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# Communications to the Editor

## Methylaluminoxane as a New Catalyst for Alternating Copolymerization between 1,3-Butadiene and Methyl Methacrylate

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**Introduction.** It was reported that alternating copolymerizations between a conjugated diene and a polar vinyl monomer could be promoted by Lewis acidic catalysts such as ethylaluminum dichloride ($EtAlCl_2$), $EtAlCl_2$/vanadium trichloride oxide ($VOCl_3$), triethylaluminum ($Et_3Al$)/chromyl chloride ($CrO_2Cl_2$), aluminum trichloride ($AlCl_3$)/vanadium trichloride oxide ($VOCl_3$)/benzoyl peroxide (BPO), etc.[1−3] Among the alternating copolymers, for instance, poly(1,3-butadiene (BD)-*alt*-acrylonitrile (AN)), poly(BD-*alt*-methyl methacrylate (MMA)), poly(isoprene-*alt*-AN), etc., poly(BD-*alt*-AN) was the most investigated one.[4] This is due to poly(BD-*alt*-AN) possessing higher tensile strength than that of the corresponding random copolymer prepared with a radical initiator.[5] However, such a copolymer has not been commercially produced so far. The reasons may be attributed to large amounts of catalyst required, insufficient activity, and the high content of halogen compounds in the product. Therefore, finding of more efficient catalysts for the alternating copolymerization is still one of the very important objectives in the field of synthetic rubbers.

Methylaluminoxane (MAO) is well-known as an effective cocatalyst for metallocene-based olefin polymerizations.[6] We have focused on MAO as a new catalyst for the alternating copolymerization, because it is a Lewis acid without any halogen atoms. We have surprisingly found that MAO can promote the copolymerization between conjugated dienes and polar vinyl monomers in good yield at room temperature. In this communication, it is reported that an alternating copolymerization between BD and MMA could be achieved in high yield with a high degree of alternation using MAO alone as a catalyst.

**Experimental Section. a. Materials.** Toluene was commercially obtained from Kanto Chemicals Co., Japan, and purified according to the usual procedures.[7] 1,3-Butadiene (BD) of polymerization grade (>99.5%), donated by Nippon Zeon Co., Japan, was distilled over triethylaluminum just prior to use. Methyl methacrylate (MMA) was commercially obtained from Kanto Chemicals Co., Japan, dried over $CaH_2$ for 12 h and distilled under a reduced pressure. MAO (2.95 M in toluene) and trimethylaluminum (TMA) were donated by Tosoh Akzo Co., Japan, and used without further purifications.

**b. Polymerization Procedure.** Copolymerizations of BD and MMA were conducted under dry nitrogen atmosphere at 25 °C in a 150 $cm^3$ glass ampule sealed with a rubber septum. Measured amounts of toluene, MMA, and BD were introduced into the ampule in this order. Copolymerizations were initiated by injecting a measured amount of MAO and terminated by adding a small portion of acidic methanol. The resulting polymer was collected by precipitation into a large amount of acidic methanol containing 2,6-di-*tert*-butyl-4-methylphenol (1.0 wt %) as an antioxidant reagent. For further purification, the crude polymer was dissolved again in chloroform. The solution included insoluble part, which was filtered off. The chloroform-soluble and -insoluble parts were reprecipitated independently into a large

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**Table 1. Results of the Copolymerization between 1,3-BD and MMA Using MAO as a New Catalyst[a]**

| runs | catalyst | [Al] (mol/L) | [BD] (mol/L) | [MMA] (mol/L) | $f_{BD}$[b] (mol %) | yield (wt %) | activity (g pol/mol [Al] h) | $M_w$[c] ($\times 10^{-5}$) | $M_w/M_n$[c] | $F_{BD}$[d] (mol %) | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MAO | 0.005 | 0.01 | 0.10 | 9.1 | 2.0 | 30 | 6.1 | 3.2 | 49.8 | −6.7 |
| 2 | MAO | 0.005 | 0.05 | 0.10 | 33.3 | 7.0 | 89 | 9.0 | 4.5 | 48.1 | −6.0 |
| 3 | MAO | 0.010 | 0.10 | 0.10 | 50.0 | 20.0 | 154 | 12.1 | 4.1 | 49.6 | −5.4 |
| 4 | MAO | 0.010 | 0.10 | 0.05 | 66.6 | 12.5 | 65 | 7.2 | 3.8 | 50.4 | −6.5 |
| 5 | MAO | 0.010 | 0.10 | 0.01 | 90.9 | 6.0 | 19 | 8.0 | 4.1 | 51.3 | −7.3 |
| 6 | TMA | 0.010 | 0.10 | 0.10 | 50.0 | 0 | 0 | | | | |
| *e* | $EtAlCl_2/VOCl_3$ | 0.080 | 0.80 | 0.80 | 50.0 | 11.7 | 14 | 0.57 | | | |

[a] Toluene, 30 cm$^3$; polymn temp, 25 °C; polymn time, 2 h. [b] Mole fraction of BD in the feeds. [c] Determined from the GPC peak on the basis of a standard polybutadiene calibration curve. [d] Mole fraction of BD in the copolymers. [e] Solvent, dichloromethane; [$VOCl_3$], 4 mmol/L; polymn temp, 0 °C; polymn time, 25 h (ref 8).

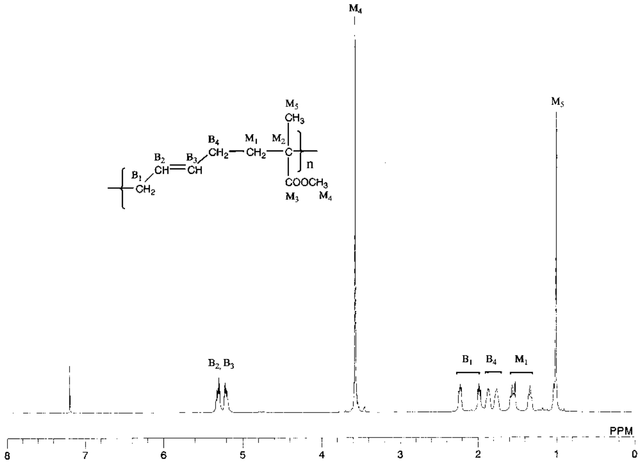

**Figure 1.** $^1H$ NMR spectrum of BD/MMA alternating copolymer (run 3).

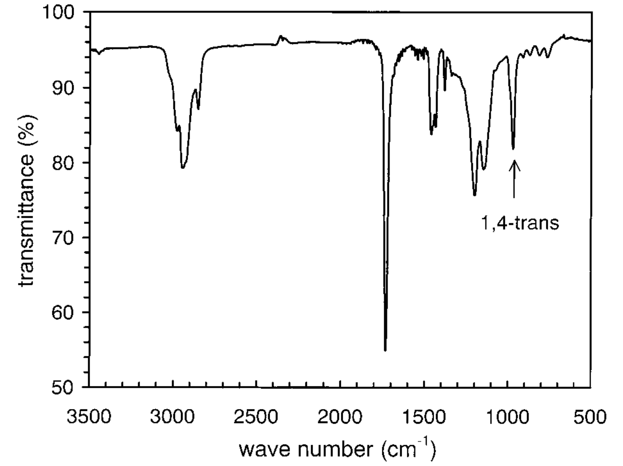

**Figure 2.** IR spectrum of BD/MMA alternating copolymer (run 3).

amount of the above methanol solution. Then those were dried under reduced pressure in vacuo at 60 °C for 8 h. Polymer yields were calculated as the percentage of the weight of whole polymer against the weight of monomers used.

**c. Polymer Characterization.** Weight-average molecular weights ($M_w$) and molar mass distributions ($M_w/M_n$) of the polymers were measured by gel permeation chromatography operated at 40 °C using chloroform as the solvent and calibrated with polybutadiene standards (Polymer Laboratories Co. Ltd.). Tosoh HLC8120, which was equipped with G4000, G5000, and G7000 (Tosoh Co., Japan) as a set of column, was used as an instrument. $^1H$ (600 MHz) and $^{13}C$ NMR (150 MHz) spectra were recorded on a JEOL LA 600 NMR spectrometer in $CDCl_3$ at room temperature. IR spectra were recorded on a Perkin-Elmer Paragon 1000 using KBr disks. For NMR, GPC, and IR measurements, chloroform-soluble parts of polymerization products were used as samples. The glass transition temperatures ($T_g$) of the whole polymer products were measured by a differential scanning calorimeter (Seiko DSC220C) at a heating rate of 10 °C/min.

**Results and Discussion.** Copolymerizations of BD and MMA were performed at 25 °C in toluene using MAO as the catalyst. Typical results are shown in Table 1. The data obtained with $EtAlCl_2/VOCl_3$,[8] which was the most active catalyst system reported so far, are also included for reference. When MAO was added into the ampule, the polymerization solution gradually became viscous and was difficult to be stirred after 2 h. It is apparent from Table 1 that the polymer yields are strongly dependent upon the molar ratios of two monomers in the feed ($f_{BD}$), reaching a maximum at $f_{BD} = 50$ mol % (run 3). The polymerization activity is about 10-fold higher than that obtained with the $EtAlCl_2/VOCl_3$ catalyst system.

The resulting polymers included the chloroform-insoluble parts, whose percentages varied from 40 to 60 wt % against the total products. The insoluble part was rubbery and gave the transparent gel swollen with much chloroform. Thus, this part is estimated to be extremely high molecular weight polymer with less cross-linking. DSC analyses were performed for the whole products. For all samples, only one glass transition was observed at about −6 °C without those of homopoly(BD) (−83 °C for 1,4-trans and −95 °C for 1,4-cis) and homo-poly(MMA) (104 °C). The result indicates that homopolymers were not produced in the present polymerization system.

Chloroform soluble parts were characterized by GPC, IR, and NMR measurements. It was found that the molecular weights of copolymers were very high as compared to those of $EtAlCl_2/VOCl_3$-based ones. However, the molar mass distributions were relatively broadened. The $^1H$ NMR spectrum of the copolymer (run 3) is illustrated in Figure 1. Signals appearing around 5.1−5.4 ppm ($B_2$, $B_3$) and 3.6 ppm ($M_4$) can be assigned to olefinic methine protons in 1,4-BD units and methoxy protons in MMA units. The BD content in the copolymers ($F_{BD}$) was estimated from the intensity ratio of these signals. As shown in Table 1, the $F_{BD}$ values were almost 50 mol % regardless of the $f_{BD}$ values. Minor signals observed around 4.8 ppm in Figure 1 might be arisen from 1,2-BD units, the content of which is calculated to be less than 1.5%. The geometric isomerism of 1,4-BD units, i.e., 1,4-cis and 1,4-trans, could be estimated from the characteristic absorptions at 738 and 967 cm$^{-1}$ in the IR spectrum, respectively.[9] The IR spectrum of the copolymer (run 3) shown in Figure 2

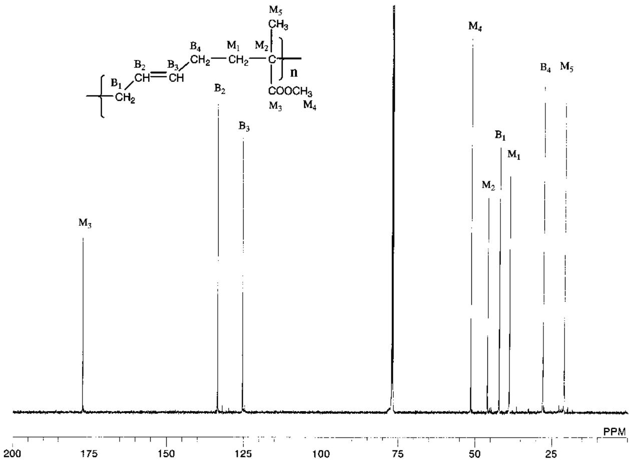

**Figure 3.** $^{13}C$ NMR spectrum of BD/MMA alternating copolymer (run 3).

reveals that the 1,4-BD units have predominantly 1,4-trans microstructure.

The main signals appearing in the $^{1}H$ and $^{13}C$ NMR spectra (Figures 1 and 3) were assigned with the aid of the $^{1}H\{^{13}C\}$-COSY and $^{1}H$-homodecoupling techniques, and the symbols defined therein are ascribed for the 1,4-trans BD and MMA units. It is worth noting that the $^{13}C$ NMR spectrum of the copolymer (run 3) has only nine sharp signals. From the result, it is obvious that the copolymer has exclusively 1,4-trans microstructure and an extremely high degree of alternation. Moreover, judging from the fact that the absence of splitting of signals arisen from $M_5$ and $M_3$ carbons, which normally indicates a structural defect of MMA units,[10] the MMA units may also have a controlled head-to-tail structure and a high stereo regularity (isotactic or syndiotactic).

To check the effect of free trimethylaluminum (TMA), which is always present in MAO (ca. 15 mol %), a copolymerization was conducted with TMA alone (run 6). However, no polymer was obtained. The result strongly supports the fact that aluminoxane plays an important role for the alternating copolymerization reaction. Furukawa et al. postulated previously that the alternating copolymerizations between a conjugated diene and a polar vinyl monomer proceeded through the formation of a ternary complex between those monomers and a Lewis acid.[1] In the present system, a ternary complex between BD, MMA, and MAO may be formed. However, it is difficult to clarify the precise mechanism due to the lack of direct information on the structure of MAO.[11]

In conclusion, MAO was found for the first time to be a highly active catalyst for the copolymerization between BD and MMA at room temperature. The resulting copolymer has an extremely high degree of alternation.

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## References and Notes

(1) Furukawa, J. In *Encyclopedia of Polymer Science & Engineering*, 2nd ed.; John Wiley & Sons: New York, 1986; Vol. 4, pp 223−261 and references therein.
(2) Cowie, J. M. G. *Alternating Copolymers*; Plenum: New York, 1985; Chapter 2.
(3) Furukawa, J. *J. Polym. Sci., Symp.* **1975**, No. 51, 105.
(4) (a) Furukawa, J.; Iseda. Y.; Haga, K.; Kataoka, N. *J. Polym. Sci., Part A-1* **1970**, *8*, 1147. (b) Furukawa, J.; Kobayashi, E.; Iseda, Y. *Polym. J.* **1970**, *1*, 155. (c) Furukawa, J.; Iseda, Y.; Kobayashi, E. *Polym. J.* **1971**, *2*, 337. (d) Furukawa, J.; Kobayashi, E.; Iseda, Y. *J. Polym. Sci., Part B* **1970**, *8*, 47.
(5) Furukawa, J. In 13th Annual Meeting of the Inter. Ins. Synth. Rub. Producer, June 19−22, 1972, Munich, Germany.
(6) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.
(7) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.
(8) Furukawa, J.; Arai, Y.; Kobayashi, E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2243.
(9) Anzai, S.; Irako, K.; Onishi, A.; Furukawa, J. *Kobunshi Kagaku Zasshi* **1969,** *72*, 2081.
(10) Deng, H.; Shiono, T.; Soga, K. *Macromolecules* **1995**, *28*, 3067.
(11) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993,** *115*, 4971 and references therein.

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