Polymerization of 1,3-Butadiene with VO(P$_{204}$)$_2$ Activated by Methylaluminoxane, Purified Methylaluminoxane, and Trimethylaluminum

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ABSTRACT: The effect of different aluminum-based cocatalysts (MAO, pMAO, and TMA) on butadiene (Bd) polymerization catalyzed by VO(P204)2 was investigated. The bimodal dependence of the polymer yield on the [MAO]/[V] molar ratio was revealed, and an highest polymer yield was achieved at a rather low [MAO]/[V] molar ratio ([MAO]/[V] = 13). The microstructures of the resulting poly(Bd)s were also significantly influenced by the ratio. In the TMA or pMAO system, the polymer yields were also very sensitive to the [Al]/[V] molar ratio. However, the microstructures of the resulting poly(Bd)s were almost independent of the ratio. In relation to the microstructures of poly(Bd)s obtained by the MAO and TMA systems at various temperatures, the 1,2-unit contents were found to be the most abundant microstructure for both systems. In the pMAO system, the *trans*-1,4-units were the most abundant. The results of the additions of Lewis bases (THF and TPP) into Bd polyerization system comfirmed the existing of the two types of the reactions of VO(P$_{204}$)$_2$-MAO catalyst and had the polymerization process controlled to some extent. The different thermal behaviors of these catalytic systems also show that multiple types of active centers were formed during the reaction between VO(P$_{204}$)$_2$ and MAO. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Synthetic polybutadiene rubbers have gained increased academic and industrial attention.[1–4] Lanthanum-based (neodymium, samarium, and so on) and first-row transition metal (TM)-based Ziegler-Natta catalysts are used to polymerize 1,3-butadiene (Bd). Depending on metal-ligand nature, these catalysts can give *cis*-1,4, *trans*-1,4, and 1,2-vinyl poly(Bd)s. Unlike fully investigated lanthanum catalysts, little is known of the nature of vanadium-based catalysts. They have been studied to prepare *trans*-1,4-poly(Bd) and syndiotactic 1,2-poly(Bd).[2–6] Using the chloride-containing catalysts V(acac)$_3$/AlRCl$_2$ (R = alkyl group) and VCl$_3$·3THF/AlR$_2$Cl, *trans*-1,4-poly(Bd) has been produced.[7,8] On the other hand, using the chloride-free catalyst V(acac)$_3$/AlR$_3$, syndiotactic 1,2-poly(Bd)s has been obtained.[9]

Since its discovery as metal-complex activator in olefins polymerization, methylaluminoxane (MAO) has also largely used in the polymerization of conjugated dienes.[10] Among them, metallocene vanadium/MAO produces poly(Bd)s consisting of 80 mol % *cis*-1,4-units.[11,12] Under certain polymerization conditions, poly(Bd)s with more than 60 mol % *cis*-1,4 structures can be obtained with the catalyst V(acac)$_3$/MAO.[13] In combination with MAO, the TM complexes of nickel,[14,15] cobalt, and iron[16,17] have also been reported for *cis*-specific Bd polymerization. Despite the TM precursors, MAO seems to be considered as the key factor for obtaining *cis*-1,4-units in poly-1,3-dienes. Ricci et al.[18–20] have reported that the V(acac)$_3$-MAO system poly/copolymerized Bd into *trans*-1,4 structures. These conflicting results may be due to the sources of MAO solutions. A considerable amount of trimethylaluminum (TMA) is well known to exist in MAO solutions and has an important effect on the catalytic activity of TM/MAO in ethylene, α-olefin, and Bd polymerizations.[21–28]

Additional Supporting Information may be found in the online version of this article.
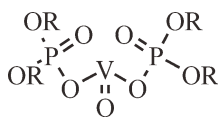
Scheme 1. Structure of $VO(P_{204})_2$. R= $CH_2CH(C_2H_5)C_4H_9$.

In our previous study,[29–31] the complex of $VO(P_{204})_2$ (Scheme 1), a chloride-free vanadium complex, has been less sensitive to air and moisture. When combined with $Et_3Al_2Cl_3$, the $VO(P_{204})_2$ system exhibits much higher catalytic activity and longer active life than the $VOCl_3/Et_3Al_2Cl_3$ system in the copolymerization of ethylene and propylene. In the Bd polymerization by $VO(P_{204})_2$/alkylaluminums, a high catalytic performance of oxovanadium phosphate complexes is observed. These encouraging results prompted us to investigate the behavior of $VO(P_{204})_2$-MAO catalysts in Bd polymerization, and to compare the results with $VO(P_{204})_2$-TMA and $VO(P_{204})_2$-pMAO catalysts.

The addition of Lewis bases to TM-mediated coordination polymerization has been found to increase the catalytic activity or modify the polymer characteristics.[23,32–35] Accordingly, tetrahydrofuran (THF) and triphenylphosphine (TPP) were used in this study, and the Bd polymerization in the presence of these two additives was also examined.

EXPERIMENTAL

Materials

MAO in toluene (10 wt %; Albar Corporation) and TMA (2.0 mol L^{-1}; Aldrich Chemical Company) were used without further purification. Purified MAO (pMAO) was prepared accord-

ing to a method described in literature[23] and obtained by treating MAO solution under high vacuum to a constant weight. The aluminum concentrations of free-TMA and pMAO in the MAO solution were estimated by the titration with EDTA to be 0.33 and 1.09 mol/L, respectively.

Bd was donated by Jinzhou Petrochemical Company, Petrochina, and dried by passing through a column packed with KOH and 4 Å molecular sieves. $VO(P_{204})_2$ was prepared according to a reference.[29–31] Toluene and THF (Beijing Reagents Factory) were refluxed over sodium benzophenone ketyl under a nitrogen atmosphere until the solution turned blue and distilled before use. TPP (99%; Aldrich Chemical Company) was used without purification. To examine the effects of additives, the cocatalysts were pretreated by adding THF and TPP ([additive]/[Al] = 1.0 mol/mol). The mixture was kept under a nitrogen atmosphere 24 h before use.

Polymerization Procedure

All manipulations were performed under a dry nitrogen atmosphere. A detailed polymerization procedure (Table I, line 3) is described as a typical example. First, a solution of Bd in toluene was prepared as follows: Bd was condensed into a vessel with volume grading, cooled at 0°C, and added via a bridge into a flask containing toluene. The Bd concentration (1.85 mol L^{-1}) was then determined by weighting the vessel before charging it with toluene, as well as before and after adding the Bd. The solution was divided via a distributor into 40 mL portions and transferred to an Ampoule bottle. After heating the reaction solution to the desired temperature (40°C) in a water bath, $VO(P_{204})_2$ (1.85×10^{-1} mol L^{-1} solution in 0.40 mL of

Table I. Effect of THF and TPP Additives on Bd Polymerization with $VO(P_{204})_2$-TMA, -pMAO, and -MAO Catalysts in Toluene at 40°C for 2 h[a]

Additive/Cocatalyst	[Al]/[V] (mol/mol)	Yield (%)	$10^{-4} M_n$	M_w/M_n	Microstructure (%)		
					Cis-1,4	1,2	Trans-1,4
–/TMA	3.7	23.8	2.68	4.74	32.6	55.0	12.4
	11.7	14.3	0.76	8.35	33.4	56.3	10.3
–/pMAO	12.3	0.7	–	–	16.3	22.8	60.9
	38.3	8.6	–	–	9.3	26.2	64.5
–/MAO	16.0	58.1	3.36	5.24	29.8	41.8	28.4
	50.0	9.5	1.11	12.30	50.6	36.2	13.2
THF/TMA	3.7	31.9	1.39	4.18	20.4	69.9	9.7
	11.7	6.2	1.58	14.66	29.2	57.2	13.6
THF/pMAO	12.3	0	–	–	–	–	–
	38.3	0	–	–	–	–	–
THF/MAO	16.0	14.4	2.07	3.75	22.2	68.5	9.3
	50.0	19.1	1.92	4.59	22.7	68.7	8.6
TPP/TMA	3.7	35.9	1.72	4.19	28.4	64.1	7.5
	11.7	3.9	0.56	11.12	35.6	55.3	9.1
TPP/pMAO	12.3	1.5	–	–	–	–	–
	38.3	6.6	–	–	–	–	–
TPP/MAO	16.0	46.5	1.40	4.66	26.6	58.0	15.4
	50.0	13.5	2.40	4.45	29.9	52.6	17.5

[a]Polymerization conditions: [Bd] = 1.85 mol L^{-1}, [V] = 1.85×10^{-3} mol L^{-1}, and [Additive]/[Al] = 1.0 mol/mol.

toluene) and MAO (1.42 mol L^{-1} solution in 0.83 mL of tolu-ene) were introduced into the reaction solution via syringes. Po-lymerization was carried out at 40°C for 2 h and quenched by adding acidified ethanol containing 2,6-di-*tert*-butyl-*p*-methyl-phenol (1 wt %) as a stabilizer. The formed polymer was coagu-lated, repeatedly washed with ethanol, and finally dried under a vacuum at 40°C to constant weight.

Polymer Characterization
The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured at 30°C by gel perme-ation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, and HMW 2 THF), and a Waters 2414 refractive index detector. THF was used as an eluent at a flow rate of 1.0 mL min^{-1}. The molecular weights of poly(Bd) were determined by polystyrene calibration. Sample solutions (1.0 mg mL^{-1}) were filtered through a 0.45-μm microfilter before injection. IR spectroscopy was used to determine the microstructure of Bd units using a Bio-Rad FIS 135 Spectrophotometer with a film sample.[36]

RESULTS AND DISCUSSION

The results of the polymerization of Bd with VO(P$_{204}$)$_2$-MAO within our research scope showed that two types of active centers were present in the catalyst system. These active centers produced polymers of different molecular weights and stereoregularities.

Effect of the [MAO]/[V] Molar Ratio on Bd Polymerization with VO(P$_{204}$)$_2$-MAO Catalyst
The effect of the [MAO]/[V] molar ratio on the polymerization of Bd with VO(P$_{204}$)$_2$-MAO catalyst was examined, and the results are shown in Figures 1(a–c). Figure 1(a) shows the GPC profiles of the formed poly(Bd)s with VO(P$_{204}$)$_2$-MAO catalyst at different [MAO]/[V] molar ratios. The molecular weight dis-tribution curves shifted toward higher molecular weight regions and showed a bimodal pattern by increasing the [MAO]/[V] molar ratios. Figure 1(b) reveals that the microstructure of the resulting poly(Bd)s was significantly influenced by the [MAO]/[V] molar ratio. The catalyst produced poly(Bd)s with mixed structures when the ratio was lower than 200, whereas pol-y(Bd)s consisting of mainly *cis*-1,4 structures were obtained when the ratios were more than 200. The bimodal dependence of the polymer yield on the [MAO]/[V] molar ratio is also observed in Figure 1(c). The polymer yield rapidly increased with increased ratio, and the highest polymer yield was achieved when the ratio was 13. This ratio was rather low when com-pared with those observed in the olefin polymerization initiated by metallocene-MAO catalysts.[37] A plateau value was reached when the ratio was more than 300. Thus, the polymerization of Bd with VO(P$_{204}$)$_2$-MAO catalyst was assumed proceed at two types of active sites.

Effect of the [Al]/[V] Molar Ratio on Bd Polymerization with VO(P$_{204}$)$_2$-pMAO and VO(P$_{204}$)$_2$-TMA Catalysts
In the Bd polymerization activated by VO(P$_{204}$)$_2$-MAO catalyst, the abovementioned results may be ascribed to the multiple reac-tions of VO(P$_{204}$)$_2$ with free-TMA and pMAO, because a mixture of different oligomers with multiple equilibria exists in the com-mercial MAO solution.[38,39] To confirm this point, the effect of

the [Al]/[V] molar ratio on Bd polymerization with VO(P$_{204}$)$_2$-TMA and VO(P$_{204}$)$_2$-pMAO catalysts were examined, and the results are shown in Figure 2(a, b). In the case of the TMA sys-tem, a high polymer yield was achieved when the [TMA]/[V] molar ratio was 4.7. The molecular weight distribution curves shifted toward lower molecular weight regions and acquired a bi-modal pattern with increased ratio [Figure 2(c)]. This finding
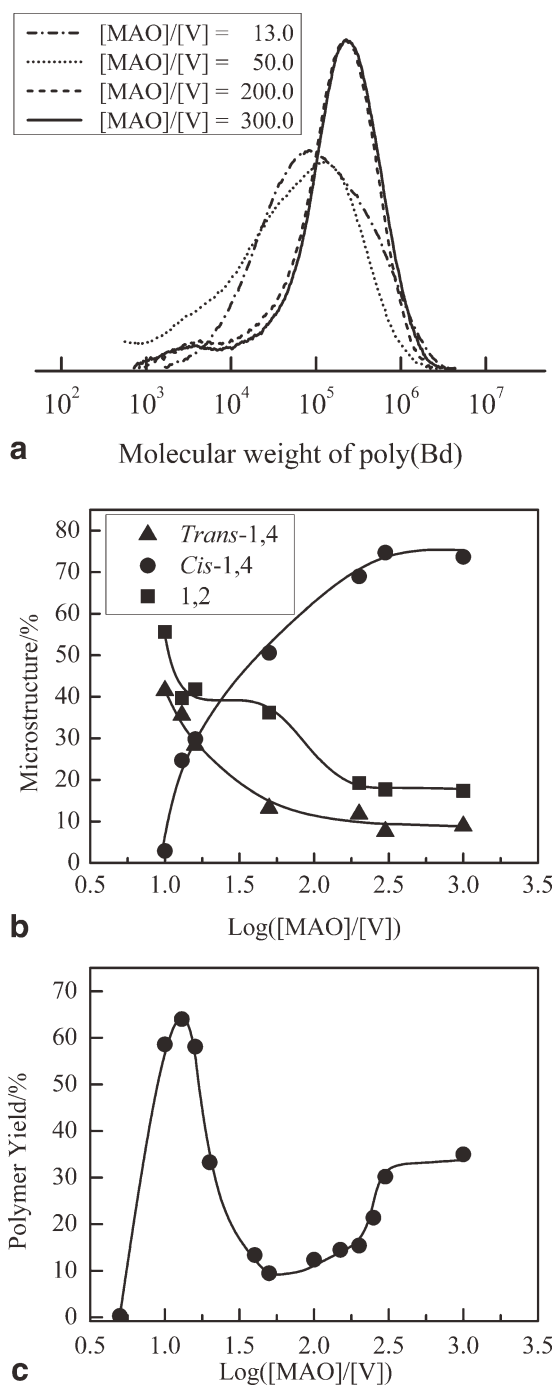

Figure 1. Effect of the [MAO]/[V] molar ratio on Bd polymerization with VO(P$_{204}$)$_2$-MAO catalyst: (a) GPC profiles, (b) microstructure, and (c) polymer yield. Polymerization conditions: 40°C for 2.0 h, [Bd] = 1.85 mol L^{-1}, [V] = 1.85 × 10^{-3} mol L^{-1}, and toluene solvent.
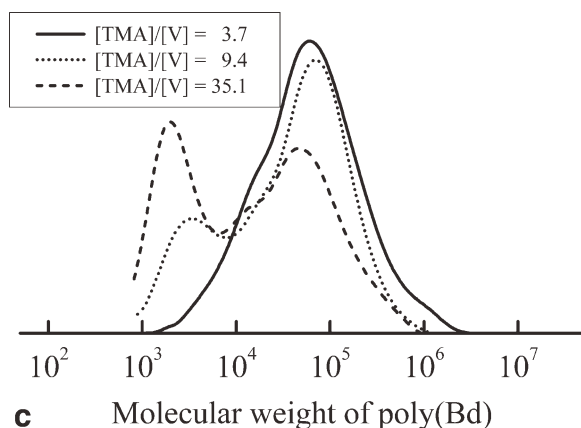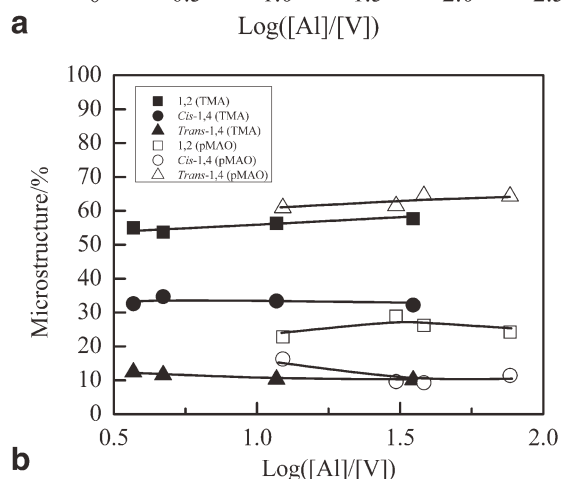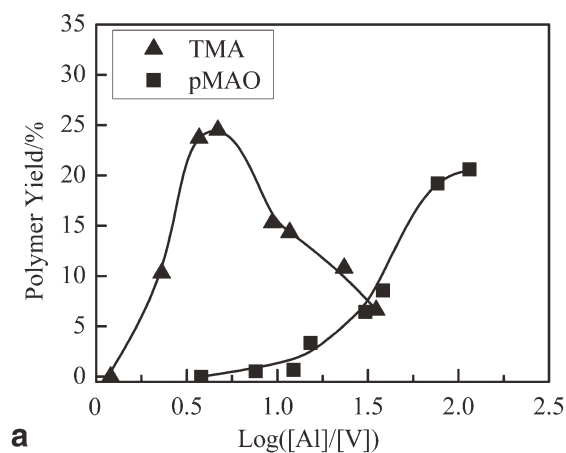
Figure 2. Effect of the [Al]/[V] molar ratio on Bd polymerization with VO(P$_{204}$)$_2$/pMAO and VO(P$_{204}$)$_2$/TMA catalysts: (a) polymer yield, (b) microstructure, and (c) GPC profiles. Polymerization conditions: 40°C for 2.0 h, [Bd] = 1.85 mol L^{-1}, [V] = 1.85 × 10^{-3} mol L^{-1}, and toluene solvent.

be obtained because the resulting poly(Bd)s were not sufficiently soluble to give a homogeneous solution in trichlorobenzene even at 150°C, which may be due to crosslinking.[40]

As shown in Figure 2(b), the microstructures of the poly(Bd)s were mixed 1,2/*cis*-1,4-unit structures for the TMA system and mainly *trans*-1,4-unit structures for the pMAO system, which were almost independent of the [Al]/[V] molar ratio. The formation of *trans*-1,4 vs. *cis*-1,4(and/or 1,2)-units with most soluble TM catalysts is well accepted to depend on the relative rate of two processes: the *anti/syn* isomerization of the η^3-allyl group and the incorporation of the coordinated monomer.[4] Therefore, the different stereospecificities of the TMA and pMAO systems may be explained by assuming that isomerization is faster than monomer incorporation in the TMA system, and the opposite occurs in the pMAO system.

Therefore, in the MAO system, the active species generated by the reactions between TMA and VO(P$_{204}$)$_2$ played a dominant role when the polymerization occurred at lower [MAO]/[V] moral ratios. In contrast, at higher [MAO]/[V] molar ratios, the multiple reactions among TMA, pMAO, and VO(P$_{204}$)$_2$ affected the catalytic activities and polymer features, leading to the observed polymeric characteristics.

Additive Effect

During the Bd polymerization with VO(P$_{204}$)$_2$-MAO catalyst, active species (especially at low [Al]/[V] molar ratios as aforementioned) were presumably generated by two types of reactions, namely, between VO(P$_{204}$)$_2$ and TMA, as well as between VO(P$_{204}$)$_2$ and pMAO. The addition of a third Lewis base component to polymerization system would give different effects on these active centers. It should be another evidence of the existing of these reactions and also give an insight to the nature of the vanadium-based catalyst systems. The influence of the addition of THF and TPP to the MAO, TMA, and pMAO systems during Bd polymerization were examined, and the results are
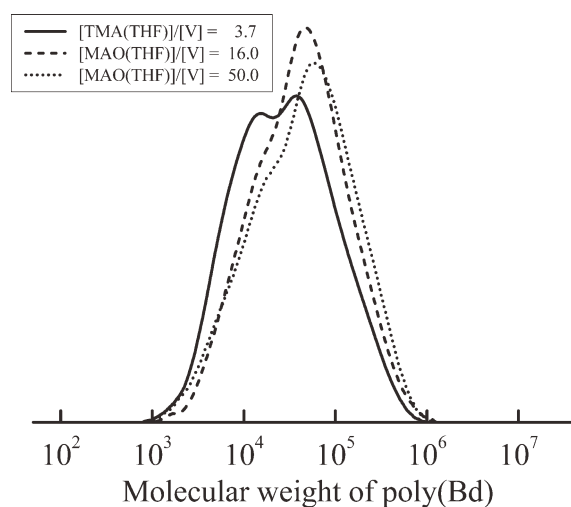
Figure 3. GPC profiles of the poly(Bd)s with VO(P$_{204}$)$_2$/MAO(THF) and VO(P$_{204}$)$_2$/TMA(THF) catalysts. Polymerization conditions: 40°C for 2.0 h, [Bd] = 1.85 mol L^{-1}, [V] = 1.85 × 10^{-3} mol L^{-1}, and [additive]/[Al] = 1.0 mol/mol, and toluene solvent.

indicated that the polymerization proceeded at two types of active centers at high a [TMA]/[V] molar ratio. In contrast, the yield of the pMAO system seemed to increase monotonically to give rise to a plateau value against the [Al]/[V] molar ratio. This result may be due to the low abundance of active sites in the pMAO structures, thus requiring the high [Al]/[V] molar ratio for polymerization.[38] However, the GPC elution profiles cannot

$$(\text{MeAlO})_6 + \text{THF} + 1/2(\text{TMA})_2 \rightarrow \{(\text{MeAlO})_6 \cdot \text{THF} \cdot \text{TMA}\} \quad \Delta E = -23.15 \text{ kcal/mol}$$

Scheme 2. One reaction among MAO cage, THF, and TMA.

summarized in Table I. The Lewis base/mono-TMA complex formed in the TMA/additive system. Although for the pMAO system, the THF/pMAO system resulted in no polymer produced. The polymers obtained by the THF/MAO system also had almost the same microstructure as those by the THF/TMA system ([Al]/[V] = 3.7). For comparison, the GPC profiles of these polymers are shown in Figure 3, and no remarkable difference was observed. These results revealed that the Bd polymerization initiated by the THF/MAO system proceeded at the same types of active centers as that initiated by the THF/TMA system obtained at lower [Al]/[V] molar ratios. A plausible explanation for this phenomenon was that in the polymerization initiated by the THF/MAO system, the vanadium precursor was actually activated by free TMA or the THF-TMA adduct, rather than the pMAO or bound TMA. Hence, because of the binding of THF to pMAO, the active species generated by the reactions between $VO(P_{204})_2$ and pMAO did not come into being, i.e., these types of reactions were deactivated. The decreased concentration of free TMA or TMA-THF adducts, as indicated by Zurek and Ziegler[38] in Scheme 2, decreases the polymer yields. On the other hand, the addition of Lewis base with bulk group (the addition of TPP) had little influence on the polymer yield of the pMAO system, lowered that of the TMA system ([TMA]/[V] = 11.7). Therefore, the Bd polymerization with the TPP/MAO system ([MAO]/[V] = 50.0) initiated by the reactions between $VO(P_{204})_2$ and pMAO. The narrow molecular weight distributions (in Table I) also indicated that the polymerization proceeded at fewer types of active centers than that in the MAO system. The poly(Bd)s obtained with the TPP/MAO system had more 1,2-units, which may be due to the active center formed

by TPP. Thus, the results of the addition of Lewis bases with the different sizes confirmed the existing of the two types of reactions in the $VO(P_{204})_2$-MAO catalyst system.

Effect of the Polymerization Temperature on the Bd Polymerization with $VO(P_{204})_2$-MAO, -pMAO, and -TMA Catalysts

The influence of the polymerization temperature on the Bd polymerization was examined when the [Al]/[V] molar ratios were 16.0, 12.3, and 3.7 for the MAO, pMAO, and TMA systems, respectively. The results are summarized in Table II, and the plot of the catalytic activity vs. temperature is shown in Figure 4. The catalytic activity in relation to the MAO system increased to give a plateau value against the polymerization temperature. In contrast, the catalytic activity in the TMA system decreased at higher polymerization temperatures. In the case of the pMAO system, the polymer yield was also found to increase with increased polymerization temperature. This finding can be explained by the disproportionation reactions of pMAO at higher temperatures, resulting in the formation of more active sites.[38] Nath et al.[23] have also observed the same results for cobalt-based catalysts. In terms of the microstructures of poly(Bd)s obtained by the MAO and TMA systems, 1,2-unit contents were found to be the most abundance microstructure for both systems. This result was evidence that TMA in the MAO solution enabled control over the polymerization at lower [MAO]/[V] molar ratios. In the pMAO system, the poly(Bd)s mainly had *trans*-1,4-units, especially when the polymerization occured at high temperatures. pMAO showed poor solubility in toluene, which led to the crosslinking in the polymer.[40]

Table II. Variation in the Polymerization Temperature for Bd Polymerization with $VO(P_{204})_2$-MAO, -TMA, and -pMAO Catalysts in Toluene for 2.0 h[a]

Cocatalyst	Temperature °C	[Al]/[V] (mol/mol)	Yield (%)	$10^{-4} M_n$	M_w/M_n	Microstructure (%)		
						Cis-1,4	1,2	*trans*-1,4
MAO	20	16.0	34.9	–	–	34.1	36.3	29.6
	40		58.1	3.36	5.24	29.8	41.8	28.4
	50		61.0	–	–	19.8	59.1	21.1
	70		63.5	1.47	6.07	13.5	57.9	28.6
TMA	20	3.7	8.9	–	–	–	–	–
	40		23.8	2.68	4.74	32.6	55.0	12.4
	50		36.3	–	–	29.3	51.3	19.4
	70		15.4	1.23	5.67	30.4	46.6	23.0
pMAO	20	12.3	0.4	–	–	–	–	–
	40		0.7	–	–	16.3	22.8	60.9
	50		7.9	n.s.[b]		12.2	21.4	66.4
	70		16.2	n.s.[b]		8.0	18.2	73.7

[a]Polymerization conditions: [Bd] = 1.85 mol L^{-1} and [V] = 1.85 × 10^{-3} mol L^{-1}.
[b]n.s. indicates not soluble. The molecular weight of the resulting poly(Bd)s was not determined because these polymers were not sufficiently soluble in trichlorobenzene to form homogeneous solutions even at 150°C.
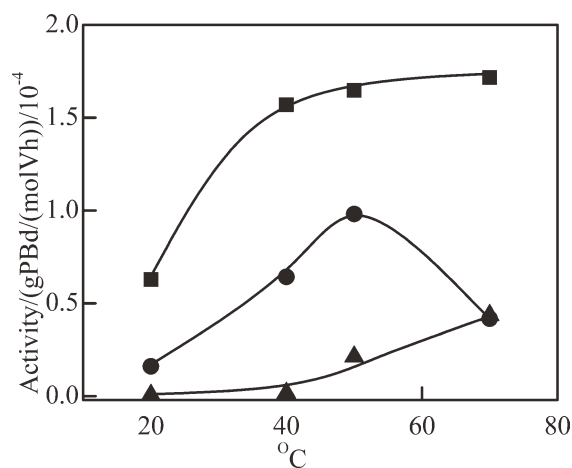
Figure 4. Effect of the variation in polymerization temperature on the activities of poly(Bd)s activated by the catalysts of VO(P$_{204}$)$_2$/MAO (■), VO(P$_{204}$)$_2$/pMAO (▲) and VO(P$_{204}$)$_2$/TMA (●). Polymerization conditions: 40°C for 2.0 h, [Bd] = 1.85 mol L^{-1}, [V] = 1.85 × 10^{-3} mol L^{-1}, [MAO]/[V] = 16.0 mol/mol, [pMAO]/[V] = 12.3 mol/mol, [TMA]/[V] = 3.7 mol/mol, and toluene solvent.

CONCLUSIONS

The effect of different aluminum-based cocatalysts (MAO, pMAO, and TMA) on Bd polymerization catalyzed by VO(P$_{204}$)$_2$ was investigated. The bimodal dependence of the polymer yield on the [MAO]/[V] molar ratio was revealed, and an highest polymer yield was achieved at a rather low [MAO]/[V] molar ratio ([MAO]/[V] = 13.0). The microstructures of the resulting poly(Bd)s were also significantly influenced by the ratio. In the TMA or pMAO system, the polymer yields were also very sensitive to the [Al]/[V] molar ratio. However, the microstructures of the resulting poly(Bd)s were almost independent of the [Al]/[V] molar ratio. As regards to the microstructures of poly(Bd)s obtained by the MAO and TMA systems at various temperatures, the 1,2-unit contents were found to be the most abundant microstructure for both systems. In the pMAO system, the *trans*-1,4-units were the most abundant. The results of the additions of Lewis bases (THF and TPP) into Bd polymerization system confirmed the existing of the two types of the reactions of VO(P$_{204}$)$_2$-MAO catalyst and had the polymerization process controlled to some extent. Upon the addition of THF, no polymer was produced by the THF/pMAO system. The polymers obtained by the THF/MAO system had almost the same microstructure as that of the THF/TMA system ([Al]/[V] = 3.7). No remarkable difference was observed from the GPC profiles of those polymers, indicating that the active species generated by the reactions between VO(P$_{204}$)$_2$ and pMAO were selectively deactivated. TPP addition had little influence on the polymer yield of the pMAO system but lowered that of the TMA system ([TMA]/[V] = 11.7). Therefore, Bd polymerization in the TPP/MAO system ([MAO]/[V] = 50.0) was selectively initiated by the reactions between VO(P$_{204}$)$_2$ and pMAO. The different thermal behaviors of these catalytic systems also indicated that multiple types of active centers were formed during the reaction between VO(P$_{204}$)$_2$ and MAO.

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