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Isotactic Polymerization of *tert*-Butyl Acrylate with Chiral Zirconocene

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Recently, the isotactic polymerization of methyl methacrylate (MMA) was realized using 4B metallocene catalysts,[1] which show a living character in the presence of an alkylzinc compound in toluene.[2] The stereochemistry of the polymerization is controlled by the chirality of the propagating site,[3] which differs from the chain end control mechanism.[4] On the other hand, isotactic poly(MMA) (PMMA) can be synthesized using organolanthanide metallocene, which shows a different stereocontrol mechanism.[5]

In anionic polymerization, it is difficult to obtain an isotactic acrylic polymer under mild conditions, because the acidic hydrogens in the α-position make alkyl acrylate monomers behave differently from MMA.[6] On the other hand, group transfer polymerization (GTP) can give living polymers of alkyl acrylates[7] that display random tacticity. Some lanthanocene catalysts were reported to afford atactic poly(alkyl acrylates) with narrow molecular mass distributions.[8]

We report herein the development of a new initiating system for the synthesis of isotactic poly(*tert*-butyl acrylate) (P-tBA) and PMMA catalyzed by typical C_2 symmetrical *ansa*-zirconocene catalysts.

Results and Discussion. Polymerization of tBA was carried out at 0 °C in toluene or in CH_2Cl_2 with the *rac*-$Et(Ind)_2ZrMe_2/Ph_3CB(C_6F_5)_4$ catalyst using $ZnEt_2$ as the activator, and no polymer was obtained. When (bis(2,6-di-*tert*-butyl-4-methylphenoxy)methyl)aluminum (BMA) was used in place of $ZnEt_2$, however, P-tBA was produced in both solvents. The results of the polymerization are displayed in Table 1, indicating that the use of CH_2Cl_2 as the solvent gives P-tBA with a narrower molecular mass distribution (MMD) in higher yield. Together with the ^{13}C NMR spectrum (Figure 1), it is obvious that highly stereoregular polymer with high molecular weight was obtained in both solvents. For reference, the polymerization of MMA was also conducted with the same catalyst using CH_2Cl_2 as the solvent (Table 1). Judging from the MMDs of both types of polymers, there is a possibility that some transfer or

Table 1. Results for the Polymerization of Acrylates[a]

run no.	monomer	solvent	[Al][b] (mM)	polym time (h)	yield[c] (%)	M_n[d] ($\times 10^3$)	M_2/M_n[d]	N/[Zr][e] (%)
1	tBA	toluene	105	24	6	48.0	2.20	12
2	tBA	toluene	60	17	13	44.0	1.91	26
3	tBA	toluene	30	17	13	48.3	1.68	24
4	tBA	CH_2Cl_2	30	17	46	76.9	1.30	52
5	tBA	CH_2Cl_2	15	17	60	70.4	1.23	80
6	MMA[f]	CH_2Cl_2	60	17	70	125	1.24	52
7	MMA	CH_2Cl_2	15	17	100	125	1.20	75

[a] Polymerization conditions: [*rac*-$Et(Ind)_2ZrMe_2$] = [$Ph_3CB(C_6F_5)_4$ = 0.25 mM, $[tBA]_0$ = 0.17 M. [b] (Bis(2,6-di-*tert*-butyl-4-methylphenoxy)methyl)aluminum. [c] Yield = weight of polymer/weight of monomer introduced. [d] Measured by GPC. [e] Calculated from polymer yield and molecular weight. [f] Methyl methacrylate: $[MMA]_0$ = 0.23 M.

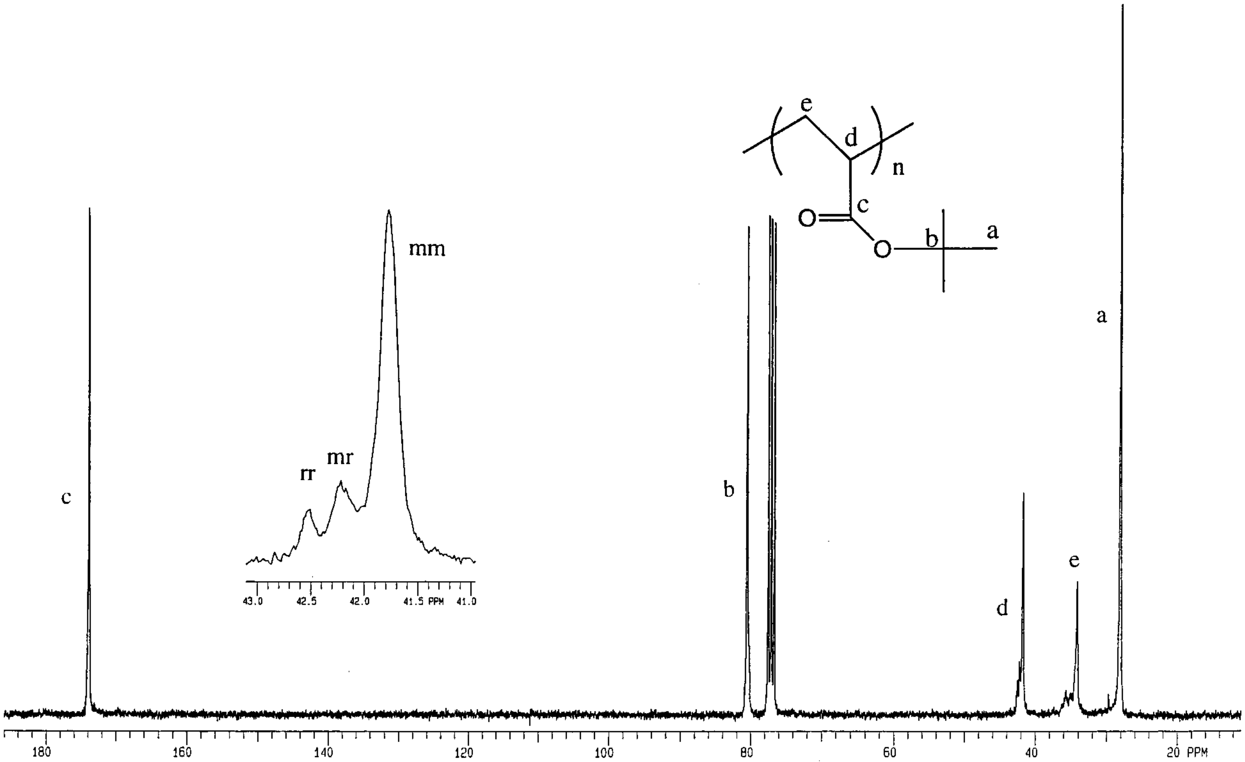

Figure 1. 75 MHz ^{13}C NMR spectrum of poly(tBA) obtained in toluene (no. 3 in Table 1).

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Table 2. Steric Triad Content (%) of P-tBA and PMMA[a]

run no.	monomer	solvent	[mm]	[mr]	[rr]
3	tBA	toluene	74.2	18.4	7.4
5	tBA	CH_2Cl_2	60.9	26.6	12.5
8[b]	tBA	toluene	75.9	15.7	8.4
7	MMA	CH_2Cl_2	97.0	2.0	1.0

[a] The triad contents in P-tBA and PMMA were measured by ^{13}C NMR and ^{1}H NMR, respectively. [b] Obtained with *rac*-$Me_2Si(Ind)_2ZrMe_2$; the other conditions are similar to those for no. 3.

termination reactions take place in the present polymerizations. By neglecting them, however, we have estimated the catalyst efficiency (N/[Zr]) from the polymer yield and molecular weight (Table 1). The catalyst efficiency seems to be not so different for the two monomers. In the case of MMA, the efficiency is higher than that observed using $ZnEt_2$ in toluene.[2]

Figure 1 shows the ^{13}C NMR spectrum of the P-tBA obtained in toluene. The resonance assigned to the methine of P-tBA at about 41 ppm splits into three peaks, which can be assigned to the mm, mr, and rr triads, respectively.[9] The isotacticity ([mm]) of P-tBA thus estimated is shown in Table 2. The use of *rac*-$Me_2Si(Ind)_2ZrMe_2$ gave a similar result (run no. 8). The stereoregularity of P-tBA is much lower than that in PMMA ([mm] $\sim$ 97%). Such a difference may originate from lower steric hindrance at the α-position of tBA. The glass transition temperature of P-tBA obtained in run no. 3 was approximately 41 °C, which is higher compared with that of P-tBA (35 °C) obtained by an anionic polymerization.[10]

From Table 2, it can be roughly concluded that [mr] = 2[rr], suggesting that this polymerization also proceeds by a site-controlled mechanism.[1,2]

Experimental Section. Monomers (MMA, tBA) and toluene was dried over calcium hydride and distilled before use. *rac*-$Et(Ind)_2ZrMe_2$,[11] *rac*-$Me_2Si(Ind)_2ZrMe_2$,[11] and $MeAl[OPh(tBu)_2Me]_2$[12] were synthesized according to the literature. $Ph_3CB(C_6F_5)_4$ was donated from Tosoh Akzo Co. Ltd. The other chemicals (research grade) were purchased from commercial sources and used without further purification.

Polymerizations were carried out under a dry nitrogen atmosphere in a 100 mL round-bottomed flask equipped with a magnetic stirrer. A typical polymerization process is as follows: toluene (16.5 mL), tBA (0.5 mL), and a 0.30 M toluene solution of BMA (1.0 mL) were injected into the flask, and the mixture was stirred for 10 min at 0 °C. After the addition of a 5.0 mM toluene solution of $Ph_3CB(C_6F_5)_4$ (1.0 mL), a 5.0 mM toluene solution of *rac*-$Et(Ind)_2ZrMe_2$ (1.0 mL) was immediately injected to start the polymerization. The polymerization was quenched at 0 °C with methanol mixed with hydrochloric acid. The polymer produced was precipitated into methanol, followed by drying in vacuo at 40 °C for 8 h.

The molecular weight and molecular mass distribution were measured by GPC (Shimadzu 9A) at room temperature using chloroform as the solvent and calibrated with PMMA standards. The glass transition temperature (T_g) was measured with a Seiko DSC-220C calorimeter at a heating rate of 10 °C/min. The ^{13}C NMR spectra were measured in chloroform-*d* at room temperature with a Varian 300 NMR spectrometer. Broad-band decoupling was used to remove the $^{13}C-^{1}H$ coupling. The center peak of chloroform-*d* was used as an internal reference (77.0 ppm).

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