Stereocontrol in the Polymerization of Methyl Methacrylate Mediated by Chiral Organolanthanide Metallocenes

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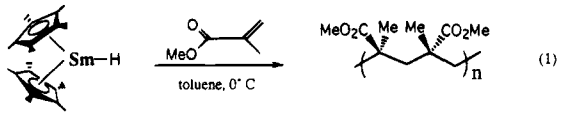
As with poly-α-olefins, the properties of poly(methyl methacrylates) (PMMAs) are highly dependent on the stereoregularity of the polymer backbone.[1-3] However, unlike α-olefin polymerization catalysis,[4] agents for stereoregular MMA polymerization have traditionally been anionic species (lithium, Grignard reagents) with highly mobile and, in most cases, poorly defined coordination spheres. Recently, an achiral organolanthanide, $[(C_5Me_5)_2SmH]_2$, was shown to efficiently catalyze the living, highly syndiospecific polymerization of methyl methacrylate (eq 1).[5,6] These results raise the intriguing question of whether



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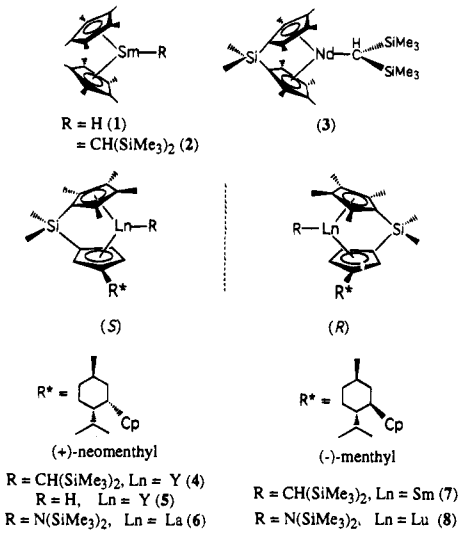
acrylate polymerizations might also be subject to enantiomorphic site control via a chiral metal−ligand template. If so, chiral organolanthanide complexes might be capable of regulating the stereochemical outcome of this polymerization. The C_1-symmetric complexes shown in Scheme 1 are effective catalysts for asymmetric olefin hydrogenation,[7] hydroamination,[7b,8] and hydrosilylation[9] with moderate to high turnover frequencies and enantioselectivities. We communicate here on the efficacy of such catalysts in the stereoregular polymerization of methyl methacrylate—the first example for a chiral metallocene catalyst.[10,11] Isotacticities (as high as >96% *mmmm* pentad content) and relative polymerization initiation rates are shown to be a sensitive function of precatalyst architecture.

Hydride, hydrocarbyl, and amide precatalysts (Scheme 1)

Scheme 1. Organolanthanide Precatalysts



were prepared as described elsewhere.[7,12] Polymerizations[13] were performed in toluene solution (polymerization is inhibited in THF) and, after a measured time interval, were quenched with acidified methanol. Polymer microstructure was characterized by ^1H and ^{13}C NMR using standard triad[14,15] and pentad[15,16] analyses. Molecular weights were characterized by GPC. Results are summarized in Table 1. C_1-symmetric catalysts bearing the (+)-neomenthyl chiral auxiliary produce *isotactic* polymers with tacticity increasing with decreasing temperature (entries 5−7, 9−12). At −35 °C with precatalyst (*R*)-**6**, ^{13}C NMR pentad analysis of the resulting PMMA indicates an *mmmm* pentad content >96% (94% triad). The agreement between entries **5** and **8** argues that the mechanism of stereoregulation is independent of the precatalyst R group. In sharp contrast to the (+)-neomenthyl results, catalysts bearing the (−)-menthyl chiral auxiliary produce *syndiotactic* polymers with stereoregularities approaching those of the parent achiral Ln complexes (>75% *rrrr* pentad content at 25 °C (73% triad)). Differences in stereoregulation between (*S*)- and (*R*)-**8** (entries 14 and 15) underscore the previously noted[7,8,12c] diastereomeric character of the catalysts.

The present results confirm earlier observations[5] that achiral hydride precatalysts yield syndiotactic PMMA with narrow

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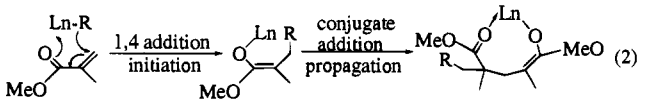
Table 1. Activity, Molecular Weight, and Tacticity Data for the Polymerization of Methyl Methacrylate by Achiral and Chiral Organolanthanide Complexes[a]

entry	precat.[c]	precat. structure	T (°C)	time (h)	yield (%)	% *mm*[d]	% *mr*[d]	% *rr*[d]	$M_w(\times 10^3)$[e]	$M_n(\times 10^3)$[e]	PDI
1[b]	**1**	$(Cp'_2SmH)_2$	0	1	99			82	59	58	1.02
2	**1**	$(Cp'_2SmH)_2$	0	2	100	3	14	83	74	69	1.06
3	**2**	$Cp'_2SmSmCH(TMS)_2$	0	2	93	6	14	80	1390	823	1.7
4	**3**	$Me_2SiCp''NdCH(TMS)_2$	0	3	90	3	15	82	284	133	2.1
5	(*R,S*)-**4**[f]	(*R,S*)-(neomenthyl)$YCH(TMS)_2$	25	10	100	55	25	20	423	236	1.8
6	(*R,S*)-**4**[f]	(*R,S*)-(neomenthyl)$YCH(TMS)_2$	0	2	92	57	23	20	479	262	1.8
7	(*R,S*)-**4**[f]	(*R,S*)-(neomenthyl)$YCH(TMS)_2$	−20	160	100	64	20	16	678	376	1.8
8	(*R,S*)-**5**[f]	(*R,S*)-(neomenthyl)YH	0	2	100	51	26	23	161	104	1.55
9	(*R*)-**6**	(*R*)-(neomenthyl)$LaN(TMS)_2$	25	10	29	75	19	6	191	38	4.1
10	(*R*)-**6**	(*R*)-(neomenthyl)$LaN(TMS)_2$	0	160	36	79	16	5	391	50	7.9
11	(*R*)-**6**	(*R*)-(neomenthyl)$LaN(TMS)_2$	−20	160	77	81	14	5	576	77	7.5
12	(*R*)-**6**	(*R*)-(neomenthyl)$LaN(TMS)_2$	−35	160	100	94	5	1	896	134	6.7
13	(*R*)-**7**	(*R*)-(menthyl)$SmCH(TMS)_2$	25	10	96	13	20	67	451	150	3.0
14	(*S*)-**8**	(*S*)-(menthyl)$LuN(TMS)_2$	25	10	59	20	23	57	725	394	1.8
15	(*R*)-**8**	(*R*)-(menthyl)$LuN(TMS)_2$	25	20	24	10	17	73	1645	521	3.2

[a] [Cat.] = 1.2 mM; MMA/cat., mol/mol = 500; 75 mL of toluene. [b] From ref 4. [c] See Scheme 1. [d] From ^1H NMR in toluene-d_8, 75 °C, 45° pulse width, 5 s delay. [e] From GPC relative to polystyrene standards. [f] (*R*) and (*S*) epimers crystallize in the same unit cell.

polydispersities ($M_w/M_n = 1.02-1.05$). As can be seen in Table 1, the polydispersity of PMMA from the chiral C_1-symmetric hydride precatalyst (R,S)-**5** is somewhat greater, while those from the chiral and achiral hydrocarbyl precatalysts are still larger, and amide precatalysts yield the largest polydispersities. Assuming that the polymerization mechanism involves initial 1,4 addition of the Ln−R functionality to MMA to generate an enolate[5] which then undergoes rapid, subsequent conjugate addition sequences (eq 2), it is reasonable that the kinetics of

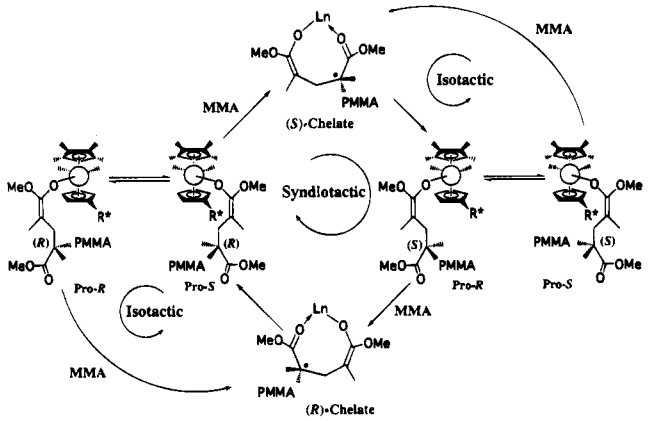


(2)

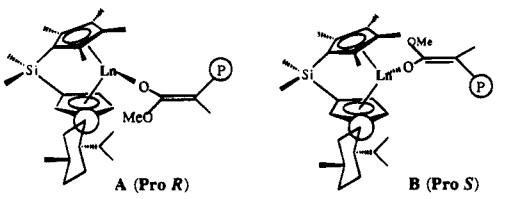
initiation should be sensitive to the steric encumbrance and operational nucleophilicity of R. Indeed, bulky R = $CH(TMS)_2$ and $N(TMS)_2$ ligands are most likely to render $k_p \gg k_i$. That **5** forms more tightly bound hydride dimers than does **1**[12] supports this scenario. Table 1 also reveals a decline in PMMA molecular weight with increasing reaction temperature for both the (*R,S*)-**4**- and (*R,S*)-**6**-mediated processes. These results and the parallel decline in polymer yield for the amido precatalysts are consistent with thermally-activated chain termination steps, some of which yield organolanthanides incompetent for further conjugate addition.

NMR statistical analysis[14-16] of the present PMMA samples reveals microstructures that cannot be associated with either exclusive Bernoullian chain-end or enantiomorphic site stereochemical control.[17,18] However, the observed stereospecificity can be rationalized on the basis of competing conjugate addition and lanthanide enolate template isomerization processes (Scheme 2). If stereoselective conjugate addition is far more rapid than isomerization or if the diastereomer equilibrium largely favors the incipient Michael product, then the resulting polymer is predicted to be predominantly syndiotactic. However, if template-mediated enolate isomerization is more rapid than conjugate addition and the diastereomer equilibrium favors the isomerized enolate, then template control is likely to produce isotactic polymer. The former scenario is proposed for the achiral and C_1-symmetric (−)-menthyl catalysts, while the latter

Scheme 2. Proposed Scenario for the Stereoregular Polymerization of Methyl Methacrylate Mediated by C_1-Symmetric Organolanthanide Complexes



appears predominant for the (+)-neomenthyl catalysts. For these laterally dissymmetric complexes, differences in the conformational energies of the two enolate species (e.g., **A** and **B**)



and the respective conjugate addition products can be expected. Nonbonding interactions between the chiral auxiliary and the enolate moiety likely contribute to these energy differences.

In summary, C_1-symmetric organolanthanides can be efficient catalysts for the stereoregular polymerization of methyl methacrylate. Stereoregulation, molecular weight, and polydispersity can be controlled by choice of precatalyst architecture and polymerization conditions.

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Supplementary Material Available: Experimental procedure and ^{13}C NMR data for isotactic poly(methyl methacrylate) (Table 1, entry 12, carbonyl region) (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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