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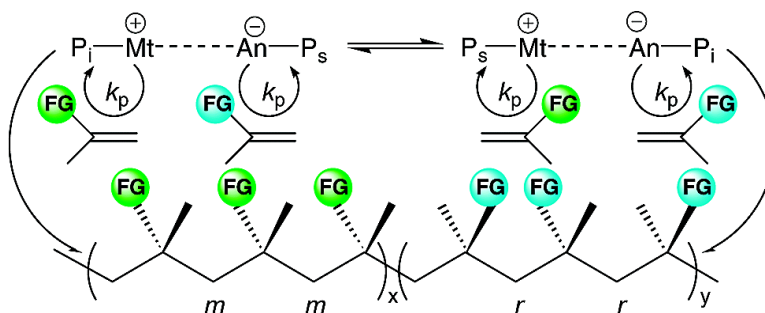
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Amphicatalytic Polymerization: Synthesis of Stereomultiblock Poly(methyl methacrylate) with Diastereospecific Ion Pairs

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Polymerization mediated by transition-metal complexes has become an increasingly important technique in polymer synthesis, due to the remarkable efficiency and high degree of control over polymerization, selectivity, and architecture that is attainable. An important strategy in transition-metal catalysis is to generate highly electron-deficient, coordinately unsaturated transition-metal cations ($Mt^{\oplus}$), paired with weakly coordinating main-group anions ($An^{\ominus}$), highly active systems for the polymerizations of olefins[1] and polar vinyl monomers such as methyl methacrylate (MMA).[2] When MMA is polymerized with rac-L_2ZrMe^+ (L_2 = EBI or SBI; EBI = Et(Ind)$_2$, SBI = Me$_2$Si(Ind)$_2$) paired with $MeAl(C_6F_5)_3^-$, instead of $MeB(C_6F_5)_3^-$, we[3] previously found that the chain propagates from the syndiospecific enolaluminate anion center, rather than the isospecific zirconocenium cation center, with a propagation mechanism analogous to group-transfer polymerization.[4] This polymer chain switching has been utilized in a sequential stereoblock polymerization for the synthesis of highly isotactic-b-syndiotactic diblock PMMA.[5]

An important challenge still remains, however: can a growing polymer chain be switched back and forth between diastereospecific cation $Mt^{\oplus}$ and anion $An^{\ominus}$ centers? If this is accomplished, a new concept for polymerizing functionalized vinyl monomers can be realized: amphicatalytic polymerization (Scheme 1),[6] which is a polymerization mediated by ion pairs $Mt^{\oplus}\cdots An^{\ominus}$ in which both the cation and the anion can catalyze independent polymer chain growth but have different stereospecificity; furthermore, two diastereospecific propagating species operating at the same time are kinetically compatible. In addition, the growing polymer chains (P_i = isotactic (mm) polymer chain; P_s = syndiotactic (rr) polymer chain) at the cation and anion centers are occasionally exchangeable, thereby leading to the production of functionalized polymers with stereomultiblock microstructures.

Earlier attempts to produce stereomultiblock PMMA using either diastereomeric or diastereospecific metallocenium cation mixtures resulted in the formation of either polymer blends with bimodal molecular weight distributions or just isotactic PMMA.[7] However, MMA polymerizations using chiral metallocenium cations paired with both methyl borate and methyl aluminate anions, rac-L_2ZrMe^+-$[MeB(C_6F_5)_3^-]_{0.5}[MeAl(C_6F_5)_3^-]_{0.5}$ (L_2 = EBI, **1**; L_2 = SBI, **2**), generated from dimethyl zirconocenes activated with a 1:1 mixture of Lewis acids $M(C_6F_5)_3$ (M = B, Al), produced unimodal PMMAs with low polydispersity indices (PDI = 1.24 in THF, 1.17 in CHCl$_3$; Table 1, entries 1 and 2). The MMA polymerizations by **1** and **2** in toluene at 23 °C are very rapid; near quantitative to quantitative polymer yields are obtained within 15 or 20 min. This is compared to a typical 2 h reaction time for similar conversions using the same cations, but paired with an individual methyl borate or aluminate anion, under otherwise identical polymerization conditions.

Several lines of evidence indicate that the PMMAs produced by **1** or **2** are stereomultiblock polymers from an amphicatalytic polymerization process. First, ¹H NMR analyses of the PMMAs

Scheme 1
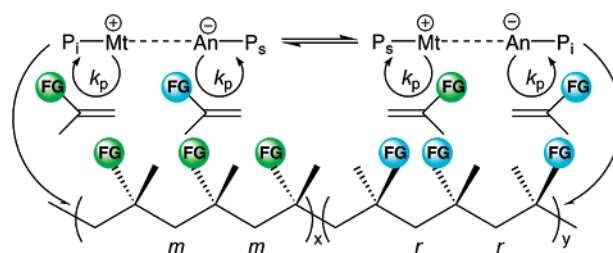
by **1** and **2** at a polymerization temperature of 23 °C revealed methyl triad distributions of [mm]/[mr]/[rr] = 40.3/22.6/37.1 and 37.0/24.3/38.7, respectively, reflecting the isotactic-b-syndiotactic stereoblock microstructures.[8]

Second, the polymers are unimodal and have single T_g values ranging from 93 to 99 °C; these values are considerably different from the T_g for isotactic (~50 °C) and syndiotactic (typically >110 °C) PMMAs, but are closer to that for atactic (~105 °C) PMMA.

Third, a possibility that such methyl triad distributions are simply a result of the blending of isotactic and syndiotactic homopolymers can be ruled out by solvent extraction studies. Because isotactic PMMA of moderate molecular weight (M_n < 50 K) is completely soluble in hot ethanol, the bulk polymer was subjected to extraction with boiling absolute ethanol for >12 h. The insoluble polymer was recovered in >95% yield, and the microstructure (triad distributions) of the polymer remains practically constant before and after the extraction, showing that the polymer product is not just a physical blend.

Fourth, GPC analyses of the PMMA using different eluents provide direct evidence for unimodality of the polymer. It is known that isotactic and syndiotactic PMMAs can form stereocomplexes in dilute solutions such as THF (complex solvent for stereoregular PMMA mixtures);[9] this behavior can complicate the GPC analysis with THF as the eluent, especially when dealing with the possibility of stereoregular polymer mixtures. On the other hand, stereocomplexes cannot be formed in CHCl$_3$[9] (noncomplex solvent), presumably because the polymer—solvent interaction is favored more than the polymer—polymer interaction. Accordingly, the PMMAs were also analyzed by GPC in CHCl$_3$. The GPC traces carried out in CHCl$_3$ showed single, sharp peaks with low PDI values of 1.17; this unambiguous result confirms unimodality of the PMMAs produced by **1** and **2**.

Interestingly, molecular weights obtained by GPC in THF of the same polymers are considerably higher than those determined in CHCl$_3$, reflecting possible aggregation of the stereoblock PMMA in THF via stereocomplexation. To verify this result, dynamic laser light scattering (DLS)[10] was used to further investigate the aggregation behavior of the stereoblock PMMA in both noncomplex (chloroform) and complex (THF and acetone) solvents. Figure 1 shows that the PMMA (Table 1, entry 1) in chloroform has an average hydrodynamic radius $\langle R_h \rangle$ of ~5 nm; this radius is doubled

Table 1. MMA Polymerization Results and PMMA Properties by Diastereospecific Ion Pairs[a]

| entry	ion pairs (mM)	T_p (°C)	t_p (min)	yield (%)	M_n[b] (kg/mol)	PDI[b]	T_g[c] (°C)	[mm][d] (%)	[mr][d] (%)	[rr][d] (%)
1	**1** (4.67)	23	15	100	31.9 (11.6)	1.25 (1.17)	93	40.3	22.6	37.1
2	**2** (4.67)	23	20	93	32.9 (12.6)	1.24 (1.18)	99	37.0	24.3	38.7
3	**1** (2.34)	23	120	100	94.0	1.19	56	90.8	4.6	4.6
4	**2** (2.34)	23	120	84	86.2	1.24	51	91.0	5.6	3.4
5	**1** (4.67)	0	120	100	70.3	1.38	120	11.8	30.9	57.3
6	**2** (4.67)	0	120	100	64.3	1.42	121	6.3	33.5	60.2
7[e]	**1** (4.67)	23	15	100	44.2	1.20	53	92.3	3.0	4.7
8[e]	**1** (4.67)	0	120	100	59.6	1.33	54	92.8	2.7	4.5

[a] **1** = rac-(EBI)ZrMe$^+$[MeB(C$_6$F$_5$)$_3$$^-$]$_{0.5}$[(MeAl(C$_6F_5$)$_3$$^-$]$_{0.5}$; **2** = rac-(SBI)ZrMe$^+$[MeB(C$_6F_5$)$_3$$^-$]$_{0.5}$[(MeAl(C$_6F_5$)$_3$$^-$]$_{0.5}$; 9.35 mmol of MMA; 10 mL of toluene. [b] Determined by GPC relative to PMMA standards with THF as the eluent; data in parentheses obtained by GPC relative to PS standards with CHCl$_3$ as the eluent. [c] Determined by DSC. [d] Determined by ^{1}H NMR spectroscopy. [e] Carried out in o-dichlorobenzene.
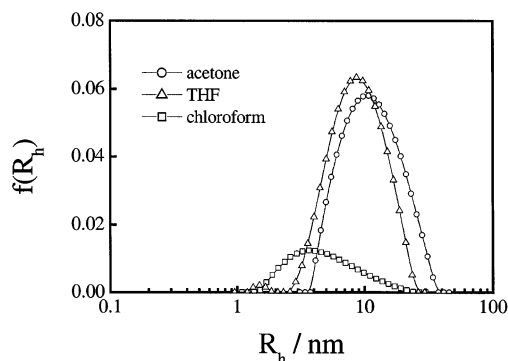
Figure 1. Hydrodynamic radius distributions $f(R_h)$ of stereoblock PMMA in different solvents at $[C_{PMMA}] = 4.3 \times 10^{-3}$ g/mL, 10 °C.

Scheme 2
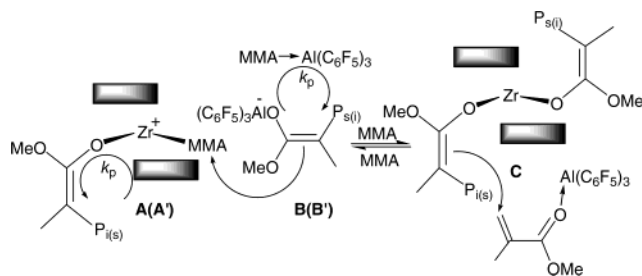
to ~10 nm in acetone or nearly doubled to ~9 nm in THF. Thus, the DLS study explains the pronounced molecular weight differences measured in two different kinds of solvents because of complexation of stereoblock PMMA in complex solvents (THF).

Finally, the formation of stereomultiblock microstructures by diastereospecific ion pairs **1** or **2** can be realized with the amphicatalytic polymerization concept, Scheme 1. Scheme 2 illustrates how diastereomeric polymer chains can be switched back and forth between the cation and anion centers. In this proposed reaction sequence, the Zr/B ion pair polymerizes MMA to isotactic block via chiral cationic zirconocene enolate **A**[2] in a unimetallic propagation, whereas the Zr/Al pair polymerizes MMA to syndiotactic block via enolaluminate anion **B**[3] in a bimetallic propagation. The occasional polymer chain exchange occurs via intermolecular Michael addition of the syndiotactic enolate ligand in **B** to Zr-activated MMA in **A**. Subsequently, the isotactic enolate ligand in the resulting bis(enolate)zirconocene intermediate **C** immediately attacks alane-activated MMA to form back to the same propagating species (**A′** and **B′**), but each propagating species is now carrying a diastereomeric block (denoted as $P_{i(s)}$ or $P_{s(i)}$). If the exchange rate is comparable to the propagation rates, stereomultiblock PMMA is formed.

Consistent with this proposal, predominantly isotactic PMMA is formed (via **A**) when the catalyst concentration is reduced to one-half (Table 1, entries 3 and 4), whereas syndiotactic PMMA is produced (via **B**) when the polymerization temperature is lowed to 0 °C (entries 5 and 6). Furthermore, when the polymerization is carried out in polar solvents such as o-dichlorobenzene, predominantly isotactic PMMA is again formed (entries 7 and 8).

In conclusion, suitable diastereospecific ion pairs promote efficient amphicatalytic polymerization of MMA, allowing for the production of stereoblock microstructures. Mechanistic studies and applications to other polar vinyl monomers are underway.

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

References

(1) For recent special review issues, see: (a) Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100*, 1167−1681 and references therein. (b) Marks, T. J., Stevens, J. C., Eds. *Top. Catal.* **1999**, *7*, 1−208 and reference therein.

(2) (a) Frauenrath, H.; Keul, H.; Höcker, H. *Macromolecules* **2001**, *34*, 14−19. (b) Bandermann, F.; Ferenz, M.; Sustmann, R.; Sicking, W. *Macromol. Symp.* **2001**, *174*, 247−253. (c) Cameron, P. A.; Gibson, V.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329−4335. (d) Nguyen, H.; Jarvis, A. P.; Lesley, M. J. G.; Kelly, W. M.; Reddy, S. S.; Taylor, N. J.; Collins, S. *Macromolecules* **2000**, *33*, 1508−1510. (e) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875−1883. (f) Deng, H.; Shiono, T.; Soga, K. *Macromolecules* **1995**, *28*, 3067−3073. (g) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222−7224. (h) Collins, S.; Ward, S. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460−5462.

(3) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943−7944.

(4) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706−5708.

(5) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2002**, *124*, 5612−5613.

(6) Use of "catalytic" here emphasizes the fundamental catalytic event of monomer enchainment, rather than polymer chain formation.

(7) See Supporting Information for experimental details.

(8) A microstructure analysis suggested the number of average lengths of isotactic and syndiotactic sequences is approximately five.

(9) For reviews, see: (a) te Nijenhuis, K. *Adv. Polym. Sci.* **1997**, *130*, 67−81, 244−246 (references). (b) Spevacek, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27*, 81−150.

(10) Berne, B. J.; Pecora, R. *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*; Dover Publications: New York, 2000.

JA035261Y