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Tetrahedron
Tetrahedron 60 (2004) 7277–7285

Poly(ε-caprolactone) macroligands with β-diketonate binding sites: synthesis and coordination chemistry

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Received 3 April 2004; revised 3 June 2004; accepted 4 June 2004

Dedicated to Robert H. Grubbs, in celebration of his many achievements and contributions to chemistry, both as a creative scientist and an inspiring mentor to us all

Abstract—Dibenzoylmethane (dbm) initiators with one and two alcohol sites were used to generate dbm end-functionalized and dbm-centered poly(ε-caprolactone) macroligands (dbmPCL and dbmPCL$_2$) with low polydispersities (~1.1). Chelation of polymeric ligands to metal ions (Eu^{3+}, Fe^{3+}, Ni^{2+} and Cu^{2+}) produced metal-centered star polymers, which were characterized by UV–vis and fluorescence spectroscopy, as well as gel permeation chromatography.

1. Introduction

Metal β-diketonates are complexes with a wide range of uses, both in materials and catalysis. For example, Europium β-diketonates are finding increasing application in technologies ranging from sensors[1–3] and molecular probes[4,5] to OLEDs.[6–10] Various Eu and other metal diketonates are also commonly used as homogeneous or heterogeneous polymer-bound catalysts for organic reactions.[11]

Eu tris(β-diketonates) figure prominently in lanthanide coordination chemistry.[12,13] Lanthanide metals are characterized by a partially filled 4f electron shell lying within and effectively shielded by lower-lying 5s and 5p shells. Due to this shielding from the surrounding environment, the electronic transitions of the lanthanide ions result in distinct, narrow line emission spectra, unlike the broad peaks arising from electronic transitions of transition metals. Europium itself has a very low molar absorptivity; however, it has been shown that certain ligands can absorb ultraviolet radiation and transfer this energy to the bound lanthanide ion, from which light is emitted.[14,15] The luminescence intensity of these Europium complexes in solution however, is often diminished due to the easy access of water molecules to the metal center, allowing energy to be dissipated non-radiatively through O–H stretching modes, and decreasing the energy available for radiative decay. The luminescence of Eu can be enhanced by the presence of a polymeric matrix.[16,17] Polymers can shield the metal centers from water and solvent molecules and lend processability to the luminescent material. These features make polymeric lanthanide complexes of interest for light-emitting materials.[8–10,18]

The concept of polymeric metal-centered β-diketonates described herein may also prove useful for supported, site-isolated catalysts in heterogeneous or homogeneous modes, which benefit from greater ease of product isolation. For example, Eu complexes are employed as catalysts for polymerizations,[19–21] epoxidation of alkenes with O_2,[22] and alkyne hydrogenation.[23] Polymer-supported nickel, copper, and iron diketonates have also been utilized in epoxidation reactions,[24] and as heterogeneous Lewis acid catalysts for hetero Diels–Alder reactions.[25]

With these many potential uses in mind, star-shaped polymeric metal β-diketonate complexes have been targeted. Hydroxyl-functionalized dibenzoylmethane (dbm) analogues, dbmOH (**5**) and dbm(OH)$_2$ (**4**), were prepared for use as initiators in the controlled polymerization of ε-caprolactone (CL), producing macroligands dbmPCL (**6**) and dbmPCL$_2$ (**7**) with dbm binding sites at the end and center of the chains, respectively. To determine the optimal conditions for preparative scale reactions, the polymerization kinetics were explored. Macroligands were chelated to Eu, Fe, Cu and Ni metal ions to produce metal-centered stars of various architectures, the spectroscopic properties of which were compared to non-polymeric M(dbm)$_n$ analogues.[26,27] This study builds upon prior

Keywords: Metallopolymer; Poly(caprolactone); β-Diketonate; Europium.
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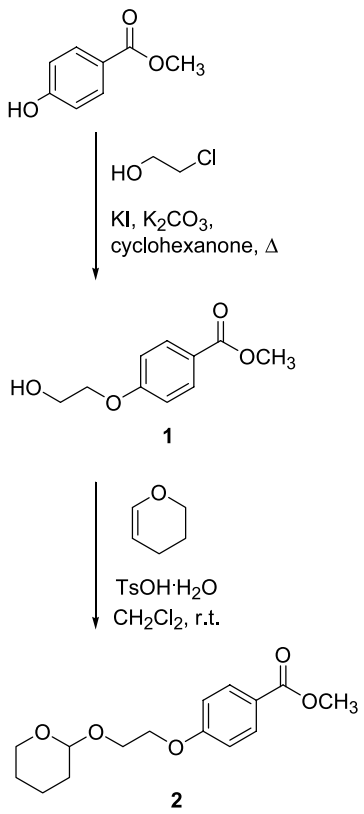
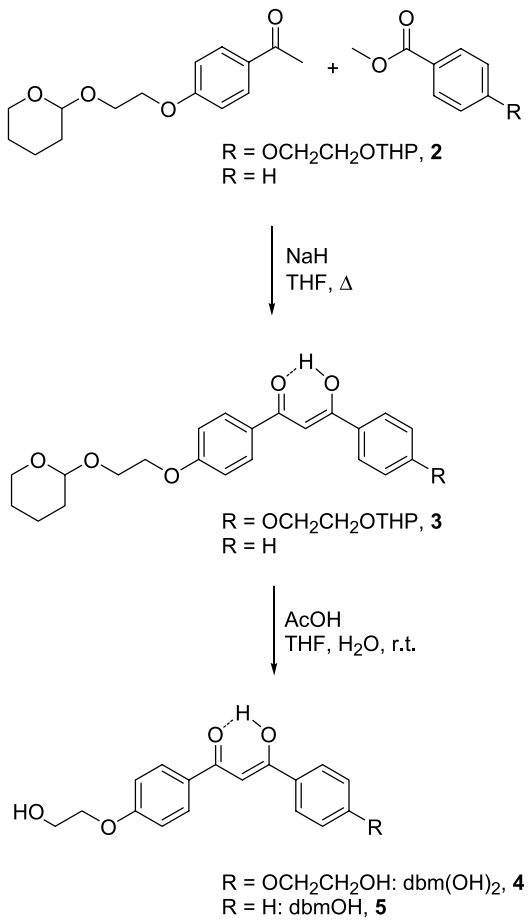
doi:10.1016/j.tet.2004.06.019



Scheme 1. Preparation of THP-protected alcohol ester **2**.



Scheme 2. Preparation of dibenzoylmethane initiators dbmOH, **5** and $dbm(OH)_2$, **4**.

work involving dbm-functionalized poly(lactic acid), dbmPLA, and its Europium complexes, thus expanding the dbm macroligand and polymeric metal complex set to include another biocompatible polyester.[15]

2. Results and discussion

2.1. Ligand initiator synthesis

A condensation reaction between ester and ketone components was used to produce diketones containing primary alcohol groups, which act as initiators for the ring-opening polymerization of ε-caprolactone. This modular synthesis allows for variation of the number and placement of initiating sites on the arene rings. Mono- and difunctional ligand initiators **5** and **4** were prepared as shown in Schemes 1 and 2. First, phenol functionalities were converted to primary alcohols by modification with alkyl linkers, as shown for the ester **1**, in Scheme 1. After protection of acidic alcohol sites as tetrahydropyranyl (THP) ethers, β-diketones were generated by condensation of the appropriate ester and ketone. The THP protecting groups were readily removed with acid and the ligand initators $dbm(OH)_2$, **4**, and dbmOH, **5** were purified by recrystallization and chromatography, respectively.

2.2. Macroligand synthesis

Macroligands were produced from the diketone alcohol initiators **4** and **5** by controlled polymerization. Living polymerization is a widely-used method for making polymers with discrete architectures, targeted molecular weights, and narrow molecular weight distributions (i.e. low polydispersity indices, PDIs).[30] Controlled polymerizations feature initiation and propagation; common side reactions such as termination and chain transfer are negligible. Criteria used to test whether a polymerization is living that are relevant to this study include the following: the polymerization proceeds until all monomer is consumed; the number-average molecular weight (M_n) is a linear function of percent monomer conversion; M_n can be predicted in advance based on the monomer to initiator ratio; resulting polymers have narrow PDIs, if initiation is fast relative to propagation; and the overall yield of chain-end functionalized polymers is quantitative.[30]

Various catalysts were screened to test whether controlled polymerization of ε-caprolactone could be achieved with the diketone initiators. Reactions were attempted with Et_3Al, $Al(O^iPr)_3$, and $Sn(Oct)_2$, all common catalysts for the living polymerization of ε-caprolactone.[31–38] Neither Et_3Al nor $Al(O^iPr)_3$ produced polymeric products, even after several days. Polymerizations employing $Sn(Oct)_2$ were successful in generating polymer; thus, further studies focused on this catalyst.

Kinetics studies were performed using $Sn(Oct)_2$ and bulk ε-caprolactone at 110 °C, to determine the optimal reaction conditions for achieving molecular weight control (e.g. low PDI and a linear relationship between M_n and percent

monomer conversion.) Catalyst to initiator ratios of 1/20, 1/40, and 1/60 were screened for the monofunctional initiator **5**. For a 1/20 loading, GPC traces show high molecular weight shoulders and broad PDIs after 1 d, corresponding to only a 10% conversion of monomer. In contrast, a catalyst loading of 1/60 yielded polymer with a low PDI (<1.1) at ~23% monomer conversion, but 3 d were required to achieve this result. With a 1/40 loading, comparable molecular weight control and conversion were achieved after 1 d. Because this loading strikes the best balance between molecular weight control, monomer conversion, and reaction time, the 1/40 ratio was employed in subsequent polymerization studies with initiators **4** and **5**.

Kinetics and molecular weight versus percent conversion plots for polymerizations with dbmOH, **5**, and dbm(OH)$_2$, **4** are compared in Figures 1 and 2. The rate of polymerization with the difunctional initiator is roughly two times that of the monofunctional reagent, as expected, and first-order kinetics plots with both **4** and **5** deviate from linearity, after ~11 and 31 h, respectively (Fig. 1). After these time points, GPC analysis reveals high molecular weight shoulders that become increasingly more pronounced over time, correlating with higher PDIs (Fig. 2). M_n versus % conversion plots are essentially linear at low monomer conversion; however, the observed molecular weights are slightly higher than the values that are predicted for a controlled reaction. Unlike lactide polymerizations with the same tin catalyst and initiator **5**, which produce dbmPLA with narrow PDIs up to high monomer conversion,[15] ε-caprolactone reactions with **4** and **5** are not controlled.

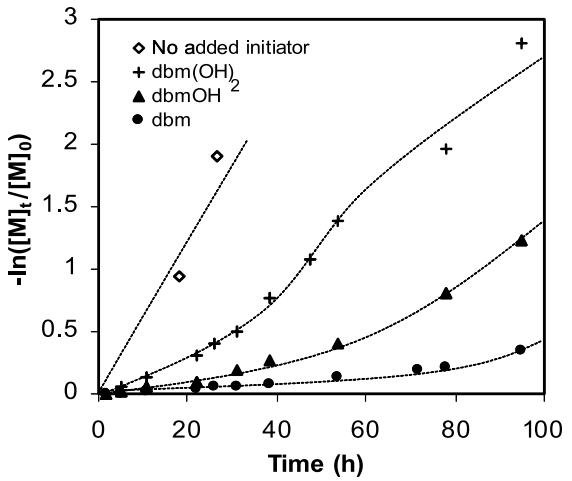


Figure 1. Kinetics plots for the polymerization of ε-caprolactone with dbm(OH)$_2$, **4**, and dbmOH, **5** (Sn(Oct)$_2$: 1° alcohol=1:40), and control reactions with dbm and no added initiator (curves are drawn through each data set to serve as a guide for the eye).

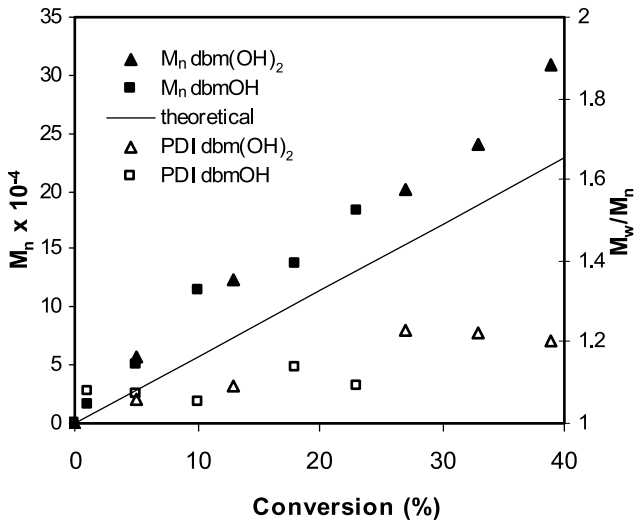


Figure 2. Number-average molecular weight versus percent conversion plots and polydispersity indices for the polymerization of ε-caprolactone with the monofunctional and difunctional initiators dbmOH, **5**, and dbm(OH)$_2$, **4**. (Sn(Oct)$_2$:1° alcohol=1:40).

To account for the diminished control, we first considered the nature of the initiators. Because dbmOH and dbm(OH)$_2$ are diketones that can tautomerize, it was theorized that the enol form could potentially act as an alcohol initiator for the polymerization of ε-caprolactone, perhaps causing the shoulder that is seen in the GPC trace over time. To test this possibility, a polymerization reaction was performed with unmodified dbm, and the reaction mixture became viscous within 1 d. The resulting solid was dissolved in CH_2Cl_2 and precipitated into cold acetone in an attempt to remove any unreacted dbm. Although ^{1}H NMR analysis of the precipitated polymeric product still showed the presence of poly(ε-caprolactone) and dbm resonances, the amount of dbm decreased upon subsequent precipitations. This suggests that the dbm peaks may arise from molecules entrapped within the polymer, and not covalently bound to it as would be the case if dbm were serving as an initiator. Furthermore, the ^{1}H NMR spectrum of the polymer grown in the presence of unfunctionalized dbm was compared with that of O-acylated diketones.[39] The vinyl and enol resonances in the polymer sample correspond to dbm rather than an enol ester, suggesting that the dbm enol is not covalently attached to the end of most polymer chains. However, the possibility of the enol site initiating the polymerization to yield an unstable enol ester that subsequently fragments to reform dbm and a carboxylic acid terminated polymer chain cannot be ruled out on the basis of these findings.

Another control reaction was run to see if polymerization can proceed in the absence of any added initiator. As shown in Figure 1, caprolactone was rapidly polymerized. This is consistent with previous reports that adventitious water from the Sn(Oct)$_2$, which is present in the catalyst even after multiple distillations,[31,37,40] can serve as an initiator. This is a negligible problem in most reactions because the Sn hydroxide and oxide initiating species produced from Sn(Oct)$_2$ and water do not compete effectively with the Sn-alkoxide initiator obtained from primary alcohols.

Although results described above suggest that dbm is not an effective initiator, it may still function as a ligand for the Sn catalyst, thus altering its normal reactivity. To test the effect of dbm on Sn(Oct)$_2$-catalyzed reactions with primary alcohol initiators, additional controls were run with ethylene glycol, in the presence and absence of dbm. As an example, for a 20:10,000:1 ethylene glycol/ε-caprolactone/Sn(Oct)$_2$ loading, a polymer with M_n=25,200 and PDI=1.14 was produced after 8 h. Under the same conditions, but in the

presence of dbm (1:1 dbm/ethylene glycol), a polymer with M_n=1000 and PDI=1.14 was generated. Consistent with data for **4** and **5** shown in Figure 1, polymerization of ε-caprolactone is slowed in the presence of dbm.

Although ε-caprolactone polymerizations with dbm initiators **4** and **5** are not strictly living, with careful selection of reaction conditions, it is still possible to prepare macroligands with low PDIs and monomodal GPC traces for use in coordination reactions. Based on the kinetics experiments, preparative scale reactions were run using a catalyst loading of 1/40 per primary alcohol initiating site. Polymerizations employing the monofunctional ligand **5** were stopped after 31 h, and polymerizations with the difunctional ligand **4** were stopped after 11 h. The resulting macroligands were analyzed by ^{1}H NMR and GPC in THF using RI detection. As shown in Figure 3 for dbmPCL, diketone resonances are clearly evident in ^{1}H NMR spectra. Number-average molecular weights were determined by relative integration of the peak at 4.06 ppm, corresponding to the $-OCH_2-$ protons of the polymer backbone against a phenyl proton peak at 7.98 ppm. GPC and NMR molecular weight data correlate reasonably well (e.g. dbmPCL: M_n(NMR)=9700; M_n(GPC)=10,000); however, discrepancies between GPC and ^{1}H NMR values are not uncommon, since the GPC molecular weights are based on polystyrene standards.[33,41]

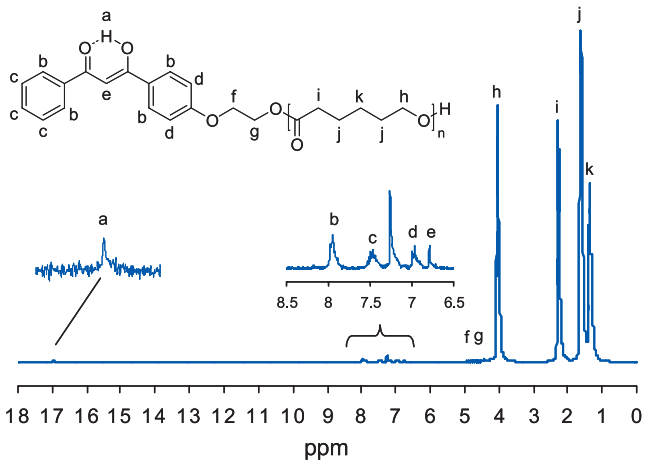


Figure 3. ^{1}H NMR spectrum of the dibenzoylmethane end-functionalized poly(ε-caprolactone) macroligand, dbmPCL **6** in $CDCl_3$.

2.3. Synthesis and characterization of Eu-centered polymers

Previously, Eu-centered star polymers based on PLA were synthesized using a mixed solvent system[15] to accommodate the polymer and the metal salt. More recently, it was noted that Eu tris and tetrakis dbm complexes are more conveniently prepared in THF, which solubilizes the macroligand, Et_3N, and anhydrous $EuCl_3$ reactants. The lability of Europium systems precludes the determination of molecular weight by GPC methods because the complexes fragment into their component parts on the columns. Characterization is accomplished by fluorescence spectroscopy and luminescence lifetime measurements of 1 mM THF solutions. Figure 4 shows representative excitation

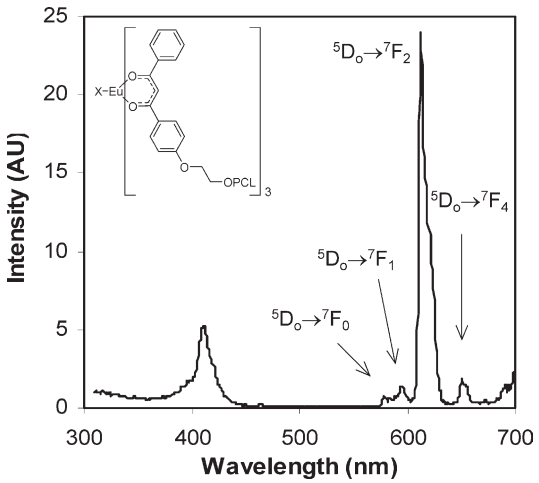


Figure 4. Excitation (~300–430 nm) and emission (~570–700 nm) spectra for a 1 mM solution of $Eu(dbmPCL)_3$ in THF with labeled transitions (X=possible donor ligand, such as H_2O or THF).

and emission spectra of $Eu(dbmPCL)_3$, the features of which are consistent with the spectra of $Eu(dbm)_3$. Europium emission spectra vary little with different ligands and solvents because the 4f electrons of the metal are well-shielded by outer-shell electrons; the 4f electronic transitions maintain much of their atomic character in solution.

A titration study was undertaken to compare the relative fluorescence intensities of solutions with different ratios of dbmPCL per Eu ion. Figure 5 shows that the intensity is greatest when 3 equiv of ligand have been added, corresponding to a tris complex, for both the macroligand and dbm. Fluorescence intensities of tris and tetrakis dbmPCL complexes are enhanced relative to the non-polymeric Europium dbm analogues. This is consistent with previous reports describing the protective nature of the polymer shell, diminishing luminescence quenching due to metal–metal encounters and access of water and other donors to the Eu center.[17,42]

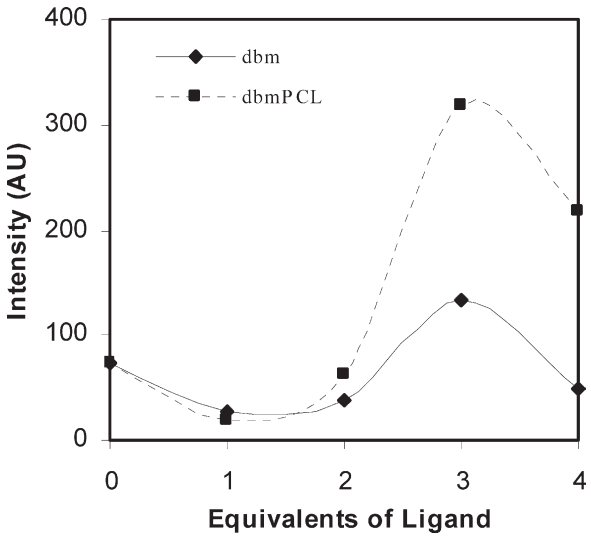


Figure 5. Europium titration experiment. Intensity versus equivalents of dbm and dbmPCL **6** (M_n(NMR)=7700) added (per equivalent of $EuCl_3$). [Eu^{3+}] held constant at 1 mM.

Luminescence lifetimes provide valuable information about sample homogeneity. In homogeneous samples with only one species emitting, the lifetime decay curve fits a single exponential equation. If, however, the decay curve fits a double or higher exponential equation, the sample may be inhomogenous, with more than one species emitting. Lifetime data for tris and tetrakis polymeric products as well as the corresponding non-polymeric Eu dbm complexes are presented in Table 1. Tris complexes of dbm, dbmPCL, and $dbmPCL_2$ all display double exponential lifetime decay curves, as is common for Lewis acidic six-coordinate Eu complexes, with solvent or water occupying remaining binding sites in a fraction of the sample.[43–45] The data obtained for the tetrakis complexes are consistent with single species in solution.

Table 1. Luminescence lifetimes[a] (τ_1 and τ_2) for Europium dibenzoylmethane complexes

Complex	MW[b] (calcd)	τ_1 (ms)	RW_1[c] (%)	τ_2 (ms)	RW_2[c] (%)
$Eu(dbm)_3$	844	0.02	86	0.30	14
$Eu(dbmPCL)_3$	25,000	0.15	94	0.68	6
$Eu(dbmPCL_2)_3$	23,500	0.13	81	0.26	19
$Eu(dbm)_4^-$	1068	0.13	100	—	—
$Eu(dbmPCL)_4^-$	33,300	0.13	100	—	—
$Eu(dbmPCL_2)_4^-$	31,200	0.13	100	—	—

[a] One millimolar THF solutions monitored at 613 nm after excitation at 465 nm.
[b] MW (calcd)=calculated molecular weight, determined from M_n(NMR) for polymeric complexes.
[c] Relative weighting (RW) of component in double exponential fits.

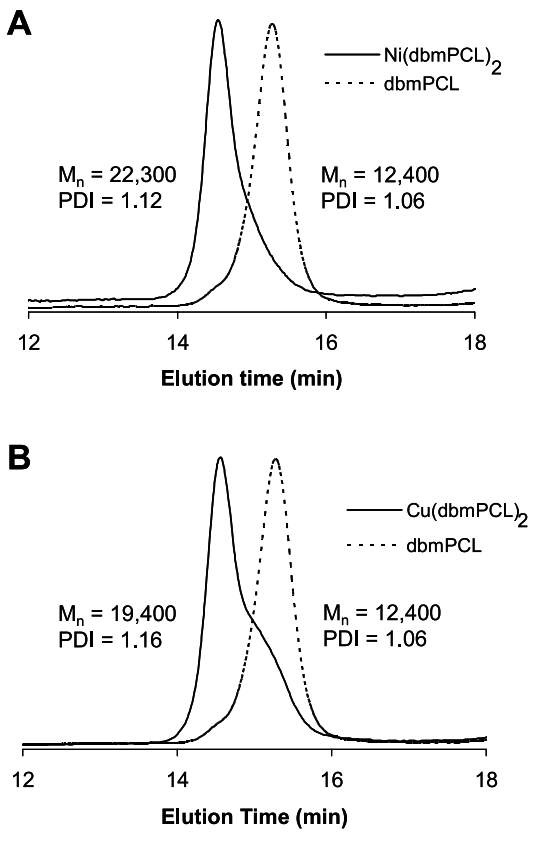


Figure 6. GPC overlay of (A) dbmPCL and a Ni bis dbmPCL complex, and (B) dbmPCL and a Cu bis dbmPCL complex in THF.

Nickel(II) and copper(II) bis β-diketonate complexes are also known[46,47] and macroligand chelation was explored for these systems as well. Because of differences in solubility between dbm and dbmPCL, literature preparations of Ni and Cu dbm complexes were modified for this study. Both $Ni(dbm)_2$ and $Ni(dbmPCL)_2$ were prepared in 1:1 DMF/THF, and copper complexes $Cu(dbm)_2$ and $Cu(dbmPCL)_2$ were prepared in THF. During the course of the macroligand chelations, small aliquots of the green Ni and Cu solutions were removed and injected directly onto the GPC for analysis. The GPC overlays of Ni(II) and Cu(II) complexes along with their component macroligands are shown in Figure 6.

The GPC molecular weights of the Ni and Cu species are roughly twice those of the component macroligands, indicative of bis complexes. Unlike the labile Europium systems, both nickel and copper complexes show little fragmentation. Low molecular weight tailing seen for Ni, and the shoulder observed for Cu may be attributed to a small fraction of unreacted, or cleaved macroligand. Sample treatment and also GPC column conditions may affect polymeric Ni and Cu complex fragmentation. Bimodal GPC traces were consistently observed upon analysis of samples that were concentrated in vacuo or isolated after precipitation from THF/hexanes or THF/MeOH. Both Ni and Cu are known to form adducts,[48,49] and solvento complexes in particular exhibit varying stability.[50,51] Substitution or removal of donors such as THF, MeOH or Et_3N during precipitation or concentration may account for decreased stability during GPC analysis. Attempts to characterize the Ni and Cu polymeric compounds by UV–vis spectroscopy were also hampered by their sensitivity to fragmentation upon concentration and by insolubility at concentrations required to visualize transitions with low extinction coefficients. Nickel and copper dbm and dbmPCL complexes were analyzed in 1:1 DMF/THF. Green solutions of the polymeric nickel complex show a broad absorbance centered at 620 nm, in accord with the $Ni(dbm)_2$ complex (λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)=507 (25sh), 620 (32), 679 (19sh)). Unfortunately, the polymeric Ni complex was insoluble at the concentration required to resolve details of the spectrum that are evident in 20 mM solutions of the Ni dbm complex. Solutions of copper dbm and dbmPCL complexes in 1:1 DMF/THF are both green in color ($Cu(dbm)_2$: λ_{max}=656 nm, ε=68 $M^{-1}\,cm^{-1}$; $Cu(dbmPCL)_2$: λ_{max}=660 nm, ε=87 $M^{-1}\,cm^{-1}$). These data compare favorably with literature values for the bis dbm species in dioxane (λ_{max}=650 nm, ε=76 $M^{-1}\,cm^{-1}$).[52]

The iron complex, $Fe(dbmPCL)_3$ was also prepared. Because the rates of reaction with polymeric ligands tend to be slower than with small-molecule ligands,[53] a chelation kinetics study was performed and the progress of reaction was monitored by UV–vis spectroscopy. After 10 min, the absorbance of the polymeric Fe species had reached a maximum value and plateaued with continued stirring. Thus, preparative scale reactions were run using reaction times of ~15 min. UV–vis spectra of $Fe(dbmPCL)_3$ and $Fe(dbm)_3$ are compared in Figure 7. Spectral data for $Fe(dbm)_3$ (λ_{max}=487 nm, ε=4292 $M^{-1}\,cm^{-1}$) and $Fe(dbmPCL)_3$ (λ_{max}=485 nm, ε=4035 $M^{-1}\,cm^{-1}$) in CH_2Cl_2 correspond reasonably well to the reported value

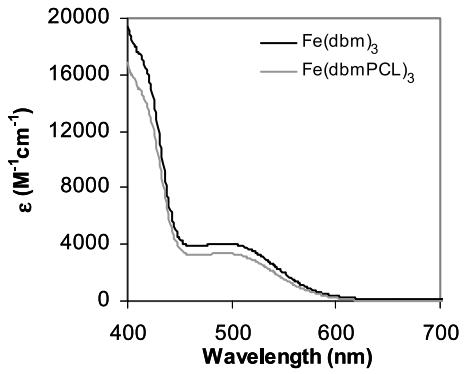


Figure 7. UV–vis spectra of $Fe(dbmPCL)_3$ (λ_{max}=485 nm, ε=4292 M^{-1} cm^{-1}) and $Fe(dbm)_3$ (λ_{max}=487 nm, ε=4035 M^{-1} cm^{-1}) in CH_2Cl_2.

for the n→d* transition in $CHCl_3$ (λ_{max}=500 nm, ε=2344 M^{-1} cm^{-1}).[54]

3. Conclusions

In summary, the polymerization of ε-caprolactone from monofunctional and difunctional alcohol diketonate ligands was explored. Although these reactions do not meet the usual criteria for a living polymerization at high conversions, narrow PDI materials were produced at low monomer conversion. Polymers thus prepared were chelated to a range of metal ions, including Eu, Ni, Cu, and Fe. This approach provides site-isolated polymeric metal complexes with spectroscopic properties that correlate well with non-polymeric analogues. The luminescence intensities of polymeric Europium complexes however, are significantly enhanced relative to Eu dbm species. Further investigation of the properties and reactivities of polymeric β-diketonate complexes will set the stage for their application as new kinds of functional materials and catalysts.

4. Experimental

4.1. Materials

ε-Caprolactone (Aldrich) was dried over CaH_2 and distilled prior to use. THF was dried and purified by distillation over sodium benzophenone ketyl. Chloroform-*d*-($CDCl_3$) was passed through a short plug of dry, activated (Brockman I) basic alumina prior to ^1H NMR spectral analysis of acid sensitive compounds. $EuCl_3$ (Cerac Inc., 99.9%), Tin(II)2-ethylhexanoate ($Sn(Oct)_2$, Aldrich) and all other reagents were used as received without further purification. 1-[4-(2-Hydroxyethoxy)-phenyl]-3-phenyl-propane-1,3-dione (dbmOH, **5**), $Eu(dbm)_3$,[15] and $Fe(dbm)_3$[28] were prepared as previously reported.

4.2. Methods

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a General-Electric QE-300 instrument in $CDCl_3$, unless indicated otherwise. ^1H NMR spectra were referenced to the signal for residual chloroform at 7.26 ppm or DMSO at 2.50 ppm. ^{13}C NMR spectra were referenced to the chloroform signal at 77.0 ppm or the DMSO signal at 39.4 ppm. Analytical thin layer chromatography (TLC) was performed on 0.2 mm silica 60 coated glass plates (Whatman) and spots were visualized by UV light (254 nm). Flash chromatography was carried out on EM Science 40–63 μm silica gel. Deactivation of silica for acid-sensitive samples was performed using 10% Et_3N in hexanes, where indicated. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. IR spectra of samples as thin films (prepared by evaporation of CH_2Cl_2 solutions onto NaCl plates) were measured using a Nicolet Impact 400D FTIR spectrophotometer. Molecular weights were determined by ^1H NMR and gel permeation chromatography (GPC) (THF, 25 °C, 1.0 mL min^{-1} vs polystyrene standards). Polymer Labs 5 μm-mixed-C columns along with Hewlett–Packard instrumentation (Series 1100 HPLC) and Viscotek software (TriSEC GPC Version 3.0, Viscotek Corp.) were used in the GPC analysis. Emission and excitation spectra were recorded on a SPEX Fluorolog 1680 instrument using right angle illumination. Emission decay curves were recorded using a Tektronix TDS-540 digital oscilloscope, with excitation by a pulsed nitrogen laser (337 nm) and emission monitored at 613 nm.

Thermogravimetric analysis (TGA) was conducted under N_2 using a TA Instruments TGA 2020 thermogravimetric analyzer over a temperature range from 30 to 500 °C with a heating/cooling rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC 2920 modulated DSC. Analyses were performed in modulated mode under a N_2 atmosphere (amplitude=±1 °C; period=60 s; heating rate=5 °C min^{-1}; range −10 to 110 °C). Reported values of thermal events are from the second heating cycle and the reversing heat flow curve (T_g=the midpoint of the change in heat capacity).

4.3. Initiator synthesis

4.3.1. 4-(2-Hydroxyethoxy)-benzoic acid methyl ester (1). Cyclohexanone (20 mL) was added to a mixture of methyl 4-hydroxybenzoate (1.0 g, 6.57 mmol), KI (0.55 g, 3.29 mmol), and K_2CO_3 (1.81 g, 13.1 mmol) under N_2 to produce a yellow suspension. 2-Chloroethanol (1.2 mL, 16.4 mmol) was added and the reaction mixture was stirred at reflux for ~1 d or until TLC showed no change. The tan suspension was cooled to room temperature and filtered to remove the solids. The yellow-orange filtrate was concentrated in vacuo to yield a mixture containing a brownish-orange oil and white solid. Addition of CH_2Cl_2 (~15 mL) to the mixture produced a cloudy yellow suspension that was gravity filtered, and the filtrate was concentrated in vacuo to yield a light brown solid. The product was purified by column chromatography (1:1 EtOAc/hexanes, R_f=0.25) to give the alcohol **1** (1.23 g, 93%) as a white solid. Spectral data corresponds to that previously reported.[29]

4.3.2. 4-[2-(Tetrahydropyran-2-yloxy)-ethoxy]-benzoic acid methyl ester (2). A solution of **1** (0.50 g, 2.55 mmol), *p*-toluenesulfonic acid monohydrate (2.4 mg, 0.0128 mmol), and 3,4-dihydro-2*H*-pyran (0.35 mL, 3.82 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for ~2 h or until no starting material was evident by TLC (R_f=0.81; 1:1 EtOAc/hexanes). Saturated

$NaHCO_3$ (aq.) (10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with additional CH_2Cl_2 (3×50 mL). The combined organic fractions were washed with brine (50 mL), dried over sodium sulfate, and then were filtered and concentrated in vacuo. The resulting residue was purified by column chromatography (deactivated silica, 1:1 EtOAc/hexanes, R_f=0.79) to afford **2** (0.69 g, 96%) as an orange oil. ^{1}H NMR δ 7.98 (d, J=8.9 Hz, 2H, 2,6-ArH), 6.95 (d, J=8.9 Hz, 2H, 3,5-ArH), 4.70 (t, J=3.5 Hz, 1H, OCHO (THP)), 4.20 (m, 2H, $ROCH_2CH_2OAr$), 4.07 (m, 2H, $ROCH_2CH_2OAr$), 3.88 (s, 3H, CH_3), 3.85 (m, 2H, OCH_2, (THP)), 3.53 (m, 2H, CH_2 (THP)), 1.79 (m, 2H, CH_2 (THP)), 1.59 (m, 2H, CH_2 (THP)). ^{13}C NMR δ 131.7, 114.5, 65.9, 62.4, 52.1, 30.7, 25.6, 19.5. Anal. calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.29; H, 7.20.

4.3.3. 1,3-Bis-{4-[2-(tetrahydropyran-2-yloxy)-ethoxy]-phenyl}-propane-1,3-dione (3). A solution of **2** (1.01 g, 3.68 mmol) and 1-{4-[2-(tetrahydropyran-2-yloxy)-ethoxy]-phenyl}-ethanone (0.95 g, 3.60 mmol) in THF (25 mL) was transferred by cannula to a suspension of sodium hydride (0.21 g, 7.35 mmol) in THF (10 mL) under N_2. The resulting mixture was heated at reflux for ~2.5 d or until TLC (1:1 EtOAc/hexanes) showed complete consumption of the ketone starting material. The resulting brown suspension was cooled to room temperature, and the reaction was quenched by the addition of H_2O (25 mL). EtOAc (50 mL) was added to the solution, and the organic layer was separated. The aqueous layer was extracted with additional EtOAc (3×50 mL). The combined organic fractions were washed with brine (25 mL), dried over sodium sulfate, and concentrated in vacuo to give a yellow-orange solid. The crude product was purified by column chromatography (deactivated silica, 1:1 EtOAc/hexanes, R_f=0.50) to give **3** (1.17 g, 63%) as a pale yellow solid. Mp=99–101 °C. ^{1}H NMR δ 17.11 (s, 1H, enol OH), 7.95 (d, J=8.5 Hz, 4H, 2′,6′-ArH, 2″,6″-ArH), 7.01 (d, J=8.5 Hz, 4H, 3′,5′-ArH, 3″,5″-ArH), 6.73 (s, 1H, COCHCO), 4.72 (t, J=3.7 Hz, 2H, OCHO (THP)), 4.22 (m, 4H, $Ar-O-CH_2$), 4.09 (m, 4H, $Ar-O-CH_2-CH_2$), 3.87 (m, 4H, OCH_2 (THP)), 3.54 (m, 2H, CH_2 diketone form), 1.90–1.46 (m, 12H, CH_2 (THP)). ^{13}C NMR δ 19.5, 25.6, 30.7, 62.4, 65.9, 67.8, 91.7, 99.2, 114.8, 128.4, 129.2, 131.5, 162.5, 184.8. Anal. calcd for $C_{29}H_{36}O_8$: C, 67.95; H, 7.08. Found: C, 67.89; H, 7.08.

4.3.4. 1,3-Bis-[4-(2-hydroxyethoxy)-phenyl]-propane-1,3-dione (4). Acetic acid (40 mL), THF (20 mL), and H_2O (10 mL) were added to **3** (1.12 g, 2.2 mmol), and the mixture was heated at 45 °C under N_2 for 1 d. The reaction was concentrated in vacuo, yielding an off-white solid, which was purified by recrystallization from THF/hexanes to yield the diketone **4** (0.48 g, 1.39 mmol, 58%) as a fluffy white solid. Mp=149–151 °C. ^{1}H NMR (DMSO-d_6) δ 17.07 (s, 1H, enol OH), 7.96 (d, J=8.3 Hz, 4H, 2′,6′-ArH, 2″,6″-ArH), 7.00 (d, J=8.9 Hz, 4H, 3′,5′-ArH, 3″,5″-ArH), 6.73 (s, 1H, COCHCO), 4.17 (t, J=4.4 Hz, 4H, $HOCH_2-CH_2OAr$), 4.01 (t, J=4.4 Hz, $HOCH_2CH_2OAr$), 1.27 (broad s, 2H, $HOCH_2CH_2OAr$). ^{13}C NMR (DMSO-d_6) δ 184.0, 162.4, 129.4, 126.9, 114.5, 91.4, 69.8, 59.3. Anal. calcd for $C_{18}H_{20}O_4$: C, 66.27; H, 5.84. Found: C, 65.97; H, 5.93.

4.4. Kinetics study of caprolactone polymerization with monofunctional initiator 5

A dry, 50 mL Kontes flask was charged with dbmOH initiator **5** (24.9 mg, 0.088 mmol), and ε-caprolactone (4.8 mL, 44 mmol). The flask was flushed with N_2, sealed, and stirred at 110 °C to ensure a homogeneous mixture, and then an 85 mM solution of $Sn(Oct)_2$ (26 μL, 2.2 μmol) in hexanes was added under N_2 and the flask was sealed. Small aliquots were removed by pipette under N_2 over a span of 5 d and were transferred to vials and quenched by immediate immersion in an ice bath. Percent monomer conversion was determined by ^{1}H NMR using relative integrations of the monomer $-OCH_2$ triplet peak (4.0–4.3 ppm) versus the triplet arising from the $-OCH_2-$ backbone protons of the polymer (3.9–4.1 ppm), which are discrete resonances for individual aliquots. GPC analysis versus polystyrene standards was used to determine molecular weights (M_n) and polydispersity indices (PDIs). For comparison, M_n was also determined by NMR integration of the polymer $-OCH_2-$ proton peaks (~4.1 ppm) relative to the phenyl initiator peak for the protons adjacent to the diketone moiety (~8.0 ppm).

4.5. Kinetics study of ε-caprolactone polymerization with difunctional initiator 4

A dry, 50 mL Kontes flask was charged with initiator $dbm(OH)_2$ (**4**) (30 mg, 0.087 mmol) and ε-caprolactone (4.8 mL, 44 mmol). The flask was flushed with nitrogen, sealed and stirred at 110 °C to ensure homogeneity, then an 85 mM solution of $Sn(Oct)_2$ in hexanes (51 μL, 4.4 μmol) was added under N_2. The flask was resealed and stirring was continued at 110 °C. Aliquots were removed and tested as described for dbmPCL.

4.6. ε-Caprolactone polymerization kinetics control reactions

(1) With dbm
A dry, 50 mL Kontes flask was charged with dibenzoylmethane (20 mg, 0.088 mmol) and ε-caprolactone (4.8 mL, 44 mmol). The flask was flushed with nitrogen, sealed and stirred at 110 °C until homogeneous, and then an 85 mM solution of $Sn(Oct)_2$ in hexanes (26 μL, 2.2 μmol) was added under nitrogen. The flask was resealed and stirring was continued at 110 °C. Aliquots were removed and tested as described above for dbmPCL.
(2) With no initiator
This control reaction was run as described above for (1), with the exception that no initiator was added.
(3) With ethylene glycol as initiator
The control reaction with ethylene glycol was run as described in (1), with the exception that ethylene glycol was added instead of dbm. Reagent loadings: ethylene glycol (4.9 μL, 0.087 mmol), ε-caprolactone (4.9 mL, 44 mmol), and $Sn(Oct)_2$ (49 μL of an 89 mM solution in hexanes).
(4) With ethylene glycol and dbm
The control reaction with ethylene glycol and dbm was run as described above for (3), with the exception that dbm (19.5 mg, 0.087 mmol) was also added.

4.7. Preparative scale reaction with dbm

Polymerizations in the presence of dibenzoylmethane were performed analogous to the corresponding kinetics control described above, but on a larger scale: dbm (50.0 mg, 0.223 mmol), ε-caprolactone (12.4 mL, 112 mol) and $Sn(Oct)_2$ (101 μL of a 55 mM solution in hexanes). After 12 h, the liquid reaction mixture was added dropwise to cold MeOH (~400 mL), the resulting solid product was collected on a fine frit, and was washed with cold acetone (3×50 mL).

4.8. Macroligand synthesis

4.8.1. Preparative scale synthesis of dbmPCL (6). A representative procedure is provided. A dry, 50 mL Kontes flask was charged with initiator **5** (24.9 mg, 0.088 mmol) and ε-caprolactone (4.8 mL, 44 mmol). The flask was flushed with nitrogen, sealed and stirred at 110 °C until homogenous, then a 69 mM solution of $Sn(Oct)_2$ in hexanes (32 μL, 2.2 μmol) was added under nitrogen. The flask was resealed and stirring was continued at 110 °C for 31 h (i.e. ~30% conversion). The reaction mixture was cooled in an ice bath, dissolved in CH_2Cl_2 (3 mL), and precipitated by dropwise addition to cold stirring MeOH (300 mL). The product was collected on a fine frit, and dried in vacuo. The resulting solid was dissolved in CH_2Cl_2 (2 mL) and precipitated by dropwise addition to cold stirring hexanes (35 mL). The product was collected by centrifugation. The mother liquor was decanted, the solid was washed with additional cold hexanes and then was dried in vacuo to provide **6** as a white solid: 0.55 g (88%; corrected for monomer conversion). T_m (DSC)=60.1 °C. ^{1}H NMR δ 16.96 (s, enol OH), 7.98 (d, J=4.6 Hz, 2′,6′-ArH, 2″,6″-ArH), 7.49 (m, H-3″, H-4″, H-5″-ArH), 7.00 (d, J=4.6 Hz, 3′,4′-ArH), 6.81 (s, COCHCO), 4.47 (t, J=4.6 Hz, $PhOCH_2CH_2$), 4.25 (t, J=4.6 Hz, $PhOCH_2CH_2$), 4.06 (t, J=6.5 Hz, RCO_2CH_2), 3.65 (m, CH_2OH), 2.30 (t, J=7.5 Hz, CH_2CO_2R), 1.64 (m, CH_2), 1.38 (m, CH_2). M_n(NMR)=8270; GPC: M_n=13,300, M_w= 14,000, PDI=1.05.

4.8.2. DbmPCL$_2$ (7). $DbmPCL_2$ samples were synthesized from **4** and ε-caprolactone in the presence of $Sn(Oct)_2$ according to the procedure for dbmPCL, but with a 1:20 $Sn(Oct)_2$:**4** loading. The reaction was heated at 110 °C for 9 h (i.e. ~20% conversion). Characterization data for a representative $dbmPCL_2$ sample is as follows: 0.47 g (69%; corrected for monomer conversion). ^{1}H NMR δ 17.06 (s, enol H), 7.96 (d, J=8.3 Hz, 2′,6′-ArH, 2″,6″-ArH), 6.98 (d, J=8.3 Hz, 3′,5′-ArH, 3″,5″-ArH), 6.74 (s, COCHCO), 4.46 (t, J=4.4 Hz, $PhOCH_2CH_2$), 4.25 (t, J=4.4 Hz, $PhOCH_2CH_2$), 4.06 (t, J=6.6 Hz, RCO_2CH_2), 3.65 (m, CH_2OH), 2.30 (t, J=7.5 Hz, CH_2CO_2R), 1.64 (m, CH_2), 1.38 (m, CH_2). M_n (NMR)=7800; GPC: M_n=9700, M_w=10,100, PDI=1.05.

4.9. Titration of Eu with dbm and dbmPCL

Dbm (27 mg, 0.12 mmol) was dissolved in THF (10 mL) to produce a 12 mM solution. In a separate volumetric flask, $EuCl_3$ (26 mg, 100 μmol) was dissolved in THF (50 mL) to produce a 2 mM solution. The dbm solution (0.5 mL, 6.0 μmol) and $EuCl_3$ solution (0.5 mL, 1.0 μmol) were combined with Et_3N (3 μL, 20 μmol) in a fluorescence cuvette equipped with a small stir bar, to produce a 6:1 dbm/Eu solution. After stirring for 30 min, the mixture was centrifuged to settle the fine white solids. The clarified solution was excited at 466 nm in the spectrofluorimeter, the emission was monitored over the range of 500–650 nm, and the maximum intensity at ~612 nm was noted. For a 4:1 dbm/Eu ratio, a second $EuCl_3$ stock solution was prepared (1 mM, 26 mg in 100 mL THF) and a portion of it (0.5 mL, 0.05 μmol) was added to the cuvette, which was clarified and analyzed as described above. Ligand to metal ratios of 3:1, 2:1 and 1:1 were prepared and studied in an analogous manner, maintaining a 1 mM Eu concentration throughout so that intensities at different ligand loadings could be compared. A titration of Eu with dbmPCL **6** (M_n=13,900) was performed in an analogous manner, starting with a 1 mM solution of $EuCl_3$ (1 mL, 1 μmol), solid dbmPCL (83 mg, 6 μmol), and Et_3N (3 μL, 20 μmol) in THF (0.5 mL).

4.10. Synthesis of polymeric metal complexes

4.10.1. Eu(dbmPCL)$_3$ and Eu(dbmPCL$_2$)$_3$. A representative procedure for $Eu(dbmPCL)_3$ is provided. DbmPCL **6** (M_n(NMR)=9500, 107 mg, 16 μmol), and Et_3N (10 μL, 72 μmol) were dissolved in THF (10 mL), and 0.9 mL of a stock solution of $EuCl_3$ (23 mg, 3.5 μmol) in THF (25 mL) was added. The reaction mixture turned pale yellow and a fine white precipitate formed in minutes. The mixture was stirred for 2 h, and then the solid byproduct was removed by centrifugation. The clarified polymer solution was decanted and concentrated in vacuo. The crude product was dissolved in a minimal amount of THF (~2 mL) and added slowly dropwise to stirring cold methanol (35 mL). The mixture was centrifuged, the supernatant was decanted, and the remaining solid was washed with cold methanol (10 mL) and dried in vacuo to give $Eu(dbmPCL)_3$ as a white powder: 0.100 g (100%).

4.10.2. Ni(dbmPCL)$_2$. $NiCl_2{\cdot}6H_2O$ (25.3 mg, 0.106 mmol) was dissolved in DMF (25 mL) to form a 4.3 mM stock solution, and a portion of it (0.5 mL, 2.2 μmol) was removed and added to a solution of dbmPCL (M_n=7100, 31 mg, 4.4 μmol) in THF (8 mL). Et_3N was added (25 μL, 17.9 μmol) to adjust the pH of the solution to ~7. The yellow-green solution was stirred for 2 h before further analysis.

4.10.3. Cu(dbmPCL)$_2$. $CuCl_2{\cdot}2H_2O$ (50 mg, 0.29 mmol) was dissolved in THF (50 mL) to form a 5.8 mM stock solution, and a portion of it (0.5 mL, 2.9 μmol) was removed and added to a solution of dbmPCL (M_n=8800, 50 mg, 5.7 μmol) in THF (5 mL). Et_3N was added (15 μL, 57 μmol) and the yellow-green solution was stirred for 2 h before further analysis.

4.10.4. Fe(dbmPCL)$_3$.

4.10.4.1. Kinetics study. DbmPCL (M_n=8300, 13 mg, 1.57 μmol) and Et_3N (0.2 μL, 10.53 μmol) were combined in CH_2Cl_2 (750 μL) in a sealed cuvette equipped with a small magnetic stir bar. A 2.1 μM solution of $FeCl_3{\cdot}6H_2O$ in MeOH was added (250 μL) and the solution was stirred for

1 min. Absorbance readings at λ_{max}=480 nm were taken every minute for 0.5 h, then every 2 min for a total of 1 h. An extinction coefficient was calculated as an average of data from three kinetics runs, collected after 10 min of stirring (i.e. after no change in absorbance).

4.10.4.2. Preparative scale. DbmPCL (M_n=10,000, 25 mg, 2.5 μmol) was dissolved in CH_2Cl_2 (3 mL) and Et_3N (1 μL, 7.5 μmol) was added. A 1.71 mM solution of $FeCl_3 \cdot 6H_2O$ (23 mg, 0.085 mmol) in MeOH (50 mL) was added (500 μL, 0.83 μmol), along with an additional 500 μL of MeOH, and the resulting red solution was stirred for 15 min. The reaction mixture was centrifuged to remove solid byproducts, and the clarified solution was added dropwise to cold stirring MeOH (35 mL) to precipitate the polymer product. The mixture was centrifuged, the supernatant was decanted, and the remaining solid was washed with cold methanol (10 mL) and dried in vacuo to give the Fe polymer as a red powder: 25 mg (98%). UV–vis (CH_2Cl_2): λ_{max}= 485 nm, ε=4035 M^{-1} cm^{-1}.

Acknowledgements

We thank the National Science Foundation and Dupont for support for this research. Prof. James Demas is gratefully acknowledged for the use of his fluorescence equipment, and for invaluable advice and technical assistance.

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