

Radical-Induced Ionic Polymerization in the Presence of Maleic Anhydride. I. Mechanism of Polymerization of Maleic Anhydride by Radical Initiators

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Synopsis

Three kinds of trapped radicals are observed in poly(maleic anhydride) (Poly-MAH) which were prepared by the use of radical initiators such as AIBN or BPO. It was found that these radicals were transformed to the active species so as to initiate the cationic polymerization. The structure of these radicals was studied by the ESR and the kinetic analysis of MAH polymerization in the presence of various additives.

INTRODUCTION

In recent years, polymerization of maleic anhydride (MAH) has been studied by Joshi¹) and Lang et al.² In this paper, the authors describe the polymerization of MAH using α, α' -azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) to elucidate the mechanism, particularly of the reaction of the primary radicals with MAH, by means of the effect of additives and by an ESR study of trapped radicals in poly-MAH.

EXPERIMENTAL

AIBN, BPO, and solvents used were purified by the usual methods. Polymerizations were carried out in vacuo, and the polymers obtained were precipitated from benzene solution. Molecular weights of the polymers were determined by the ebulliometric method in acetone solution.

RESULTS AND DISCUSSION

Table I shows the polymer yields in the polymerization of MAH by the use of AIBN and BPO as catalysts. The molecular weights of the polymers obtained were in the range of 500-1000. The polymer yield increases

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TABLE I
 Polymerization of Maleic Anhydride *in vacuo* at 60°C

No.	Initiator, mole/l.	MAH, mole/l.	Time, hr	Yield, %	Solvents	Condition	
755	AIBN	0.13	1	5	1.7	dichloroethane	heterogeneous
752	AIBN	0.13	1	10	3.6	dichloroethane	heterogeneous
749	AIBN	0.13	1	20	4.4	dichloroethane	heterogeneous
804	AIBN	0.013	1	20	7.0	benzene	heterogeneous
805	AIBN	0.032	1	20	10.4	benzene	heterogeneous
806	AIBN	0.065	1	20	14.5	benzene	heterogeneous
758	AIBN	0.13	1	20	10.2	benzene	heterogeneous
807	AIBN	0.26	1	20	10.1	benzene	heterogeneous
650	AIBN	0.13	4	20	4.5	benzene	homogeneous
816	AIBN	0.26	4	20	7.5	benzene	homogeneous
817	AIBN	0.52	4	20	11.1	benzene	homogeneous
750	BPO	0.082	1	20	10.2	dichloroethane	heterogeneous
800	BPO	0.021	1	20	4.2	benzene	heterogeneous
758	BPO	0.082	1	20	10.2	benzene	heterogeneous
911	BPO	0.164	1	20	20.5	benzene	heterogeneous

linearly with polymerization time. At constant polymerization time, the yield increases linearly with the square root of the AIBN concentration in the low concentration range, but at AIBN concentrations above 0.065 mole/l., polymer yield is reduced. The maximum yield is varied depending on the ratio of AIBN and MAH concentrations. At higher MAH concentrations, such a phenomenon was not observed. On the other hand, BPO does not show a diminution in polymer yield at higher concentrations of initiator.

The rates of polymerizations initiated by a fixed concentration of both initiators are proportional to the concentration of MAH, as shown in Figure 1. This result indicates that MAH has no influence on the decomposition of BPO. The rate of decomposition of AIBN is much larger than that of BPO, as observed in the polymerization of styrene under the same condition. However, MAH is polymerized by both these initiators with the same magnitude of polymerization rate in benzene solution. In

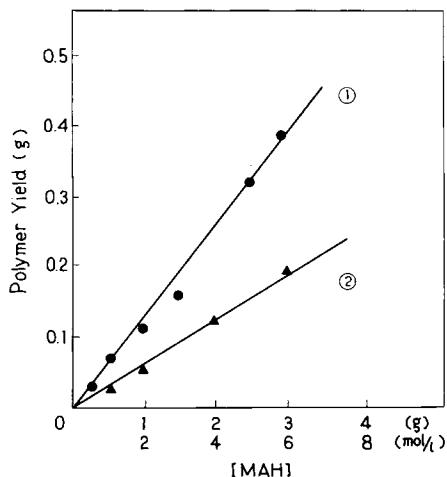


Fig. 1. Polymerization of maleic anhydride in dichloroethane: total volume = 5 cc; polymerization time = 5 hr; temperature = 60°C; ① BPO, 100 mg (0.082 mole/l.); ② AIBN, 100 mg (0.13 mole/l.).

dichloroethane solution, BPO initiates the polymerization of MAH two times faster than AIBN. These results could be explained by less efficiency of the reaction between MAH and the primary radical from AIBN. The attack of the 2-cyanoisopropyl radical on MAH is hindered by a steric effect and by the electrostatic repulsion between the two species. Moreover, the AIBN radical has no ability to abstract hydrogen atom from MAH or the solvent, contrary to BPO.¹ For this reason, the AIBN radical possibly exists freely in the solution and disappears by radical recombination of each other or with the MAH radical. The primary radical of BPO also hardly attacks MAH¹ in the usual way, but its strong ability to abstract the hydrogen atom makes it possible to form an MAH radical through the solvent radical, and another possibility is the formation of a phenyl radical³ by successive decomposition of BPO radicals which experience less electric hindrance for attacking MAH.

The large rate of polymerization in benzene induced by AIBN can be explained as a molecular complex formation between MAH and benzene, in which the electropositive charge of MAH is moderated by electron transfer from benzene. Under such conditions electric hindrance for the propagation reaction in the polymerization of MAH is minimized. On the other hand, the polymerization by BPO in dichloroethane solution is accelerated by solvent radicals which are produced owing to the strong hydrogen affinity of BPO radical and easily attack MAH. In the polymerization by BPO, the rates of polymerizations in both solvents have the same magnitude, and this can be attributed to the two reasons mentioned above.

Table II shows the relation between polymer yield, trapped radicals, and UV absorption spectra of the polymers obtained in these polymerizations. The numbers of radicals are measured in the solid phase by ESR.

TABLE II
Properties of Poly-MAH Obtained Under Various Polymerization Conditions (20 Hr, 60°C in vacuo)

Sample no.	Initiator, moles/l.	Solvents	MAH mol./l.	Condition	Yield, %	Trapped radical, number/g			Electronic spectra in cyclohexanone	
						35.9 gauss ^c	14.7 gauss ^c	18.3 gauss ^c	λ_{max} nm	ϵ_0 cc/g
1 ^a	AIBN 0.13	benzene	1	heterogeneous	10.3	1.2×10^{16}	1.0×10^{16}	—	460	1.3×10^3
2	AIBN 1.7	bulk	—	homogeneous	14.	2.0×10^{16}	2.6×10^{16}	—	450	1.5×10^3
3	AIBN 0.13	dioxane	1	homogeneous	20.	4.0×10^{14}	6.5×10^{14}	—	450	1.8×10^2
4	AIBN 0.13	dichloroethane	1	heterogeneous	5.	5.0×10^{15}	5.3×10^{15}	—	465	3.1×10^3
5 ^b	BPO 0.082	benzene	1	heterogeneous	—	—	—	4.0×10^{16}	445	4.1×10
6	AIBN 0.13	benzene:THF 9:1	1	heterogeneous	34.	7.0×10^{14}	6.3×10^{14}	—	455	2.7×10
7	AIBN 0.26	benzene	4	homogeneous	7.5	1.0×10^{16}	1.3×10^{16}	—	450	8.3×10^2
8	AIBN 0.013	benzene	1	heterogeneous	7.4	2.0×10^{15}	3.5×10^{15}	—	450	5.3×10^2

^a Fig. 2a.

^b Fig. 2b.

^c Peak-to-peak width in Fig. 2.

TABLE III
Decay of Trapped Radicals (*in vacuo* at Room Temperature)

Polymerization	Nature of radical (peak-to-peak width in Fig. 2)	No. of radicals after 8 days no. of radical after 1 day $\times 100$	Polymeri- zation rate of IBVE after 8 days polymeri- zation rate of IBVE after 1 day $\times 100$
(a)	3.5 gauss	31%	20%
Expt. 1 in Table II	14.7 gauss	17%	
(b)			
Expt. 5 in Table II	18.5 gauss	40%	33%

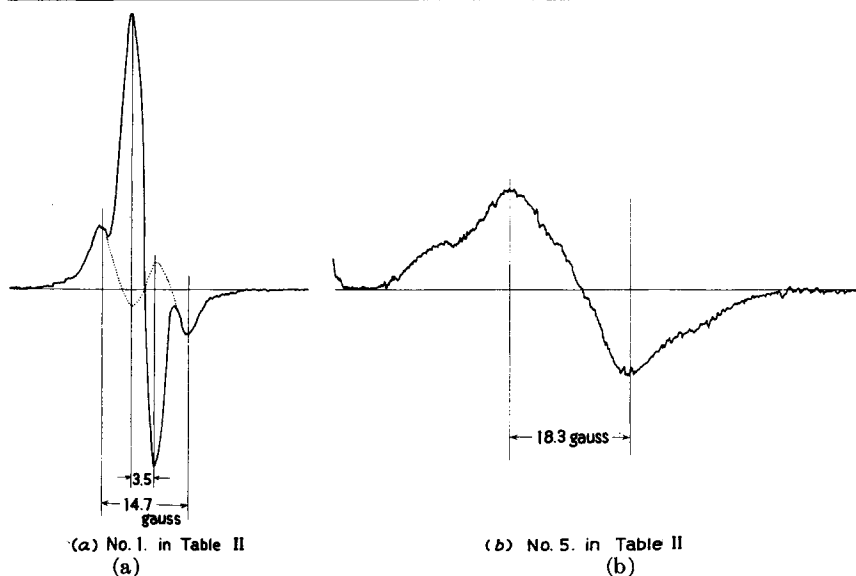


Fig. 2. ESR spectrum of trapped radical in poly-MAH one day after polymerization of MAH.

Typical ESR spectra are shown in Figures 2a and 2b, where (a) and (b) correspond to samples 1 and 5 in Table II, respectively. The decay of these radicals is indicated in Table III. The decaying behavior of the polymer radical in Figure 2a indicates the existence of two kinds of radicals. A very narrow peak (3.5 gauss) is thought to correspond to the trapped electron in a large conjugated molecular system.

The results of Figure 3 represent the radical polymerization of styrene by poly-MAH radicals formed by both AIBN and BPO. Poly-MAH radicals were used after one week of storage; under this condition, the radical corresponding to the 3.5-gauss peak is the major component of the trapped radicals (a) in Figures 2 and 3. The rate of polymerization in-

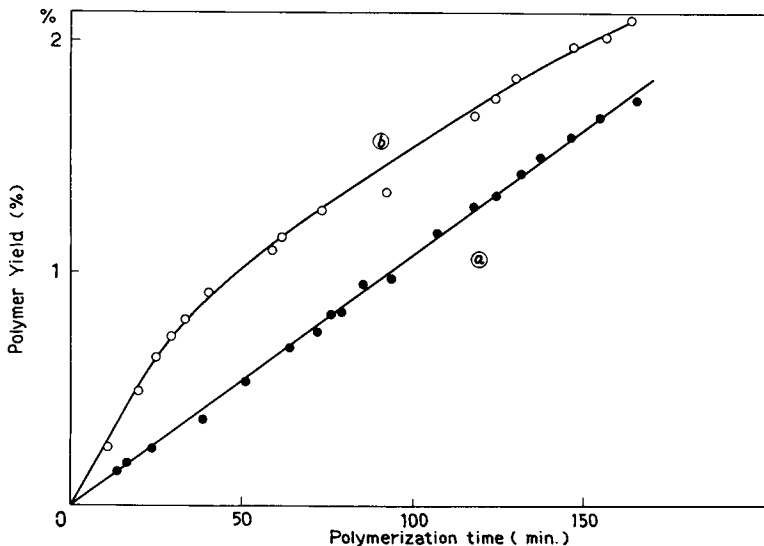


Fig. 3. Polymerization of styrene in cyclohexanone using poly-MAH: styrene, 4.1 mole/l. at 60°C, in vacuo; (a) 4.0 g/l. Poly-MAH formed by AIBN; (b) 7.0 g/l. Poly-MAH formed by BPO.

duced by radicals (a) was found to be constant irrespectively of polymerization time, but the diminution of rate was observed with radical (b). This result indicates that, though both radicals are sufficiently stable, the former is more strongly stabilized owing to its large conjugation than radical (b).

The radical nature of this polymerization mechanism is supported by the following facts. First, this rate of polymerization is proportional to the square root of the poly-MAH concentration. Secondly, the copolymerization of methyl methacrylate and styrene initiated by this poly-MAH(a) imports the copolymer a composition corresponding to the radical mechanism. On the other hand, poly-MAH induced the cationic polymerization of isobutyl vinyl ether (IBVE), which is known to be a very active monomer for cationic polymerization.⁴ It was found that the polymerization of the mixture of IBVE and MAH (1:1 mole composition), initiated by poly-MAH, gives only the homopolymer of IBVE at 20°C and 60°C, though the usual radical polymerization of IBVE in the presence of MAH always produces a copolymer of 1:1 composition. The rate of this cationic polymerization at 20°C is not changed by the presence of MAH. If the radical polymerization occurred partially in the mixed system of IBVE and MAH, the rate of cationic polymerization would be reduced by the consumption of active species owing to radical polymerization, because the rate of the radical polymerization of IBVE is much smaller than that of the cationic polymerization. That is, if the 14.5-gauss radicals are consumed by radical polymerization in the mixed system of MAH and IBVE, the overall rate of polymerization by poly-MAH(a) should be reduced.

These results indicate that two small conjugated radicals [radicals of 14.5 gauss in (a) and 18.3 gauss in (b)] are not propagating radicals of MAH in the usual radical polymerization. When the polymerization of styrene by poly-MAH(a), in which the radical of 3.5 gauss is dominant, was examined, a larger rate was observed in THF solution than in dioxane and cyclohexanone, although the usual radical initiators show the smallest rate in THF as observed by the authors. This result should be attributed to the electric positive charge of this radical which causes formation of a molecular complex and then THF radical formation by hydrogen transfer. THF is a good hydrogen transfer agent for electrically positive radicals, as shown later. This THF radical formed easily initiates the polymerization of styrene instead of the very stable radicals of 3.5 gauss in poly-MAH of (a). The formation of cationic, active species from these radicals indicates the strong electron-positive charge localized in the radicals.

The radical corresponding to 14.7 gauss in (a) should be considered as a superposition of a doublet over a singlet, as shown by the dotted curve of Figure 2a. On the other hand, it is thought that the broad spectrum of 18.3 gauss formed by BPO (Fig. 2b) has a triplet structure.

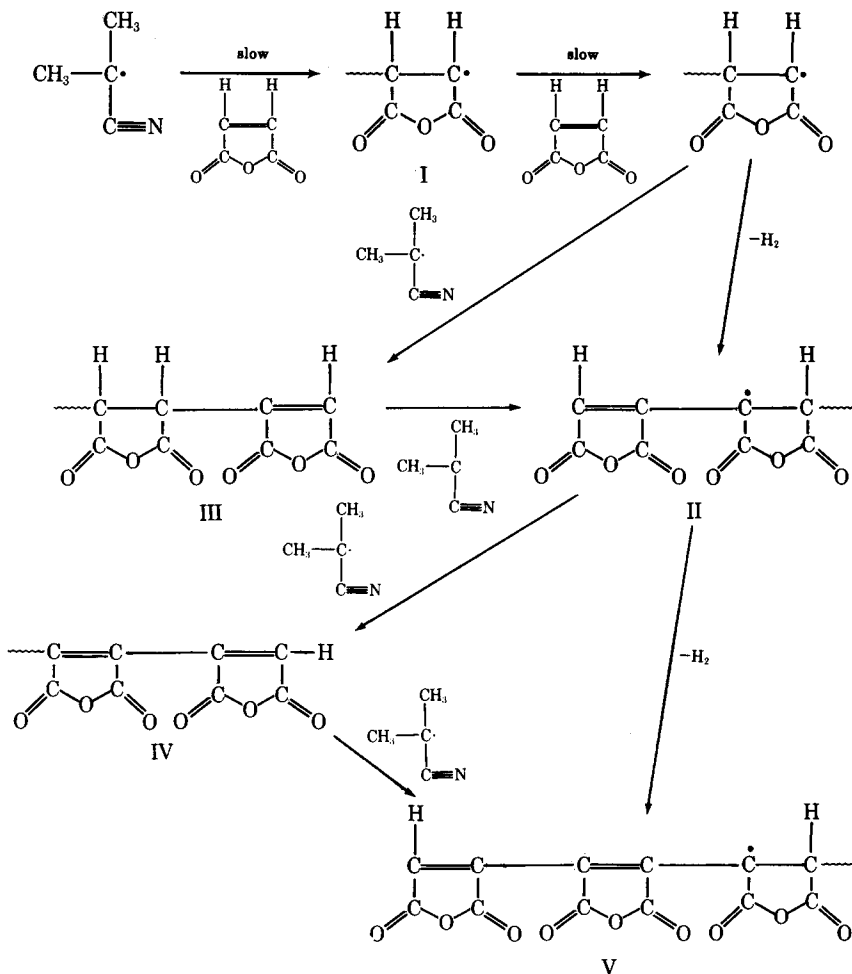
In the ionic polymerization induced by poly-MAH, the radical of 14.7 gauss in (a) shows a similar behavior as the radical of 18.3 gauss in (b), but the 3.5-gauss radical in (a) is quite different from the other two radicals (see the part III of this series⁴).

All poly-MAH samples show an absorption in the range of 450 nm accompanied by a small shoulder at 550 nm. These absorptions did not decrease after storage of poly-MAH, and it was confirmed that this absorption of 450 nm has no correlation with the concentration of any radical. However, this absorption appeared considerably in the course of the polymerization of MAH by AIBN, in which a large conjugated radical is possibly formed. For example, system no. 2 in Table II, which shows a strong absorption of 450 nm, indicates the possibility of the formation of a large conjugated radical because of the high concentration of AIBN. Of course, a homogeneous system is not suitable for accumulation of radical, and the polymer obtained from a homogeneous system has only a small number of radicals.

Another experimental proof is the inversely parallel relationship between number of radicals and absorption intensity of 450 nm, which is shown in experiments 1 and 4 of Table II. Considering the low polymer yield of experiment 4, this condition is very suitable to the formation of a large conjugated radical in spite of low concentration of trapped radicals. This is caused by the fact that the precipitate produced in dichloroethane is less rigid than that in benzene and is not suitable for the accumulation of radicals. In this sense, it is possible to attribute this absorption to a large conjugated molecular system which remains even after termination of the large conjugated radical. In addition, we have other evidence for this assumption; that is, the polymerization system of citraconic anhydride by AIBN does not give this absorption, though the polymerization of this monomer was followed by dilatometry. In this case, the growth of the con-

jugated system by the elimination of hydrogen is inhibited by an α -methyl group of this monomer.

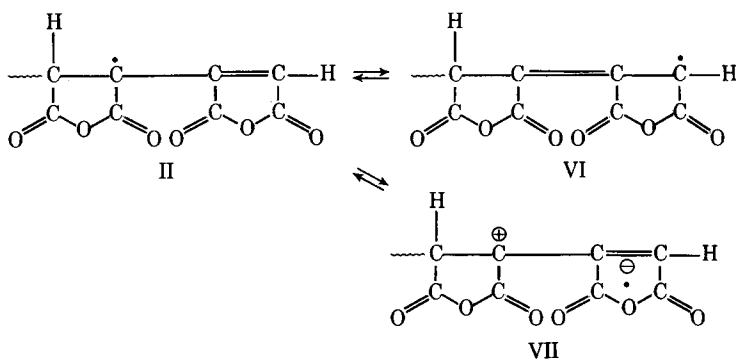
By examining Tables I and II, it is found that a large conjugated radical is effectively produced under unfavorable condition for the polymerization reaction in the presence of an excess of AIBN. At low concentration of AIBN, the number of small conjugated radicals is relatively increased (see samples 1 and 8 in Table II). From these results, the following mechanism of the formation of trapped radicals is assumed:



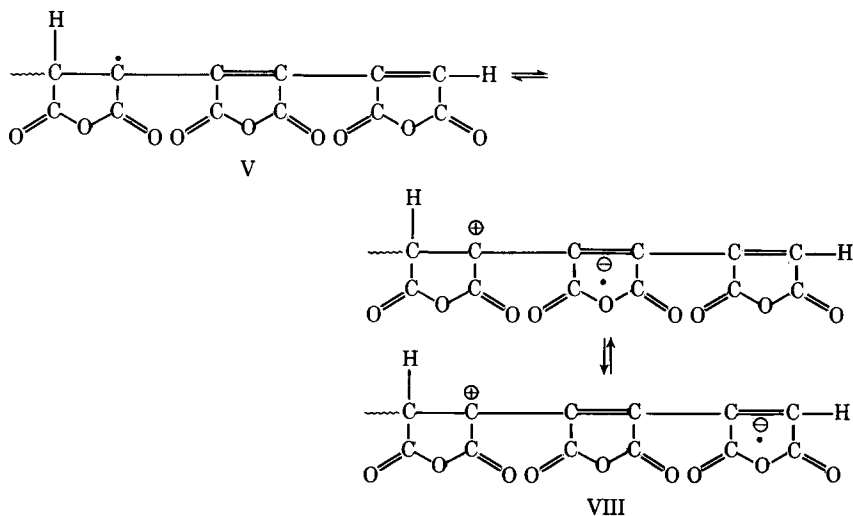
The AIBN radical exists freely in the solution, because of the difficulty of the attack on MAH and weak affinity for the hydrogen atom, in contrast with the BPO radical. The propagating radical of MAH (I) also hardly attacks MAH owing to their electrostatic repulsion. On the other hand, as MAH is a 1,2-disubstituted monomer, the hydrogen at the β -carbon in type I is easily released accompanying the abstraction of geminate hydrogen atoms to form the radical of type II. The propagation of the conjugated system becomes more difficult after type II radical, owing to the stabiliza-

tion of the π -electron system. The formation of type V radical is probably achieved by the existence of a free AIBN radical in the solution. The 14.7-gauss radical is too stable to be assigned as propagating radical I, because this could exist in poly-MAH obtained by homogeneous polymerization. Moreover, the behavior of polymerization of IBVE initiated by this active species confirms this conclusion.

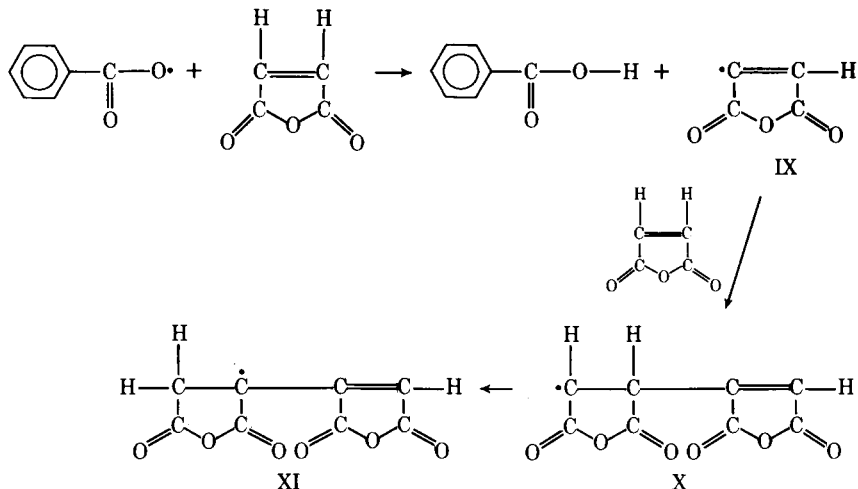
The ESR spectrum of 14.7 gauss is assigned to a radical of type II, having a doublet structure due to one β -hydrogen. However, the radical nature of this active species is rather weak owing to two electrophilic groups of carbonyl and MAH. The hydrogen on the MAH ring also splits off owing to the electrophilic nature of the MAH group. But this splitting might be very weak and gives only a broad peak. That unpaired π -electron is delocalized in the MAH ring, and the contribution of resonance between radical II and radical VII in the following illustration is more important than that between radical II and radical VI:



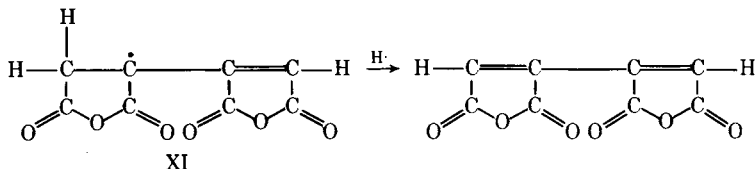
The resonance structure of VII makes the initiation of cationic polymerization a possibility. In radical V, the unpaired π -electron is strongly attracted by two MAH groups which have a very high electron affinity, so that this electron seems to be trapped in the MAH group. This structure gives a very narrow ESR spectrum:



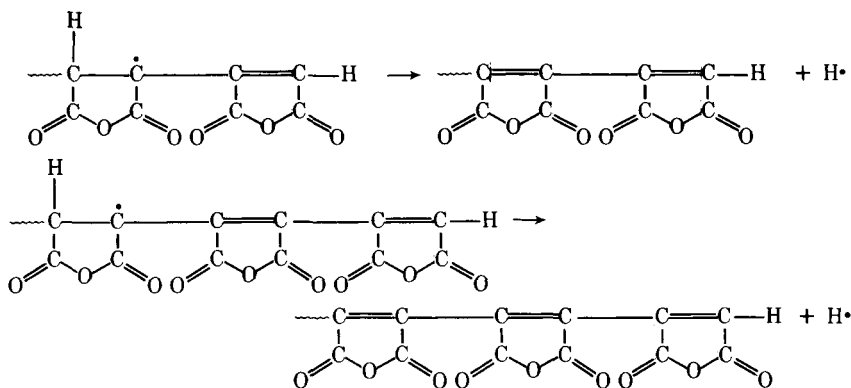
In the polymerization in benzene solution initiated by BPO, the radical formation is illustrated as follows:



BPO radical abstracts a hydrogen from MAH by its high hydrogen affinity.¹ This radical hardly attacks the double bond of MAH owing to electron repulsion. The hydrogen in radical X, which is surrounded by an unpaired electron, a carbonyl group, and an MAH group, is very mobile and is easily transformed into radical XI. The ESR spectrum of radical XI should be a triplet signal due to two β -hydrogens, which is deformed as a broad line owing to the hydrogen on the conjugated MAH ring, as discussed for radical II. In consequence the broad triplet 18.3-gauss signal (b) is assigned as radical XI. In this case, the extension of conjugated system hardly takes place, and the resulting ESR spectra also show no existence of such a large conjugated radical. The absorption of 450 nm, which had been assigned to a large conjugate system, was very weak in this case. The identical behavior in cationic polymerizations of IBVE⁴ induced by 14.7-gauss radicals in (a) and 18.3-gauss radicals in (b) in Figure 2 are reasonably explained by assigning them to structures similar to those of radicals II and XI. On the basis of these assumptions, the slow decay of the 18.3-gauss radical (b) as shown in Table III is explained by the following reaction:



In this case, the decomposition of the radical occurred with the release of secondary hydrogen. On the other hand, the other two radicals decomposed easily releasing tertiary hydrogen atoms according to the following reactions: The difference between these two decays is probably caused by the difference in stability of these radicals.



Heating the cyclohexanone solution of poly-MAH obtained by AIBN in the presence of newly added AIBN at 60°C did not change the absorption at 450 nm. However, in the case of BPO, the absorption at 450 nm decreased under the same conditions, accompanied by an increase in absorption at 550 nm. The shift in absorption to a long wavelength range is caused by the extension of the conjugated system. The BPO radical attacks even the rather stable hydrogen at the β -position of the long conjugate system, which is not abstracted by an AIBN radical of low hydrogen affinity.

In the polymerization of MAH in dioxane, the increase in MAH concentration from 1 mole/l. to 4 moles/l. increases the dependence of the rate of polymerization on AIBN concentration (from 0.6 to 0.8). This phenomenon is explained by the increase of one molecular termination, which is discussed above. The interaction between the propagating radical of MAH (electron acceptor) and dioxane (electron donor) has an influence on the nature of these radicals and increases the ratio of mutual termination against one molecular termination. It has been mentioned that the radicals have a strong electron affinity.^{5,6} Moreover the complex formation of dioxane and MAH, as mentioned later, influences the rate of polymerization as shown in the case of benzene, and the interaction between AIBN radical and dioxane might inhibit the formation of conjugate system owing to the deactivation of AIBN radical in the sense of steric hindrance. In fact, the polymer obtained in dioxane solution contains a small number of radicals and has a weak absorption at 450 nm (see Table II).

Additional evidence for the low efficiency of primary radicals formed directly from AIBN and BPO in attacking MAH is obtained from the polymerization of MAH in the presence of a small amount of ether. For example, a five-membered cyclic ether such as tetrahydrofuran (THF) is a very suitable chain transfer agent for an electropositive radical, and such an ether radical attacks MAH very favorably. In fact, considerable decrease in molecular weight of the resulting polymer was observed in the polymerization of methyl methacrylate, methyl acrylate, maleimide, *N*-butylmaleimide, and acrylic acid in THF solution as compared with dioxane and benzene solution, in spite of the small change of the rate of polymerization.

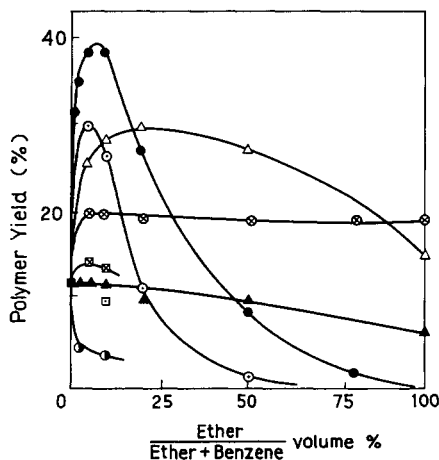
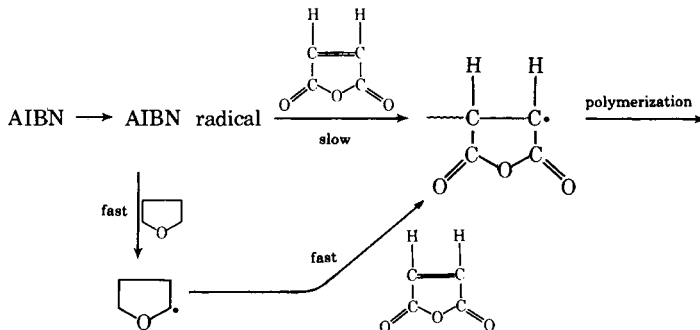
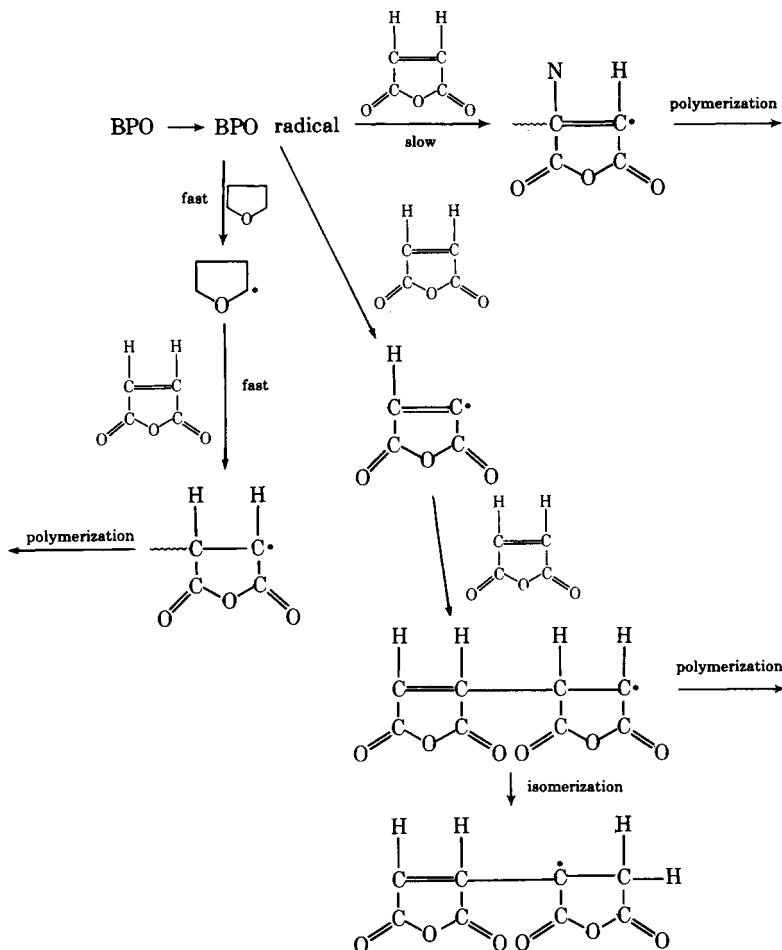


Fig. 4. Polymerization of maleic anhydride in mixed solution of various ethers and benzene: (●) THF; (○) dioxolane; (▲) tetrahydropyran; (◻) 1,3-dioxane; (●) butylene oxide; (Δ) 1,2-dimethoxyethane; (⊗) *n*-propyl ether; (■) pure benzene; (⊗) dioxane; MAH, 1 mole/l.; AIBN, 0.13 mole/l.; time = 20 hr; temperature, 60°C.

Figure 4 shows a remarkable increase in the rates of polymerization by the addition of a small amount of five-membered cyclic ethers. These data were obtained using AIBN as initiator in benzene solution; the same phenomenon was also observed in dichloroethane. In another polymerization initiated by BPO, 10% THF addition in benzene solution gives a four times higher yield than in the absence of THF. The yields are estimated from the precipitated polymer in benzene. The addition of large amounts of THF reduces the molecular weight of polymer owing to the chain transfer reaction between propagating MAH radical and THF. The reaction of MAH in an excess of THF is reported to produce a 1:1 adduct of MAH and THF.⁷

The decrease in yield by increasing the THF concentration suggests a decrease in precipitated polymer, that is, the molecular weights of the polymers are reduced with increase in the THF ratio, as shown in Figure 8. As a consequence, the rates of volume contraction increase with THF ratio, as shown in Figure 5. This acceleration is due to the new route for attacking MAH through the THF radical which is produced by the reaction between THF and AIBN radical or BPO radical:





Figures 6 and 7 show the relationship between AIBN concentration and polymerization rate in benzene solution containing 20% THF at two different concentrations of MAH. A higher concentration of AIBN in comparison with MAH reduces the polymer yields, as shown in the polymerization in pure benzene solution (see Table I). But this maximum point shifts to higher AIBN concentration in comparison with pure benzene solution. The saturation phenomenon of the time conversion curve in Figure 6 indicates that an unfavorable reaction occurs at a later stage of polymerization. It seems to be due to a disturbance of the conjugated systems which are accumulated during the polymerization time. The presence of a sufficient amount of MAH eliminates such an unusual phenomenon, as shown in Figure 7. In a mixed solution (THF and benzene), a new route for forming MAH radicals through THF radicals is produced, but in the case of AIBN initiator the direct route is not negligible because of the weak hydrogen affinity of the AIBN radical. The same discussion as in the case of pure benzene solution is possible at very low concentration of MAH.

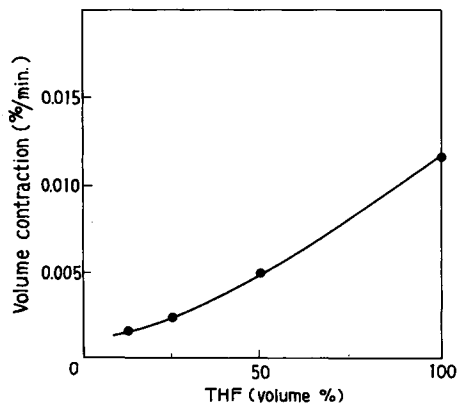


Fig. 5. Volume contraction of THF and MAH system in benzene at 60°C: AIBN, 0.043 mole/l.; MAH, 2 mole/l.

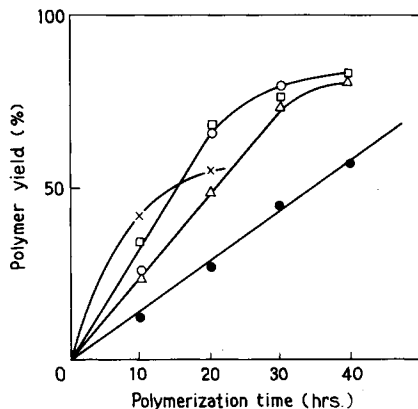


Fig. 6. Polymerization of maleic anhydride in the presence of THF: temperature, 60°C; THF:benzene, 1:4 (in volume); MAH, 0.4 mole/l.; AIBN: (●) 0.033 mole/l. (△) = 0.065 mole/l.; (□) 0.13 mole/l.; (○) 0.26 mole/l.; (×) 0.39 mole/l.

Figure 8 shows the effect of THF addition on the rate of polymerization at various MAH concentrations. This accelerating effect is not clear in high concentrations of MAH, in which the direct attack on MAH by AIBN radical seems to be more important than the route via THF radical. Considering the acceleration of the propagating steps owing to the complex formation between MAH radical and THF, a large acceleration should be expected also at high concentrations of MAH. The idea of a new route in the initial step seems to be the most probable. The increase in absolute polymer yield in benzene solution in comparison with bulk polymerization at the same AIBN concentration is certainly attributable to the complex formed by MAH and benzene. The polymer yield is reduced with an insufficient amount of benzene without any variation in the ratio between AIBN and MAH (3 and 5 in Fig. 8). Figure 9 is the result of the MAH

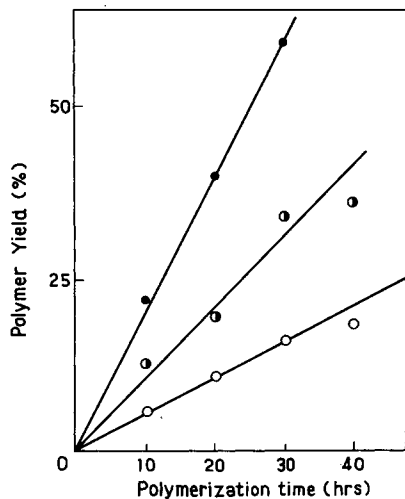


Fig. 7. Polymerization of maleic anhydride in the presence of THF: temperature, 60°C; THF:benzene, 1:4 (volume); MAH, 4 mole/l.; AIBN: (O) 0.065 mole/l.; (◐) 0.13 mole/l.; (●) 0.26 mole/l.

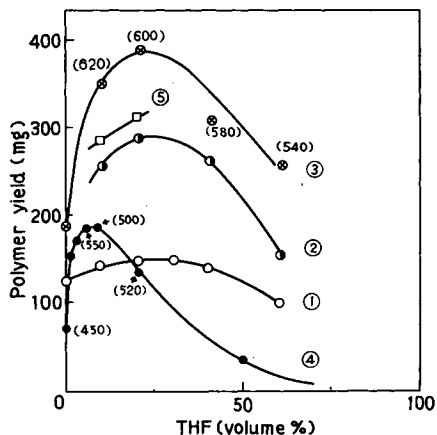


Fig. 8. Polymerization of maleic anhydride in the mixed solution of THF in benzene: AIBN, 0.13 mole/l.; time, 20 hr; temperature, 60°C; MAH: ① bulk, total volume 5 cc; ② 8 mole/l., total volume 5 cc; ③ 4 mole/l., total volume 5 cc; ④ 1 mole/l., total volume 5 cc; ⑤ 8 mole/l., AIBN, 0.26 mole/l., total volume, 25 cc; () molecular weight of polymer formed.

polymerization in the THF-benzene mixture, initiated by various concentrations of AIBN. The acceleration in rate is pronounced at high concentrations of AIBN. The results could be explained in terms of enhanced initiation reaction or the reduction of termination, but not of increase in propagation rate, because the ratio of acceleration by THF addition is independent of the concentration of AIBN in this case. All these results indicate that the increase of efficiency in the initial step is the most probable

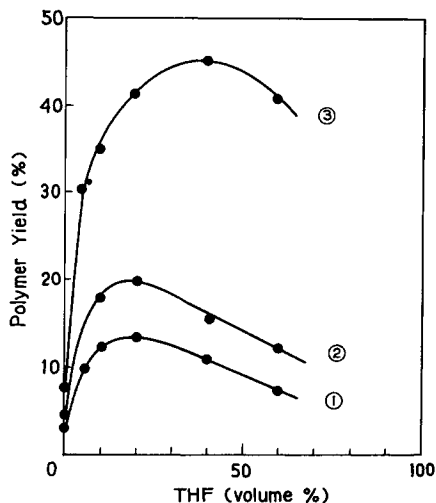






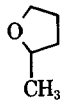
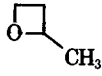
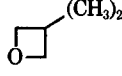
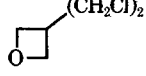
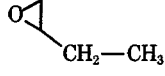
Fig. 9. Polymerization of maleic anhydride in THF and benzene mixed solution using various concentrations of initiator: temperature, 60°C; time, 20 hr; MAH, 4 mole/l.; ① AIBN, 0.065 mole/l.; ② AIBN, 0.13 mole/l.; ③ AIBN, 0.26 mole/l.

in order to explain these acceleration phenomena. Another mechanism, for example, the reduction of termination or the increase in propagating rate, could not explain all these results without inconsistency.

Table IV shows a volume contraction in the MAH-ether system, caused by polymerization initiated by AIBN. It is known that in the case of these four-membered cyclic ethers, these rates of volume contraction shows the polymerization rate of these ethers.^{8,9} In the case of 1,2-dimethoxyethane, dioxane, and tetrahydropyran, the volume contractions are caused by both polymerization of MAH and mutual addition reaction. Poly-MAH was not obtained in five-membered cyclic ether solution. In this case, the volume contraction indicates the rate to produce a 1:1 adduct of MAH and ether in which the chain transfer reaction is extremely fast as compared with the polymerization reaction.⁷ In such reaction, the complex between acceptor radical and donor ether may be considered an intermediate because of the strong electron affinity of usual radicals.^{5,6} The large rate in THF in comparison with dioxolane suggests that this rate of the chain transfer reaction is decided by the formation of a complex between MAH radical and cyclic ether, in which the basicity of ether plays an important role. In the case of 2-methyl-THF, the methyl group introduces another factor, that of steric hindrance. Such a conclusion is also valuable for the results of six-membered cyclic ethers. In tetrahydropyran, which is characterized by its high basic property, the polymer yield is smaller than in dioxane, but the volume contractions are increased because of the high rate of the chain transfer reaction.

The large rate of five-membered cyclic ether in comparison with that of six-membered cyclic ether can be attributed to the facility of forming

TABLE IV
Volume Contraction of Maleic Anhydride and Ether System
in the Presence of Radical Initiator^a

Ether	Volume contraction, %/min
$\text{CH}_3\text{---O---CH}_2\text{---CH}_2\text{---O---CH}_3$	0.00075
	0.0013
	0.0003
	0.0117
	0.003
	0.006
	0.0125 (acceleration)
	0.0098 (acceleration)
	0.0003
	0.0091

^a [AIBN] = 0.043 mole/l.; [MAH] = 2 mole/l., at 60°C.

oxonium ion, as indicated in the cationic copolymerization of cyclic ethers.¹⁰ In this complex, cyclic ether seems to form a kind of oxonium ion, particularly in the intermediate state.

The strong electropositive charge on the MAH radical inhibits the attack of this radical on MAH, which also has electropositive charge. The complex between MAH and the solvents may release this inhibition, because the electropositive charge on MAH is reduced by the electron transfer from solvent to MAH. Figure 10 shows the UV absorption spectra of MAH in various ether solutions in an attempt to examine the possibility of complex formation. Dioxane shows the strongest absorption above 360 nm, in spite of its weak basicity. This absorption has a maximum at 1:1 ratio of MAH and dioxane. Two symmetric oxygens in dioxane facilitate the formation a complex. Indeed, the polymerization of MAH in dioxane gives

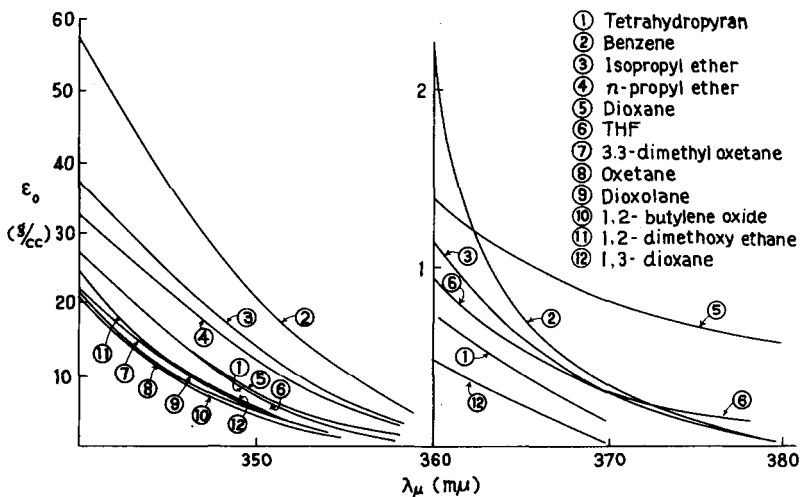


Fig. 10. Optical absorption of MAH in various ethers and benzene solution: MAH, 0.1 g/cc; ① tetrahydrofuran; ② benzene; ③ isopropyl ether; ④ *n*-propyl ether; ⑤ dioxane; ⑥ THF; ⑦ 3,3-dimethyloxetane; ⑧ oxetane; ⑨ dioxane; ⑩ 1,2-butylene oxide; ⑪ 1,2-dimethoxy ethane; ⑫ 1,3-dioxane.

the highest polymer yield in all the solvents used. However, in this system, the interaction between the MAH radical and the oxygens of dioxane should be considered. Since the acceleration by addition of dioxane occurred at low concentrations of dioxane, as shown in Figure 4. As the acceleration occurring by the addition of benzene to dichloroethane is dependent on the ratio of benzene and dichloroethane, complex formation seems to be responsible for this acceleration. A π -donor such as benzene seems to form a π -complex with MAH rather than with the MAH radical. But the acceleration by toluene, xylene, and mesitylene is much smaller than that by benzene in spite of their large tendency of complex formation with MAH (observed by UV absorption spectra). This is explained by the large chain transfer reaction between these additives. The radicals obtained do not effectively attack MAH, because these radicals have no electronegative charge, in contrast to THF radicals. The addition of durene and hexamethylbenzene, which have a very large ability to form complexes with MAH, shows an acceleration of the polymerization rate at very high concentrations of AIBN, but not at low concentrations. Although the former additives, i.e., toluene, xylene, and mesitylene, which have much less of a possibility to form such a complex, do not show acceleration at any concentration of AIBN, this fact may be explained by a complex formation; however, in these cases, the coexistence of the following factors complicates the reaction: (1) The complex formation between MAH and substituted benzene accelerates the polymerization rate. (2) The elimination of excess initiator radical by the charge transfer reaction with substituted benzenes accelerates the polymerization rate. (3) On

the contrary the chain transfer reactions with substituted benzene for propagating and initiator radicals reduce the polymerization rate.

In conclusion, the polymerization of MAH is suppressed by the strong electrostatic repulsion between MAH monomer and MAH radical in each step of the polymerization, and initiator radicals which have the same electropositive charge have only a small efficiency in the first step on the attacks of MAH. Moreover, according to the specific nature of α,β -disubstituted monomer, MAH radical has always one hydrogen which is easily released, leading to the formation of large conjugated system in the resultant polymers. This nature makes MAH more difficult to polymerize.

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