

POLYMERIZATION OF ISOBUTYL VINYL ETHER CATALYSED BY DINUCLEAR HALF-TITANOCENES*

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Abstract Polymerization of isobutyl vinyl ether (IBVE) has been studied with mononuclear half-titanocene, CpTiCl_3 [**1**] and dinuclear half-titanocenes, $[(\text{C}_5\text{H}_4)_2(\text{CH}_2)_n][(\text{TiCl}_3)_2]$ [**2** ($n = 3$), **3** ($n = 6$)], and $[(\text{C}_5\text{H}_4)_2(\text{CH}_2)_n][(\text{TiCl}_2\text{OR})_2]$ ($\text{R} = 2,6$ -diisopropylphenoxy) [**4** ($n = 3$), **5** ($n = 6$)], in the presence of methyl aluminoxanes (MAO) as cocatalyst in methylene chloride. The influences of the length of polymethylene bridge and the substitution of aryloxy group at the metal center have been investigated at three polymerization temperature (25°C, –10°C, and –30°C). It was observed that the structure of catalyst displayed significant effects on not only the polymerization behavior but also the properties of the produced polymers. At –30°C it was noted that polymerization catalyzed by dinuclear titanocenes indicated a living character where a linear relation between molecular weight of the polymers and monomer conversion. The catalytic activity decreased in the order of **1** > **2** > **4** > **3** > **5** whereas the stereoregularity of PIBVE, calculated by racemic dyad value, r , increased in the order of **1** < **2** < **3** < **4** < **5**. The collected polymers have the high molecular weight (1×10^5 – 3×10^5) and narrow molecular weight distribution ($\text{PDI} \leq 2.3$). Very interestingly the dinuclear half-titanocenes containing a different bridge and substituent generated the polymers containing a different level of syndiotacticity from 47% to 56% according to the employed catalyst, which clearly demonstrated the property of aryloxy substituent at the metal center played a key role to adjust polymer stereoregularity.

Keywords: Dinuclear half-titanocene; Poly(isobutyl vinyl ether); Vinyl ether polymerization by metallocene; Stereoregularity control by metallocene.

INTRODUCTION

Since 1980, metallocene complexes can be activated by methylaluminoxane (MAO) cocatalyst and used as organometallic catalyst to polymerize α -olefin^[1–4]. Metallocene polymerization system has been improved remarkably for the last 20 years because of its superior controllability of molecular parameters of polymer. However, it turned out that metallocene systems were not able to be employed to polymerize polar vinyl monomers containing electron donor atom such as nitrogen and oxygen since those atoms may coordinate with the active site to block monomer coordination. Poly(vinyl ethers), which were first made in Germany before 1940, have been widely used in adhesive industry^[5]. Poly(isobutyl vinyl ether) (PIBVE), one of the most useful poly(vinyl ethers), has found the first economically important application as adhesives, impregnating agents for textile, paper, leather whilst the latter has found use in surface coatings^[6, 7]. It is well known that the polymerization of IBVE can be readily accomplished with cationic initiators to produce polymer by addition polymerization mechanisms. A variety of initiators such as $\text{HCl}/\text{SnCl}_4/n\text{Bu}_4\text{NCl}$ ^[8], p -methoxystyrene in aqueous

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media with $\text{Yb}(\text{OSO}_2\text{CF}_3)_3$ ^[9], aromatic acetals/ MtX_n ^[10], IBVE-HCl adduct/ $\text{TiCl}_2\{\text{OC}_6\text{H}_4i\text{-Pr}_2(2,6-)\}_2$ ^[11], and $\text{AlCl}_3/\text{LiAlH}_4$ ^[12] have been reported as catalyst systems with better control on molecular weight as well as on tacticity to form isotacticity rich PIBVE. Generally, the development of polymerization route to produce polymers with high stereoregularity, high molecular weight (M_n), and narrow molecular weight distribution (PDI) has always been a challenging job in the polymer synthetic area. In many cases, extreme reaction conditions may be employed in order to do it, for example, the very low reaction temperature (-78°C) must be applied to get isotactic PIBVE with a high meso dyad contents ($m = 90\%–92\%$)^[11]. Recently a few reports to prepare PIBVE by use of metallocene catalyst have also been published. Baird and coworkers polymerized vinyl ethers with $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ ^[13] (where Cp^* is η^5 -pentamethylcyclopentadienyl) *via* carbocationic mechanism at -78°C to obtain polymers with high molecular weights ($4 \times 10^4–1 \times 10^5$), narrow molecular weight distribution (PDI = 1.7–2.4) and syndiotactic fraction of 33%–56%. Shaffer and Ashbaugh was able to make PIBVE with $\text{Cp}_2^*\text{ZrMe}_2$ and Cp_2HfMe_2 ^[14]. However, their polymers suffered from the low M_n (3800–28300) and high PDI (4.02–8.8). In 2005, Cadenas-Pliego group published the formation of PIBVE having a high M_n of 94900 and low PDI of 1.79 but low syndiotacticity ($r = 36\%$) with IndTiCl_3 catalyst system (where Ind is indenyl) at -78°C ^[15].

Recently, dinuclear half-titanocene compounds which contain two mechanically linked metallocene units have been known to be able to be employed efficiently as a new type of metallocene catalyst to control the stereoregularity, molecular weight and molecular weight distribution of syndiotactic polystyrene^[16]. In this paper, we would like to describe the first application of dinuclear half-titanocene to polymerize IBVE to figure out not only the difference between mononuclear and dinuclear catalyst but also the effects of the bridging ligand structure in controlling molecular weight and syndiotacticity. Moreover, the effect of aryloxy substituent at titanium on the catalytic properties in polymerization was explored.

EXPERIMENTAL

Materials

IBVE was obtained from Aldrich and distilled over CaH_2 before use. MAO was purchased from Akzo, USA and used without further purification. Methylene chloride (CH_2Cl_2) was distilled from CaH_2 prior to use. Cyclopentadienyl titanium trichloride (CpTiCl_3) was purchased from Aldrich and used without further purification. Catalysts **2**, **3**, **4**, and **5** were synthesized in the laboratory according to reported methods^[17–19].

Polymerization

The polymerization was carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passing through a column of molecular sieve (0.4 nm) and Drierite (8 mesh) before use. Firstly, CH_2Cl_2 solution containing the calculated quantity of catalyst was added to the Schlenk flask through degassed syringe. The resulting flask was introduced to the polymerization temperature followed by the addition of the designed amount of MAO solution. After the activation of the catalyst system for 5 min, IBVE was injected to start the polymerization. After the designed reaction time, the polymerization was stopped by methanol/HCl 10% solution. The formed polymer was precipitated in methanol to be separated by filtration followed by drying under reduced pressure.

Characterization

M_n and PDI were measured by gel permeation chromatography (GPC) using Waters columns (styragel, HR5E) equipped with a Waters 515 pump and a Waters 2410 differential refractometer using diphenyl ether as an internal standard. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. Linear polystyrene standards (1.31×10^3 g/mol – 3.58×10^6 g/mol) were used for calibration.

The stereoregularity of the generated polymers was determined by ^{13}C -NMR spectra. They were recorded on a Bruker DPX-300 FT-NMR spectrometer in CDCl_3 at 50°C .

RESULTS AND DISCUSSION

Polymerization of IBVE

In reality the dinuclear half-metallocene with polymethylene bridge systems displayed not only the distinguished characters from the well-defined mononuclear metallocenes, but also a strong influence of the nature of the bridging ligand on the syndiospecific styrene polymerization^[20]. As reported, a variety of half-titanocenes containing aryloxy group showed remarkable catalytic activities for ethylene copolymerization and syndiospecific styrene polymerization^[21, 22]. Four different dinuclear half-titanocenes (Fig. 1) along with CpTiCl₃, **1**, were investigated for the polymerization of IBVE to study the relation of catalyst structure to the polymerization behavior. In all cases, the same molar ratio of IBVE to catalyst to MAO (8000:1:100) in methylene chloride has been applied to the reaction at low temperature (−10°C and −30°C). Polymerization results are summarized in Tables 1 and 2.

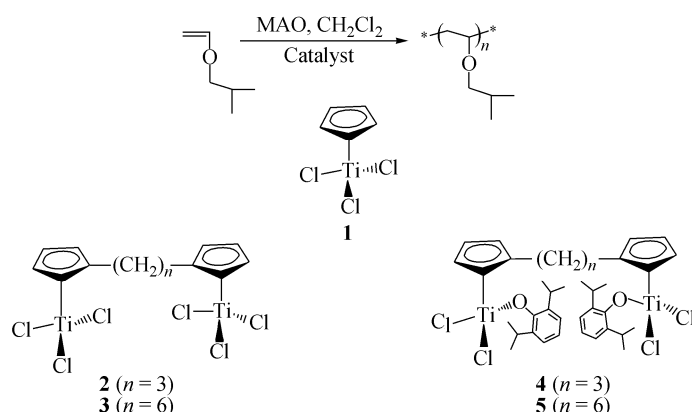


Fig. 1 Scheme of polymerization of PIBVE and structure of the catalyst **1** to **5**

Table 1. Results of IBVE polymerization by use of dinuclear half-titanocenes at −10°C^a

Catalyst	Time (h)	Conversion (%)	Activity ^b	M_n	PDI
1	2	14.00	56	70400	2.1
1	4	21.35	43	72400	1.9
1	5	26.39	42	97600	2.0
1	7	63.25	72	118100	2.0
2	3	10.21	27	73100	1.5
2	5	25.73	41	125800	1.8
2	6	88.02	118	162600	1.8
2	7	89.56	103	171600	1.8
3	5	3.96	6	15600	1.9
3	7	6.77	8	16400	1.9
3	9	14.24	13	100400	2.0
3	10	63.76	51	153500	2.1
3	11	86.50	63	172300	2.0
4	2	28.23	113	45900	1.8
4	4	31.94	64	85700	1.8
4	5	58.85	94	117400	1.8
4	7	77.29	88	129500	1.8
5	6	0.46	1	17900	2.1
5	7	4.56	5	18900	2.1
5	9	20.35	18	99400	1.9
5	10	60.03	48	149900	1.9
5	11	80.15	58	210900	2.0

^a Reaction condition: [IBVE]/[catalyst]/[MAO] = 8000:1:100;

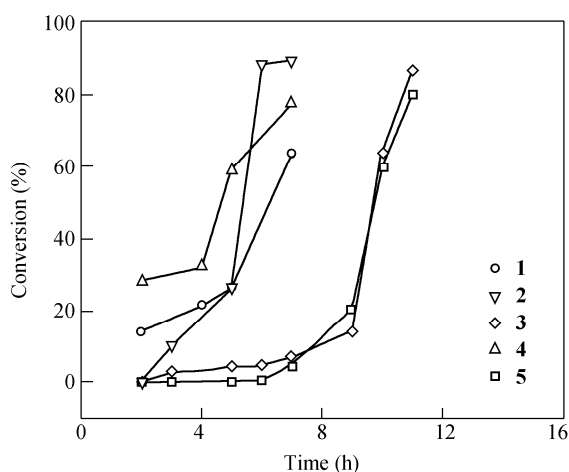
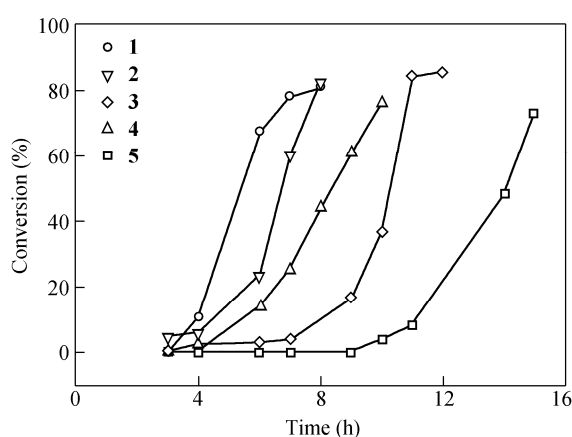
^b kg PIBVE/(mol of catalyst·h)

Table 2. Results of IBVE polymerization by use of dinuclear half-titanocenes at $-30^{\circ}\text{C}^{\text{a}}$

Catalyst	Time (h)	Conversion (%)	Activity ^b	M_n	PDI
1	4	10.63	21	164200	2.1
1	6	67.36	90	241800	2.1
1	7	78.13	89	252600	2.2
1	8	80.80	81	259800	2.0
2	3	4.69	13	36800	2.1
2	4	6.25	13	41300	2.1
2	6	23.44	31	106400	2.1
2	7	59.90	69	219000	1.9
2	8	82.78	83	282300	1.9
3	4	2.40	5	22100	2.8
3	7	3.75	4	31000	2.2
3	9	16.56	15	54000	2.0
3	10	36.46	29	117500	2.0
3	11	84.38	61	265100	1.9
4	6	13.85	19	63800	2.4
4	7	25.31	29	115600	2.0
4	8	44.14	44	187200	2.0
4	9	60.76	54	242500	1.9
4	10	76.20	61	268200	1.9
5	10	3.65	3	19300	2.3
5	11	8.20	6	20900	2.0
5	14	47.92	27	213700	1.9
5	15	73.07	39	324600	1.9

^a Reaction condition: [IBVE]/[catalyst]/[MAO] = 8000:1:100;^b kg PIBVE/(mol of catalyst·h)**Polymerization Activity**

It was found that the catalytic behaviors of dinuclear half-titanocenes were dependent on both the structure of catalyst and the polymerization temperature. To easily discuss results, conversion versus time for polymerization of IBVE using five catalysts at -10°C and -30°C were described in Fig. 2 and Fig. 3, respectively.

**Fig. 2** Correlation of conversion with the polymerization time with the catalyst 1 to 5 at -10°C **Fig. 3** Correlation of conversion with the polymerization time with the catalyst 1 to 5 at -30°C

It is very interesting that there was a very intimate relation between the catalytic activity and the length of the bridging ligand of the dinuclear half-titanocene. The mononuclear catalyst **1** and dinuclear catalysts **2** and **4** which contain three methylenes as a bridge exhibited similarly high activity. In contrast, the catalysts **3** and **5** were found to have much lower activities particularly at the early stage of the polymerization. At -30°C , the influence of polymerization temperature on the activity of the catalyst was able to be exerted more clearly probably due to the reduced mobility of dinuclear active sites. Initiation time of polymerization at -30°C increased, *i.e.* initiation of polymerization was slowed down, according to the catalyst in the order of $1 < 2 < 4 < 3 < 5$. This may reflect that the presence of bridge at dinuclear half-titanocene contribute to play a crucial role to delay the initiation step of the reaction at low temperature. Consequently, it is not unreasonable to suggest that the length of bridging unit have an effect on the reaction which is actually consistent with the observed results^[23]. The feature concerned with the catalytic activity was the manifested difference among mononuclear half-titanocene and dinuclear half-titanocenes with trimethylene and hexamethylene bridges. The adoption of methylene linkage at dinuclear metallocene would be a positive factor to stabilize the electron deficient active site electronically. However, the steric disturbance due to the interaction by the sway movement of polymethylene between two active sites may cause a more difficult coordination of monomer to the cationic species. Now the question is why the dinuclear catalysts with six methylenes exhibited such a low activity comparing to the corresponding those with three methylenes. It is understandable that trimethylene linkage is so short that it may be hard to cause a significant interaction between the two sides. On the other hand, hexamethylene is sufficiently flexible to draw a close contact of two active centers *via* the formation of six-membered ring intermediate (Fig. 4). This kind of process would be able to provide each other not only the opportunity to transfer electronic information of the cationic active site but also the perturbation to make a contact between two sides to lead to reduce a monomer coordination probability. It is suggested that these effects should contribute to slow down the propagation rate.

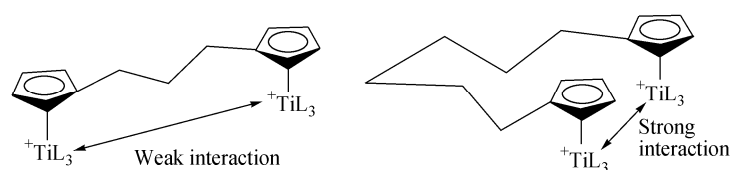


Fig. 4 Intramolecular interaction between two metal centers in dinuclear half-titanocene

In addition, another important factor related to the sluggishness of dinuclear half-titanocenes may be the property of substituent at titanium center. The diisopropyl phenoxy group is known as a π electron donor to stabilize the electron deficient active species. In terms of steric point of view 2,6-diisopropyl aryloxy group is bulky enough to give a negative effect on monomer coordination at the metal center. The experimental outcomes that the catalysts with aryloxy group exhibited slower polymerization rate than those with chloride displayed the steric environment around the active site are actually more influential factor to determine the polymerization behavior of the dinuclear catalysts.

Finally, the relation between the activity of dinuclear half-titanocenes and polymerization temperature was able to be represented clearly in Fig. 5 when the IBVE monomer was polymerized at 25°C , -10°C and -30°C with the catalyst **2**, $[(\text{C}_5\text{H}_4)_2(\text{CH}_2)_3][(\text{TiCl}_3)_2]$, in the presence of MAO in methylene chloride solvent. General tendency was observed between the activity of catalysts and the polymerization temperature. At 25°C , the monomer has been polymerized most quickly among three temperatures. Monomer solution became very sticky just after one hour polymerization, whereas at -10°C and -30°C polymers could not be collected up to three or four hours of reaction.

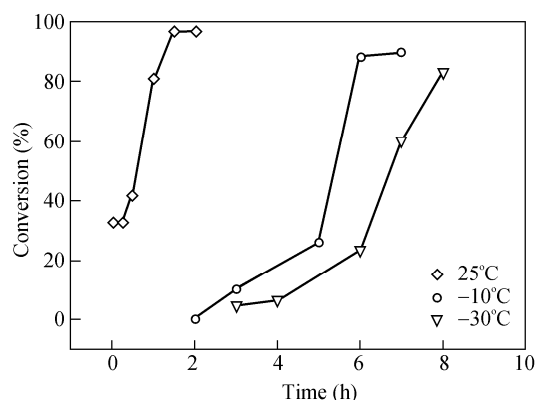


Fig. 5 The effect of temperature on conversion of IBVE polymerization versus time using dinuclear half-titanocene catalyst **2**

Molecular Weight of PIBVE

The variation of molecular weight and molecular weight distribution of PIBVE seems to be sensitive to the polymerization conditions as well as the nature of the catalyst. It has been noted that the polymerization at higher temperature produced the polymer with the smaller molecular weight (Fig. 6). It was notable that the molecular weights of the formed polymers at 25°C were close to 25000 regardless of conversion. On the other hand, molecular weight values of the polymers generated at -10°C and -30°C were getting larger according to the increase of conversion from 36000 to 282000. It was pointed that narrow PDIs of the polymers (near 2.0) had been maintained through the whole process of the reaction, which was known as the general trend of single site catalyst polymerization. One interesting feature may be pointed out from these results about the effect of polymerization temperature on molecular weight of PIBVE. The experimental molecular weights at -30°C were more closed to the calculated molecular weight than those at -10°C. The theoretical molecular weight values are calculated by $M_n(\text{cal}) = ([M]_0/2[\text{cat.}]_0)M_M C_M$, where $[M]_0$ and $[\text{cat.}]_0$ are the initial concentrations of the monomer and dinuclear half-titanocene catalyst, respectively; M_M is the molecular weights of monomer and C_M is the monomer conversion^[8,9]. In order to confirm the effects of temperature on the control on molecular weight of polymer the polymerization of IBVE was conducted with all five catalysts in this study. It was observed that the molecular weight values of the polymers formed at -30°C were fitted better than those formed -10°C on the calculated values as shown in Fig. 7 and Fig. 8. In these graphs, the experimental molecular weight values were higher than the theoretical ones until less than 40% of conversion. However, as the conversion increases the molecular weights of polymers become smaller than the calculated ones probably because of the inefficient

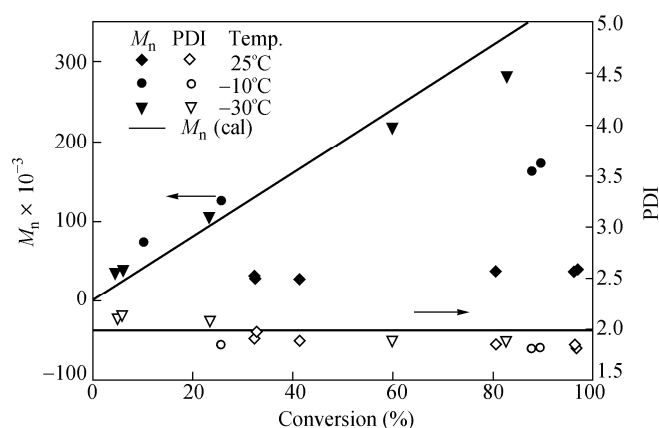


Fig. 6 M_n and PDI versus conversion for polymerization of IBVE using dinuclear half-titanocene catalyst **2** at three different temperatures

initiation with the slow growing carbocation and the fast termination at high conversion. Meanwhile, PDI of resulting polymer almost did not change during the whole reaction period and the range of value was quite narrow ($\text{PDI} \leq 2.3$) due to the single active site of catalyst.

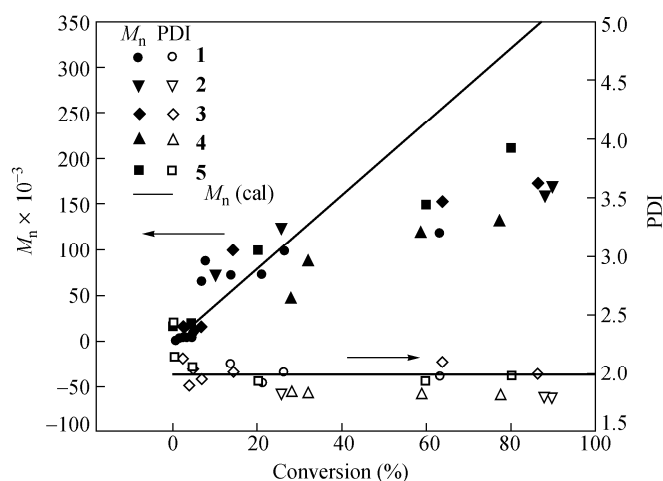


Fig. 7 M_n and PDI versus conversion for polymerization of IBVE using dinuclear half-titanocene catalyst at -10°C

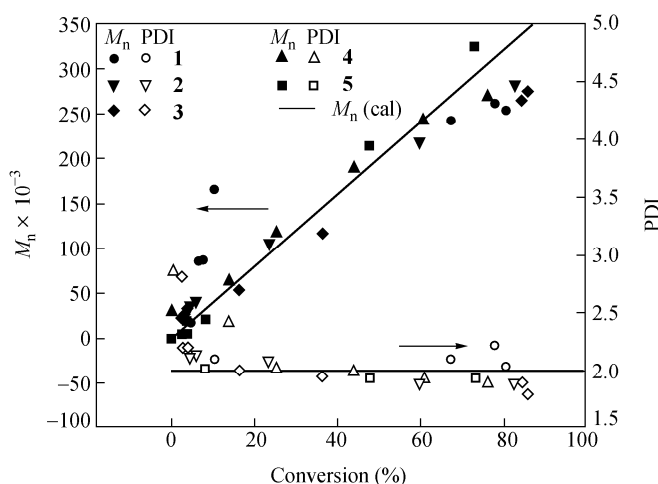


Fig. 8 M_n and PDI versus conversion for polymerization of IBVE using dinuclear half-titanocene catalyst at -30°C

Dependence of molecular weight of PIBVE upon polymerization temperature should be explained by β -H elimination rate of the reaction. At high temperature the termination step through β -H elimination would proceed frequently to liberate a constant length of polymer chain as indicated by the experiment. However, as the temperature becomes lower the rate of β -H elimination should be suppressed significantly to lead to a longer chain of polymer molecule. The range of termination suppression may be directly related to the activation energy of β -H elimination. Our experiment demonstrated very well that β -H elimination may be completely inhibited around the temperature of -30°C since almost living character has been observed at this temperature as shown in Fig. 6, in which a linear relation of molecular weight with the conversion is well coincided with the line of theoretical polymerization. Another explanation may be applied that these catalysts also polymerize both *via* coordination insertion mechanism and *via* cationic mechanism below the change in polymerization temperature. This explanation is similar to the case of Baird and coworkers. In the first example of

polymerization of vinyl ether by metallocene, Baird and coworkers reported that the polymerization of vinyl ethers could be induced by $\text{Cp}^*\text{TiMe}_3\text{-B}(\text{C}_6\text{F}_5)_3$: the polymers were formed *via* carbocationic initiation by the titanium-containing cationic complex $(\text{Cp}^*\text{TiMe}_2)^+$ rather than *via* Ziegler-Natta process^[13]. Later, some reports showed that resultant polystyrene possessed both atactic (*via* carbocationic mechanism) and syndiotactic (*via* coordination insertion mechanism) stereo regularity with Cp^*TiMe_3 catalyst under conditional polymerization temperature, beside, the mechanism of polymerization of ethylene and α -olefins was also explored^[24–26]. In our case, the polymerization happened with coordination insertion mechanism at 25°C, chain termination was dominant factor to control molecular weight, and the active species of the polymerization should be cationic at low temperature. The cationic complex formed by methylation of metal by MAO may initiate the polymerization and the propagating cationic end may be stabilized by MAO, preventing termination with the chloride anion.

It was found out that the nature of catalyst had effect on the variation of molecular weight of PIBVE as well. For example, in order to reach about 120000 g/mol of molecular weight the required conversion has been varied according to the catalyst in the order of **1** (63%) > **4** (60%) > **2** (25%) > **5** (20%) > **3** (15%) at –10°C, which may be considered as the correlation of catalyst character with the molecular weight of the produced polymer. This result proposes that two factors seem to act as an important role to determine the molecular weight of the polymer. The first one is the effect of the bridging ligand of the dinuclear half-titanocene. The dinuclear catalysts formed a longer polymer chain than CpTiCl_3 . Among dinuclear catalysts the hexamethylene bridged catalysts **3** and **5** were able to form higher molecular weight polymer than the trimethylene bridged ones **2** and **4**, which indicated that the six methylene bridge is more influential to generate a longer chain. An extremely interesting outcome has been found from the change of chloride to aryloxy group. For instance, the catalyst **3** containing not only hexamethylene bridge but also trichlorides at titanium was found to form the highest molecular weight polymer. However, catalyst **5** having hexamethylene bridge with aryloxy group was observed to form the polymers with lower molecular weight. This result represents clearly that the substituent effect at the titanium center exerted a less significant influence than the bridge nature to control molecular weight of the polymers. This result showed that the higher activity catalysts were good to make a shorter PIBVE, which is a general tendency in metallocene polymerization.

Stereoregularity of PIBVE

Since stereoregulation in vinyl ether polymerization is an issue of great importance many researchers have attempted to control the stereoregularity of PIBVE by the desired catalyst design^[10–12]. In recent years, dinuclear half-titanocene has been successfully employed for the preparation of highly syndiotactic polystyrene^[16–19]. Substituent effect of half-titanocene on structure of polymer has been demonstrated very well by Nomura^[21]. Even if the isobutyl ether does not have the steric bulk as the phenyl group in styrene monomer, the dinuclear catalysts with the rich-electron property of –OR group may have a positive effect on the control of syndiotacticity of PIBVE. Figure 9 displayed ¹³C-NMR spectra of samples obtained by the catalyst **1**, **2**, **3**, **4** and **5** at –30°C. The dyad distribution of PIBVE can be determined from the peak intensity ratios of the main chain methylene carbons [–CH₂–CH(O*i*Bu)–] around $\delta = 39\text{--}42$ where the meso (*m*) and racemic (*r*) dyads are well resolved.

The result showed that the syndiotactic fraction of PIBVE with five catalysts was arranged in the order of **1** < **2** < **3** < **4** < **5**. It is remarkable that the tendency of stereoregularity is pretty different from not only that of activity of the catalyst but also that of molecular weight of polymer. In terms of the catalyst structure there are two factors to adjust polymerization scheme, which are the effect of bridge and substituent. The mononuclear, normal catalyst **1** was turned out to prepare PIBVE with the lowest syndiotactic diad of 45%. Two catalysts **2** and **3** with trichlorides as an anionic ligand formed the polymer with 47% and 49% of syndiotacticity, respectively. Finally, the catalysts with aryloxy group made the highest syndiotactic diad of PIBVE with 52% and 56%. It can be summarized that the dinuclear half-titanocenes are able to make slightly higher syndiotactic PIBVE than CpTiCl_3 . In addition, the catalysts **4** and **5** with aryloxy group exhibited higher syndiotacticity than the catalysts **2** and **3** without substituent group. It is noteworthy that the catalysts **5** and **3** with hexamethylene bridge prepared polymer with greater stereoregularity than the catalysts **4** and **2** with trimethylene bridge,

respectively. This result indicates that the length of bridge at the dinuclear half-titanocene affected less powerfully on stereochemical control of the polymerization than the aryloxy substitution at titanium. From the stereochemical characterization of PIBVE one very important observation has been revealed. The structural variation of the half-titanocene plays a major role to guide the stereochemical control of the polymerization in reality. The prime feature of the experiment strongly suggests that if sophisticatedly designed dinuclear catalyst could be prepared the highly stereoregular PIBVE should be manufactured.

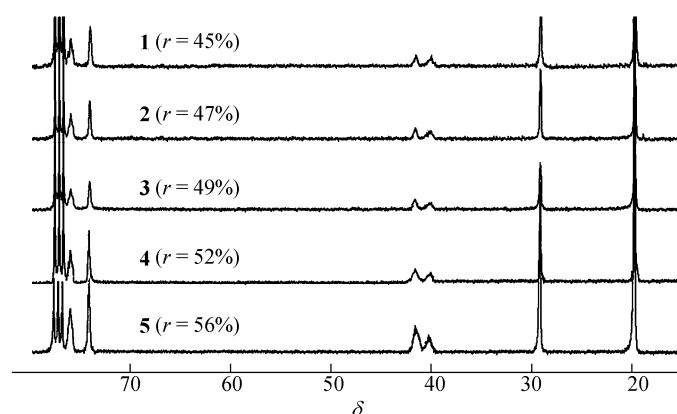


Fig. 9 ^{13}C -NMR spectrum of PIBVE using catalyst **1**, **2**, **3**, **4**, **5** system in CDCl_3 at 50°C

CONCLUSIONS

Four different dinuclear half-titanocenes (Fig. 1) along with CpTiCl_3 were investigated for the polymerization of IBVE to study the relation of catalyst structure to the polymerization behavior. It was found that the polymerization behaviors of dinuclear catalysts were dependent on both the structure of catalyst and the polymerization temperature. The mononuclear catalyst **1** and dinuclear catalysts **2** and **4** which contain three methylenes as a bridge exhibited similarly high activity. In contrast, the catalysts **3** and **5** were found to have much lower activities particularly at the early stage of the polymerization. The steric disturbance due to the interaction by the sway movement of polymethylene between two active sites may be attributed to control the activity of the dinuclear catalysts. The variation of molecular weight and molecular weight distribution of PIBVE seems to be sensitive to the polymerization conditions as well as the nature of the catalyst. It was pointed that narrow PDIs of the polymers (near 2.0) had been maintained through the whole process of the reaction, which was known as the general trend of single site catalyst polymerization. The experimental molecular weights at -30°C were more closed to the calculated molecular weight than those at -10°C . Dependence of molecular weight of PIBVE upon polymerization temperature should be explained by β -H elimination rate of the reaction. At high temperature the termination step through β -H elimination would proceed frequently to liberate a constant length of polymer chain as indicated by the experiment. However, as the temperature becomes lower the rate of β -H elimination should be suppressed significantly to lead to make a longer chain of polymer molecule. Among dinuclear catalysts the hexamethylene bridged catalysts **3** and **5** were able to form higher molecular weight polymer than the trimethylene bridged ones **2** and **4**. The polymerization showed that the syndiotactic fraction of PIBVE with five catalysts was arranged in the order of $\mathbf{1} < \mathbf{2} < \mathbf{3} < \mathbf{4} < \mathbf{5}$. It turned out that the dinuclear half-titanocenes are able to make slightly higher syndiotactic PIBVE than CpTiCl_3 . It is noteworthy that the catalysts **5** and **4** with aryloxy group at titanium prepared greater stereoregularity than the catalysts **3** and **2** with chloride group. This result indicates that the aryloxy substituent at titanium affected more powerfully on stereochemical control of the polymerization than the length of bridge at the dinuclear half-titanocene. This study suggests if the well and intentionally designed dinuclear catalyst could be prepared on the basis of the reported knowledge the stereochemical control of PIBVE should be established by the metallocene polymerization system.

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