

## 양이온 중합을 이용한 폴리알파올레핀의 미세구조 조절에 관한 연구

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### A Study on the Control of Microstructures of Polyalphaolefins via Cationic Polymerization

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**초록:** 폴리알파올레핀(PAO)은 유동점, 점도지수, 열/산화 안정성이 광유 기반의 윤활유보다 우수한 합성 윤활유이다. 본 연구에서는 1-펜텐, 1-헥센, 1-옥텐, 및 1-도데센을 단량체로 사용하고 세가지 종류의 알루미늄계 루이스 산 촉매로 양이온 중합을 수행하여 다양한 PAO를 합성하였다. PAO 중합 성능과 제조된 PAO의 분자량, 동점도, 유동점과 점도지수를 다양한 중합 조건에서 조절할 수 있었다. 알킬 알루미늄 할라이드계 촉매가 기존의  $AlCl_3$ 계 촉매에 비하여 촉매 성능이 우수하였다. PAO의 미세구조를 비행-시간형 질량분석기(TOF-MS) 해석을 통하여 PAO의 미세구조와 윤활유로의 성능(점도지수, 유동점)과의 상관관계를 규명하였다. 특히, PAO의 점도지수는 알파 올레핀의 탄소수 증가에 따라 상승하여, PAO의 분지길이가 점도지수와 밀접한 상관관계가 있음을 확인하였다.

**Abstract:** Polyalphaolefin (PAO) is a synthetic lubricant that is superior to mineral-based lubricants in the terms of physical and chemical characteristics such as low pour point, high viscosity index (VI), and thermal and oxidation stability. Several kinds of PAOs have been synthesized by using 1-pentene, 1-hexene, 1-octene, or 1-dodecene as monomer with three kinds of aluminum-based Lewis acid catalysts via cationic polymerization. The control of the catalytic performance and physical properties of PAO such like molecular weight, kinematic viscosity, pour point, and viscosity index was done by changing polymerization parameters. The alkyl aluminum halide-based catalysts show better catalytic activity than that of the conventional  $AlCl_3$  catalyst. The microstructure of PAO was investigated by means of TOF-MS (time of flight-mass spectroscopy) analysis in order to elucidate the correlation between the performances of the lubricant (VI, pour point) and the molecular structure of PAO. The VI of PAO increases with increases in the carbon number of  $\alpha$ -olefin. In other words, the performances of PAO as a lubricant strongly depended on the branch length of PAO.

**Keywords:** polyalphaolefin, cationic polymerization, alkyl aluminum halide,  $AlCl_3$ , lubricant, viscosity index, pour point.

## Introduction

Polyalphaolefins (PAOs) are hydrocarbon oligomers produced via catalytic polymerization of  $\alpha$ -olefins. The typical synthetic procedure includes the following three steps: (i) catalytic oligomerization of the  $\alpha$ -olefins that have carbon num-

bers of  $C_4$ - $C_{20}$ , (ii) hydrogenation process for the creation of saturated oligomer, and (iii) distillation for separating various grades of synthetic lubricants from 2 to 100 cSt on a viscosity grade.<sup>1,2</sup> In the petroleum industry, the PAO-based synthetic lubricants have generated interest due to their superior physical and chemical properties such as thermal/oxidation stability, low pour point, high viscosity index (VI), low toxicity, and biodegradable properties as compared with those of mineral oils. For this reason, PAOs have been used in high-end lines of

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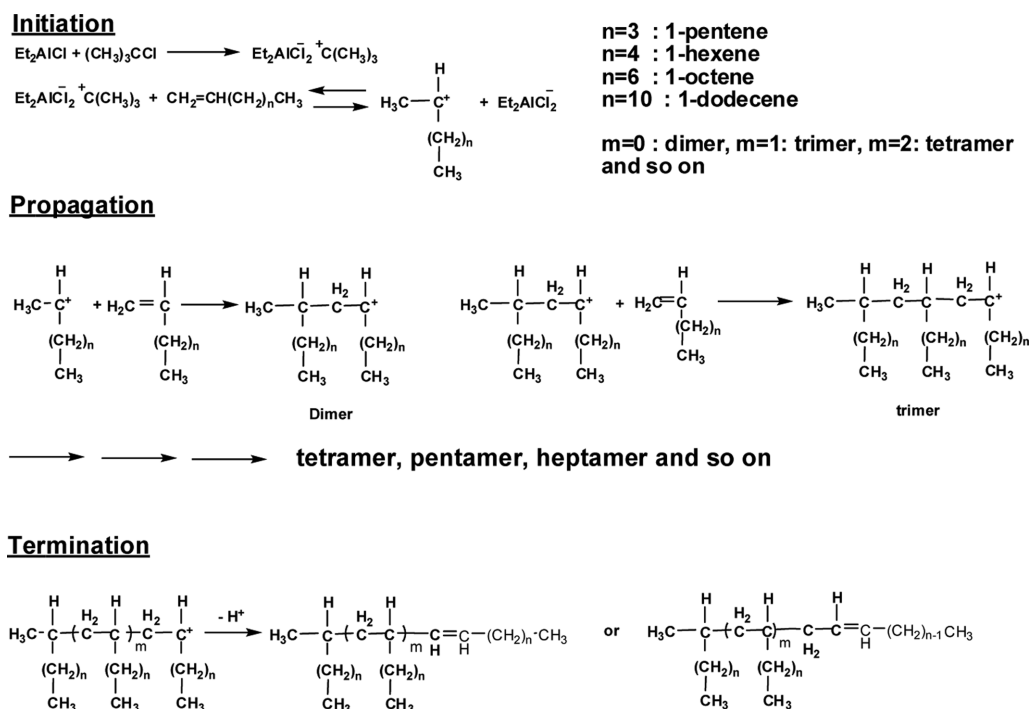
products such as engine oil, gear oil, transmission fluid, compressor/pump oil etc. Therefore related petroleum industry has made efforts to improve important properties for lubricant such as VI value and pour point.<sup>3-5</sup> The representative syntheses for PAOs have been performed *via* cationic polymerization mechanism by using Lewis acid catalysts such as  $\text{BF}_3$ <sup>6-8</sup> and aluminum compounds.<sup>9-12</sup> Considering yield, difficulty or ease in degree of polymerization, molecular weight control, and catalyst handling and removal, aluminum-based liquid catalysts are more preferred to the gas phase of conventional  $\text{BF}_3$  catalyst. A typical PAO manufacturing process involves the use of Lewis acid, in combination with a protic source such as alcohol or water, to induce the cationic oligomerization of linear  $\alpha$ -olefin. In the case of alkyl aluminum halide, the catalyst essentially needs tertiary carbon chloride as a promoter as well. The simple mechanism for cationic oligomerization using alkyl aluminum halide with *tert*-butylchloride (*t*BuCl) is described in Scheme 1.

However, the described mechanism does not fully explain the high number of isomers observed in these polymerization reactions. Chromatographic studies of hydrogenated dimer show that over 50 different isomers are generated during the reaction.<sup>13,14</sup> Moreover, NMR analyses of dimer and other higher oligomers have shown that all of the skeletal rearrangement may occur at the dimerization stage, and much ana-

lytical work has focused on the dimer fraction.<sup>15</sup> A more detailed reaction mechanism for the origin of multiple skeletal isomers in the polymerization of 1-decene has been reported by J. C. Gee *et al.*<sup>16</sup>

In general, the pour point and the VI value of PAO increase with increases in the number of carbon in  $\alpha$ -olefin.<sup>4</sup> Therefore PAOs has been synthesized mostly based on 1-decene as a monomer because  $\alpha$ -olefins with high carbon number would be preferable to obtain PAO with optimum VI value and low pour point property. 1-decene-based PAO made by oligomerization using  $\text{BF}_3$  catalyst as an alcohol promoter was reported to have a kinematic viscosity in the range of 4 to 6 cSt, at 100 °C, and a VI value in the range of 120 to 135, and a pour point of -55 °C.<sup>2</sup> However the price of 1-decene is relatively high compared with the price of  $\alpha$ -olefins with low carbon number (<10). To overcome these drawbacks, the co-oligomerization using relatively cheap  $\alpha$ -olefins have been extensively performed to obtain similar properties to those of PAO that employs 1-decene.<sup>2-4</sup> However there are no systematic studies regarding the correlation between the properties of PAO (VI and pour point) and its microstructure such as molecular weight, molecular weight distribution, side chain length and so on.

In this study, various PAOs were prepared by using four kinds of  $\alpha$ -olefins:  $\text{C}_5$  (1-pentene),  $\text{C}_6$  (1-hexene),  $\text{C}_8$  (1-octene),



**Scheme 1.** Simple mechanism for cationic polymerization of  $\alpha$ -olefins using an  $\text{Et}_2\text{AlCl}$ -*t*-BuCl catalyst.

and C<sub>12</sub> (1-dodecene) as well as three kinds of aluminum-based Lewis acid catalysts (AlCl<sub>3</sub>-H<sub>2</sub>O, Et<sub>2</sub>AlCl-*t*BuCl, and Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-*t*BuCl). In addition, polymerization parameters such as monomer concentration, type of catalyst, and polymerization temperature have also been performed to investigate the cationic polymerization behaviors of various  $\alpha$ -olefins. The typical microstructures of the PAOs have been analyzed by means of gel permeation chromatography (GPC) and time of flight mass spectrometer (TOF-MS).

## Experimental

**Materials.** 1-pentene (C<sub>5</sub>H<sub>10</sub>, Tokyo Chemical Industry, Japan), 1-hexene (C<sub>6</sub>H<sub>12</sub>, Aldrich, USA), 1-octene (C<sub>8</sub>H<sub>16</sub>, Aldrich, USA), and 1-dodecene (C<sub>12</sub>H<sub>24</sub>, Aldrich, USA) were used as monomers for the synthesis of PAOs. All  $\alpha$ -olefins were purified by passing them through molecular sieves. Aluminum chloride (AlCl<sub>3</sub>, Aldrich, USA), diethylaluminum chloride (Et<sub>2</sub>AlCl, Aldrich, USA), diethylaluminum sesquichloride (Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, Aldrich, USA) were used as catalysts for cationic polymerization. Et<sub>2</sub>AlCl and Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> were diluted as 1 M using *n*-hexane (Junsei Chemical Co., Japan). Distilled H<sub>2</sub>O and diluted *tert*-buthylchloride (*t*BuCl, Aldrich, USA) were used as promoters for cationic polymerization.

**Preparation of PAO Using Aluminum-based Lewis Acid Catalyst.** The synthesis of PAO by using AlCl<sub>3</sub>-H<sub>2</sub>O catalyst was performed as follows. AlCl<sub>3</sub> as a cationic catalyst was added to a three necked 100 mL glass reactor equipped with a magnetic bar in an argon filled glove box. The glass reactor was placed in a water bath, which controlled the reaction temperature. An adequate amount of hexane and monomer (1-pentene, 1-hexene, 1-octene or 1-dodecene) was poured into the reactor and stirred for 30 min to stabilize the reaction temperature. H<sub>2</sub>O as a promoter was slowly added over the course of 30 min. Subsequently, the polymerization reaction was maintained for 1 h with vigorous stirring of the magnetic bar. After the completion of the reaction, unreacted olefin was removed by vacuum at room temperature. Residual catalyst in the product was removed by 5 wt% NaOH aqueous solution. The product was transferred into a separatory funnel and washed with a sufficient amount of distilled water for three times. The resultant product was vacuum-dried at 120 °C for 1 h to obtain the final synthesized PAO. The preparation procedure of PAO by using alkyl aluminum halide (Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>)-*t*BuCl catalyst was similar to that of using AlCl<sub>3</sub>-H<sub>2</sub>O catalyst except for using a different catalyst and promoter.

**Characterizations of Synthesized PAO.** The molecular weight and polydispersity index (PDI) of synthesized PAOs were measured by means of gel permeation chromatography (GPC). The instrument was equipped with a Waters 1515 pump, a Waters 2414 RI detector, and two styragel columns (HR 4E and HR 5E). The columns were eluted with tetrahydrofuran (1 mL/min rate at 40 °C). Polystyrene standards were used for calibration. Kinematic viscosity of PAO was measured by means of capillary tube type automatic HOUILLON viscometer from ISL. Reference oils from CANNON Instrument Company were used for calibration of viscometer. This HOUILLON viscometer requested less than 1 mL sample for each measurement. ISL's automated MPP 5Gs was used for measuring pour point of PAO. MPP 5Gs provided highly accurate pour point result using only 0.5 mL sample. The molecular mass distribution of the synthesized PAO was determined by means of a field-desorption-time-of-flight mass spectrometer (FD-TOF-MS, JMS-T100GC; JEOL, JAPAN). Roughly diluted in hexane, a 1% solution of PAO was prepared. Using 1 drop (about 1~1.5  $\mu$ L) of the solution, an emitter was wetted and dried out for about 1 min. The emitter was putted back in FD ion source of the mass spectrometer. A mass range 200~2000 was scanned to measure mass distribution of PAO samples. The emitter is a 5  $\mu$ m thin filament covered with carbon dendrimer structure. Between the emitter and ion extraction electrode, 10 kV electric potential was introduced. At the same time, 10~50  $\mu$ A current also was added in the filament. Then electric resistance increase the temperature of emitter to 100~400 °C, and PAO molecule dropped on the dendrimer needle is desorbed off in the air near the dendrimer (so called FD, field desorption). The other hands 10 kV potential makes over 10<sup>8</sup> V/cm high density electric field near the needle top of the dendrimer, and the PAO molecule passed on the needle top is ionized by the quantum tunneling effect occurred in the over 10<sup>8</sup> V/cm high density electric field. FD source makes molecular ion effectively because it is soft ionization technique. Almost all ions in the spectrum can be interpreted as molecule ion. The resolution of the mass analyzer (resolution 3000~4000) was enough to distinguish molecule ions in the range over *m/z* 1000.

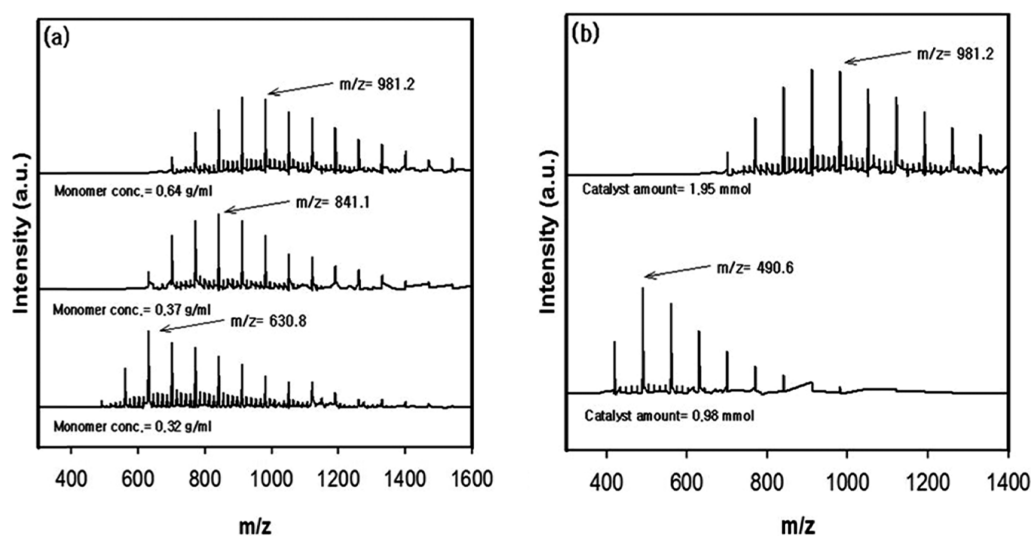
## Results and Discussion

As preliminary experiments, the various 1-pentene-based PAOs were synthesized by using AlCl<sub>3</sub>-H<sub>2</sub>O catalyst in order to determine their appropriate polymerization conditions, as

**Table 1. Polymerization Yield and Properties of 1-pentene-based PAO Prepared with Different 1-pentene Concentrations Using  $\text{AlCl}_3$  Catalyst<sup>a</sup>**

Catalyst concentration (M)	Hexane/1-pentene volume ratio	Yield (%)	Kinematic viscosity		VI	Pour point (°C)	$M_n$	$M_w$	PDI
			cSt @40 °C	cSt @100 °C					
$6.25 \times 10^{-2}$	1	61.2	257	21	97	-22.5	609	1418	2.33
$6.25 \times 10^{-2}$	0.75	67.0	320	24	95	-20.0	651	1524	2.34
$6.25 \times 10^{-2}$	0	73.0	509	30	94	-17.5	724	1760	2.43

<sup>a</sup>1-pentene=31.2 mL, catalyst:  $\text{AlCl}_3$ , promoter:  $\text{H}_2\text{O}$ ,  $\text{AlCl}_3/\text{H}_2\text{O}$  mole ratio=0.5, polymerization proceeded under room temperature.

**Figure 1.** TOF-MS spectra of the various 1-pentene-based MAOs prepared with (a) different monomer concentrations; (b) different catalyst amounts.

shown in Table 1. Polymerization yield tends to slightly increase as a function of 1-pentene concentration. Moreover, the kinematic viscosity and molecular weight of the PAO clearly increase with increasing monomer concentration. By the way the VI value ( $\sim 95$ ) and pour point ( $\sim 20^\circ\text{C}$ ) were similar under these experimental conditions.

Figure 1 shows the molecular mass distribution of the various 1-pentene-based PAO. TOF-MS spectra revealed that the major product can be controlled by changing monomer concentration. Mass peak ( $m/z$ ) located in 981.2, 841.2, and 630.8 stands for tetradecamer, dodecamer, and nonamer, respectively. Moreover, the intervals of peaks reflecting the carbon number of  $\alpha$ -olefin were exactly consistent with the molecular structure of 1-pentene.<sup>17</sup> Bulk polymerization has been proceeded to increase the polymerization yield and molecular weight of PAO for subsequent experimental procedures.

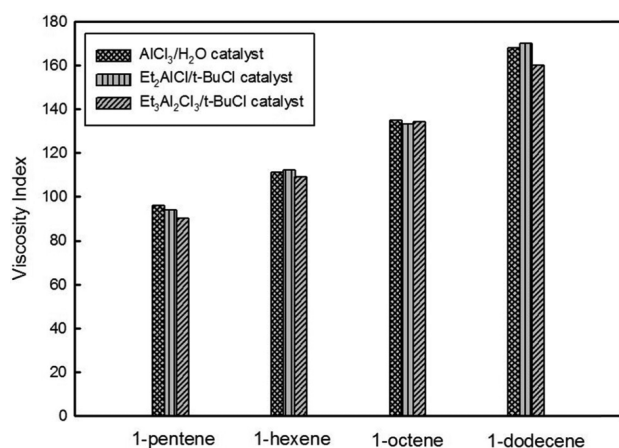
The catalytic performance and properties of various  $\alpha$ -olefin-based PAOs are presented by changing the type of aluminum-based catalyst, as shown in Table 2. The yield of alkyl

aluminum halide-based catalyst ( $\text{Et}_2\text{AlCl}$  or  $\text{Et}_3\text{Al}_2\text{Cl}_3$ ) was much superior to that of conventional  $\text{AlCl}_3$  catalyst. Moreover the molecular weight of PAO prepared by  $\text{Et}_3\text{Al}_2\text{Cl}_3$  catalyst was the highest among the used catalysts under the same experimental condition. It was observed that the correlation between the order of the molecular weight of synthesized PAO and the number of ethyl groups in the catalyst ( $\text{AlCl}_3 < \text{Et}_2\text{AlCl} < \text{Et}_3\text{Al}_2\text{Cl}_3$ ). It would be postulated that an ethyl group, as an electron donating group, may effectively stabilize the aluminum metal center in intermediate catalyst such as  $\text{Et}_2\text{AlCl}_2^-$  (see Scheme 1). Interestingly, the effect of catalyst types on the molecular weight increment depended on the length of  $\alpha$ -olefin. The difference of molecular weight of PAO by changing the aluminum based catalyst was not significant in the case of 1-pentene polymerization. Indeed, when 1-dodecene, having a relatively long carbon chain, was used as a monomer, the increase of molecular weight of PAO by changing the type of catalyst was apparent. The role of an ethyl group in the alkyl aluminum halide catalyst as an electron donating group may

**Table 2. Polymerization Yield and Properties of Various PAOs Prepared with Different Types of Catalysts and  $\alpha$ -Olefins<sup>a</sup>**

Monomer	Catalyst	Yield (%)	Kinematic viscosity		VI	Pour point (°C)	$M_n$	$M_w$	PDI
			cSt @40 °C	cSt @100 °C					
1-pentene	AlCl <sub>3</sub>	71.8	351.9	25.64	96	-17.5	507	1483	2.92
	Et <sub>2</sub> AlCl	73.4	262.4	20.84	94	-22.5	533	1011	1.90
	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	70.6	355.0	24.74	90	-17.5	608	1106	1.82
1-hexene	AlCl <sub>3</sub>	74.1	123.5	13.99	111	-35.0	567	1047	1.84
	Et <sub>2</sub> AlCl	95.7	219.0	20.86	112	-30.0	634	1199	1.89
	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	91.4	214.5	20.18	109	-25.0	857	1272	1.48
1-octene	AlCl <sub>3</sub>	75.4	91.8	13.99	135	-24.0	658	1133	1.72
	Et <sub>2</sub> AlCl	87.9	134.4	16.62	133	-42.5	770	1350	1.75
	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	88.6	234.7	24.91	134	-32.5	1128	1710	1.52
1-dodecene	AlCl <sub>3</sub>	72.8	6.5	2.27	168	n. m. <sup>b</sup>	160	860	5.36
	Et <sub>2</sub> AlCl	94.6	35.9	7.22	170	n. m. <sup>b</sup>	738	1110	1.50
	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	91.8	215.7	26.9	160	-12.5	1278	2024	1.58

<sup>a</sup>Volume of  $\alpha$ -olefins=50 mL, catalyst: concentration of aluminum based catalyst= $6.25 \times 10^{-2}$  M, AlCl<sub>3</sub>/H<sub>2</sub>O mole ratio=0.5, Cl/Al mole ratio=5 in the case of Et<sub>2</sub>AlCl-*t*-BuCl, and Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-*t*-BuCl catalysts, polymerization temperature=0 °C. Bulk polymerization proceeded. <sup>b</sup>n.m. means not measured.

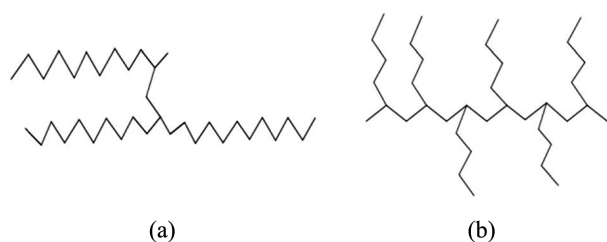
**Figure 2.** Variation of viscosity index of synthesized PAO prepared with different  $\alpha$ -olefins and aluminum based catalysts.

tend to be more dominant with regard to increasing the carbon number of  $\alpha$ -olefin.

The VI value of various  $\alpha$ -olefin-based PAO was strongly dependent on the chain length of  $\alpha$ -olefin, as shown in Figure 2. In other words, VI value drastically increases as a function of the carbon number of  $\alpha$ -olefin in the case of PAO synthesis using cationic polymerization.

However, the differences of VI values of the PAOs prepared using the three kinds of aluminum-based catalyst were not great. VI values of PAOs prepared using Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-*t*-BuCl catalyst was slightly lower than those using the other catalysts. It

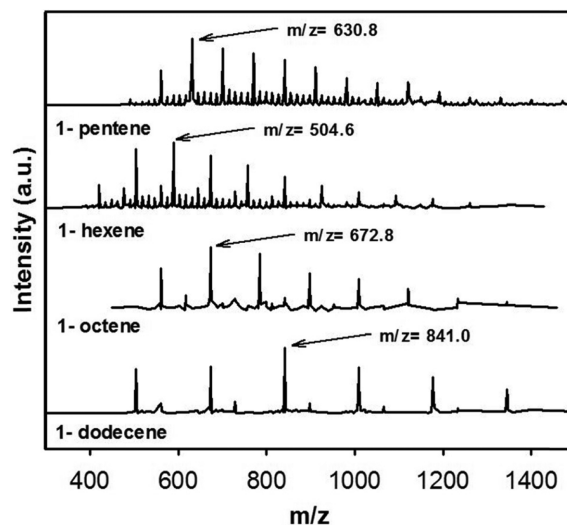
may be related to the tendency of  $M_n$  of PAO (see Table 2), which effect molecular movement of PAO. Pour points of various PAOs made by using 1-pentene, 1-hexene, 1-octene, and 1-dodecene with the Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-*t*-BuCl catalyst were -17.5, -25, -32.5, and -12.5 °C, respectively. The pour points of the various PAOs tend to decrease with increases in the number of carbon in  $\alpha$ -olefin, except for 1-dodecene. In general, the variation of pour point can be determined by two factor : (i) increase of viscosity due to limitation of molecular movement, and (ii) wax crystallization. Considering VI value of various PAOs, the variation of pour point of PAOs, which were synthesized 1-pentene, 1-hexene, and 1-octene can be explained by increase of viscosity with decreasing temperature. By the way, the pour point of PAO prepared by 1-dodecene was higher than that by 1-octene even though VI value of 1-dodecene-based PAO is higher than that of 1-octene-based PAO. This might be due to the wax crystallization of linear -CH<sub>2</sub>- chains in 1-dodecene-based PAO. When compared with the representative molecular structure of the PAOs that consist of 36 carbons made from 1-dodecene and 1-hexene, 1-dodecene based-PAO is more linear in structure compared with 1-hexene-based PAO, as depicted in Figure 3. Hydrocarbon molecules with paraffin like linear structure are prone to stack each other as decreasing temperature. It makes easy to form wax crystallite that inducing drastic increase of the viscosity of substance under certain low temperature.



**Figure 3.** Plausible molecular structure of PAOs consisting of 36 carbon atoms: (a) trimer from 1-dodecene; (b) hexamer from 1-hexene.

Figure 4 shows the molecular mass distribution of the various  $\alpha$ -olefin-based PAO by using an  $\text{Et}_3\text{Al}_2\text{Cl}_3$ - $t\text{BuCl}$  catalyst system. TOF-MS spectra revealed that the major products differed depending on the kinds of  $\alpha$ -olefin even though polymerization conditions were the same. The major mass peak ( $m/z$ ) of 1-pentene-based PAO was located in 630.8, which indicates the presence of a nonamer. Hexamer was major product for 1-hexene and 1-octene-based PAO (1-hexene:  $m/z = 504.6$ , 1-octene:  $m/z = 672.8$ ). The major mass peak ( $m/z$ ) of 1-dodecene-based PAO was located in 841.0, which indicates the presence of a pentamer. The degree of polymerization decreased with increases in the carbon number of  $\alpha$ -olefin due to steric hindrance of the side chain during the cationic polymerization, as shown in Scheme 1. The intervals of peaks reflecting the carbon number of  $\alpha$ -olefin were consistent with the molecular structure of  $\alpha$ -olefin, as expected.<sup>17</sup>

The polymerization of 1-hexene, 1-octene, and 1-dodecene as  $\alpha$ -olefin using an  $\text{Et}_3\text{Al}_2\text{Cl}_3$ - $t\text{BuCl}$  catalyst were performed



**Figure 4.** TOF-MS spectra of MAOs prepared with various  $\alpha$ -olefins.

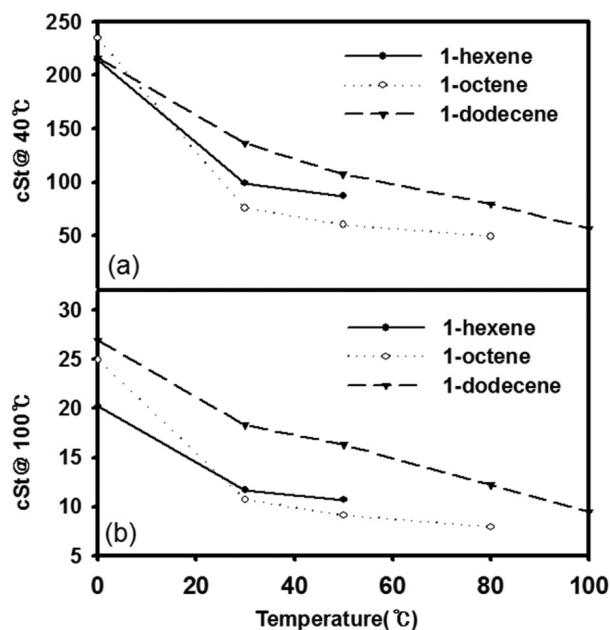
to investigate the effect of the reaction temperature (see Table 3).

The polymerization yield and VI were similar with changing polymerization temperature regardless of  $\alpha$ -olefin type such as 1-hexene, 1-octene, and 1-dodecene. However, polymerization temperature strongly affected the kinematic viscosity and molecular weight of PAO, as shown in Figure 5. The kinematic viscosity of PAO drastically decreases as a function of polymerization temperature, due to the decrease of molecular weight of PAO in the all case of the  $\alpha$ -olefins. In the case of coordination polymerization, catalyst and monomer concentration and polymerization temperature can be used as the

**Table 3.** Polymerization Yield and Properties of Various PAOs Prepared with Different  $\alpha$ -Olefins as a Function of Polymerization Temperature<sup>a</sup>

Monomer	Reaction temp. (°C)	Yield (%)	Kinematic viscosity		VI	$M_n$	$M_w$	PDI
			cSt @40 °C	cSt @100 °C				
1-hexene	0	88.6	214.5	20.2	109	857	1272	1.48
	30	85.4	99.1	11.7	107	545	958	1.76
	50	82.7	87.1	10.7	128	505	912	1.81
1-octene	0	88.6	234.7	24.9	134	1128	1710	1.52
	30	88.6	75.9	10.7	128	669	1144	1.71
	50	85.5	59.9	9.1	131	697	1176	1.69
	80	84.6	49.2	7.9	129	629	1137	1.81
1-dodecene	0	91.8	215.7	26.9	160	1278	2024	1.58
	30	89.2	136.4	18.3	150	1068	1983	1.86
	60	93.0	107.6	16.3	163	1008	1519	1.51
	80	92.7	79.4	12.2	151	859	1291	1.50
	100	93.8	56.7	9.5	150	661	999	1.51

<sup>a</sup>Volume of  $\alpha$ -olefins=50 mL, catalyst: concentration of  $\text{Et}_3\text{Al}_2\text{Cl}_3$ = $6.25 \times 10^{-2}$  M, Cl/Al mole ratio=5. Bulk polymerization was proceeded.



**Figure 5.** Variation of kinematic viscosity of PAOs synthesized by different  $\alpha$ -olefins as a function of polymerization temperature: (a) kinematic viscosity at 40 °C; (b) kinematic viscosity at 100 °C.

main parameters for controlling the molecular weight of polyolefin prepared by Ziegler type metallocene catalyst. The  $\beta$ -hydrogen elimination, i.e. chain transfer reaction, has widely been known as a typical termination step in the metallocene-based olefin polymerization.<sup>18</sup>

In relatively higher polymerization temperatures, the chain transfer reaction is accelerated compared with the propagation reaction in cationic polymerization as well as coordination polymerization.<sup>19</sup> This means that lower temperatures should be more favorable to obtain higher molecular weight of PAO. The chain transfer effect was not significant above 50 °C. It seems to be that the increase tendency of kinetic constant for chain transfer diminishes above 50 °C.

## Conclusions

We have successfully shown the synthesis of various PAOs by using various  $\alpha$ -olefins such as 1-pentene, 1-hexene, 1-octene, and 1-dodecene with aluminum-based Lewis acid catalysts. The  $\text{Et}_3\text{Al}_2\text{Cl}_3$ - $t\text{BuCl}$  catalyst system shows the highest catalytic performance among the used catalysts in terms of polymerization yield and molecular weight of PAO. This might be due to the ethyl group, which as an electron donating group, may effectively stabilize the catalytic intermediate dur-

ing the cationic polymerization. Major oligomeric product can be controlled by changing polymerization parameters such as monomer concentration and reaction temperature. The VI values of various  $\alpha$ -olefin-based PAOs significantly depend on the chain length of  $\alpha$ -olefin due to the molecular structures of PAO. VI values can be controlled in a range of 90 to 170 by changing the carbon number of  $\alpha$ -olefin and types of catalyst. Furthermore, the pour point of PAO was also affected by the carbon number of  $\alpha$ -olefin. The properties of PAO using  $\alpha$ -olefin above carbon number 12 seem to be inadequate in terms of pour point due to wax crystallization under low temperature.

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