1,2-Polymerization of 1,3-Butadiene with $Cr(acac)_3$-Alkylaluminum Catalysts

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ABSTRACT: The polymerization of butadiene (Bd) with chromium(III) acetylacetonato [$Cr(acac)_3$]-trialkylaluminum (AlR_3) or methylaluminoxane (MAO) catalysts was investigated for the synthesis of 1,2-poly(Bd). The polymerization of Bd was found to proceed with $Cr(acac)_3$-AlR_3 (R-Me, Et, *i*-Bu) catalysts to give poly(Bd) with a high 1,2-vinyl content, but highly isotactic 1,2-poly(Bd) was not synthesized. The $Cr(acac)_3$-MAO catalyst gave a polymer consisting of low 1,2 units. The effects of the Al/Cr mole ratios on the polymerization of Bd with the $Cr(acac)_3$-AlR_3 catalysts were observed. With an increase of Al/Cr mole ratios, the isotactic (mm) content of the polymer increased but the 1,2-vinyl contents decreased. The effects of the aging time and temperatures of the catalysts on the polymerization of Bd with the $Cr(acac)_3$-AlR_3 catalysts were also observed, and the lower polymerization temperature and the prolonged aging time were favored to produce the 1,2-vinyl structure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1621–1627, 2000

Key words: butadiene; chromium(III) acetylacetonato; trialkylaluminum; methylaluminoxane; microstructure; 1,2-poly(butadiene)

INTRODUCTION

Stereospecific polymerizations are interesting and important from the viewpoints of polymer design and use as polymer materials. In the polymerization of butadiene (Bd), many works on stereospecific polymerization of Bd with transition metal catalysts were reported to make such polymers.[1–3] Among the isometric structures of poly(Bd), the synthesis of cis-1,4 and trans-1,4 polymers were studied extensively; e.g., *cis*-1,4-poly(Bd) was synthesized with Ziegler catalysts such as TiI_4-trialkylaluminum (AlR_3),[4,5] $CoCl_2 \cdot$ 2pyridine-Et_2AlCl,[6] and $[(\eta^3\text{-allyl})NiOCOCF_3]_2$[7] catalysts. *Trans*-1,4-poly(Bd) was prepared with $Ni(C_{12}H_{18})$-HI,[8] VCl_3-AlR_3,[9,10] and $RhCl_3$-EtOH (ref. 11) catalysts.

On the other hand, 1,2 polymerizations of Bd were also investigated. Researchers found that Cr, Mo, and Nd salts containing nonhalogen ligands favor the formation of 1,2-poly(Bd).[12–18] 1,2-Poly(Bd) has stereoregularity, as well as polyolefins; and syndiotactic 1,2-poly(Bd) was synthesized with $CoCl_2$-$AlEt_3$, $CoBr_2$-$(PPh_3)_2$-Al(i-Bu)$_3$-H_2O, $V(acac)_3$-$AlEt_3$, and $Ti(OBu)_4$-$AlEt_3$ catalysts.[12–16] Natta et al.[17,18] reported that isotactic 1,2-poly(Bd) could be synthesized from the polymerization of Bd with $Cr(CNC_6H_5)_6$-$AlEt_3$ and chromium(III) acetylacetonato [$Cr(acac)_3$]-$AlEt_3$ catalysts, depending on the polymerization conditions, but the polymers were not determined by NMR spectroscopy. To elucidate this point we investigated the polymerization of Bd with $Cr(acac)_3$ in combination with various AlR_3 compounds, including methylaluminoxane (MAO),

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and the polymer structure was estimated by NMR spectroscopy.

In this article we describe the results of the polymerization of Bd with Cr(acac)$_3$-AlR$_3$ catalysts from the viewpoint of the synthesis of 1,2-poly(Bd).

EXPERIMENTAL

Materials

The Cr(acac)$_3$ was purchased from Dojin Chem. Co. and was used without purification. Commercially available AlR$_3$ (R-Me, Et, *i*-Bu) was used without purification. MAO diluted with toluene was kindly supplied by Tosoh-Akuzo Co. and was used as received Ethylbenzoate (EB) and CS$_2$ were purified by distillation before use. Solvents were used after purification by conventional methods.

Polymerization Procedure

Polymerization was carried out in a sealed glass tube with a rubber stopper with a connection to a vacuum system. The required amounts of reagents were introduced into the tube by a syringe under a dry nitrogen atmosphere. After aging the catalyst at a constant temperature for given time, the required amount of Bd was charged. The tube was then sealed off under high vacuum. Polymerization was carried out in the sealed tube at a constant temperature for a given time. After the polymerization, the tube was opened and the contents in the tube were poured into a large amount of methanol containing a few percent of hydrochloric acid and a small amount of *p*-*tert*-butylcatechol to precipitate the polymer formed. The resulting polymers were isolated by decantation, washed with a large amount of methanol, and dried under high vacuum at room temperature. Polymer yields were determined by gravimetry.

Hydrogenation of Polymer

Hydrogenation of the polymer was carried out as follows[19]: 135 mg of the polymer dissolved in 6.0 mL of *p*-xylene was placed in a Schlenk tube. To this solution was added 3.0 g of tosyl hydrazide containing a trace amount of *p*-*tert*-butylcatechol. The mixture was then degassed twice through a freeze pump–thaw cycle and a reflux condenser was assembled under a dry nitrogen atmosphere. The Schlenk tube was heated to 110°C until a homogeneous solution was obtained, and the temperature was maintained for 2 h to proceed to complete hydrogenation. After the reaction, the product was cooled to room temperature; the contents of the tube was poured into a large amount of methanol containing a few percent of hydrochloric acid to isolate the reaction product. The product was isolated by decantation, washed with a large amount of methanol, and dried under high vacuum. The product was identified by ^{13}C-NMR spectroscopy.

Characterization of Polymers

The number- and weight-average molecular weight (M_n and M_w, respectively) and molecular weight distribution (M_w/M_n) of the polymers were estimated by GPC in THF at 38°C as calibrated with polystyrene standards. The 1,2 and 1,4 contents of the poly(Bd) were determined from its ^{1}H-NMR spectra.[20] Tacticity in the 1,2 unit of the hydrogenated polymer as poly(1-butene) was determined from the ^{13}C-NMR spectrum of the

Table I Polymerization of Bd with Cr(acac)$_3$-AlR$_3$ or MAO Catalyst in Toluene at 50°C for 5 h

						Tacticity in 1,2 Unit (%)		
Catalyst	Al/Cr Mole Ratio	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	1,2 Content (%)	mm	mr	rr
AlMe$_3$	5	78.8	6.4	2.19	70	30	15	55
AlEt$_3$	5	100	6.4	2.08	69	27	12	61
Al(*i*-Bu)$_3$	5	88.5	7.3	1.92	72	26	11	63
MAO[a]	100	74.6	2.6	1.69	8[b]	67	14	19

The general concentrations were [Bd] = 3.0 mol/L and [Cr] = 2.0×10^{-2} mol/L.

[a] [Cr] = 2.0×10^{-3} mol/L.

[b] The cis-1,4 was 65%, and the trans-1,4 was 27%.

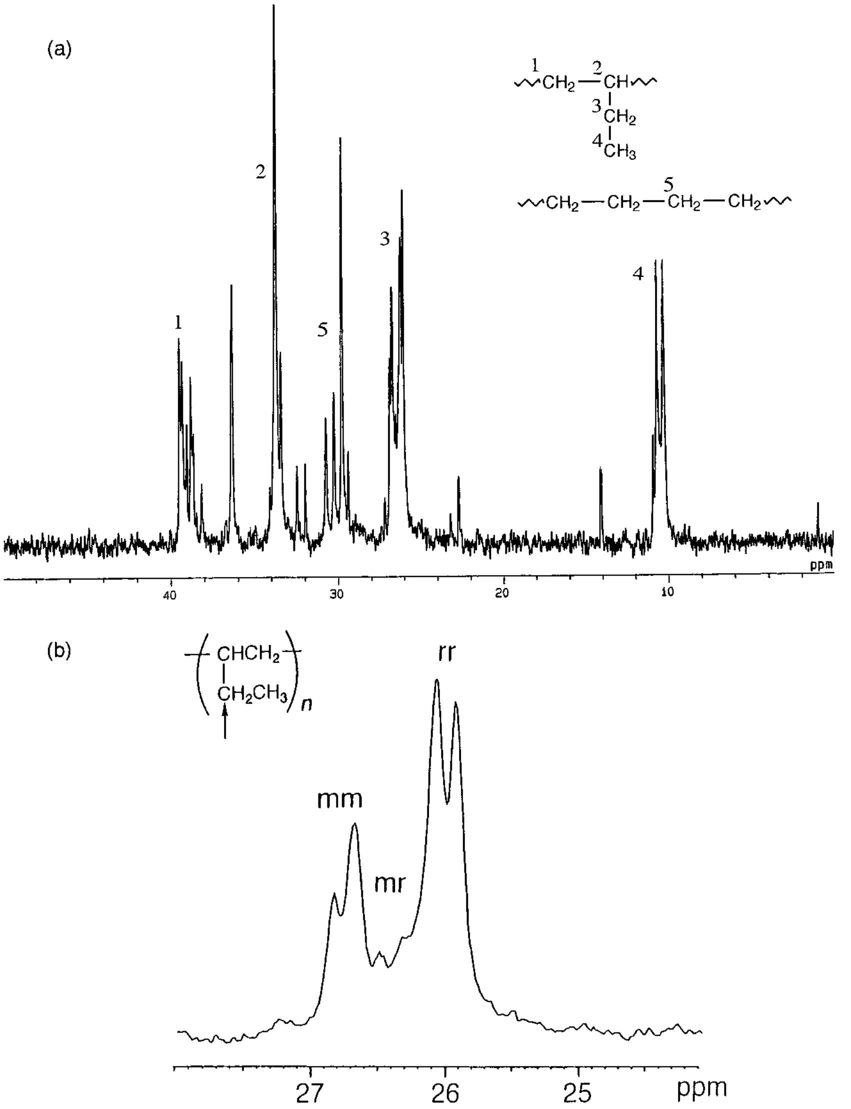

Figure 1 (a) The ^{13}C-NMR spectrum of hydrogenated poly(Bd). (b) The expanded spectrum of the methylene region of the side chain.

hydrogenated polymer.[21,22] The NMR spectra of the polymers were recorded on a Jeol JNM-A-400 FT NMR system in CDCl$_3$ solvent at 45°C.

RESULTS AND DISCUSSION

Polymerization of Bd with Cr(acac)$_3$-AlR$_3$ or MAO Catalysts

Table I shows the results of the polymerization of Bd with Cr(acac)$_3$-AlR$_3$ (R-Me, Et, *i*-Bu) and Cr(acac)$_3$-MAO catalysts. The polymerization of Bd took place easily with all catalysts examined giving polymers bearing molecular weights of 3–7 × 10^3, depending on the AlR$_3$ and MAO, and M_w/M_n of around 2. This suggests that the polymerization of Bd with these catalysts proceeded at a single active site. The polymerization activities were found to be influenced by the cocatalysts and decreased in the following order: AlEt$_3$ > Al(*i*-Bu)$_3$ >AlMe$_3$ > MAO. The catalytic activity for the polymerization of Bd with the Cr(acac)$_3$-MAO catalyst was low. This was in contrast with the previous results that the MAO revealed a higher active cocatalyst than AlR$_3$ for the polymerization of styrene and Bd with NiX$_2$ (X-ligand) in combination with alkylaluminums including MAO.[23]

The resulting poly(Bd) was hydrogenated with a tosyl hydrazide to determine the tacticity. In the ^{1}H-NMR spectra of the polymers before and after the hydrogenation, the signals at around 4.9 and 5.4 ppm based on olefinic protons of 1,2 and 1,4 units of the poly(Bd), respectively, disappeared completely after the hydrogenation of the polymers. In the ^{13}C-NMR spectra of the polymer, the peaks at 114, 130, and 143 ppm based on the olefinic carbon of the poly(Bd) disappeared completely after the hydrogenation. Accordingly, it is clear that the poly(Bd) was hydrogenated completely with the tosyl hydrazide under the reaction conditions as described in the Experimental section.

The expanded ^{13}C-NMR spectrum of the hydrogenated polymers is shown in Figure 1. The peaks at 25.0, 30.2, 34.1, and 43.6 ppm based on the isolated 1,2-vinyl (surrounded by cis-1,4 or trans-1,4 units) were very small compared with the peaks based on the 1,2-vinyl sequence appearing at 10.5, 26.8, 33.5, and 38.1 ppm as broad peaks due to splitting by the tacticity.[24] Thus, the 1,2-vinyl units in the resulting polymers seem to present mostly as a block sequence. Then the peaks appearing at around 26.8 ppm were used to estimate the tacticity of the 1,2 structure.[21,22] The triad tacticity of the polymers thus determined is also listed in Table I. Although high 1,2-vinyl content polymers were produced, stereoregular 1,2-poly(Bd) was not synthesized with the Cr(acac)$_3$-AlR$_3$ catalysts. The microstructure of the poly(Bd) obtained with the Cr(acac)$_3$-MAO catalyst was different from that obtained with the Cr(acac)$_3$-AlR$_3$ catalysts [i.e., the Cr(acac)$_3$-MAO catalyst gave a polymer with low 1,2-vinyl content]. Because we focused on the synthesis of 1,2-poly(Bd) in this study, we did not determine the cis- and trans-1,4 contents, although the signals based on the cis- and trans-1,4 structure were observed in the ^{13}C-NMR spectra of the polymers.

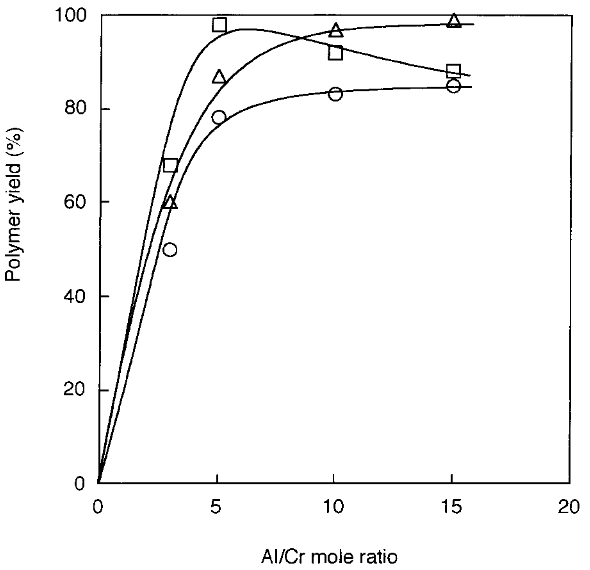

Figure 2 The relationship between the Al/Cr mole ratio and yield on the polymerization of Bd with the Cr(acac)$_3$-AlR$_3$ catalysts in toluene at 50°C for 5 h; R = (□) Me, (△) Et, (○) *i*-Bu; [Bd] = 3.0 mol/L; [Cr(acac)$_3$] = 2.0 × 10^{-2} mol/L.

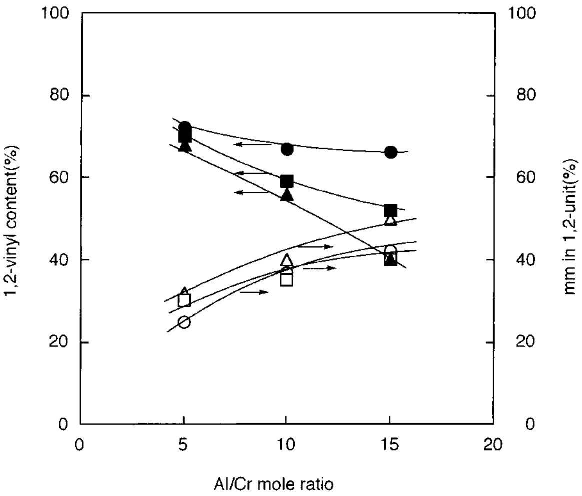

Figure 3 The relationships between the Al/Cr mole ratio and 1,2 content or tacticity of the polymer on the polymerization of Bd with the Cr(acac)$_3$-AlR$_3$ catalysts in toluene at 50°C for 5 h; R = (□, ■) Me, (△, ▲) Et, (○, ●) *i*-Bu, [Bd] = 3.0 mol/L; [Cr(acac)$_3$] = 2.0 × 10^{-2} mol/L.

Table II Polymerization of Bd with Cr(acac)$_3$-MAO Catalyst in Toluene at 50°C for 5 h

Al/Cr Mole Ratio	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	1,2 Content (%)
20	67.0	2.1	1.49	9
50	74.8	2.2	1.58	9
100	74.6	2.6	1.69	8
150	74.5	2.5	1.79	9

The concentrations were [Bd] = 3.0 mol/L and [Cr] = 2.0 × 10^{-3} mol/L.

Table III Polymerization of Bd with Cr(acac)$_3$-AlR$_3$ Catalysts in Toluene

AlR$_3$	Al/Cr Mole Ratio	Temp. (°C)	Time (h)	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	1,2 Content (%)	Tacticity in 1,2 Unit (%) mm	mr	rr
AlMe$_3$	5	0	24	41.4	8.7	1.51	80	35	29	36
″	5	50	5	78.8	6.4	2.19	70	31	15	54
AlEt$_3$	5	0	24	23.5	6.7	1.94	73	28	16	56
″	5	50	5	100	6.4	2.08	69	27	12	61
″	5	70	3	69.7	6.4	2.49	70	30	12	58

The concentrations were [Bd] = 3.0 mol/L, and [Cr] = 2.0 × 10^{-2} mol/L.

Effect of Al/Cr Mole Ratios on Polymerization of Bd with Cr(acac)$_3$-AlR$_3$ Catalysts

It was reported that the ratio component determines the prevailing isomeric structure, and the Cr(CNC$_6$H$_5$)$_6$-AlEt$_3$ catalyst gave isotactic 1,2-poly(Bd) at the Al/Cr mole ratio above 10. So, the effects of the Al/Cr mole ratios on the polymerization of Bd with the Cr(acac)$_3$-AlR$_3$ catalysts were examined. The results are shown in Figure 2. The content of 1,2 units did not significantly depend on the Al/Cr mole ratios, but the polymer yields increased with an increase of the Al/Cr mole ratio. However, highly isotactic 1,2-poly(Bd) was not synthesized with the Cr(acac)$_3$-AlR$_3$ catalysts at any Al/Cr mole ratio examined. Among the Cr(acac)$_3$-AlR$_3$ catalysts, the Cr(acac)$_3$-Al(*i*-Bu)$_3$ catalyst gave the polymer with the highest 1,2-vinyl contents.

The isotactic mm contents in the 1,2 units of the polymer against the Al/Cr mole ratios were plotted, and the results are depicted in Figure 3. The mm contents of the 1,2 units of the polymer increased with increasing the Al/Cr mole ratios, indicating that a higher Al/Cr mole ratio is favorable polymerization conditions for producing the 1,2 structure.

Effect of Al/Cr Mole Ratio on Polymerization of Bd with Cr(acac)$_3$-MAO Catalysts

The effect of the Al/Cr mole ratio on the polymerization of Bd with the Cr(acac)$_3$-MAO catalyst was examined, and the results are shown in Table II. In the polymerization of 1-olefins with metallocene-MAO catalyst, a high MAO/metallocene mole ratio (>500) is required to reach a high activity for the polymerization.[25] However, in the polymerization of Bd with the Cr(acac)$_3$-MAO catalyst, such a high MAO/Cr mole ratio was not required to reach a high catalytic activity for the

Table IV Polymerization of Bd with Cr(acac)$_3$-EB-AlR$_3$ Catalysts in Toluene at 50°C for 5 h

AlR$_3$	Al/Cr Mole Ratio	EB ($\times 10^2$ mol/L)	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	1,2 Content (%)	Tacticity in 1,2 Unit (%) mm	mr	rr
AlMe$_3$	5	—	78.8	6.4	2.19	70	31	15	54
″	5	2.0	27.2	9.5	1.50	78	27	8	65
″	15	—	88.2	4.6	2.08	51	41	19	40
″	15	2.0	69.6	2.9	2.53	45	50	16	34
AlEt$_3$	5	—	100	6.3	2.08	69	27	12	61
″	5	2.0	14.4	3.8	2.67	73	32	13	55
″	15	—	88.1	2.8	3.39	36	57	14	29
″	15	2.0	68.6	3.8	2.30	50	48	16	36

The concentrations were [Bd] = 3.0 mol/L and [Cr] = 2.0 × 10^{-2} mol/L.

Table V Polymerization of Bd with $Mt(acac)_3$-$AlMe_3$-H_2O-CS_2 Catalyst in Benzene at 40°C for 0.5 h

				Tacticity in 1,2 Unit (%)		
$Mt(acac)_3$	Al/Mt Mole Ratio	Yield (%)	1,2 Content (%)	mm	mr	rr
$Co(acac)_3$	1	4.9	100	7	8	85
$Co(acac)_3$	5	16.4	100	2	4	94
$Cr(acac)_3$	5	Trace	—	—	—	—

The total volume was 7.7 mL, and there was 1.0 mL of H_2O. The concentrations were [Bd] = 3.0 mol/L, $[CS_2] = 2.15 \times 10^{-2}$ mol/L; and $[Mt] = 2.0 \times 10^{-3}$ mol/L.

polymerization of Bd. Similar results were reported in the polymerization of Bd with NiX_2-MAO catalysts.[23] Thus, it is clear that a large amount of MAO was not required for reaching high activity for the polymerization of vinyl and diene monomers with $Mt(acac)_x$-MAO catalysts.

The M_n and the M_w/M_n of the polymers did not depend on the MAO/Cr mole ratio in the polymerization of Bd with the $Cr(acac)_3$-MAO catalyst. The microstructure of the polymers was mainly a cis-1,4 microstructure, and the 1,2-vinyl contents of the polymers was quite low as compared with the $Cr(acac)_3$-AlR_3 catalysts. We reported that $Mt(acac)_x$-MAO catalysts (Mt═V, Fe, Co, Ni) gave mainly *cis*-1,4-poly(Bd), regardless of the $Mt(acac)_x$.[23] Accordingly, it is obviously that MAO may play an important role in producing the cis-1,4 microstructure of the poly(Bd), although the distinct function of MAO is not clear.

Effect of Temperature on Polymerization of Bd with $Cr(acac)_3$-AlR_3 Catalysts

Table III shows the results for the effect of the polymerization temperature on the polymerization of Bd with the $Cr(acac)_3$-AlR_3 catalysts. Raising the reaction temperatures increased the polymerization rates, but the molecular weight of the polymers decreased. When the $AlMe_3$ was used as a cocatalyst, the effect of temperature on the 1,2-vinyl contents in the polymers was observed and the 1,2-vinyl units in the polymers obtained at 0°C were higher than those obtained at 50°C.

Effect of Additives on Polymerization of Bd with $Cr(acac)_3$-AlR_3 Catalyst

Because the addition of EB is known to enhance an isotactic fraction of the polymer in the polymerization of 1-olefins with a Ti-based catalyst,[26] the mm contents in the 1,2-vinyl units of the polymer will be expected to be increased in the polymerization of Bd by adding EB to the $Cr(acac)_3$-AlR_3 (R-Me, Et) catalysts. To check this point, the effect of EB on the polymerization of Bd with the $Cr(acac)_3$-AlR_3 catalysts was examined; the results are shown in Table IV. Adding EB to the $Cr(acac)_3$-AlR_3 catalysts increased the 1,2-vinyl contents, but the activity for the polymerization and the mm contents of the 1,2-vinyl units in the polymers decreased.

Table VI Polymerization of Bd with $Cr(acac)_3$-$AlMe_3$ Catalyst in Toluene at 50°C for 5 h

						Tacticity in 1,2 Unit (%)		
Al/Cr Mole Ratio	Aging Time (h)	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	1,2 Content (%)	mm	mr	rr
5	—	78.8	6.4	2.19	70	31	15	54
5	24	3.8	3.9	2.02	70	26	13	61
10	—	85.8	5.2	2.07	58	42	17	41
10	24	54.2	1.9	2.40	16	51	18	31
15	—	88.2	4.6	2.08	51	41	19	40
15	24	36.3	1.8	2.75	14	60	14	26

The concentrations were [Bd] = 3.0 mol/L and $[Cr] = 2.0 \times 10^{-2}$ mol/L. The catalyst was aged at 25°C.

Highly syndiotactic poly(Bd) was reported to be synthesized by the addition of CS_2 to the $CoBr_2(PPh_3)_2$-$AlEt_3$-H_2O catalyst in the polymerization of Bd.[13] So, the additive effect of H_2O and CS_2 to the Mt(acac)$_x$-AlR_3 catalyst on the polymerization of Bd was examined, and the results are shown in Table V. Although the Co(acac)$_3$-$AlMe_3$-H_2O-CS_2 catalyst gave a highly 1,2-poly(Bd) with highly syndiotactic content, which is consistent with the previously reported results for the polymerization of Bd with Co-based catalysts,[13] such behavior was not observed with the Cr(acac)$_3$-$AlMe_3$-H_2O-CS_2 catalyst and it gave a trace polymer.

Effect of Catalyst Aging on Polymerization of Bd with Cr(acac)$_3$-AlR_3 Catalyst

Natta et al.[17] pointed out that the stereoregularity of the poly(Bd) depended on the catalyst aging time in the polymerization of Bd with the Cr-based catalyst, and isotactic 1,2-poly(Bd) was synthesized by a longer aging time. The effects of the catalyst aging on the polymerization of Bd with the Cr(acac)$_3$-$AlMe_3$ catalyst were examined, and the results are listed in Table VI. At the Al/Cr mole ratio of 5, the 1,2 contents and the mm contents of the polymer did not depend on the aging time of the catalyst. At the Al/Cr mole ratio of 10–15, the mm contents in the 1,2 units of the polymer increased with an increase of the aging time. Thus, we presumed that the active species for producing the isotactic poly(Bd) are a lower valence of Cr and more stable than that for the syndiotactic polymer in the polymerization of poly(Bd) with the Cr(acac)$_3$-$AlMe_3$ catalyst.

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