Unexpected Entropy-Driven Ring-Opening Polymerization in a Reversible Supramolecular System

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Viscosity is a fundamental feature of polymer melts and solutions, and controlling this property is a key issue in polymer science and technology. In many covalent polymers, a high degree of control is only feasible during synthesis, when covalent bonds are reversibly made and broken. In linear supramolecular polymers,[1] the monomeric units are held together by reversible noncovalent interactions, such as hydrogen bonding,[2] metal-coordination,[3] or hydrophobic forces.[4] Because these polymers are always at equilibrium, they present unique opportunities for viscosity control.

Previously, we have reported the use of strong quadruple hydrogen bonding between 2-ureido-4[1H]-pyrimidinone (UPy) units[5] attached to hexamethylene spacers in compound **1** (Chart 1) to form linear supramolecular polymers with a high degree of polymerization.[6] A concentration-dependent ring-chain equilibrium in conformationally biased trimethyl derivative **2** in its racemic form[7] results in striking differences in viscosity between solutions of **1** and **2**; the specific viscosity of $CHCl_3$ solutions of **2** is more than a decade lower than that of **1** at low concentrations, where **2** is present as cycles, but increases very rapidly at higher concentrations where polymeric chains are formed. Here we report the temperature dependence of this equilibrium, and its unexpected effect on solution viscosity.

^{1}H NMR spectra of solutions of **2** in chloroform show two distinct sets of signals, with a relative intensity that is concentration dependent. The chemical shifts of the N−H signals in each set indicate that all signals arise from hydrogen-bonded aggregates. At low concentration, two peaks of equal intensity are observed for every proton, indicating that these signals originate from well-defined asymmetric cycles or a mixture of isomeric structures.

The relative sizes of the species present at different concentrations were investigated by using DOSY ^{1}H NMR (diffusion ordered spectroscopy[8]) with heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin as internal reference. Figure 1 shows part of the DOSY-NMR spectrum of a 250 mM solution of **2** in chloroform. The signal labeled "p" displays a low value of the diffusion constant, showing that it belongs to an aggregate with a high molecular weight. The other signals (labeled "c") exhibit diffusion constants which are just slightly lower than the diffusion constant of the cyclodextrin (molecular mass 1429 g mol^{-1}), indicative for dimeric cycles of **2** (molecular mass 2 × 797 g mol^{-1}). Using the assignment of the signals, the temperature dependence of the ring-chain equilibrium was analyzed. ^{1}H NMR spectra of a 145 mM solution of **2** in $CDCl_3$ at different temperatures (Figure 2) reveal that approximately 8% of **2** is present as polymer at 223 K, while at 313 K, close to 35% of **2** is polymeric. Based on a K_a value of the UPy groups[5b] of 5.7 × 10^7, the degree of polymerization (DP) of the polymeric fraction is estimated to be 3.2 × 10^3 at 298 K (see Supporting Information), but it is difficult to estimate DP at other temperatures because the K_a value is also temperature dependent. Notably, a plot of the specific viscosity (η_{sp}) vs temperature of a 145 mM solution of **2** in $CHCl_3$ (Figure 3) reflects the temperature dependence of the ring-chain equilibrium: η_{sp} increases from 1.14 to 4.40 when the temperature is increased from 253 to 323 K. The effect is completely reversible; upon cooling the solution, η_{sp} returns to its original value. In contrast to this, η_{sp} of a 180 mM solution of **2** shows a maximum of 20.6 at 273 K and decreases to 14.6 at 323 K.

The observed shift of the equilibrium toward linear chains at higher temperatures is indicative of an entropy-driven ring-opening polymerization. Almost all ring-opening polymerizations, e.g. of THF,[9] are enthalpy driven, with an equilibrium degree of polymerization that decreases with temperature, and a critical

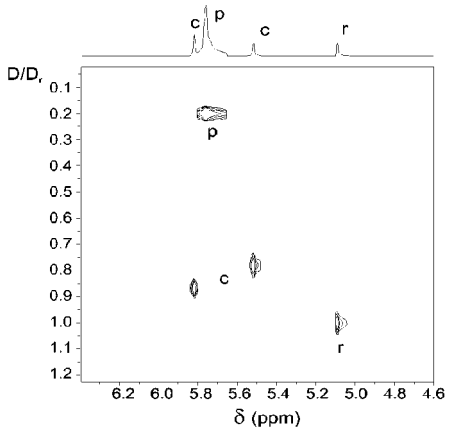
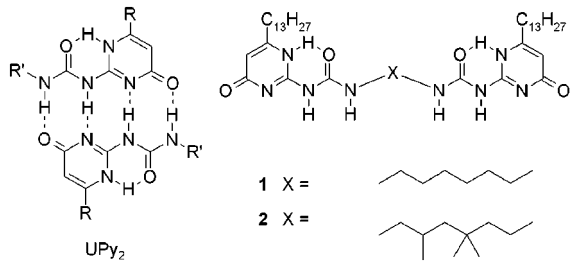


Figure 1. Part of the DOSY-NMR spectrum of a 250 mM solution of compound **2** in $CDCl_3$. Signals originating from cyclic aggregates are labeled "c", those from polymeric aggregates are labeled "p", and those from cyclodextrin added as internal reference are labeled "r". Diffusion constants are given relative to the diffusion constant of the internal reference.

Chart 1. Structure of the Ureidopyrimidinone Dimer and Bifunctional Molecules **1** and **2**



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(7) The racemate of **2** is isolated from a mixture of geometrical isomers (see Supporting Information).

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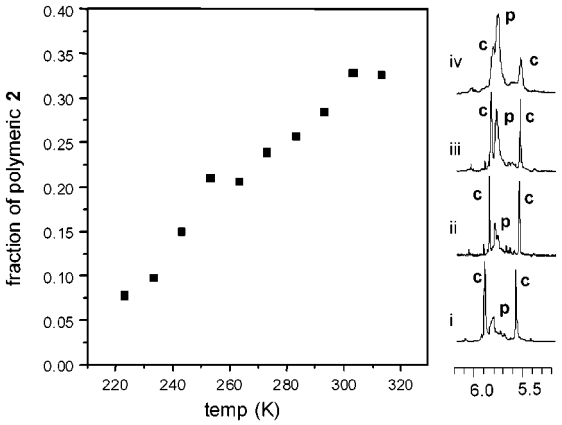

Figure 2. Fraction of polymer from deconvoluted ^{1}H NMR peak intensities in the 5.5−6.0 ppm region of a 145 mM solution of **2** in $CDCl_3$. Spectra recorded at 223 (i), 273 (ii), 298 (iii), and 323 K (iv) are shown. Signals originating from cyclic aggregates are labeled "c", and those from polymeric aggregates are labeled "p".

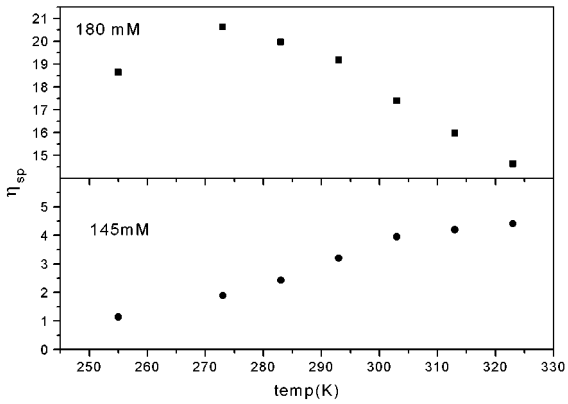

Figure 3. Specific viscosity (η_{sp}) versus temperature of solutions of **2** in chloroform at 145 (●) and 180 mM (■).

temperature, the ceiling temperature, above which virtually all species are cyclic. Very few polymerizations[10,11] have been reported with a floor temperature,[12] owing to an entropy-driven polymerization. The best studied example is the ring-opening polymerization of cyclic S_8 in liquid sulfur, in which the viscosity increases by a factor of 2000 when it is heated from 432 to 439K, and decreases again at still higher temperatures[13] due to dissociation and increased dynamics.[14] The increase in viscosity in a 145 mM solution of **2** (by a factor of 3.9) is less dramatic than that in liquid sulfur, because the fraction of polymer (and hence its concentration) is changing by a factor of only 1.57 in the experimentally accessible temperature range, between 253 and 313 K. If it is assumed that η_{sp} is determined by the polymer concentration c, and increases with $c^{3.75}$ (like it does in **1**[6]), the conversion of cycles into chains in **2** is expected to increase viscosity by a factor of at most $1.57^{3.75} = 5.44$. Stronger effects can be expected close to the floor temperature, where the polymer fraction is closer to 0, and can easily be varied by a factor of >10. However, viscosity measurements below 253 K are difficult, and increasing the floor temperature through lowering the concentration reduces η_{sp} to very low values. Inversion of the effect, on the other hand, is readily observed by increasing the concentration to 180 mM (Figure 3). This solution reaches its maximum viscosity already at 273 K, because the more concentrated solution contains a higher fraction of linear chains; above 273 K, little additional polymer is formed, and increased dissociation in combination with faster dynamics leads to a decrease in viscosity. Present work is directed at conformation design of monomers which maximize the observed temperature-induced solution thickening.

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Supporting Information Available: Synthesis and characterization of compound **2**, ^{1}H NMR spectra of **2** in $CDCl_3$ at different concentrations, concentration-dependent relative diffusion constants of cyclic and polymeric aggregates of **2** in $CDCl_3$, and calculation of DP at 298 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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