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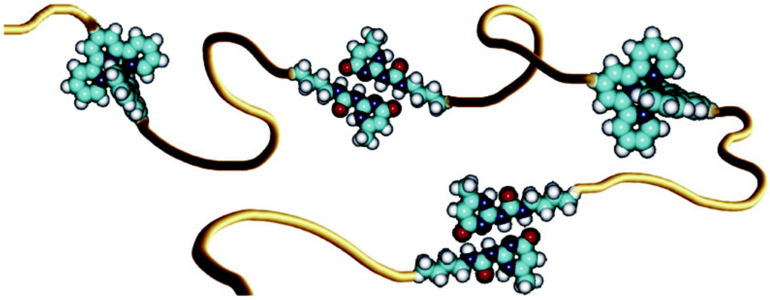

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High Molecular Weight Supramolecular Polymers Containing Both Terpyridine Metal Complexes and Ureidopyrimidinone Quadruple Hydrogen-Bonding Units in the Main Chain

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Abstract: Using a hydroxy-functionalized terpyridine as initiator, a poly(ϵ-caprolactone) containing one terpyridine endgroup was prepared by tin octanoate-catalyzed controlled ring-opening polymerization. The ω-hydroxy group of this polymer was subsequently reacted with an isocyanato−ureidopyrimidinone, resulting for the first time in polymers bearing a metal-coordinating ligand on the one and a hydrogen-bonding unit on the other chain end. Hydrogen-bonded supramolecular dimers were shown to be present in chloroform solution. The subsequent addition of iron(II) ions resulted in the formation of high molecular weight supramolecular polymers with novel properties resulting from the combination of both types of noncovalent interactions in the main chain, as could be shown using capillary viscosimetry and rheometry.

Introduction

The introduction of noncovalent interactions into the main chain of a polymer leads to reversible supramolecular materials, whose properties can be tuned by external stimuli. One popular approach toward such new materials includes strong quadruple hydrogen-bonding units of ureidopyrimidinone with a high association constant ($K_a = 6 \times 10^7$ M^{-1} in chloroform)[1,2] with the corresponding noncovalent polymers showing response to concentration, temperature, and solvent conditions.[3−6] Also, grafted architectures[7] and networks[8] were reported using hydrogen bonding.

The other type of supramolecular interactions extensively used for the construction of new polymeric architectures is metal coordination.[9] The chemistry of terpyridine metal complexes is a particularly powerful tool for the construction of supramolecular architectures[10] and polymers[11−14] since terpyridine ligands[15] are able to form directed, stable, and inert, but under certain conditions, reversible complexes with a variety of metal ions (K_a between 10^5 (Zn, Cd) and 10^{18} (Ru)).[16−18] Cyclic,[19] dendritic,[20] and chiral[21] assemblies could also be obtained utilizing the chemistry of terpyridine metal complexes. Moreover, metal ions, such as ruthenium(II),[22] osmium(II), and iridium(II), possess special photophysical properties,[10,23] making these compounds interesting for applications (e.g., in solar cells or LEDs).

Novel noncovalent polymers containing multiple "orthogonal" supramolecular interactions (supramolecular interactions of different types that do not interact with each other; the concept has already been presented on different types of polymers and

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(1) Söntjens, S. H. M.; Sijbesma, R. P.; Genderen, M. H. P. v.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487−7493.

(2) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761−6769.

(3) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J.; Hirschberg, J. H.; Lange, R. F.; Lowe, J. K.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.

(4) Hirschberg, J. H. K. K.; Beijer, F. H.; Aert, H. A. v.; Magusin, P. C. M. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **1999**, *32*, 2696−2705.

(5) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; Rijt, J. A. J. v. d.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874−878.

(6) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.

(7) Ilhan, F.; Gray, M.; Rotello, V. M. *Macromolecules* **2001**, *34*, 2597−2601.

(8) Rieth, L. R.; Eaton, R. F.; Coates, G. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2153−2156.

(9) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926.

(10) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399.

(11) Kelch, S.; Rehahn, M. *Macromolecules* **1998**, *31*, 4102−4106.

(12) Hofmeier, H.; Schmatloch, S.; Wouters, D.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 2197−2203.

(13) Schmatloch, S.; Fernandez-González, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 957−961.

(14) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043−1068.

(15) Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69−121.

(16) Andres, P. R. Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 2004.

(17) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 622−625.

(18) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341−350.

(19) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Mohapatra, P. P.; Godinez, L. A. *Chem.*−*Eur. J.* **2004**, *10*, 1493−1500.

(20) Newkome, G. R.; He, E.; Godinez, L. A.; Baker, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 9993−10006.

(21) Ziegler, M.; Monney, V.; Stoeckli-Evans, H.; von Zelewsky, A.; Sasaki, I.; Dupic, G.; Daran, J.-C.; Balavoine, G. G. A. *J. Chem. Soc., Dalton Trans.* **1999**, 667−676.

(22) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759−2767.

(23) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019.

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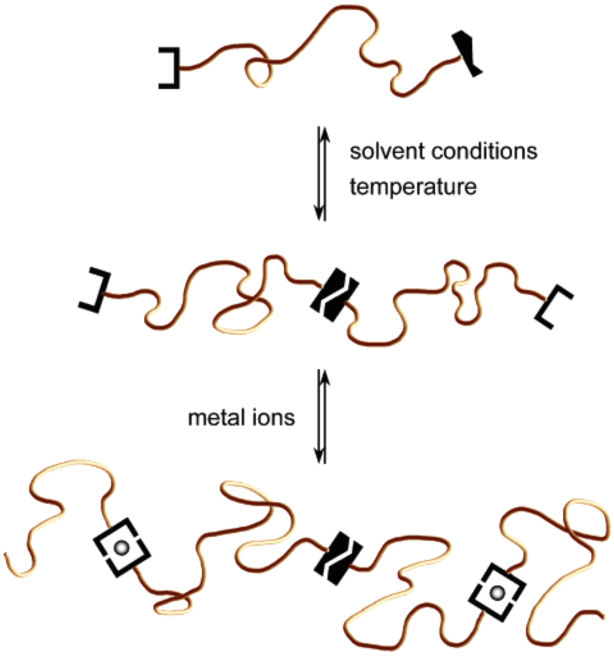

Figure 1. Schematic representation of a supramolecular polymer containing alternating terpyridine metal complexes and quadruple hydrogen bonds in the main chain.

noncovalent interactions[24]) can be prepared through combination of terpyridine complex moieties and ureidopyrimidinone units in the main chain of a synthetic polymer. Such self-organizing polymers could be tuned by various external stimuli through addressing either the metal complex moiety or the hydrogen-bonding unit. Moreover, the advantages of the hydrogen-bonded polymers (e.g., strong response to temperature or solvent conditions) can be combined with the specific properties of the metal complexes (response to strong chelating ligands or redox chemistry as well as interesting photophysical or electrochemical properties). A general structure of this type of polymer is shown in Figure 1.

It has very recently been reported that small organic molecules containing a terpyridine ligand as well as a ureidopyrimidinone moiety were able to form polymeric species involving both types of noncovalent interactions alternating in the polymer chain.[25] However, these systems contained only a short spacer (C_{10}) between the two functional groups. The corresponding supramolecular coordination polymers were characterized by a high metal complex content (high charge density), resulting in a rather low solubility in apolar solvents that promote hydrogen bonding, whereas good solvents for the complexes resulted in cleavage of the hydrogen bonds. To overcome these problems and to improve the properties of the coordination polymers, telechelic polymers with the two functional groups separated by a chain of variable length and with good solubility characteristics represent an ideal solution. It has already been demonstrated for terpyridine−iron(II) and ruthenium(II) metallopolymers that polymeric precursors lead to improved polymer properties compared to small organic telechelics.[12,26] In this contribution, we describe the synthesis and characterization of supramolecular polymers from precursors based on poly(ϵ-caprolactone), bearing both a terpyridine ligand and a ureidopyrimidinone hydrogen-bonding motif.

Results and Discussion

Controlled ring-opening polymerization of cyclic esters is a versatile route for the preparation of tailor-made functional polymers.[27] Using this approach, two different endgroups can easily be introduced.[28] In the present case, 4′-hydroxypropyloxyterpyridine, **1**, was employed as initiator for the tin octanoate-catalyzed ring-opening polymerization of ϵ-caprolactone, **2** (Scheme 1).

Poly(L-lactide)s from a terpyridine initiator have already been reported in the literature, although they were prepared using a different polymerization method.[29] The resulting polymer **3** was precipitated in methanol/water in 68% yield and purified by column chromatography (Al_2O_3) to remove water-initiated byproduct. ^1H NMR spectroscopy revealed the successful incorporation of the terpyridine moiety into the polymer (Figure 2).

GPC confirmed this observation; the polymer could be detected by the RI- as well as the UV-detector (at 290 nm, where poly(ϵ-caprolactone) does not show absorption). A number average molecular weight of 3600 was calculated from the NMR integral ratios. The endgroup obtained by this ring-opening polymerization is a hydroxy group that allows further functionalization. Utilizing the isocyanate coupling reaction, we introduced a ureidopyrimidinone group (see also ref 5). Compound **5** could be isolated in 69% yield after precipitation, followed by two preparative size-exclusion columns in dichloromethane and THF, respectively. The polymeric spacer is expected to offer sufficient solubility properties both for the uncomplexed telechelic system and for the corresponding coordination polymers. Polymer **5** showed indeed a good solubility in chloroform, and the ^1H NMR spectrum confirmed a high degree of endgroup functionalization with both the terpyridine and the ureidopyrimidinone moiety (Figure 2, middle). The signals of the hydrogen-bonded protons were found at 10.2, 11.8, and 13.1 ppm, and the resonances for the terpyridine moiety were detected between 7.3 and 8.7 ppm.

GPC analysis revealed $\bar{M}_n$ values of 2500 for **3** and 3100 for **5**, which is below the values calculated by integration of the NMR signals (a polystyrene calibration was used). Polydispersity indices of around 1.2 showed that the polymerization was indeed controlled. An iron(II) complex (**6**) and a zinc(II) complex (**7**) were obtained in 87 and 79% yield by addition of a solution of $FeCl_2$ and $(CH_3COO)_2Zn$, respectively. The polymers were isolated by precipitation after counterion exchange by addition of ammonium hexafluorophosphate. Compared to the opaque and brittle precursors **3** and **5**, the coordination polymer **6** shows film-forming properties and transparency at lower film thicknesses (Figure 3).

The coordination polymers **6** and **7** were also well-soluble in chloroform, and both the hydrogen-bonded protons and the terpyridine signals could be detected by ^1H NMR spectroscopy.

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(24) Pollino, J. M.; Stubbs, L. P.; Weck, M. *J. Am. Chem. Soc.* **2004**, *126*, 563−567.

(25) Hofmeier, H.; El-Ghayoury, A.; Schenning, A. P. H. J.; Schubert, U. S. *Chem. Commun.* **2004**, 318−319.

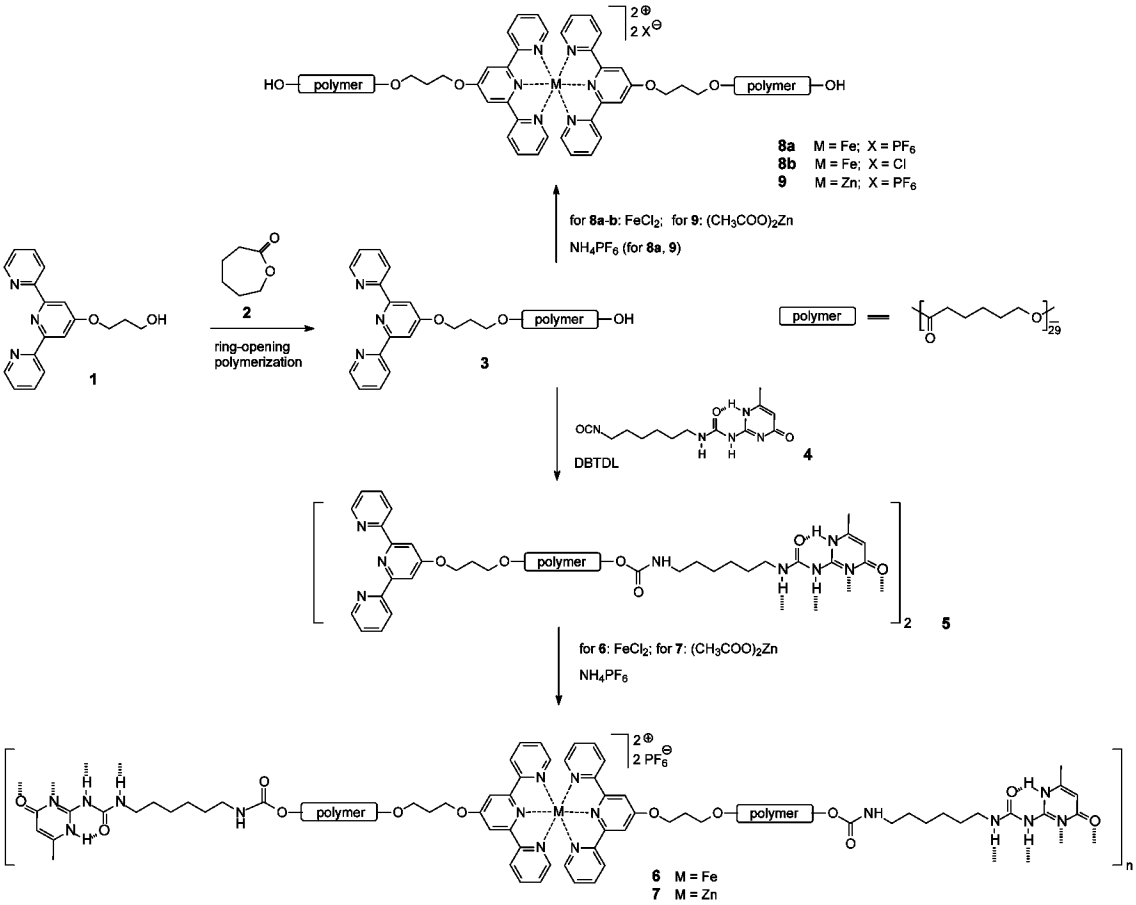
(26) Schmatloch, S.; van den Berg, A. M. J.; Alexeev, A. S.; Hofmeier, H.; Schubert, U. S. *Macromolecules* **2003**, *36*, 9943−9949.

(27) Stridsberg, K. M.; Ryner, M.; Albertsson, A.-C. *Adv. Polym. Sci.* **2001**, *157*, 41−65.

(28) Corbin, P. S.; Webb, M. P.; McAlvin, J. E.; Fraser, C. L. *Biomacromolecules* **2001**, *2*, 223−232.

(29) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, *22*, 1358−1363.

Scheme 1. Schematic Representation of the Synthesis of Polymers **3** and **5** as well as the Subsequent Complexation with Iron(II) and Zinc(II) Ions, Leading to the Supramolecular Polymers **6**−**9**



A comparison of the ^{1}H NMR spectra of **3**, **5**, **6**, and **7** is shown in Figure 2. However, the aromatic signals were relatively broad in this solvent. The resolution could be significantly improved by recording spectra in acetonitrile (insets in the spectra of **6** and **7**). However, the hydrogen bonds are not present under these conditions.

To study the effect of the hydrogen-bonding moiety on the polymer and to discern its influence from the metal complex, the iron(II) complex **8a** of polymer **3** (without ureidopyrimidinone moiety) was prepared. The aromatic as well as the aliphatic region (poly(ϵ-caprolactone)) of the ^{1}H NMR spectrum of **8a** resembles the spectrum of **6**.

Characterization of polymers **6**−**9** by UV−vis spectroscopy showed the bathochromic shift of the ligand-centered bands (from 245 to 274 nm and from 278 to 318 nm) for all polymers, the characteristic band for the zinc(II) complexes **7** and **9** (323 nm), and the metal-to-ligand charge transfer (MLCT) band of the iron(II) complexes **6** and **8a**,**b** at 558 nm, giving evidence for the successful complex formation. A UV−vis titration was performed with polymer **5** by adding stepwise a solution of $FeCl_2$ to a chloroform solution of the ligand (Figure 4, top; insert: magnification of the ligand-centered bands). The intensities of the absorptions at 318 (LC) and 558 nm (MLCT) were plotted against the equivalents of $FeCl_2$ to obtain a titration curve (Figure 4, bottom). The equivalence point (for both wavelengths) was found at 0.5 equiv of iron(II) ions, in accordance to a number average molecular weight of 3900, which corresponds to the molecular weight obtained by NMR spectroscopy.

To study the polymeric behavior of the coordination polymers **6** and **7** in solution, capillary viscosimetry was performed in chloroform, and the results were compared to those of precursors **3** and **5** (Figure 5). The ureidopyrimidinone-functionalized polymer **5** revealed a slightly higher relative viscosity than that of **3**, in accordance with the formation of hydrogen-bonded dimers. The relative viscosity of the metallo−supramolecular polymer **6** is much higher and increases strongly with concentration, providing direct evidence for the formation of high molecular weight polymers.

Compared to linear coordination polymers containing only terpyridine iron(II) or ruthenium(II) complexes (with an almost linear dependence of the relative viscosity on concentration[12,26]), an exponential behavior was found for polymer **6**, showing a strong dependence of the chain length with concentration; this behavior was also observed for hydrogen-bonded polymers.[3] At very low concentrations, the viscosity values approach the value of the model polymer **8a** (iron(II) hexafluorophosphate complex of the terpyridinyl caprolactone **3**). This can also be seen in the double-logarithmic plots: a change of slope can be observed at about 0.25 mmol/L (2.1 mg/mL). Above this value, a slope of 2.2 was found; below this concentration and for compounds **3** and **5**, a slope of 1.1 could be interpolated. The onset of the steeper slope is expected to be the critical concentration, below which mainly macrocycles can be expected (ring-chain equilibrium[30,31]). Chain-extended polymers are formed above this concentration with the amount of cyclic

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(30) Jacobsen, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18,* 1600−1606.

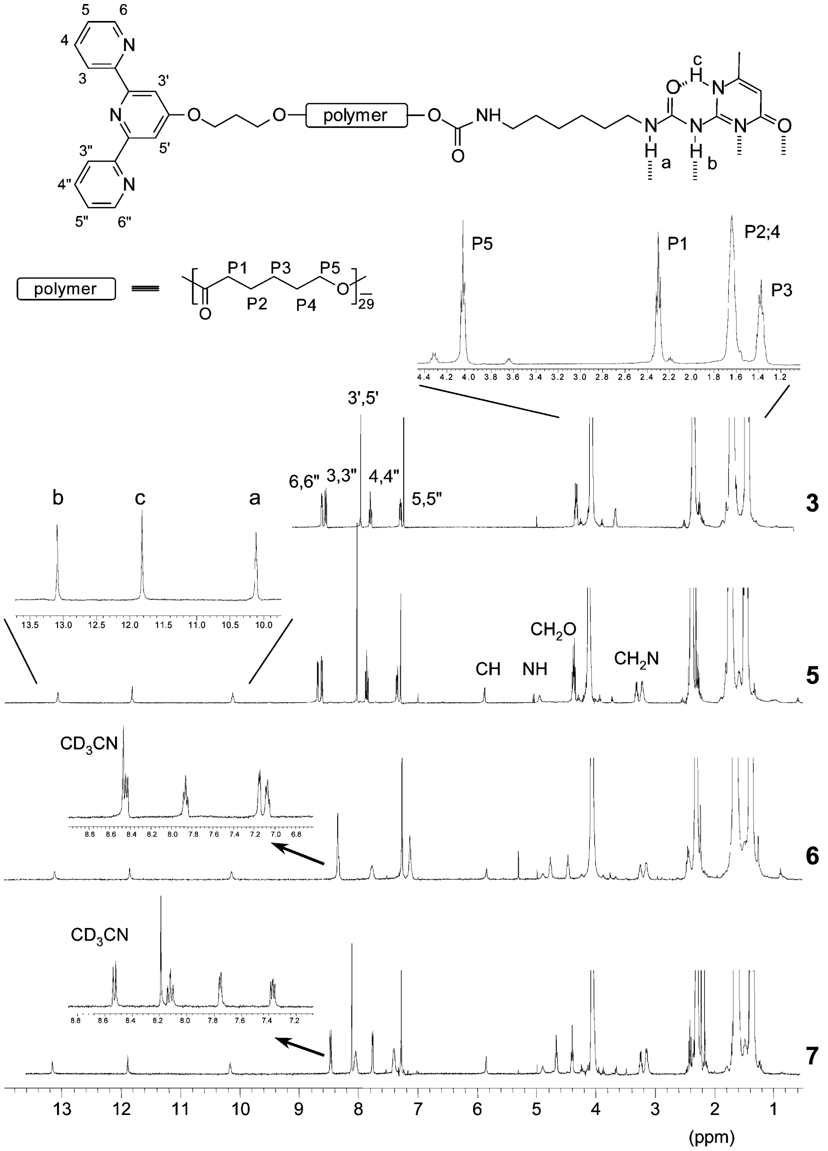

Figure 2. ^{1}H NMR spectra of **3**, **5**, **6**, and **7** (from top to bottom). Inset in spectrum for **3**: signals of poly(caprolactone). Inset in spectrum for **5**: magnification of the signals of the hydrogen-bonded protons. Inset in spectra for **6** and **7**: aromatic region in CD$_3$CN. All spectra were recorded in CDCl$_3$ unless indicated otherwise.

species being constant. A similar behavior (with slopes of 2.8−3.0) is described in the literature for bisureidopyrimidinone compounds with small alkyl spacers, where (due to strong effects of the conformation of the linker) a large influence of the spacer (length, branches) on the viscosity behavior was found.[32] For poly(siloxane)s bearing ureidopyrimidinone endgroups, a constant slope of 3.9 was found in the viscosity plot.[4] A slope of 1 (linear relationship) corresponds to noninteracting species of constant size, whereas the steeper slopes (exponential relationship) indicate the formation of reversible polymers of increasing size.[33] Theoretical calculations predict a slope of 3.5−3.7 for reversible polymers.[34] The explanation for the lower slope found here could be impurities in the material that could act as a chain stopper. In literature, a slope of 2.5 corresponds to an amount of chain stopper (monofunctional hydrogen-bonding systems) of 5%.[3] In the present case, an amount of chain stopper of around 5−7% could be assumed. Two parameters have to be considered regarding the degree of polymerization: the hydrogen-bonding unit and the terpyridine complex. For the hydrogen-bonding interaction, small amounts of polymer **3** could still be present (resulting in mono-UP-functionalized complexes that act as a chain stopper), which could be the cause for a small NMR signal at 3.6 ppm (CH$_2$OH) in compound **5**. Moreover, traces of ureidopyrimidinone starting material may also be present. For the formation of the terpyridine iron(II) complexes, unavoidable deviations of the stoichiometry of iron(II) chloride could result in a small amount of uncomplexed terpyridine moieties. Finally, Fe(III) ions (which also act as an endcapper through formation of monocomplexes) may be present in the FeCl$_2$ salt. The reversibility of the iron(II) complexes should not play a role since the association constant (K_a) of such complexes is several orders of magnitude higher than the quadruple hydrogen bonding. Actually, terpyridine metal com-

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(31) Ercolani, G.; Luigi, M.; Mencarelli, P.; Roelens, S. *J. Am. Chem. Soc.* **1993**, *115*, 3901−3908.

(32) ten Cate, A. T.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 3801−3808.

(33) ten Cate, A. T.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094−1112.

(34) Cates, M. E. *Macromolecules* **1987**, *20*, 2289−2296.

Figure 3. Photograph of a film of polymer **6**. Inset: visualization of precursor **3** (**5** has a similar appearance).

plexes have two association constants, K_1 for monocomplexes and K_2 for biscomplexes. In the case of iron(II) ions, K_2 (6×10^{13} M^{-1}) is much higher than K_1 (10^7 M^{-1}), thus virtually only biscomplexes are present.

Compared to the iron(II) polymer, **6**, the zinc(II)-containing supramolecular polymer **7** revealed lower viscosities that lie between the viscosities of **6** and the precursors. Still an exponential relationship (slope of 1.6 in the logarithmic plot) could be observed. Zinc(II) complexes of terpyridine are weaker than the corresponding iron(II) complexes[17] and undergo ligand exchange via a monocomplex. K_1 (10^6 M^{-1}) is slightly higher than K_2 in this case. Therefore, monocomplexes are present at the equivalence point, which also act as a chain stopper. Therefore, the viscosities of zinc(II) coordination polymers are significantly lower. This has also been shown for linear supramolecular polymers[26] and cross-linked systems[35] containing terpyridine zinc(II) complexes.

For a comparison to the coordination polymers (and to study the influence of the complex moiety on the viscosity), the iron(II) complex of polymer **3** (**8a**) was also investigated. The values of the relative viscosity are in the range of the ureidopyrimidinone−terpyridine-functionalized polymer **5** (in accordance with a comparable molecular weight), and a slope of 1 (no dependence on the concentration) was found in the double-logarithmic plot.

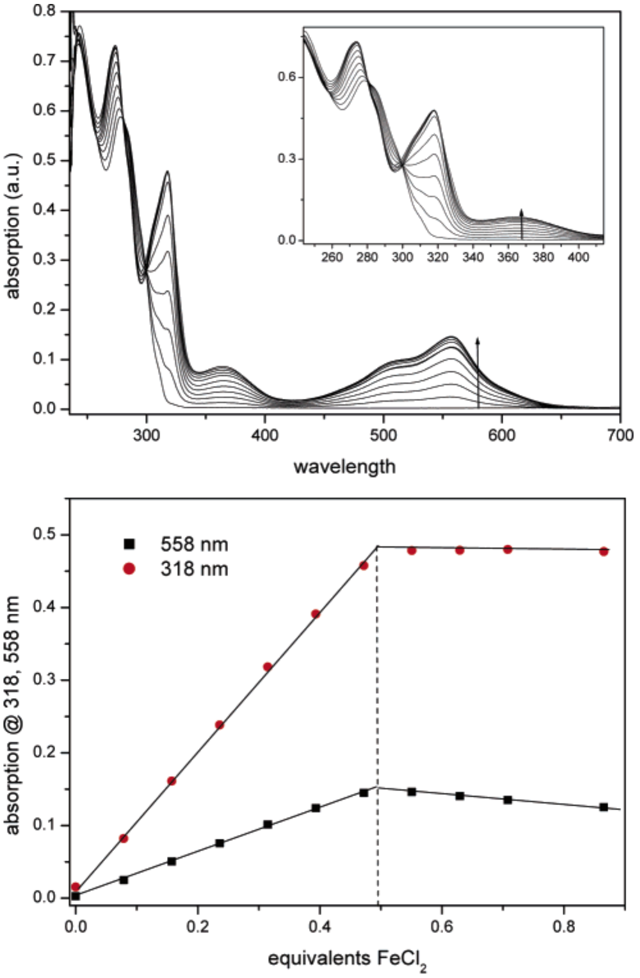

Figure 4. Top: UV−vis titration of **5** with $FeCl_2$ (in chloroform) (insert: magnification of the ligand-centered absorption bands). Bottom: Plot of the absorptions at 318 and 558 nm versus the equivalents of $FeCl_2$.

A temperature dependence of the viscosity was observed in accordance with a shortening of the lifetime of the hydrogen bonds at elevated temperatures (Figure 6). The equilibrium between the open and the hydrogen-bonded form is shifted to the open form, thus the degree of polymerization is decreased.[36]

The rheological properties of the poly(ϵ-caprolactone) systems were examined in bulk using a rheometer with a parallel plate setup within the linear viscoelastic regime (Figure 7, top). A drop in the melt viscosities was found at around 45 °C for precursors **3** and **5**, in accordance with the low molecular weights of these compounds and corresponding to the melting points determined by DSC. Coordination polymer **6**, however, revealed significantly higher viscosities above the melting point, providing evidence for the existence of high molecular weight entities.

In addition to the sudden viscosity decrease around the melting point of the poly(ϵ-caprolactone) backbone from 60 to 66 °C (this value is closer to the value obtained from the first DSC heating run; however, the rheometry was performed at 5 °C/min, allowing a better recrystallization), a second, more gradual decrease is found between 90 and 120 °C. Furthermore, a continuous decreasing slope was observed that could be attributed to an increasing exchange rate of the hydrogen

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(35) Hofmeier, H.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1391−1397.

(36) Folmer, B. J. B., Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 2000.

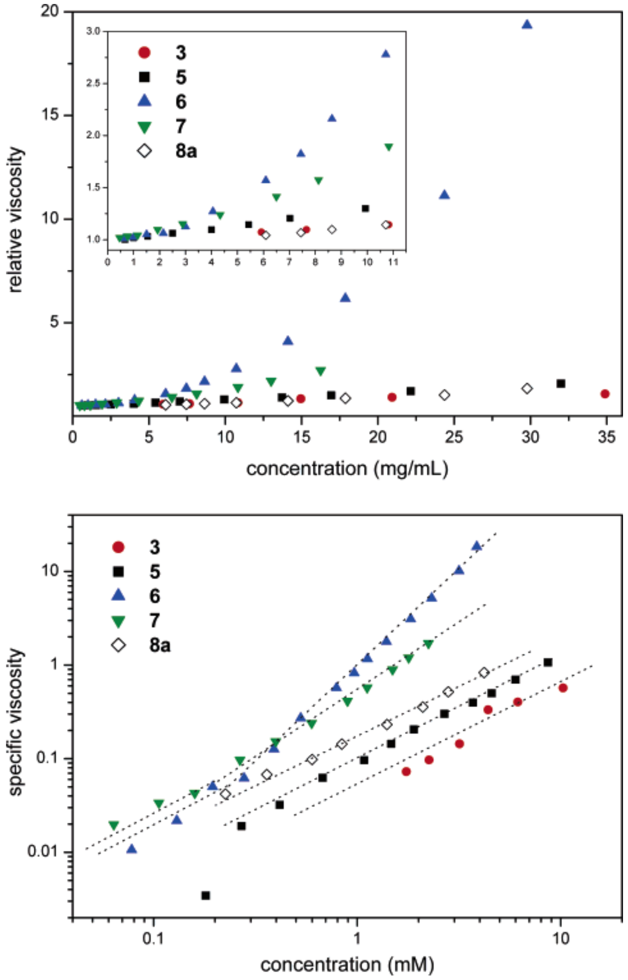

Figure 5. Top: Relative viscosities of **3**, **5**, **6**, **7**, and **8a** at different concentrations (Ubbelohde viscosimeter, chloroform). Bottom: double-logarithmic plot of the specific viscosities of **3**, **5**, **6**, **7**, and **8a**.

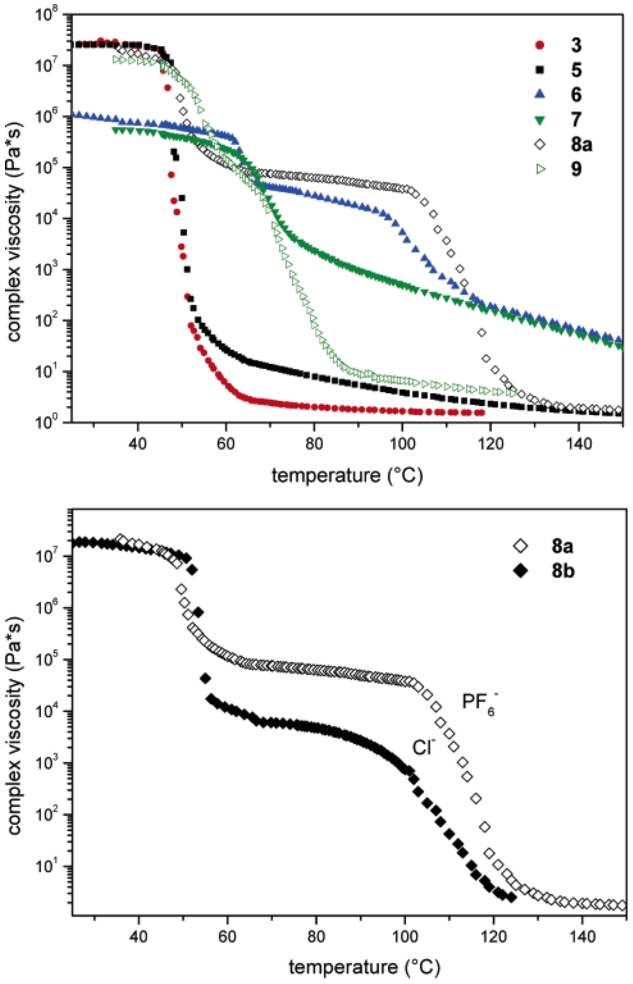

Figure 7. Top: Complex viscosities of **3**, **5**, and **6**−**9**, determined by rheometry. Bottom: Influence of the counterions on the rheological behavior, curves of **9a** and **9b**.

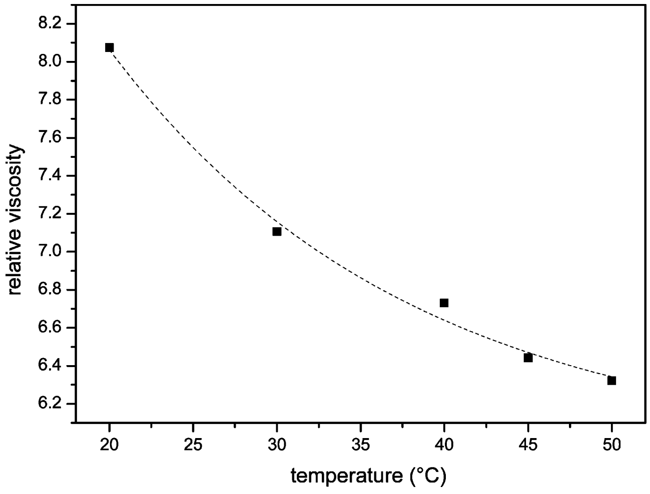

Figure 6. Relative viscosity of **6** (4.31 M) at different temperatures (in chloroform).

bonding due to a decreasing lifetime of the bond with increasing temperature. An explanation of the second step could be a weakening of the coordinative bonds in the metal complex moieties above ∼90 °C. This would result in a dynamic exchange of the ligands, resulting in a decreasing melt viscosity. To verify this assumption, model compound **8a** was also investigated. At room temperature, the material revealed the same melt viscosity as that in compounds **3** and **5**. After a decrease of the viscosity during the melting transition around 46 °C, a second step was observed between 102 and 127 °C, which lies in the same range as that for coordination polymer **6**, indicating that the metal complexes are indeed responsible for this transition. Eventually, the viscosity reached the same low values as those for **3** and **5**. However, despite the low molecular weight (of the bispoly(ϵ-caprolactone) terpyridine iron(II) unit), a plateau of high viscosity (comparable to that of **6**) was found between the steps, which could be explained by electrostatic interactions caused by the charges, resulting in aggregates of high molecular weight.

The corresponding zinc(II) complexes, **7** (with ureido-pyrimidinone) and **9** (model complex), were also investigated. In the case of **7**, only one step around 70−80 °C was found, but the viscosity values at low and at high temperatures are in the same range as those for the iron(II) polymer, **6**. For the model system **9**, two transitions at 50−60 (poly(ϵ-caprolactone) melting) and 70−80 °C were found. These findings can be explained by the fact that zinc(II) complexes are weaker and exchange ligands at lower temperatures (compared to the iron(II) complexes) via monocomplexes. Therefore, the formation of aggregates of high molecular weight is inhibited. A likely explanation for this behavior of terpyridine−metal complexes is that the K_2 constant (and also K_1) is temperature-dependent;

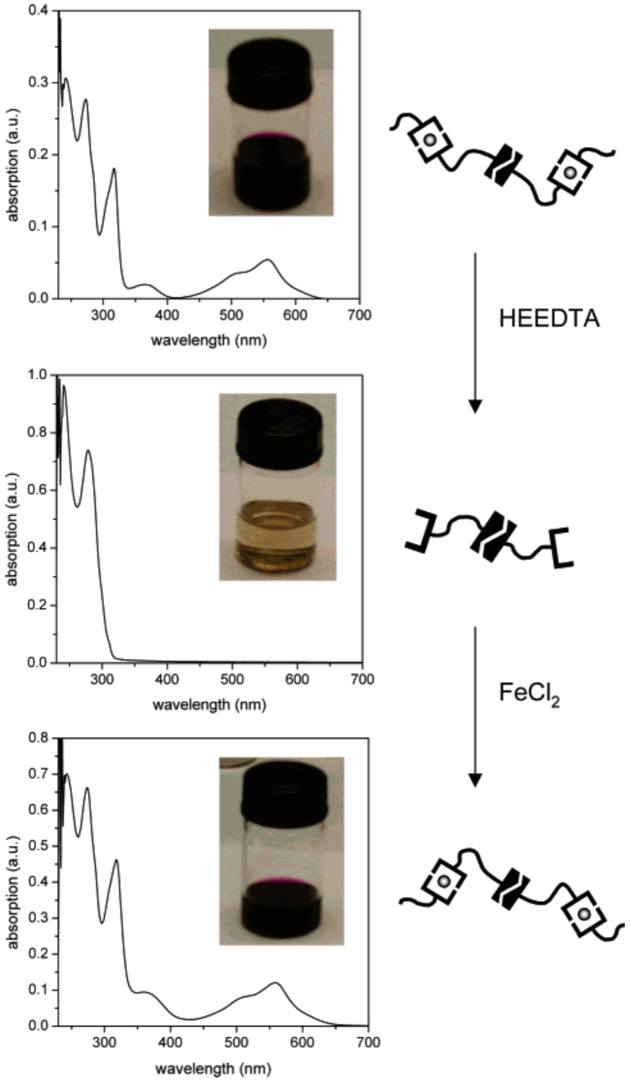

Figure 8. Decomplexation of polymer **6** with the competing ligand HEEDTA, followed by recomplexation with iron(II) chloride: schematic representation (top), UV−vis spectra (bottom), and photographic images of the solution (insets in UV−vis spectra).

it is lowered with increasing temperature, eventually leading to dynamic ligand exchange.

Finally, the effect of the counterions was investigated; the results of **8b** (Cl^- counterions) were compared to those of **8a** (PF_6^- counterions) (Figure 7, bottom). The first transition (melting of poly(ϵ-caprolactone)) of **8b** occurs about 3 K higher than in the case of **8a**, suggesting a slightly different crystallization due to the smaller Cl^- counterions. This was confirmed by DSC, where a higher ΔH was found for **8b**. The following plateau was lower than that for **8a**, and the second transition was observed earlier (around 90 °C), which can be also explained by the smaller Cl^- ions. The ion pairs between the chloride ion and the metal center are tighter, as in the case of the hexafluorophosphate ions. As a result, the chlorides are spatially closer to the cations, whereas the large PF_6^- ions have a better ability to form intermolecular interactions (physical cross-linking), resulting in a higher viscosity. In addition, the chloride ions are characterized by a higher charge density. Therefore, they could act as competing ligand, and the reversible opening of the complexes could occur at lower temperatures. Besides a dynamic ligand exchange, a complete dissociation of the complexes could also be discussed for the heating process; a film, applied on a microscopic slide, was investigated on an optical microscope equipped with a heating stage. No fading of the purple color could be observed up to 210 °C. Therefore, no complete dissociation of the coordinative bonds can be expected under the discussed conditions.

These results clearly demonstrate the possibility to drastically change the mechanical properties of a well-known classical polymer (poly(ϵ-caprolactone)) by the incorporation of different supramolecular moieties. Moreover, the tunability of the materials by the use of different metal ions and counterions was shown.

The reversibility of the complex formation was investigated by applying HEEDTA (hydroxyethyl ethylenediaminetriacetic acid). HEEDTA represents a very strong chelating ligand for transition-metal ions with the ability to open terpyridine metal complexes through ligand exchange.[13] It has also been shown that iron(II) complexes, forming cross-links of terpyridine-functionalized copolymers, could be opened again.[35] The addition of an aqueous solution of HEEDTA to a $CHCl_3$/MeOH solution of **6** resulted in a decoloration of the solution of the coordination polymer within 2 min, a result of the decomplexation of the terpyridine moieties (Figure 8).

UV−vis spectroscopy revealed the bands of the free terpyridine. After extraction with water, the addition of iron(II) chloride to the organic phase led to the reformation of the metal complex, which was indicated by the immediate reappearance of the purple color and confirmed by UV−vis spectroscopy. However, in the decomplexation process, a rupture of the hydrogen bonds can be expected, mainly due to the solvent conditions (water and methanol). Nevertheless, the HEEDTA could be extracted with water and the uncomplexed polymer transferred to pure chloroform phase, allowing a re-establishment of the hydrogen bonds. This could be confirmed by ^1H NMR spectroscopy.

Conclusions and Outlook

The preparation of a series of polymers bearing a terpyridine ligand on the one and a ureidopyrimidinone unit on the other end (separated by a poly(ϵ-caprolactone) spacer) is described for the first time. These polymers were prepared by controlled ring-opening polymerization, and polymers with a low polydispersity index were obtained. Subsequently, the ω-hydroxy group was functionalized with a ureidopyrimidinone moiety. Iron(II) as well as zinc(II) complexes were prepared, leading to the first extended supramolecular polymers containing alternating metal coordination and quadruple hydrogen-bonding interactions. The resulting polymers were well-soluble in chloroform and were characterized in detail. The formation of high molecular weight species was concluded from viscosity measurements. Rheometry revealed improved material properties compared to those of the precursors and a strong influence of the metal ions as well as the counterions to the properties in bulk. Through addition of a competing ligand, a reversible opening of the metal complex could be achieved, opening a pathway toward new “switchable” functional polymers. Further studies will include more detailed investigations, including the employment of polymeric spacers of different composition and chain length, and more detailed studies of the materials’ properties.

Experimental Section

Materials and Instrumentation. Basic chemicals were obtained from Sigma-Aldrich. Compound **1**[37] was synthesized from 4′-chloro-2,2′:6′,2′′-terpyridine,[38] and 6-[3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]hexyliscyanate **4** was prepared according to ref 5. NMR spectra were measured on a Varian Mercury 400 NMR spectrometer. The chemical shifts were calibrated to the residual solvent peaks. UV−vis spectra were recorded on a Perkin-Elmer Lamda-45 (1 cm cuvettes). Solution viscosimetry was performed at 20 °C on a Schott AVS 350 viscosimetry system using Ubbelohde viscosimeters with a capillary diameter of 0.4 mm and chloroform as solvent. GPC was performed on a Waters GPC, equipped with a 1515 pump and a 717plus autosampler, using a Waters StyraGel HT4 column at 50 °C and DMF containing 5 mM NH$_4$PF$_6$ as eluent. A polystyrene calibration was applied. Differential scanning calorimetry (DSC) investigations were performed on a Perkin-Elmer Pyris-1 DSC system with a heating rate of 40 K/min (glass transitions, T_g) and 10 K/min (melting points, T_m, and crystallization points, T_c). Rheological experiments were carried out on a Paar Physica UDS 200 rheometer. A parallel plate with a diameter of 8 mm was used, and the measurements were performed within the linear viscoelastic regime at an oscillating frequency of 1 Hz and a strain amplitude of 1%. Temperature scans were carried out from 30 to 120 °C (**3**) or 150 °C (**6** and **7**) with a heating rate of 5 °C/min.

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-ω-hydroxypoly(ε-caprolactone), 3. Two hundred milligrams (0.65 mmol) of 4′-hydroxypropyloxy-2,2′:6′,2′′-terpyridine **1**, 1.49 g (13.07 mmol, 1.2 mL) of ε-caprolactone **2**, and 2 drops of Sn(Oct)$_2$ were added into a sealed polymerization tube, which was dried and flushed with argon prior to the experiment. The mixture was stirred for 3 h at 110 °C. Subsequently, the reaction mixture was dissolved in THF and precipitated into 50 mL of a 60:40 mixture of methanol/water. The dried raw product was purified through filtration (alox column, chloroform containing 5% methanol) to remove any water-initiated byproduct, yielding 1.16 g (68%) of **3** as a white powder. UV−vis (CHCl$_3$): λ_{max} (ϵ) = 245 (23 500), 279 (23 600) nm (L mol^{-1} cm^{-1}). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.37 (m, 62 H, CH$_2$ (poly(caprolactone))), 1.64 (m, 122 H, CH$_2$ (poly(caprolactone))), 2.19 (t, 2 H, J = 6.22 Hz, CH$_2$ (propyl)), 2.30 (t, 56 H, J = 7.32 Hz, CH$_2$CO (poly(caprolactone))), 3.64 (m, 2 H, CH$_2$OH (poly(caprolactone))), 4.05 (t, 40 H, J = 6.59 Hz, OCH$_2$ (poly(caprolactone))), 4.30 (t, 2 H, J = 6.59 Hz, OCH$_2$), 4.32 (t, 2 H, J = 6.59 Hz, OCH$_2$), 7.33 (ddd, 2 H, J = 8.06, 8.06, 1.47 Hz, H$_{5,5''}$), 7.84 (ddd, 2 H, J = 8.06, 8.06. 2.20 Hz, H$_{4,4''}$), 8.01 (s, 2 H, H$_{3',5'}$), 8.61 (d, 2 H, J = 8.06 Hz, H$_{3,3''}$), 8.68 (d, 2 H, J = 4.89 Hz, H$_{6,6''}$). $\bar{M}_n$ (NMR) = 3600 g/mol. DSC: T_g = −43 °C (second heating run, 40 °C/min), T_m = 44, 51 °C (third heating run, 10 °C/min), T_c = 20 °C (third cooling run, 10 °C/min). MALDI-TOF: $\bar{M}_n$ = 3310, PDI = 1.04. GPC (DMF containing 5 mM NH$_4$PF$_6$, RI-detector): $\bar{M}_n$ = 2500, PDI = 1.21.

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-ω-{6-[3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]hexyl}carbamic Acid Poly-(ε-caprolactone)yl Ester, 5. Seven hundred milligrams (0.20 mmol) of **3**, 80 mg (0.26 mmol) of **4**, and 10 μL of dibutyltin dilaureate (DBTL) were dissolved in 20 mL of chloroform. The mixture was refluxed for 16 h, followed by the addition of another 70 mg (0.23 mmol) of **4** and further refluxing (12 h) to ensure complete reaction. Subsequently, the product was precipitated into a 60:40 mixture of methanol/water, followed by two BioBeads SX-1 columns in dichloromethane and THF, respectively, and finally precipitated into methanol containing 10% of water. Yield: 613 mg (69%). UV−vis (CHCl$_3$): λ_{max} (ϵ) = 242 (28 700), 279 (23 100) nm (L mol^{-1} cm^{-1}). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.37 (m, 64 H, CH$_2$ (poly(caprolactone))), 1.22 (m, 4 H, CH$_2$), 1.37 (m, 64 H, CH$_2$ (poly(caprolactone))), 1.48 (m, 4 H, CH$_2$), 1.63 (m, 118 H, CH$_2$ (poly(caprolactone))), 2.18 (t, 2 H, J = 5.86 Hz, CH$_2$ (propyl)), 2.29 (t, 56 H, J = 7.82 Hz, CH$_2$CO (poly(caprolactone))), 3.13 (m, 2 H, NHCH$_2$), 3.23 (m, 2 H, NHCH$_2$), 4.05 (t, 56 H, J = 6.84 Hz, OCH$_2$ (poly(caprolactone))), 4.29 (t, 2 H, J = 6.59 Hz, OCH$_2$), 4.31 (t, 2 H, J = 6.59 Hz, OCH$_2$), 5.83 (s, 1 H, CH), 7.32 (dd, 2 H, J = 7.82, 4.89 Hz, H$_{5,5''}$), 7.84 (ddd, 2 H, J = 7.82, 7.82, 1.96 Hz, H$_{4,4''}$), 8.00 (s, 2 H, H$_{3',5'}$), 8.61 (d, 2 H, J = 7.82 Hz, H$_{3,3''}$), 8.67 (d, 2 H, J = 4.89 Hz, H$_{6,6''}$), 10.12 (s, 1 H, NH), 11.84 (s, 1 H, NH), 13.11 (s, 1 H, NH). $\bar{M}_n$ (NMR) = 3900 g/mol. DSC: T_g = −37 °C (second heating run, 40 °C/min), T_m = 44, 52 °C (third heating run, 10 °C/min), T_c = 3 °C (third cooling run, 10 °C/min). GPC (DMF containing 5 mM NH$_4$PF$_6$, RI-detector): $\bar{M}_n$ = 3100, PDI = 1.23. MALDI-TOF: $\bar{M}_n$ = 3340, PDI = 1.04.

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-ω-{6-[3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]hexyl}carbamic Acid Poly-(ε-caprolactone)yl Ester Iron(II) Hexafluorophosphate, 6. To a solution of **8** (144 mg, 0.041 mmol) in chloroform (8 mL) was added a methanolic solution of FeCl$_2$ (2.7 mg, 0.021 mmol). Product **6** was isolated after adding 100 mg of ammonium hexafluorophosphate and diethyl ether (20 mL) as a purple precipitate in 136 mg (87%) yield. UV−vis (CHCl$_3$): λ_{max} (ϵ) = 241 (68 500), 273 (61 900), 317 (40 500), 363 (4400), 556 (12 100) nm (L mol^{-1} cm^{-1}). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.38 (m, 58 H, CH$_2$ (poly(caprolactone))), 1.64 (m, 116 H, CH$_2$ (poly(caprolactone))), 2.23 (t, 2 H, J = 6.22 Hz, CH$_2$ (propyl)), 2.30 (t, 54 H, J = 7.32 Hz, CH$_2$CO (poly(caprolactone))), 2.45 (m, 2 H, CH$_2$OCON (poly(caprolactone))), 3.14 (m, 2 H, NHCH$_2$), 3.24 (m, 2 H, NHCH$_2$), 4.05 (t, 54 H, J = 6.59 Hz, OCH$_2$ (poly(caprolactone))), 4.46 (t, 2 H, J = 5.86 Hz, OCH$_2$), 4.76 (t, 2 H, J = 5.86 Hz, OCH$_2$), 4.89 (s, 1 H, NH), 5.83 (s, 1 H, CH), 7.13 (br, 4 H, H$_{5,5''}$, H$_{6,6''}$), 7.77 (br, 2 H, H$_{4,4''}$), 8.34 (br, 4 H, H$_{3,3''}$, H$_{3',5'}$), 10.13 (s, 1 H, NH), 11.85 (s, 1 H, NH), 13.12 (s, 1 H, NH). ^{1}H NMR (CD$_3$CN): δ (ppm) = 7.07 (dd, 2 H, J = 7.82, 4.89 Hz, H$_{5,5''}$), 7.15 (d, 2 H, J = 4.89 Hz, H$_{6,6''}$), 7.86 (dd, 2 H, J = 7.82, 7.82 Hz, H$_{4,4''}$), 8.43 (d, 2 H, J = 7.82 Hz, H$_{3,3''}$), 8.46 (s, 2 H, H$_{3',5'}$). DSC: T_g = −60 °C (second heating run, 40 °C/min), T_m = 43 °C (third heating run, 10 °C/min).

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-ω-{6-[3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido]hexyl}carbamic Acid Poly-(ε-caprolactone)yl Ester Zinc(II) Hexafluorophosphate, 7. To a solution of **5** (77 mg, 0.022 mmol) in chloroform (8 mL) was added a methanolic solution of (CH$_3$COO)$_2$Zn hydrate (2.45 mg, 0.011 mmol). Product **7** was isolated after adding 60 mg of ammonium hexafluorophosphate and diethyl ether (20 mL) as a white precipitate in 79 mg (97%) yield. UV−vis (CHCl$_3$): λ_{max} (ϵ) = 244 (69 000), 274 (47 900), 311 (29 600), 323 (33 300) nm (L mol^{-1} cm^{-1}). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.37 (m, 54 H, CH$_2$ (poly(caprolactone))), 1.64 (m, 108 H, CH$_2$ (poly(caprolactone))), 2.22 (m, 2 H, CH$_2$ (propyl)), 2.16 (t, 50 H, J = 7.82 Hz, CH$_2$CO (poly(caprolactone))), 2.41 (t, 2 H, J = 6.84 Hz, CH$_2$OCON (poly(caprolactone))), 43.14 (m, 2 H, NHCH$_2$), 3.24 (m, 2 H, NHCH$_2$), 4.05 (t, 50 H, J = 6.84 Hz, OCH$_2$ (poly(caprolactone))), 4.39 (t, 2 H, J = 5.86 Hz, OCH$_2$), 4.65 (t, 2 H, J = 5.86 Hz, OCH$_2$), 4.88 (s, 1 H, NH), 5.83 (s, 1 H, CH), 7.38 (br, 2 H, H$_{5,5''}$), 7.77 (d, 2 H, J = 3.91 Hz, H$_{6,6''}$), 8.02 (br, 2 H, H$_{4,4''}$), 8.09 (s, 4 H, H$_{3',5'}$), 8.44 (d, 2 H, J = 7.89 Hz, H$_{3,3''}$), 10.13 (s, 1 H, NH), 11.85 (s, 1 H, NH), 13.12 (s, 1 H, NH). ^{1}H NMR (CD$_3$CN): δ (ppm) = 7.37 (dd, 2 H, J = 7.82, 4.89 Hz, H$_{5,5''}$), 7.76 (d, 2 H, J = 4.89 Hz, H$_{6,6''}$), 8.12 (dd, 2 H, J = 7.82, 7.82 Hz, H$_{4,4''}$), 8.19 (s, 2 H, H$_{3',5'}$), 8.53 (d, 2 H, J = 7.82 Hz, H$_{3,3''}$). DSC: T_g = −55 °C (second heating run, 40 °C/min), T_m = 51 °C (third heating run, 10 °C/min).

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-ω-hydroxypoly(ε-caprolactone) Iron(II) Hexafluorophosphate, 8a. To a solution of **3** (125 mg, 0.04 mmol) in chloroform (10 mL) was added a methanolic solution of FeCl$_2$ (2.6 mg, 0.02 mmol), and the mixture was stirred for 30 min. Product **8a** was isolated after addition of 100

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[37] Schubert, U. S.; Eschbaumer, C.; Hien, O.; Andres, P. R. *Tetrahedron Lett.* **2001**, *42*, 4705−4707.

[38] Schmatloch, S.; Precup, A. A.; Schubert, U. S. *Des. Monom. Polym.* **2002**, *5*, 211−221.

mg of ammonium hexafluorophosphate in 5 mL of methanol/water (1:1) and diethyl ether (20 mL) as a purple precipitate in 125 mg (82%) yield. UV−vis ($CHCl_3$): λ_{max} (ϵ) = 246 (66 800), 273 (78 000), 317 (58 800), 363 (4900), 556 (16 800) nm (L mol^{-1} cm^{-1}). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 1.35 (m, 56 H, CH_2 (poly(caprolactone))), 1.59 (m, 108 H, CH_2 (poly(caprolactone))), 2.12 (m, 2 H, CH_2 (propyl)), 2.27 (t, 54 H, J = 7.32 Hz, CH_2CO (poly(caprolactone))), 3.42 (m, 2 H, C*H*$_2$OH (poly(caprolactone))), 4.01 (t, 50 H, J = 6.59 Hz, OCH_2 (poly(caprolactone))), 4.42 (t, 2 H, J = 5.86 Hz, OCH_2 (propyl)), 4.68 (t, 2 H, J = 5.86 Hz, OCH_2 (propyl)), 7.07 (dd, 2 H, J = 7.82, 4.89 Hz, $H_{5,5''}$), 7.15 (d, 2 H, J = 4.89 Hz, $H_{6,6''}$), 7.86 (dd, 2 H, J = 7.82, 7.82 Hz, $H_{4,4''}$), 8.43 (d, 2 H, J = 7.82 Hz, $H_{3,3''}$), 8.46 (s, 2 H, $H_{3',5'}$). DSC: T_g = −57 °C (weak, second heating run, 40 °C/min), T_m = 49 °C (third heating run, 10 °C/min).

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-*ω*-hydroxypoly(*ϵ*-caprolactone) Iron(II) Chloride, 8b. To a solution of **3** (189 mg, 0.06 mmol) in chloroform (10 mL) was added a methanolic solution of $FeCl_2$ (4 mg, 0.03 mmol), and the mixture was stirred for 30 min. Product **8b** was isolated by precipitation through addition of diethyl ether (50 mL) as a purple powder in 179 mg (93%) yield. UV−vis ($CHCl_3$): λ_{max} (ϵ) = 246 (46 200), 275 (63 800), 318 (45 000), 364 (6000), 557 (14 900) nm (L mol^{-1} cm^{-1}). ^1H NMR (400 MHz, CD_3Cl): δ (ppm) = 1.36 (br, 58 H, CH_2 (poly(caprolactone))), 1.62 (br, 112 H, CH_2 (poly(caprolactone))), 1.92 (br, 2 H, CH_2 (propyl)), 2.28 (br, 56 H, CH_2CO (poly(caprolactone))), 3.61 (br, 2 H, C*H*$_2$OH (poly(caprolactone))), 4.03 (br, 50 H, OCH_2 (poly(caprolactone))), 4.45 (br, 2 H, OCH_2 (propyl)), 5.11 (br, 2 H, OCH_2 (propyl)), 7.03 (br, 2 H, $H_{5,5''}$), 7.08 (br, 2 H, $H_{6,6''}$), 7.87 (br, 2 H, $H_{4,4''}$), 9.12 (br, 4 H, $H_{3,3''}$, $H_{3',5'}$). DSC: T_m = 49 °C (third heating run, 10 °C/min).

α-(2,2′:6′,2′′-Terpyridin-4′-yloxypropyloxy)-*ω*-hydroxypoly(*ϵ*-caprolactone) Zinc(II) Hexafluorophosphate, 9. To a solution of **3** (182 mg, 0.06 mmol) in chloroform (10 mL) was added a methanolic solution of $(CH_3COO)_2Zn$ (6.6 mg, 0.03 mmol), and the mixture was stirred for 30 min. Product **9** was isolated after addition of 100 mg of ammonium hexafluorophosphate in 5 mL of methanol/water (1:1) and diethyl ether (20 mL) as a white precipitate in 164 mg (87%) yield. UV−vis ($CHCl_3$): λ_{max} (ϵ) = 244 (69 100), 274 (47 800), 311 (29 500), 323 (33 100) nm (L mol^{-1} cm^{-1}). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 1.35 (m, 52 H, CH_2 (poly(caprolactone))), 1.59 (m, 102 H, CH_2 (poly(caprolactone))), 2.12 (m, 2 H, CH_2 (propyl)), 2.27 (t, 48 H, J = 7.32 Hz, CH_2CO (poly(caprolactone))), 2.48 (br, 1 H, OH), 3.46 (t, 2 H, J = 6.59 Hz, C*H*$_2$OH (poly(caprolactone))), 4.02 (t, 50 H, J = 6.59 Hz, OCH_2 (poly(caprolactone))), 4.36 (t, 2 H, J = 5.86 Hz, OCH_2 (propyl)), 4.60 (t, 2 H, J = 5.86 Hz, OCH_2 (propyl)), 7.37 (dd, 2 H, J = 7.82, 4.89 Hz, $H_{5,5''}$), 7.76 (d, 2 H, J = 4.89 Hz, $H_{6,6''}$), 8.12 (dd, 2 H, J = 7.82, 7.82 Hz, $H_{4,4''}$), 8.19 (s, 2 H, $H_{3',5'}$), 8.53 (d, 2 H, J = 7.82 Hz, $H_{3,3''}$). DSC: T_m = 47, 53 °C (double peak, third heating run, 10 °C/min).

Titration Experiments. The UV titration was performed by dissolving **5** (0.851 mg, 2.18 mmol) in 10 mL of chloroform and adding a 1.02×10^{-3} molar solution of iron chloride (in methanol) in steps of 20 μL. After every addition, a UV−vis spectrum was recorded after 5 min. The absorption value of the maximum of the ligand-centered absorption band at 318 nm as well as the metal-to-ligand charge-transfer band (MLCT) at 558 nm was used in order to obtain the titration curve.

The viscosity titration of the chain stopper (butyl ureidopyrimidinone) was performed by dissolving 114 mg of polymer **6** in 10 mL of chloroform and adding a solution of the chain stopper in steps of 40 μL into that solution. Four to eight viscosity measurements were recorded after each addition (after approximately 1 min waiting to check for constancy of the viscosity value).

Decomplexation of Polymer 10 with HEEDTA and Recomplexation. Ten milligrams of **6** were dissolved in a 1:1 mixture of chloroform/methanol (1.5 mL), and 0.2 mL of a concentrated aqueous solution of HEEDTA was added. After the mixture was shaken, the purple color disappeared within 2−3 min. The solution was extracted with water, and 0.2 mL of a methanolic solution of $FeCl_2$ (0.5 mg) was added to the organic phase, resulting in a reappearance of the color.

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