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Asymmetric Coordination Polymerization of Acrylamides by Enantiomeric Metallocenium Ester Enolate Catalysts

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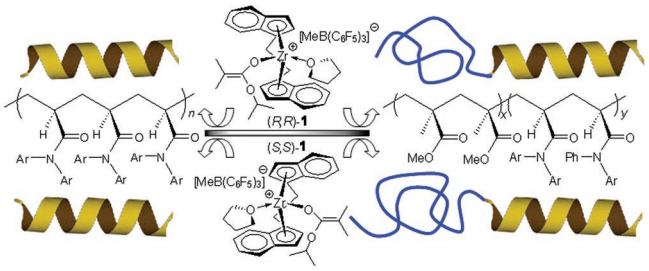
Most stereoregular vinyl polymers[1] with configurational main-chain chirality cannot be optically active even with significant asymmetric induction at the stereogenic centers of the main chain because they possess mirror planes of symmetry, excluding chain-end and chiral side groups.[2] Chiral template polymerization and asymmetric cyclopolymerization present two unique strategies leading to chiral polymers;[3] for tactic vinyl polymers without complex configurational architectures, single-handed helical conformations can render their optical activity.[4] Many stereoregular vinyl polymers adopt helical conformations in the solid state (e.g., isotactic polypropylene, *it*-PP); however, such solid-state helical conformations cannot be maintained in solution because of the fast solution dynamics of the polymer chain. Thus, the *it*-PP produced by an optically active zirconocene catalyst can exhibit a large optical rotation in suspension, but the optical activity is lost when the polymer is completely dissolved or heated.[5] Okamoto and co-workers[2,4,6] pioneered a strategy addressing the above issue; they employed achiral vinyl monomers incorporating bulky side groups (e.g., triarylmethyl methacrylates[7] and *N*,*N*-diaryl acrylamides[8]) so that the helical conformation is sustainable in solution even at room temperature by steric repulsion of the bulky side groups of the highly isotactic polymers accessible through the so-called helix-sense-selective polymerization.[9]

Asymmetric *anionic* polymerization by chiral organolithium initiators was utilized to convert prochiral functionalized vinyl monomers such as *N*,*N*-diphenyl acrylamide (DPAA) to optically active polymers with rigid one-handed helical conformation in solution.[7,8] However, such polymerization must be carried out at low temperatures (−78 °C or lower) to achieve an appreciable level of polymerization control as well as the polymer isotacticity and optical activity. Furthermore, in the chiral-initiator-controlled polymerization the enchaining monomer experiences varied degrees of asymmetric induction as a function of the growing chain length, giving rise to a large disparity in stereoregularity and optical activity of the polymer; even in the chiral-ligand-controlled anionic polymerization, such a disparity still exists.[8a] Hence, a hypothesized *ideal* asymmetric polymerization system for the synthesis of optically active polymers from achiral vinyl monomers should possess the following advanced features: (a) the reaction can be carried out at ambient or higher temperatures; (b) it exhibits a high degree of polymerization control and high stereospecificity; and (c) the reaction proceeds in a manner such that each enchaining monomer must coordinate to the chiral catalyst center before enchainment and is regulated by the same degree of chiral induction of the same asymmetric center, thereby producing chiral polymers of uniform asymmetric induction. Communicated herein is such an *asymmetric coordination polymerization* system rendered by enantiomeric *ansa*-zirconocenium ester enolate catalysts for the synthesis of optically active helical poly(*N*,*N*-diaryl acrylamide)s and their block copolymers with methyl methacrylate (MMA) (Chart 1).

Chart 1. Synthesis of Right- and Left-Handed Rigid Helical Poly(*N*,*N*-Diaryl Acrylamide)s and Their Rigid-Coil Block Copolymers with P(MMA).



We have recently developed the living and stereospecific coordination polymerization of *N*,*N*-dialkyl acrylamides[10] using the highly active racemic (*R*,*R*/*S*,*S*)-*ansa*-zirconocenium ester enolate catalyst (EBI)Zr^+(THF)[OC(O^{i}Pr)═CMe_2][$MeB(C_6F_5)_3$]$^-$ [**1**; EBI = $C_2H_4(\eta^5\text{-Ind})_2$][11] under ambient conditions; the polymer produced has a quantitative isotacticity [*mm*] of >99%, a controlled number-average molecular weight (M_n), a narrow molecular weight distribution (MWD) of 1.07, and a high melting-transition temperature (T_m) of >306 °C. To examine the catalyst reactivity toward *N*,*N*-diaryl acrylamides for rendering solution helical conformations of the corresponding isotactic polymers, we polymerized DPAA using *rac*-**1** to produce rigid helical P(DPAA) (runs 1 and 2, Table 1) with T_{max} (maximum rate decomposition temperature) as high as 484 °C in a narrow, one-step decomposition window.[12] The P(DPAA) produced is insoluble in common organic solvents, precluding its direct MW measurements by GPC. Accordingly, it was converted to poly(methyl acrylate) by treatment with concentrated H_2SO_4 in MeOH at 90 °C for 24 h, followed by methylation with CH_2N_2.[8a] The measured M_n and M_w/M_n values of the poly(methyl acrylate) derivative (runs 1 and 2) demonstrate the controlled/living nature of the DPAA polymerization.

To produce optically active P(DPAA)s with excess one-handed helices, enantiomeric catalysts (*R*,*R*)- and (*S*,*S*)-**1** are required. They were obtained by two mirror-image syntheses of 11 steps,[12] starting from enantiomeric 2,4-pentanediol to (*R*,*R*)- and (*S*,*S*)-(EBI)$ZrCl_2$ using Jordan's chelate-controlled synthesis;[13] the enantiomeric *ansa*-zirconocene dichlorides were then transformed to enantiomeric neutral methyl ester enolate precatalysts (*R*,*R*-pre-**1**, $[\alpha]^{23}_D$ = −285°; *S*,*S*-pre-**1**, $[\alpha]^{23}_D$ = +290°) and last to the cationic ester enolate catalysts (*R*,*R*)-**1** and (*S*,*S*)-**1**, following our established route for the synthesis of *rac*-**1**.[11,14]

Polymerization of DPAA by (*S*,*S*)-**1** and (*R*,*R*)-**1** successfully afforded optically active, one-handed helical P(DPAA)s. Specifically, the enantiomeric catalysts produce the P(DPAA)s of opposite optical rotations (run 3 vs 4); the P(DPAA)s also exhibit opposite optical rotations to those of the respective catalysts used, thereby arguing against a possibility that the optical activity could arise from the catalyst residue (although it was carefully removed during

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Table 1. Results of Asymmetric Polymerization of *N,N*-Diaryl Acrylamides by **1**[a]

run no.	M/co-M	[M]/[**1**]	catalyst form	yield[b] (conv)	10^{-4} M_n[c] (g/mol)	MWD[c] (M_w/M_n)	$[\alpha]^{23}_D$ (deg)
1	DPAA	50	*rac*	96	1.03	1.13	0.0
2	DPAA	200	*rac*	97	3.85	1.03	
3	DPAA	50	*S,S*	96	n.d.	n.d.	−15.5
4	DPAA	50	*R,R*	97	n.d.	n.d.	+19.5
5	MMA/DPAA	400/50	*rac*	>99	105	1.72	0.0
6	MMA/DPAA	400/50	*S,S*	>99	108	1.76	−8.5
7	MMA/DPAA	400/50	*R,R*	>99	122	1.76	+11.0
8	PTAA	50	*rac*	(100)	n.d.	n.d.	0.0
9	PTAA	50	*S,S*	(100)	n.d.	n.d.	−159
10	PTAA	50	*R,R*	(100)	n.d.	n.d.	+180
11	MMA/PTAA	400/50	*rac*	>99	94.7	1.61	0.0
12	MMA/PTAA	400/50	*S,S*	>99	117	1.52	−27.0
13	MMA/PTAA	400/50	*R,R*	>99	116	1.53	+32.0

[a] Carried out in 5 mL of CH_2Cl_2 at ambient temperature for 10 min (for MMA) or 3 h (for acrylamides). [b] Isolated polymer yield or monomer conversion in parenthesis, (conv), measured by ^{1}H NMR. [c] Determined by GPC relative to P(MMA) standards; results for runs 1 and 2 were based on poly(methyl acrylate) derivative.

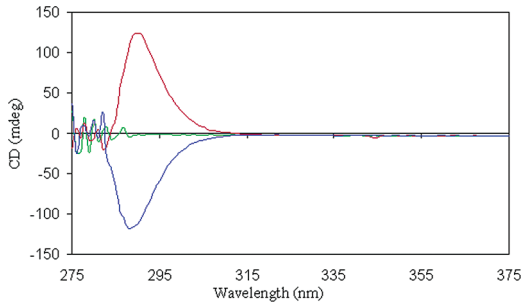

Figure 1. CD spectra of P(MMA)-*b*-P(DPAA) by catalysts (*S,S*)-**1** (red), *rac*-**1** (green), and (*R,R*)-**1** (blue).

the workup procedure[12]). To overcome the solubility issue of helical P(DPAA), we synthesized the flexible random coil−rigid helical block copolymer P(MMA)-*b*-P(DPAA) (Chart 1; Table 1, runs 5−7). The copolymer is soluble in $CHCl_3$, enabling direct GPC analysis. Based on linear P(MMA) standards, the measured MWs of the copolymers produced by all three forms of catalyst **1** are ∼20 times higher than the calculated, most likely due to the large hydrodynamic volume of the rigid-rodlike helical P(DPAA) block and association of the chains. For the reason described above, the P(MMA) (MWD = 1.04) derived from the enantiomeric catalysts is optically inactive. On the other hand, the optical activity of P(MMA)-*b*-P(DPAA) hinges on the nature of the catalyst; while *rac*-**1** affords the optically inactive copolymer, (*S,S*)-**1** and (*R,R*)-**1** lead to the copolymers of opposite optical rotations (run 6 vs 7). These results were further confirmed by their circular dichroism (CD) spectra (Figure 1) which show no, positively signed, and negatively signed Cotton effects for the copolymers produced by *rac*-**1**, (*S,S*)-**1**, and (*R,R*)-**1**, respectively, and that the latter two are near mirror images of each other.

We also examined possible modulation of optical activity of the polymer by unsymmetrical substitution of the phenyl groups of poly(*N,N*-diaryl acrylamide)s. To this end, we extended this asymmetric coordination polymerization system to *N*-phenyl-*N*-(4-tolyl)acrylamide (PTAA).[8a] Specifically, polymerizations of PTAA by *rac*-**1**, (*S,S*)-**1**, and (*R,R*)-**1** are as effective as the DPAA polymerizations, producing rigid helical P(PTAA) and random coil-rigid helical P(MMA)-*b*-P(PTAA) whose screw-sense helices are determined by the form of the catalyst employed (runs 8−13). Of significance in this study are the observed considerably higher $[\alpha]^{23}_D$ values and CD intensities (Figure 2) for the PTAA-based polymers than for the ones derived from DPAA.

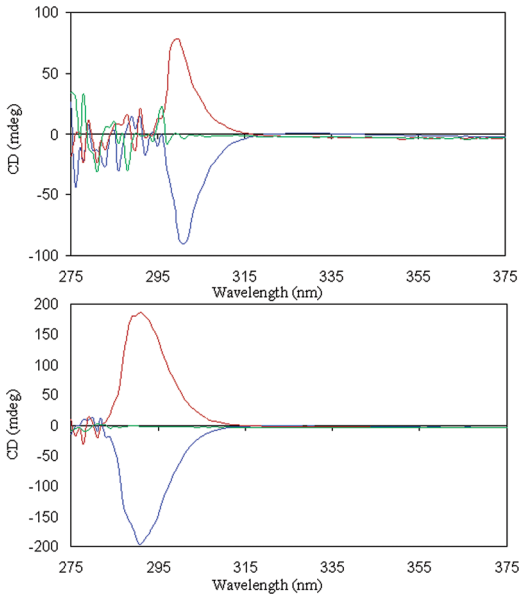

Figure 2. CD spectra of P(PTAA) (top) and P(MMA)-b-P(PTAA) (bottom) by catalyst (*S,S*)-**1** (red), *rac*-**1** (green), and (*R,R*)-**1** (blue).

In summary, we have developed the asymmetric coordination polymerization of functionalized alkenes using enantiomeric *ansa*-zirconocenium ester enolate catalysts for the synthesis of optically active, rigid one-handed helical poly(acrylamide)s and their co-polymers with random-coil methacrylate blocks under ambient conditions. Embraced by its three advanced features, this polymerization should offer excellent opportunities for the production of optically active chiral polymers from other types of achiral monomers via asymmetric polymerization catalysis mediated by readily available chiral metallocene catalysts.

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

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