Copolymerization of CO_2 and cyclohexene oxide using a lysine-based (salen)$Cr^{III}Cl$ catalyst†

Liping Guo,[a] Congmin Wang,[a] Wenjia Zhao,[a] Haoran Li,*[a] Weilin Sun[b] and Zhiquan Shen[b]

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A new, natural lysine-based (salen)$Cr^{III}Cl$ ((lys-salen)$Cr^{III}Cl$) complex was prepared and its catalytic activity for the copolymerization of CO_2 and cyclohexene oxide (CHO) was described in the presence of PPNCl (PPN^+ = bis(triphenylphosphoranylidene)ammonium) as cocatalyst. The influence of the reaction time, operating temperature and the molar ratio of the catalyst components on the copolymerization was investigated in detail. The results showed that the (lys-salen)$Cr^{III}Cl$, synthesized from non-*ortho*-diamine, could effectively catalyze the alternating copolymerization (carbonate linkages = 94.6–99.0%). The selectivity was >95%, and was less sensitive to the temperature and the molar ratio of catalyst components, compared to that of the copolymerization catalyzed by traditional salen–metal complexes. The ESI-MS analyses of oligomer and (lys-salen)$Cr^{III}Cl$ indicated that a possible chain-transfer reaction had taken place, which might be induced by the water coordinating to the central metal ion.

Introduction

A series of investigations have been performed in the area of CO_2 utilization, since CO_2 is an abundant, economical and biorenewable resource. One of the most promising reactions in this area is the copolymerization of CO_2 with epoxides announced in 1960's by Inoue *et al.*[1] to prepare polycarbonates, which have displayed great potential as biodegradable polymeric materials.[2] Among the numerous metal-based catalyst systems,[2] the salen–metal complex (Fig. 1) system is of special interest.[3] Using a binary catalyst system of a salen–metal complex as catalyst in conjunction with ionic organic ammonium salt or Lewis base as cocatalyst could markedly increase turnover frequency (TOF) and gave the alternating copolymer with high selectivity.[4,5] Recently, the effects of different slicylaldehyde-modified H_2salen ligands [6,7] and various cocatalysts[8] on the copolymerization have been investigated in detail. The results showed that the steric and electronic structure of salicylaldehyde and cocatalyst played an important role in the copolymerization. Up to now, diamines, as the framework for H_2salen ligands, were only focused on some *ortho*-diamines, such as 1,2-cyclohexenediamine, 1,2-phenylenediamine, 1,2-ethylenediamine and some derivatives of 1,2-ethylenediamine.[3,6] So far as we know, the copolymerization catalyzed by a salen–metal complex obtained from non-*ortho*-diamine was absent. This prompted us to verify whether the salen–metal complex synthesized from non-*ortho*-diamines such as amino acids could effectively catalyze the copolymerization of CO_2 and epoxides.

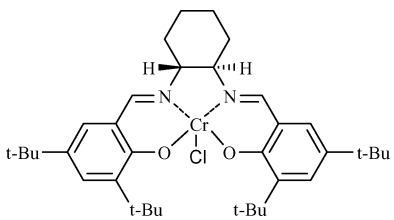
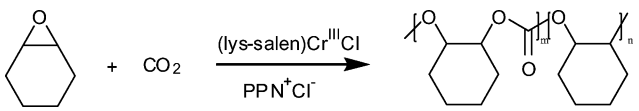


Fig. 1 (*R*,*R*)-(salen)$Cr^{III}Cl$ for the copolymerization of CO_2 and epoxide.

It is well known that natural amino acids, as renewable natural sources, are highly economic and scientific materials for the chemistry industry. What is more, natural amino acids are attractive sources of chirality. A lot of metal complexes with Schiff base ligands composed of one salicylaldehyde and one natural amino acid have been synthesized and applied.[9] However, few studies on metal complexes with salen ligands composed of two salicylaldehydes and one amino acid were reported. This has inspired us to determine whether we could develop a new lysine-based salen–metal catalyst for the copolymerization of CO_2 and epoxides. Herein we report the synthesis of a natural lysine-based (salen)$Cr^{III}Cl$ complex **4**, [(lys-salen)$Cr^{III}Cl$], and investigate its catalytic activity in the copolymerization of 1,2-cyclohexene oxide (CHO) and CO_2 (Scheme 1) for the first time.



Scheme 1 Copolymerization of CO_2 and CHO catalyzed by (lys-salen)$Cr^{III}Cl$.

[a]*Department of Chemistry, Zhejiang University, Hangzhou, 310027, People's Republic of China. E-mail: lihr@zju.edu.cn; Fax: (86)-571-8795-1895; Tel: (86)-571-8795-2424*
[b]*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, People's Republic of China*

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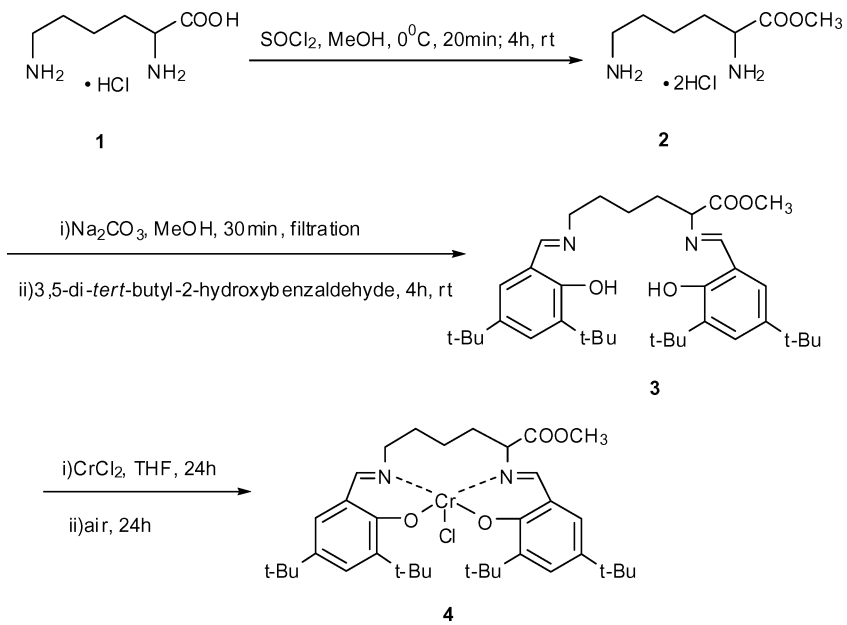

Scheme 2 Synthesis of (lys-salen)$Cr^{III}Cl$.

Results and discussion

Synthesis and characterization of the (lys-salen)$Cr^{III}Cl$

The synthesis of (lys-salen)$Cr^{III}Cl$ **4** started with commercially available (*S*)-lysine monohydrochloride (Scheme 2). Firstly, the (*S*)-lysine monohydrochloride was esterified by thionyl chloride and methanol[10] to obtain lysine methyl ester dihydrochloride **2** in 95% yield. The product was characterized by ^1H NMR spectroscopy, and the signal at 3.74 ppm corresponded to the methoxyl group.

Complex **2** was treated with sodium carbonate,[11] and then 3,5-di-*tert*-butylsalicylaldehyde was added to afford the lysine-based H_2salen ligand **3**. After recrystallization from methanol, the ligand was obtained in 45% yield as a bright yellow solid. It was characterized by IR and NMR spectroscopies and elemental analysis. The signals at 8.38 and 8.34 ppm in the ^1H NMR spectrum, and the absorbance at 1632 cm^{-1} in the IR spectrum both indicated the formation of C=N bonds.

Finally, the H_2salen ligand **3** was metalated by $CrCl_2$ and oxidized in air to form the desired (lys-salen)$Cr^{III}Cl$ **4**. Complex **4** was characterized by IR spectroscopy, ESI-MS and elemental analyses. Upon binding **3** to the metal center, there was a remarkable shift of the ν(C=N) vibration to the frequency at 1617 cm^{-1}. The ESI-MS measurement showed that the m/z was 660.3, which corresponded to $[(C_{37}H_{54}N_2O_4Cr)\cdot(H_2O)]^+$ (= [(**4** – Cl)·$(H_2O)]^+$). It indicated that one molecule of water per molecule of **4** was strongly coordinating to the central metal ion.

Catalytic copolymerization of CO_2 and CHO

The copolymerization of CO_2 and CHO was carried out in neat CHO at 4.5 MPa of CO_2 with the (lys-salen)Cr^{III}Cl-PPNCl (PPN^+=bis(triphenylphosphoranylidene)ammonium) as catalyst system. As shown in Table 1, the (lys-salen)$Cr^{III}Cl$, combined with

Table 1 Copolymerization of CO_2 and CHO by the (lys-salen)Cr^{III}Cl–PPNCl system[a]

Entry	Time/h	Temp/°C	Equiv of cocatalyst	Yield/%	TOF[b]/h^{-1}	Selectivity/% PCHC[c]	% carbonate[c]	M_n[d]/g mol^{-1}	M_w/M_n[d]
1	4	80	2.25	31	76.3	99.9	94.6	895	1.83
2	12	80	2.25	67	55.9	98.8	98.1	3430	1.25
3	24	80	2.25	87	36.4	99.1	98.6	7661	1.32
4	32	80	2.25	89	27.9	99.0	99.0	9138	1.39
5	18	60	2.25	44	24.5	100	95.9	1876	1.64
6	18	70	2.25	72	40.2	100	98.2	2136	1.75
7	18	80	2.25	81	44.9	99.4	98.9	7695	1.20
8	18	90	2.25	89	49.3	97.6	98.7	5862	1.22
9	18	100	2.25	99	55.0	95.0	98.8	6607	1.27
10	24	80	0.5	54	22.3	100	98.0	7369	1.15
11	24	80	1	75	31.1	99.6	98.8	9865	1.16
12	24	80	3	86	35.8	98.8	97.8	5984	1.14
13	24	80	5	81	33.6	97.9	97.8	3515	1.22

[a] Copolymerizations run in neat cyclohexene oxide (CHO) (14.7 g, 150 mmol; [CHO] : [Cr]=1000 : 1) at 4.5 MPa of CO_2. [b] Measured in moles of CHO consumed (mol Cr)$^{-1}$ h^{-1}. [c] Estimated based on ^1H NMR. [d] Estimated by gel permeation chromatography in THF at 30 °C on the basis of polystyrene standard.

PPNCl, could effectively catalyze the alternating copolymerization with high selectivity. All isolated copolymers appeared narrow molecular weigh distributions, ranging from 1.14 to 1.83, along with high carbon dioxide incorporation (greater than 94%), and only trace quantities of cyclic carbonate, as a byproduct, were produced.

The effect of reaction conditions on the copolymerization was investigated in detail. Firstly, when the reaction time increased from 4 to 32 h (Table 1, entries 1–4), the conversion of monomer continued increasing, and the molecular weight of copolymers increased from 895 to 9138. Meanwhile, the selectivity was not sensitive to the reaction time and remained at about 99%.

Secondly, higher temperature led to higher yields and greater molecular weights (Table 1, entries 5–9). At 60 °C, the yield was only 44% and the molecular weight of the copolymer was only 1876 after 18 h. The yield increased significantly to 99% at 100 °C, and the molecular weight was 7695 at 80 °C. A previous report had demonstrated that the increase of the temperature for the copolymerization of CHO and CO_2 resulted in a sharp increase in cyclic carbonate formation.[12] The activation barrier for cyclic carbonate formation was higher than that of polycarbonate, therefore cyclic carbonate tended to form at elevated temperatures.[12] For **4**–PPNCl, the selectivity decreased slightly from 100% to 95% when the temperature increased from 60 to 100 °C.

Finally, a slight increase in cyclic carbonate formation and a decrease in the molecular weight were observed with an increase in the cocatalyst loading (Table 1, entries 3, 10–13). The molar ratio of cocatalyst to catalyst also played an important role in the cyclic carbonate formation[8d,13] because excessive anions of the cocatalyst could displace the growing polymer chain from the metal center,[5] which then led to an increased rate of chain degradation and the formation of cyclic carbonate. When the ratio of **4** : PPNCl was 0.5, there was no cyclic carbonate produced. Increasing the ratio to 5 resulted in a slight (2%) decrease in selectivity. However, for the copolymerization of CHO and CO_2, catalyzed by the aluminium–salen complex–ammonium salt system in similar reaction conditions,[13] the increase of the ratio from 0.5 to 5 decreased the selectivity by over 50%. The decrease in the molecular weight might be caused by accompanying water of the cocatalyst.[14]

The GPC curve for the copolymer obtained from the reaction showed a bimodal molecular weight distribution. This phenomenon has been reported several times.[7a,13,15] Using MS characterization, in combination with GPC and the corresponding UV spectra of the copolymer, Sugimoto and coworkers have demonstrated that a possible chain-transfer reaction with concomitant water occurred, resulting in the bimodal distribution of the obtained copolymer.[13] Accordingly, an oligomer produced at 80 °C for 1 h catalyzed by **4**–PPNCl(1 : 2.25), was measured by ESI-MS, which was applied to defining the end groups of the copolymer in the copolymerization of CO_2 and epoxides.[8d,13,15] Similar to previous reports,[13,15] two series of signals having the same regular intervals of a repeating unit (142) were observed. They matched copolymer **a** and copolymer **b** (Fig. 2), respectively. Copolymer **a** had a –OH group at the end, which was probably introduced by the chain transfer by water,[13] and copolymer **b** had a terminal –Cl group, which was an initiating group for the copolymerization of CO_2 and CHO. The effect of water on the copolymerization was investigated. It was seen from Table 2 that

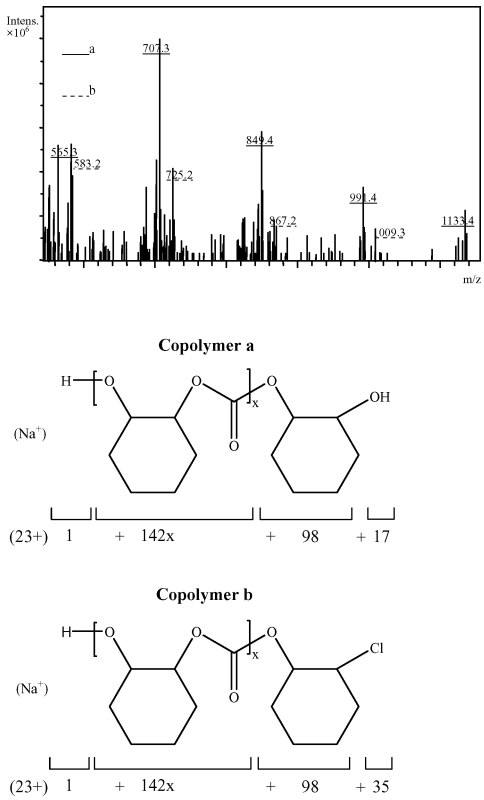

Fig. 2 ESI-MS spectrum of the Na^+-ionized polymer obtained with the catalytic system (CHO : (lys-salen)$Cr^{III}Cl$: PPNCl= 1000 : 1 : 2.25) at 80 °C and a 4.5 MPa CO_2 pressure for 1 h, and possible structures of copolymer **a** and copolymer **b**.

there was no obvious change in the TOF when the quantity of water was increased, while the molecular weight of the copolymer decreased significantly. In order to remove the concomitant water, the autoclave reactor containing **4** and PPNCl was heated at 100 °C for 6 h *in vacuo* and then cooled in a N_2 atmosphere before the copolymerization. However, the copolymer obtained still showed a bimodal GPC curve. The ESI-MS of **4** indicated that one molecule of water was coordinating to the central metal ion, and this might be the source of the water, which resulted in the chain transfer.[15]

The (*R*,*R*)-(salen)Co^{III} catalysts, which have two chiral centers, have been proven to be active in enantioselective copolymerization

Table 2 Copolymerization of CO_2 and CHO by the **4**–PPNCl system with added water[a]

Entry	Equiv of H_2O[b]	TOF[c]/h^{-1}	M_n[d]/g mol^{-1})	M_w/M_n[d]
1[e]	0	35.6	10592	1.26
2	0	36.4	7661	1.32
3	5	34.2	2472	1.31
4	40	33.3	1636	1.24

[a] Copolymerizations run in neat cyclohexene oxide (CHO) (14.7 g, 150 mmol; [CHO] : [Cr] : [PPNCl] = 1000 : 1 : 2.25) at 4.5 MPa of CO_2 for 24 h. [b] The equiv. of H_2O to **4**. [c] Measured in mole of CHO consumed (mol Cr)$^{-1}$ h^{-1}. [d] Estimated by gel permeation chromatography in THF at 30 °C on the basis of polystyrene standard. [e] Before the copolymerization, the autoclave reactor containing **4** and PPNCl was heated at 100 °C for 6 h *in vacuo* and then cooled in a N_2 atmosphere.

of CO_2 and CHO.[16] However, the study of Darensbourg and co-workers on the tacticity of copolymers formed by the copolymerization of CO_2 and CHO catalyzed by chiral (salen)Cr^{III} catalysts, showed a lack of stereocontrol in the CHO ring-opening step.[4,6] Accordingly, we wondered if the (lys-salen)$Cr^{III}Cl$ was active for enantioselective copolymerization of CO_2 and CHO, since it is unsymmetric and has a chiral center. To determine the tacticity of the polymer, ^{13}C NMR spectroscopy was employed and analyzed, following the description of Nozaki and Coates.[17] However, chemical shifts observed at 153.9, 153.4, and 153.2 ppm indicated the production of a largely atactic polymer.

Conclusions

In summary, we prepared a natural lysine-based (salen)$Cr^{III}Cl$, and investigated the copolymerization of CO_2 and CHO catalyzed by this catalyst. The results showed that the (lys-salen)$Cr^{III}Cl$, synthesized from non-*ortho*-diamine, could effectively catalyze the alternating copolymerization. The ESI-MS measurement of (lys-salen)$Cr^{III}Cl$ indicated that one molecule of water coordinated to the central metal ion, responding to the bimodal GPC curve of copolymers. In addition, the study on the tacticity of the copolymer showed a lack of stereocontrol in the CHO ring-opening step catalyzed by (lys-salen)$Cr^{III}Cl$ catalyst. In contrast to the traditional salen–metal catalysts, the (lys-salen)$Cr^{III}Cl$ catalyst was prepared from lysine, which is commercially available and optically pure. Although the activity of (lys-salen)$Cr^{III}Cl$ catalyst is not better than traditional salen–metal catalysts, it shows some advantages such as high carbonate linkage, narrow molecular weight distribution and good selectivity. Further studies are focused on exploring the reaction mechanism and developing new amino acid-based salen catalyst systems that exhibit higher stereoselectivity for epoxide ring-opening.

Experimental

Reagents and methods

THF was dried by distillation over sodium–benzophenone and stored over 4 Å molecular sieves under dry nitrogen. Cyclohexene oxide was freshly distilled over calcium hydride before use. Other reagents and starting materials were all used as received unless otherwise stated. The NMR spectra were recorded with a 500 MHz Bruker spectrometer in $CDCl_3$, D_2O and calibrated with tetramethylsilane (TMS) as the internal reference. Infrared spectra measurements were performed on a Nicolet 470 FT-IR spectrometer using KBr optics. ESI-MS analyses were performed on an Esquire3000plus mass spectrometer. Elemental analyses were measured by EA-1112 elemental analyser. The relative molecular weights were measured at 30 °C in THF with a flow rate of 1.0mL min^{-1}, using the polystyrene standards, on Waters1525/2414/717 GPC (waters 1525 HPLC pump, 2414 differential refraction detector, and 717 plus autosampler) equipped with three series-connected Styragel HR_3-HR_2-HR_1 columns.

Synthesis of (lys-salen)$Cr^{III}Cl$

(*S*)-lysine methyl ester dihydrochloride 2. [10] (*S*)-lysine monohydrochloride (3.65 g, 20 mmol) was partly dissolved in 150 mL methanol and cooled to 0 °C, then thionyl chloride (10.7 mL, 150 mmol) was added dropwise over 30 min. The reaction mixture quickly became homogeneous and was stirred for 20 min at 0 °C. After heating at reflux for 4 h, the solution was concentrated *in vacuo*. The crude product was diluted with methanol, the solution was concentrated again to remove any residual acid, and then dried under vacuum overnight to afford **2** (4.41 g, 95%) as a white solid. Melting point: 197.8–198.4 °C, ^1H NMR (D_2O): δ 4.08–4.06 (t, 1H), 3.74 (s, 3H), 2.92–2.89 (t, 2H), 1.93–1.85 (m, 2H), 1.63–1.60 (m, 2H), 1.33–1.39 (m, 2H) ppm.

Lysine-based H_2salen ligand 3. **2** (1.16 g, 5 mmol) was dissolved in 20 mL methanol and stirred together with Na_2CO_3 (1.06 g, 10 mmol) at room temperature for 30 min.[11] After removing the precipitate by filtration, a solution of 3,5-di-*tert*-butylsalicylaldehyde (2.34 g, 10 mmol) in 30 mL methanol was dropped slowly into the filtrate. Then, the reaction mixture was heated under reflux for 4 h. After distilling most of the solvent off and cooling to 0 °C, the crude product was collected by filtration. Recrystallization from methanol afforded the desired compound **3** as a bright yellow solid (1.33 g, 45%). ^1H NMR ($CDCl_3$): δ 13.87 (s, 1H), 13.30 (s, 1H), 8.38 (s, 1H), 8.34 (s, 1H), 7.42 (d, 1H), 7.38 (d, 1H), 7.12 (d, 1H), 7.08 (d, 1H), 4.00–3.97 (m, 1H), 3.75 (s, 3H), 3.59–3.58 (m, 2H), 2.08–1.92 (m, 2H), 1.77–1.74 (m, 2H), 1.47–1.45 (m, 2H), 1.46 (s, 9H), 1.44 (s, 9H), 1.32 (s, 9H), 1.31 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 172.14, 168.14, 166.12, 158.38, 158.31, 140.52, 140.17, 137.12, 136.90, 127.84, 126.99, 126.62, 126.01, 118.09, 117.88, 71.78, 59.45, 52.56, multiple peaks were present between 23–36 ppm. IR (KBr, ν_{max}/cm^{-1}):, 2955 and 2866 (CH), 1632 (C=N), 1597 and 1470 (C=C, Ar). Anal. calcd for $C_{37}H_{56}N_2O_4$: C, 74.96; H, 9.52; N, 4.73. Found: C, 74.92; H, 9.55; N, 4.73.

(lys-salen)$Cr^{III}Cl$ 4. Under a nitrogen atmosphere, $CrCl_2$ (0.27 g, 2.2 mmol) was added to a solution of **3** (1.18 g, 2 mmol) in 40 mL THF. The reaction mixture was stirred under nitrogen for 24 h and then in air for an additional 24 h. The reaction mixture was poured into 200 mL ethyl acetate and washed with aqueous saturated NH_4Cl (3 × 100 mL) and brine (3 × 100 mL). The organic layer was dried with Na_2SO_4, and solvent was removed under vacuum, yielding **4** (0.85 g, 63%) as a dark brown power. IR (KBr, ν_{max}/cm^{-1}): 2960, 2904 and 2869 (CH), 1617 (C=N), 1533 and 1458 (C=C, Ar). Anal. calcd for $C_{37}H_{54}N_2O_4CrCl{\cdot}H_2O$: C, 63.82; H, 8.11; N, 4.02. Found: C, 64.13; H, 8.31; N, 3.98. MS (ESI^+, *m*/*z*): 660.3 (calcd for $[(C_{37}H_{54}N_2O_4Cr){\cdot}(H_2O)]^+$ (= [(**4** – Cl)·$(H_2O)]^+$) 660.3).

Copolymerization of cyclohexene oxide and CO_2 catalyzed by (lys-salen)$Cr^{III}Cl$

In a typical experiment, a 100 mL stainless steel autoclave was charged with CHO, catalyst **4** and PPNCl. The autoclave was heated to 80 °C and held at 4.5 MPa for 24 h, and then quickly cooled to room temperature, and the residual CO_2 vented in a fume hood. A ^1H NMR spectrum was immediately taken to obtain the ratio of polycarbonate to cyclic carbonate and the percentage of carbonate linkage in the copolymer, where the amount of ether linkages was determined by integrating the peaks corresponding to the methane proton of polyether at *ca.* 3.5 ppm, cyclic carbonate at *ca.* 4.0 ppm and polycarbonate at *ca.* 4.6 ppm. A ^{13}C NMR spectrum was also taken to determine the tacticity of the polymer

formed. The polymer was extracted from a dichloromethane solution and dried under vacuum at 100 °C overnight. The isolated polycarbonate was weighted to calculate the yields. Molecular weight was determined through GPC in tetrahydrofuran (THF) (5 wt) and was calculated relative to polystyrene.

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