

파라이소프로필 - α - 메틸스티렌과 말레산 무수물의 자유라디칼 혼성중합에 관한 연구

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Free-Radical Copolymerization of p-Isopropyl- α -methylstyrene and Maleic Anhydride

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요약 : p-이소프로필 - α -메틸스티렌과 말레산 무수물의 자유라디칼 혼성중합을 클로로포름 용액중에서 행하여 반응속도론적인 연구를 행하였다. 이 단위체 쌍은 초기 단위체 농도비에 무관하게 1:1 교대 혼성중합제를 형성하며, 혼성중합속도는 60°C에서 단위체농도에 대하여 1.07, 개시제 (과산화 벤조일)에 대하여 0.65의 차수를 보여주었고, 두 단위체의 농도비가 1:1일때 가장 컸다. 이 혼성중합의 총괄 활성화 에너지는 7.6kcal/mole이었다. 혼성중합속도가 두단위체의 농도와 농도비에 의존하는 양상으로 보아 두 단위체간의 착물이 형성되어 이 착물이 전파단계에 참여하는 메카니즘 만으로는 혼성중합 결과를 모두 설명할 수 없음을 알았다.

ABSTRACT: Kinetics of free-radical copolymerization of p-isopropyl- α -methylstyrene and maleic anhydride in chloroform at 60°C have been studied. The monomer pair formed 1:1 alternating copolymers regardless monomer feed composition with the highest copolymerization rate at the equimolar feed. General kinetic studies at equimolar feeds and various initiator concentrations showed an order of 1.07 and 0.65 with respect to monomer and initiator concentrations. The overall activation energy for this polymerization was found to be 7.6 kcal/mole. The dependence of copolymerization rate on the monomer concentration and monomer feed ratio indicates that participation of intermolecular charge-transfer complexes between the two monomers is yet to be proven.

INTRODUCTION

Recently a great deal of works have been

published on the free radical copolymerization systems which give rise to 1:1 alternating copolymers.

Copolymerization characteristics of vinyl monomers in ordinary cases can be satisfactorily described by the familiar copolymer composition equation which was derived independently in 1944 by Alfrey and Goldfinger¹, Mayo and Lewis², Wall³ and Sakurada⁴. This equation contains two kinetic parameters, so-called monomer reactivity ratios (r_1 and r_2) which define the relative reactivities of the two monomers involved in the copolymerization. Moreover, the magnitude of the $r_1 r_2$ product has been regarded as an index for alternating tendency of the two monomers along the copolymer chain. This relation was qualitatively rationalized by Mayo and Walling⁵ in terms of polar effect of the substituents attached to the double bond. Alfrey and Price⁶ introduced, based on polar and resonance effects, a relatively simple semi-empirical "Q-e" scheme to correlate structures of vinyl monomers to their reactivities. This approach also predicts that the alternating tendency of certain monomer pair depends solely on the polar effects of the substituents on the vinyl group.

These reasonings, however, have been lately scrutinized especially for strongly or perfectly alternating systems such as styrene/maleic anhydride⁷⁻¹¹, α -methylstyrene/maleic anhydride¹²⁻¹⁴, vinyl ether/maleic anhydride¹⁵⁻¹⁷, sulfur dioxide/ α -olefins¹⁸, and many others¹⁹⁻²⁵.

Since these monomer pairs form 1 : 1 donor-acceptor complexes and polymerizations are usually fastest at equimolar feed compositions, participation of the intermolecular complexes between the two monomers in propagation reactions have been claimed to occur by many authors^{9, 12, 13, 19, 20, 21, 22}. It has been also suggested that, for example, alternating copolymerization of styrene and maleic anhydride results from the resonance stabilization of the transition state between a radical and the comonomer²⁶. Barb⁶

interpreted the kinetic results of styrene/maleic anhydride copolymerizations in terms of penultimate group effect.

Participation of monomer complex is more convincing in the case of copolymerization of α -methylstyrene and maleic anhydride. Although these two monomers do not homopolymerize well under ordinary conditions, this monomer pair readily form 1 : 1 copolymers when either free radical initiator or γ -ray irradiation¹⁴ is employed. Seymour and Garner^{12, 13} recently drew the conclusion that 1 : 1 charge transfer complexes of the two monomers play important role in the copolymerization. Yoneho et al.¹⁴, also, in their study of the γ -ray induced copolymerization of these two monomers, interpreted their results by the kinetic scheme which counted on the participation of monomer complexes in propagation reactions. Baldwin²⁷ studied the rate of copolymerizations of vinyl isobutyl ether/diethyl fumarate, vinyl isobutyl ether/maleic anhydride, and 1-octene/maleic anhydride pairs. He explained the kinetic results for the first two systems by a modified copolymerization equation based on the simple terminal model. All the pairs are known to form only alternating copolymers. Observed in those polymerizations are however many experimental phenomena which need further clarification. This paper reports a study of the free radical copolymerization of *p*-isopropyl α -methylstyrene and maleic anhydride mainly in chloroform solvent. The purpose of the present work is to understand the copolymerization kinetic features of this pair of monomers and to see if the mechanism involving propagation reactions via monomer complexes is adequate to explain all the experimental results.

EXPERIMENTAL

1. Chemicals and Instruments

Chemicals. p-Isopropyl- α -methylstyrene obtained from Aldrich Chemical Company (U. S. A.) was freshly vacuum distilled prior to use. Gas chromatographic analysis of the distilled monomer showed that it was 99.5+% pure.

Maleic anhydride(Merck AG) was used after recrystallization from chloroform solution and drying under a reduced pressure (mp, 53.0°C; lit. value, 52.8°C). Benzoyl peroxide used as an initiator throughout the present work was obtained from Kanto Chemical Co. (Japan) and purified using chloroform/methanol. Chain stopper, hydroquinone, from Showa Chemical Co. (Japan) was used as received. All the solvents and chemicals employed without purification for this work were of extra pure reagent grade.

Instruments. Vapor pressure osmometer used for the measurements of molecular weights of polymers was of Herbert Knauer Co. (W. Germany) equipped with a electronic universal temperature measuring device and an X-Y recorder. Automatic recording differential analysis system Model 4-4442 of American Instrument Co. and thermogravimetric analyzer (Model TGS-1) of Perkin Elmer were used for the study of thermal behaviors of polymers.

2. Copolymerization of p-Isopropyl- α -methylstyrene and Maleic Anhydride

Required amounts of the two monomers and benzoyl peroxide were placed in a volumetric flask and the mixture was diluted to the mark by chloroform. A certain amount of the solution was pipetted and transferred to a polymerization tube, which was immediately stoppered and the mixture was frozen in a dryice/acetone bath. The tube was then connected to a vacuum line and the air in the tube was removed by the usual freeze-thaw method. The polymerization tube with its empty space filled with nitrogen was placed in a water bath whose temperature was

maintained at the polymerization temperature within $\pm 0.1^\circ\text{C}$. Polymerization was stopped by placing the reaction mixture in a dry-ice/acetone bath and then by mixing the mixture with a small quantity of chloroform solution containing hydroquinone. Copolymer formed was separated by pouring the reaction mixture into an excess amount of chilled absolute diethyl ether. Copolymer was purified by dissolution and precipitation cycles using chloroform and diethyl ether. Copolymer purified was finally dried to a constant weight at 70-80°C under a reduced pressure (15mmHg). Variations of polymerization condition are described later in the Results and Discussion section.

3. Determination of Copolymer Composition.

Copolymer compositions were determined by a simple acid-base titration method. Copolymer sample of 100-200mg was dissolved in 10ml DMF, and 25-30ml of standard 0.1N NaOH solution added to the solution. The mixture was heated at 100°C until it became clear. After cooled to room temperature, the solution was titrated against a standard 0.1N HCl solution. By calculating the amount of NaOH consumed by the copolymer sample, the content of maleic anhydride unit in the copolymer was determined.

RESULTS AND DISCUSSION

1. Copolymer Composition vs. Composition of Monomer Feed

Copolymers were prepared from a wide range of monomer feeds in chloroform and in a mixture of benzene and acetonitrile (1 : 3 by volume) at 60°C.

Overall monomer concentration was 2.55mole/l and the concentration of the initiator 0.16 mole % based on the monomer mixtures when

Table I. Copolymerization of Maleic Anhydride (M_1) and p-Isopropyl- α -Methylstyrene (M_2)*

Exp. No.	M_1 (g)	M_2 (g)	M_1/M_2 (mole ratio in feed)	Conversion (wt. %)	M_1 content (mole % in copolymer)
1	2.6425	1.4363	3.01	8.75	49.0
2	2.2588	3.7275	0.990	10.2	50.5
3	2.2580	3.7279	0.990	11.4	51.0
4	1.1798	3.8423	0.502	6.35	49.2
5	1.0726	5.2864	0.332	9.04	50.1

* Copolymerized in chloroform at 60°C. Total monomer concentration was 2.55mole/l and the concentration of benzoyl peroxide was 0.16mole % based on monomer mixtures.

Table II. Copolymerization of Maleic Anhydride (M_1) and p-Isopropyl- α -Methylstyrene (M_2)*

Exp. No.	M_1 (g)	M_2 (g)	M_1/M_2 (mole ratio in feed)	Conversion (wt. %)	M_1 content (mole % in copolymer)
1	4.2313	0.7681	9.00	10.9	49.0
2	3.2363	1.7679	2.99	11.2	51.3
3	3.2365	1.7668	2.99	8.29	50.9
4	2.9368	2.5137	1.91	9.17	51.5
5	2.9365	2.3799	2.02	8.55	50.9
6	2.2586	3.7281	0.990	5.32	50.5
7	1.8979	3.1101	0.997	7.81	51.6
8	1.1799	3.8487	0.501	9.20	50.6
9	1.1795	3.8422	0.502	8.75	50.0
10	1.0716	5.2878	0.331	11.6	48.8
11	1.0726	5.2870	0.332	5.34	49.9

* Copolymerized at 60°C using 0.16mole% benzoyl peroxide as initiator in a mixture of benzene (1.5ml) and acetonitrile (4.5ml).

Table III. Dependence of Copolymerization Rate on Overall Monomer Concentration ($[M_1] + [M_2]$)*

Exp. No.	$[M_1] + [M_2]$ (mole/l)	R_p (mole/l·sec.)	R_p (wt. %/sec.)
1	2.46	84.6×10^{-6}	68.8×10^{-4}
2	1.55	38.6×10^{-6}	44.5×10^{-4}
3	0.982	11.9×10^{-6}	24.2×10^{-4}
4	0.490	3.03×10^{-6}	12.4×10^{-4}
5	0.155	0.280×10^{-6}	3.61×10^{-4}

* Copolymerized at equimolar feed and initiator concentration of 2.48×10^{-3} mole/l. Copolymerization temperature was 60°C.

copolymerizations were conducted in chloroform. Copolymerizations were stopped at the conversion of about 10wt%. Copolymerization proceeded homogeneously in both solvent systems. Table I and II suggest that all the copolymers formed

are presumably of 1 : 1 alternating composition. We have observed the fact that p-isopropyl- α -methylstyrene homopolymerized extremely slowly while maleic anhydride produced practically no homopolymer under the same condition. This

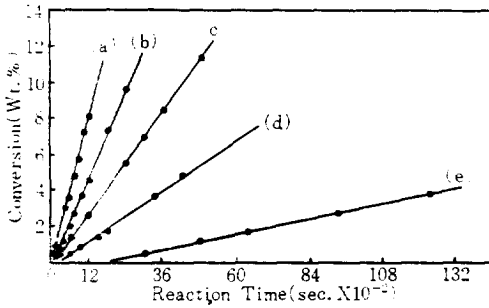


Figure 1. Copolymerization for an equimolar feed of p-isopropyl- α -methylstyrene and maleic anhydride in chloroform at 60°C and benzoyl peroxide concentration of 2.48×10^{-3} mole/l.

- (a) $[M_1] + [M_2] = 2.46$ mole/l
- (b) $[M_1] + [M_2] = 1.55$ mole/l
- (c) $[M_1] + [M_2] = 0.982$ mole/l
- (d) $[M_1] + [M_2] = 0.490$ mole/l
- (e) $[M_1] + [M_2] = 0.155$ mole/l

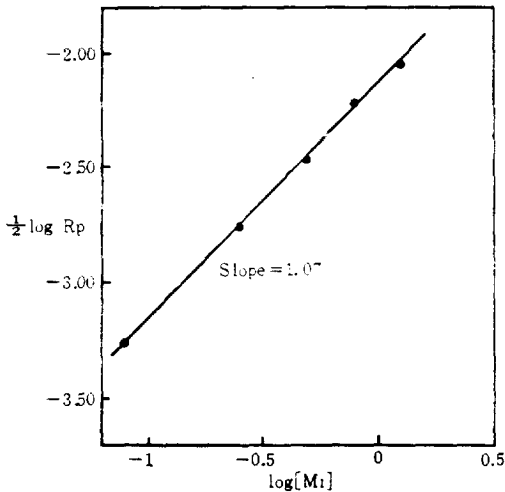


Figure 2. Dependence of copolymerization rate on individual monomer concentration. Reaction conditions are the same as presented in Figure 1.

point will be further discussed later (Figure 7).

2. General Kinetics of Copolymerization

The overall kinetic features of copolymerization were examined by measurement of the rates of copolymerization for an equimolar feed of p-isopropyl- α -methylstyrene and maleic an-

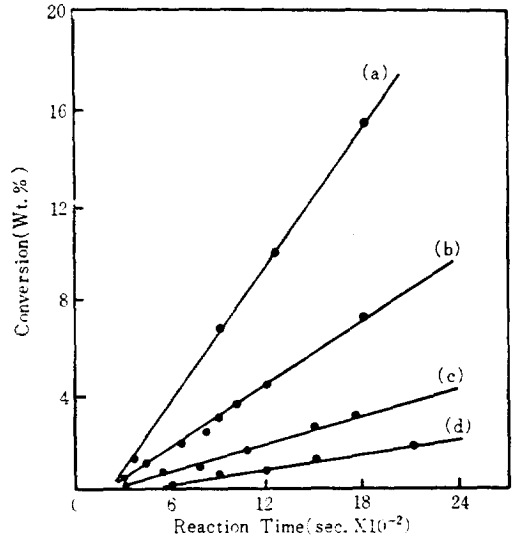


Figure 3. Copolymerization for an equimolar feed (total monomer concentration of 1.55 mole/l) of maleic anhydride and p-isopropyl- α -methylstyrene in chloroform at 60°C and various benzoyl peroxide concentrations.

- (a) $[I] = 7.76 \times 10^{-3}$ mole/l
- (b) $[I] = 2.48 \times 10^{-3}$ mole/l
- (c) $[I] = 7.76 \times 10^{-4}$ mole/l
- (d) $[I] = 2.48 \times 10^{-4}$ mole/l

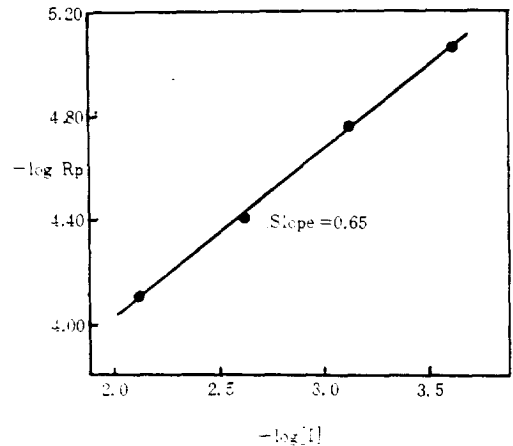


Figure 4. Dependence of copolymerization rate on initiator (benzoyl peroxide) concentration. Reaction conditions are the same as shown in Figure 3.

Table IV. Copolymerization of Maleic Anhydride and p-Isopropyl- α -Methylstyrene in Chloroform at Various Initiator Concentrations ($[I]$)*

Exp. No.	$[I]$ (mole/l)	R_p (mole/l. sec.)	R_p (wt. %/sec.)
1	7.76×10^{-3}	77.0×10^{-6}	95.5×10^{-4}
2	2.48×10^{-3}	38.6×10^{-6}	44.5×10^{-4}
3	0.776×10^{-3}	17.1×10^{-6}	21.3×10^{-4}
4	0.248×10^{-3}	8.75×10^{-6}	10.0×10^{-4}

* Copolymerized at an equimolar feed of the two monomers with overall monomer concentration of 1.55 mole/l. Polymerization temperature was 60°C.

Table V. Dependence of Copolymerization Rate on Temperature*

Exp. No.	Temp. (°C)	R_p (wt. %/sec.)	R_p (mole/l. sec.)
1	60	44.5×10^{-4}	38.6×10^{-6}
2	55	36.4×10^{-4}	28.1×10^{-6}
3	50	28.7×10^{-4}	22.2×10^{-6}
4	45	23.0×10^{-4}	17.8×10^{-6}

* Copolymerized at the overall monomer concentration of 1.55mol/l and initiator concentration of 2.48×10^{-3} mole/l.

Table VI. Rates of Copolymerization of Maleic Anhydride (M_1) and p-Isopropyl- α -Methylstyrene (M_2) in Chloroform at 60°C*

Exp. No.	$[M_1]/[M_2]$	R_p (mole/l. sec.)	R_p (wt. %/sec.)
1	0.333	17.3×10^{-6}	1.74×10^{-4}
2	1.00	38.6×10^{-6}	4.45×10^{-4}
3	3.00	30.8×10^{-6}	4.31×10^{-4}

* Overall monomer and initiator concentrations were 1.55mole/l and 2.48×10^{-3} mole/l, respectively.

hydride. Copolymerizations were conducted in chloroform at 60°C and at various overall monomer feed and initiator concentrations. The results are presented in Figure 1 to 4, and in Table III and IV.

Copolymerization rates at benzoyl peroxide concentration of 2.48×10^{-3} mole/l and overall monomer concentrations between 2.46 and 1.55×10^{-1} mole/l (Figure 1) showed an order with respect to each monomer concentration of 1.07 (Figure 2). Dodgson and Ebdon¹⁰ reported a value of 1.05 for the copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C. Rate of copolymerization at an

overall monomer concentration of 1.55mole/l and the concentration of benzoyl peroxide between 7.76×10^{-3} and 2.48×10^{-4} mole/l (Figure 3 and 4) gave an order of 0.65 with respect to the initiator.

A value of 0.62 was reported by Yoneho et al.¹⁴ for the γ -ray induced copolymerization of α -methylstyrene and maleic anhydride in chloroform solvent. Therefore, the overall copolymerization rate (R_p) for this monomer pair can be expressed as follows:

$$R_p \propto [M_1]^{1.07} [I]^{0.65}$$

Induction periods observed in the present experiments were taken into account in the calcula-

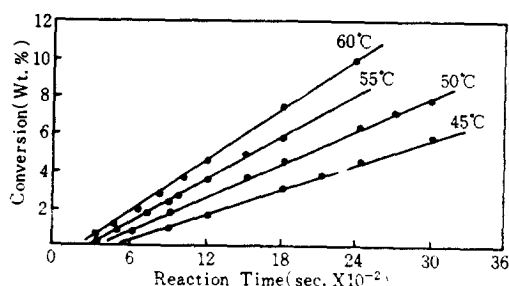


Figure 5. Copolymerization for an equimolar feed (total monomer concentration of 1.55mole/l) of maleic anhydride and p-isopropyl- α -methylstyrene in chloroform at various temperatures. Initiator concentration was kept constant at 2.48×10^{-3} mole/l.

tion of copolymerization rates from the experimental data.

The overall activation energy for the copolymerization of the monomer pair was obtained from the temperature-dependence of copolymerization rate at an equimolar feed. Initiator and total monomer concentrations were kept constant at 1.55 and 2.48×10^{-3} mole/l, respectively. Copolymerizations were conducted in chloroform at 45, 50, 55, and 60°C. The results are shown in Figure 5 and 6, and Table V. Thus obtained overall activation energy of this copolymerization is 7.6 kcal/mole, which is close to the value of 6.7kcal/mole reported by Yoneho et al.¹⁴ for the γ -ray induced copolymerization of α -methylstyrene and maleic anhydride in chloroform.

3. Dependence of Copolymerization Rates on the Initial Monomer Feed Composition

Copolymerization rates were measured at an overall monomer concentration of 1.55mole/l and the initiator concentration of 2.48×10^{-3} mole/l at the three different feed compositions of 1:1, 3:1, and 1:3. The results show (Table VI) copolymerization at the 3:1 feed

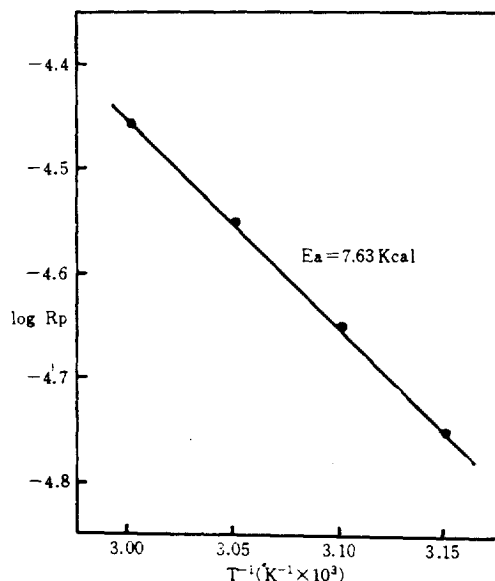


Figure 6. Activation energy for the free-radical copolymerization of maleic anhydride and p-isopropyl- α -methylstyrene in chloroform.

is greatly different from that at 1:3 feed. When the copolymerizations at a wide range of monomer feed ratios were stopped after 30 minutes, the results showing the dependence of the rates of copolymerization on monomer feed composition is much distorted in shape (Figure 7). Nonetheless it is clear that copolymerization proceeds fastest at the 1:1 monomer feed. One can also see from this figure that the homopolymerization of p-isopropyl- α -methylstyrene proceeds very slowly compared with copolymerizations. Such observations have been reported for many other systems where participation of donor-acceptor complexes between the monomers was claimed to occur in propagation reactions^{17, 20, 21, 23}.

4. Participation of Monomer Complexes in Propagation Reactions

The facts that (1) the present monomer pair form 1:1 alternating copolymers regardless monomer feed composition, (2) copolymerizat-

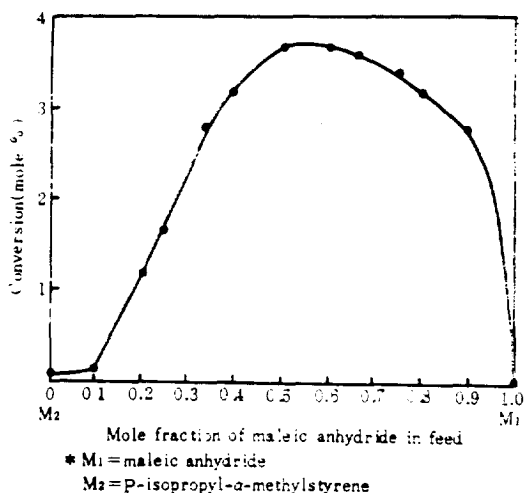


Figure 7. Dependence of rate of copolymerization of maleic anhydride and p-isopropyl- α -methylstyrene on the monomer feed composition in chloroform at 60°C. Overall monomer and initiator concentrations were 1.55 and 2.48×10^{-3} mole/l, respectively. Copolymerizations were stopped at 30 minutes of reaction.

ion rate is greatest at equimolar monomer feed, and (3) the two monomers form charge transfer complex which could be qualitatively verified by uv spectroscopy and by visual observation (They formed yellowish solution when mixed in chloroform) suggest the participation of π -complexes of the two monomers in propagation reaction. Each compound formed colorless solution when dissolved separately in chloroform.

There are, however, certain kinetic features unexplainable by the complex mechanism. The general kinetic studies of this system, as discussed above, showed that the copolymerization rate is almost directly proportional to concentration of the each monomer at equimolar feeds.

Moreover, it is difficult to justify why the profile of copolymerization rate vs. monomer feed ratio is not symmetrical as shown in

Figure 7. If complexes are the sole propagating species, copolymerization rate, for example, at $[M_1] : [M_2] = 3 : 1$ should be same as that at $[M_1] : [M_2] = 1 : 3$ because the concentration of complexes would be same or almost so at the two feed compositions (Table VI). Dodgson and Ebdon¹⁰ concluded in their study of the copolymerization of styrene and maleic anhydride that the penultimate effect mechanism is to be preferred to complex mechanism.

5. General Characteristics of Copolymers

Equimolar copolymers prepared in chloroform at 60°C (overall monomer concentration of 1.55 mole/l; benzoyl peroxide concentration of 2.48×10^{-3} mole/l or 0.3 wt. %) had intrinsic viscosity of 0.710 (measured at 25°C for chloroform solution) and number average molecular weight of 29,000 (measured at 45°C for chloroform solution). The copolymers are soluble in wide variety of solvents such as acetone, DMF, THF, and chloroform. The homopolymer of p-isopropyl- α -methylstyrene prepared for the purpose of comparison in bulk at 70°C using 0.5 wt. % of benzoyl peroxide had intrinsic viscosity of 0.119 (measured 25°C in chloroform) and number average molecular weight of only 4000. Thermograms (Figure 8) indicate that the copolymers undergo major thermal break-down around 300°C. Copolymer samples left substantial amount of char when heated up to 500°C indicating random thermal decomposition of copolymers. Poly (p-isopropyl- α -methylstyrene) and poly (maleic anhydride) practically left no chars. Poly (maleic anhydride) used in this study was prepared at 70°C in N, N-dimethylformamide according to the reported method^{28,29}. The intrinsic viscosity and number average molecular weight of the polymer were 0.072 (measured at 25°C in DMF) and 700 (measured at 85°C in DMF), respectively.

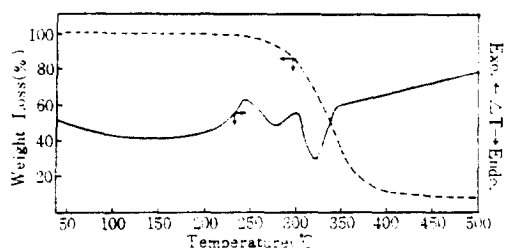


Figure 8. Thermograms of 1 : 1 copolymer of maleic anhydride and p-isopropyl- α -methylstyrene (DTA in air; heating rate 8°C/min, TGA in air; heating rate 20°C/min).

Conclusions

Following conclusions on the copolymerization of p-isopropyl- α -methylstyrene and maleic anhydride are drawn in light of the results of present investigation:

- (1) These two monomers form 1 : 1 copolymers regardless of monomer feed composition.
- (2) General kinetic feature for equimolar feeds can be written as following:

$$R_p \propto [M_1]^{1.07} [I]^{0.65}$$

- (3) Activation energy for the copolymerization at an equimolar feed is 7.6kcal/mole.
- (4) Copolymerization rate is greatest at the equimolar feed composition. It does not, however, show symmetrical dependence on the monomer feed composition.
- (5) The mechanism in which only intermolecular charge-transfer complexes participate in propagation reactions needs further proof.

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