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Isotactic-*b*-Syndiotactic Stereoblock Poly(methyl methacrylate) by Chiral Metallocene/Lewis Acid Hybrid Catalysts

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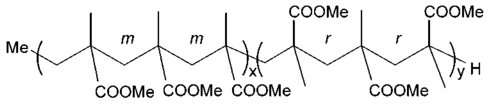
One of the growing interests in polymer synthesis has been to develop catalyst systems for producing stereoblock polymers from a single vinyl monomer. Successes on this front include the synthesis of isotactic-*b*-atactic thermoplastic elastomeric polypropylene by bridged[1] or nonbridged[2] group 4 metallocene catalysts. Although controlled homopolymerization of methyl methacrylate (MMA) by lanthanocene[3] and metallocene[4] initiators, discovered by Yasuda and Collins et al., respectively, has been well documented, synthesis of stereoblock poly(methyl methacrylate) (PMMA) with industrially important group 4 metallocene catalysts/initiators still remains a challenge.[5] We communicate here the synthesis of isotactic-*b*-syndiotactic stereoblock PMMA (**A**) using *ansa*-metallocene *rac*-(EBI)ZrMe$_2$ (**1**, EBI = Et(Ind)$_2$)[6] or *rac*-(SBI)ZrMe$_2$ (**2**, SBI = Me$_2$Si(Ind)$_2$)[7] and strong Lewis acid M(C$_6$F$_5$)$_3$ (M = B[8] or Al[9]) hybrid catalysts.



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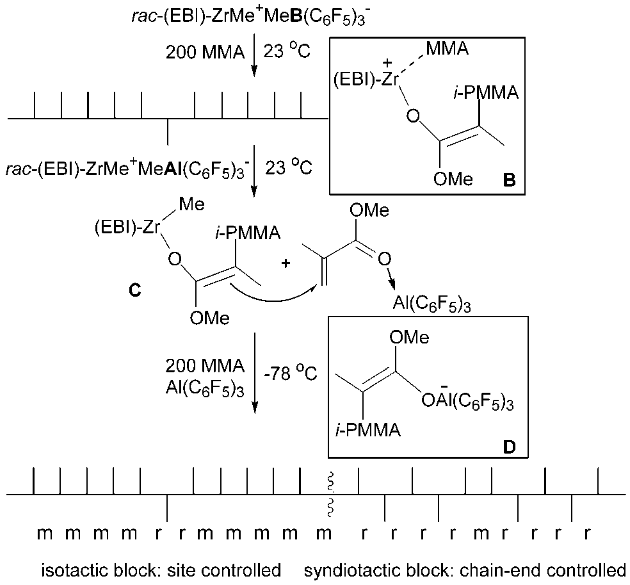
The observation that well-controlled polymerizations of MMA by *rac*-**1** and -**2** produce highly isotactic PMMA when activated with the borane, but low syndiotactic PMMA when activated with the alane (entries 1−4, Table 1), suggested a unique catalyst system to possibly construct stereoblock PMMA microstructures. Indeed, a sequential stereoblock polymerization procedure outlined in Scheme 1 has successfully produced the stereoblock PMMA.

The first portion of MMA was polymerized at 23 °C with *rac*-(EBI)ZrMe$^+$MeB(C$_6$F$_5$)$_3^-$, generated cleanly by in situ mixing *rac*-**1** and the borane, to an isotactic block via isospecific cationic zirconocene enolate propagating species **B**.[4] Next, *rac*-(EBI)ZrMe$^+$-MeAl(C$_6$F$_5$)$_3^-$ was added to convert the orange red **B** to yellow neutral methyl zirconocene enolate **C** and adduct MMA•Al(C$_6$F$_5$)$_3$. The reaction mixture was cooled to −78 °C and a second portion of MMA then added to construct a syndiotactic block via syndiospecific enoaluminate propagating species **D**.[4a] The stereoblock polymerization is highly efficient and a quantitative polymer yield is obtained in <2 h of total polymerization time (entry 5). The stereoblock polymerization with the SBI analogue behaves similarly (entry 6).

Evidence that the materials obtained are real stereoblock polymers and not simply mixtures of homopolymers derives from several lines. First, the polymer has unimodality, narrow molecular weigh distribution, and a single T_g value of 87 °C. This T_g value lies somewhat between that of typical isotactic and syndiotactic PMMAs.

Scheme 1



Second, methyl triad distributions (tacticity) from the ^{1}H NMR reveal high stereoregularity of both isotactic and syndiotactic blocks with [*mm*]/[*rr*]/[*mr*] = 46.4/45.7/7.9 (entry 5). Consistent with this ratio, the ^{13}C NMR spectrum of the C=O pentad region (Figure 1) features a pentad distribution of [*mmmm*] = 42.8, [*rrrr*] = 39.6, [*mmmr*] = 0.9, [*rrrm*] = 7.4, [*mmrr*] + [*rrmr*] = 8.5, [*mrrm*] = 0.8, and no detectable *mmrm*, *rmrm*, and *rmmr* pentad peaks. These spectroscopic characteristics are in agreement with the microstructures of the stereoblock polymer depicted in Scheme 1, where the isotactic block is produced via an enantiomorphic-site controlled mechanism, whereas the syndiotactic block is produced by a chain-end controlled mechanism.

Third, solubility test and solvent fractionation studies confirm the uniformity of the stereoblock polymers obtained from entries 5 and 6. While both isotactic and syndiotactic PMMAs are soluble in boiling 2-propanol, the stereoblock polymers are not. After extracting the bulk polymer with boiling 2-propanol for >12 h, only a trace amount of materials is extracted, and the tacticity of the polymer remains unchanged before and after the extraction.

Finally, model reactions shown in Scheme 2 have provided critical support for the reaction sequence in the stereoblock polymerization proposed in Scheme 1. Thus, neutral zirconocene enolate **E**[10] is first converted to the corresponding cationic zirconocene enolate **F** with the borane, where the enolate moiety and THF are used to simulate the growing polymer chain and the coordinated MMA monomer in the polymerization, respectively. Next, zirconocenium aluminate *rac*-(SBI)ZrMe$^+$ MeAl(C$_6$F$_5$)$_3^-$ is added, and the reaction leads to formation of **E**, *rac*-(SBI)ZrMe$^+$

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Table 1. MMA Polymerization Results and Polymer Properties by Metallocene/Lewis Acid Hybrid Catalysts[a]

entry	initiator	T_p (°C)	t_p (h)	yield (%)	10^4 M_n[b]	M_w/M_n[b]	T_g[c] (°C)	[*rr*][d] (%)	[*mr*][d] (%)	[*mm*][d] (%)
1	*rac*-(EBI)ZrMe$_2$/B	23	2	100	2.97	1.18	54.9	1.2	2.8	96.0
2	*rac*-(SBI)ZrMe$_2$/B	23	2	80	2.84	1.13	54.7	3.1	6.5	90.4
3	*rac*-(EBI)ZrMe$_2$/Al	23	2	100	1.77	1.23	110.3	60.2	35.8	4.0
4	*rac*-(SBI)ZrMe$_2$/Al	23	2	85	2.88	1.19	110.5	60.6	35.1	4.3
5	(i) *rac*-(EBI)ZrMe$^+$(MeB)$^-$	23	0.75	100	5.43	1.61	86.9	45.7	7.9	46.4
	(ii) *rac*-(EBI)ZrMe$^+$(MeAl)$^-$	−78	1							
6	(i) *rac*-(SBI)ZrMe$^+$(MeB)$^-$	23	0.75	100	5.38	1.45	86.6	47.1	9.9	43.0
	(ii) *rac*-(SBI)ZrMe$^+$(MeAl)$^-$	−78	1							
7	$Cp_2Zr(Me)O(O^iPr)C=CMe_2$	23	2	0						
8	$Cp_2Zr(Me)O(O^iPr)C=CMe_2/2Al$	23	0.08	100				68.9	28.3	2.7
9	$Cp_2Zr(Me)O(O^iPr)C=CMe_2/2Al$	−78	1.75	98				77.7	20.8	1.5

[a] Polymerization conditions: 46.7 μmol initiator (I); mole ratio [MMA]/[I] = 200; 10 mL of toluene; B = $B(C_6F_5)_3$; Al = $Al(C_6F_5)_3$. [b] Determined by GPC relative to PMMA (entries 1−4) or polystyrene (entries 5 and 6) standards. [c] Determined by DSC. [d] Determined by ^{1}H NMR spectroscopy.

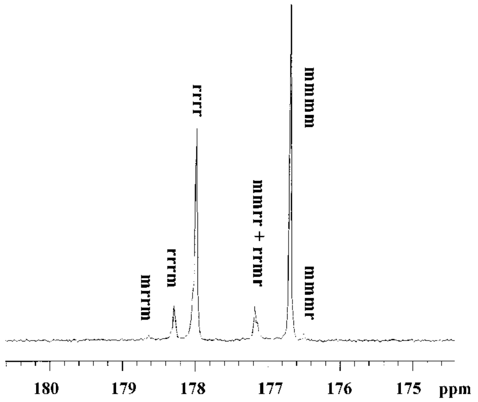
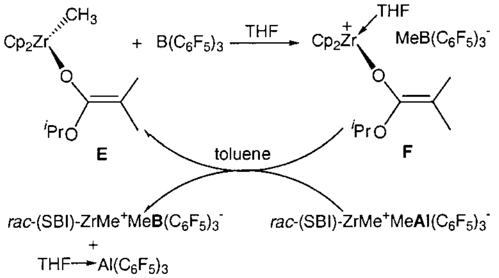


Figure 1. ^{13}C NMR spectrum of an isotactic-PMMA-*b*-syndiotactic-PMMA sample (entry 5): pentad distributions in the C═O region.

Scheme 2



$MeB(C_6F_5)_3^-$, and THF → $Al(C_6F_5)_3$. Although the neutral zirconocene enolate **E** by itself has no polymerization activity, the polymerizations via monomer activation with the alane are highly active at both 23 and −78 °C, producing syndiotactic PMMA (entries 7−9). It is worth noting that zirconocene dimethyls exhibit no activity in the alane-activated MMA polymerization at −78 °C, suggesting that the second step of the stereoblock polymerization must involve the transfer of the polymeric enolate moiety to an activated monomer, rather than a reinitiation via methyl transfer to an activated monomer, a process that would produce a mixture of homopolymers.

In summary, we have developed an efficient stereoblock polymerization system based on group 4 metallocene and group 13 Lewis acid hybrid catalysts capable of switching stereospecificity of the MMA polymerization for production of highly stereoregular isotactic-*b*-syndiotactic stereoblock PMMA. Efforts are underway to construct multi-stereoblock polar vinyl polymers using a similar catalyst system.

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Supporting Information Available: Experiment details and block copolymerization procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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