


Article

Chemoselective Polymerization of Polar Divinyl Monomers with Rare-Earth/Phosphine Lewis Pairs

Pengfei Xu ¹, Lei Wu ¹, Liqiu Dong ^{1,2} and Xin Xu ^{1,*} 

¹ Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China; 20164009015@stu.suda.edu.cn (P.X.); 1509401010@stu.suda.edu.cn (L.W.); dongliqiufrank@gmail.com (L.D.)

² Suzhou International Academy, BFSU, Suzhou 215200, China

* Correspondence: xinxu@suda.edu.cn; Tel.: +86-512-65882921

Received: 6 January 2018; Accepted: 6 February 2018; Published: 8 February 2018

Abstract: This work reports the chemoselective polymerization of polar divinyl monomers, including allyl methacrylate (AMA), vinyl methacrylate (VMA), and 4-vinylbenzyl methacrylate (VBMA), by using simple Lewis pairs comprised of homoleptic rare-earth (RE) aryloxy complexes RE(OAr)₃ (RE = Sc (**1**), Y (**2**), Sm (**3**), La (**4**), Ar = 2,6-*t*Bu₂C₆H₃) and phosphines PR₃ (R = Ph, Cy, Et, Me). Catalytic activities of polymerizations relied heavily upon the cooperation of Lewis acid and Lewis base components. The produced polymers were soluble in common organic solvents and often had a narrow molecular weight distribution. A highly syndiotactic poly(allyl methacrylate) (PAMA) with *rr* ~88% could be obtained by the scandium complex **1**/PEt₃ pair at −30 °C. In the case of poly(4-vinylbenzyl methacrylate) (PVBMA), it could be post-functionalized with PhCH₂SH. Mechanistic study, including the isolation of the zwitterionic active species and the end-group analysis, revealed that the frustrated Lewis pair (FLP)-type addition was the initiating step in the polymerization.

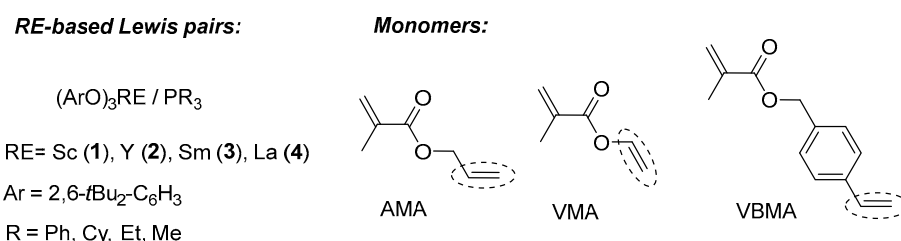
Keywords: Lewis pairs; rare-earth; phosphines; chemoselective polymerization

1. Introduction

The post-modification of polymers containing reactive vinyl groups offers a great opportunity to obtain many advanced functional materials [1–7]. The chemoselective polymerization of polar divinyl monomers represents one of the most powerful methods to produce such polymers. Among the enormous efforts which have been made so far, anionic [8,9] and radical [10–13] polymerization have been extensively investigated. However, achieving complete chemoselectivity and preventing crosslinking during the whole process remains a great challenge, especially in the later stage of the polymerization [14]. To maintain the chemoselectivity of the polymerization at the later stage, harsh reaction conditions (e.g., low temperature or suitable Lewis acid additive) were often required [15,16]. Limited catalyst systems have been developed for the chemoselective polymerization of polar divinyl monomers under mild conditions [15]. Chen's group recently reported an elegant example of the chemoselective polymerization of polar divinyl monomers by using chiral ansa-zirconocene enolates, affording a highly stereotactic polymer [17,18]. The same group achieved complete chemoselectivity in the polymerization of multivinyl-functionalized γ -butyrolactones by utilizing *N*-heterocyclic carbene (NHC) catalysts [19]. Chemoselective polymerization of allyl methacrylate was also realized by a yttrium monoalkyl complex [20].

Inspired by flourishing frustrated Lewis pairs (FLPs) chemistry [21,22], Lewis pair polymerization (LPP) of polar alkenes by main-group Al- or B-based Lewis pairs was successfully achieved in recent years [23–28]. We reported the polymerization of methyl methacrylate (MMA) and its cyclic analogues

by using the intramolecular cationic rare-earth (RE)-based Lewis pairs [29]. Subsequently, enhanced polymerization activity and extended monomer scope were realized by utilizing simple intermolecular Lewis pairs which are composed of homoleptic rare-earth metal tris-aryloxides $\text{RE}(\text{OAr})_3$ and phosphines PR_3 [30]. We herein found that such rare-earth/phosphine systems also enabled the chemoselective polymerization of polar divinyl monomers, affording polymers with the retention of pendant $\text{C}=\text{C}$ bonds (Scheme 1). These results will be described and discussed in this article.



Scheme 1. Rare-earth (RE)-based Lewis pairs and monomers examined in this work. AMA: allyl methacrylate; VBMA: 4-vinylbenzyl methacrylate; VMA: vinyl methacrylate.

2. Results and Discussion

First, we examined the polymerization of allyl methacrylate (AMA) using our RE-based Lewis pairs. Polymerization experiment was conducted with the 1/ PPh_3 pair in a Lewis acid/Lewis base (LA/LB) ratio of 2 and a $[\text{AMA}]/[\text{LB}]$ ratio of 200, and no polymer was yielded up to 24 h (Table 1, entry 1). Replacement of the Lewis base PPh_3 with a more basic tris-alkyl phosphine tricyclohexylphosphine (PCy_3) led to a 100% monomer conversion after 25 min (Table 1, entry 2). The $^1\text{H-NMR}$ spectrum of the resulting polymer clearly showed that the allylic $\text{C}=\text{C}$ bond remained unreacted. The high M_n (12.3×10^4 g/mol) of the polymer probably resulted from the steric hindrance of the zwitterionic propagating species [26,30]. We thus performed the same polymerization with the less-sterically hindered triethylphosphine (PEt_3), which yielded a polymer with a more controlled M_n of 5.03×10^4 g/mol and a syndiotacticity of 79.9% (Table 1, entry 3). A higher syndiotactic PAMA (*rr* value of 87.8%) could be obtained by conducting the polymerization at -30 °C, albeit with a low activity (Table 1, entry 4). Even switching to a less-sterically hindered trimethylphosphine (PMe_3) did not obviously change the polymerization results (Table 1, entry 5). It is well-established that the catalytic reactivity of rare-earth metal complexes highly relies on the metal ionic radii [31,32]. Subsequently, the larger metals in the series were employed as the Lewis acid components in the polymerization, with PEt_3 as the Lewis base component. Excitingly, all of the polymerizations showed complete chemoselective behaviors. Quantitative monomer consumptions were achieved in 3 min for 2 (Table 1, entry 6) and 1 min for 3 and 4 (Table 1, entries 7 and 8), respectively. The polydispersity (PDI) of the produced polymer was also narrow (1.34–1.42). This showed that the polymerization activity increased with the increasing of metal ionic radius ($\text{La} > \text{Sm} > \text{Y} > \text{Sc}$). For the 4/ PEt_3 pair, with a very small amount of catalyst loading (0.25 mol %), quantitative monomer conversion could be achieved in 5 min, producing syndiotactic-rich PAMA with high molecular weight (Table 1, entry 9). Notably, control experiments by using either the Sc complex 1 or the La complex 4 alone in the AMA polymerization under standard conditions led to no monomer conversion, even up to 24 h (Table S1, entries 12 and 13).

Table 1. Chemoselective polymerization of polar divinyl monomers with homoleptic rare-earth aryloxide-based Lewis pairs ^a.

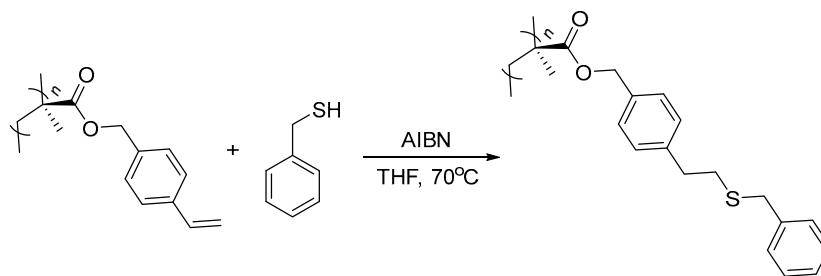
Entry	Monomer	LA	LB	[M]/[LB]	T (min)	Conv. (%)	M _n (10 ⁴ g/mol)	PDI (M _w /M _n)	M _n (theo) ^b (10 ⁴ g/mol)	rr (%)	mr (%)	mm (%)
1	AMA	1	PPh ₃	200	1440	0	-	-	-	-	-	-
2	AMA	1	PCy ₃	200	25	100	12.3	1.33	2.55	79.8	19.6	0.6
3	AMA	1	PEt ₃	200	15	100	5.03	1.23	2.54	79.9	19.5	0.6
4 ^c	AMA	1	PEt ₃	200	1440	75	10.8	1.38	2.54	87.8	11.4	0.8
5	AMA	1	PMe ₃	200	30	90	5.09	1.23	2.53	79.2	20.0	0.8
6	AMA	2	PEt ₃	200	3	100	8.57	1.41	2.54	75.3	23.5	1.2
7	AMA	3	PEt ₃	200	1	100	9.16	1.34	2.54	75.0	23.7	1.7
8	AMA	4	PEt ₃	200	<1	100	10.0	1.42	2.54	72.5	26.0	1.5
9	AMA	4	PEt ₃	400	5	100	15.3	1.76	5.06	72.8	25.4	1.8
10	VMA	1	PEt ₃	100	10	100	5.62	1.36	1.13	75.6	22.6	1.8
11	VMA	1	PMe ₃	100	10	100	7.59	1.31	1.13	76.8	21.6	1.6
12	VMA	4	PEt ₃	100	1	100	4.74	1.76	1.13	69.3	29.1	1.6
13	VBMA	1	PEt ₃	100	45	100	2.55	1.87	2.03	75.0	22.5	2.5
14	VBMA	1	PMe ₃	100	45	100	2.42	1.99	2.03	76.2	22.8	1.0
15	VBMA	4	PEt ₃	100	5	100	2.92	2.00	2.03	72.1	26.3	1.6

^a Conditions: polymerizations were conducted at room temperature in toluene ($V_{\text{monomer}}/V_{\text{solvent}}$: 1:2) and a Lewis acid (LA)/Lewis base (LB) ratio of 2, where $n_{[\text{LA}]} = 40 \mu\text{mol}$. Monomer conversions were determined by ¹H-NMR spectroscopy and confirmed by gravimetric methods; *rr*, *mr*, *mm* were measured by ¹H-NMR spectroscopy. M_n and polydispersity (PDI) were determined by gel permeation chromatography (GPC) in *N,N*-dimethylformamide (DMF) relative to the poly(methyl methacrylate) (PMMA) standards; ^b $M_n(\text{theo}) = M_w(M) \times [M]/[I] \times \text{conversion} (\%) + MW$ (chain-end groups); ^c Polymerization was conducted at -30°C .

We next examined our RE/P catalytic system for the polymerization of VMA, an analogue of AMA. The 1/PEt₃ pair exhibited good activity for the polymerization of VMA, achieving 100% monomer conversion after 10 min. The produced PVMA had a M_n of 5.62×10^4 g/mol and a PDI of 1.34 (Table 1, entry 10). Switching to trimethylphosphine (PMe₃) did not noticeably change the polymerization results (Table 1, entry 11). The La complex 4/PEt₃ pair also showed high activity in the polymerization, which consumed 100 equivalent monomers within only 1 minute and yielded polymer with a relatively broad PDI of 1.76 (Table 1, entry 12). We then conducted the same polymerization in CH₂Cl₂, and the resulting polymer showed a narrower PDI of 1.43 (Table S1, entry 17).

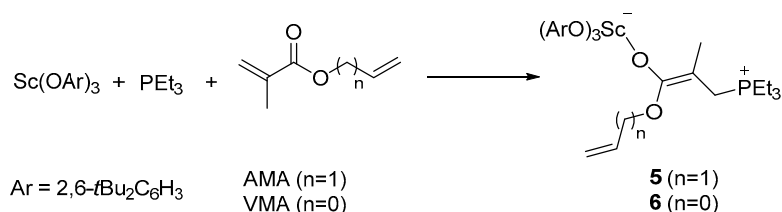
A more challenging monomer was VBMA, because the relative reactivity ratio for the methacrylic C=C and the styrenic vinyl group is quite small ($r_1/r_2 = 1.2$) [33,34]. Gratifyingly, our intermolecular RE/P systems were found to be active for the chemoselective polymerization of VBMA with the retention of styrenic C=C bonds. This monomer was quantitatively converted to PVBMA in 45 min by the Sc complex 1/PEt₃ (or PMe₃) pair (Table 1, entries 13 and 14). When using the La complex 4/PEt₃ pair as a catalyst, polymerization proceeded rapidly and gave 100% monomer conversion in only 5 min (Table 1, entry 15). The resulting PVBMA had a syndiotacticity of 72.1% *rr*.

Since the polymer obtained in the current polymerization still possessed reactive pendant C=C bonds, we decided to examine if it could undergo post-functionalization reaction. Treatment of the PVBMA with a stoichiometric excess amount of benzyl thiol (PhCH₂SH), using catalytic amount of 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator, afforded functionalized product as expected (Scheme 2). The produced polymer had an increased M_n of 6.80×10^4 g/mol and a broader PDI of 3.27, which indicated some degree of cross-linking during the post-functionalization reaction. The ¹H-NMR spectrum of the product showed a full conversion of the pendant C=C double bonds, which was evidenced by complete disappearance of the signals corresponding to the olefinic protons in PVBMA (δ 6.64, 5.71 and 5.22 ppm) and appearance of new saturated CH₂ signals at δ 2.76 and 2.61 ppm ascribed to [S]CH₂CH₂[Ph] units (Figure S10).



Scheme 2. Post-functionalization of PVBMA with PhCH₂SH. AIBN: 2,2'-azobis(2-methylpropionitrile).

To explore the mechanism of the current polymerizations, we investigated stoichiometric reactions of the Sc complex **1**/PEt₃ pair with the abovementioned polar divinyl compounds. First, treatment of the **1**/PEt₃ pair with AMA in a 1:1 molar ratio in toluene at room temperature yielded the addition product **5** as a white crystalline solid (Scheme 3, 79% yield). Complex **5** could be readily characterized by NMR for the phosphonium cation Et₃P⁺ [δ 36.9 ppm in ³¹P-NMR; δ 2.05 (m, CH₂), 1.25 (m, CH₃) ppm in ¹H-NMR] and for the ester enolate moiety [δ 5.84 (m, 1H, CH=CH₂), 5.08 (m, 2H, CH=CH₂), 4.32 (m, 2H, OCH₂) ppm in ¹H-NMR]. The molecular structure of **5** was also confirmed by single-crystal X-ray diffraction analysis (Figure 1), which clearly showed that a kinetically-controlled 1,4-addition reaction occurred during the reaction to produce *trans*-configured product with an enolate moiety (Sc1-O1 1.9671(11) Å, O1-C1 1.3117(19) Å, C1-C2 1.350(2) Å, O1-C1-C2-C4 4.284(153)°) and an unreacted terminal C=C bond (C6-C7 1.309(3) Å). The analogous reaction of the **1**/PEt₃ pair with VMA also yielded the *trans* Sc/P 1,4-addition complex **6** as a white crystalline solid (77% yield, Scheme 3), which was also comprehensively characterized by multinuclear NMR spectroscopy, elementary analysis, and single-crystal X-ray diffraction (Figure S7). Complex **6** showed similar structural features and spectroscopy properties to those of the AMA addition product **5** (for details, see the Supporting Information). Notably, the 1,4-addition reaction occurred through the conjugated C=C bond, leaving the non-conjugated C=C intact, which is at the origin of the high level of chemoselectivity observed in the polymerization reaction. Subsequently, the polymerizations with the isolated complexes **5** and **6** as initiators were performed. Complex **5** exhibited a low activity for the polymerization of AMA in CH₂Cl₂, achieving 32% monomer conversion after 24 h (Table 2, entry 1). On the other hand, highly active polymerization could be achieved by adding an additional equivalent of the Lewis acidic Sc complex **1**, affording a 100% monomer conversion in 20 min (Table 2, entry 2). The polymerization of VMA catalyzed by complex **6** with [VMA]/[**6**] = 100 in CH₂Cl₂ led to no monomer conversion up to 24 h (Table 2, entry 3). Nevertheless, a quantitative monomer consumption was realized in 20 min by adding an additional equivalent of the Sc complex **1** (Table 2, entry 4). These observations indicated that the polymerization requires another equivalent of Lewis acid to activate monomer, which is consistent with the activated monomer propagation mechanism [23–26,29,30].



Scheme 3. 1,4-Addition reactions of the Sc/P Lewis pair to AMA and VMA.

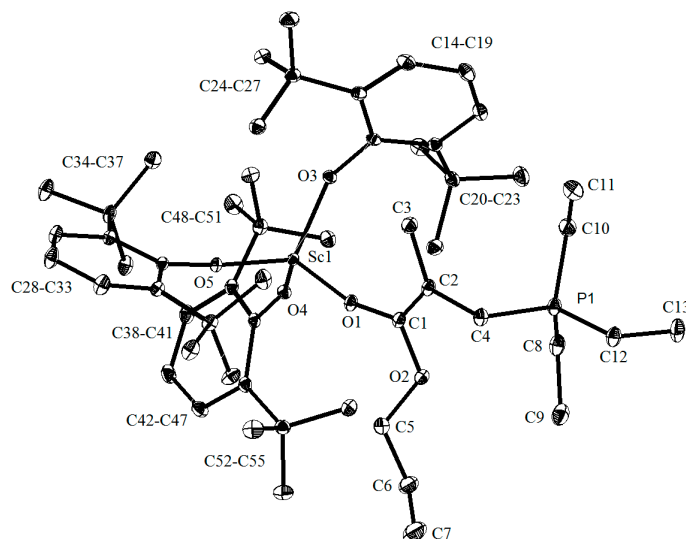


Figure 1. Molecular structure of the AMA addition product **5**. Hydrogen atoms are omitted for clarity, ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles(°): Sc1-O1 1.9671(11); O1-C1 1.3117(19); C1-C2 1.350(2); C2-C3 1.498(2); C2-C4 1.516(2); C5-C6 1.482(3); C6-C7 1.309(3); P1-C4 1.8091(17); O1-C1-O2 115.40(14); O1-C1-C2 127.30(16); O2-C1-C2 117.29(14); C1-C2-C3 122.71(15); C4-C2-C3 117.94(15); C4-C2-C1 119.25(15).

Table 2. Chemoselective polymerization of AMA and VMA with complexes **5** and **6**.^a

Entry	Monomer	Cat.	LA	[M]/[Cat.]	T (min)	Conv. (%)	M_n (10^4 g/mol)	PDI (M_w/M_n)	<i>rr</i> (%)	<i>mr</i> (%)	<i>mm</i> (%)
1	AMA	5	-	100	1440	32	2.12	1.45	75.3	21.5	3.2
2	AMA	5	1	100	20	100	4.23	1.42	78.4	19.6	2.0
3	VMA	6	-	100	1440	0	-	-	-	-	-
4	VMA	6	1	100	20	100	4.89	1.42	77.4	21.7	0.9

^a Conditions: polymerizations were conducted at room temperature in CH_2Cl_2 ($V_{\text{monomer}}/V_{\text{solvent}}$: 1:2) by using 20 μmol catalyst. Monomer conversions were determined by $^1\text{H-NMR}$ spectroscopy and confirmed by gravimetric methods; *rr*, *mr* and *mm* were measured by $^1\text{H-NMR}$ spectroscopy. M_n and PDI were determined by GPC in DMF relative to the PMMA standards.

Finally, we also conducted an oligomerization reaction using the scandium complex **1**/ PEt_3 pair in an $[\text{AMA}]/[\text{PEt}_3]$ molar ratio of 20. After quenching with wet MeOH, the resulting oligomer was then analyzed by MALDI-TOF MS spectrum (Figure S11). It clearly showed a major series of mass ions with a repeat unit of 126.10, which corresponded to the mass of the AMA monomer. A plot of m/z values of this series versus the number of AMA repeat units produced a straight line with a slope of 126.10 and an intercept of 119.47 (Figure S12). The intercept is equal to the sum of H^+ and PEt_3 , suggesting that the produced oligomer has a structural formula of $\text{Et}_3\text{P}^+(\text{AMA})_n\text{-H}$, where the phosphorus atom is attached to AMA. Thus, the polymerization was initiated by an FLP-type 1,4-addition reaction of the RE/P Lewis pair to the monomer.

3. Materials and Methods

3.1. General Information

All manipulations were performed under a dry Argon atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer (Bruker (Beijing) Scientific Technology Co., Ltd., Beijing, China). Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of

NMR data were supported by 1D and 2D-NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument (CE Instruments Ltd, Wigan, UK). AMA and VMA were purchased from TCI (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). The VBMA was synthesized by following the literature procedures [35]. These monomers were dried over CaH₂ and distilled prior to use. Phosphines—including PPh₃, PCy₃, PEt₃, and PMe₃—were purchased from Alfa Aesar (Alfa Aesar (China) Chemical Co., Ltd., Shanghai, China) and used as received. RE(OAr)₃ (RE = Sc (**1**), Y (**2**), Sm (**3**), La (**4**), Ar = 2,6-*t*Bu₂C₆H₃) were synthesized by following the literature procedures [36]. The AIBN was purchased from TCI and purified by recrystallization from methanol prior to use.

3.2. Procedures and Compound Characterization

3.2.1. Preparation and Characterization of Complex 5

To a solution of Sc(OAr)₃ (132 mg, 0.2 mmol) and AMA (25 mg, 0.2 mmol) in toluene (0.5 mL), PEt₃ (24 mg, 0.2 mmol, in 0.5 mL of toluene) was added. After standing at room temperature for 1 h, a large amount of colorless crystalline solid was precipitated, which was then washed with hexane (2 × 0.5 mL) to give complex **5** (150 mg, 79%). Crystals suitable for the single-crystal X-ray structure analysis were grown from a benzene solution of **5** at room temperature. ¹H-NMR (400 MHz, CD₂Cl₂, 298 K): δ = 7.04 (m, 6H, *m*-OAr), 6.50 (m, 3H, *p*-OAr), 5.84 (m, 1H, CH=CH₂), 5.08 (m, 2H, CH=CH₂), 4.32 (m, 2H, OCH₂), 2.88 (d, ²J_{PH} = 11.1 Hz, 2H, PCH₂C=), 2.05 (m, 6H, PCH₂CH₃), 1.52 (m, 3H, CH₃C=), 1.42 (s, 54H, C(CH₃)₃), 1.25 (m, 9H, PCH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 298 K): δ = 163.4 (*i*-OAr), 159.5 (d, ³J_{PC} = 8.9 Hz, OC=), 139.0 (*o*-OAr), 135.6 (CH=CH₂), 125.1 (*m*-OAr), 116.8 (CH=CH₂), 115.8 (*p*-OAr), 68.3 (d, ⁵J_{PC} = 1.4 Hz, OCH₂), 67.2 (d, ²J_{PC} = 9.6 Hz, CH₃C=), 35.8 (C(CH₃)₃), 32.7 (C(CH₃)₃), 24.1 (d, ¹J_{PC} = 45.7 Hz, PCH₂C=), 18.5 (d, ³J_{PC} = 1.0 Hz, CH₃C=), 12.5 (d, ¹J_{PC} = 47.1 Hz, PCH₂CH₃), 6.0 (d, ²J_{PC} = 5.1 Hz, PCH₂CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 298 K): δ = 36.9 (ν_{1/2} ~5 Hz). Elemental Analysis: calculated for C₅₅H₈₈O₅PSc·0.5C₇H₈: C, 73.86; H, 9.75. Found: C, 73.75; H, 9.30.

X-ray crystal structure analysis of complex **5**: formula C₅₅H₈₈O₅PSc·C₆H₆, M = 944.24, colorless, 0.25 × 0.25 × 0.20 mm, a = 18.7281(8), b = 18.5836(7), c = 16.1009(7) Å, β = 100.6070°, V = 5507.9(4) Å³, ρ_{calc} = 1.139 g cm⁻³, μ = 0.207 mm⁻¹, Z = 4, monoclinic, space group P2(1)/c, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 87,725 reflections collected (±h, ±k, ±l), 12,616 independent (R(int) = 0.0565) and 9925 observed reflections [I > 2σ(I)], 608 refined parameters, R = 0.0381, wR2 = 0.1267, max. (min.) residual electron density 0.550 (−0.625) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

3.2.2. Preparation and Characterization of Complex 6

Following the procedure described for **5**, reaction of Sc(OAr)₃ (132 mg, 0.2 mmol) and VMA (22 mg, 0.2 mmol) with PEt₃ (24 mg, 0.2 mmol) gave **6** as colorless crystals (151 mg, 77%). Crystals suitable for the X-ray single-crystal structure analysis were grown from a benzene solution of **6** at room temperature. ¹H-NMR (400 MHz, CD₂Cl₂, 298 K): δ = 7.05 (m, 6H, *m*-OAr), 6.98 (overlapped, 1H, CH=CH₂), 6.51 (m, 3H, *p*-OAr), 4.36 (m, 1H, CH=CH₂), 3.99 (m, 1H, CH=CH₂), 2.90 (d, ²J_{PH} = 11.5 Hz, 2H, PCH₂C=), 2.07 (m, 6H, PCH₂CH₃), 1.48 (d, ⁴J_{PH} = 2.9 Hz, 3H, CH₃C=), 1.41 (s, 54H, C(CH₃)₃), 1.28 (m, 9H, PCH₂CH₃). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 298 K): δ = 163.3 (*i*-OAr), 157.3 (d, ³J_{PC} = 9.0 Hz, OC=), 148.1 (OCH=CH₂), 139.0 (*o*-OAr), 125.1 (*m*-OAr), 116.0 (*p*-OAr), 89.8 (OCH=CH₂), 68.4 (d, ²J_{PC} = 9.4 Hz, CH₃C=), 35.7 (C(CH₃)₃), 32.6 (C(CH₃)₃), 23.4 (d, ¹J_{PC} = 45.7 Hz, PCH₂C=), 18.2 (d, ³J_{PC} = 1.0 Hz, CH₃C=), 12.4 (d, ¹J_{PC} = 47.3 Hz, PCH₂CH₃), 6.0 (d, ²J_{PC} = 5.2 Hz, PCH₂CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 298 K): δ = 36.9 (ν_{1/2} ~5 Hz). Elemental Analysis: calculated for C₅₄H₈₆O₅PSc·C₇H₈: C, 74.51; H, 9.64. Found: C, 74.66; H, 9.26.

X-ray crystal structure analysis of complex **6**: formula C₅₄H₈₆O₅PSc·0.5C₆H₆, M = 930.21, colorless, 0.25 × 0.20 × 0.15 mm, a = 18.8243(9), b = 18.4532(8), c = 16.0590(8) Å, β = 100.998(2)°, V = 5475.9(4) Å³, ρ_{calc} = 1.128 g cm⁻³, μ = 0.208 mm⁻¹, Z = 4, monoclinic, space group P2(1)/c, λ = 0.71073 Å, T = 120(2) K,

Multi-scan, 118,961 reflections collected ($\pm h, \pm k, \pm l$), 12,526 independent ($R(\text{int}) = 0.0499$) and 10,196 observed reflections [$I > 2\sigma(I)$], 599 refined parameters, $R = 0.0358$, $wR2 = 0.1288$, max. (min.) residual electron density 0.601 (-0.713) $\text{e}\cdot\text{\AA}^{-3}$, hydrogen atoms were calculated and refined as riding atoms.

3.2.3. General Polymerization Procedures

Polymerizations were performed in 20 mL oven-dried glass reactors at room temperature inside the glovebox. A predetermined amount of $\text{RE}(\text{OAr})_3$ (2 equiv.) was first dissolved in the solvent and monomer. Then, the polymerization was started by rapid addition of a solution of Lewis base via a pipette to the above solution under vigorous stirring. After the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture and quickly quenched into a 4-mL vial containing 0.6 mL of undried “wet” CDCl_3 . The quenched aliquots were later analyzed by $^1\text{H-NMR}$ to obtain the monomer conversion data. After the removal of the aliquot, the polymerization was immediately quenched by the addition of 5 mL 5% HCl-acidified methanol. The quenched mixture was poured into 50 mL methanol, stirred for 1 h, filtered, washed, and dried in a vacuum oven at $50\text{ }^\circ\text{C}$ overnight to a constant weight to verify the polymer conversions determined by $^1\text{H-NMR}$.

3.2.4. Polymer Characterizations

Polymer number (M_n) and weight (M_w) average molecular weights and polydispersity index ($\text{PDI} = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at $40\text{ }^\circ\text{C}$ and a flow rate of $0.8\text{ mL}/\text{min}$ with DMF as the eluent, on a Waters University 1515 GPC instrument coupled with a Waters RI detector and equipped with four PLgel $5\text{ }\mu\text{m}$ mixed-C columns. The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower 2 software.

4. Conclusions

In summary, we have reported the complete chemoselective polymerization of a series of polar divinyl monomers under mild condition by the utilization of homoleptic rare-earth aryloxide-based Lewis pairs. Catalytic activities of polymerizations were highly dependent on the ionic radii of RE ions and electronic/steric profiles of the Lewis bases. The resulting polymers, bearing pendant $\text{C}=\text{C}$ double bonds, could easily undergo post-functionalization with the thiol reagent. Remarkably, a highly syndiotactic PAMA with $rr \sim 88\%$ could be produced by such an RE-based Lewis pair system. The isolation of zwitterionic propagating species and the end-group analysis suggested that current polymerization was initiated by an RE/P FLP-type 1,4-addition, rather than RE covalent bond insertion or single-electron transfer in the traditional RE-catalyzed polymerizations.

Supplementary Materials: The Supplementary Materials are available online: supplementary materials contain part of experimental procedures, characterizations of the 1,4-addition complexes and oligomers; CCDC 1814864 (complex 5) and 1814865 (complex 6) contain 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.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Grant No. 21502132), the Natural Science Foundation of Jiangsu Province (Grant No. BK20150316), Jiangsu Specially-Appointed Professor Plan, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the project of scientific and technologic infrastructure of Suzhou (SZS201708).

Author Contributions: X.X. conceived and designed the experiments; P.X. performed the experiments and analyzed the data; L.W. and L.D. performed part of the experiments; X.X. and P.X. wrote the paper. All authors have read and proofed the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References and Note

1. Cherian, A.E.; Sun, F.C.; Sheiko, S.S.; Coates, G.W. Formation of nanoparticles by intramolecular cross-linking: Following the reaction progress of single polymer chains by atomic force microscopy. *J. Am. Chem. Soc.* **2007**, *129*, 11350–11351. [[CrossRef](#)] [[PubMed](#)]
2. Sui, X.; Hempenius, M.A.; Vancso, G.J. Redox-active cross-linkable poly(ionic liquid)s. *J. Am. Chem. Soc.* **2012**, *134*, 4023–4025. [[CrossRef](#)] [[PubMed](#)]
3. Wendland, M.S.; Zimmerman, S.C. Synthesis of cored dendrimers. *J. Am. Chem. Soc.* **1999**, *121*, 1389–1390. [[CrossRef](#)]
4. Powell, K.T.; Cheng, C.; Wooley, K.L. Complex amphiphilic hyperbranched fluoropolymers by atom transfer radical self-condensing vinyl (co)polymerization. *Macromolecules* **2007**, *40*, 4509–4515. [[CrossRef](#)] [[PubMed](#)]
5. Zhou, J.; Chen, P.; Deng, C.; Meng, F.; Cheng, R.; Zhong, Z. A simple and versatile synthetic strategy to functional polypeptides via vinyl sulfone-substituted L-cysteine *N*-carboxyanhydride. *Macromolecules* **2013**, *46*, 6723–6730. [[CrossRef](#)]
6. Stevens, D.M.; Tempelaar, S.; Dove, A.P.; Harth, E. Nanosponge formation from organocatalytically synthesized poly(carbonate) copolymers. *ACS Macro Lett.* **2012**, *1*, 915–918. [[CrossRef](#)] [[PubMed](#)]
7. Coates, G.W.; Grubbs, R.H. Quantitative ring-closing metathesis of polyolefins. *J. Am. Chem. Soc.* **1996**, *118*, 229–230. [[CrossRef](#)]
8. Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S. Anionic polymerization of monomers containing functional groups. 13. Anionic polymerizations of 2-, 3- and 4-(3,3-dimethyl-1-butynyl)styrenes, 2-, 3-, and 4-(1-hexynyl)styrenes, and 4-(phenylethynyl)styrene. *Macromolecules* **1998**, *31*, 3764–3774. [[CrossRef](#)]
9. Tanaka, S.; Goseki, R.; Ishizone, T.; Hirao, A. Synthesis of well-defined novel reactive block polymers containing a poly(1,4-divinylbenzene) segment by living anionic polymerization. *Macromolecules* **2014**, *47*, 2333–2339. [[CrossRef](#)]
10. París, R.; de la Fuente, J.L. Bulk atom transfer radical polymerization of allyl methacrylate. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 2395–2406. [[CrossRef](#)]
11. París, R.; de la Fuente, J.L. Solvent effect on the atom transfer radical polymerization of allyl methacrylate. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 6247–6261. [[CrossRef](#)]
12. Nagelsdiek, R.; Mennicken, M.; Maier, B.; Keul, H.; Höcker, H. Synthesis of polymers containing cross-linkable groups by atom transfer radical polymerization: Poly(allyl methacrylate) and copolymers of allyl methacrylate and styrene. *Macromolecules* **2004**, *37*, 8923–8932. [[CrossRef](#)]
13. Sugiyama, F.; Satoh, K.; Kamigaito, M. Regiospecific radical polymerization of vinyl methacrylate in the presence of Lewis acids into soluble polymers with pendent vinyl ester substituents. *Macromolecules* **2008**, *41*, 3042–3048. [[CrossRef](#)]
14. Vardareli, T.K.; Keskin, S.; Usanmaz, A. Synthesis and characterization of poly(allyl methacrylate) obtained by free radical initiator. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2008**, *45*, 302–311. [[CrossRef](#)]
15. Vidal, F.; Chen, E.Y.-X. Precision polymer synthesis via chemoselective, stereoselective, and living/controlled polymerization of polar divinyl monomers. *Synlett* **2017**, *28*, 1028–1039.
16. Murali Mohan, Y.; Raghunadh, V.; Sivaram, S.; Baskaran, D. Reactive polymers bearing styrene pendants through selective anionic polymerization of 4-vinylbenzyl methacrylate. *Macromolecules* **2012**, *45*, 3387–3393. [[CrossRef](#)]
17. Vidal, F.; Gowda, R.R.; Chen, E.Y.-X. Chemoselective, stereospecific, and living polymerization of polar divinyl monomers by chiral zirconocenium catalysts. *J. Am. Chem. Soc.* **2015**, *137*, 9469–9480. [[CrossRef](#)] [[PubMed](#)]
18. Vidal, F.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E.Y.-X. Robust cross-linked stereocomplexes and C₆₀ inclusion complexes of vinyl-functionalized stereoregular polymers derived from chemo/stereoselective coordination polymerization. *J. Am. Chem. Soc.* **2016**, *138*, 9533–9547. [[CrossRef](#)] [[PubMed](#)]
19. Gowda, R.R.; Chen, E.Y.-X. Organocatalytic and chemoselective polymerization of multivinyl-functionalized γ -butyrolactones. *ACS Macro Lett.* **2016**, *5*, 772–776. [[CrossRef](#)]
20. Xu, T.; Liu, J.; Lu, X.B. Highly active half-metallocene yttrium catalysts for living and chemoselective polymerization of allyl methacrylate. *Macromolecules* **2015**, *48*, 7428–7434. [[CrossRef](#)]
21. Welch, G.C.; Juan, R.R.S.; Masuda, J.D.; Stephan, D.W. Reversible metal-free hydrogen activation. *Science* **2006**, *314*, 1124–1126. [[CrossRef](#)] [[PubMed](#)]

22. Stephan, D.W.; Erker, G. Frustrated Lewis pair chemistry: Development and perspectives. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441. [[CrossRef](#)] [[PubMed](#)]
23. Zhang, Y.; Miyake, G.M.; Chen, E.Y.-X. Alane-based classical and frustrated Lewis pairs in polymer synthesis: Rapid polymerization of MMA and naturally renewable methylene butyrolactones into high-molecular-weight polymers. *Angew. Chem. Int. Ed.* **2010**, *49*, 10158–10162. [[CrossRef](#)] [[PubMed](#)]
24. Zhang, Y.; Miyake, G.M.; John, M.G.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E.Y.-X. Lewis pair polymerization by classical and frustrated Lewis pairs: Acid, base and monomer scope and polymerization mechanism. *Dalton Trans.* **2012**, *41*, 9119–9134. [[CrossRef](#)] [[PubMed](#)]
25. Xu, T.; Chen, E.Y.-X. Probing site cooperativity of frustrated phosphine/borane Lewis pairs by a polymerization study. *J. Am. Chem. Soc.* **2014**, *136*, 1774–1777. [[CrossRef](#)] [[PubMed](#)]
26. Knaus, M.G.M.; Giuman, M.M.; Pöthig, A.; Rieger, B. End of frustration: Catalytic precision polymerization with highly interacting Lewis pairs. *J. Am. Chem. Soc.* **2016**, *138*, 7776–7781. [[CrossRef](#)] [[PubMed](#)]
27. Jia, Y.B.; Ren, W.M.; Liu, S.J.; Xu, T.; Wang, Y.B.; Lu, X.B. Controlled divinyl monomer polymerization mediated by Lewis pairs: A powerful synthetic strategy for functional polymers. *ACS Macro Lett.* **2014**, *3*, 896–899. [[CrossRef](#)]
28. Chen, J.; Chen, E.Y.-X. Lewis pair polymerization of acrylic monomers by *N*-heterocyclic carbenes and B(C₆F₅)₃. *Isr. J. Chem.* **2015**, *55*, 216–226. [[CrossRef](#)]
29. Xu, P.; Yao, Y.; Xu, X. Frustrated Lewis pair-like reactivity of rare-earth metal complexes: 1,4-addition reactions and polymerizations of conjugated polar alkenes. *Chem. A Eur. J.* **2017**, *23*, 1263–1267. [[CrossRef](#)] [[PubMed](#)]
30. Xu, P.; Xu, X. Homoleptic rare-earth aryloxide based Lewis pairs for polymerization of conjugated polar alkenes. *ACS Catal.* **2018**, *8*, 198–202. [[CrossRef](#)]
31. Arndt, S.; Spaniol, T.P.; Okuda, J. Homogeneous ethylene-polymerization catalysts based on alkyl cations of the rare-earth metals: Are dicationic mono(alkyl) complexes the active species? *Angew. Chem. Int. Ed.* **2003**, *42*, 5075–5079. [[CrossRef](#)] [[PubMed](#)]
32. Hong, S.; Marks, T.J. Organolanthanide-catalyzed hydroamination. *Acc. Chem. Res.* **2004**, *37*, 673–686. [[CrossRef](#)] [[PubMed](#)]
33. Greenley, R.Z. *Polymer Handbook*, 3rd ed.; Immergut, E.H., Brandup, J., Eds.; Wiley: New York, NY, USA, 1989; pp. 267–274.
34. The divinyl monomers was regarded as a copolymerization system of two independent and competing vinyl monomers.
35. Pugh, C.; Percec, V. Synthesis and group transfer polymerization and copolymerization of *p*-vinylbenzyl methacrylate. *Polym. Bull.* **1985**, *14*, 109–116. [[CrossRef](#)]
36. Lappert, M.F.; Singh, A.; Smith, R.G. Hydrocarbon-soluble homoleptic bulky aryl oxides of the lanthanide metals [Ln(OAr^R)₃]. *Inorg. Synth.* **1990**, *27*, 164–168.

Sample Availability: Samples of the compounds are available from the authors.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).