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Isospecific polymerization of methyl methacrylate by intramolecular rare-earth metal based Lewis pairs

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ummary of main observation and conclusion A series of cationic rare-earth aryloxide complexes, *i.e.*, [LREOAr']⁺[B(C₆F₅)₄]⁻ (L = CH₃C(NAr)CHC(CH₃)(NCH(R)CH₂PPh₂); RE = Y, Lu; Ar' = 2,6-*t*Bu₂-C₆H₃, 2,6-(PhCMe₂)₂-4-Me-C₆H₂; Ar = 2,6-*i*Pr₂-C₆H₃, 2,6-(Ph₂CH)₂-4-*i*Pr-C₆H₂; R = H, CH₃, *i*Pr, ⁿh), were prepared and applied to the Lewis pair polymerization of methyl methacrylate (MMA). The stereoregularity of the resulting PMMA was significantly affected by the R substituent on the pendant arm of the tridentate NNP ligand, and was found to increase with increases in the steric hindrance of R. When using a Ph group as R, the Y complex produced a highly isotactic polymer with an *mm* value of 95% and a *T_g* of 54.6 °C. In contrast, ne steric hindrance of the Ar and Ar' groups had no effect on the tacticity of the resulting polymer, presumably because these two substituents were situated such that they pointed outward from the cyclic intermediates. Kinetics studies demonstrated that the polymerization was a first-order process with regard to the monomer concentration prior to catalyst deactivation. End group analysis indicated that the polymerization was accompanied by two ossibly competing chain-termination side reactions that proceeded *via* intramolecular backbiting cyclization.

Background and Originality Content

Since the discovery of frustrated Lewis pairs (FLPs) in 2006 by Stephan and coworkers,¹ FLP chemistry has become one of the most promising research fields in main group chemistry.^{2,3} FLPs ypically comprise sterically bulky main group Lewis acids and bases and can react with a large number of small molecules via ynergistic acid/base interactions.⁴ This has led to the applications of FLPs in various organic syntheses, such as hydrogenation,⁵ ydroamination,⁶ and C-H functionalization.⁷ Notably, FLPs can also be used in the field of polymer synthesis. In a seminal work, Chen and coworkers found that FLPs based on the main group lane, Al(C₆F₅)₃, effectively promoted the polymerization of methyl methacrylate (MMA) and its cyclic analogues.⁸ A novel onjugate-addition mechanism was proposed based on a FLP-type 1,4-addition as the initiating step. Stimulated by this research, has been significant development in the study of Lewis pairs polymerization (LPP) over the past decade.⁹ As an example, the cope of monomers has been expanded to include a variety of polar alkenes, including Michael-type compounds and their derivatives¹⁰ esters.11 well heterocyclic The as as ving/controlled¹² and complete chemoselective (co)polymerization¹³ have been successfully achieved through the use of LPP. Furthermore, application of LPP as a platform for the reparation of advanced materials have also realized.¹⁴ However, despite these advances, there are still various challenges in the field of LPP. One issue is that, although the stereoregularity of the olymer backbone plays a crucial role in defining the properties of the material, there have been few reports concerning the synthesis of polymers with a high degree of stereospecificity via LPP. Chen et al. demonstrated the highly stereospecific polymerization of MMA to obtain syndiotactic PMMA with a rr

value of 91% using an Al/P Lewis pair at -78 °C.¹⁵ Several chiral phosphines were also examined for use as Lewis bases in LPP as a means of increasing stereoselectivity under mild conditions. However, these compounds only gave syndio-rich PMMA with *rr* values of 74-75%, with no enhancement compared with PMMA derived from achiral LPs. These results can likely be attributed to binding of the Lewis base to the initiating chain end, which has a negligible effect on the polymer tacticity when the polymer chain becomes sufficiently long. It is also noteworthy that there have been no reports concerning the synthesis of isotactic or iso-rich PMMA using LPP.

Recently, the replacement of the main group Lewis acid in FLP chemistry by a transition-metal Lewis acid has emerged and shown some unique and promising results, because the Lewis acidity of transition-metals is diverse and can be finely-tuned.¹⁶ Specifically, employing rare-earth (RE) metals as Lewis acids is expected to provide new opportunities in both FLP and RE chemistry.¹⁷ On this basis, our group previously designed a new type of tridentate NNP ligand and prepared the corresponding cationic RE aryloxide complexes (Scheme 1),¹⁸ which were found to be active for the polymerization of MMA. The isolation of active intermediates (Scheme 1) and end group analysis indicated that this polymerization was initiated by an internal RE/P FLP-type 1,4-addition rather than the traditional and ubiquitous initiation pathway in RE metal-catalyzed MMA polymerization, *i.e.*, covalent RE-E (E = H, C, N) bond insertion or single-electron transfer.¹⁹

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However, the resulting polymers were found to be atactic. In ngle-site metal-catalyzed MMA polymerization, the steric hindrance of ancillary ligands usually exerts considerable fluence on the stereoregularity of the resulting polymer.²⁰ Thus, with the aim of achieving a high degree of stereospecificity, we odified NNP ligand precursor and prepared new RE aryloxide complexes (Scheme 1). A systematic study of polymerization promoted by various RE complexes with different NNP ligands dicated that isotactic PMMA could be obtained with an *mm* value of up to 95%. The study reported herein assessed the fects of the supporting ligands, the RE Lewis acids, and the reaction conditions on the catalytic activity and on the stereoregularity of the polymeric product.

Results and Discussion

synthesis and characterization of new tridentate NNP ligand ecursors and corresponding cationic RE complexes. Ligand precursors were prepared by the condensation reactions of enamines **1** with β -aminophosphines **2** in the presence of a atalytic amount of p-toluenesulfonic acid (Scheme 2). The starting materials **2b** and **2c** were accessed through well-established protocols from naturally-occurring chiral amino acids,²¹ while 2d was obtained from the chiral sulfinamide.²² To achieve satisfactory yields, these condensation reactions ed relatively harsh conditions (>110 °C, several days). Consequently, partial racemization of compounds 3 occurred, as c nfirmed by further transformations (vide infra). In all cases, no somer from tautomerization of the resulting products was observed in solution. Compound 3c was also characterized by ngle crystal X-ray diffraction and the molecular structure is provided in Supporting Information.

1 R R PPh_{2} R R PPh_{2} R R PPh_{2} $PPh_$

$$r = 2,6-(Ph_2CH)_2-4-iPr-C_6H_2, R = H(3e)$$

Scheme 1. Cationic RE aryloxide complexes and corresponding cyclic intermediates in LPP of MMA.

Scheme 2. Preparation of the NNP ligand precursors 3.

Our previous work indicated that complexes containing Sc, the smallest RE metal, showed significantly lower activity in the LPP of MMA compared with the performance obtained from the Y and Lu analogues.¹⁸ Thus, Sc complexes with new NNP ligands were not prepared in this study. The target RE complexes were synthesized using a three-step process based on our prior research, as depicted in Scheme 3. The alkane elimination reactions of the ligand precursors 3 with RE(CH₂SiMe₃)₃(THF)₂ (RE = Y, Lu) afforded the RE dialkyl complexes 4b - 4d in moderate yields under mild conditions. However, attempts to prepare complex 4e-Y using this same method failed, likely due to the presence of the bulky aryl group. Thus, the salt elimination reaction was applied and gave the desired dialkyl complex 4e-Y in a 70% isolated yield (for detail, see Supporting Information). Treatment of the RE dialkyls 4 with one equivalent of alkyl-substituted phenol in toluene generated the mixed alkyl/aryloxide species 5. Notably, complexes 5b - 5d were isolated as mixtures of two diastereomers, for which the respective molar ratios were determined by ^1H and ^{31}P NMR spectroscopy (see Supporting Information for details). This outcome is attributed to the coexistence of the unsymmetrical RE center and the chiral carbon at the ligand backbone.^{18,23} These results suggest that partial racemization occurred during the preparation of the ligand precursors. Finally, the target cationic RE aryloxide complexes 6 were obtained by the protonolysis of 5 amounts of the with equimolar Brønsted acid [PhNMe₂H][B(C₆F₅)₄]. Selected NMR spectroscopic data for complexes 6 are presented in Table 1 for comparisons. Based on the present ³¹P NMR spectroscopic observations together with the results of our previous work, we propose that internal RE-P interactions were present in complexes 6 in the solution state.²⁴ RE complexes 4c-Lu and 5c-Y were also characterized by single crystal X-ray diffraction. The molecular structure of complex 5c-Y is depicted in Figure 1, while structure of 4c-Lu is provided in Supporting Information.



cheme 3. The synthetic pathway to the cationic RE aryloxide complexes



Figure 1. Molecular structure of complex **5c-Y**. Hydrogen atoms are mitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Y1-O1 2.107(3); 2.346(4); Y1-N2 2.324(4); Y1-C49 2.396(6); Y1-P1 3.0650(12); N1-C2 1.319(6); C2-C3 1.416(7); C3-C4 1.395(7); N2-C4 1.338(6); N2-C6 490(6); C6-C7 1.555(8); C6-C10 1.490(6); N1-Y1-N2 81.54(14); 01-Y1-C49 109.86(17); N2-Y1-P1 64.77(10).

 Table 1. Selected NMR spectroscopic data for cationic RE aryloxide

 omplexes 6.°

(Insertion here)

Polymerization of MMA by intramolecular rare-earth metal ased Lewis pairs. We first examined the polymerization of MMA using 2 mol% of complex **6c-Y** by varying both the reaction temperature and solvent, and the results are summarized in Table 2. The polymerization led to a monomer conversion of 43% after 12 h when the reaction was conducted in PhCl at room temperature (Table 2, entry 1). However, the resulting polymer showed an isotacticity of 70% mm, in sharp contrast to our prior research. Upon lowering the temperature to -30 °C, the polymerization became much more rapid such that 90% of the MMA was consumed after 5 h, and PMMA with an 77% mm was obtained [molecular weight (Mn) = 8400 g/mol, polydispersity (PDI) = 1.62; Table 2, entry 2]. However, the stereoregularity of the resulting polymer was significantly reduced (mm = 57%) when polymerization was performed at -40 °C, and the activity was also lower such that only 65% MMA conversion was observed after 12 h (Table 2, entry 3). PhF, PhBr, and toluene were also investigated as solvents for the polymerization at -30 °C under the same conditions. These polymerizations achieved 83-91% monomer conversions after 12 h but only produced isotactic-rich polymers (59% mm in PhF, 58% mm in PhBr, and 60% mm in toluene; Table 2, entries 4-6). Thus, complex 6c-Y showed superior performance when polymerization was conducted in PhCl at -30 °C, likely because the corresponding cyclic, zwitterionic intermediate involved in the polymerization was relatively stable under these conditions.

Table 2. Polymerization of MMA by using complex 6c-Y.^a

(Insertion here)

A series of cationic RE aryloxide complexes based on tridentate NNP ligands were subsequently examined in LPP of MMA under the optimized conditions (2 mol% of catalyst loading, -30 °C, 0.4 mL of PhCl as a solvent, Table 3). Both 6a-Y and 6a-Lu generated atactic PMMA while exhibiting moderate activity (Table 3, entries 1 and 2). In contrast, the RE complexes 6b-Y and 6b-Lu, in which a methyl group was present on the pendant arm, polymerized MMA to isotactic-rich PMMA (6b-Y: 67% mm, 6b-Lu: 50% mm; Table 3, entries 3 and 4). Complex 6c-Lu achieved a 60% monomer conversion after 12 h and yielded a polymer with an isotacticity of 63% mm (M_n = 9300g/mol, PDI = 1.31; Table 3, entry 5). The incorporation of a more sterically hindered phenyl group on the pendant arm resulted in the formation of highly isotactic PMMA (95% mm) but of a low monomer conversion of 20% (Table 3, entry 6). The resulting polymer had a glass transition temperature (T_a) of 54.6 °C (Figure S88 in Supporting Information), which is consistent with the reported values for it-PMMA.25 These observations indicate that the substituent on the pendant arm of the NNP ligand had a significant effect on the stereoregularity of the resulting polymer, with stereoregularity decreasing in the order of Ph > iPr > Me > H. In addition, the polymerization results were affected by the RE metal ion and the Y complexes showed higher activity and gave more stereoregular products than the Lu analogues. Increasing the steric hindrance of the NAr (in the case of the 6e-Y) and OAr groups (in the case of the 6f-Lu) did not improve the stereoregularity of the polymeric product, but rather afforded atactic PMMA (Table 3, entries 7 and 8). This most probably occurred because these two Ar substituents extended outward from the cyclic intermediate, and so had a negligible effect on the stereoregularity during polymerization. The effects of the RE catalyst and monomer concentrations on the polymerization were also examined, and lower concentrations were found to greatly improve the ability to regulate the stereospecificity of the

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polymer. As an example, complex **6c-Y** produced highly isotactic PMMA (mm = 90%, $M_n = 7800$ g/mol, PDI = 1.33, $T_g = 56.2$ °C), although with a sacrifice of the catalytic activity (12 h, 58% MMA conversion; Table 3, entry 9).

Table 3. Polymerization of MMA by various cationic RE aryloxide complexes. $\!\!\!^{a}$

(Insertion here)

Kinetic and mechanistic studies of polymerization. To obtain additional information concerning the RE-based LPP of MMA, we e amined the polymerization kinetics using the RE catalysts 6b-Y, oc-Y, 6c-Lu, and 6d-Y with an initial MMA concentration of 2.5 M in PhCl at -30 °C. As shown in Figure 2, all of four systems rapidly initiated the polymerization but suffered from catalyst deactivation after approximately 2 h, after which there were no rther increases in MMA conversion. Plots of $ln([MMA]_0/[MMA]_t])$ vs. time (prior to catalyst deactivation) for trials generated good straight lines (Figure 3), indicating a first-order dependence on the MMA concentration. Notably, this * pe of polymerization kinetics is different with those observed during the LPP of MMA with main-group Lewis acids, for which zero-order kinetics are characteristic.9



r gure 2. Plots of conversion (%) vs. time (min) for the polymerization of MMA by RE catalysts **6b-Y** (●), **6c-Y** (■), **6c-Lu** (▲) and **6d-Y** (▼) in PhCl at -30 °C, [MMA]₀ = 2.5 M.



Figure 3. Plots of the first-order kinetics of $In([MMA]_0/[MMA]_t])$ vs. time (min) for the polymerization of MMA by RE catalysts **6b-Y** (\bullet), **6c-Y** (\blacksquare), **6c-Lu** (\bigstar) and **6d-Y** (\blacktriangledown) in PhCl at -30 °C, [MMA]_0 = 2.5 M.

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Figure 4. MALDI-TOF MS spectrum of the isolated PMMA produced by 5 mol% of 6c-Y at -30 °C in PhCl.

It is well-established that chain initiation in LPP is caused by he cooperative activation of the monomer substrate by the Lewis acid and base. In our previous work, we established that the cationic RE aryloxide complex based on NNP ligand 3a underwent an FLP-type RE/P 1,4-addition to conjugated carbonyl compounds such as MMA, affording product with a nine-membered metallocyclic framework (Scheme 1, vide supra), hat was found to serve as the initiating species for the MMA r olymerization.¹⁸ This result is in contrast to the traditional initiating process during polymerization catalyzed by RE complexes, which involves σ -bond insertion or single-electron ansfer. To provide further evidence for this initiation mechanism and to better understand the chain termination or ratalyst deactivation processes that occur during the polymerization, we subsequently investigated the chain end structure of the polymer. An oligomerization of 20 equivalents of 1 1MA using the 6c-Y at -30 °C was performed and the resulting A was analyzed by MALDI-TOF MS spectrum. As can be seen from Figure 4, a major series of ions were observed at m/zintervals of 100.2, which corresponds to the mass of the MMA



Figure 5. Plot of m/z values from the MALDI-TOF MS spectrum vs. the number of MMA repeating units (n).

monomer.²⁶ A plot of the m/z values associated with this series against the number of MMA repeating units gave a straight line with a slope of 100.17 and an intercept of 781.9 (Figure 5). This intercept value is not equal to the sum of the masses (513.3) of H⁺ and the ligand precursor **3c**, as was observed following polymerization with **6a** in our previous work, indicating a distinct chain termination pathway. We propose that side reactions occurred during the RE-based LPP of MMA and competed with chain propagation, and that this phenomenon also resulted in low activity in the present system during polymerization. Given that the chain initiation end is believed to comprise the ligand precursor **3c** (with a mass of 512.3), the value of 269 for the

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residual segment obtained by subtracting this value from the intercept would be expected to equal the mass of the chain termination end. We assume that intramolecular nucleophilic backbiting of the growing polymer at the adjacent ester group occurred to generate a six-membered lactone chain end, as has been reported to occur during the LPP of polar alkenes by Al-based systems.²⁷ The sum of the masses of such a six-membered lactone moiety (169) and an MMA repeating unit corresponds to the segment mass of 269. It should be noted here that there is another possible pathway for intramolecular b ckbiting cyclization that generates a β -ketoester chain end with a mass of 269,^{27b} but we cannot differentiate between these two nossible chain ends at present. Even so, based on the above observations, we can assume that growth of the polymer chains was hampered by the occurrence of the backbiting side reaction ring the late stage of polymerization. This process formed either six-membered lactone or β -ketoester chain ends, and led complete catalyst deactivation. Overall, these data show that the polymerization of MMA by cationic RE aryloxide complexes hised on tridentate NNP ligands is initiated by a RE/P 1,4-addition and terminated by a backbiting cyclization reaction.

The stereospecific polymerization of MMA to give a highly inptactic polymer is a remarkable feature of our RE-based Lewis pair catalyst system. The triad analysis of the resulting polymer st ereomicrostructure by ¹H NMR indicated that the stereocontrol mechanism cannot be simply associated with either chain end control $(4[rr][mm]/[mr]^2 = 1)^{25a-c,28}$ or enantiomorphic site control $(2[rr]/[mr] = 1)^{25a-d,29}$. This was further confirmed by the pentad analysis of the polymers using quantitative ¹³C NMR (for more details, see Supporting Information).^{25a,29a,30} On the basis of plymerization results, it appears that the stereospecificity of the product is greatly affected by the substituent on the ligand endant arm. In addition, the isotacticity of the resulting PMMA is increased with increasing steric hindrance of the corresponding substituent. Therefore, we tentatively propose that increasing le steric effect of the cyclic chain propagation intermediate may result in a slower rate of the subsequent conjugated addition action compared with that of enolate isomerization, thus render MMA coordination at the same site. This stereocontrol mechanism has been previously suggested to occur during the isospecific polymerization of MMA promoted by a chiral RE ocene amide.³¹

Conclusions

In summary, we synthesized a series of tridentate NNP ligand frameworks and prepared the corresponding cationic RE ryloxide complexes, which were systematically investigated in LPP of MMA. The results clearly demonstrated that the s ereoregularity of the resulting PMMA was strongly affected by the steric hindrance of the ligand motif, and that isospecific polymerization could be realized by introducing substituents on e pendant arm of the ligand. Remarkably, the isotacticity of the PMMA was increased with increasing steric hindrance of the substituent on the ligand backbone, achieving an *mm* value of up to 95% when a phenyl group was introduced. The outcome of the polymerization was also dependent on the nature of RE metal, and an Y complex showed higher activity and greater stereocontrol compared with those achieved using its Lu analogue. Kinetics data confirmed that the current polymerization exhibits a first-order dependence on the monomer concentration prior to catalyst deactivation, which is different from the behavior previously reported for the Al-based LPP of MMA. End group analysis indicated that the polymerization was terminated by an unexpected backbiting cyclization reaction, resulting in the low activity of this RE-based LP system during MMA polymerization. This study provides a comprehensive understanding of cationic RE aryloxide complexes during the LPP of MMA and also represents the first example of the isospecific polymerization of acrylate monomers by this process.

Supporting Information

The supporting information for this article is available on the WWW under <u>https://doi.org/10.1002/cjoc.2018xxxxx</u>.

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Table 1. Selected NMR spectroscopic data for cationic RE aryloxide complexes 6.^a

		Complex		6a ^b	6b		6c	(6d-Y	6e	-Y	6f-Lu
	¹ H	NC <i>H</i> R	3.22 (Y)		3.45 (Y)		3.25 (Y)		4.36	3.5	53	2.43
				3.38 (Lu)	3.60 (Lu)		3.34 (Lu)					
		PCH ₂		2.24 (Y)	2.32 (Y)		2.68 (Y)	:	2.65	2.5	56	2.43
				2.26 (Lu)	2.38 (Lu)		2.62 (Lu)					
		γ-C <i>H</i>		4.98 (Y)	4.69 (Y)		4.66 (Y)	4	4.95	5.0)8	4.79
\mathbf{i}				4.94 (Lu)	4.84 (Lu)		4.81 (Lu)					
1	${}^{13}C{}^{1}H{}$	N <i>C</i> HR		46.8 (Y)	53.9 (Y)		64.5 (Y)	(62.1	48	.5	44.6
				45.7 (Lu)	53.8 (Lu)		64.4 (Lu)					
		PCH ₂		28.8 (Y)	34.5 (Y)		32.2 (Y)	1	36.8	34	.0	28.7
1				27.5 (Lu)	34.0 (Lu)		31.2 (Lu)					
		γ- <i>C</i> H		94.5 (Y)	89.2 (Y)		88.0 (Y)	9	94.7	97	.6	98.3
			1	101.5 (Lu)	93.0 (Lu)		89.4 (Lu)					
	³¹ P{ ¹ H}			-6.8 (Y)	-10.9 (Y)		-13.2 (Y)		-9.0	-10	-10.3	
5			6.8 (Lu)		-1.8 (Lu)		-4.4 (Lu)					
_	³¹ P{ ¹ H} ^c			-21.5	-22.0		-22.0	-	22.0	-21	.4	-21.
۵NM	VR in PPM. "Re	et. 18. * **P{*H} of	correspondi	ng ligand precu	rsor.							
.ab	ile 2 . Polymeri	zation of MMA b	by using comp	plex 6c-Y.ª								
.ab	ble 2 . Polymeri	zation of MMA k Temp.	by using comp	olex 6c-Y .ª Time	Conv. ^b	M _n ^c		PDI ^c		mm ^d	mr ^d	r
. <u>ab</u>	ble 2 . Polymeri Entry	zation of MMA b Temp. (°C)	oy using comp Solvent	olex 6c-Y . ^a Time (h)	Conv. ^b (%)	Mn ^c (g/mol)	(PDI ^c M _w /M _n)		mm ^d (%)	mr ^d (%)	rı (9
. <u>ab</u>	ble 2 . Polymeri Entry 1	zation of MMA t Temp. (°C) 25	by using comp Solvent PhCl	Diex 6c-Y . ^{<i>a</i>} Time (h) 12	Conv. ^b (%) 43	Mn ^c (g/mol) 4100	(PDI ^c M _w /M _n) 1.93		mm ^d (%) 70	mr ^d (%) 18	r (9
	ble 2 . Polymeri Entry 1 2	Temp. (°C) 25 -30	by using comp Solvent PhCl PhCl	Deex 6c-Y." Time (h) 12 5	Conv. ^b (%) 43 90	M ^{n^c} (g/mol) 4100 8400	(PDI ^c M _w /M _n) 1.93 1.62		mm ^d (%) 70 77	mr ^d (%) 18 13	r (9 1 1
ab.	Entry 1 2 3	Temp. (°C) 25 -30 -40	by using comp Solvent PhCl PhCl PhCl	Delex 6c-Y . ^{<i>a</i>} Time (h) 12 5 12	Conv. ^b (%) 43 90 65	Mn ^c (g/mol) 4100 8400 5500	(PDI ^c Mw/Mn) 1.93 1.62 1.47		mm ^d (%) 70 77 57	mr ^d (%) 18 13 21	(9 1 1 2
. <u>at</u>	De 2. Polymeri Entry 1 2 3 4	zation of MMA I Temp. (°C) 25 -30 -40 -30	by using comp Solvent PhCl PhCl PhCl PhF	blex 6c-Y . ^{<i>a</i>} Time (h) 12 5 12 12 12	Conv. ^b (%) 43 90 65 83	M ^{n^c} (g/mol) 4100 8400 5500 5700	(PDI ^c Mw/Mn) 1.93 1.62 1.47 1.30		mm ^d (%) 70 77 57 59	mr ^d (%) 18 13 21 18	rr (% 1 2 2
	De 2. Polymeri Entry 1 2 3 4 5	zation of MMA I Temp. (°C) 25 -30 -40 -30 -30	Solvent Solvent PhCl PhCl PhCl PhF PhF PhBr	blex 6c-Y." Time (h) 12 5 12 12 12 12	Conv. ^b (%) 43 90 65 83 91	Mn ^c (g/mol) 4100 8400 5500 5700 6300	(PDI ^c Mw/Mn) 1.93 1.62 1.47 1.30 1.29		mm ^d (%) 70 77 57 59 58	mr ^d (%) 18 13 21 18 18 17	rr (% 1 1 2 2 2

able 2. Polymerization of MMA by using complex 6c-Y.^a

1		Temp.		Time	Conv. ^b	M _n ^c	PDI ^c	mm ^d	mr ^d	rr ^d
	Entry	(°C)	Solvent	(h)	(%)	(g/mol)	(M _w /M _n)	(%)	(%)	(%)
	1	25	PhCl	12	43	4100	1.93	70	18	12
1	2	-30	PhCl	5	90	8400	1.62	77	13	10
	3	-40	PhCl	12	65	5500	1.47	57	21	22
- i -	4	-30	PhF	12	83	5700	1.30	59	18	23
	5	-30	PhBr	12	91	6300	1.29	58	17	25
<u> </u>	6	-30	toluene	12	87	4600	1.44	60	20	20

Conditions: Polymerizations were conducted in 0.4 mL of solvent, where n_[6C-Y] = 20 µmol, [M]/[C] = 50/1. ^bMonomer conversions were determined by ¹H JMR spectroscopy. ^cMn and PDI were determined by GPC in THF relative to PS standards. ^drr, mr, mm = polymer methyl triads were measured by ¹H NMR (PMMA).

Table 3. Polymerization of MMA by various cationic RE aryloxide complexes.^a

	Entry	Cat.	Time	Conv. ^b	M_n^c	PDI ^c	mm ^d	mr ^d	rr ^d
			(n)	(%)	(g/mol)	(IVIw/IVIn)	(%)	(%)	(%)
Ce	1	6a-Y	12	71	7900	1.48	28	22	50
	2	6a-Lu	12	54	6900	1.67	20	22	58
	3	6b-Y	12	68	6400	1.48	61	18	21
	4	6b-Lu	12	43	6100	1.25	50	19	31
	5	6c-Lu	12	60	9300	1.31	63	19	18
0	6	6d-Y	24	20	2800	1.20	95	3	2
	7	6e-Y	12	83	5300	1.19	28	21	51
	8	6f-Lu	8	93	7300	1.15	24	39	37
	9 ^e	6c-Y	24	58	7800	1.33	90	7	3

^aConditions: Polymerizations were conducted at -30 °C in 0.4 mL of PhCl, where n_[cat.] = 20 μmol, [M]/[C] = 50/1. ^bMonomer conversions were determined by ¹H NMR spectroscopy. ^cMn and PDI were determined by GPC in THF relative to PS standards. ^drr, mr, mm = polymer methyl triads were measured by ¹H NMR (PMMA). ^ePolymerization was conducted in 0.8 mL of PhCl.



Accepted Article

Entry for the Table of Contents

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Isospecific polymerization of methyl methacrylate by intramolecular rare-earth metal based Lewis pairs



Cationic rare-earth aryloxide complexes based on tridentate NNP ligands are prepared and applied for RE/P Lewis pair polymerization of methyl methacrylate, which afford isotactic polymers when using ligands with substituent on the pendant arm.