The Reaction of Polypropylene with Maleic Anhydride

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Synopsis

An addition reaction of maleic anhydride with polypropylene takes place in the presence of radical reagents or sunlight. The initial rate of the reaction was proportional to the concentration of polypropylene and maleic anhydride, and one-half power of the concentration of the radical reagents. The increase in the temperature from 80 to 120°C increased the rate of the reaction and di-cumyl peroxide was effective as a radical reagent for this reaction.

Ionic crosslinked rubber-like polymers were obtained from the reaction of maleic polypropylene with some alkali metal compounds. They showed the characteristic absorption band due to —COO° in their infrared spectra.

INTRODUCTION

There have been many investigations of the reaction of maleic anhydride with high polymers, but the high polymer that has been mainly used is rubber. Bacon, Farmer,[1-3] and Alder[4] have shown that maleic anhydride reacts with natural rubber in the presence of benzoyl peroxide and they have proposed that maleic anhydride adds to the double bonds and α-methylene groups in the rubber chain. Also, Compagnon and Le Bras,[5] Delaland,[6] and Pinnazi,[7] have confirmed the addition reaction of maleic anhydride with rubber in the solid phase and in solution.

Recently, it was reported that maleic anhydride was applied to the modification of polystyrene,[8] polyvinylchloride,[9] and ethylene propylene copolymer,[10] but little basic research has been carried out to date. In this paper, the reaction of polypropylene with maleic anhydride in the presence of benzoyl peroxide was carried out, and the effects of the concentrations of polypropylene, maleic anhydride, the radical reagent, and the kind of various radical reagents, at the same concentration and reaction temperature, on the reaction rate, were studied. It was found that the polymer product obtained by the reaction was able to react with various alkali metal compounds and was converted to polymers having an ionic crosslinked structure.[11,12]

The physical properties of the ionic crosslinked polymer were also measured.

EXPERIMENTAL

Materials and Reagents

Isotactic polypropylene (IPP) and atactic polypropylene (APP) which were used for the reaction, were refined by the reprecipitation method. The melt flow-rate of IPP was about 5.0 (230°C, 2.16 kg). The intrinsic
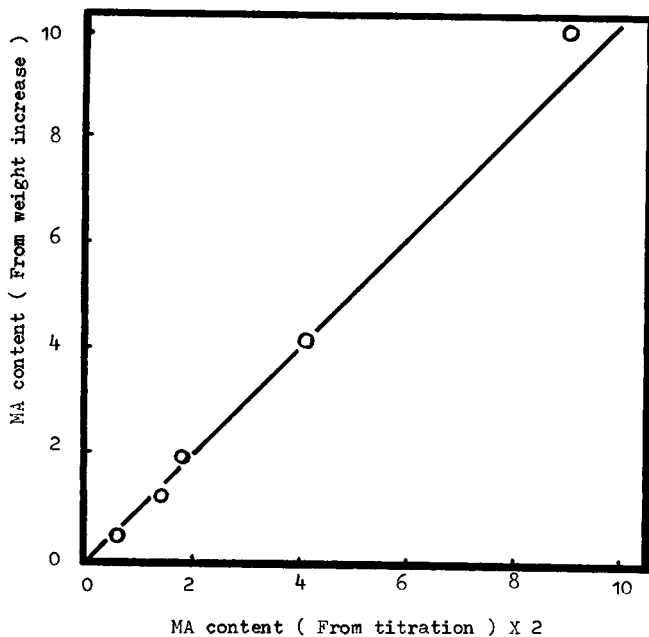

Fig. 1. Relationship between MA content values from weight method and from titration method.
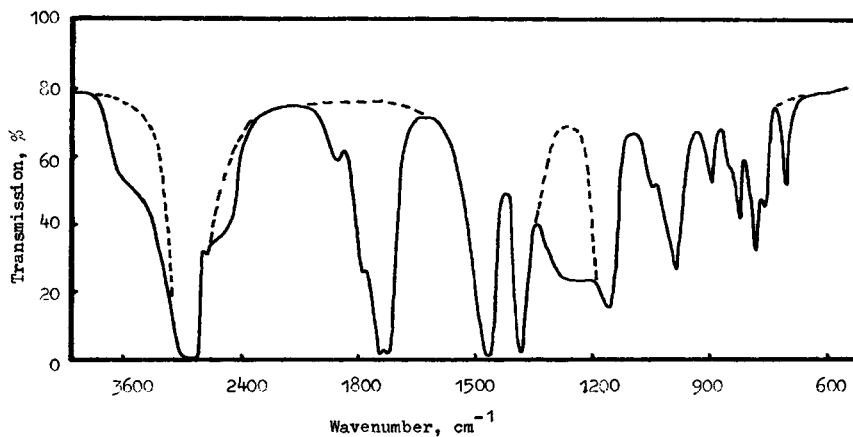

Fig. 2. Infrared spectra of the reaction product of atactic polypropylene with maleic anhydride. - - -: atactic polypropylene film from chloroform solution. ———: reaction product film from chloroform solution.

viscosity in tetraline and the iodine value (Wijs method) of APP were, 0.322 and 1.71, respectively.

Maleic anhydride (MA) was recrystallized from benzene. The melting point was 54°C. Benzoyl peroxide (BPO), azo-bis-iso-butyronitrile (AIBN), and dicumyl peroxide (DCP), used as radical reagents, were purified by recrystallization. The melting points of BPO, AIBN, and DCP were 140°C, 106°C, and 39°C, respectively. Also, commercially supplied di-tert-butyl peroxide (DTBP), of which the content of active peroxide measured by iodine titration was 65%, was used as a radical reagent without further purification. Benzene and xylene etc., used as solvents, were refined by the usual methods.

Reaction of PP with MA

The reaction of PP with MA was carried out in a tube containing the required amounts of MA, PP, the radical reagent, and the solvent. The tube was degassed and sealed off under vacuum at 1 mm Hg. The reaction was carried out from 0 to 8 hr at 80 to 120°C in an oil bath. The total volume of the reactants was 10 ml. The reaction product was precipitated in methanol, filtered after 24 hr, washed with methanol, and dried in vacuum at room temperature.
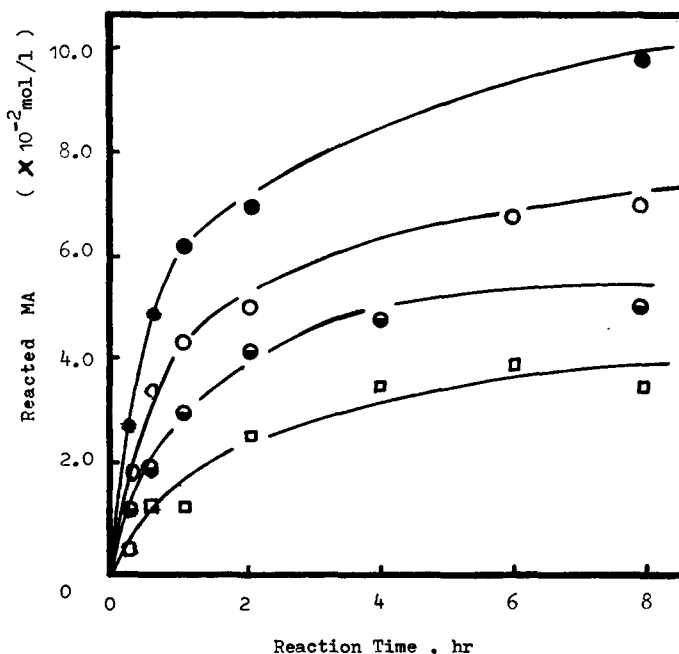

Fig. 3. Effect of the concentration of atactic polypropylene on the reaction of polypropylene with maleic anhydride. Conditions: atactic polypropylene: ●, 3.04 mol/l.; ○: 2.28 mol/l; ◓, 1.52 mol/l.: □: 0.76 mol/l.; maleic anhydride = 1.224 mol/l; benzoyl peroxide = 2×10^{-1} mol/l at 120°C in benzene.

Characterization of the Reaction Product. The infrared absorption spectra were obtained by films of APP and the reaction products formed from chloroform solution on a NaCl crystal plate and by a film of IPP made by hot pressing, by means of Perkin-Elmer model 337 Infrared Spectrophotometer.

The MA contents of the reaction products were determined by titration with 0.1 N-KOH alcoholic solution[13] and by the weight increase of the reaction product. Their relationship was linear, as shown in Figure 1. In this paper, MA content means the average number of molecules of MA attached to a segment of the chain consisting of 100 C_3H_6 units. As the relationship in Figure 1 is linear and the slope of the straight line is about 1, it is considered that the MA content can be determined by the weight increase method as well as the titration method.

Viscosity measurements were carried out using an Ubbelohde viscometer at 30°C and tetraline as solvent.

Preparation of Ionic Crosslinked Polymer and its Properties. The reactions of maleic APP with alkali metal compounds were carried out, and ionic crosslinked polymers were obtained.

The preparation of the ionic crosslinked polymers was as follows. Three milliliters of saturated solutions of sodium hydroxide, potassium hydroxide, lead acetate, or magnesium acetate in methanol were added to 10% benzene solutions of maleic APP from a dropping funnel with stirring, and then the mixture was heated for 10 ~ 30 min at 50 ~ 80°C on a water bath. The
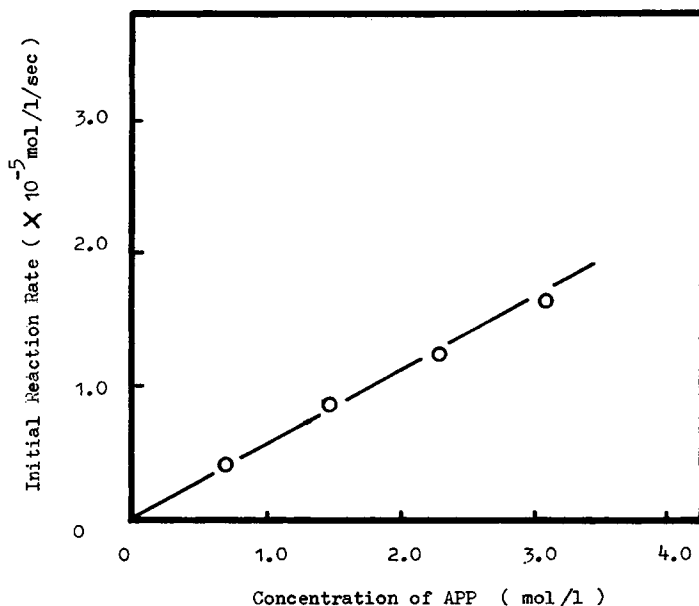

Fig. 4. Relationship between the concentration of atactic polypropylene and the initial reaction rate of polypropylene with maleic anhydride. Conditions: maleic anhydride = 1.224 mol/l., benzoyl peroxide = 2×10^{-1} mol/l, in benzene, at 120°C, from 0 to 8 hr.

products which precipitated from the reaction system were filtered, washed with methanol, and dried in vacuo at room temperature. Infrared spectra were obtained from films made by hot pressing using the same apparatus as described above. The apparent melting point and elasticity were measured by the usual methods.

RESULTS AND DISCUSSION

Confirmation of the Reaction

The infrared spectrum of the product, which was obtained under the reaction conditions described in Table I is shown in Figure 2. New characteristic absorption bands at 1840 cm^{-1}, 1775 cm^{-1}, 1740 cm^{-1}, 1710 cm^{-1}, $3000 \sim 2500$ cm^{-1}, and $1300 \sim 1200$ cm^{-1} were observed. The absorption bands at 1840 cm^{-1} and 1775 cm^{-1} support the addition of anhydrosuccinic residues to APP. The carbonyl bands due to the carboxylic group at $3000 \sim 2500$ cm^{-1} and 1710 cm^{-1} and the strong ester carbonyl bands at 1740 cm^{-1} and $1300 \sim 1200$ cm^{-1} suggest the mono-esterification reaction of anhydrosuccinic residue with methanol.

Moreover, the absorption bands in the 700 to 850 cm^{-1} range do not appear usually in APP. But these absorption bands were found in this
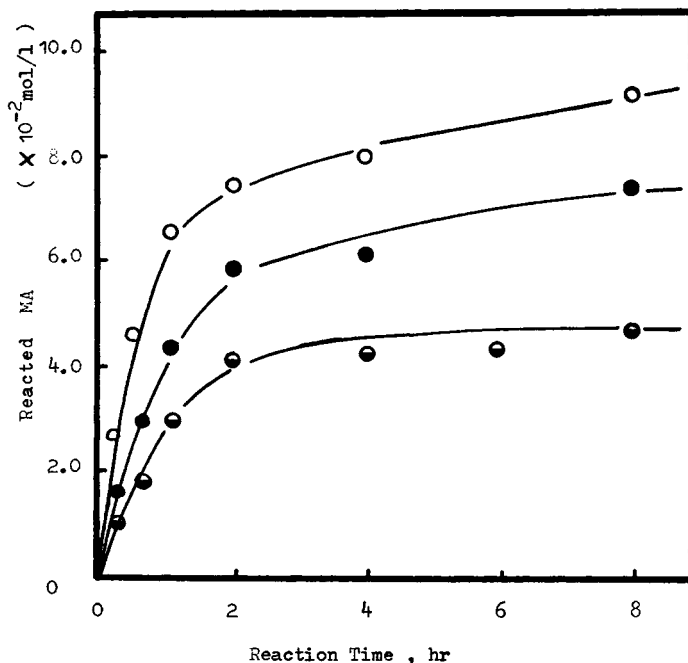

Fig. 5. Effect of the concentration of maleic anhydride on the reaction of polypropylene with maleic anhydride. Conditions: maleic anhydride; O, 2.448 mol/l; ●, 1.836 mol/l; ◒: 1.224 mol/l; atactic polypropylene = 1.52 mol/l; benzoyl peroxide = 2×10^{-1} mol/l in benzene at 120°C.

TABLE I
Reaction of Polypropylene with Maleic Anhydride[a]

Run no.	APP g/10 ml	IPP g/10 ml	MA g/10 ml	BPO g/10 ml	Reaction time (hr)	Reaction temperature (°C)	MA amounts attached to PP (g)	Percentage of reaction (%)	MA content (from weight increase)
1	0.64	—	1.2	0.968	8	120	0.151	12.6	10.1
2	0.32	—	0.6	—	640[b]	room temperature	0.035	5.9	4.6
3	—	0.64	1.8	0.484	8	135		From IR spectrum	

[a] Remarks; solvent: xylene,
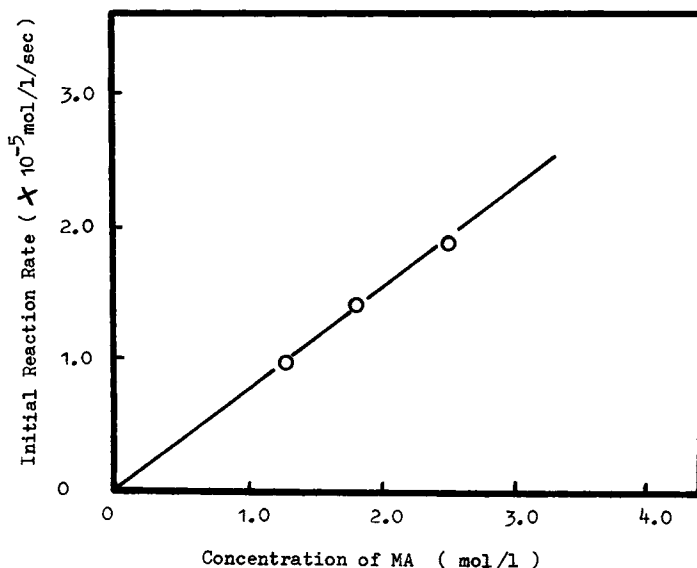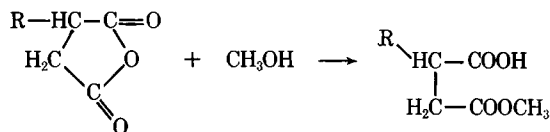[b] Irradiation time of sunlight.

Fig. 6. Relationship between the concentration of maleic anhydride and the initial reaction rate of polypropylene with maleic anhydride. Conditions: atactic polypropylene = 1.25 mol/l; benzoyl peroxide = 2×10^{-1} mol/l, in benzene, at 120°C, from 0 to 8 hr.

work and did not disappear by means of drying up the films from the polymer solutions for 8 hr under 1 mm Hg at room temperature. Probably, it was considered that these absorption bands are dependent upon chloroform used for the preparation of infra-red spectra's sample.

The MA content of the product described above was determined by both titration and the weight increase methods, it was 10.1 for the weight increase method and 4.5 for the titration method. This disagreement suggests that the following reaction between anhydrosuccinic residues and methanol could have taken place.

$$R-HC-C{=}O$$
$$H_2C\diagdown\diagup O \quad + \quad CH_3OH \quad \longrightarrow \quad R\diagdown HC-COOH$$
$$C \qquad\qquad\qquad\qquad\qquad\qquad H_2C-COOCH_3$$
$$O$$

Moreover, MA could be added to APP in the absence of a radical reagent under the irradiation of sunlight, and IPP reacted with MA as well. These results are shown in Table I.

Here, the reaction of IPP with MA was confirmed from the infrared spectrum obtained using a film of maleic IPP, and the reaction of APP with MA was confirmed similarly. It was made clear that MA added to IPP as well as APP.

From these results, it was confirmed that the reaction of APP with MA could take place. It may be considered that this reaction is as follows:
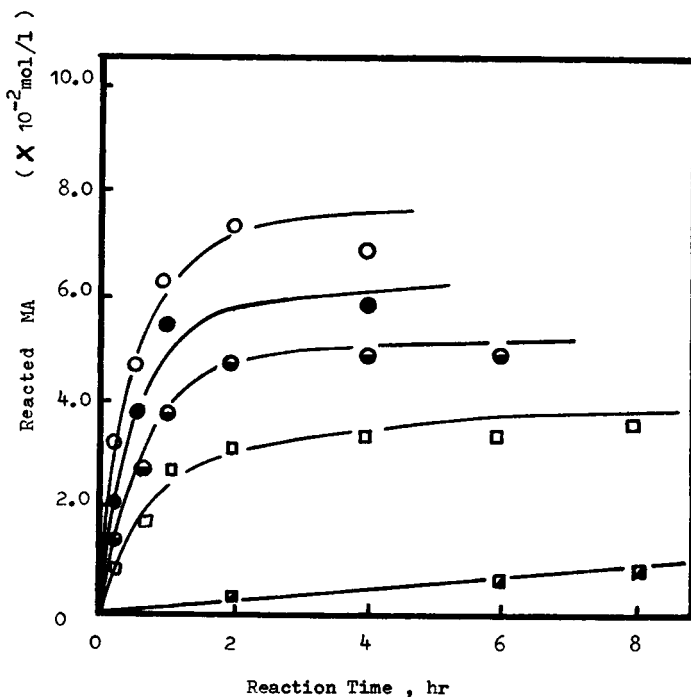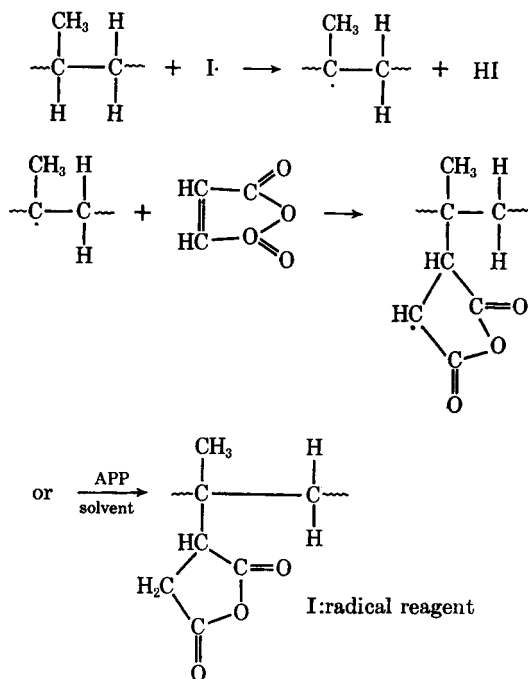
Fig. 7. Effect of the concentration of radical reagent on the reaction of polypropylene with maleic anhydride. Conditions: radical reagent: O, 4×10^{-1} mol/l; ●: 3×10^{-1} mol/l; ◐: 2×10^{-1} mol/l; □: 1×10^{-1} mol/l; ■: 0 mol/l; atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l, in benzene, at 120°C.
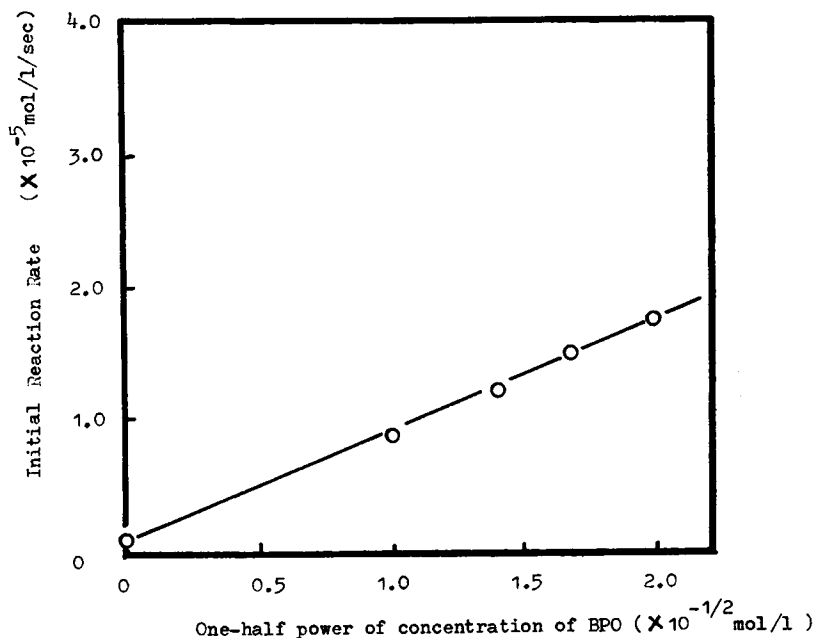
Fig. 8. Relationship between the initial reaction rate and the concentration of benzoyl peroxide. Conditions: atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l, in benzene, at 120°C from 0 to 8 hr.

The Effect of the Concentration of APP, MA, and the Radical Reagent on the Initial Rate of the Reaction.

The effects of the concentrations of APP, MA and BPO on the reaction of APP with MA are shown in Figure 3-8. The initial consumption rates of MA were obtained from the slope of respective curves in the initial period of the reaction. From Figure 3, it was made clear that the initial consumption rate of MA increased with increase in the concentration of APP. The contents of MA in the products at the same reaction time were almost the same. A linear relationship was obtained, between the initial consumption rate of MA and the concentration of APP, as shown in Figure 4. That is, the initial rate of the reaction of APP with MA is proportional to the concentration of APP.

For the variation of the concentration of MA, it was found from Figures 5 and 6 that the initial consumption rate of MA was proportional to the concentration of MA.

The effect of the concentration of BPO on the reaction of APP with MA is shown in Figures 7 and 8. It was made clear that the initial consumption rate of MA increased with the concentration of BPO and was proportional to one-half power of the concentration of BPO. From Figure 7, it was found that the reaction of APP with MA also takes place in the absence of BPO. Presumably, this reaction should be dependent upon the terminal double bond and the active hydrogen of APP.
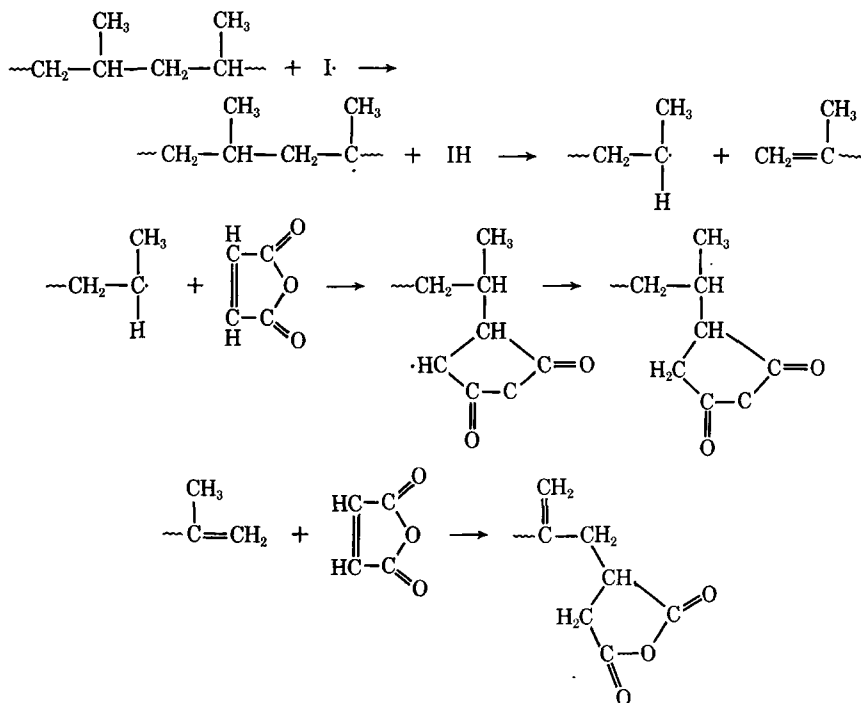
From these results, the initial rate of the reaction of APP with MA may be expressed as follows. $R_p = k[\text{APP}][\text{MA}][\text{BPO}]^{1/2}$.

In the next place, this reaction was carried out at 80°C, 100°C, and 120°C. These results are shown in Figure 9. It was confirmed that the initial consumption rate of MA increased as the reaction temperature was raised.

The changes in the intrinsic viscosity of the reaction product are shown in Figures 10 and 11. The intrinsic viscosity of the reaction product decreased linearly with increase in the concentration of BPO in the presence of BPO, but the degradation of the product did not take place in the absence of BPO. When the concentration of BPO was constant, the intrinsic viscosity of the reaction product decreased rapidly at first with the reaction time, and then approached a constant value gradually. But gelation did not take place during the reaction. These facts show that within the range of this experiment the reaction of APP with MA is accompanied by the chain scission of APP.
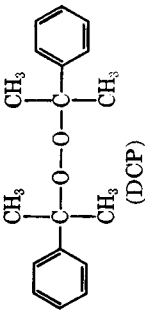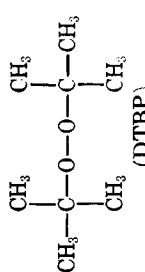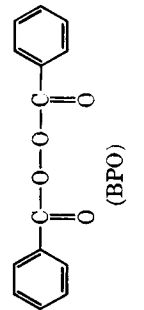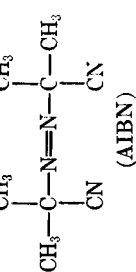
From these results, the following mechanism is considered as well.

Chain Scission

$$
\begin{array}{c}
\underset{|}{\overset{\text{CH}_3}{\text{}}} \quad \underset{|}{\overset{\text{CH}_3}{\text{}}}\\
\sim\!\text{CH}_2\!-\!\text{CH}\!-\!\text{CH}_2\!-\!\text{CH}\!\sim \;+\; \text{I}\cdot \;\longrightarrow
\end{array}
$$

$$
\sim\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\underset{}{\text{CH}}}\!-\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\underset{\cdot}{\text{C}}}\!\sim \;+\; \text{IH} \;\longrightarrow\; \sim\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\cdot \;+\; \text{CH}_2\!=\!\overset{\text{CH}_3}{\text{C}}\!\sim
$$

$$
\sim\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\cdot \;+\; \text{(maleic anhydride)} \;\longrightarrow\; \sim\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\text{CH}} \;\longrightarrow\; \sim\!\text{CH}_2\!-\!\overset{\text{CH}_3}{\text{CH}}
$$

$$
\sim\!\overset{\text{CH}_3}{\text{C}}\!=\!\text{CH}_2 \;+\; \text{(maleic anhydride)} \;\longrightarrow\; \sim\!\overset{\text{CH}_2}{\text{C}}\!-\!\text{CH}_2
$$

The Effect of the Kind of Radical Reagent on the Initial Rate of Reaction. The effect of different radical reagents such as BPO, AIBN, DTBP, and DCP on the initial reaction rate were investigated. The results are shown in Figure 12 and Table II. As the decomposition rates of these radical

TABLE II
Ratio of Radical Initiator Decomposition Rate and Initial Rate[a]

Radical reagents	Decomposition rate of radical reagent (at 120°C)(mol/1/sec)	Initial reaction rate at 120°C (mol/1/sec)	Ratio of initial reaction rate to decomposition rate
(DCP)	4.6×10^{-5} [14]	7.67×10^{-3}	1.67×10^{2}
(DTBP)	1.39×10^{-6} [15]	2.2×10^{-4}	1.58×10
(BPO)	3.1×10^{-3} [16]	6.82×10^{-4}	2.2×10^{-1}
(AIBN)	1.26×10^{-2} [17]	4.57×10^{-5}	3.36×10^{-3}

[a] Remarks; solvent: benzene; total volume: 10 ml; APP: 1.52 mol/l; MA: 1.224 mol/l; radical reagent: 2×10^{-1} mol/l.
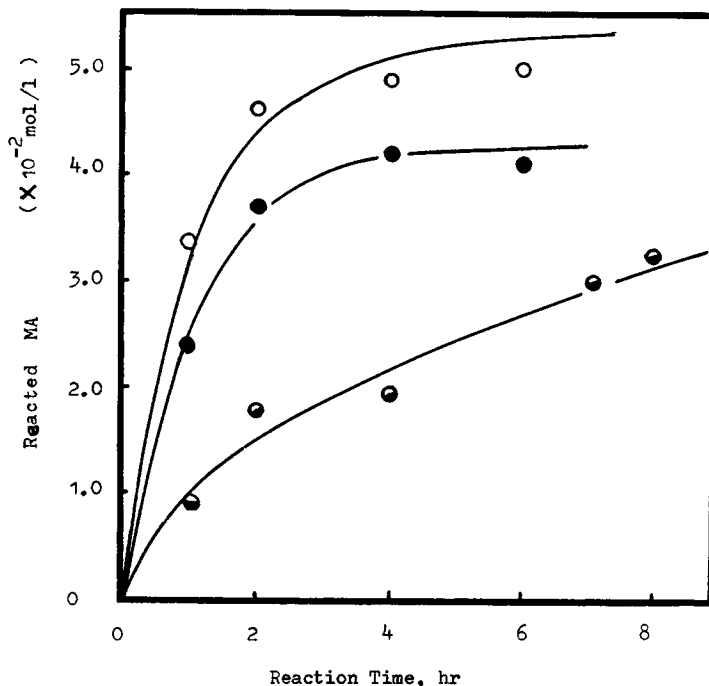
Fig. 9. Effect of reaction temperature on the reaction of polypropylene with maleic anhydride. Conditions: reaction temperature; O: 120°C; ●: 100°C; ◒: 80°C; atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l; benzoyl peroxide 2 × 10⁻¹ mol/l; in benzene.

reagents at 120°C are different, the efficiency of these radical reagents must be estimated at the same level of free radical concentration during the reaction. This problem may be accomplished by using the ratio of the initial reaction rate and the decomposition rate. From the results, it was found that the order of the efficiency of these radical reagents was DCP > DTBP

TABLE III
Properties of ionic crosslinked polymer

Maleic APP and its ionic crosslinked polymer (ICP)	Apparent melting point (°C)	Elasticity	Solubility[b]
Maleic APP[a]	55	Not elastic	soluble
Lithium ICP	195	elastic	insoluble
Sodium ICP	195	elastic	insoluble
Potassium ICP	200	elastic	insoluble
Lead ICP	165	elastic	insoluble
Magnesium ICP	230	elastic	insoluble

[a] This polymer was contend 1.01 mol % of MA and was used for the proportions of ICP.

[b] Solubility: benzene, toluene, xylene, and carbon tetrachloride.
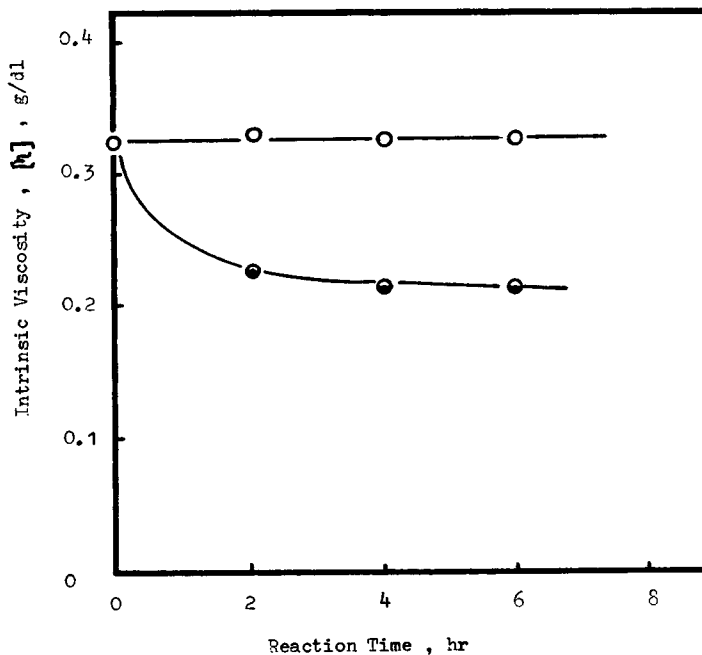
Fig. 10. Relationship between reaction time and intrinsic viscosity of the reaction product of polypropylene with maleic anhydride. Conditions: O: no radical reagent; ◓: radical reagent 2×10^{-1} mol/l; atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l, in benzene, at 120°C.

> BPO > AIBN, as shown in Table II.   In this case the efficiency of the radical reagent DCP was particularly large compared to the other radical reagents.   This fact suggests that the stability and polarizability of the free radicals which are produced during the reaction affect the hydrogen withdrawing reaction.

Properties of Maleic APP and its Ionic Crosslinked Polymer.   The hardness and tensile strength of maleic APP tended to increase relative to those of APP as the MA content increased.   For example, the tensile strength, elongation at break, and hardness of APP were 5.4 kg/cm², 110%, and 10 ~ 15 (Japan Industrial Standard), but the values of maleic APP with an MA content of 4.5, were 19.5 kg/cm², 400%, and 50 ~ 55. Maleic APP was possible to cure using ethylene diamine, hexamethylene diamine, and magnesium oxide as crosslinking agents.   A change in the solubility of maleic APP in some APP-solvents was not observed.

The infrared spectrum of the reaction product of maleic APP with NaOH is shown in Figure 13.   A new characteristic absorption band that was not observed with maleic APP, appeared at 1590 cm^{-1}.   This absorption band is due to the ionized carboxylic group.   In contrast to this, the absorption strength due to the carboxylic group decreased.   When metal compounds such as KOH, LiOH, Pb(OCOCH₃)₂, and Mg(OCOCH₃)₂ were used, analo-
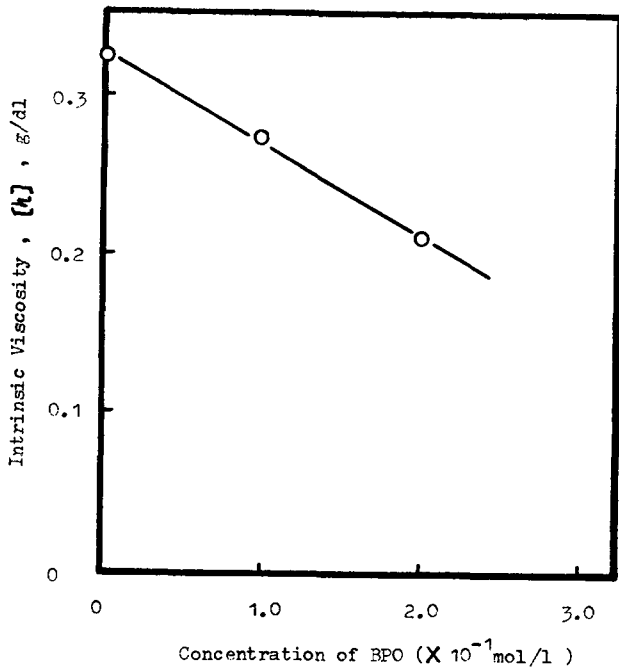
Fig. 11. Relationship between the concentration of benzoyl peroxide and intrinsic viscosity of reaction product of polypropylene with maleic anhydride for 4 hr. Conditions: atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l, at 120°C, in benzene.
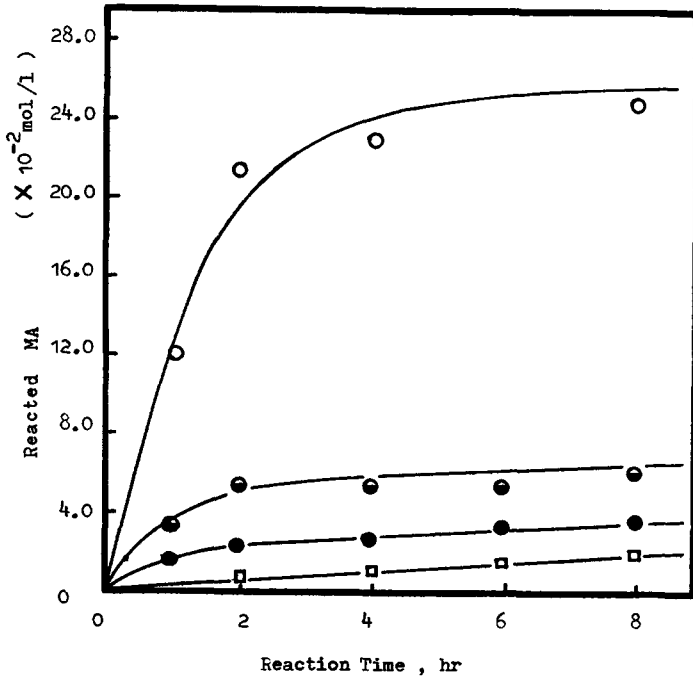

Fig. 12. Effect of some radical reagents on the reaction of polypropylene with maleic anhydride. Conditions: radical reagents; O: DCP; ◑: DTBP; ●: BPO; □: AIBN; atactic polypropylene = 1.52 mol/l; maleic anhydride = 1.224 mol/l; (radical reagent = 2 × 10^{-1} mol/l, in benzene, at 120°C.

gous results to the case of NaOH were also confirmed from their infrared spectra. Thus, it was made clear that maleic APP was neutralized with alkali metal compounds and turned to the ionic polymer. The properties of these ionic polymers are shown in Figure 14 and Table III. Here, the
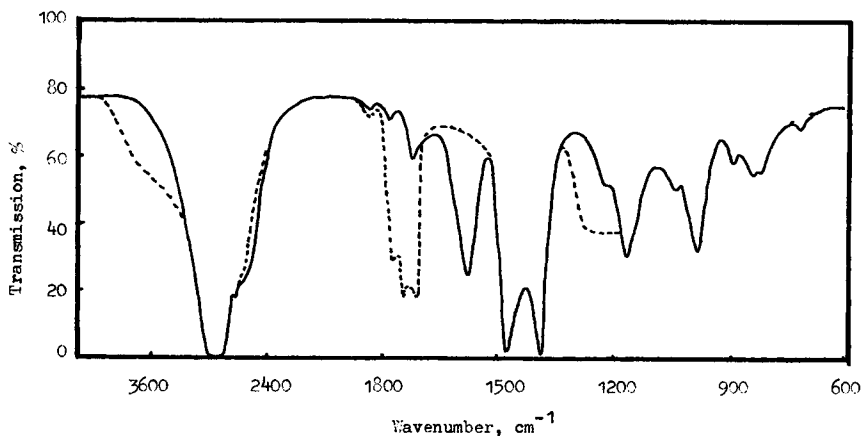

Fig. 13. Infrared spectra of the reaction product between carboxylic polypropylene and sodium hydr. - - -: carboxylic polypropylene; ———: reaction product.
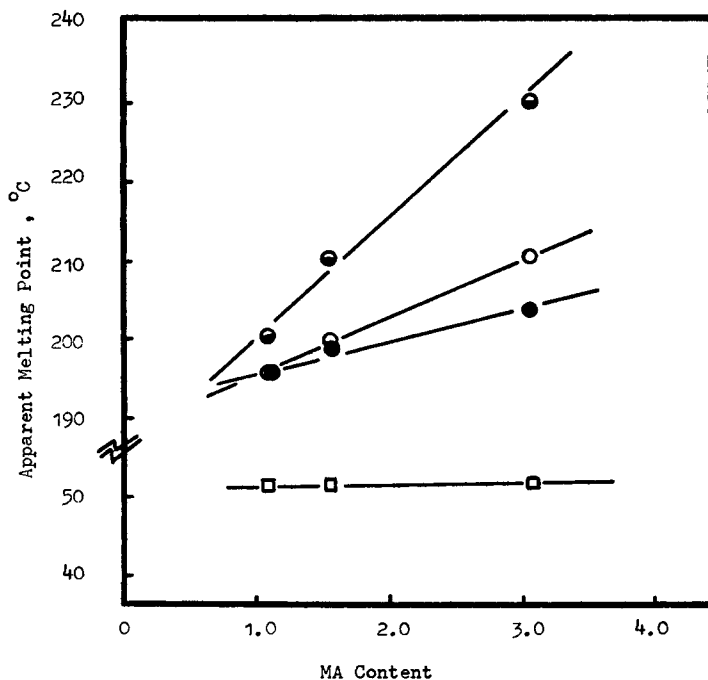

Fig. 14. Relationship between MA content and apparent melting points of some ionic crosslinked polymers (ICP). ◓: potassium ICP; ○: sodium ICP; ●: lithium ICP; □: carboxylic polypropylene.

apparent melting point is the temperature at which the polymer is fluid under a force of 0.5 kg. From Figure 14 and Table III, it was found that the apparent melting point increased with increase in the MA content and was also influenced by the kind of alkali metal. These ionic polymers were insoluble in maleic APP solvents and were elastic. These results support the hypothesis that the ionic crosslinked structure may be formed by an ionic attractive force operating between the carboxylate anion and the metallic cation in polymer. Thus the ionic crosslinked structure will account for the increase in the apparent melting point, insolubility, and elasticity. Namely, the insolubility and elasticity are caused by gelation, and, in general, an apparent melting point is not observed for a polymer in which a three-dimensional network is made up of covalent bonds.

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