Controlled Ring-Opening Polymerization Initiated via Self-Complementary Hydrogen-Bonding Units

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ABSTRACT: Controlled anionic ring-opening polymerization of ϵ-caprolactone (ϵ-CL) in toluene using self-complementary quadruple hydrogen bonding array 2-ureido-4[1*H*]-pyrimidinone (UPy)-functionalized initiators with stannous(II) octanoate has been achieved to yield UPy−poly(ϵ-caprolactone) chains capable of undergoing supramolecular self-assembly. Molecular weights of these polymers varied from 2000 to 20 000 g/mol and were determined using ^{1}H NMR end-group analysis as well as gel permeation chromatography. Furthermore, using Ubbelohde solution viscometry, samples demonstrated a marked increase in viscosity-average molecular weight when measured in chloroform, indicating that the UPy chain ends are in a dimerized form when compared to polymer solutions in dimethylformamide (DMF).

Introduction

Multiple hydrogen bonding arrays play a fundamental role in nature within complex biological systems such as DNA complexation. The same principles convey well to similar systems in supramolecular chemistry. The directionality and versatility possessed by such systems have been widely used to prepare interesting, dynamic materials in both solution and the bulk.[1] Although not the strongest of supramolecular interactions, hydrogen bonds can work in parallel as part of a linear array to increase their strength, resulting in noncovalent interactions of greater stability. The quadruple hydrogen bonding unit 2-ureido-4[1*H*]-pyrimidinone (UPy) first introduced by Meijer et al. is a prime example;[2] the rich tautomerism inherent within UPy allows for both self-complementary and complementary (with a correct partner such as naphthyridines)[3−5] bonding to occur. Furthermore, UPy exhibits a strong self-association constant ($K_{dim} \geq 10^7$ M^{-1} in chloroform)[6] using a donor−donor−acceptor−acceptor (DDAA) self-complementary array.

UPy has proven effective in the preparation of telechelic polymers as well as pendant units off a polymer backbone to improve material properties.[7,8] A wide range of polymers have been functionalized with UPy end groups and exhibit low melt viscosities typical of small organic molecules.[1] Until recently,[9] telechelic polymers of this nature were prepared using a "post-polymerization" strategy. Long et al. demonstrated the coupling of complementary hydrogen bonding nucleobase pairs adenine and thymine to the chains ends of poly(DL-lactide)[10] and poly(tetrahydrofuran),[11] the former polymer being both biocompatible and biodegradable. Also demonstrated by several groups is the coupling of a UPy building block to the ends of hydroxy- or amine-terminated polymers.[12] However, these methods of polymer end-group modification have all been via a post-polymerization route, and quantitative conversion cannot be guaranteed. In order to overcome this problem and ensure that end-group functionality is present at every polymer chain end, polymers can be initiated from small molecules already bearing the desired end-group functionality as depicted in Scheme 1. Here we demonstrate the synthesis and use of a UPy-functionalized self-complementary initiator for the ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) to yield UPy-functionalized polycaprolactone (PCL). This method of polymerization ensures that each polymer chain bears a UPy group at exactly one terminus.

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Experimental Section

Unless otherwise stated, all materials were used as received.

Instrumentation. ^{1}H NMR (400 MHz) spectra was recorded using a Bruker Avance QNP 400. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ with the internal reference set to δ 7.26 ppm. ^{13}C NMR (125 MHz) spectra were recorded using a Bruker Avance Cryobrobe ATM TCI DRX 500 or a Bruker Avance 500 BB-ATM. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ and dimethyl-d_6 sulfoxide with the internal reference set to δ 77.16 ppm and δ 39.52 ppm, respectively. ATR FT-IR spectroscopy was performed using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. High-resolution mass spectra were recorded on a Bruker BioASpex II 4.7e FT-ICR mass spectrometer liquid chromatography−mass spectrometry Waters ZQ. UV−vis studies were performed on a Varian Cary 4000 UV−vis spectrophotometer. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) on two PLgel 5 μm mixed C columns, with pore sizes ranging from 10 to 10^5 Å (Polymer Laboratories), connected in series with a SPD-M20A prominence diode array detector (Shimadzu) and a differential refractometer/viscometer model 200 (Viscotek) calibrated in relation to polystyrene standards. Samples were filtered over 0.45 μm PTFE filters before injection using a 1.0 mL/min flow rate. Solution viscosities were measured using Schott-Geräte Ubbelohde microviscometers with a suspended level bulb using a PVS1 measuring device, and the microviscometers were thermostated in a PV15 water bath at 25.00 or 30.00 (±0.01) °C using a DLK10 thermostat unit (all manufactured by Lauda). Samples were filtered over stainless steel filters before measurement. Intrinsic viscosities were corrected using the appropriate Hagenbach correction factors.

Materials. Tetrahydrofuran was obtained by distillation from sodium benzophenone; toluene and triethylamine from calcium hydride. Chloroform and 1-pentanol (98+%) were dried over 4 Å molecular sieves and purchased from Fisher Scientific and Alfa Aesar, respectively. 5-Amino-1-pentanol (95+%) was purchased from Sigma-Aldrich and used as received. Stannous(II) ethylhexanoate (~95%) was purchased from Sigma-Aldrich and azeotropically distilled from toluene three times prior to use unless stated otherwise. ϵ-Caprolactone (99+%) was purchased from Sigma-Aldrich and freshly distilled from calcium hydride prior to use unless stated otherwise. 2-Amino-6-(heptan-3-yl)pyrimidin-4(1*H*)-one and UPy−imidazolide were prepared as reported by Keizer et al.[13]

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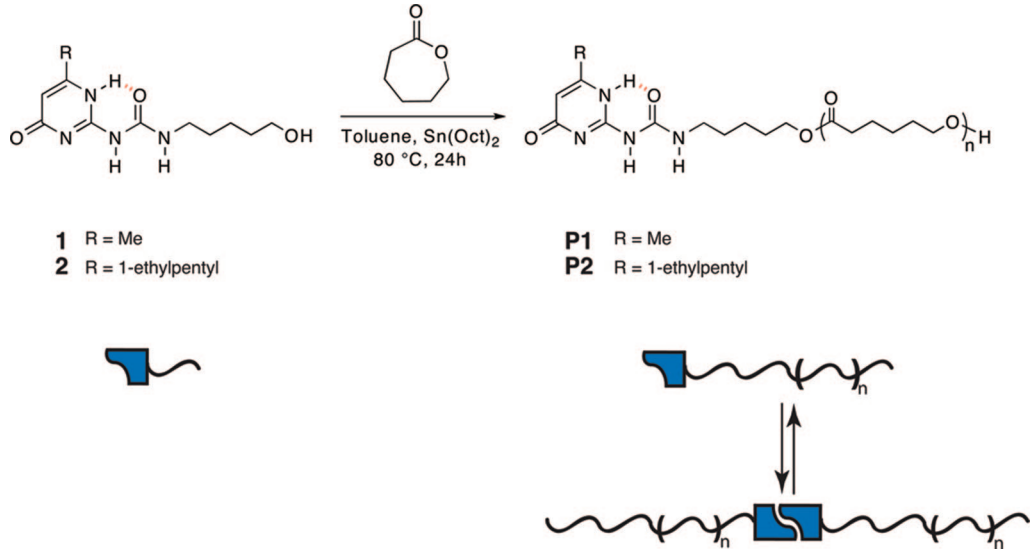
Scheme 1. Ring-Opening Polymerization of ϵ-Caprolactone with a Ureidopyrimidinone Initiator



Synthesis of 1-(5-Hydroxypentyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (1). 5-Amino-1-pentanol (1.99 g, 19.3 mmol), 6-methyl-UPy−imidazolide (2.00 g, 9.12 mmol), and $CHCl_3$ (24 mL) were stirred under a nitrogen atmosphere. Dry triethylamine (3 mL, 21.5 mmol) was added to the white suspension, and then the mixture was stirred at 50 °C for 18 h. The solution was allowed to cool to room temperature and was washed with $CHCl_3$ (200 mL) and saturated ammonium chloride solution (150 mL) at such point a white precipitate appeared in the aqueous layer. The white precipitate was filtered on a Büchner funnel, washed with water (5 × 20 mL), and dried by suction. The white solid was further dried in a 50 °C vacuum oven overnight to yield **1** (1.92 g, 83% yield). ^{1}NMR spectroscopy ($CDCl_3$, δ): 13.20 (1H, s, UPy-amine), 11.79 (1H, s, ureido α to pyrimidinone), 9.91 (1H, s, ureido α to pyrimidinone), 5.86 (1H, s, UPy-aryl), 3.67 (2H, t, methylene α to ureido, J = 5.8 Hz), 3.29 (2H, q, methylene α to alcohol, J = 5.5 Hz), 2.78 (1H, br s, alcohol), 2.23 (3H, s, 6-methyl-UPy), 1.62−1.53 (6H, m, 3 × methylene). FT-IR (ATR): ν = 3390 (alcohol), 2936 (ureido N−H), 1698 cm^{-1} (ureido carbonyl); mp 186−188 °C.

Synthesis of 1-(6-(Heptan-3-yl)-4-oxo-1,4-dihydropyrimidin-2-yl)-3-(5-hydroxypentyl)urea (2). 5-Amino-1-pentanol (0.535 g, 5.20 mmol), dry chloroform (20 mL), *N*-(6-(heptan-3-yl)-4-oxo-1,4-dihydropyrimidin-2-yl)-1*H*-imidazole-1-carboxamide (0.87 g, 2.9 mmol), and dry triethylamine (0.80 mL, 5.7 mmol) were stirred at 40 °C for 18 h under a nitrogen atmosphere. Chloroform (50 mL) was then added, and the organic phase was washed with water (50 mL) and brine (50 mL) and dried over anhydrous sodium sulfate. Chloroform (50 mL) was added to the filtered solution which was then concentrated under reduced pressure. Diethyl ether (50 mL) was then added and reduced to dryness under reduced pressure to give an off-white/yellow solid, the crude product. The crude mixture was purified by flash chromatography with a methanol/chloroform 5% v/v mobile phase. The title compound (0.73 g, 75% yield) was isolated after reducing to dryness under reduced pressure and drying in an ambient vacuum oven overnight. ^{1}H NMR spectroscopy ($CDCl_3$, δ): 13.33 (1H, s, UPy-amine), 11.86 (1H, s, ureido α to pyrimidinone), 9.98 (1H, s, ureido α to pyrimidinone), 5.83 (1H, s, UPy-aryl), 3.66 (2H, t, methylene α to ureido, J = 5.7 Hz), 3.29 (2H, q, methylene α to alcohol J = 6.3 Hz), 2.78 (1H, br s, alcohol), 2.29 (1H, m, 6-ethylpentyl-UPy-CH), 1.78−1.49 (10H, m, 6-ethylpentyl-UPy-CH_2 × 2 and 3 × methylene), 1.30 (4H, m, 6-ethylpentyl-UPy-CH_2), 0.85 (6H, m, 6-ethylpentyl-UPy-CH_3). ^{13}C NMR spectroscopy ($CDCl_3$, δ): 173.61 (pyrimidinone 6-position), 156.72 (pyrimidinone carbonyl), 155.87 (urea carbonyl), 154.92 (pyrimidinone α to urea), 106.07 (pyrimidinone 5-position), 61.53 (α to alcohol), 45.36 (6-ethylpentyl-UPy-CH), 40.05 (α to urea), 32.92 (α to urea), 31.90 (6-ethylpentyl-UPy-CH_2), 29.35 (6-ethylpentyl-UPy-CH_2), 27.76 (α to alcohol), 26.59 (α to alcohol), 22.74 (6-ethylpentyl-UPy-CH_2), 22.46 6-ethylpentyl-UPy-CH_2), 13.87 (6-ethylpentyl-UPy-CH_3), 11.74 (6-ethylpentyl-UPy-CH_3). LC-MS: (*m*/*z*) calcd 338.23; obsd 339.8 (M + H$^+$). FT-IR (ATR): ν = 3345 (alcohol), 2925 (uriedo N−H), 1693 cm^{-1} (ureido carbonyl); mp 96−98 °C.

Ring-Opening Polymerization of ϵ-Caprolactone. A Typical Synthesis of 1-(5-Hydroxypentyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea−Poly(ϵ-caprolactone) (P1). Tetrahydrofuran/chloroform (1:1 (v/v) mixture, 3.25 mL total volume), **1** (0.053 g, 0.208 mmol), and ϵ-caprolactone as is (2.23 mL, 20.1 mmol) were added to a round-bottomed flask. The mixture was thoroughly degassed three times consecutively using a freeze, pump, and thaw method. Stannous(II) octanoate (0.1 mL) was then added via syringe as is, and the mixture was stirred at 80 °C for 24 h under nitrogen. The off-white/yellow gelled mixture was dissolved in dichloromethane (10 mL) and precipitated into stirring methanol (150 mL). The white precipitate was filtered on a Büchner funnel, washed with methanol (4 × 50 mL), and dried in a 40 °C vacuum oven for 18 h to give **P1** (2.07 g, 86% yield). ^{1}H NMR spectroscopy ($CDCl_3$, δ): 5.85 (1H, end group UPy-pyrimidinone, s), 4.08 (polymer, t, J = 6.7 Hz), 3.67 (2H, end group CH_2 α to ester, t, J = 6.4 Hz), 3.30 (2H, end group CH_2 α to urea, q), 2.43 (3H, end group CH_3 α to pyrimidinone ring, s), 2.33 (polymer, t, J = 7.5 Hz), 1.62 (6H, end group CH_2, m), 1.41 (polymer, m).

A Typical Synthesis of 1-(6-(Heptan-3-yl)-4-oxo-1,4-dihydropyrimidin-2-yl)-3-(5-hydroxypentyl)urea−Poly(ϵ-caprolactone) (P2). Stannous(II) octanoate (azeotropically distilled from toluene three times, 0.2 M in toluene, 1.5 mL, 0.30 mmol), **2** (0.051 g, 0.15 mmol), toluene (3.25 mL, dried over calcium hydride for 72 h, distilled, and degassed), and finally ϵ-caprolactone (0.25 mL, 2.3 mmol, dried over calcium hydride for 72 h, distilled, and degassed using three freeze−pump−thaw cycles) were added into vials under a nitrogen atmosphere and stirred at 80 °C for 24 h. Dichloromethane (2 mL) was added to the mixture, which was then added dropwise to cold methanol (100 mL). The white precipitate

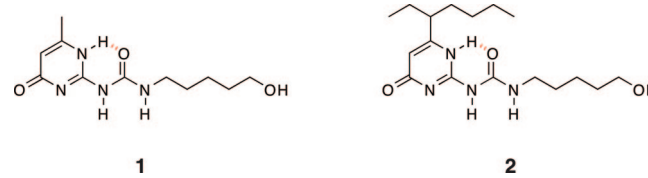


Figure 1. Ureidopyrimidinone−alcohol initiators for anionic ring-opening polymerization.

Table 1. Physical Measurements Determined for Polymer Samples P2 and P3 and Commercially Available PCL Samples

sample	[M]/[I]	M_n ($\times 10^{-3}$)[a]	M_n ($\times 10^{-3}$)[b]	M_w/M_n	[η] (cm^3 g^{-1})	M_v ($\times 10^{-3}$)[c]	M_v ($\times 10^{-3}$)[d]	% yield
P1a	71	8.36	[g]	[g]				73
P1b	48	19.7	[g]	[g]				79
P2a	15	2.05	2.68	1.34	8.55	4.31	6.58	95
P2b	25	4.33	5.48	1.50	12.5	7.23	11.9	82
P2c	36	5.93	7.49	1.55	16.1	10.2	15.1	93
P2d	42	6.73	8.71	1.51	17.8	11.7	16.4	82
P2e	57	9.13	11.1	1.55	20.8	14.5	20.4	94
P2f	69	10.6	12.1	1.56	23.1	16.7	23.5	92
P2g	179	[f]	19.1	1.35	29.1	22.9	29.1	94
P3a	50	5.19	3.59	1.17	11.9	6.76		52
P3b	100	8.65	7.98	1.36	17.7	11.6		67
PCL[e]					7.64	3.67		n/a
PCL[e]					9.89	5.23		n/a
PCL[e]					64.9	68.8		n/a

[a] Determined by ^{1}H NMR spectroscopy using UPy aryl proton, δ: 5.80 ppm and polymer methylene α to ester, δ: 4.04 ppm. [b] Determined using GPC (THF) apparatus referenced to poly styrene standards. [c] Determined using Ubbelohde viscometry (DMF, with Mark−Houwink constants of $K = 19.1 \times 10^3$ mL g^{-1} and $\alpha = 0.73$ at 30 °C,[17] Hagenbach correction applied). [d] Determined using Ubbelohde viscometry ($CHCl_3$ at 25 °C, with Mark−Houwink constants of $K = 26.5 \times 10^3$ mL g^{-1} and $\alpha = 0.79$. [e] Commercially available PCL. [f] Molecular weight too high for accurate end-group analysis via ^{1}H NMR integration. [g] Unable to characterize using GPC (THF) due to insolubility.

was filtered on a Büchner funnel, washed with cold methanol (2 × 25 mL), and dried in a 40 °C vacuum oven for 18 h to give **2** (0.28 g, 95% yield). ^{1}H NMR spectroscopy ($CDCl_3$, δ): 13.21 (1H, end group pyrimidinone-amine, s), 11.89 (1H, end group urea α to pyrimidinone ring, s), 10.23 (1H, end group urea, s), 5.80 (1H, end group pyrimidinone, s), 4.04 (polymer, t, $J = 6.6$ Hz), 3.63 (2H, end group CH_2 α to ester, t, $J = 6.6$ Hz), 3.25 (2H, end group CH_3 α to urea, q, $J = 6.9$ Hz), 2.29 (polymer, t, $J = 7.5$ Hz), 1.63 (polymer, m), 1.78−1.49 (9H, end group UPy-ethylpentyl CH_2 and CH, m), 1.37 (polymer, m), 1.30 (6H, end group UPy-pentanol linker CH_2, m), 0.85 (6H, end group UPy-ethylpentyl CH_3, m). ^{13}C NMR spectroscopy ($CDCl_3$, δ): 173.51 (polymer, carbonyl), 64.07 (polymer, α to oxygen), 62.59 (end group, α to ester), 34.20 (polymer, α to ester), 32.30 (end group, α to urea), 28.32 (polymer, α to oxygen), 25.50 (polymer, α to ester), 24.54 (polymer, α to ester), 22.44 (end group, 6-ethylpentyl-UPy-CH_2), 13.85 (end group, 6-ethylpentyl-UPy-CH_3), 11.67 (end group, 6-ethylpentyl-UPy-CH_3).

A Typical Synthesis of 1-Pentanol−Poly(ϵ-caprolactone) (P3). 1-Pentanol (0.013 mL, 0.12 mmol), tetrahydrofuran (3.7 mL), and ϵ-caprolactone (1.2 mL, 10.72 mmol) were added to a round-bottomed flask (RBF). The mixture was degassed by three freeze−pump−thaw cycles. Stannous(II) octanoate (0.1 mL, 0.3 mmol) was then added via syringe, and the mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere. Dichloromethane (10 mL) was then added to the mixture, and the solution was then added dropwise to methanol (150 mL). The white precipitate was filtered on a Büchner funnel, washed with methanol (4 × 50 mL), and dried in a 40 °C vacuum oven for 18 h to give **3** (0.46 g, 38% yield). ^{1}H NMR spectroscopy ($CDCl_3$, δ): 4.04 (polymer, t, $J = 6.5$ Hz), 3.62 (2H, end group α to ester, t, $J = 6.5$ Hz), 2.28 (polymer, t, $J = 7.7$ Hz), 1.63 (polymer, m), 1.36 (polymer, m), 1.23 (6H, end group CH_2, m), 0.88 (3H, end group CH_3, t, $J = 7.2$ Hz). ^{13}C NMR spectroscopy ($CDCl_3$, δ): 173.52 (polymer carbonyl), 64.07 (polymer, α to oxygen), 62.56 (end group, α to ester), 34.08 (polymer, α to ester), 32.28 (end group, α to ester), 28.31 (polymer, α to oxygen), 25.48 (polymer, α to ester), 24.63 (polymer, α to ester), 22.26 (end group, α to ester), 13.95 (end group, δ to ester), 11.67 (end group, ϵ to ester).

Results and Discussion

ROP Initiator Design and Synthesis. The aim of this work was to demonstrate that UPy-functionalized initiators can be used for the anionic ROP of ϵ-CL to afford controlled self-complementary supramolecular polymers bearing UPy moieties at one terminus of every polymer chain. A major difficulty encountered was the varying solubilities of UPy-initiators, **1** and **2**, as shown in Figure 1.

UPy initiator **1** was the first to be investigated for the ROP of ϵ-CL for its relative ease of synthesis. However, the solubility

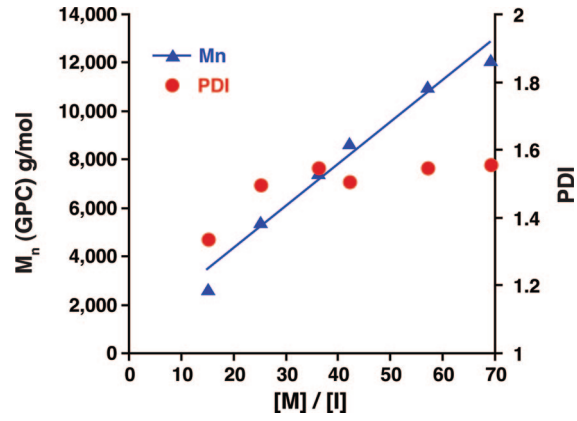


Figure 2. Number-average molecular weight control (M_n) and polydispersity (PDI) for **P2** as measured by gel permeation chromatography (tetrahydrofuran).

of UPy initiator **1**, which contains a methyl group at the 6-position on the pyrimidinone ring, is poor in organic solvents typically used for ROP such as THF and toluene.[14,15] Therefore, it was necessary to employ a mixture of $CHCl_3$ and THF in a 1:1 (v/v) ratio for solubilizing **1**. Unfortunately, while the THF:$CHCl_3$ mixture allowed for sufficient solubility, it proved to be detrimental for the controlled ROP of ϵ-CL as indicated by the modest polymerization yields and uncontrolled molecular weights in Table 1, entries **P1a** and **P1b**.

In order to increase solubility of the initiator in a single organic solvent, an initiator containing a branched alkyl chain at the 6-position on the pyrimidinone ring, **2**, was investigated and was found to greatly increase the solubility in THF and toluene. According to many literature reports, THF is commonly used as the solvent of choice for the ROP of ϵ-CL with a stannous(II) octanoate catalyst.[15,16] Unfortunately, polymerizations with **2** were difficult to control in THF. This can be attributed to both the fact that THF acts as a hydrogen-bond disruptor and that the available heteroatoms present on the UPy could then interfere with the $Sn(oct)_2$ catalyst, preventing alkoxide formation of the alcohol initiator. To overcome this problem, toluene was employed as the solvent for the ROP of ϵ-CL. It is known that UPy units exhibit a high association constant in toluene ($K_{dim} = 6 \times 10^8$ M^{-1}).[6] Hence, **2** should initiate the ROP while mainly in its dimerized form and therefore lower the chance of the UPy heteroatoms interfering with the $Sn(oct)_2$ catalyst.

Controlled ROP of ϵ-CL. A variety of **P2** polymers ranging in molecular weights from 2000 to 20 000 g/mol were prepared

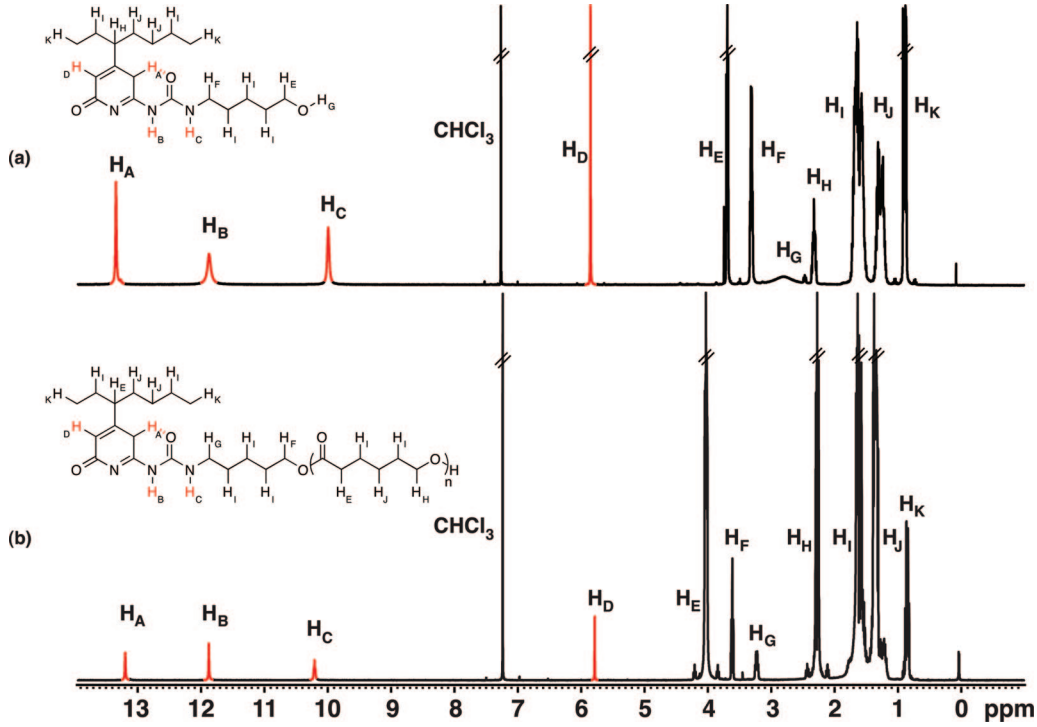


Figure 3. ^{1}H NMR spectra of (a) ureidopyrimidinone (UPy)−pentanol initiator and (b) UPy−poly(ϵ-caprolactone).

in a controlled manner, as shown in Figure 2. This was achieved by varying the ϵ-CL to **2** ratio, entries **P2a**−**P2g** in Table 1. Polymerizations were carried out in toluene[14] to ensure UPy dimerization and reached high yields after 24 h. The polydispersity indices (PDIs) were between 1.3 and 1.6; this is slightly higher than what has previously been observed for the ROP of ϵ-CL with $Sn(oct)_2$.[18] A possible explanation for the increased PDIs is the polymerization temperature of 80 °C, which leads to an increased rate of on/off UPy dimerization. While the UPy heteroatoms are certainly not interfering with the $Sn(oct)_2$ catalyst in the dimerized form, a small proportion of UPy monomer may become available over the course of the polymerization, leading to a slight increase in PDI but without substantially affecting molecular weight control. As the ROP of ϵ-CL has been studied by many groups, the $Sn(oct)_2$ catalyst concentration was kept at 0.5 mol equiv relative to the hydroxy initiator to generate the tin alkoxide, as indicated in the literature.[18] It was necessary to use freshly distilled catalyst as the commercially available $Sn(oct)_2$ contained a significant amount of water and thus an amount of octanoic acid which was detrimental for ROP. Additionally, a set of control polymers **P3** were prepared using 1-pentanol; a few of these are shown in Table 1. This initiator was chosen as the linking unit between the UPy and the initiating hydroxy functionality on **2** contained five methylenes.

^{1}H NMR Spectroscopy. A range of monomer-to-initiator ratios ([M]/[I]) were employed to investigate both the level of control and the range of molecular weights which could be achieved via this method. At lower [M]/[I] ratios, where end-group analysis is possible, the DP determined by ^{1}H NMR demonstrated a linear relationship indicating an efficient initiation process. The DP of the PCL polymers was determined by integration of proton H_D existing on the UPy end group (one per chain) against protons H_E existing on each monomer unit which has been incorporated into the PCL backbone, as depicted in Figure 3b. Proton H_D was chosen to calculate the DP as it is not subject to any intramolecular interactions with the pyrimidinone carbonyl group or intermolecular interactions with another UPy unit in its dimerized form and can therefore be integrated far more accurately.

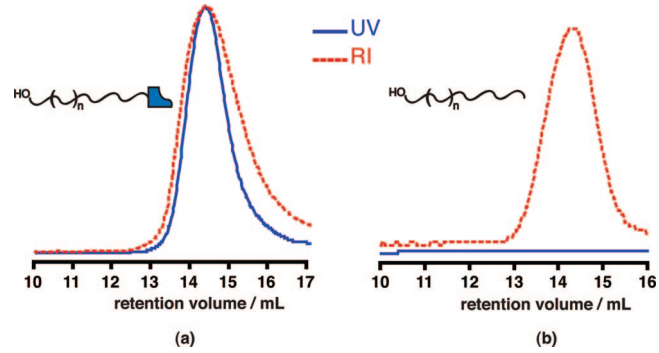


Figure 4. Gel permeation chromatography traces of (a) ureidopyrimidinone (UPy)−poly(ϵ-caprolactone) (PCL) and (b) pentanol-initiated PCL.

GPC Analysis. In order to demonstrate that each polymer chain does in fact possess the desired UPy functionality, GPC analysis with both an RI and UV/vis detector was carried out. As native PCL does not contain any UV chromophore, no substantial absorbance was anticipated for the series of control PCLs (**P3**) which had been initiated from 1-pentanol. This is the case as can be seen in Figure 4, trace b. On the other hand, when the ROP of ϵ-CL was initiated with UPy initiator **2**, a clear UV absorbance at 280 nm can be observed in the GPC trace. Moreover, the UV/vis trace overlays the unimodal elution curve measured by the RI detector, indicating that each PCL chain carries the desired UPy chain end.

Viscosity Measurements. All PCL samples were characterized by Ubbelohde solution viscometry in DMF at 30 °C using the appropriate Mark−Houwink constants obtained from the *Polymer Handbook*.[17] The resulting intrinsic viscosities, $[\eta]$, allowed for determination of the viscosity-average molecular weights (M_v) by the Mark−Houwink equation, $[\eta] = KM_v^{\alpha}$, where $K = 19.1 \times 10^3$ mL g^{-1} and $\alpha = 0.73$. As shown in

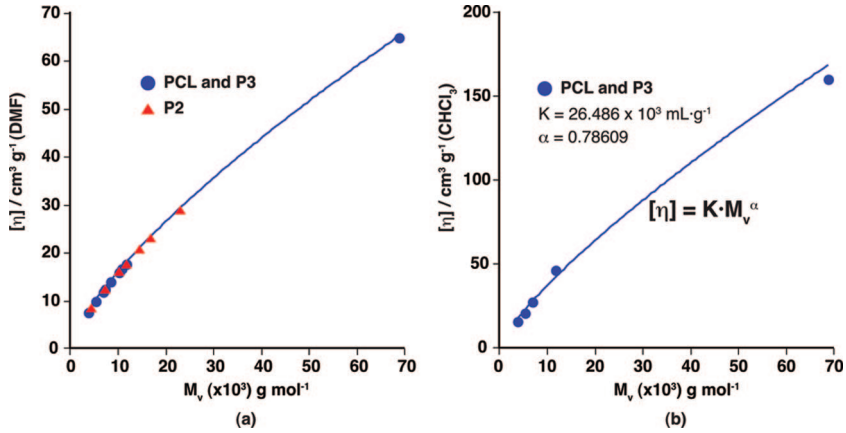


Figure 5. Ubbelohde viscometry (a) determination of poly(ϵ-caprolactone) (PCL) M_v values in DMF using Mark−Houwink constants $K = 19.1 \times 10^3$ mL g^{-1} and $\alpha = 0.73$ at 30 °C. (b) Plot of [η] measured in $CHCl_3$ at 25 °C vs previously calculated M_vs for commercially available PCLs and **P3** samples; a curve fit to a power expression yielded Mark−Houwink constants $K = 26.486 \times 10^3$ mL g^{-1} and $\alpha = 0.786\,09$.

Figure 5a, when DMF was used as solvent for the Ubbelohde experiments, all M_v values determined for PCL, including **P2**, initiated with UPy end groups, **P3**, initiated with 1-pentanol, and commercially available PCLs fall onto a single curve that could be fit with a single power expression. This suggests that each PCL chain is acting discretely and does not dimerize. Subsequently, the **P3** samples as well as the commercially available PCL samples were run in $CHCl_3$, a good solvent for UPy dimerization. Again, the intrinsic viscosities in $CHCl_3$ were obtained and plotted against the previously determined M_v values (from the DMF experiments), shown in Figure 5b. A new set of Mark−Houwink parameters were then obtained upon curve fitting with a power expression $K = 26.5 \times 10^3$ mL g^{-1} and $\alpha = 0.79$. These K and α values could then be used to acquire the M_v for the dimerized UPy−PCL (**P2**) complexes. A comparison of the M_v values for samples **P2a**−**g** run in both DMF and $CHCl_3$ are shown in Table 1. While a doubling of the molecular weight is not quite apparent, a marked increase is discernible.

Conclusion

The synthesis and use of UPy-functionalized initiators for the controlled ROP of ϵ-CL have been successfully demonstrated. It was necessary to employ toluene during the polymerizations to ensure UPy dimerization and prevent any detrimental interactions of the UPy heteroatoms with the $Sn(oct_2)$ catalyst. The molecular weights of the **P2** samples were determined using both end-group analysis via ^{1}H NMR spectrometry as well as by GPC vs PS standards. To confirm that **P2** samples bear UPy at one terminus, GPC analysis was carried out in THF, in which UPy exhibits little to no dimerization. A UV absorbance at 280 nm was observed and overlaid the unimodal elution curves measured with an RI detector while the UV signals were absent in **P3** samples. Furthermore, **P2** samples demonstrated a marked increase in viscosity-average molecular weight when measured in chloroform, indicating that the UPy chain ends are in a dimerized form when compared to DMF. These polymers have been demonstrated to be reversible in nature and are a step toward dynamic systems mirroring those observed in biological contexts.

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References and Notes

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