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### Preparations of Propylene and Ethylene Ionomers with Solvay-Type $TiCl_3$ Catalyst

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## PREPARATIONS OF PROPYLENE AND ETHYLENE IONOMERS WITH SOLVAY-TYPE $\text{TiCl}_3$ CATALYST

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**Key Words:** Polymerization, Catalyst, Ionomer, Crosslinking

### ABSTRACT

Terpolymerizations of propylene/1-hexene/ethylchloroaluminum-10-undecenoate (ECAU) and ethylene/1-hexene/ECAU systems were carried out with Solvay-type  $\text{TiCl}_3$  and diethylaluminum chloride to prepare the propylene ionomer and ethylene ionomer, respectively. By adding 1-hexene, the ECAU contents of polymer could be enhanced. The acid contents of the propylene terpolymer was higher than that of the ethylene one. This indicated polar monomer (ECAU) was incorporated more easily into propylene-based polymer chain. With increasing ECAU in both systems, the rate of terpolymerization decreased while the induction periods of polym-

erization increased. The propylene terpolymer salts exhibited higher  $T_m$  and  $T_c$  than the acid form of terpolymers due to the ionic cross-linking of terpolymer salts.

## INTRODUCTION

Recently, the research on the structures and properties of polymeric materials containing salt groups has been carried out [1-5]. These polymeric materials which contain salt groups are called "ionomer", and this is a polymer with a hydrocarbon backbone and some pendant acid groups which are neutralized partially or completely to form salts [2]. The important thing in understanding the structure of ionomer is the concept of ionic crosslinking. These are understood by neutralizing carboxylated elastomer into cation-like zinc ion when the carboxylated elastomer needs to have properties of vulcanized rubber. This ionic crosslinking usually represents the connection of  $Zn^{2+}$  ion and two carboxylate ions. This ionomer, as a copolymer having acid groups on a hydrocarbon backbone, is adequate to improve adhesion and dyeability .

Until the mid-1970s, the synthesis of functional  $\alpha$ -olefin was, for the most part, limited to ethylene and conjugated carboxylic monomers polymerized by free-radical processes. Typically, carboxyl-containing ethylene ionomers were obtained by copolymerization of ethylene with acrylic acid or methacrylic acid comonomer by free-radical process [1]. Recent advances in the ethylene ionomers have broadened the array of new functionalized polymer structures. However, despite the considerable industrial and academic research efforts which have been expended on ionomers, there is still a lack of general agreement about their structure.

There have been a number of reports on the preparation of propylene ionomers by copolymerization. These propylene ionomers were synthesized by copolymerization with aluminum salts of  $\omega$ -alkenoic acids, such as undecenoic acid, and these aluminum salts were usually prepared by reaction of the acid with diethylaluminum chloride [6-13]. Landol and Breslow reported a detailed study of the synthesis and properties of the propylene ionomers prepared in this way [9]. However, the incorporation of undecenoate complex into propylene copolymer was not high in the absence of hydrogen.

In this paper, we have carried out a study of the synthesis and properties of the propylene and ethylene ionomers by terpolymerization of propylene or ethylene/undecenoate/1-hexene system, our goal being the increase of incorporation of undecenoate complex into the polymer and the observation of effects of 1-hexene as comonomer.

## EXPERIMENTAL

### Materials

Propylene and ethylene of polymerization grade (99.5% purity) were supplied by the Korea Petrochemical Industrial Co. and dried by passing through two columns of preactivated molecular sieve 4A. Neat diethylaluminum chloride (DEAC) was supplied by Tosoh Akzo Corp., Japan and used without further purification. *n*-Hexane (Tokyo Kasei Co., Japan) was dried over preactivated molecular sieve 4A for at least 24 hours and contained less than 5 ppm of water. 1-Hexene (Fluka Chemie AG Co., Switzerland) and 10-undecenoic acid (Aldrich Chemical Co., U.S.A) were purified by the usual methods. Solvay-type titanium trichloride (Tosoh Akzo Corp., Japan) was used as received.

### Preparation of Ethylchloroaluminum-10-undecenoate

Ethylchloroaluminum-10-undecenoate (ECAU) was prepared by addition of 77.4 g (0.42 mol) of 10-undecenoic acid in 100 ml of *n*-hexane to 523 ml of 15 wt%-DEAC (0.45 mol) in *n*-hexane with stirring and cooling [6, 9-13]. After the addition was complete, the reaction mixture was heated at 55°C for 1 hour to complete the formation of the complex with a deep burnt-orange color. The reverse order for addition essentially gave the same result, and this was more convenient for a large scale preparation.

### Terpolymerization Conditions and Procedure

The semibatch polymerization for the synthesis of  $\alpha$ -olefin ionomers was carried out in a 2L stainless-steel autoclave (Taiatsu Glass Co., Japan) equipped with mass flow meter and regulator, using *n*-hexane as diluent. The whole system was repeatedly evacuated and filled with dry nitrogen several times. The 400 ml of *n*-hexane was charged under nitrogen atmosphere, and then 14 ml of 15 wt%-DEAC (12 mmol), 1-hexene (0-50 ml) and ECAU (0-28 g) were charged in sequence. The dilute DEAC solution in *n*-hexane was first added to *n*-hexane in order to scavenge any oxygen or moisture left in the diluent. After evacuation, the reactor temperature increased to 50°C with stirring, and propylene or ethylene was fed to reactor through mass flow meter with regulator. When the flow quantity on the flow meter became zero, the Solvay-type  $\text{TiCl}_3$  catalyst ( $[\text{Al}]/[\text{Ti}] = 4.3$ ) was added and then the polymerization was started, and at the same time, the polymerization rate was recorded on a computer. The terpolymerization temperature was controlled at 50°C, while propylene and ethylene was fed continuously to keep the pressure constant at 0.3 and 0.5 Kg/cm<sup>2</sup>G, respectively. After 2 hours, the propylene or ethylene feed was stopped and the pressure of the reactor was vented to

atmospheric pressure. Then, the reactor contents were poured into a mixture of water and hydrochloric acid and stirred at 40°C for at least 1 hour. The obtained polymer was filtered, washed with water and ethanol in sequence, and dried in vacuum at 40°C for 24 hours.

### Preparation of Zn Salts [2, 9]

To convert the obtained polymer into zinc salt, it was treated with an excess of 15 wt%-ZnCl<sub>2</sub> solution in water at 55°C for 24 hours. After 24 hours, the reaction mixture was filtered, washed with water, and dried in vacuum at 40°C for 24 hours.

### Analytical Procedures

Infrared spectra of polymer were recorded on Hitachi Model 270-30 spectrophotometer. The crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) for polymer samples were determined on a differential scanning calorimeter, Du Pont Instruments 90, at a heating rate of 10°C/min. <sup>13</sup>C-NMR spectra of selected polymers were recorded on a Varian Unity-Inova-300 spectrometer for the analysis of acid contents in polymer samples. The spectra were obtained at 130°C in 1,2,4-trichlorobenzene/benzene-d<sub>6</sub> (8/2) solution. The differences between acids contents calculated from the titration method [9] and those by <sup>13</sup>C-NMR spectra were less than 6%. Therefore, acid contents were determined by titrating 0.5 g of terpolymer in hot chlorobenzene with standardized alcoholic KOH solution using thymolphthalein as an indicator.

## RESULTS AND DISCUSSION

### Preparation of Ethylchloroaluminum-10-undecenoate (ECAU)

10-undecenoic acid (UDA) was complexed with DEAC by a modification of the method described by Clark [6] and Landol [9]. ECAU could be prepared by two methods: one is adding the DEAC solution to the solution of UDA, the other is reverse addition. In case of the former, a hexane solution of DEAC was added to the acid with stirring under nitrogen. After 0.5 mol of DEAC had been added, a highly viscous solution was formed, which thinned out on the addition of the remaining DEAC. The viscous material is presumably chloroaluminum bisundecenoate, as a dimer or higher associate, which then disproportionated with DEAC added to form the final product, ethylchloroaluminum 10-undecenoate as described below:

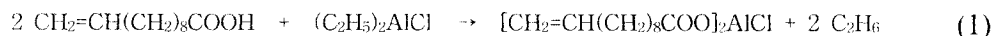


TABLE 1. Terpolymerization of Propylene with 1-Hexene and ECAU at the Constant Amount of 1-Hexene

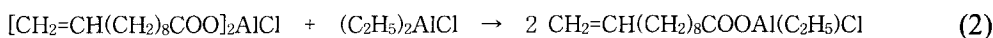
Run No.	ECAU (mmol/L)	1-Hexene (mmol/L)	Activity <sup>a)</sup>	Acid wt(%)	T <sub>c</sub> /T <sub>m</sub> (°C) Acid <sup>b)</sup>	T <sub>c</sub> /T <sub>m</sub> (°C) Salt <sup>c)</sup>
P0	0	0	152.7	0	117/163	
P1	0	500	175.8	0	84/150	
P2	63.7	500	66.7	5.1	98/150	
P3	127.4	500	62.0	6.5	99/151	
P4	254.7	500	59.1	9.4	100/150	106/156

Polymerization conditions : TiCl<sub>3</sub>, 12.6 mmol/L; mol ratio of [Al]/[Ti] = 4.3; 50 °C; 2 h

<sup>a)</sup> Catalytic activity, g-polymer/g-Ti · atm · h

<sup>b)</sup> Acid form of polymer

<sup>c)</sup> Zn salt form of polymer

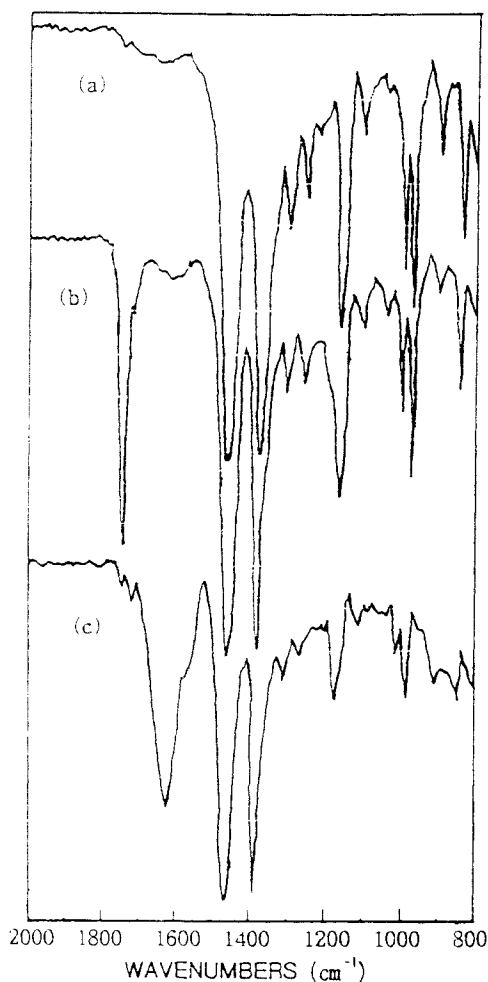


But in the latter case, i.e., adding a solution of UDA to DEAC solution, the viscosity problem could be avoided and the product obtained by one-step mechanism with little difference in activity. Therefore, in our work the latter method was chosen.

### Terpolymerization of Propylene/1-Hexene/ECAU

Preliminary tests on the terpolymerization of propylene or ethylene with 1-hexene and ECAU were carried out in autoclaves. Little difference was observed between polymerizations in toluene or in aliphatic hydrocarbons (*n*-hexane or *n*-heptane). Therefore, *n*-hexane was selected as a diluent.

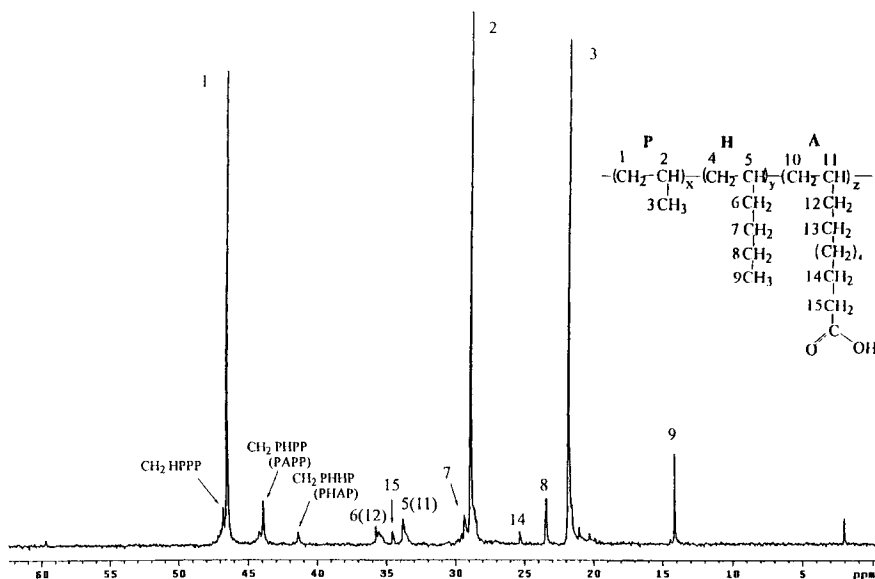
The results of polymerization behavior and characterization of polymers produced for propylene/1-hexene/ECAU system are given in Table 1. As well-known in Ziegler-Natta catalysts [14], copolymerization (P1) of propylene with 1-hexene shows an increase in activity compared with that of propylene polymerization (P0). Under the constant quantity of 1-hexene (P1-P4), activity was greatly decreased with increasing ECAU. This seems to be caused by the fact that induction periods for the interaction between ECAU and active sites of catalyst is required followed by deactivation of active sites by ECAU, and then polymerization occurs from the coordination between  $\alpha$ -olefins and active sites of catalyst. Acid contents increased with the increase of ECAU, tending to decrease in activity. Although there is no change in melting temperature ( $T_m$ ), the crystallization temperature ( $T_c$ ) of



**Figure 1.** Comparison of infrared spectra of polyolefin copolymer (P1) and terpolymer (P3): (a) poly(propylene-*co*-hexene); (b) poly(propylene-*co*-hexene-*co*-10-undecenoic acid), (c) poly(propylene-*co*-hexene-*co*-10-undecenoic acid zinc salt), Ionomer.

terpolymers (P2, P3, P4) is about 15°C higher than that of copolymer (P1). This seems to be slightly due to the nucleating effect of heterogeneous phase [15] in acid groups of terpolymer.

In order to clarify whether or not ECAU is terpolymerized with propylene and 1-hexene, the polymers obtained were molded into a transparent thin film. The infrared spectra of the film is shown in Figure 1. Clear differences can be found between infrared spectrum of the propylene/1-hexene copolymer (a) and that of the



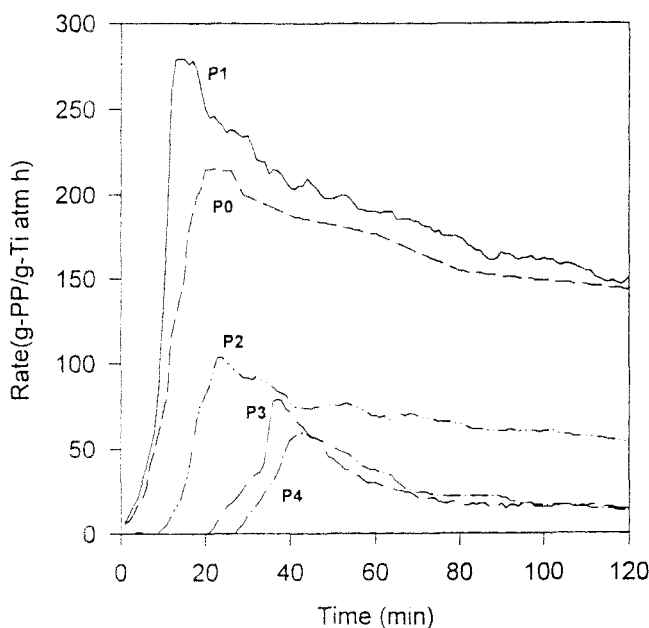
**Figure 2.**  $^{13}\text{C}$  NMR spectrum of poly(propylene- $\omega$ -hexene-*co*-10-undecenoic acid). P, H, and A are abbreviations for propylene, 1-hexene, and acid units in chain sequences, respectively.

acid form (b) and salt form (c) of terpolymer. The most significant difference is the presence of an absorption band at around  $1750\text{ cm}^{-1}$ , which is assigned to the carbonyl group, in the spectrum of the acid terpolymer (b). This is evidence for the terpolymerization of propylene with 1-hexene and 10-undecenoic acid. Infrared analysis also indicates almost total conversion to the polycarboxylate salt (Ionomer), as demonstrated by a shift in the carbonyl absorption from  $1750\text{ cm}^{-1}$  (C=O stretch, carboxylic acid) to  $1620\text{ cm}^{-1}$  (C=O stretch, carboxylate salt) [9, 10, 16].

$^{13}\text{C}$ -NMR spectrum of the acid terpolymer (P3), which is poly(propylene- $\omega$ -hexene-*co*-10-undecenoic acid), is illustrated in Figure 2. In addition to the resonances of main chain carbons of propylene units (21.8, 28.9, 46.5 ppm) [17], weak resonances are observed at around 14.1, 23.4, 25.3 and 34.5 ppm, which could be assigned to 1-hexene [17] and undecenoic acid [16] units, respectively. All peaks of the  $^{13}\text{C}$ -NMR spectrum were also assigned, referred to the literature [16-20]. The result indicates that terpolymerization of 10-undecenoic acid with propylene and hexene occurs in the present system.

Terpolymerization rate of propylene with the change of undecenoate complex (ECAU) under the constant quantity of 1-hexene is shown in Figure 3.





**Figure 3.** Comparison of polymerization rates on the variation of undecenoate complex (ECAU) under the constant 1-hexene (see Table 1).

The copolymerization rate (P1) is greater than homopolymerization rate (P0) due to the effect of 1-hexene as comonomer [21a]. The rate of terpolymerization decreased and induction periods for polymerization increased with the increase of EAU. This indicates that the interaction between ECAU and transition metal part of catalyst is greatly stronger than that between the  $\pi$ -electron of  $\alpha$ -olefin and transition metal part, followed by the deactivation of the active sites by polar monomer [13, 22]. After the induction periods, the complexes between  $\alpha$ -olefins and active sites of catalyst are formed and then terpolymerization seems to have occurred.

As shown in Table 2, copolymerization of propylene with ECAU (P5) shows an abrupt decrease in activity compared with that of propylene/1-hexene system. However, under the constant quantity of ECAU, terpolymerization of propylene with the increase of 1-hexene initially showed an increase in activity by up to two times of magnitude and then slightly decreased with excess of 1-hexene. But acid contents increased with the increase of 1-hexene. This indicates that 1-hexene, showing the comonomer effect [23], play a important part in increasing incorporation of ECAU into polymers. The  $T_m$  and  $T_c$  of terpolymers (P6-P10) are lower than that of copolymer of propylene/ECAU system (P5).

TABLE 2. Terpolymerization of Propylene with 1-Hexene and ECAU at the Constant Amount of ECAU

Run No.	ECAU (mmol/L)	1-Hexene (mmol/L)	Activity <sup>a)</sup>	Acid wt(%)	Tc/Tm(°C) Acid <sup>b)</sup>	Tc/Tm(°C) Salt <sup>c)</sup>
P5	127.4	0	20.4	3.1	117/161	
P6	127.4	200	46.8	3.0	104/150	
P7	127.4	360	55.5	5.4	98/149	
P8	127.4	500	62.0	6.5	99/151	
P9	127.4	700	55.4	7.2	92/148	
P10	127.4	1000	54.8	11.1	97/150	104/156

Polymerization conditions : TiCl<sub>3</sub>, 12.6 mmol/L; mol ratio of [Al]/[Ti] = 4.3; 50 °C; 2 h

<sup>a)</sup> Catalytic activity, g-polymer/g-Ti · atm · h

<sup>b)</sup> Acid form of polymer

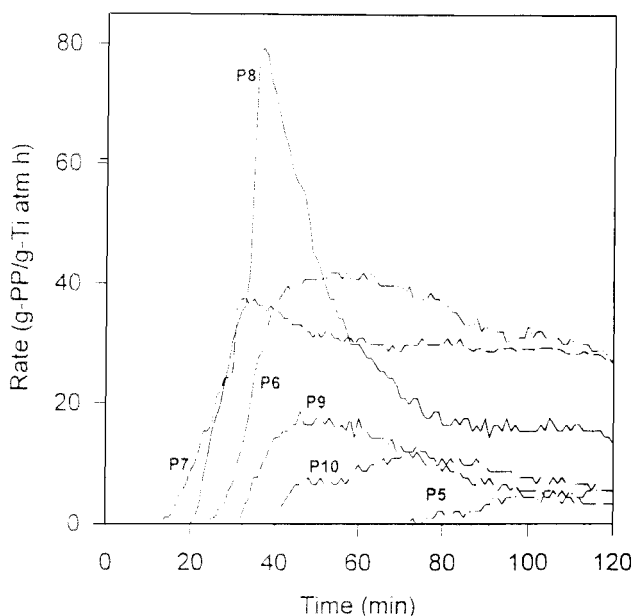
<sup>c)</sup> Zn salt form of polymer

The rate profile of terpolymerization of propylene with the change of 1-hexene under the constant quantity of ECAU is shown in Figure 4. In the absence of 1-hexene (P5), the polymerization rate did not increase until about 75 minutes and the magnitude of the rate is also smaller. However, in the presence of 1-hexene, the polymerization rate initially increased with the increase of 1-hexene, and then decreased with an excess of 1-hexene. On the other hand, induction periods for polymerization initially decreased with the increase of 1-hexene and then increased due to the increased concentration of 1-hexene.

### Terpolymerization of Ethylene/1-Hexene/ECAU

The results of polymerization behaviors and characterization of polymers obtained in terpolymerization of ethylene/1-hexene/ECAU system are given in Table 3. Copolymerization (E1) of ethylene with 1-hexene also shows an increase in activity compared with that of ethylene polymerization (E0). Under the constant quantity of 1-hexene (E1-E4), a decrease in activity and an increase in acid contents with the increase of ECAU was also shown apparently, as in terpolymerization of propylene/1-hexene/ECAU system.

The terpolymerization rate of ethylene with the change of undecenoate complex (ECAU) under the constant quantity of 1-hexene is shown in Figure 5. In the case of copolymerization of ethylene with 1-hexene, the rate (E1) is also greater than the homopolymerization rate (E0) due to the effect of 1-hexene as comonomer



**Figure 4.** Comparison of polymerization rates on the variation of 1-hexene under the constant ECAU (see Table 2).

**TABLE 3.** Terpolymerization of Ethylene with 1-Hexene and ECAU at the Constant Amount of 1-Hexene

Run No.	ECAU (mmol/L)	1-Hexene (mmol/L)	Activity <sup>a)</sup>	Acid wt(%)	T <sub>c</sub> /T <sub>m</sub> (°C) Acid <sup>b)</sup>	T <sub>c</sub> /T <sub>m</sub> (°C) Salt <sup>c)</sup>
E0	0	0	109.8	0	116/136	
E1	0	200	118.5	0	113/130	
E2	63.7	200	101.6	0.9	112/127	
E3	127.4	200	76.6	1.6	109/127	
E4	254.7	200	58.9	2.0	110/127	112/130

Polymerization conditions: TiCl<sub>3</sub>, 12.6 mmol/L; mol ratio of [Al]/[Ti] = 4.3; 50 °C; 2 h

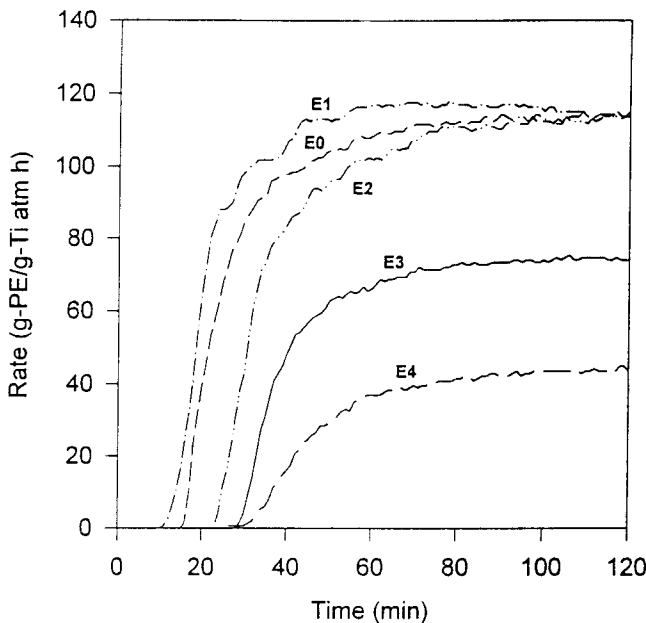
<sup>a)</sup> Catalytic activity, g-polymer/g-Ti · atm · h

<sup>b)</sup> Acid form of polymer

<sup>c)</sup> Zn salt form of polymer

[21b]. The rate of terpolymerization decreased with the increase of ECAU and induction periods for polymerization increased with the increase of ECAU, as in terpolymerization of propylene/1-hexene/ECAU system (Figure 3).

On the other hand, as shown in Table 4, under the constant quantity of ECAU, activity in polymerization without 1-hexene was very low, but terpolym-



**Figure 5.** Comparison of polymerization rates on the variation of undecenoate complex (ECAU) under the constant 1-hexene (see Table 3).

**TABLE 4.** Terpolymerization of Ethylene with 1-Hexene and ECAU at the Constant Amount of ECAU

Run No.	ECAU (mmol/L)	1-Hexene (mmol/L)	Activity <sup>a)</sup>	Acid wt(%)	T <sub>c</sub> /T <sub>m</sub> (°C) Acid <sup>b)</sup>	T <sub>c</sub> /T <sub>m</sub> (°C) Salt <sup>c)</sup>
E5	127.4	0	16.9	0.4	116/135	
E6	127.4	100	65.3	0.8	112/129	
E7	127.4	200	76.6	1.6	109/127	
E8	127.4	500	86.3	1.5	110/127	
E9	127.4	1000	105.6	1.6	110/127	112/130

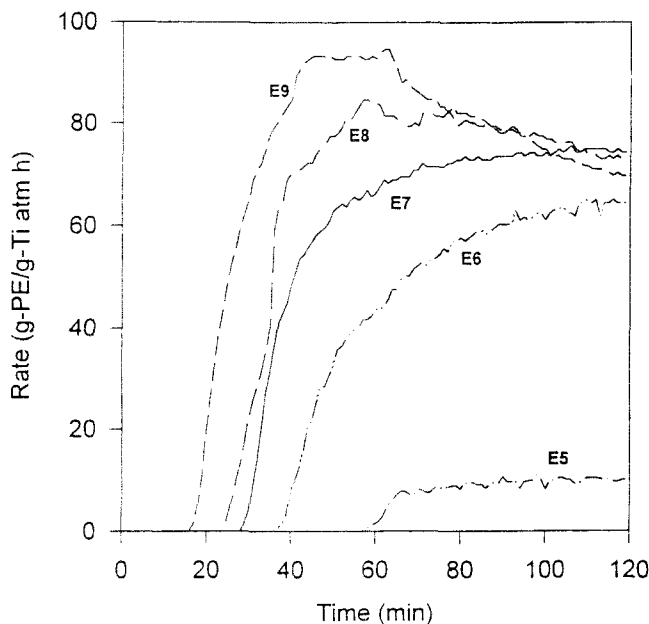
Polymerization conditions: TiCl<sub>3</sub>, 12.6 mmol/L; mol ratio of [Al]/[Ti] = 4.3; 50 °C; 2 h

<sup>a)</sup> Catalytic activity, g-polymer/g-Ti · atm · h

<sup>b)</sup> Acid form of polymer

<sup>c)</sup> Zn salt form of polymer

erization activity increased with the increase of 1-hexene, showing the comonomer effect [23]. Acid contents initially increased with the increase of 1-hexene and then remained constant regardless of quantity of 1-hexene (E7-E9). An increase in the acid contents and a decrease in T<sub>m</sub> and T<sub>c</sub> was smaller than that of propylene/1-hexene/ECAU system. This indicates it is more difficult for polar monomer



**Figure 6.** Comparison of polymerization rates on the variation of 1-hexene under the constant ECAU (see Table 4).

(ECAU) to be incorporated into ethylene-based polymer chain than propylene-based one.

The rate profile of terpolymerization of ethylene with the change of 1-hexene under the constant quantity of ECAU is shown in Figure 6. In the absence of 1-hexene (E5), the polymerization rate was smallest, whereas induction period was longest, as in copolymerization of propylene/ECAU system (P5 shown in Figure 4). With the increase of 1-hexene, the rate of terpolymerization increased, whereas induction periods for polymerization decreased.

From these results (Figure 3-6), it was confirmed that the polymerization rate decreased while induction periods increased, with the increase of ECAU in terpolymerization of both propylene/1-hexene/ECAU and ethylene/1-hexene/ECAU system. On the other hand, the polymerization rate increased while induction periods decreased, with the increase of 1-hexene under the constant quantity of ECAU for terpolymerization of ethylene/1-hexene/ECAU system. However, for terpolymerization of propylene/1-hexene/ECAU system, the polymerization rate initially increased with 1-hexene and then decreased with excess of 1-hexene under the constant quantity of ECAU, but the induction periods showed the opposite trend compared with the polymerization rate.

The results of the DSC analysis for the neutralized terpolymer salts are given in Table 1-4. Some terpolymer salts, neutralized by zinc chloride solution at 55°C for 24 hours, exhibit about 6°C and 7-10°C higher in both  $T_m$  and  $T_c$ , respectively than the acid form for the propylene terpolymers (P4, P10). From this result, it is confirmed that terpolymer salts are vulcanized by an ionic crosslinking, i.e., the  $Zn^{+2}$  ion bridging two carboxylate ions. However,  $T_m$  and  $T_c$  of salt forms for the ethylene terpolymers were increased only by about 3°C. This was caused by less contents of acid group able to do ionic crosslinking in comparison with the propylene terpolymers.

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