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Stereospecific, Coordination Polymerization of Acrylamides by Chiral *ansa*-Metallocenium Alkyl and Ester Enolate Cations

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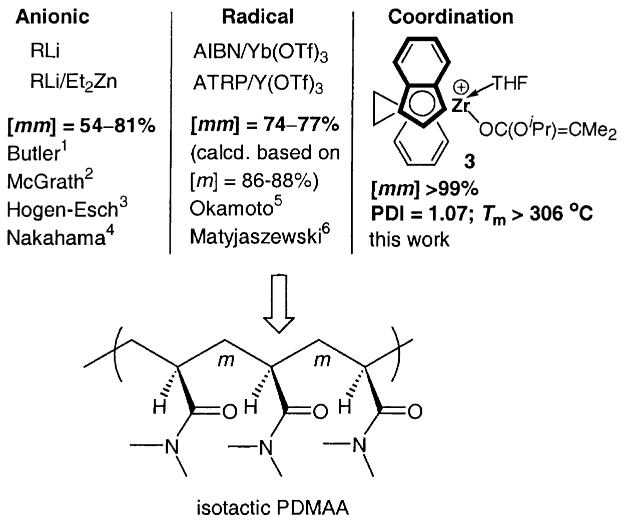
A high degree of control over polymerization stereochemistry still remains as a challenge for many technologically important polymerization reactions. For example, both anionic and radical polymerizations of *N,N*-dimethylacrylamide (DMAA) with various initiators that can promote tacticity control yielded poly(*N,N*-dimethylacrylamide) (PDMAA) with moderate isotacticities (Chart 1).[1−6] Butler and co-workers reported the first isoselective polymerization of DMAA using an anionic initiator (EtLi) in toluene, producing a crystalline polymer.[1] Two decades later, McGrath et al. analyzed the tacticity of PDMAA produced by *s*-BuLi with ^{1}H and ^{13}C NMR and concluded the polymer to be highly isotactic ([*mm*] ∼ 81%).[2] Hogen-Esch et al. found that the PDMAA produced by Ph_3CLi or $(Ph_2CCH_2CH_2CPh_2)Li_2$ in THF at −78 °C was also isotactic ([*mm*] = 54%).[3] Nakahama and co-workers used anionic initiators modified with Lewis acids such as Et_2Zn and Et_3B to effect the tacticity of the resulting PDMAA.[4] The presence of the Lewis acid additive typically reduces the PDMAA isotacticity and thus enhances the syndiotacticity for anionic polymerization; however, the trend is reversed for radical polymerization where Lewis acids such as $M(OTf)_3$ (M = Y, Sc, Yb) are shown to enhance isotacticity, as demonstrated by the work of Okamoto and co-workers.[5] Most recently, Matyjaszewski et al. utilized this Lewis acid effect to synthesize the well-defined atactic-*b*-isotactic stereoblock PDMAA by adding $Y(OTf)_3$ at a given time to an atom-transfer radical polymerization (ATRP) of DMAA, initially started without the Lewis acid.[6]

Chart 1



Despite these significant advances, the highest reported isotacticity [*mm*] for PDMAA is ∼81% (Chart 1). Recognizing the difficulty in achieving a higher degree of isotacticity of DMAA polymerization via either an anionic or a radical mechanism, we sought to explore the possibility of using the coordination polymerization mediated by chiral *ansa*-metallocene complexes to achieve this significant goal. It is known that chiral, cationic *ansa*-zirconocene complexes promote highly isospecific polymerization of alkyl methacrylates via an enantiomorphic-site control mechanism;[7] however, we were not aware of any reports on polymerization of *acrylamides* by metallocene complexes. We communicate here the first stereospecific, coordination polymerization of DMAA for the synthesis of highly isotactic PDMAA ([*mm*] > 99%) using the following cationic, chiral *ansa*-zirconocene complexes: *rac*-(EBI)ZrMe$^+$MeM$(C_6F_5)_3^-$ (EBI = $C_2H_4(Ind)_2$; M = B, **1**; M = Al, **2**) and *rac*-(EBI)-Zr$^+$(THF)[OC(O^{i}Pr)=CMe$_2$][MeB$(C_6F_5)_3$]$^-$ (**3**).[7a]

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Table 1. Results of DMAA Polymerization and Properties of PDMAA[a]

entry no.	complex/radical inhibitor	solvent, time (h)	yield (%)	M_n[b] (kg/mol)	PDI[b] (M_w/M_n)	T_g[c] (°C)	T_m[c] (°C)	$T_{int,end}$[d] (°C)	T_{max}[d] (°C)	$[mm]/[mr + rr]$[e] ($[m/r]$)[f]
1	*rac*-(EBI)$ZrMe_2$	toluene, 24	>99	11800	7.33	126		395−448	433	(52/48)
2	$Al(C_6F_5)_3$	toluene, 24	>99	44.3	8.82	122				(51/49)
3	$B(C_6F_5)_3$	toluene, 24	0							
4	**1**	toluene, 24	>99	30.2	1.51		310	403−441	430	93/7
5	**2**	toluene, 24	>99	106	1.97	111	313	393−437	429	61/39
6	**1**/galvinoxyl	toluene, 24	>99	544	3.21		312	398−436	427	98/2
7	**2**/galvinoxyl	toluene, 24	>99	613	7.91		308	396−438	429	98/2
8	**1**	CH_2Cl_2, 24	>99	270	1.90	112	306	389−434	422	82/18
9	**1**/galvinoxyl	CH_2Cl_2, 24	92	1140	7.00		316	392−440	431	>99
10	**3**	CH_2Cl_2, 2	93	92.7	1.07		306	393−436	428	>99
11	**3**/galvinoxyl	CH_2Cl_2, 2	93	104	1.07		318	381−430	420	>99

[a] All polymerizations were carried out in an argon-filled glovebox (oxygen and moisture <1.0 ppm) at ambient temperature (~25 °C); 5 mL of solvent; $[DMAA]_0/[complex]_0 = 400:1$. [b] Number-average molecular weight and polydispersity index were determined by GPC in $CHCl_3$ relative to PMMA standards. [c] Glass (T_g) and melting (T_m) transition temperatures were determined by DSC from a second scan. [d] Decomposition onset ($T_{int,end}$) and d(wt %)/dT peak max for maximum rate decomposition (T_{max}) temperatures were determined by TGA. [e] Carbonyl triads were determined by ^{13}C NMR spectroscopy in D_2O at 80 °C. [f] Data in parentheses are methylene dyads (m/r) determined by ^1H NMR spectroscopy in $CDCl_3$ at 50 °C.

Initial DMAA polymerizations using the in situ generated **1** or **2** yielded PDMAA of low isotacticity. The control runs showed that the neutral metallocene dimethyl and the activator alane themselves, but not the borane, are active for the polymerization (entries 1−3, Table 1). The PDMAA obtained, however, is atactic with a high polydispersity index (PDI), and the polymerization can be completely shut down by adding an established, effective radical inhibitor (galvinoxyl);[8] all evidence points to a radical process. It should be noted that none of these neutral alkylmetallocenes and the Lewis acid activators is active for polymerization of methacrylates.

On the basis of this finding, we subsequently used the *isolated* alkyl cations **1** and **2** for polymerization of DMAA (entries 4, 5). The cation **1** now produced highly isotactic PDMAA ($[mm]$ = 93%), whereas **2** afforded PDMAA with a moderate isotacticity of $[mm]$ = 61%, presumably due to the greater propensity for **2** to dissociate back to the neutral metal alkyl and the activator in solution than for **1**.[9] Nevertheless, both PDMAAs formed exhibit high melting transition temperatures (T_m) of > 310 °C and moderate PDI of < 2.0. To inhibit any possible radical processes initiated by the neutral species derived from the dynamic ion pair reorganization processes of the alkyl cation,[10] the addition of 2 equiv of galvinoxyl to the polymerization led to enhanced isospecificity of both cations ($[mm]$ = 98%, entries 6, 7), but gave high PDI of > 3.2. Although both the polymerizations with and without galvinoxyl gave quantitative polymer yields for 24 h, the polymerization activity difference is much more pronounced at a shorter reaction time. For example, the yields for the 2 h polymerization reaction by **1** without and with galvinoxyl were 78% and 24%, respectively.

The considerably increased PDI value with galvinoxyl is initially surprising, but this may be attributed to the inhomogeneity of the reaction in toluene, as a result of the enhanced PDMAA isotacticity ($[mm]$ = 98%) and high M_n (> 5 × 10^5). In attempts to overcome the inhomogeneity, we used CH_2Cl_2 for polymerizations by **1** and **1**/galvinoxyl (entries 8, 9). The substantially increased and uncontrolled M_n of PDMAA produced in CH_2Cl_2 vs in toluene (e.g., 1.14 × 10^6 in entry 9 vs 5.44 × 10^5 in entry 6) continued creating the inhomogeneity problem, leading to high PDI values.

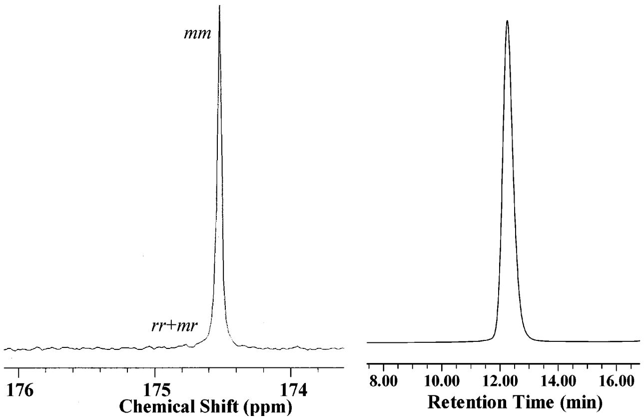

Figure 1. Left: ^{13}C NMR spectrum (D_2O, 80 °C) of highly isotactic PDMAA by cation **3** (entry 10) showing carbonyl triad $[mm]$ >99%. Right: GPC trace of the same PDMAA showing PDI = 1.07.

A demonstrated strategy for controlling polymer M_n and PDI in the case of methacrylate polymerization is to use the cationic zirconocene *ester enolate* initiator, because it simulates the active propagating species that has bypassed the slow initiation step starting from the cationic alkyl initiator.[7a,h,j,11] Although the anticipated propagating species for DMAA polymerization is a cationic zirconocene *amide* enolate, the chiral zirconocene *ester* enolate initiator should impose a similar effect on M_n and PDI of PDMAA. Indeed, the DMAA polymerization using the isolated cationic ester enolate **3** is much more reactive than that by the alkyl cation **1** (2 h in entry 10 vs 24 h in entry 8), and more importantly, the polymerization now is much more controlled, as indicated by M_n of 9.27 × 10^4 and low PDI of 1.07 (right column, Figure 1). The formation of a virtually stereodefect-free isotactic PDMAA by ^{13}C NMR ($[mm]$ > 99%; left column, Figure 1), even in the absence of the radical inhibitor, is another remarkable feature of this polymerization. The same polymerization, but in the presence of 2 equiv of galvinoxyl, gave nearly identical polymerization results (entry 11 vs 10), except for a noticeably higher T_m of 318 °C, presumably due to a higher M_n of 1.04 × 10^5. These results show that the DMAA polymerization initiated by the cationic ester enolate **3** is free of radical processes, well controlled, and highly isospecific.

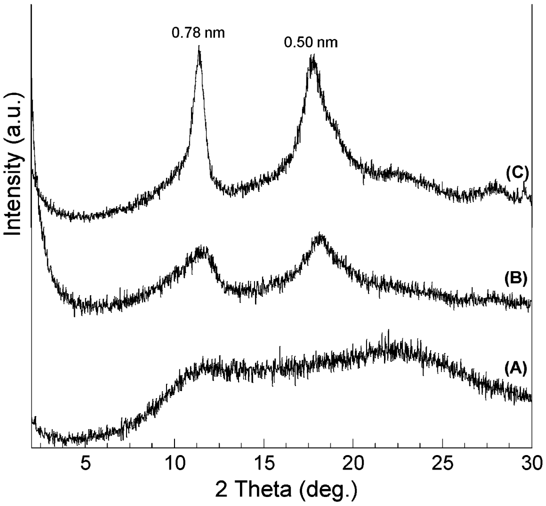

Figure 2. Overlay of XRD plots for PDMAA: (A) atactic (entry 1); (B) isotactic (entry 6); (C) same as plot B, but annealed at 140 °C for 60 h.

All highly isotactic PDMAAs obtained from this study are insoluble in toluene, diethyl ether, THF, or DMF, but soluble in methanol, water, and chloroform. They exhibit high T_m (> 306 °C) and single, high decomposition temperatures as shown by maximum rate decomposition temperatures (T_{max}) of 420−430 °C with narrow decomposition temperature windows (Table 1).

Unlike the amorphous or moderately isotactic PDMAAs, which exhibit defined glass transition temperature (T_g) endothermic peaks on DSC traces (entries 1, 2, 5, and 8), the PDMAAs with isotacticity [*mm*] > 90% do not show noticeable T_g's (or are too broad to define)[12] because of their high crystallinity. The crystallization temperature (T_c) of isotactic PDMMA is typically in the range of 260−270 °C under our DSC conditions.[12] The isotactic PDMAAs are crystalline when isolated (quenched) directly from a polymerization reaction. As shown by the X-ray diffraction (XRD) plots in Figure 2, no annealing treatment is necessary for isotactic PDMAA to develop substantial crystallinity (plot B, Figure 2), although annealing can further increase the crystallinity as the two characteristic scattering peaks (*d* spacing: 0.78 and 0.50 nm) increase their intensity and sharpness after being annealed at 140 °C for 60 h (plot C, Figure 2). The XRD of atactic PDMAA produced by *rac*-(EBI)ZrMe$_2$ is included in the plot for comparison (plot A, Figure 2).

In summary, we discovered the coordination acrylamide polymerization by the cationic, chiral *ansa*-zirconocene ester enolate complex. Remarkable features about this polymerization include the high degree of control over polymerization stereochemistry and polymer molecular weight distribution. Thus, PDMMA with unprecedented isotacticity ([*mm*] >99%), high M_n, low PDI (1.07), and T_m as high as 318 °C has been synthesized. Efforts are underway to synthesize other types of stereoregular polyacrylamides using this technique.

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Supporting Information Available: Text giving experimental details and figures showing representative NMR spectra and GPC, DSC, and TGA traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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