Article

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

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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) aryloxide complexes RE(OAr)₃ (RE = Sc (1), Y (2), Sm (3), La (4), Ar = 2,6-tBu₂C₆H₃) 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) (PVBMMA), 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-butyrrolactones 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 [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 RE(OAr)₃ and phosphines PR₃ [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 C=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/PPh₃ pair in a Lewis acid/Lewis base (LA/LB) ratio of 2 and a [AMA]/[LB] ratio of 200, and no polymer was yielded up to 24 h (Table 1, entry 1). Replacement of the Lewis base PPh₃ with a more basic tris-alkyl phosphine tricyclohexylphosphine (PCy₃) led to a 100% monomer conversion after 25 min (Table 1, entry 2). The ¹H-NMR spectrum of the resulting polymer clearly showed that the allylic C=C bond remained unreacted. The high Mₙ (12.3 × 10⁴ 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 (PEt₃), which yielded a polymer with a more controlled Mₙ of 5.03 × 10⁴ 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 (PMe₃) 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 PEt₃ 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 (La > Sm > Y > Sc). For the 4/PEt₃ 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.

| Entry | Monomer | LA     | LB     | [M]/[LB] | T (min) | Conv. (%) | \(M_n\) (10^4 g/mol) | PDI (Mw/Mn) | Meth/\text{theo} \(b\) (10^6 g/mol) | \(rr\) (%) | \(mr\) (%) | \(mm\) (%) |
|-------|---------|--------|--------|----------|---------|-----------|---------------------|-------------|-------------------------------------|-----------|-----------|----------|
| 1     | AMA     | PPh\(_3\) | 200    | 1440     | 0       |            | 12.3                | 1.33        | 2.55                                | 79.8      | 19.6      | 0.6      |
| 2     | AMA     | PCy\(_3\) | 200    | 25       | 100     | 2         | 3.33                | 2.54        | 79.9                                | 91.4      | 8.6       | 0.4      |
| 3     | AMA     | PEt\(_3\) | 200    | 15       | 100     |            | 5.03                | 1.23        | 2.54                                | 79.9      | 91.5      | 0.6      |
| 4\(^c\) | AMA     | PEt\(_3\) | 200    | 1440     | 75      | 100       | 10.8                | 1.38        | 2.54                                | 88.6      | 11.4      | 0.8      |
| 5     | AMA     | PMe\(_3\) | 200    | 30       | 90      |            | 5.09                | 1.23        | 2.53                                | 79.2      | 20.0      | 0.8      |
| 6     | AMA     | PEt\(_3\) | 200    | 3        | 100     |            | 8.57                | 1.41        | 2.54                                | 75.3      | 23.5      | 1.2      |
| 7     | AMA     | PEt\(_3\) | 200    | 1        | 100     |            | 9.16                | 1.34        | 2.54                                | 75.6      | 23.8      | 1.7      |
| 8     | AMA     | PEt\(_3\) | 200    | <1       | 100     |            | 10.0                | 1.42        | 2.54                                | 72.5      | 26.0      | 1.5      |
| 9     | AMA     | PEt\(_3\) | 400    | 5        | 100     |            | 15.3                | 1.76        | 5.06                                | 72.8      | 25.4      | 1.8      |
| 10    | AMA     | PEt\(_3\) | 100    | 10       | 100     |            | 5.62                | 1.36        | 1.13                                | 75.6      | 22.6      | 1.8      |
| 11    | VMA     | PMe\(_3\) | 100    | 10       | 100     |            | 7.59                | 1.31        | 1.13                                | 76.8      | 21.6      | 1.6      |
| 12    | VMA     | PEt\(_3\) | 100    | 1        | 100     |            | 4.74                | 1.76        | 1.13                                | 69.3      | 29.1      | 1.6      |
| 13    | VBMA    | PEt\(_3\) | 100    | 45       | 100     |            | 2.55                | 1.87        | 2.03                                | 75.0      | 22.5      | 2.5      |
| 14    | VBMA    | PMe\(_3\) | 100    | 45       | 100     |            | 2.42                | 1.99        | 2.03                                | 76.2      | 22.8      | 1.0      |
| 15    | VBMA    | 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 \(n_{[LA]} = 40 \text{ µmol}\). Monomer conversions were determined by \(^1\)H-NMR spectroscopy and confirmed by gravimetric methods; \(rr\), \(mr\), \(mm\) were measured by \(^1\)H-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; \(^b\) \(M_n\)(theo) = \(M_w(M) \times [M]/[L] \times \text{conversion (%) + MW (chain-end groups)}\). \(^c\) Polymerization was conducted at \(-30^\circ\)C.

We next examined our RE/P catalytic system for the polymerization of VMA, an analogue of AMA. The 1/PEt\(_3\) 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 \times 10^4 g/mol and a PDI of 1.34 (Table 1, entry 10). Switching to trimethylphosphine (PMe\(_3\)) did not noticeably change the polymerization results (Table 1, entry 11). The La complex 4/PEt\(_3\) 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 CH\(_2\)Cl\(_2\), 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/PEt\(_3\) (or PMe\(_3\)) pair (Table 1, entries 13 and 14). When using the La complex 4/PEt\(_3\) 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 (PhCH\(_2\)SH), 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 \times 10^4 g/mol and a broader PDI of 3.27, which indicated some degree of cross-linking during the post-functionalization reaction. The \(^1\)H-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 (\(\delta 6.64, 5.71\) and 5.22 ppm) and appearance of new saturated CH\(_2\) signals at \(\delta 2.76\) and 2.61 ppm ascribed to [S]CH\(_2\)CH\(_2\)[Ph] units (Figure S10).
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 2. Post-functionalization of PVBMA with PhCH2SH. AIBN: 2,2′-azobis(2-methylpropionitrile).

Scheme 3. 1,4-Addition reactions of the Sc/P Lewis pair to AMA and VMA.
Finally, we also conducted an oligomerization reaction using the scandium complex 1/PEt\textsubscript{3} pair in an [AMA]/[PEt\textsubscript{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 \( \text{H}^+ \) and \( \text{PEt}_3^- \), 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 \( \delta \) 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-(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), PPh₃ (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 complex 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, 2JFH = 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, 3JPC = 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, 5JPC = 1.4 Hz, OCH₂), 67.2 (d, 2JPC = 9.6 Hz, CH₃C=), 35.8 (C(CH₃)₃), 32.7 (C(CH₃)₃), 24.1 (d, 3JPC = 45.7 Hz, PCH₂C=), 18.5 (d, 3JPC = 1.0 Hz, CH₃CH₂C=), 12.5 (d, 1JPC = 47.1 Hz, PCH₂CH₃), 6.0 (d, 2JPC = 5.1 Hz, PCH₂CH₃). ³¹P[¹H] NMR (162 MHz, CD₂Cl₂, 298 K): δ = 36.9 (v₁/₂ ~5 Hz). Elemental Analysis: calculated for C₅₅H₆₈O₅PSc·0.5C₇H₄: C, 73.86; H, 9.75. Found: C, 73.75; H, 9.30.

X-ray crystal structure analysis of complex 5: formula C₅₅H₆₈O₅PSc·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, ρcalc = 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 PPh₃ (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, 2JFH = 11.5 Hz, 2H, PCH₂C=), 2.07 (m, 6H, PCH₂CH₃), 1.48 (d, 4JPH = 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, 3JPC = 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, 2JPC = 9.4 Hz, CH₃C=), 35.7 (C(CH₃)₃), 32.6 (C(CH₃)₃), 23.4 (d, 1JPC = 45.7 Hz, PCH₂C=), 18.2 (d, 1JPC = 1.0 Hz, CH₃CH₂C=), 12.4 (d, 1JPC = 47.3 Hz, PCH₂CH₃), 6.0 (d, 2JPC = 5.2 Hz, PCH₂CH₃). ³¹P[¹H] NMR (162 MHz, CD₂Cl₂, 298 K): δ = 36.9 (v₁/₂ ~5 Hz). Elemental Analysis: calculated for C₅₅H₆₈O₅PSc·0.5C₇H₄: C, 74.51; H, 9.64. Found: C, 74.66; H, 9.26.

X-ray crystal structure analysis of complex 6: formula C₅₅H₆₈O₅PSc·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, ρcalc = 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 (±h, ±k, ±l), 12,526 independent (R(int) = 0.0499) and 10,196 observed reflections [I > 2σ(I)], 599 refined parameters, R = 0.0358, wR2 = 0.1288, max. (min.) residual electron density 0.601 (−0.713) e Å−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 RE(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” CDCl3. The quenched aliquots were later analyzed by 1H-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 °C overnight to a constant weight to verify the polymer conversions determined by 1H-NMR.

3.2.4. Polymer Characterizations

Polymer number (Mn) and weight (Mw) average molecular weights and polydispersity index (PDI = Mw/Mn) were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 0.8 mL/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 µm 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 C=C double bonds, could easily undergo post-functionalization with the thiol reagent. Remarkably, a highly syndiotactic PAMA with rr ~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.

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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. Pariš, 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. Pariš, 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.; Usamnaz, A. Synthesis and characterization of poly(allyl methacrylate) obtained by free radical initiator. *J. Macromol. Sci. 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 zirconocene 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-metalloocene 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, 7776–7781. [CrossRef] [PubMed]

26. Knaus, M.G.M.; Guiman, M.M.; Pöthig, A.; Rieger, B. End of frustration: Catalytic precision polymerization with highly interacting Lewis pairs. *J. Am. Chem. Soc.* 2016, 138, 1263–1267. [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(C_6F_5)_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.