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Isotactic copolymerization of methyl methacrylate (MMA) with alkyl acrylates

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Summary

Copolymerization of methyl methacrylate(MMA) and alkyl acrylates [t-butyl(tBA) and 2-ethylhexyl(OA)] was realized from a short living pre-PMMA. The poly(MMA-co-tBA) and poly(MMA-co-OA) obtained with rac-$Me_2Si(Ind)_2ZrMe_2$ were characterized as random isotactic copolymers. Whereas, corresponding syndio-rich atactic random copolymers were obtained with Cp_2ZrMe_2.

Introduction

Recently, highly isospecific polymerization of methyl methacrylate(MMA) has been realized with a C_2 symmetrical ansa-zirconocene (1), while the syndio-rich PMMA is obtained with Cp_2MtMe_2(Mt = Zr, Hf) (2). The stereochemistry in the isotactic polyinsertion is proved to be controlled by the chirality of propagating site. The mechanism differs from the chain end-controlled mechanism in the isotactic polymerization catalyzed by Grignard reagents (3).

The living polymerization of alkyl acrylates has been realized by the group transfer polymerization(GTP), which results in syndiotactic polymers via a chain end-controlled mechanism(4,5). Yasuda et al.(6) recently reported that some lanthanocene catalysts also afford to produce atactic poly(alkyl acrylate) and poly(MMA-b-alkyl acrylate). However, isotactic random copolymerization of MMA and alkyl acrylates has not been reported yet.

This paper reports the first example on the isotactic random copolymerization of MMA and some alkyl acrylates catalyzed by a C_2 symmetrical ansa-zirconocene.

Experimental

Monomers(MMA, tBA, MA and OA) and toluene were dried over calcium hydride and distilled before use. Cp_2ZrMe_2 (7) and rac-$Me_2Si(Ind)_2ZrMe_2$ (8) were synthesized according to the literatures. $ZnEt_2$ and $Ph_3CB(C_6F_5)_4$ were donated from Tosoh Akzo Co. Ltd. The other chemicals (research grade) were purchased from commercial sources and used without further purification.

Copolymerizations were carried out under dry nitrogen atmosphere in a 100 mL round-bottomed flask equipped with a magnetic stirrer. Typical polymerization process is as follows: toluene(16 mL), MMA(1.0 mL) and 2.0 M toluene solution of $ZnEt_2$(1.0 mL) were injected into the flask, and the mixture was stirred for 1 h at 0 °C. After the addition of 5.0 mM toluene solution of $Ph_3CB(C_6F_5)_4$(1.0 mL), 5.0 mM toluene solution of rac-$Me_2Si(Ind)_2ZrMe_2$ (1.0 mL) was immediately injected to start the pre-polymerization. After a defined time, tBA(0.5 mL) or other acrylates was injected into the system allowing to be copolymerized with MMA for 24 h. The copolymerization was quenched at 0 °C with

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methanol mixed with hydrochloric acid. The polymer produced was precipitated into methanol, followed by drying in vacuo at 60 °C for 8 h.

The molecular weight and molecular mass distribution were measured by GPC (Shimazu 9A) at room temperature using chloroform as the solvent and calibrated with standard PMMAs. The glass transition temperature (Tg) 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 JEOL GX-400 NMR spectrometer. Broad band decoupling was used to remove the ^{13}C-^{1}H coupling. The center peak of chloroform-d was used as internal reference(77.0 ppm).

Results and discussion

Three kinds of alkyl acrylates were employed in the present study, i.e. methyl acrylate(MA), t-butyl acrylate(tBA) and 2-ethylhexyl acrylate(OA). Polymerization was conducted using the equimolar mixture of rac-$Me_2Si(Ind)_2ZrMe_2$ and $Ph_3CB(C_6F_5)_4$ in the presence of $ZnEt_2$ as reported previously(1). The results of copolymerization are summarized in Table 1. Homopolymerizations of these acrylates did not give any polymer under similar conditions. The copolymerization starting from the mixture of MMA and tBA gave no polymer. However, when MMA was prepolymerized for 3 h before additon of acrylate monomers, polymerization ran smoothly, indicating that the initiation is difficult in the presence of acrylate monomers. The copolymerizations of MMA with tBA and OA from the propagating species of PMMA resulted in the corresponding copolymers with high molecular weights (Runs No.4, 6), whereas the polymerization of the mixture of MMA and MA gave only PMMA.

Figure 1 shows the ^{13}C NMR spectra of poly(MMA-co-tBA) and poly(MMA-co-OA) obtained with rac-$Me_2Si(Ind)_2ZrMe_2$. The signals assignable to tBA units(e.g. 22.8 ppm for $OC(\underline{C}H_3)_3$) and OA units(e.g. 13.3 ppm for $(CH_2)_3\underline{C}H_3$) are observed. The results together with the higher polymer yields and the higher molecular weights relative to the prepolymer(Run No.1), indicate the formation of copolymers.

Table 1. Copolymerization of MMA with alkyl acrylates [a].

Run No.	Catalyst[b]	Prepolym. time (h)	$CH_2CHCO_2\underline{R}$ (mL)	Yield [c] (g)	M_n [d] ($\times 10^3$)	M_w/M_n [d]
1[e]	rac-$Me_2Si(Ind)_2ZrMe_2$	3.0	-------	0.05	4.4	1.35
2	rac-$Me_2Si(Ind)_2ZrMe_2$	3.0	methyl	0.14	137	1.63
3	rac-$Me_2Si(Ind)_2ZrMe_2$	3.0	t-butyl	0.10	142	1.57
4	rac-$Me_2Si(Ind)_2ZrMe_2$	3.0	t-butyl	0.13	133	1.63
5	rac-$Me_2Si(Ind)_2ZrMe_2$	6.5	t-butyl	0.18	175	1.57
6	rac-$Me_2Si(Ind)_2ZrMe_2$	3.0	2-ethylhexyl	0.10	141	1.28
7[e]	Cp_2ZrMe_2	2.5	-------	0.07	5.2	1.40
8	Cp_2ZrMe_2	2.5	t-butyl	0.24	106	1.50
9[f]	Cp_2ZrMe_2	2.5	2-ethylhexyl	0.11	65	1.90
10	Cp_2ZrMe_2	2.5	2-ethylhexyl	0.36	117	1.80

a) $[MMA]_0 = 0.47$ M, copolymerization was carried out for 24 h at 0°C after the addition of alkyl acrylate. b) 1) $[Me_2Si(Ind)_2ZrMe_2]_0 = [Ph_3CB(C_6F_5)_4]_0 = 0.25$ mM, $[ZnEt_2]_0 = 98$ mM; 2) $[Cp_2ZrMe_2]_0 = [Ph_3CB(C_6F_5)_4]_0 = 0.50$ mM, $[ZnEt_2]_0 = 4.3\times 10^2$ mM. c) Yield = weight of polymer obtained. d) Measured by GPC calibrated with PMMA standards. e) polymerization of MMA for 3.0 h with $Me_2Si(Ind)_2ZrMe_2$, and 2.5 h with Cp_2ZrMe_2 respectively. f) $[MMA]_0 = 0.14$ M.

Table 2. Content of alkyl acrylates in the copolymer.

Run No.	Feed of Alkyl Acrylates (ml)	Content (%)[a]	
		MMA	Alkyl Acrylate
2	0.5	100	0.0
3	0.2	94.5	5.5
4	0.5	89.0	11.0
5	0.5	95.0	5.0
6	0.5	93.8	6.2
8	0.5	86.2	13.8
9	0.5	70.0	30.0
10	0.5	90.0	10.0

a) Calculated from the ^{13}C NMR spectra according to the relative intensities of the methyl resonances of MMA and alkyl acrylates.

A more detail analysis of the resonance in the carbonyl region (Figure 2) suggests that highly isotactic PMMA segments are formed in the copolymer, where a new weak peak (indicated by an arrow) is observed close to the mmmm resonance which might be caused by the effect from the tBA unit. On the other hand, when the content of tBA is low, only one peak assignable to the carbonyl of tBA is observed at 174.9 ppm (Figure 2(B)), implying that the tBA units distribute randomly in the PMMA segments.

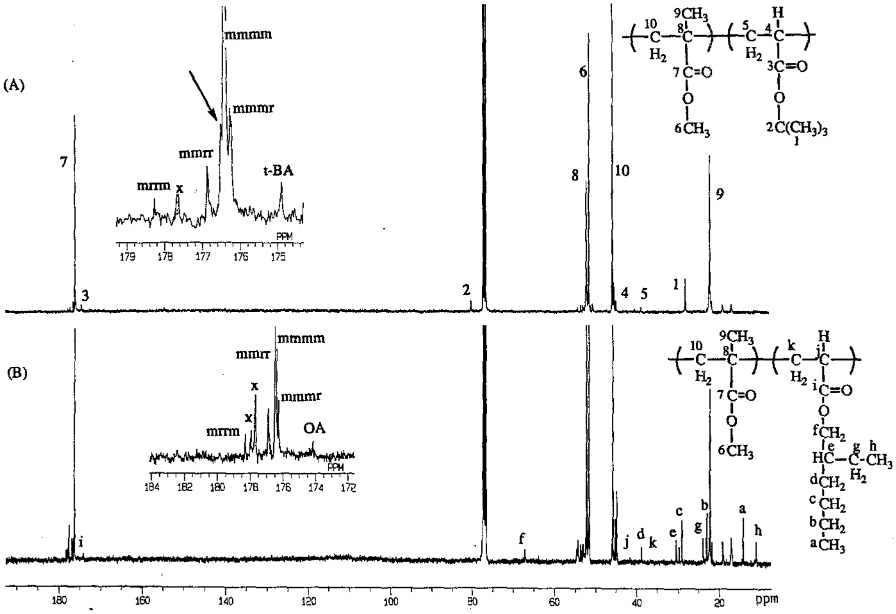

Figure 1. 100 MHz ^{13}C NMR spectra of isotactic copolymers: (A)poly(MMA-co-tBA)(Run No.3), (B) poly(MMA-co-OA) (Run No.6). The signals indicated by the mark (x) may be originated from other species(see ref.10).

Recently, an atactic poly(tBA) was obtained by Yasuda's group using lanthanocene catalyst, which displayed a broad peak attributed to the methyne group of tBA at around 42 ppm (9). The poly(MMA-co-tBA) obtained with Cp_2ZrMe_2 showed a similar peak at 42 ppm, whereas the poly(MMA-co-tBA) obtained with rac-$Me_2Si(Ind)_2ZrMe_2$ displayed a sharp peak at 40.8 ppm as illustrated in Figure 3. More recently, we also obtained an isotactic poly(tBA) with rac-$Me_2Si(Ind)_2ZrMe_2$ in the presence of an aluminium activator showing an isotactic methine peak at about 41.7 ppm(11). The different chemical shift of copolymer might reflect the isotactic MMA environment. It may be considered, therefore, that the copolymer from rac-$Me_2Si(Ind)_2ZrMe_2$ is an isotactic copolymer of MMA and tBA.

When the amount of tBA in the feed was increased, the content of tBA in the copolymer increased(Runs No. 2, 3, Table 2). With an increase in the content of tBA, the resonance attributed to the carbonyl of tBA was divided into a few peaks, which may reflect the sequence distributions of tBA units(Figure 2A). The same phenomenon was also observed in the copolymer produced from a longer pre-PMMA(Figure 2C).

Finally, the ^{13}C NMR spectra of poly(MMA-co-tBA) and poly(MMA-co-OA) obtained with Cp_2ZrMe_2 are illustrated in Figures 4A and 4B for reference. The ^{13}C NMR spectrum of the poly(MMA-co-tBA) displays two resonances attributed to the carbonyl of tBA at around 174 ppm with equal intensity. Poly(MMA-co-OA) also gave a similar spectrum.

On the other hand, the poly(MMA-co-OA) obtained with Cp_2ZrMe_2 (Run No.9), which contains a high concentration of OA(30%), showed two Tg at 38 and 126 °C. Considering that the

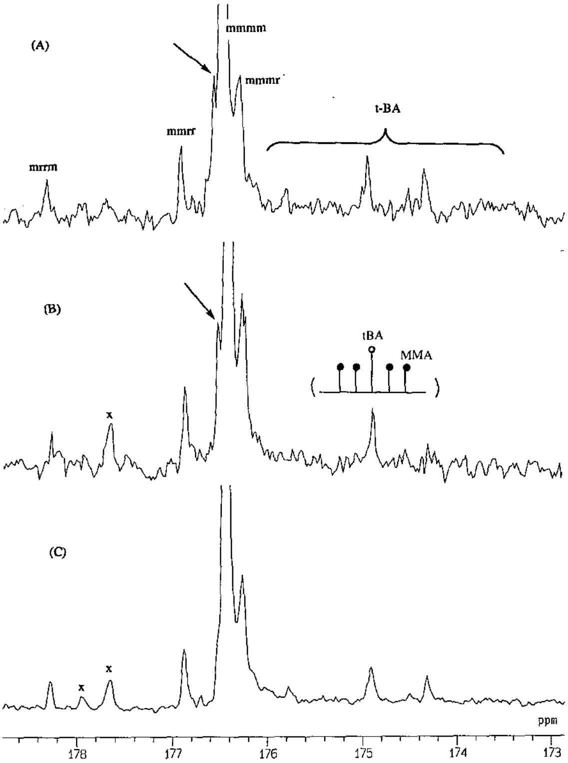

Figure 2. Expanded ^{13}C NMR spectra in the carbonyl region of isotactic poly(MMA-co-tBA) obtained with different conditions: (A)Run No.4, (B)Run No.3, (C)Run No.5.

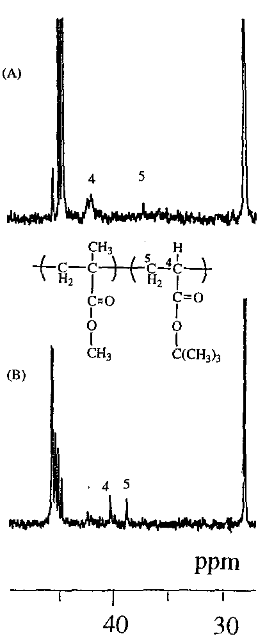

Figure 3. Expanded ^{13}C NMR spectra in the methine region of tBA unit in poly(MMA-co-tBA): A) atactic (Run No.8); B) isotactic (Run No.4).

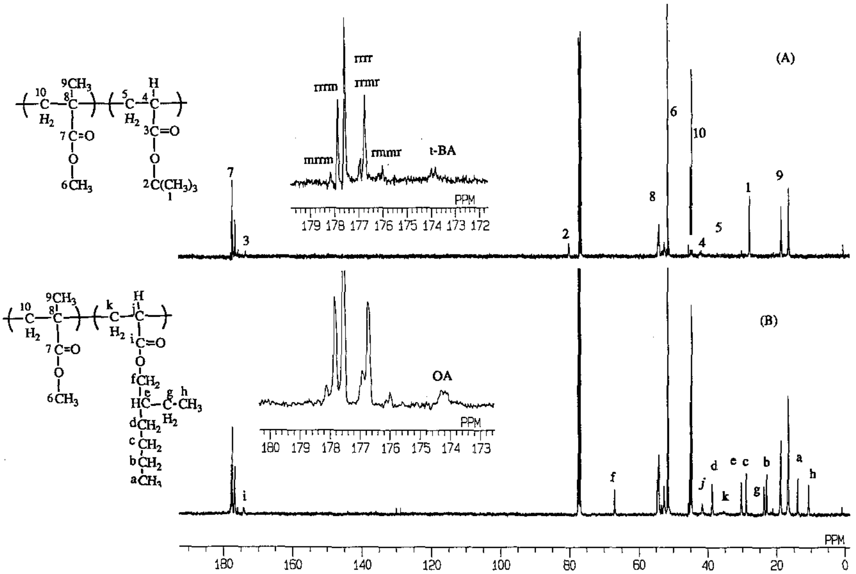

Figure 4. 100 MHz ^{13}C NMR spectra of syndio-rich atactic copolymers: (A) Poly(MMA-co-tBA)(Run No.8), (B) Poly(MMA-co-OA)(Run No.9).

Tg's of syndiotactic PMMA and poly(OA) are 131 °C (6) and -56°C (12) respectively, the new Tg at 38°C might results from a syndio-rich atactic copolymer. In the isotactic copolymer(Run No.6), however, only one Tg was observed at around 54 °C, which is different from the Tg of isotactic poly(OA)(-60°C)(11) but close to the Tg of PMMA(52°C).

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