g/l. Poly-MAH was used one day after formation.

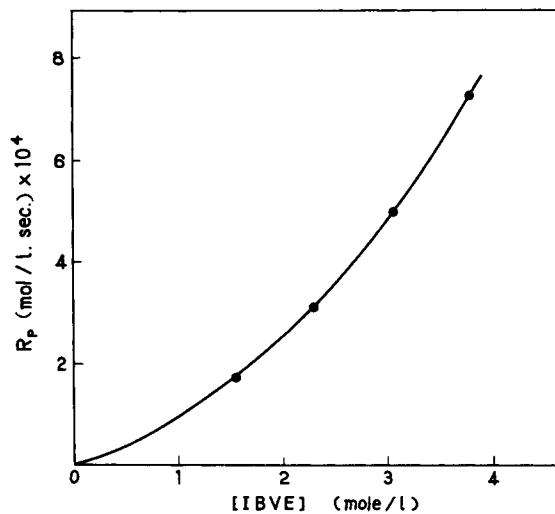


Fig. 7. Polymerization of IBVE in cyclohexanone at 20°C, initiated by Poly-MAH formed by AIBN. Influence of monomer concentration: P-MAH, 1.0 g/l. Poly-MAH (no. 1) was used eight days after formation.

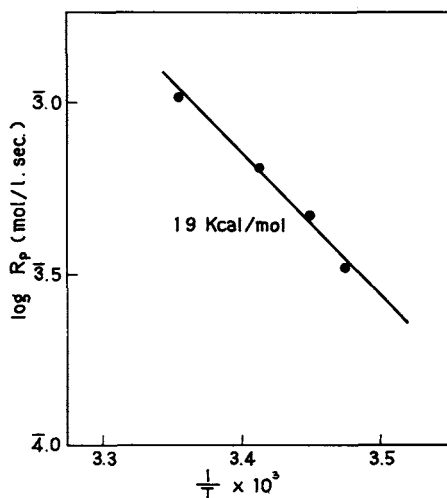


Fig. 8. Polymerization of IBVE in cyclohexanone initiated by fresh Poly-MAH formed by AIBN. Influence of polymerization temperature: P-MAH, 1.0 g/l. (no. 1), used immediately after preparation; IBVE, 2.29 moles/l.

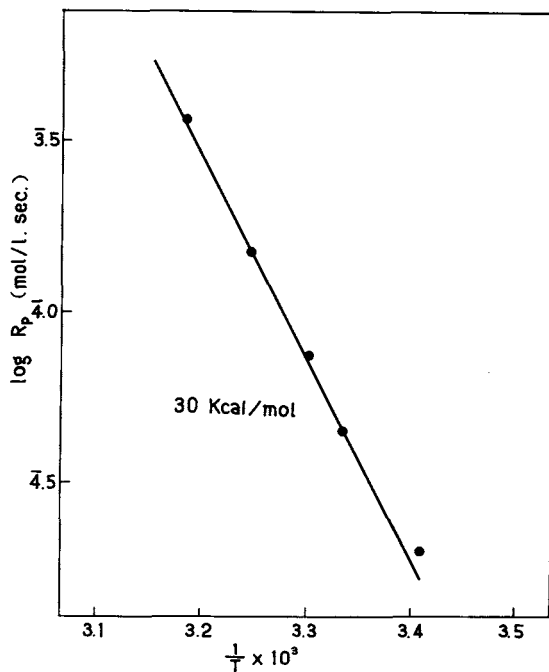


Fig. 9. Polymerization of IBVE in cyclohexanone initiated by Poly-MAH formed ten days after formation: P-MAH, 1.0 g/l. (no. 1), used ten days after formation; IBVE, 2.29 moles/l.

species. Of course, it is one of the possible reactions, but this probably explains the very high activation energy in the ionic polymerization induced by this large conjugated radical in comparison with the other two radicals.

When the addition of IBVE takes place 10 min after dissolving sample 1 in cyclohexanone at 20°C, the rate of polymerization is reduced to 80% in comparison with the case of dissolving it in a mixed solution of cyclohexanone and IBVE. Considering the decrease to 1/3 in the case of sample 8, the small decrease of sample 1 is caused by only part of a small conjugated radical contained in it rather than a large conjugated radical.

The induction period of these polymerizations is inversely proportional to the concentration of the added Poly-MAH and is remarkably extended by the addition of a small amount of water, but polymerization occurred after a certain time. Almost all the water in the solution disappeared by the reaction with anhydride group of Poly-MAH, and the minor part which was not caught by the anhydride group reacted with the cationic species produced by the reaction between IBVE and radical. The induction period is thought to be the time in which this reaction is complete. A proportional relationship between rate of polymerization and induction period was observed for each sample of Poly-MAH. But this relation did not always hold true for various samples of PolyMAH, for example, sample 1 in Figure 1 shows a fast rate of polymerization and long induction period in comparison with sample 8 in the same figure. This phenomenon can also be explained by the assumption of a solvated ion pair or free ion, which seems likely for cationic species obtained by large conjugated radicals. Such cationic species are hardly produced according to the high activation energy (30 kcal/mole), but the rate of polymerization by each species is very large because of weak hindrance by counter ion, as mentioned above.

It is reported² that the electrical conductivity of the ether-MAH system is increased by UV irradiation or heating with BPO. The authors also observed such conductivity in the cyclohexanone-MAH system in the presence of AIBN and BPO as well as the dioxane-MAH system. Comparing the two initiators (AIBN and BPO), AIBN is about eight times more effective than BPO. Poly-MAH sample 1 shows a 350 times larger conductivity than sample 8. Sample 5 and the copolymer (styrene and MAH) show no electrical conductivity. But sample 2 shows as high a conductivity as sample 1, and these high conductivities were not decreased with preservation time, in spite of a decrease in radical concentration and in activity for initiation of polymerization. Moreover, this conductivity is too high to consider the result of a radical in Poly-MAH and shows rather good relationship with the absorption at 450 nm. It may be caused by dissociation of carboxylic acid group, which is activated by the conjugated system.

References

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