Macromolecules **1999,** *32,* 2696−2705

Supramolecular Polymers from Linear Telechelic Siloxanes with Quadruple-Hydrogen-Bonded Units

J. H. K. Ky Hirschberg,[†] Felix H. Beijer,[†] Huub A. van Aert,[†] Pieter C. M. M. Magusin,[‡] Rint P. Sijbesma,*,[†] and E. W. Meijer*,[†]

Eindhoven University of Technology, Laboratory of Macromolecular and Organic Chemistry, and Schuit Institute of Catalysis, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

Received December 18, 1998; Revised Manuscript Received January 28, 1999

ABSTRACT: Telechelic oligo- and poly(dimethylsiloxanes) **1** and **2**, with two ureidopyrimidone (UPy) functional groups, have been prepared via a hydrosilylation reaction. The compounds have been characterized in solution by ^{1}H NMR and viscometry and in the solid state by ^{1}H NMR and ^{13}C NMR, FTIR, and rheology measurements. The measurements show that the UPy groups of **1** and **2** are associated via quadruple hydrogen bonds in a donor−donor−acceptor−acceptor (DDAA) array. In many aspects, the materials behave like entangled, high molecular weight polymers. Compound **2** has a T_g at −119 °C and shows melting of microcrystalline domains of associated UPy units at −25 °C. Compound **1** has a crystalline form (T_m = 112 °C) and an amorphous modification with a T_g of 25 °C. Solid-state NMR was used to investigate the mobility of these phases. WISE spectra show a higher mobility of the UPy groups in the amorphous phase than in the crystals of **1**. Amorphous **1** and **2** behave like entangled polymers. Their mechanical behavior is characterized by a rubbery plateau and a relatively high activation enthalpy for stress relaxation (ΔH = 127 kJ/mol for **1**; ΔH = 54 kJ/mol for **2**), which was derived from the temperature dependence of the zero-shear viscosity. Estimates for the degree of polymerization (DP) of **1** and **2**, based on the mechanical properties, give DP > 100 for **1** and approximately 20 for **2**. Like in condensation polymerization, the DP's of reversible supramolecular polymers are presumably limited by the presence of small amounts of monofunctional impurities.

Introduction

The physical properties of linear polymers and organic molecules are strongly modified when they are provided with associating end groups.[1−4,7,8] When the end groups associate through nondirectional interactions, like for example coulomb forces in telechelic ionomers[1] and hydrophobic interactions in hydrophobically endcapped urethanes[2] (HEUR), clusters of end groups are formed, and a reversible network results. These materials exhibit interesting and useful rheological properties. Polymers with partly directional hydrogen-bonding end groups have also been studied. Stadler[3] has made a detailed study of the effect of hydrogen bonding of the functional groups in urazole-modified polyolefins. In these materials, the hydrogen-bonding groups aggregate in a cooperative fashion to form ordered clusters, leading to thermoplastic elastomers. Lillya[4] has shown that modest changes in rheological properties result when poly(THF) is capped with carboxylic acid-containing functionalities, capable of dimerization. The changes in properties were ascribed to the formation of large crystalline domains of end groups. In these polymers, like in the urazole-modified polyisobutylene, other interactions than hydrogen bonds also play a role and cause further aggregation to give microcrystalline domains.

Polymers in which the end groups exclusively form dimers, but do not aggregate further, are of great interest. Telechelic polymers with such end groups would form long chains by concatenation of molecules, without physical cross-links. When the aggregation of end groups is sufficiently strong and directional, even low molecular weight telechelic building blocks (M_w < 10^3) would give materials in which chain entanglements give rise to polymer-like properties, such as rubber elasticity. Although the directionality required for specific dimerization is inherently present in hydrogen bonds, the strength of this type of interaction is limited (an average value of −7.9 kJ/mol for a single hydrogen bond in chloroform is reported[5]), and high degrees of polymerization are not readily achieved, unless anisotropy of the medium in liquid-crystalline material imposes end-to-end association.[6] Examples of linear self-assembly in liquid-crystalline phase are reported by Lehn, who used triple hydrogen bonding between diaminopyridine and uracil end groups,[7] and by Griffin, who studied complexes of diacids with bis- and tetrapyridyls.[8] We are interested in reversible polymerization in the absence of any long-range order. Flexible spacer units and stronger hydrogen-bonding interactions than the ones used by Griffin and Lehn are required to obtain isotropic polymer melts and solutions with high degrees of polymerization (DP). Recently we have shown[9] that a self-complementary hydrogen-bonding unit based on ureidopyrimidone (UPy) (Figure 1) features dimerization constants in excess of 10^6 M^{-1}, and we have found[10] that low molecular weight bifunctional molecules containing this functional group in many ways behave like polymers. In the present article we describe the full details of the synthesis and properties of the first series of telechelic poly(dimethylsiloxanes) **1** and **2**, in which the assembly of UPy end groups leads to strong modification of its properties. Even in compound **1**, with only 13 atoms in the main chain of the spacer, many properties that are typical for polymers are observed. Throughout this work, the properties of the bifunctional

---

[†] Laboratory of Macromolecular and Organic Chemistry.

[‡] Schuit Institute of Catalysis.

10.1021/ma981950w CCC: $18.00

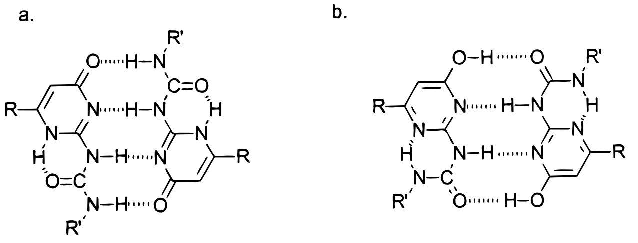


Figure 1. Modes of dimerization of the UPy functional group via quadruple hydrogen bonding: keto tautomer (a) and enol tautomer (b).

materials are compared with those of analogues **1-Bn** and **2-Bn**, in which quadruple hydrogen bonding of the functionalities is prevented by benzyl-protecting groups.

Results

Synthesis. Because telechelic, hydride-terminated dimethylsiloxanes of various lengths are commercially available compounds, which can be functionalized in high yields by a hydrosilylation reaction with alkenes,[11] we decided to prepare telechelic siloxanes using the 6-butenyl-substituted UPy **5** and its benzyl-protected derivative **6**. These compounds were synthesized according to Scheme 1. First, the dianion of ethyl acetoacetate was alkylated with allyl bromide,[12] followed by condensation of the resulting β-keto ester with guanidinium carbonate. The product of this reaction, isocytosine **4**, was reacted with butyl isocyanate to yield UPy **5**, which in turn was O-benzylated in moderate yield with benzyl bromide in DMF to give **6**.

Attempts to couple compound **5** with hydride-terminated dimethylsiloxanes were not fully successful. ^{1}H NMR of the crude reaction mixture showed that a side product was formed in which the siloxane was attached to the oxygen atom of the enol tautomer of **5**. The side product could not be separated from the product, and therefore we decided to use O-benzyl derivative **6** in the hydrosilylation reaction.

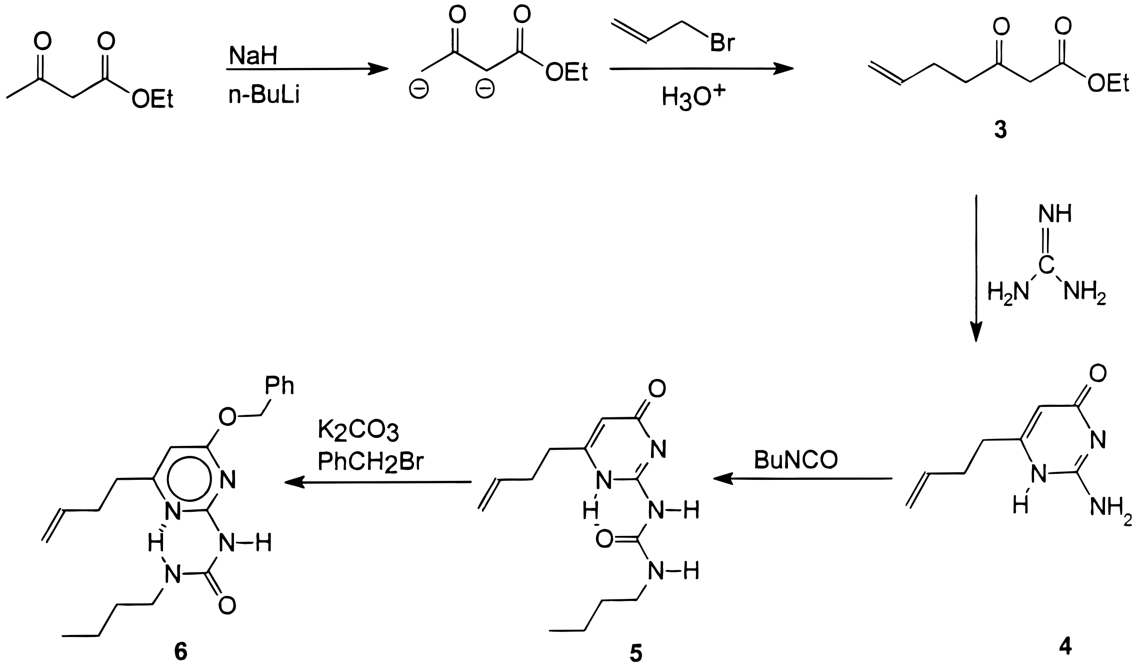
Hydrosilylation reactions of **6** with α,ω-bishydride-terminated hexamethyltrisiloxane or poly(dimethylsiloxane) (M_n = 6000 g/mol) were carried out in toluene under a dry nitrogen atmosphere, using the platinum–divinyltetramethyldisiloxane complex as a catalyst (Scheme 2). A small excess of **6** was employed to ensure complete conversion of the silane end groups. During the reaction, the disappearance of Si–H signals at 4.7 ppm was monitored by ^{1}H NMR spectroscopy. Reactions were complete after 48 h. Compound **1-Bn** was purified by column chromatography followed by recrystallization from hexane, while compound **2-Bn** was triturated several times with methanol in order to remove very soluble **6**. End group analysis of **2-Bn** by ^{1}H NMR showed that due to fractionation in the trituration procedure M_w had increased from 80 to 100 repeat units.

Hydrogenolysis of **1-Bn** and **2-Bn** was performed in THF/ethanol using activated palladium on carbon as a catalyst. Compound **1** was purified by column chromatography followed by recrystallization from ethyl acetate, yielding analytically pure white needles in 85% yield with a melting point of 112 °C. Purification of compound **2** using trituration was not successful; therefore, the crude product was dissolved in a mixture of chloroform and ethanol, from which the chloroform was selectively evaporated at low vacuum, resulting in a precipitation of the product as a viscous oil. Although NMR and IR showed only resonances of pure product, it seems reasonable to assume that **1** is more pure than **2**.

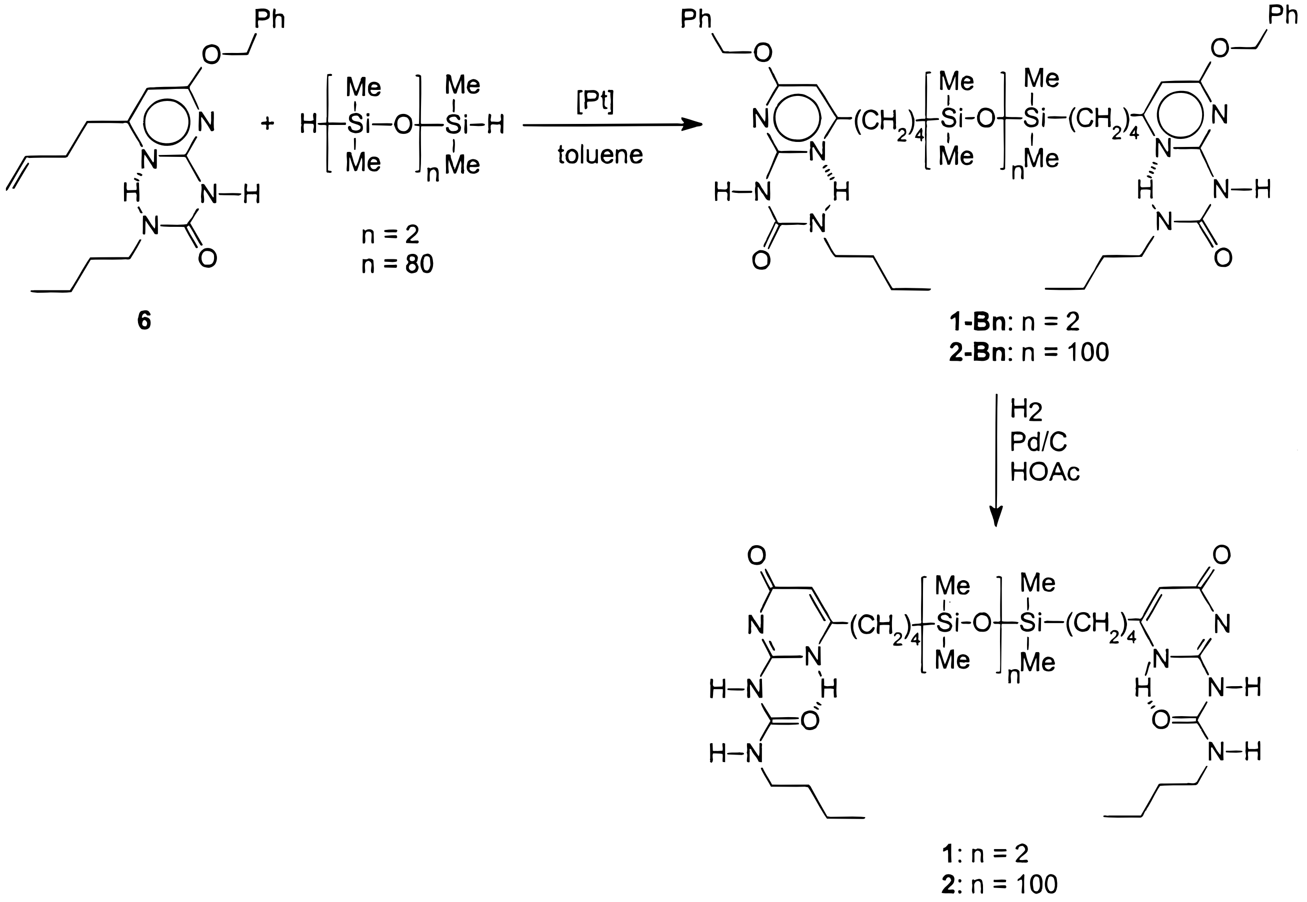
The reaction scheme used here proves to be a general route in which reasonable amounts of telechelic polysiloxanes can be made, from which the precursors can be used as nonsticky model compounds.

Hydrogen Bonding of the Functional End Groups. In a previous study,[9] we established that the UPy functional group dimerizes with high dimerization constants in solvents such as $CDCl_3$ or toluene. In the solid state, the molecules are also present as dimers. However, the exact mode of association was shown to

Scheme 1. Synthesis of 6-(3-Butenyl)-2-butylureido-4-pyrimidinone 5 and 4-Benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine 6



Scheme 2. Synthesis of Telechelic UPy Functionalized Siloxanes



be dependent on solvent and the substituents. Specifically, the functional group may be present as dimers of either a keto tautomer or of an enol tautomer (Figure 1). Each of these tautomers is easily identified by characteristic features in the ^{1}H NMR and FTIR spectra. Consequently, it is relatively straightforward to establish the extent and mode of association of the UPy groups in **1** and **2** in solution and in bulk. The ^{1}H NMR spectrum of compound **1** in $CDCl_3$ is shown in Figure 2. The positions of the NH signals at 13.2, 11.8, and 10.2 ppm, along with a pyrimidyl resonance at 5.8 ppm, indicate that the functional groups are dimerized and that the molecules are exclusively present in the keto tautomeric form. IR spectroscopy is very sensitive for detecting changes in hydrogen bonding of the UPy group. The FTIR spectrum of the keto form of the ureidopyrimidone functional group shows a characteristic band at 1696 cm^{-1} of the pyrimidone carbonyl stretch vibration, which is absent in the enol tautomer. The spectra in Figure 3, of **1** in $CDCl_3$ solution, of crystalline and amorphous **1**, and of amorphous **2**, display a band at this characteristic position, showing that the UPy functionalities remain dimerized in the keto tautomer in all these phases.

Thermal Properties. Several properties distinguish polymers from low molecular weight compounds. Among these are a propensity to form glasses and pronounced differences in rheological behavior. Phase behavior of compounds **1** and **2** was investigated with DSC. The thermal behavior of compound **1** shows pronounced effects of hydrogen bonding (Figure 4). When obtained by precipitation from solvent, compound **1** is crystalline, with a melting point of 112 °C, as shown by a first heating scan. A subsequent cooling and heating scan reveals a glass transition at 25 °C. Crystallization of **1** from the bulk is remarkably difficult, since even annealing at 100 °C for 3 h does not result in reappearance of the melting isotherm (data not shown).

In the compounds with the polymeric spacers, it is instructive to compare the differences between the protected and unprotected material. Compound **2-Bn**, which cannot associate via quadruple hydrogen bonds, shows a DSC thermogram (Figure 5a) similar to that of unfunctionalized PDMS, with a T_g at -129 °C, crystallization at -75 °C, and subsequent melting at -50 °C. Hydrogen-bonded product **2**, on the other hand, displays different behavior. A glass transition is present at the same temperature as in **2-Bn**, but the strong crystallization exotherm of the siloxane spacers is absent (Figure 5b). Crystallization does also not occur when **2** is annealed at -60 °C for 2 h (Figure 5c). A small but significant endotherm is observed at -25 °C, which has a much lower ΔH (0.8 J/g) than the melting endotherm of **2-Bn** (13.5 J/g).

Solid-State NMR. The crystalline and amorphous phases of **1** were characterized further by solid-state ^{13}C and ^{1}H NMR. The ^{13}C NMR spectrum of the amorphous phase shows a broadening of the lines relative to the crystalline phase (Figure 6). The width of the line at 105 ppm remarkably increases from 90 to 300 Hz. On the basis of its chemical shift and fast cross-polarization behavior ($T_{CH} = 30\ \mu s$), this resonance is assigned to the protonated heteroaromatic carbon at position d in the molecular structure (Figure 2). Its measured transverse relaxation time T_2 in the amorphous phase is 3.7 ms, which corresponds to only a minor homogeneous

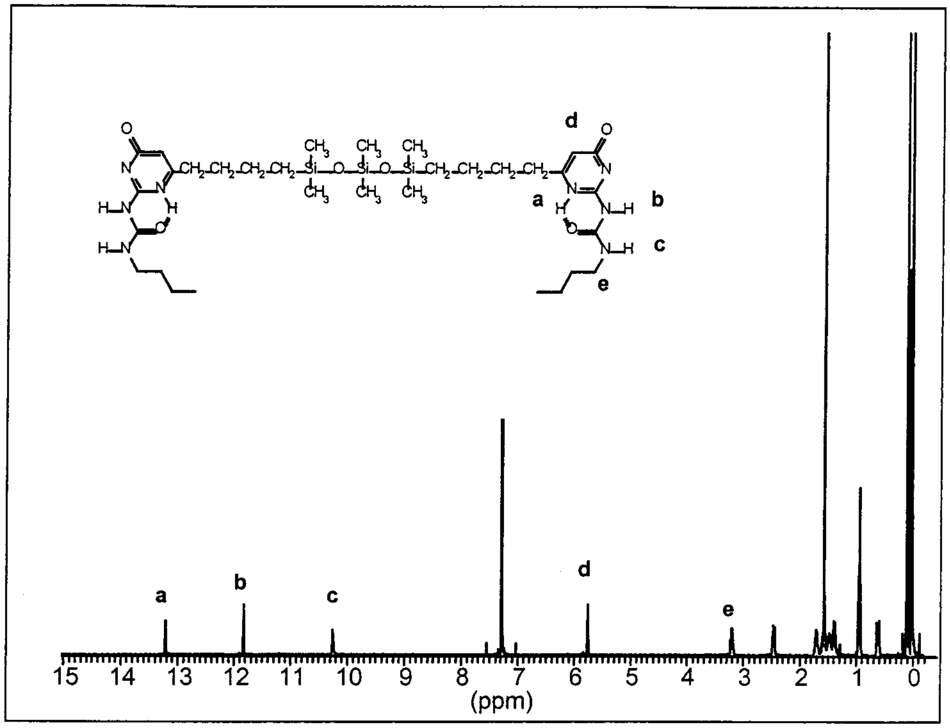


Figure 2. ${}^{1}H$ NMR spectrum of compound **1** in $CDCl_3$.

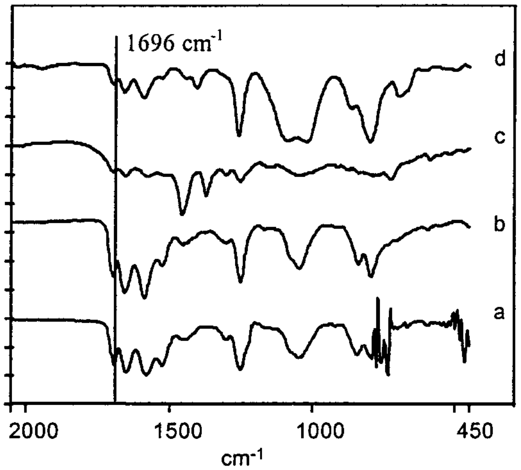


Figure 3. FTIR spectra: compound **1** in $CDCl_3$ solution (a), amorphous **1** (b), crystalline **1** (c), and amorphous **2** (d).

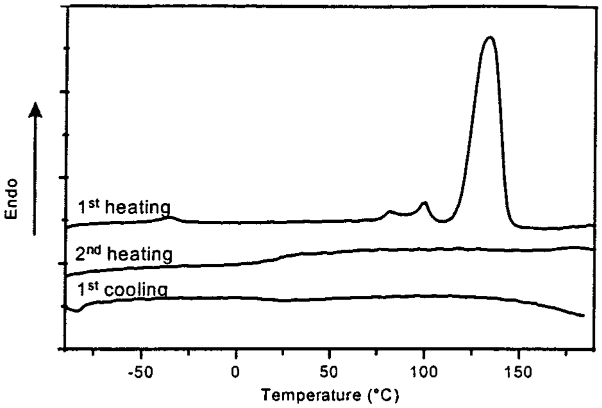


Figure 4. DSC traces of compound **1**.

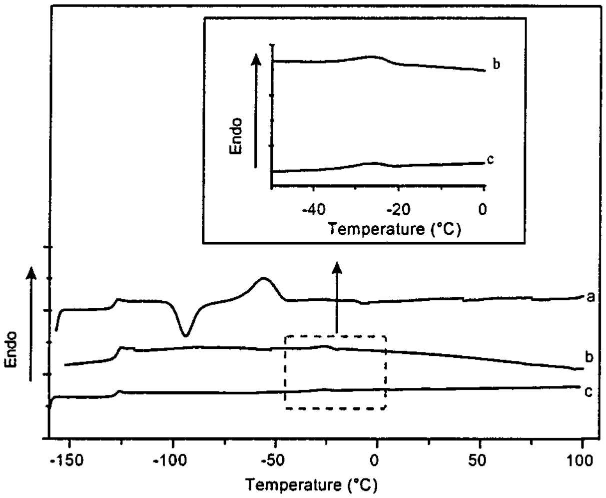


Figure 5. DSC traces of telechelic PDMS derivatives at a heating rate of 20 °C/min: compound **2-Bn** (a); compound **2**, second heating run (b); compound **2** after annealing for 2 h at −60 °C (c).

contribution of 86 Hz to the total line width. Apparently the resonance at 105 ppm is mainly affected by strong inhomogeneous broadening. This probably reflects heterogeneous packing effects in the amorphous material, indicating that the regular stacking of hydrogen-bonding units in the crystal is hardly present in the amorphous phase. This picture is confirmed by broadening of the other resonances in the spectrum.

To compare the molecular mobility of **1** in the crystalline and the amorphous phase, WISE experiments were carried out. This NMR technique links the capacity of ${}^{13}C$ NMR to resolve chemically inequivalent ${}^{13}C$ nuclei with the power of ${}^{1}H$ NMR to yield mobility information by combining the two in a two-dimensional correlation experiment.[13] A horizontal trace in the WISE spectrum in Figure 7 at the vertical position of a specific ${}^{13}C$ resonance shows the NMR line shape of the protons within a 5 Å distance of the selected carbon. Residual molecular motions in organic materials at a time scale $\leq 10^{-5}$ s cause narrowing of the proton line. The wider

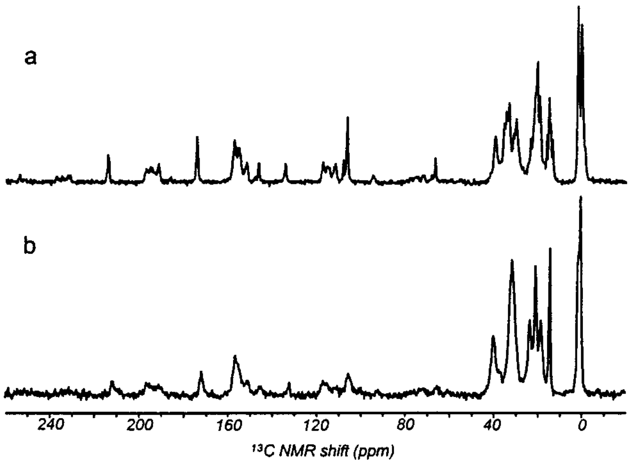


Figure 6. CPMAS ^{13}C NMR spectrum of crystalline **1** (a) and amorphous **1** (b). The sharper resonances of the crystalline material as compared to the amorphous material reflect the perfect regular packing in the crystalline phase.

the proton line shape, the more rigid the corresponding part of the molecule. The four traces shown in Figure 7 illustrate the line shapes of the proton of the heterocycle in the hydrogen-bonding units and the methyl groups of the siloxane spacers in the crystalline and amorphous phase. The line shapes show that the methyl groups are more mobile than the UPy groups in both the crystalline and amorphous phase and that the amorphous material is characterized by a higher mobility of both the flexible and the more rigid parts of the molecule, as expected from the increased free volume. Other types of ^{13}C and ^{1}H NMR relaxation confirm the increased molecular mobility in amorphous relative to the crystalline material. For instance, proton $T_{1\rho}$ values were measured via the ^{13}C resonances after cross-polarization. Due to spin diffusion, no distinction between spacers and hydrogen-bonding units can be made. The proton $T_{1\rho}$ of amorphous **1**, being 5.5 ms, is much smaller than that of the crystalline material, ca. 150 ms, indicating a strongly increased mobility in the 10^{-4} s range. Averaged by the spin diffusion, these proton $T_{1\rho}$ values predominantly reflect the mobility of the proton-rich siloxane spacers and alkyl side groups. To specifically study the mobility of separate hydrogen-bonding units, ^{13}C transverse relaxations (T_2) of the two modifications of **1** were compared. In contrast to various sorts of proton relaxation, ^{13}C relaxation times reflect more localized features of molecular fragments. The values for the sp$_2$ resonances in amorphous **1** are about half as large as for its crystalline modification. For example, the ^{13}C T_2 value of the carbonyl resonance in the hydrogen-bonding unit is 3.6 ms in the amorphous and 9.4 ms in the crystalline material. A major cause for T_2 relaxation of the sp$_2$ resonances with their large chemical shift anisotropy is probably rotational mobility in the range $\leq 10^{-3}$ s. This indicates that in the amorphous material the hydrogen-bonding units have a high mobility as well.

Solution Viscosity. The viscosity behavior of telechelic siloxane **1** and its protected precursor **1-Bn** in CHCl$_3$ solution strongly differs. The differences become particularly clear in a double-logarithmic plot of the specific viscosity $\eta_{sp} = (\eta/\eta_{solvent})^{-1}$ against the concentration (Figure 8). The viscosity of **1** is significantly higher at all concentrations and has a much higher concentration dependence than the viscosity of **1-Bn**. Straight lines can be fitted reasonably well to the viscosity data of both compounds, indicating that a simple power law relates the viscosity and the concentration. The lines have slopes of 3.9 and 1.06, respectively. The latter value agrees well with the Stokes–Einstein law for the viscosity of solutions of hard spheres, indicating there is no concentration-dependent association of molecules of **1-Bn**. The concentration dependence for compound **1** is much higher, and the slope is in reasonable agreement with the predicted value[14] of 3.55–3.75 for the solution viscosity of reversible polymers.

Rheological Measurements. Dynamic oscillatory shear measurements were performed on compounds **1**, **1-Bn**, **2**, and **2-Bn**. The contrast between protected and hydrogen-bonding compounds is very large in the analogues **1** and **1-Bn** with short spacers: whereas the

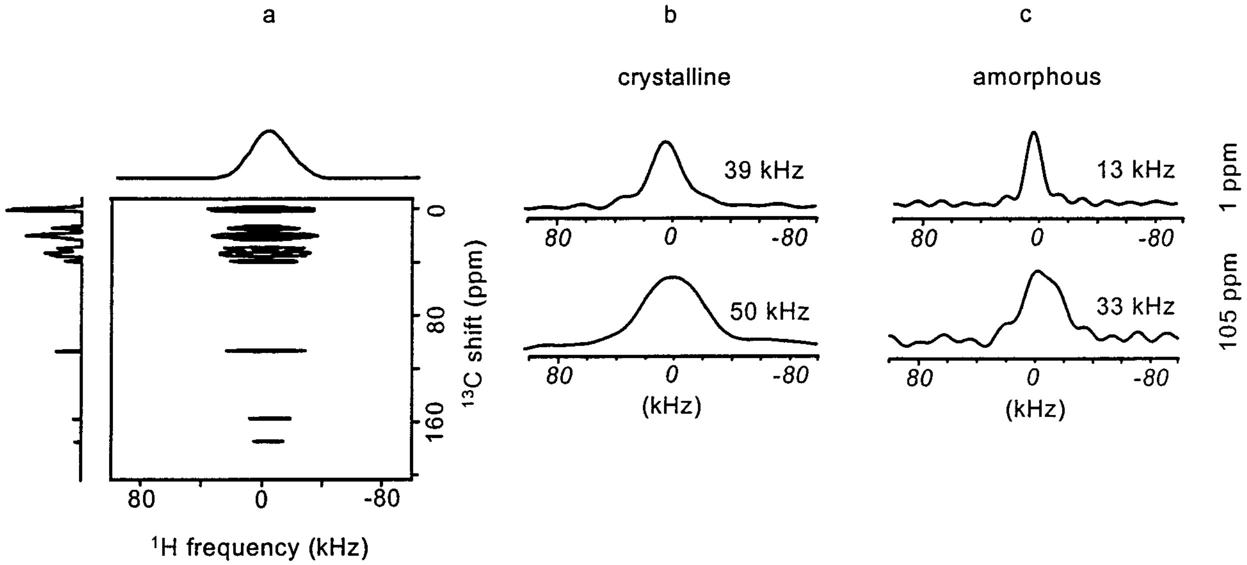


Figure 7. (a) Two-dimensional WISE spectrum of crystalline **1** correlating ^{1}H NMR line shapes to ^{13}C resonance positions in the MAS spectrum. (b) Horizontal traces at 1 and 105 ppm for the crystalline modification of **1** representing the proton line shape of the methyl groups in the siloxane spacer and the C–H proton in the Upy hydrogen-bonding unit, respectively. (c) Same two traces for the amorphous material. Line widths at half-height as determined from Gaussian line shape fitting are indicated.

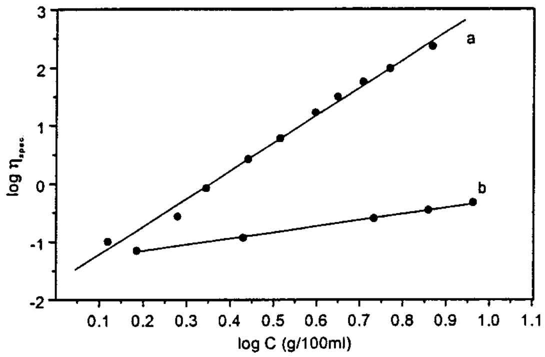


Figure 8. Specific viscosities of compounds **1** (a) and **1-Bn** (b) in $CHCl_3$ as a function of concentration at 20 °C.

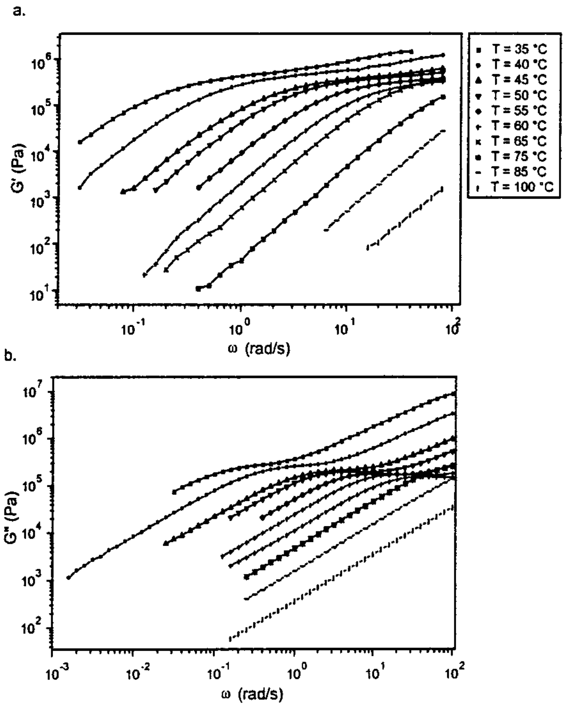


Figure 9. Storage moduli (a) and loss moduli (b) of **1** between 35 and 100 °C.

mechanical properties of compound **1-Bn** could not be determined due to its low viscosity above, and fast crystallization below its melting point, viscoelastic properties of the amorphous modification of compound **1** above T_g are distinctly polymer-like (Figure 9). At temperatures below 70 °C, a narrow rubbery plateau is observed with a storage modulus of approximately 2×10^5 Pa. The plateau modulus is only slightly dependent upon temperature. At 35 and 45 °C, an upturn of the storage modulus to the glassy state is observed at high frequencies. In the absence of physical cross-links, the rubber plateau implies the presence of elastically active polymeric chains of **1** between entanglements. The degree of polymerization of **1** must be substantially higher than the critical entanglement molecular weight (which is on the order of 3×10^4 g/mol for poly(dimethylsiloxane)) to give rise to a plateau of the width observed in Figure 9. The observed mechanical properties of **1** are therefore caused by polymeric chains with a DP exceeding 100.

Storage moduli of compound **2** in a range of temperatures are shown in Figure 10. It is evident that in this case mechanical measurements are very sensitive to phase transitions. At the lowest temperature (−39 °C), below the weak endotherm observed in DSC, G' is nearly independent of frequency. At temperatures above this transition, the compound shows a transition from viscous flow at low frequencies to rubbery behavior at higher frequencies. In contrast to this, benzyl-protected compound **2-Bn** exhibits only fluidlike behavior in the whole temperature range. The differences between the two compounds at a single temperature are discernible in a plot of G' and G'' (Figure 11). Compound **2-Bn** is fluidlike ($G' < G''$) at all frequencies, whereas in compound **2** the lines of G' and G'' cross each other at a frequency of 2 Hz.

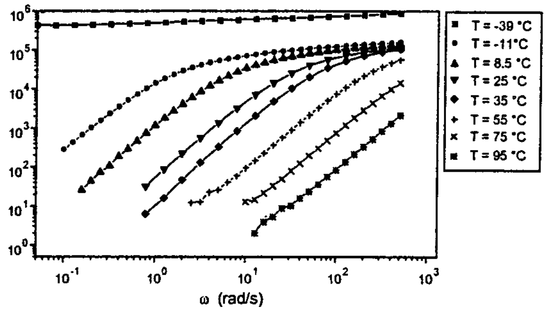


Figure 10. Storage modulus isotherms of **2**.

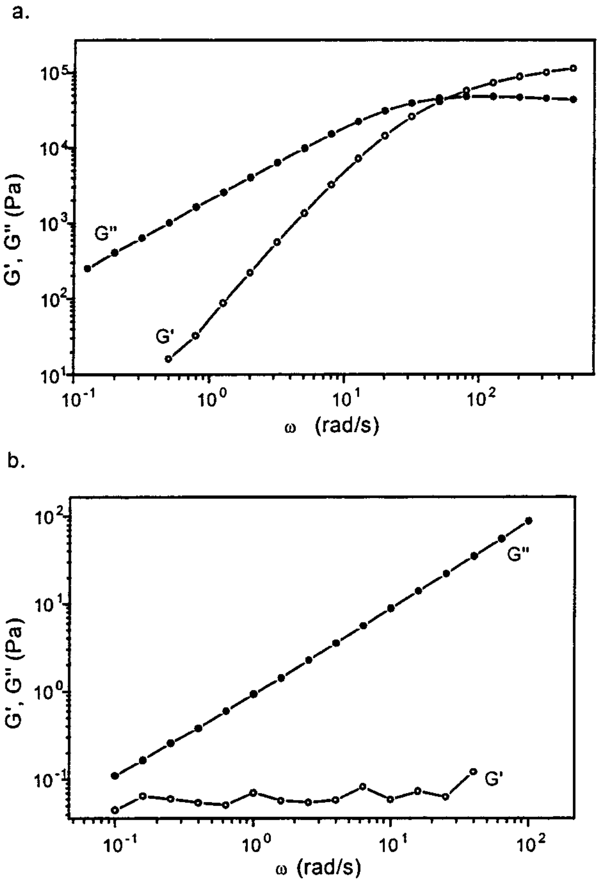


Figure 11. Storage (○) and loss (●) moduli of compounds **2** (a) and **2-Bn** (b) at 25 °C.

Frequency-independent complex viscosities are observed for compound **2-Bn** at all temperatures measured (Figure 12), which is typical for low molecular weight polymers below their entanglement molecular weight, whereas the complex viscosity of **2** decreases strongly at higher frequencies. At low frequencies, the complex viscosity of compound **2** at 30 °C is 2×10^3 times the viscosity of **2-Bn**. Using this ratio, and

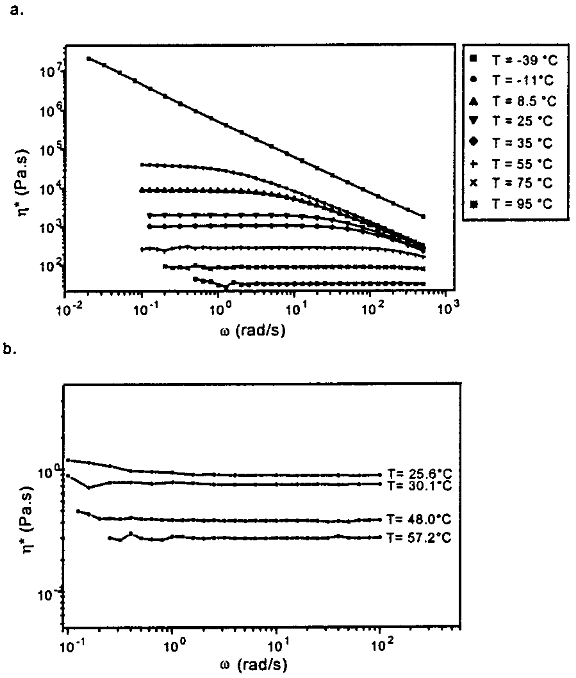


Figure 12. Complex viscosities of compounds **2** (a) and **2-Bn** (b).

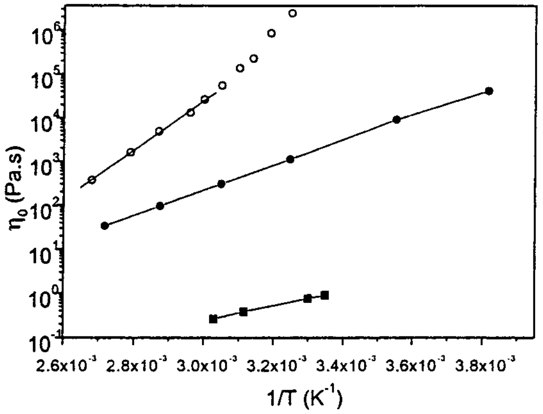


Figure 13. Semilogarithmic plot of the zero shear viscosity (η_0) of **1** (○), **2** (●), and **2-Bn** (■) against the reciprocal of the absolute temperature.

assuming that the viscosity of linear aggregates of **2** depends on the molecular weight in the same way as in PDMS,[15] a rough estimate of the degree of polymerization of **2** can be made. Such a calculation indicates that an average of 20 molecules of **2** ($M_n = 7.5 \times 10^3$) associate to form a chain with a M_n of 1.5×10^5.

Activation parameters for stress relaxation of compounds **1** and **2** were determined from the temperature dependence of the zero-shear viscosity. At low frequencies, the complex viscosity is equivalent to the zero-shear viscosity η_0. From the slope of a semilogarithmic plot of η_0 vs $1/T$ (Figure 13), activation parameters for stress relaxation were calculated using the following relationship:

$$\eta = c\mathrm{e}^{\Delta H/RT}$$

For compound **1**, the glass transition at 25 °C results in a curved plot, and only the data above 60 °C were used. This results in activation parameters of 127 kJ/mol for **1**, 54 kJ/mol for **2**, and 37 kJ/mol for **2-Bn**. Clearly, association results in a higher barrier, by inhibiting local relaxation.

Discussion and Conclusions

Telechelic siloxanes **1** and **2** are readily synthesized in good yields. Use of benzyl-protecting groups allows coupling via a high yielding hydrosilylation step and also affords analogues that do not have the possibility to associate via quadruple hydrogen bonds. In compounds **1** and **2**, the NMR and IR data show that the UPy functional groups are present as the keto tautomer, which associate via four hydrogen bonds in a DDAA array. The dramatic differences between protected compounds **1-Bn** and **2-Bn** on one hand and the hydrogen-bonding compounds **1** and **2** on the other are strong evidence for the hydrogen-bond-induced polymeric character of the latter. In solution, there is good agreement between the concentration dependence of the viscosity of solutions of **1** with the behavior predicted by Cates[14,16] for entangled solutions of reversible polymers, in which the zero-shear viscosity is calculated to scale with the concentration to the power 3.5−3.7. The results suggest that the solutions of **1** are semidilute; i.e., the supramolecular chains of **1** overlap at the concentrations studied.

Bulk phase characterization of **1** indicates that it has two completely different modifications. The compound can be obtained as either a completely crystalline material or an amorphous material. The crystalline material is very much like any other low molecular weight crystalline compound. In contrast to this, the amorphous modification of **1** in many respects behaves like a high molecular weight amorphous polymer. The inhomogeneous line broadening in solid-state ^{13}C NMR spectra of amorphous **1** indicates that the hydrogen-bonding units are not regularly stacked, as they are in the crystalline material. The absence of such microcrystalline domains in macroscopically amorphous **1** is confirmed by ^{1}H−^{13}C correlation spectra and ^{13}C T_2 values of the sp$_2$ resonances, which show that the hydrogen-bonding units are more mobile in the amorphous state than in the crystalline modification. The amorphous material does not show any sign of crystallization or formation of microcrystalline domains, but instead forms a glass below 25 °C. We propose that the reluctance with which this modification of **1** crystallizes is a result of the high viscosity and the presence of entanglements in the supramolecular polymer and reflects the high degree to which the short spacers restrict the functional groups to organize in ordered domains. The mechanical properties of **1** are also very unlike those of a low molecular weight compound but have many of the features, such as a rubbery plateau, of a high molecular weight polymer.

The properties of compound **2** also indicate extensive association. In contrast to the benzyl-protected analogue **2-Bn**, the siloxane spacers of **2** do not crystallize, because association of the end groups prevents the polymer chain from disentangling. Although the siloxane spacers of this compound do not crystallize, their length and flexibility are sufficient to allow the formation of microcrystalline domains of dimerized UPy end groups. The small endotherm in DSC at −25 °C is ascribed to melting of these domains. Above this temperature the functional groups exclusively interact in a pairwise manner. This melting behavior is comparable to what was reported by Stadler[3b] for crystalline domains of urazole end groups in telechelic polybutadienes, which melt, however, at a much higher temperature (123 °C). The phase transition of **2** at −25 °C is very important for the interpretation of the rheological data. In general, the presence of a broad rubber plateau in the modulus of a linear polymer is either due to entanglements or physical cross-links in microcrystalline domains. The DSC results indicate that the physical cross-links disappear at −25 °C. Consequently, we interpret the viscoelastic properties of **2** above −25 °C as being the result of entanglements of associated chains in an amorphous matrix.

The degree of polymerization is a primary parameter of these reversible polymers. If the DP were solely limited by the dimerization constant of the UPy functional group (which is estimated[9,10] to be on the order of 10^6-10^8 in $CDCl_3$ at 25 °C), extremely high degrees of polymerization (DP $> 10^6$) would be obtained. The actual DP's are difficult to determine, but analysis of the rheological data allows an estimate to be made. The presence of a significant rubber plateau in the storage modulus of **1** implies a DP of at least 100, but possibly it is significantly higher. In compound **2**, a DP of 20 is calculated from comparison of the zero-shear viscosities of **2** and **2-Bn**. These DP's are lower than the values based on the dimerization constant for analogous reasons as the DP is limited in a condensation polymer. When molecules with only one UPy end group are present (i.e., the functionality of the telechelic monomer is lower than 2), these molecules will act as chain stoppers and reduce the effective chain length of the polymer. Compound **1** can be purified by chromatography to a purity higher than 99%. However, for compound **2** it is not feasible to remove monofunctional impurities completely, because the chromatographic properties of **2** are dominated by the polymeric spacer. Consequently, the DP of **1** is higher than the DP of **2**.

In conclusion, this study shows that amorphous supramolecular polymers can be obtained by association of telechelic monomers via hydrogen bonds. These polymers have high DP's, resulting in chain lengths well above the critical length for entanglements. This has been achieved by utilizing the unique properties of the UPy functional group, which dimerizes with a high association constant but has little tendency to associate further in microcrystalline domains.

Experimental Section

All experiments were performed under a nitrogen atmosphere. Dry tetrahydrofuran (THF) was obtained by distillation over sodium/potassium/benzophenone. Dry toluene was obtained by distillation and degassed by repeated freeze−thaw cycles. Pyridine, ethanol, and dimethylformamide (DMF) were dried over 4 Å molecular sieves. All solvents were of p.a. quality unless otherwise stated. Solution ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or a Brucker AC 400 with TMS as internal reference. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Solid-state ^{13}C NMR spectra were recorded at room temperature on a Bruker MSL400 spectrometer. $^1H-^{13}C$ cross-polarization (CP) was used to enhance the polarization of the ^{13}C nuclei and reduce the required relaxation delay between subsequent scans. Magic-angle spinning (MAS) at a sample rotation rate of 4 kHz was employed to eliminate the line broadening caused by the chemical shift anisotropy. The ^{13}C signals were acquired with high-power proton decoupling. Typical 90° pulses on both ^{13}C and ^1H were 5 μs. Standard CPMAS spectra were recorded with a contact time of 1 ms. A contact time of 50 μs was selected for the WISE spectrum to suppress proton spin diffusion.[13] Proton $T_{1\rho}$ relaxation was studied by measuring the decay of the ^{13}C resonances versus the varied duration of the ^1H lock pulse preceding the constant $^1H-^{13}C$ contact pulse of 0.5 ms in the pulse sequence. ^{13}C T_2 values were extracted from the decay of the Hahn echo produced by a 180° pulse as a function of the echo time. Echo times equal to even multiples of the sample rotation time $T_r = 250\ \mu s$ were chosen to avoid interference with the magic-angle spinning.

Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Thermogravimetric analysis (TGA) measurements were performed with a Perkin-Elmer TGA 7. All samples were heated from 20 to 700 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were obtained with a Perkin-Elmer Pyris-1 at a heating rate of 20 °C/min. Melting points were determined with a Jenaval polarizing microscope equipped with a Unkam THMS 600 heating device. Elemental analysis were obtained using a Perkin-Elmer 240 and a Perkin-Elmer 2400. Solution viscosities were determined with Ubbelohde microviscometers with a suspended level bulb of different capillary tube diameters. Before measurements, low-viscosity samples were passed through a filter of 5 μm. Dynamic mechanical measurements were performed on a Rheometrics fluid spectroscopy RFSII, a Rheometrics RDS, and a Rheometrics RMS800 in a cone−plate geometry.

Ethyl 3-Oxo-6-heptenoate (3) was prepared according to a literature method[12] (bp 106−108 °C at 15 mmHg, lit. 106−108 °C). ^1H NMR ($CDCl_3$): δ 5.82 (m, 1H, $HC{=}CH_2$), 5.01 (m, 2H, $CH_2{=}CH$), 4.20 (q, 2H, OCH_2), 3.45 (s, 2H, CH_2), 2.66 (t, 2H, CH_2), 2.34 (m, 2H, CH_2), 1.30 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 202.4, 167.6, 137.1, 116.04, 61.9, 49.9, 42.5, 27.92, 14.6 ppm. IR (KBr): ν = 3040, 2981, 1744, 1641, 1236 cm^{-1}.

6-(3-Butenyl)isocytosine (4). A dry two-neck flask containing guanidine carbonate (18.02 g, 0.10 mol) was flushed with nitrogen and stoppered with a septum cap. Then dry ethanol (200 mL) was added. While stirring, crude ethyl 3-oxo-6-heptenoate (from 26 g, 0.2 mol of ethyl acetoacetate) was slowly added. The reaction mixture was stirred vigorously and heated under reflux for 24 h. Part of the solvent was distilled off, and the product was precipitated by addition of water. The precipitate was filtered, washed with water, cold ethanol, and cold acetone, and dried under vacuum (13.73 g, 42%). ^1H NMR (DMSO-d_6): δ 10.74 (s, 1H, N−H), 6.54 (s, 2H, NH_2), 5.80 (m, 1H, $HC{=}CH_2$), 5.40 (s, 1H, pyrimidyl), 5.01 (m, 2H, $H_2C{=}C$), 2.3 (m, 2*2H, $2CH_2$) ppm. ^{13}C NMR (DMSO-d_6): δ 166, 164.5, 155.8, 137.7, 115.2, 100.0, 35.6, 31.5 ppm. IR (KBr): ν = 3377, 3134, 2692, 1677, 1640, 1618, 1552, 1398 cm^{-1}. Anal. Calcd for $C_8H_{11}N_3O$: C, 58.17; H, 6.71; N, 25.44. Found: C, 58.14; H, 6.68; N, 25.53. Mp: 200 °C.

6-(3-Butenyl)-2-butylureido-4-pyrimidinone (5). Butyl isocyanate (2.86 mL, 25.4 mmol) was added slowly to a solution of 6-(3-butenyl)isocytosine (**4**) (3.0 g, 18.2 mmol) in dry pyridine (36 mL). The reaction mixture was heated under reflux for 3 h. The pyridine was removed by evaporation. The crude product was recrystallized from ethanol to give 4.2 g (87%) of **5**. ^1H NMR ($CDCl_3$): δ 13.24 (s, 1H, N−H), 11.87 (s, 1H, N−H) 10.14 (s, 1H, N−H), 5.84 (s, 1H, pyrimidyl), 5.79 (m, 1H, $-HC{=}CH_2$), 5.09 (m, 2H, $CH_2{=}CH-$), 3.25 (m, 2H, J = 7.4 Hz, $N-CH_2$), 2.58 (t, 2H, J = 7.5 Hz, $Ar-CH_2CH_2$), 2.43 (m, 2H, J = 7.6 Hz, $Ar-CH_2CH_2$), 1.59 (m, 2H, J = 7.6 Hz, $N-CH_2CH_2$), 1.39 (m, 2H, J = 7.5 Hz, $N-CH_2CH_2CH_2$), 0.96 (t, 3H, J = 7.4 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 173.1, 156.6, 154.7, 151.4, 135.1, 116.9, 106.1, 39.8, 31.9, 31.5, 30.8, 20.2, 13.8 ppm. IR (KBr): ν = 3424, 2957, 1700, 1662, 1586, 1527, 1257 cm^{-1}. Anal. Calcd for $C_{13}H_{20}N_4O_2$: C, 59.07; H, 7.63; N, 21.20. Found: C, 59.26; H, 7.91; N, 21.50. Mp: 118 °C.

4-Benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine (6). Using a syringe, benzyl bromide (1.58 mL, 13.24 mmol) was added to a suspension of compound **5** (1.0 g, 3.8 mmol) and potassium carbonate (1.83 g, 13.24 mmol) in dry DMF (25 mL). The suspension was stirred vigorously at 80 °C for 24 h. Acetone was poured into the reaction mixture, the resulting suspension was filtrated, and the residue was washed with DMF and acetone. Water was then added to the filtrate. The white precipitate was filtered and washed with water. Recrystallization from ethanol/water (3:1 v/v), followed by recrystallization from hexane yielded 1.04 g (78%) of pure **6**. ^{1}H NMR ($CDCl_3$): δ 9.21 (s, 1H, NH), 7.39 (m, 5H, Ph−H) 7.13 (s, 1H, NH), 6.22 (s, 1H, pyrimidyl), 5.84 (m, 1H, $-HC{=}CH_2$), 5.33 (s, 2H, CH_2-Ph), 5.10 (m, 2H, $CH_2{=}CH-$), 3.37 (m, 2H, CH_2 butyl), 2.70 (t, 2H, $J = 7.6$ Hz, CH_2), 2.46 (m, 2H, $J = 7.6$ Hz, CH_2), 1.59 (m, 2H, $J = 7.5$ Hz, CH_2 butyl), 1.45 (m, 2H, $J = 7.5$ Hz, CH_2 butyl), 0.96 (t, 3H, $J = 7.4$ Hz, CH_3 butyl) ppm. ^{13}C NMR ($CDCl_3$): δ 170.1, 170.0, 157.4, 154.3, 136.8, 136.0, 128.6, 128.2, 115.7, 100.1, 68.2, 39.6, 36.5, 32.0, 31.8, 20.2, 13.7 ppm. IR (KBr): $\nu = 3217$, 3075, 3002, 2956, 1687, 1601, 1548, 1326, 1275 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_4O_2$: C, 67.77; H, 7.39; N, 15.81. Found: C, 67.81; H, 7.36; N, 15.88. Mp: 85 °C.

1,5-Di(4-benzyloxy-6-butyl-2-butylureidopyrimidinyl)-1,1,3,3,5,5-hexamethyl-1,3,5-trisiloxane (1-Bn). In a glovebox, a solution of 1,3,5-hexamethyltrisiloxane (6.99 g, 33.56 mmol; ABCR), compound **6** (23.92 g, 67.49 mmol), and platinum catalyst PC072 (ABCR, Gelest) (136 μL of a 2.1%−2.4% solution in xylene, ±0.0136 mmol) in toluene (135 mL) was prepared. Outside the glovebox, the solution was heated to 80 °C and stirred for 24 h under a nitrogen atmosphere. After evaporation of the solvent, the crude product was purified by column chromatography. The product was finally recrystallized from hexane to give 18.5 g (60%) of pure **1-Bn**. ^{1}H NMR ($CDCl_3$): δ 9.27 (s, 2H, N−H), 7.35 (m, 10H, Ph−H), 7.19 (s, 2H, N−H), 6.19 (s, 2H, pyrimidyl), 5.30 (s, 4H, CH_2-Ph), 3.36 (q, 4H, $N-CH_2$), 2.58 (t, 4H, $J = 7.6$ Hz, $Si-CH_2CH_2CH_2CH_2$), 1.70 (m, 4H, $J = 7.6$ Hz, $Si-CH_2CH_2CH_2$), 1.57 (m, 4H, $J = 7.3$ Hz, $N-CH_2CH_2$), 1.41 (m, 2 × 4H, $N-CH_2CH_2CH_2$ and $Si-CH_2CH_2$), 0.95 (t, 6H, $J = 7.3$ Hz, CH_3 butyl), 0.56 (t, 2H, $Si-CH_2$), 0.06 (s, 12H, $Si-CH_3$), 0.01 (s, 6H, $Si-CH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 170.1, 170.0, 157.4, 154.5, 135.9, 128.5, 128.2, 99.8, 68.0, 39.5, 37.0, 31.9, 31.8, 22.9, 20.2, 18.1, 13.7, 1.2, 0.14 ppm. IR (KBr): $\nu = 3216$, 3070, 3000, 2957, 1677, 1603, 1550, 1344, 1256, 1042, 796 cm^{-1}. Anal. Calcd for $C_{46}H_{72}N_8O_6Si_3$: C, 60.22; H, 7.91; N, 12.21. Found: C, 60.74; H, 7.98; N, 12.22. Mp: 78 °C.

1,5-Di(6-butyl-2-butylureido-4-pyrimidinoyl)-1,1,3,3,5,5-hexamethyl-1,3,5-trisiloxane (1). Compound **1-Bn** (1.8 g, 1.96 mmol), Pd/C (10 wt %; 0.3 g, 0.282 mmol), THF (60 mL), EtOH (30 mL), and acetic acid (0.1 g, 1.66 mmol) were mixed together in a Parr reactor. The reaction mixture was flushed several times with nitrogen and then with hydrogen. Then the reactor was shaken under a hydrogen atmosphere of approximately 4 atm for 24 h. After filtering off the catalyst, the solvent was evaporated. The crude product was purified by column chromatography and finally recrystallized from EtOAc to yield 1.23 g (85%) of **1**. ^{1}H NMR ($CDCl_3$): δ 13.19 (s, 2H, N−H intramolecular), 11.87 (s, 2H, N−H intermolecular) 10.15 (s, 2H, N−H), 5.81 (s, 2H, pyrimidyl), 3.23 (q, 4H, $N-CH_2$ butyl), 2.46 (t, 4H, $J = 7.5$ Hz, $SiCH_2CH_2CH_2CH_2$), 1.65 (m, 4H, $J = 7.5$ Hz, $SiCH_2CH_2CH_2$), 1.58 (m, 4H, $J = 7.3$ Hz, CH_2 butyl), 1.38 (m, 4*2H, CH_2 butyl and $SiCH_2CH_2$), 0.94 (t, 6H, $J = 7.3$ Hz, CH_3 butyl), 0.56 (t, 4H, $SiCH_2$), 0.07 (s, 12H, $SiCH_3$), 0.01 (s, 6H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 173.0, 156.6, 154.7, 152.3, 105.7, C-5, 39.8, 32.4, 31.5, 30.5, 22.7, 20.2, 17.9, 13.8, 1.3, 0.15 ppm. IR (KBr): $\nu = 3211$, 2958, 1699, 1660, 1585, 1526, 1304, 1255, 1041, 795 cm^{-1}. Anal. Calcd for $C_{32}H_{60}N_8O_6Si_3$: C, 52.14; H, 8.20; N, 15.20. Found: C, 52.25; H, 8.22; N, 15.17. Mp 112 °C.

α,ω-Di(4-benzyloxy-6-butyl-2-butylureidopyrimidinyl)poly(dimethylsiloxane) (2-Bn). This compound was prepared in a similar way as compound **1-Bn**. Starting with poly(dimethylsiloxane) bishydride (27 g, 4.5 mmol; $M_n = 6 \times 10^3$, ABCR), a product was obtained which was triturated three times with 30 mL of methanol, yielding 24.42 g (90%) of a low viscous oil which showed no impurities in ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 9.37 (s, 2H, N−H), 7.99 (s, 2H, N−H), 7.34 (m, 10H, Ph−H), 6.20 (s, 2H, pyrimidyl), 5.37 (s, 4H, CH_2-Ph), 3.41 (q, 4H, $N-CH_2$), 2.60 (t, 4H, $J = 7.6$ Hz, $Si-CH_2CH_2CH_2CH_2$), 1.72 (m, 4H, $J = 7.5$ Hz, $Si-CH_2CH_2CH_2$), 1.61 (m, 4H, $J = 7.2$ Hz, $N-CH_2CH_2$), 1.41 (m, 2*4H, $N-CH_2CH_2CH_2$ and $Si-CH_2CH_2$), 0.97 (t, 6H, $J = 7.3$ Hz, CH_3 butyl), 0.60 (t, 2H, $Si-CH_2$), 0.1 (s, m*6H, $(CH_3)_2Si$) ppm. IR (KBr): $\nu = 3224$, 3070, 3000, 2963, 1688, 1598, 1344, 1261, 1092, 803 cm^{-1}. Mp: −55 °C. Anal. Calcd for $C_{240}H_{654}N_8O_{104}Si_{100}$: C, 35.5; H, 8.1; N, 1.4. Found: C, 35.56; H, 8.40; N, 1.30.

α,ω-Di(6-butyl-2-butylureido-4-pyrimidinoyl)poly(dimethylsiloxane) (2). Compound **2-Bn** (10 g, 1.17 mmol), Pd/C (10 wt %; 0.11 g, 0.1 mmol), THF (100 mL), EtOH (50 mL), and acetic acid (0.03 g, 0.5 mmol) were mixed together and transferred into a Parr reactor. The reaction mixture was flushed several times with nitrogen and then with hydrogen. The reactor was shaken under a hydrogen atmosphere of approximately 4 atm for 24 h. After filtration of the catalyst, the solvent was evaporated. The crude product was dissolved in dichloromethane/EtOH (3:1), and then dichloromethane was evaporated. The title product precipitated at the bottom of the flask, and the upper EtOH layer was removed. After being dried under vacuum, the yield was approximately 9 g of a highly viscous oil. ^{1}H NMR ($CDCl_3$): δ 13.21 (s, 2H, N−H), 11.89 (s, 2H, N−H) 10.17 (s, 2H, Bu−N−H), 5.84 (s, 2H, pyrimidyl), 3.25 (q, 4H, $N-CH_2$), 2.47 (t, 4H, $J = 7.4$ Hz, $Si-CH_2CH_2CH_2CH_2$), 1.68 (m, 4H, $J = 7.4$ Hz, $Si-CH_2CH_2CH_2$), 1.59 (m, 4H, $J = 7.2$ Hz, $N-CH_2CH_2$), 1.41 (m, 4H, $N-CH_2$-CH_2CH_2), 1.41 (m, 4H, $Si-CH_2CH_2$), 0.94 (t, 6H, $J = 7.2$ Hz, CH_3 butyl), 0.56 (t, 4H, $Si-CH_2$), 0.06 (s, m*6H, $Si-CH_3$) ppm. IR (KBr): $\nu = 2962$, 1700, 1652, 1593, 1550, 1260, 1018, 800 cm^{-1}. Anal. Calcd for $C_{226}H_{642}N_8O_{103}Si_{100}$: C, 34.2; H, 8.2; N, 1.4. Found: C, 34.45; H, 8.23; N, 1.27.

Acknowledgment. This work has been supported by Netherlands Foundation for Chemical Research (CW) with financial aid from Netherlands Organization for Scientific Research (NOW). We thank DSM for an unrestricted research grant and K. te Nijenhuis (Delft University of Technology) for useful discussions and suggestions.

References and Notes

(1) (a) Eisenberg, A.; Hurd, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098. (b) Eisenberg, A. *Macromolecules* **1970**, *3*, 147. (c) Eisenberg, A.; King, M. *Ion Containing Polymers*; Academic Press: New York, 1977.

(2) (a) Tam, K. C.; Jenkins, R. D.; Winnik, M. A.; Basset, D. R. *Macromolecules* **1998**, *31*, 4149. (b) Semenov, A. N.; Joanny, J. F.; Khoklov, A. R. *Macromolecules* **1995**, *28*, 1066. (c) Yekta, A.; Bai, X.; Duhamel, J.; Adiwidjaja, H.; Winnik, M. A. *Macromolecules* **1995**, *28*, 956. (d) Yekta, A.; Duhamel, J.; Brochard, P.; Adiwidjaja, H.; Winnik, M. A. *Macromolecules* **1993**, *26*, 1829. (e) Walderhaug, H.; Hansen, F. K.; Abrahamsen, S.; Perssen, K.; Stilbs, P. *J. Phys. Chem.* **1993**, *97*, 8336.

(3) (a) Bica, C. I. D.; Burchard, W.; Stadler, R. *Eur. Polym. J.* **1997**, *33*, 1759. (b) Muller, M.; Dardin, A.; Seidel, U.; Balsamo, V.; Ivan, B.; Spiess, H. W.; Stadler, R. *Macromolecules* **1996**, *29*, 2577. (c) C. Hilger, M.; Dräger, R.; Stadler, R. *Macromolecules* **1992**, *25*, 2498. (d) Hilger, C.; Stadler, R. *Polymer* **1991**, *32*, 3244. (e) Abetz, V.; Hilger, C.; Stadler, R. *Makromol. Chem., Macromol. Symp.* **1991**, *52*, 131. (f) de Lucca Freitas, L.; Auschra, C.; Abetz, V.; Stadler, R. *Colloid Polym. Sci.* **1991**, *269*, 566. (g) de Lucca Freitas, L.; Stadler, R. *Colloid Polym. Sci.* **1988**, *266*, 1095. (h) de Lucca Freitas, L.; Stadler, R. *Colloid Polym. Sci.* **1988**, *266*, 1102. (i) de Lucca Freitas, L.; Stadler, R. *Makromol. Chem., Macromol. Symp.* **1988**, *26*, 451. (j) de Lucca Freitas, L.; Stadler, R. *Macromolecules* **1987**, *20*, 2478. (k) Stadler, R.; de Lucca Freitas, L. *Colloid Polym. Sci.* **1986**, *264*, 773.

(4) Lillya, C. P.; Baker, R. J.; Huette, S.; Winter, H. H.; Lin, H.-G.; Shi, J.; Dickinson, L. C.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 2076.

(5) Sartorius, J.; Schneider, H.-J. *Chem. Eur. J.* **1996**, *2*, 1446.

(6) When the imposed order of a liquid-crystalline phase is present, small telechelic hydrogen-bonded molecules may form linear reversible polymers with significant degrees of polymerization. In these mesophases, excluded-volume interactions raise the energy of the dissociation of end groups, which results in coupling between long-range order and assembly: Matsuyama, A.; Kato, T. *J. Phys. Soc. Jpn.* **1998**, *67*, 204.

(7) (a) Kotera, M.; Lehn, J.-M.; Vigneron, J.-P. *J. Chem. Soc., Chem. Commun.* **1994**, 197. (b) Gulik-Krzywicki, T.; Fouquey, C.; Lehn, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 163. (c) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254.
(8) (a) Lee, C. M.; Griffin, A. C. *Macromol. Symp.* **1997**, *117*, 281. (b) St. Pourcain, C. B.; Griffin, A. C. *Macromolecules* **1995**, *28*, 4116. (c) Lee, C. M.; Jariwala, C. P.; Griffin, A. C. *Polymer* **1994**, *35*, 4550. (d) Alexander, C.; Jariwala, C. P.; Lee, C. M.; Griffin, A. C. *Macromol. Symp.* **1994**, *77*, 283. (e) Bladon, P.; Griffin, A. C. *Macromolecules* **1993**, *26*, 6604.
(9) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761.
(10) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
(11) Yilgör, I.; McGrath, J. E. Polysiloxane Containing Copolymers; A Survey of Recent Development, 1988.
(12) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.
(13) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(14) Cates, M. E. *Macromolecules* **1987**, *20*, 2289.
(15) Below 3.3×10^4 g/mol, the viscosity of PDMS is proportional to the molecular weight, while at higher molecular weights, it is proportional to $M^{3.9}$.
(16) The model has also been applied to aqueous solutions of wormlike micelles (Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869) and to complexes of copper(II) with carboxylic acids in decalin (Dammer, C.; Maldivi, P.; Terech, P.; Guenet, J.-M. *Langmuir* **1995**, *11*, 1500).

MA981950W