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Toolbox of Nonmetallocene Lanthanides: Multifunctional Catalysts in Group-Transfer Polymerization

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S Supporting Information

ABSTRACT: Herein, we present a fundamental study of isostructural 2-methoxyethylamino-bis(phenolate)-lanthanide complexes $[(ONOO)^{R}M(X)(THF)]$ (M = Lu, Y; R = ^tBu, CMe₂Ph, X = CH₂TMS, collidine; THF = tetrahydrofuran; TMS = trimethylsilyl) for rare-earth metal-mediated group-transfer polymerization (GTP). This analysis includes the differentiation of electron-donating and non-donating vinyl monomers and two metal centers with regard to the ionic radius (yttrium and lutetium). In addition, highly nucleophilic alkyl initiators are compared with electron-donating heteroaromatic initiators. Our examinations include the impact of these parameters on the activity, initiator efficiency, and tacticity of the obtained polymers. Density functional theory calculations and proposed catalyst structure determinations via X-ray analysis support these investigations. This facilitates the selection of the best metal and initiator combination to



address efficient and stereospecific polymerization of a broad range of Michael monomers. $[(ONOO)^{tBu}Lu(X)(THF)]$ shows the highest activity of 2220 h⁻¹ (normalized turnover frequency) for the polymerization of 2-vinylpyridine due to the higher Lewisacidity of lutetium. Through $C(sp^3)$ -H bond activation, catalysts with higher initiator efficiency in *N*,*N'*-dimethylacrylamide (DMAA) and diethylvinylphosphonate polymerization were synthesized. Remarkably, $[(ONOO)^{tBu}Y(collidine)(THF)]$ was capable of stereospecifically polymerizing DMAA to highly isotactic poly(DMAA) ($P_m = 0.94$). Overall, the kinetics studies reveal a living-type GTP mechanism for all of the tested catalysts, enabling precise molecular-weight predeterminations with narrow molecular weight distributions ($D \leq 1.06$).

INTRODUCTION

One of the core challenges in polymer synthesis is the creation of highly complex and well-defined structures from simple molecules. To synthesize polymers for high-tech applications, it is necessary to accurately influence the mechanical and thermal properties via changes in the microstructure or molecular weight. Therefore, the availability of catalysts for the precise synthesis of these polymers is an essential requirement. The living character and high activity of rare-earth metal-mediated group-transfer polymerization (REM-GTP) are two advantages of this polymerization method. Beyond that, molecular weights are precisely controllable, and narrow molecular weight distributions are observed. Currently, different types of Michael-type polar vinyl monomers have been homopolymerized and copolymerized via REM-GTP (Figure 1).¹⁻⁸ The possibility of using different phosphorus and nitrogencontaining polar vinyl monomers leads to different functionalities, which enables access to various fields for application. 1,9-12

REM-GTP with a symmetric 2-aminoalkoxy-bis(phenolate)yttrium trimethylsilylmethyl complex (1a) is one of the first examples of a nonmetallocene system. This catalyst showed



Figure 1. REM-GTP of Michael-type oxygen-, phosphorus-, and nitrogen-containing vinyl monomers.

good activities for various monomers without inducing tacticity.^{13,14} Recently, two different approaches toward highly

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stereospecific polymerization of prochiral 2-vinylpyridine (2VP) with nonmetallocene lanthanides have been established by the groups of Rieger and Lu.^{6,15,16} As lanthanocenes show insufficient polymerization activity and stereospecificity for various monomers, the scope of bis(phenolate)lanthanide complexes is further broadened by this contribution.^{11,13} A systematic study on the activity, initiator efficiency, and stereospecificity (with reference to three different parameters) is presented herein. The experimental investigations are substantiated with detailed density functional theory (DFT) calculations and proposed catalyst structure determinations via X-ray analysis. For the first parameter, a distinction was made between electron-donating and nonelectron-donating monomers. For the second parameter, changes in the metal center (from yttrium to lutetium) were performed with regard to the influence of the ionic radius on the polymerization. The last parameter was generated by the introduction of a new heteroaromatic electron-donating initiator. This initiator was then compared with highly basic alkyl initiators. Two different types of initiators were investigated, as different initiation mechanisms can occur. Strongly basic alkyl initiators can be inefficient if they favor deprotonation of an acidic α -CH and do not initiate polymerization via nucleophilic attack (see Figure 2).^{13,17} To eliminate side reactions and the slow deprotonationmediated initiation, heteroaromatic initiators can be used instead.



Figure 2. Initiation pathways for REM-GTP of DAVP via deprotonation (A) or nucleophilic transfer (B).

To introduce these heteroaromatic initiators, C–H bond activation can be utilized.^{12,18–26} Lanthanide complexes are able to activate compounds such as 2,4,6-trimethylpyridine (*sym*-collidine) via σ -bond metathesis. This type of C–H bond activation is a common way to access C–H bond cleavage, because oxidative addition and reductive elimination reactions

are not possible with trivalent lanthanides. This σ -bond metathesis was first shown by Watson et al. in 1983 via the activation of isotopically labeled methane, benzene, and pyridine with a cyclopentadienyl-lutetium-methyl complex.^{27,28}

RESULTS AND DISCUSSION

Synthesis and Characterization of Alkyllanthanide Complexes. The symmetrically substituted 2-methoxyethylamino-bis(phenolate) ligand (L1) was synthesized via a modified Mannich reaction of 2,3-di-*tert*-butylphenol with 2methoxyethylamine in a formaldehyde solution.²⁹ The asymmetric ligand (L2) was only accessible through a multistep reaction. The final nucleophilic substitution reaction of the cumyl-substituted 2-methoxyethylaminophenolate with the *tert*butyl-substituted phenol-methylenebromide led to the desired ligand in moderate yield (see Supporting Information).¹⁵

For the synthesis of $(ONOO)^{\hat{R}}Ln(CH_2TMS)(THF)$ (1a– 3a) (Ln = Y, Lu; TMS = trimethylsilyl; THF = tetrahydrofuran) complexes, 1 equiv of the respective ligand was reacted with 1 equiv of the precursor, $Ln(CH_2TMS)_3(THF)_3$, in a mixture of toluene/pentane at 0 °C and stirred overnight at room temperature (Supporting Information). As yttrium complexes 1a and 3a were isolated in moderate yields (43 to 47%), lutetium analogue 2a was synthesized in good yields of up to 75%. The monomeric structure of every complex was verified via ¹H NMR spectroscopy.^{15,30}

C–H Bond Activation. Initially, we tested the reactivity of complexes 1a-3a toward *sym*-collidine (Scheme 1). Time-resolved ¹H NMR experiments of the reaction were performed at room and elevated temperatures (60 and 80 °C, respectively) to investigate the tendency to activate *sym*-collidine. These experiments revealed strongly varying ambitions for the catalysts to undergo C–H bond activation (Figure 2 and Supporting Information, Figures S1–S3).

For all complexes, only very slow activation was observed at room temperature. Increased temperatures led to significant changes in the reactivity, and catalyst **1a** was transformed to complex **1b** in the presence of 1 equiv of 2,4,6-trimethylpyridine within 4 h at 60 °C (see Figure 3). ¹H NMR examinations revealed that after the addition of *sym*-collidine (Figure 3, spectrum 2: 6.77, 2.47, and 2.24 ppm), the signals for the CH₂TMS initiator of complex **1a** decreased (comparison with spectrum 1). The concurrent increase of the tetramethylsilane signal (SiMe₄: 0 ppm) indicated the ongoing metathesis reaction. In the same manner, two new signals arose in the aromatic region, representing the binding of collidine. Two signals in the aliphatic region show the two new methyl groups (spectrum 4). The reaction was straightforward, and no side

Scheme 1. C-H Bond Activation of Catalysts 1a-3a with sym-Collidine in Toluene to Obtain Complexes 1b-3b

^tBu ^tBu -0 ^tBu (toluene) `о́Ме `о́Ме ĊH₂ TMS L1 R = t Bu L2 R = CMe₂Ph 1a Ln = Y, L1 **1b** Ln = Y, L1 (yield: 31%) 2a Ln = Lu, L1 2b Ln = Lu, L1 (yield: 64%) 3a Ln = Y, L2 **3b** Ln = Y, L2 (yield: 48%)



Figure 3. ¹H NMR kinetic experiments for the C–H bond activation of *sym*-collidine with complex 1a in C_6D_6 . (1) Complex 1a. (2) Immediately after addition of *sym*-collidine. (3) 40 min; 60 °C. (4) 4 h; 60 °C. (5) Complex 1b.

reactions occurred, which enabled us to scale up the catalyst synthesis of **1b** in toluene. Purification was performed via recrystallization from pentane at -30 °C (spectrum 5). The interaction between the metal center and the initiator via an activated CH₂ group was verified by ¹H- and ¹³C NMR spectroscopy. ²*J*-Coupling (J = 2.9 Hz) of the CH₂ signal at 2.80 ppm in the ¹H NMR spectrum (spin = 1/2, leading to a splitting as a doublet) and a splitting of the carbon atom at 52.5 ppm (¹*J* = 6.0 Hz) in the ¹³C NMR spectra underscored the successful C–H bond activation.

Compound 2a was more reluctant in its reactivity toward sym-collidine; nevertheless, quantitative C-H bond activation could be achieved after 9 d at 80 °C. As the 4f electrons have no contribution to the binding valence orbitals, lutetium can be seen as an isoelectronic equivalent to yttrium. Therefore, the σ bond metathesis was investigated to determine the influence of the effective ionic radius. Lutetium is more Lewis-acidic/ electrophilic owing to its higher effective nuclear charge, leading to a stronger binding of the nucleophilic CH₂TMS initiator.³¹ This led to a prolonged reaction time for C-H bond activation. These observations and suggestions were in accordance with hard-soft acid-base (HSAB) theory. Complex 2b was isolated in good yields via recrystallization in pentane. No formation of side products was observed during the activation with compound 1a and 2a, which highlighted the remarkable stability of the catalysts. Only complex 3a slowly decomposed at elevated temperatures. Hence, complex 3b was generated through the reaction of 3a with sym-collidine at room temperature over 6 d in moderate yield. In all reactions, the Lu complexes were generated in higher yields than the Y analogues due to the higher insolubility in pentane. For all C-H bond-activated compounds, recrystallization in pentane afforded the desired complexes with the general structure $(ONOO)^{tBu,R}Ln((4,6-dimethylpyridin-2-yl)methyl))(THF)$

(1b-3b) (Scheme 1). All C-H bond-activated compounds were characterized via NMR spectroscopy and elemental analysis. In the case of complex 1b, X-ray diffraction analysis was used to analyze the proposed complex structure.

Structure Analysis. Crystals of complex 1b were grown through recrystallization from pentane at -30 °C. Against all expectations, and in contrast to the NMR spectra, the complex crystallized as two independent molecules without tetrahydrofuran as a coordinating solvent (see Figure S4, Supporting Information). As a consequence, the yttrium is coordinated in a sevenfold manner and not in the generally favored octahedral coordination sphere. Nevertheless, the 2-methoxy-bis-(phenolate) ligand coordinated in the same way as in complex 1a.³² The solid-state structure of one independent molecule of complex 1b is shown in Figure 4. The three Y-O bonds are equatorial, whereas the nitrogen is ordered axial to the yttrium center. Owing to the missing tetrahydrofuran, which coordinates equatorial to the yttrium in 1a, the bond angles between the yttrium and the oxygen atoms differ in these two compounds and are larger in 1b. Fundamental for the performed C-H bond activation is the coordination of the (4,6-dimethylpyridine-2-yl)-methyl initiator to the metal center. The Y-N bond is shorter than the Y- C_{α} bond; thus, the initiator is primarily coordinated via the Y-N moiety.

The C–C bond lengths in the aromatic ring were all similar and lay between double- and single-bond lengths (1.362[1.364] to 1.423[1.424] Å; Figure 4), as might be expected for aromatic systems (bond lengths for the second independent molecule are given in parentheses). Remarkably, the C(sp³)–H activated methyl–methyl bond ($C_{34,\alpha}$ – $C_{35,ipso}$) had a reduced length of 1.400[1.399] Å. Consequently, double-bond character was predominant, and the activated methyl group was conjugated in the aromatic system. One C–C bond of the heteroaromatic system (1.423[1.424] Å, Figure 4, $C_{35,ipso}$ – $C_{36,ortho}$) was even



Figure 4. ORTEP-style representation of **1b**. Hydrogen atoms and the second independent molecule are omitted for clarity. Ellipsoids with 50% probability. Selected bond lengths (Å) and angles (deg): Y(1)-O(1), 2.1130(15); Y(1)-O(2), 2.1318(16); Y(1)-O(3), 2.3641(16); Y(1)-N(1), 2.5385(19); Y(1)-N(2), 2.3950(19); Y(1)-C(34), 2.608(2); Y(1)-C(35), 2.740(2); N(2)-C(35), 1.386(3); N(2)-C(39), 1.361(3); C(34)-C(35), 1.400(4); C(35)-C(36), 1.423(3); C(36)-C(37), 1.362(4); C(37)-C(38), 1.413(4); C(38)-C(39), 1.366(3); C(39)-C(41), 1.493(3); C(37)-C(40), 1.508(4); O(1)-Y(1)-O(2), 119.74(6); O(1)-Y(1)-O(3), 123.02(6); O(2)-Y(1)-O(3), 99.09(6); N(1)-Y(1)-N(2), 167.93(6); O(1)-Y(1)-C(34), 91.17(7); N(2)-Y(1)-C(34), 55.94(7).

slightly longer than the activated methyl group, indicating the high charge delocalization of the latter group. The tilt of the phenyl ring was calculated with the help of the C_{α} –Y– C_{ipso} angle. The value of 80.12° and a relatively short Y– C_{ipso} bond (2.740[2.715] Å) indicated binding of the collidine occurred via an allylic motif. From these findings, the η^3 -(*C*,*C*,*N*)-aza-allylic binding to the yttrium center was evident. This coordination type is an intermediate between an η^2 -alkyl-amine and an η^1 -amido-olefin coordination, as Teuben and co-workers investigated in bis(alkoxysilylamido)-yttrium-pyridyl complexes.²⁰ The two other methyl groups possessed single-bond character with bond lengths of 1.493[1.496] and 1.508[1.502] Å; therefore, they were not integrated into the conjugated system.

As the deprotonated collidine species can be seen as a benzyl-type ligand, 1b was compared to the literature-known complex $[Y(CH_2Ph)_3(THF)_3]$ with respect to the charge

delocalization and allylic binding motif (see Figure S5 and Table S3, Supporting Information). Whereas the benzyl ligand in $[Y(CH_2Ph)_3(THF)_3]$ was primary bond via the Y-C_a, the collidine ligand in 1b is coordinated via Y-N binding. The longer $Ln-C_{\alpha}$ bond of **1b** and the shorter $C_{\alpha}-C_{ipso}$ bond (higher double bond character) indicated a more pronounced multihapto binding due to the higher charge delocalization (see Table 1). The η^3 -allylic binding in 1b was also confirmed by the higher phenyl tilt (80.12° vs 117.17°) and the shorter $\text{Ln}-\text{C}_{\text{ipso}}$ bond. The same parameters can be used to compare the collidine structures regarding the impact of the metal size. As we were not able to isolate crystals of 2b, we used DFT calculations instead. Harder et al. stated that within benzyllanthanide(III) complexes, some parameters do not vary significantly along the lanthanide series.³³ Nevertheless, we compared the DFT-calculated structures fully aware that only slight trends might be observed. Overall, these calculations predicted a higher end-on coordination in place of a side-on coordination, as found in the solid-state structure of 1b (see Table 1). Less allylic bindings were calculated for both metals, as indicated by the longer Ln-C_{ipso} bonds and the broader $C_{ipso} - C_{\alpha}$ - Ln angles. Within these calculations, the same trends as in the series of different benzyl lanthanides were observed.³³⁻³⁵ Because of the higher Lewis acidity of lutetium, a higher charge localization is provoked. The $C_{\alpha}-C_{ipso}$ bond elongates on account of weaker charge delocalization. As lutetium polarizes the negative charge more than yttrium, the allylic binding motif becomes weaker. As a result, the ${\rm Ln-C_{ipso}}$ bond was longer, and the $C_{ipso}-C_{\alpha}$ -Ln angle was broader. The less distinct multihapto binding with decreasing ion size is also shown by the $Ln-C_{\alpha}$ bond shortening.

Group-Transfer Polymerization. The isolated catalysts (1a-3b) were employed in the GTP of vinyl monomers diethylvinylphosphonate (DEVP), N,N'-dimethylacrylamide (DMAA), and 2VP to evaluate the general activities, initiator efficiencies, and the microstructures of the isolated polymers. Poly-2-vinylpyridine (P2VP) is a polymer for high-performance applications due to its pH-dependent solubility. Several examples of block copolymers containing hydrophobic 2VP are known in the literature where micelle formation occurs due to their amphiphilic character.^{36–43} Therefore, our attention was directed to enhancements in 2VP polymerization. First, the initiation mechanisms of the C-H bond-activated complexes were elucidated by end-group analysis of oligomeric 2VP. This was produced by reacting catalyst 1b with 10 equiv of 2VP and monitoring the reaction via NMR spectroscopy. Electrospray ionization mass spectrometry (ESI-MS) analysis of the

Table 1. REM-GTP Po	lymerization F	Results of Cataly	yst $1a-3b$ of $2VP^a$
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entry	[cat]	time [min]	conversion [%]	$M_{\rm n,calc} (1 \times 10^4) [\rm g/mol]^b$	$M_{ m n,exp}~(1 imes 10^4)~[m g/mol]$	\mathcal{D}^{c}	I^d	$TOF^{*e} [h^{-1}]$	$P_{\rm m}^{f}$
1 ¹³	1a	90	99	2.1	2.3	1.01	0.99	1110	0.55
2	2a	130	99	2.3	7.4	1.06	0.30	1750	0.56
3 ¹⁵	3a	120	99	2.2	3.9	1.00	0.71	440	0.57
4	1b	60	99	2.0	4.1	1.01	0.42	1080	0.54
5	2b	45	99	2.0	4.9	1.06	0.43	2220	0.54
6	3b	180	99	2.0	4.7	1.06	0.42	470	0.56

"Reactions performed with $[2VP] = 2.7 \text{ mmol}, [2VP]/[Cat] = 200/1, at 25 °C in 2 mL of solvent, conversions determined by ¹H NMR spectroscopy and <math>M_{n,expd}$ determined by GPC-MALS. ${}^{b}M_{n,calc}$ from $M_{n,calc} = M \times (([M]/[Cat]) \times \text{conversion})$. Polydispersity calculated from $M_{w,expd}/M_{n,expd}$ as determined by GPC-MALS. ${}^{d}I = M_{n,calc}/M_{n,exp}$ at the end of the reaction. "TOF* = TOF/*I*; normalized TOF for the active metal centers." ${}^{f}P_{m}$ is the probability of *meso* linkages between monomer units and was determined by ¹³C NMR spectroscopy of the quaternary carbon atom (Supporting Information)." 15,44



Figure 5. (left) Catalytic activity of catalysts **1a**/**b** and **2a**/**b** (Y = line; Lu = dashed; CH₂TMS = black; *sym*-collidine (coll) = gray; catalyst: 135 μ mol, 2VP: 27 mmol, toluene: 20 mL, T = 25 °C) measured via the aliquot method. (right) Linear growth of the absolute molecular weight (M_n) (determined by GPC-MALS) as a function of monomer conversion (gravimetrically determined).

respective oligomers showed signals corresponding to $n \times M_{2VP}$ + $M_{collidine}$ with either H⁺ or Na⁺ as the charge carrier (Supporting Information, Figure S6). The initiating groups were clearly visible in the ESI-MS; a nucleophilic transfer reaction of the initiator via monomer insertion into a Y–C bond is apparent (Figure 2). The evidence of a nucleophilic transfer reaction for the initiation of 2VP polymerization with Ia has already been reported in a previous study.¹³ On the basis of the observed mechanism, these findings were further elucidated via DFT calculations (vide infra).

To determine conversions and kinetic parameters of the polymerization, aliquots were taken at regular time intervals during polymerization. The conversion was gravimetrically calculated. Absolute molecular masses and mass distributions were measured by gel-permeation chromatography multiangle light scattering (GPC-MALS). The polymerization of 2VP with all 2-methoxyethylamino-bis(phenolate) catalysts proceed in a living fashion, as indicated by the narrow polydispersities (1.00 $\leq D \leq 1.06$) and good agreement between the experimentally determined and theoretically expected $M_{\rm p}$ values (Table 1). The plots of conversion against the absolute molecular mass reveal a linear relationship between M_n and conversion, underlining the living fashion of the polymerization (Figure 5 and Supporting Information, Figures S9, S10, S12, and S13). If the conversion is plotted against time, the polymerizations can be compared with regard to the activity of the different catalysts. Catalysts 1a and 3a were tested in the GTP of 2VP in a previous contribution from our group, and we had already shown that the increased steric demand of the bis(phenolate) ligand led to a decrease in catalyst activity and initiator efficiency (Table 1, Entries 1 and 3). In both cases, only atactic P2VP was obtained.¹⁵ As expected, changing the initiator to sym-collidine did not impact the normalized turnover frequencies (TOF*), since the activity is solely influenced by the metal center and the ligand, which are both involved in the propagation mechanism (Table 1, Entries 4 and 6).

The introduction of the collidine initiator led to a decrease in initiator efficiency of the complexes from 99% (1a)/71% (3a) to 42% (1b/3b); therefore, no improvement was found for the yttrium-based bis(phenolate)-mediated 2VP polymerization. Remarkably, the change of the metal center to lutetium increased the catalytic activity; complexes 2a and 2b were the

most active catalysts (TOF* = 1750–2220 h⁻¹) in the polymerization of 2VP while maintaining accurate control over the molecular masses (D = 1.06). Owing to the higher Lewis-acidity of lutetium, the stronger polarization of the coordinating monomer in the propagation mechanism may be decisive for the higher activity. The stronger binding of the CH₂TMS initiator in compound **2a** (vide supra) was reflected in the initiator efficiency, which was lower in comparison to the respective yttrium compounds. In contrast to the yttrium complexes, the change in initiator from **2a** to **2b** was a suitable approach for improving the initiator efficiency and led to an increase of ~45%. As the tacticity of P2VP is influenced by an enantiomorphic site control mechanism, the change of metal has no effect on the tacticity.¹⁵

Recently, we reported on nontoxic phosphorus-containing poly(dialkylvinylphosphonate)s (DAVPs) in combination with P2VP as advanced micellar systems for drug-release applications.^{26,45} On the basis of these results, our study also included the detailed investigation of DEVP polymerization (alkyl chain = ethyl) with the above-mentioned catalysts. Complexes 1a-3a, with an alkyl initiator, all showed relatively low initiator efficiency in the polymerization of DEVP (Supporting Information, Table S4). In the case of DEVP, basic alkyl initiators are inefficient due to deprotonation of the acidic α -CH of the first monomer (see Figure 2). Especially, complex 2a demonstrates a low initiator efficiency, leading to a time-shifted and slower initiation, resulting in an increase of the molecular mass distribution (D = 1.48 - 1.50). Initiation via the collidine initiator led to an increase in efficiency up to 80%. The polydispersity (D = 1.03 - 1.14) of the polymers was improved as slow initiation via deprotonation was eliminated. In contrast to 2VP polymerization, the two metal species showed similar tendencies when the initiator was changed. In addition, the activity and initiator efficiency of the lutetium species seemed to be lower than for the yttrium catalysts.

Poly(DMAA) (PDMAA) is of special interest regarding the application as stimuli-responsive materials (micelles, hydrogels, and nanocomposites).^{46–51} The polymerization of DMAA was investigated with regard to catalyst activity and the microstructure of PDMAA. Because of the exothermic nature of the polymerization, the reaction was performed at low temperatures (-78, -50, and -20 °C). When refrigerated monomer

entry	[cat]	$T_{\mathrm{Add}} [^{\circ}\mathrm{C}]^{b}$	$T_{\text{Polym}} [^{\circ}C]^{c}$	conversion [%]	$M_{\rm n,calc}^{e}$ (1 × 10 ⁴) [g/mol]	$M_{\rm n,exp} (1 \times 10^4) [g/mol]$	Đ	If	P_m^{g}
1	1a	-78	-50	99	1.9	18.4	1.42	0.10	0.91
2	1a	-50	-50	99	2.1	24.4	1.49	0.09	0.91
3	1a	-20	-20	99	1.9	8.5	1.66	0.22	0.89
4	1a	0	0	99	2.0	4.3	2.12	0.47	0.83
5	2a	-78	-20	99	2.1	57.7	1.17	0.04	0.56
6^d	2a	-78	-20	94	1.9	48.3	1.34	0.04	0.56
7	2a	-15	-15	99	2.0	18.8	1.69	0.11	
8	2a	0	0	99	2.0	7.5	2.22	0.26	
9	3a	-78	-50	99	2.3	15.1	1.30	0.15	0.90
10	1b	-78	-78	99	2.0	6.6	1.06	0.30	0.94

Table 2. REMPOTT TOTYMETIZATION Results of Catalyst Ta-Ja and TD for DIMAR	Table 2	. REM-GTP	Polymerization	Results of	Catalyst	1a-3a and	1b for DMAA
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"Reactions performed with [DMAA] = 2.15 mmol (-35 °C), [DMAA]/[Cat] = 200/1, in 4.5 g of dichloromethane, conversions determined by ¹H NMR spectroscopy, and $M_{n,expd}$ determined by GPC-MALS. Several attempts to polymerize DMAA with catalysts **2a** and **3a** failed. ^bTemperature of the reaction mixture at addition of monomer. ^cEstimated temperature when polymerization occurred; observed through the increase in viscosity and end of stirring. ^dQuenching after 3 min; first time for the nonquantitative conversion of the slowest catalyst. ^e $M_{n,calc}$ from $M_{n,calc} = M \times (([DMAA]/[cat]) \times \text{conversion})$. ^f $I = M_{n,calc}/M_{n,exp}$ at the end of the reaction. ^g P_m is the probability of *meso*-linkages between monomer units and was determined by high-temperature ¹H NMR spectroscopy in DMSO-d₆ at 140 °C.



Figure 6. (A) Carbonyl region of the ¹³C NMR spectra (126 MHz, $CDCl_3$, 25 °C) of PDMAA prepared with catalyst **1b**. (B) Backbone methylene signal in the ¹H NMR spectra (300 MHz, deuterated dimethyl sulfoxide (DMSO- d_6), 140 °C) of PDMAA prepared with catalyst **1b**. ⁵² (C) Carbonyl region of the ¹³C NMR spectra (126 MHz, $CDCl_3$, 25 °C) of PDMAA prepared with catalyst **2a**. (D) Backbone methylene signal in the ¹H NMR spectra (300 MHz, DMSO- d_6 , 140 °C) of PDMAA prepared with catalyst **2a**.

was added to the reaction mixture at a certain temperature, and no polymerization initiation was observed, the mixture was slowly warmed. The end of polymerization was apparent through the increased viscosity and the immediate end of stirring. Kinetic measurements were not possible. At 0 °C the reaction was not controllable. The alkyl-yttrium complexes 1a and 3a showed no activity at -78 °C; warming to -50 °C led to an immediate reaction but with low initiator efficiencies (Table 2, entries 1 and 9). Because of a delayed and spontaneous reaction, as well as the rapidly rising viscosity of the reaction mixture, the molecular mass distributions were higher than expected for a living-type polymerization mechanism ($D \leq 1.49$). Reactions were also performed at higher temperatures to investigate the influence of temperature on initiator efficiency and tacticity. These polymerizations indeed demonstrated a higher initiator efficiency, as more catalytic centers were active at higher temperatures; however, a higher molecular mass distribution, up to 2.22 (Table 2, entries 3, 4, 7, and 8), was found. Polymerizations that were gradually warmed from -78 °C, in comparison with those performed directly at elevated temperatures, showed similar results, which attests the reproducibility of the results (Table 2, entries 1 and 2). The stronger binding of the alkyl initiator to electrophilic

lutetium (complex 2a) was expressed by a very low initiator efficiency, since the polymerization did not start until warming to -20 °C. As a consequence, it was possible to quench the polymerization before quantitative conversion. A conversion of 94% in 3 min for complex 2a showed the high activity of this catalyst and all of the other tested catalysts. In comparison to previous studies on coordinative-DMAA polymerization, these bis(phenolate)lanthanides were highly active.⁵²⁻⁵⁴ We searched for initiators that were also active at -78 °C to overcome the problem of high molecular mass distributions and the low initiator efficiency for the yttrium complexes. The introduction of sym-collidine led to an improvement for DMAA polymerization (Table 2, entry 10) since the initiator efficiency was improved, facilitating a polymerization at -78 °C. Because of this fact, a very low polydispersity of 1.06 was observed, demonstrating the high suitability of complex 1b for the polymerization of DMAA.

The polymerization of DMAA was also studied in regard to the resulting microstructures. Figure 6 depicts the carbonyl region of the ¹³C NMR spectra and the backbone methylene signal in the high-temperature (HT) ¹H NMR spectra of PDMAA prepared with catalysts **1b** and **2a**. Assignment of the *m*- and *r*-dyad of the methylene proton was performed



Figure 7. Reaction path for the initiation process: catalyst 1a (black) and 1b (red) with 2VP and DMAA.

analogously to the method of Kakuchi et al. For the triad distribution of the carbonyl signal, assignment was performed analogously to the method of San Román et al.^{52,55} For DMAA, higher initiator efficiencies were found for the heteroaromatic compound 1b; therefore, polymerization was possible at -78 °C. This was reflected by the increasing percentage for mesolinkages in the polymer. Catalyst 1b produced PDMAA with the highest isotacticity ($P_m = 0.94$). This value was determined as the proportion of *m*-dyad in the methylene region of the 1 H NMR spectrum. Complexes 1a and 3a, which were active at -50 °C, both produced PDMAA with slightly lower isotacticity $(P_{\rm m} = 0.91 \text{ and } 0.90, \text{ respectively})$. The slight increase in steric demand of ligand L2 in 3a did not affect the tacticity. On account of this, it was obvious that the lutetium complex (2a), which was only active at -20 °C, would produce PDMAA with a lower tacticity. Figure 6 shows that only atactic polymer was obtained. To analyze if this decrease in tacticity was only caused by the increase in temperature, polymerizations with 1a were performed at -20 and 0 °C. The temperature rise led, in fact, to a decrease in isotacticity, but the catalyst still produced isotactic PDMAA ($P_m = 0.89$). Remarkably, not only the temperature but also the metal center has an impact on the tacticity. Because of these findings, different mechanisms for determining the stereoselectivity were expected for polymerizations with 2VP (enantiomorphic site control) and DMAA (chain-end control).

Radical and anionic polymerizations are only able to produce PDMAA with moderate isotacticity ([mm] = 54-81). Chiral *ansa*-zirconocenium catalysts, developed by Chen et al., exclusively produce isotactic PDMAA; however, the applic-

ability of those systems on the additional vinyl monomers, beyond acrylamides, was not investigated.^{53,54} In comparison, catalyst **1b** is a suitable generalist for DMAA polymerizations. This catalyst combines high activity and increased initiator efficiency with a low polydispersity and high polymer isotacticity.

Density Functional Theory Calculations on the Initiation Process. DFT calculations at the B3LYP level of theory, coupled with the LANL2DZ basis set, were used to uncover the mechanistic proceedings during the initiation process of GTP with 2VP (electron-donating monomer) and DMAA (nonelectron-donating monomer). These calculations were performed to assess the feasibility of the initiation reaction for the two different initiators (alkyl initiator (1a) vs collidine (1b)). Gas-phase geometry optimization of 1a, 1b, DMAA, and 2VP gave the starting-point geometries for the ensuing reaction path (Figure 7) and reference energies. Then, the monomers were chelated to the isolated complexes (THF served as the exchange molecule) as the first step of initiation, resulting in structures $I_a - I_d$.¹³ The chelated structures were optimized again to obtain the respective coordination energies. Finally, the products II_a-II_d generated via a nucleophilic transfer reaction were calculated to gain insights into the relative energies of the product with respect to the reactants and the isolated systems. The electronic energies associated with the reaction path are depicted in Figure 7 and refer to the minimum-energy geometry of the isolated monomers and catalysts. The stepwise profiles of the initiation process reaction sequence for DMAA and 2VP are depicted in black for catalyst 1a and red for catalyst **1b**. It is evident for DMAA that initiation with either



Figure 8. Optimized structures II_{a-d} after nucleophilic attack of the initiator to the monomer (light blue = yttrium; red = oxygen; purple = nitrogen; yellow = silicon; gray = carbon).

catalyst leads to a net favorable driving force for nucleophilic transfer ($\mathbf{II}_{c} = -84 \text{ kJ/mol}$; $\mathbf{II}_{d} = -139 \text{ kJ/mol}$) confirming our experimental observations. Both catalysts were able to initiate the polymerization, and cooling was necessary to avoid thermal desorption and to ensure isothermal conditions. Whereas both catalysts show a thermodynamically favored process, the calculations indicate that the initial coordination step, as well as the nucleophilic transfer reaction, are energetically more preferred using collidine as an initiator (catalyst 1b). This was manifested in lower-energy products \mathbf{I}_{d} and \mathbf{II}_{d} . These computations were in good agreement with the experimental findings. The experiments of DMAA with catalyst 1a could be performed at -50 °C, whereas the reactions with catalyst 1b had to be cooled to -78 °C for a controlled reaction due to the significantly stronger exothermic nature of the reaction.

Attempts at raising the temperatures led to the evaporation of the solvent, as the heat dissipation was not sufficient. Polymerizations with 2VP were conducted at room temperature, since the reaction was less exothermic. Again, this was supported by the calculations, which indicated a slightly endothermic process, which was associated with the coordination step ($I_a = +11 \text{ kJ/mol}$; $I_b = +16 \text{ kJ/mol}$). Consequently, reactions at -78 °C were not successful.¹³ The calculated energy differences between the initiation of 2VP with 1a and 1b show only small differences. Contrary to DMAA initiation, 1a seems to be slightly energetically favored for initiating 2VP polymerization (II_a = -21 kJ/mol; II_b = -6 kJ/mol). Again, this is in accordance with the experimental results, in which 1a shows a higher initiator efficiency. We were able to calculate two transition states for initiation with complexes 1a and 1b $(I_{h} \rightarrow II_{h} \text{ and } I_{c} \rightarrow II_{c})$. In both cases, the transition states were ~1 eV above the reactant energy levels ($I_b \rightarrow II_b = 1.2 \text{ eV}$; $I_c \rightarrow II_c$ = 0.9 eV). Given the stabilization gained by the initial monomer coordination (barrierless, since this represents a long-range attraction) and the zero-point energy, the energy barrier is not expected to hinder the reactivity as also confirmed by the experiment. Attempts in optimizing all other transition states along the nucleophilic transfer path proved challenging and were limited by convergence problems as well as high computational costs.

As the experimental finding shows a less-efficient initiation in 2VP polymerization with collidine than with the alkyl initiator, we were interested in the electronic and steric properties of the optimized geometries (I_{a-d} and II_{a-d}). By comparing structures II_a and II_b (after nucleophilic transfer of the respective initiator to 2VP) it seemed that the collidine moiety of II_b was

completely detached from the metal center (Figure 8). As known, 2VP is a strong electron donor, and when used in tandem with an electron-donating molecule like the pyridine moiety in 1b, an overload of electron density to the metal center is provoked. This overload in electron density weakens the binding energy of the collidine moiety, which explains the detachment from yttrium in the optimized geometry. The geometry I_b of the initial coordination step already confirmed dissociation of one electron-donating molecule (Figure 9).



Figure 9. Geometry of I_b (light blue = yttrium; red = oxygen; purple = nitrogen; gray = carbon).

Because of the coordination of the electron-donating collidine initiator, coordination of the 2VP via the nitrogen atom is disfavored. This led to the detachment of the monomer from yttrium. It appears that high electron density/charge localization on the nucleophilic carbon atom of the initiator (predominant in alkyl initiators) is essential for nucleophilic attack of barely coordinated 2VP. The combination of an electron-donating nitrogen atom and reduced electron density on the activated CH_2 group of collidine (due to charge delocalization) was not sufficient for efficient nucleophilic transfer to 2VP. These assumptions were in accordance with the experimental findings, as initiation with collidine was less efficient than initiation via an alkyl species.

We were interested in the initiator efficiencies of 1a and 1b in IPOx polymerization (Supporting Information, Table S5) to verify our examinations on the validity for all nitrogencoordinating Michael monomers. The results underline our postulation, as they were very similar to 2VP polymerization results. High initiator efficiency was observed for alkyl initiators (I = 0.93), whereas less-efficient initiation was predominant with the heteroaromatic collidine initiator (I = 0.47).

Table 3.	Comparison and	d Advantages of	the Best Suitable	Catalysts According	g to the Re	spective Monomer
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mone	meta	metal center initiator		ator		
N-coordinating	O-coordinating	Y	Lu	CH ₂ TMS	collidine	advantage of catalyst
2VP		+		+		high initiator efficiency
			+	+	+	high activity
	DEVP	+	+ ^a		+	improved initiator efficiencies
						improved D
	DMAA	+			+	high activity
						high isotacticity of PDMAA
						improved D
^a 2b shows just a slightly b	roader <i>Đ</i> and initiator effi	ciency in con	mparison to	1b.		

To show that the opposite trend is evident in DMAA polymerization, the isolated structures II_b and II_c were compared (see Figure 8). An eight-membered cycloadditiontype nucleophilic transfer reaction of I_d involving the CH_2 substituent of collidine leads to the formation of an aliphatic chain (II_d) . The N-Y bond was not completely cleaved after the addition process, since the pyridine moiety remained coordinated to the metal center. In comparison, the CH₂TMS moiety of structure II_c shows a complete detachment from the Y atom and is solely bound via the oxygen atom of DMAA. This can be understood by considering that the CH₂TMS moiety in 1a is a poor electron donor when compared with the pyridine moiety of 1b and, thus, has weaker binding energy. In addition, DMAA itself has electron-withdrawing character, and electron density overload is not caused by initiation with electron-donating collidine. The coordination of DMAA simultaneously with the attached electron-donating collidine does not provoke an electron overload at the metal center, neither in I_d nor in II_d . Therefore, the calculation results underline our experimental findings and enable a comparison between the different initiators, metal centers, and monomers during the initiation process.

CONCLUSION

In this study, REM-GTP with isostructural 2-aminoalkoxybis-(phenolate)yttrium and lutetium complexes 1a-3b was examined. This study showed moderate-to-exceptionally high catalyst activities with various polar monomers. Kinetic studies in 2VP polymerization revealed that all of the tested catalyst systems followed a living-type mechanism, allowing precise molecular weight control with very narrow molecular-weight distributions. A heteroaromatic molecule was efficiently introduced as an initiator via C-H bond activation. Altogether, these structure variations made it possible to tune the activity, initiator efficiency, and the resulting microstructures of 2VP, DEVP, and DMAA polymerization. Lutetium catalysts $[(ONOO)^{tBu}Lu(X)(THF)]$ (2a/2b), with a higher effective nuclear charge, demonstrated the highest activity for GTP of 2VP. Bis(phenolate)yttrium complexes with heteroaromatic initiators showed decreased efficiency in polymerization with electron-donating monomers (2VP and IPOx), because electron density overload was provoked at the yttrium center. Computational studies underline that the coordination of nitrogen-donating monomers (containing a free electron pair) is hindered with yttrium catalysts when an electron-donating initiator is used. Since all of the other monomers were nonelectron-donating systems, the change of initiator via C-H bond activation with 2,4,6-collidine led to an enhancement in initiator efficiency. Deprotonation of the acidic α -CH is avoided with heteroaromatic initiators, which, until now, was solely

assumed for DEVP polymerization while neglecting the electronic effects. For DMAA polymerization, yttrium catalyst **1b** was highly active, and the resulting polymer microstructure exhibited high isotacticity ($P_m = 94\%$) while maintaining a narrow molecular mass distribution. In summary, this study facilitates the selection of the ideal initiator and metal combination for obtaining the most efficient and stereospecific polymerization system for a broad range of polar vinyl monomers. Table 3 summarizes the most suitable catalysts for each monomer type studied.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01261.

Experimental section, further analytic data, DFT calculations, X-ray data (CCDC 1547971), and polymer characteristics (PDF)

Accession Codes

CCDC 1547971 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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REFERENCES

(1) Soller, B. S.; Salzinger, S.; Rieger, B. Rare Earth Metal-Mediated Precision Polymerization of Vinylphosphonates and Conjugated Nitrogen-Containing Vinyl Monomers. *Chem. Rev.* **2016**, *116* (4), 1993–2022.

(2) Soller, B. S.; Zhang, N.; Rieger, B. Catalytic Precision Polymerization: Rare Earth Metal-Mediated Synthesis of Homopolymers, Block Copolymers, and Polymer Brushes. *Macromol. Chem. Phys.* **2014**, *215* (20), 1946–1962.

(3) Chen, E. Y. X. Coordination Polymerization of Polar Vinyl Monomers by Single-Site Metal Catalysts. *Chem. Rev.* **2009**, *109* (11), 5157–5214.

(4) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. New Approach to Block Copolymerizations of Ethylene with Alkyl Methacrylates and Lactones by Unique Catalysis with Organolanthanide Complexes. *Macromolecules* **1992**, *25* (19), 5115–5116.

(5) Ihara, E.; Morimoto, M.; Yasuda, H. Living Polymerizations and Copolymerizations of Alkyl Acrylates by the Unique Catalysis of Rare Earth Metal Complexes. *Macromolecules* **1995**, *28* (23), 7886–7892.

(6) Xu, T.-Q.; Yang, G.-W.; Lu, X.-B. Highly Isotactic and High-Molecular-Weight Poly(2-Vinylpyridine) by Coordination Polymerization with Yttrium Bis(Phenolate) Ether Catalysts. *ACS Catal.* **2016**, *6* (8), 4907–4913.

(7) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. Synthesis of Monodispersed High Molecular Weight Polymers and Isolation of an Organolanthanide(Iii) Intermediate Coordinated by a Penultimate Poly(Mma) Unit. *J. Am. Chem. Soc.* **1992**, *114* (12), 4908–4910.

(8) Collins, S.; Ward, D. G. Group-Transfer Polymerization Using Cationic Zirconocene Compounds. J. Am. Chem. Soc. **1992**, 114 (13), 5460–5462.

(9) Seemann, U. B.; Dengler, J. E.; Rieger, B. High-Molecular-Weight Poly(Vinylphosphonate)S by Single-Component Living Polymerization Initiated by Rare Earth Metal Complexes. *Angew. Chem., Int. Ed.* **2010**, *49* (20), 3489–3491.

(10) Salzinger, S.; Seemann, U. B.; Plikhta, A.; Rieger, B. Poly(Vinylphosphonate)S Synthesized by Trivalent Cyclopentadienyl Lanthanide-Induced Group Transfer Polymerization. *Macromolecules* **2011**, *44* (15), 5920–5927.

(11) Zhang, N.; Salzinger, S.; Soller, B. S.; Rieger, B. Rare Earth Metal-Mediated Group-Transfer Polymerization: From Defined Polymer Microstructures to High-Precision Nano-Scaled Objects. J. Am. Chem. Soc. 2013, 135 (24), 8810–8813.

(12) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. End-Functionalized Polymerization of 2-Vinylpyridine through Initial C-H Bond Activation of N-Heteroaromatics and Internal Alkynes by Yttrium Ene-Diamido Complexes. *J. Am. Chem. Soc.* **2011**, *133* (49), 19626–19629.

(13) Altenbuchner, P. T.; Soller, B. S.; Kissling, S.; Bachmann, T.; Kronast, A.; Vagin, S. I.; Rieger, B. Versatile 2-Methoxyethylaminobis-(Phenolate)Yttrium Catalysts: Catalytic Precision Polymerization of Polar Monomers Via Rare Earth Metal-Mediated Group Transfer Polymerization. *Macromolecules* **2014**, 47 (22), 7742–7749.

(14) Carpentier, J. F. Rare-Earth Complexes Supported by Tripodal Tetradentate Bis(Phenolate) Ligands: A Privileged Class of Catalysts for Ring-Opening Polymerization of Cyclic Esters. *Organometallics* **2015**, *34* (17), 4175–4189.

(15) Altenbuchner, P. T.; Adams, F.; Kronast, A.; Herdtweck, E.; Pöthig, A.; Rieger, B. Stereospecific Catalytic Precision Polymerization of 2-Vinylpyridine Via Rare Earth Metal-Mediated Group Transfer Polymerization with 2-Methoxyethylamino-Bis(Phenolate)-Yttrium Complexes. *Polym. Chem.* **2015**, *6* (38), 6796–6801.

(16) Kronast, A.; Reiter, D.; Altenbuchner, P. T.; Vagin, S. I.; Rieger, B. 2-Methoxyethylamino-Bis(Phenolate)Yttrium Catalysts for the Synthesis of Highly Isotactic Poly(2-Vinylpyridine) by Rare-Earth Metal-Mediated Group Transfer Polymerization. *Macromolecules* **2016**, 49 (17), 6260–6267.

(17) Salzinger, S.; Soller, B. S.; Plikhta, A.; Seemann, U. B.; Herdtweck, E.; Rieger, B. Mechanistic Studies on Initiation and Propagation of Rare Earth Metal-Mediated Group Transfer Polymerization of Vinylphosphonates. *J. Am. Chem. Soc.* **2013**, *135* (35), 13030–13040.

(18) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. Bis(Trimethylsilyl)Benzamidinate: A Promising Spectator Ligand in Organoyttrium Chemistry. Synthesis and Reactivity of {[C6h5c-(Nsime3)2]2y-.Mu.-R}2 (R = H, C.Tplbond.Ch) and X-Ray Structure of {[C6h5c(Nsime3)2]2y-.Mu.-C.Tplbond.Ch}2. J. Am. Chem. Soc. **1993**, 115 (11), 4931–4932.

(19) Duchateau, R.; van Wee, C. T.; Teuben, J. H. Insertion and C– H Bond Activation of Unsaturated Substrates by Bis(Benzamidinato)-Yttrium Alkyl, [Phc(Nsime3)2]2yr ($R = Ch2ph\cdotThf$, Ch(Sime3)2), and Hydrido, {[Phc(Nsime3)2]2y(M-H)}2, Compounds. Organometallics **1996**, 15 (9), 2291–2302.

(20) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. Synthesis and Reactivity of Bis(Alkoxysilylamido)Yttrium H2-Pyridyl and H2-A-Picolyl Compounds. *Organometallics* **1997**, *16* (25), 5506–5516.

(21) Ihara, E.; Koyama, K.; Yasuda, H.; Kanehisa, N.; Kai, Y. Catalytic Activity of Allyl-, Azaallyl- and Diaza-Pentadienyllanthanide Complexes for Polymerization of Methyl Methacrylate. *J. Organomet. Chem.* **1999**, 574 (1), 40–49.

(22) Labinger, J. A.; Bercaw, J. E. Understanding and Exploiting C-H Bond Activation. *Nature* **2002**, *417* (6888), 507–514.

(23) Rad'kov, V.; Dorcet, V.; Carpentier, J.-F.; Trifonov, A.; Kirillov, E. Alkylyttrium Complexes of Amidine–Amidopyridinate Ligands. Intramolecular C(Sp3)–H Activation and Reactivity Studies. *Organometallics* **2013**, 32 (5), 1517–1527.

(24) Shibata, Y.; Nagae, H.; Sumiya, S.; Rochat, R.; Tsurugi, H.; Mashima, K. 2,2[Prime or Minute]-Bipyridyl Formation from 2-Arylpyridines through Bimetallic Diyttrium Intermediate. *Chem. Sci.* **2015**, *6* (10), 5394–5399.

(25) Soller, B. S.; Salzinger, S.; Jandl, C.; Pothig, A.; Rieger, B. C-H Bond Activation by Sigma-Bond Metathesis as a Versatile Route toward Highly Efficient Initiators for the Catalytic Precision Polymerization of Polar Monomers. *Organometallics* **2015**, *34* (11), 2703–2706.

(26) Altenbuchner, P. T.; Werz, P. D.; Schöppner, P.; Adams, F.; Kronast, A.; Schwarzenböck, C.; Pöthig, A.; Jandl, C.; Haslbeck, M.; Rieger, B. Next Generation Multiresponsive Nanocarriers for Targeted Drug Delivery to Cancer Cells. *Chem. - Eur. J.* **2016**, *22* (41), 14576– 84.

(27) Watson, P. L. Facile C-H Activation by Lutetium-Methyl and Lutetium-Hydride Complexes. J. Chem. Soc., Chem. Commun. 1983, No. 6, 276–277.

(28) Watson, P. L. Methane Exchange Reactions of Lanthanide and Early-Transition-Metal Methyl Complexes. J. Am. Chem. Soc. 1983, 105 (21), 6491–6493.

(29) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. [Onxo]-Type Amine Bis(Phenolate) Zirconium and Hafnium Complexes as Extremely Active 1-Hexene Polymerization Catalysts. *Organometallics* **2002**, *21* (4), 662–670.

(30) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. Exploring Electronic Versus Steric Effects in Stereoselective Ring-Opening Polymerization of Lactide and B-Butyrolactone with Amino-Alkoxy-Bis(Phenolate)-Yttrium Complexes. *Chem. - Eur. J.* 2011, *17* (6), 1872–1883.

(31) Arndt, S.; Okuda, J. Cationic Alkyl Complexes of the Rare-Earth Metals: Synthesis, Structure, and Reactivity. *Adv. Synth. Catal.* **2005**, 347 (2–3), 339–354.

(32) Cai, C.-X.; Toupet, L.; Lehmann, C. W.; Carpentier, J.-F. Synthesis, Structure and Reactivity of New Yttrium Bis(Dimethylsilyl)-Amido and Bis(Trimethylsilyl)Methyl Complexes of a Tetradentate Bis(Phenoxide) Ligand. J. Organomet. Chem. 2003, 683 (1), 131–136. (33) Harder, S.; Ruspic, C.; Bhriain, N. N.; Berkermann, F.; Schürmann, M. Benzyl Complexes of Lanthanide (Ii) and Lanthanide (Iii) Metals: Trends and Comparisons. Zeitschrift für Naturforschung B 2008, 63 (3), 267–274.

(34) Ge, S.; Meetsma, A.; Hessen, B. Scandium, Yttrium, and Lanthanum Benzyl and Alkynyl Complexes with the N-(2-Pyrrolidin-1-Ylethyl)-1, 4-Diazepan-6-Amido Ligand: Synthesis, Characterization, and Z-Selective Catalytic Linear Dimerization of Phenylacetylenes. *Organometallics* **2009**, *28* (3), 719–726.

(35) Behrle, A. C.; Schmidt, J. A. Synthesis and Reactivity of Homoleptic A-Metalated N, N-Dimethylbenzylamine Rare-Earth-Metal Complexes. *Organometallics* **2011**, *30* (15), 3915–3918.

(36) Martin, T. J.; Procházka, K.; Munk, P.; Webber, S. E. Ph-Dependent Micellization of Poly(2-Vinylpyridine)-Block-Poly-(Ethylene Oxide). *Macromolecules* **1996**, *29* (18), 6071–6073.

(37) Atanase, L. I.; Riess, G. Micellization of Ph-Stimulable Poly(2-Vinylpyridine)-B-Poly(Ethylene Oxide) Copolymers and Their Complexation with Anionic Surfactants. *J. Colloid Interface Sci.* **2013**, 395, 190–197.

(38) Kang, N.-G.; Kang, B.-G.; Koh, H.-D.; Changez, M.; Lee, J.-S. Block Copolymers Containing Pyridine Moieties: Precise Synthesis and Applications. *React. Funct. Polym.* **2009**, *69* (7), 470–479.

(39) Kumar, S.; Changez, M.; Murthy, C. N.; Yamago, S.; Lee, J.-S. Synthesis of Well-Defined Amphiphilic Block Copolymers by Organotellurium-Mediated Living Radical Polymerization (Terp). *Macromol. Rapid Commun.* **2011**, 32 (19), 1576–1582.

(40) Klinger, D.; Wang, C. X.; Connal, L. A.; Audus, D. J.; Jang, S. G.; Kraemer, S.; Killops, K. L.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. A Facile Synthesis of Dynamic, Shape-Changing Polymer Particles. *Angew. Chem., Int. Ed.* **2014**, 53 (27), 7018–7022.

(41) Talingting, M. R.; Munk, P.; Webber, S. E.; Tuzar, Z. Onion-Type Micelles from Polystyrene-Block-Poly(2-Vinylpyridine) and Poly(2-Vinylpyridine)-Block-Poly(Ethylene Oxide). *Macromolecules* **1999**, 32 (5), 1593–1601.

(42) Changez, M.; Kang, N.-G.; Kim, D. W.; Lee, J.-S. Hollow Flower Micelles from a Diblock Copolymer. *Nanoscale* **2013**, *5* (23), 11554–11560.

(43) Borchert, U.; Lipprandt, U.; Bilang, M.; Kimpfler, A.; Rank, A.; Peschka-Süss, R.; Schubert, R.; Lindner, P.; Förster, S. Ph-Induced Release from P2vp-Peo Block Copolymer Vesicles. *Langmuir* **2006**, *22* (13), 5843–5847.

(44) Brigodiot, M.; Cheradame, H.; Fontanille, M.; Vairon, J. P. Microstructure of Poly(2-Vinylpyridine): Correlation between 13c and 1n.M.R. Determinations. *Polymer* **1976**, *17* (3), 254–256.

(45) Adams, F.; Altenbuchner, P. T.; Werz, P. D. L.; Rieger, B. Multiresponsive Micellar Block Copolymers from 2-Vinylpyridine and Dialkylvinylphosphonates with a Tunable Lower Critical Solution Temperature. *RSC Adv.* **2016**, *6* (82), 78750–78754.

(46) Mariott, W. R.; Chen, E. Y. X. Stereochemically Controlled Pmma-Exfoliated Silicate Nanocomposites Using Intergallery-Anchored Metallocenium Cations. J. Am. Chem. Soc. 2003, 125 (51), 15726–15727.

(47) Aoki, T.; Kawashima, M.; Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. Temperature-Responsive Interpenetrating Polymer Networks Constructed with Poly(Acrylic Acid) and Poly-(N,N-Dimethylacrylamide). *Macromolecules* **1994**, 27 (4), 947–952.

(48) Barker, I. C.; Cowie, J. M. G.; Huckerby, T. N.; Shaw, D. A.; Soutar, I.; Swanson, L. Studies of the "Smart" Thermoresponsive Behavior of Copolymers of N-Isopropylacrylamide and N,N-Dimethylacrylamide in Dilute Aqueous Solution. *Macromolecules* **2003**, *36* (20), 7765–7770.

(49) Jayachandran, K. N.; Takacs-Cox, A.; Brooks, D. E. Synthesis and Characterization of Polymer Brushes of Poly(N,N-Dimethylacrylamide) from Polystyrene Latex by Aqueous Atom Transfer Radical Polymerization. *Macromolecules* **2002**, *35* (11), 4247–4257.

(50) Mueller, K. F. Thermotropic Aqueous Gels and Solutions of N,N-Dimethylacrylamide-Acrylate Copolymers. *Polymer* **1992**, *33* (16), 3470–3476.

(51) Bekiari, V.; Sotiropoulou, M.; Bokias, G.; Lianos, P. Use of Poly(N,N-Dimethylacrylamide-Co-Sodium Acrylate) Hydrogel to

Extract Cationic Dyes and Metals from Water. Colloids Surf., A 2008, 312 (2-3), 214–218. (52) Fuchise, K.; Sakai, R.; Satoh, T.; Sato, S.-i.; Narumi, A.;

Kawaguchi, S.; Kakuchi, T. Group Transfer Polymerization Ofn,N-Dimethylacrylamide Using Nobel Efficient System Consisting of Dialkylamino Silyl Enol Ether as an Initiator and Strong Brønsted Acid as an Organocatalyst. *Macromolecules* **2010**, *43* (13), 5589–5594.

(53) Mariott, W. R.; Chen, E. Y. X. Stereospecific, Coordination Polymerization of Acrylamides by Chiral Ansa-Metallocenium Alkyl and Ester Enolate Cations. *Macromolecules* **2004**, 37 (13), 4741–4743.

(54) Mariott, W. R.; Chen, E. Y. X. Mechanism and Scope of Stereospecific, Coordinative-Anionic Polymerization of Acrylamides by Chiral Zirconocenium Ester and Amide Enolates. *Macromolecules* **2005**, 38 (16), 6822–6832.

(55) Bulai, A.; Jimeno, M. L.; Alencar de Queiroz, A.-A.; Gallardo, A.; San Román, J. 1h And13c Nuclear Magnetic Resonance Studies on the Stereochemical Configuration of Bis(N,N-Dimethyl-2,4-Dimethylglutarylamide) and Poly(N,N-Dimethylacrylamide). *Macromolecules* **1996**, *29* (9), 3240–3246.