

Structural and Rheological Study of a Bis-urea Based Reversible Polymer in an Apolar Solvent[†]

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Received January 9, 2002. In Final Form: March 14, 2002

The structure of a bis-urea based reversible polymer is investigated using capillary viscosimetry, infrared spectroscopy, small-angle neutron scattering, and rheology. The highly viscoelastic solutions obtained in toluene are due to the formation of long and rigid fibrillar species. The cross section of these wires is measured and is shown to likely contain two or three molecules per axial repetition unit.

Introduction

Numerous low molecular weight compounds that are able to turn a free flowing liquid into a gel-like material have been reported.¹ The increasing interest in these systems is motivated both by the current industrial applications (lubrication, cosmetics, food processing, etc.) and by the interesting fundamental questions raised by the existence of these systems, such as the structure of the assemblies at the molecular level and the consequences on the properties at the macroscopic level. On the basis of their rheological properties, these systems, which are typically composed of 99% solvent and 1% low molecular weight additive, fall into two broad categories: gels and jellies.² In this context, gels are soft solids, characterized by a high yield stress and a sharp sol-to-gel phase transition. On the opposite, jellies are viscoelastic liquids, which show a weak or no yield stress and a gradual increase of viscosity with increasing concentration or decreasing temperature. In addition, the storage modulus of jellies shows a very strong dependence on the frequency of the applied oscillatory stress. Although a lot of examples of the first category have been reported in the literature, there are very few examples of jellies in an organic medium.^{3–5}

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[†] This article is part of the special issue of *Langmuir* devoted to the emerging field of self-assembled fibrillar networks.

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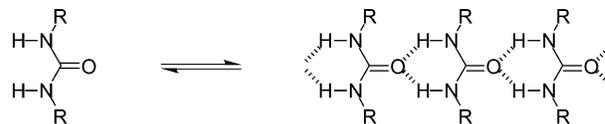
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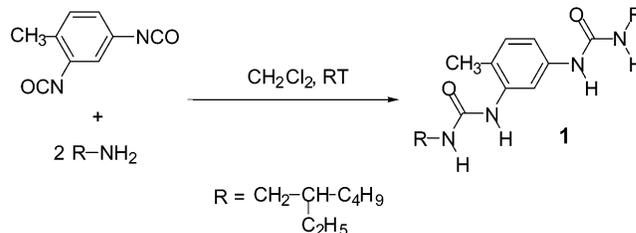
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Scheme 1



Scheme 2



To design such a jelly-forming system, we initially focused our attention on disubstituted urea compounds, which are known to form reversible polymers in solution, due to hydrogen bonding (Scheme 1).^{6,7} In the next step, the strength of the association was increased by linking two urea functions through a spacer (Scheme 2). This approach had already been exploited to design gel-forming systems.^{8–12} However, we showed that by choosing a rigid and dissymmetrical spacer, as well as branched substituents, it is possible to disturb the crystalline packing and thus obtain a bis-urea which dissolves at room temperature and forms very viscous solutions in nonpolar solvents.^{7,13} We presently report our understanding of the structure of the assemblies formed by bis-urea **1** in toluene, as

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deduced from capillary viscosimetry, infrared spectroscopy, small-angle neutron scattering, and rheology experiments.

Experimental Section

Synthesis. *Bis-urea 1.* To a stirred solution of 2,4-toluene diisocyanate (99%, Fluka, 12.7 g, 73 mmol) in 250 mL of dichloromethane (distilled over phosphorus pentoxide), 2-ethylhexylamine (Aldrich, 19.2 g, 149 mmol) in 100 mL of dichloromethane was slowly added under nitrogen. After 2 h, the precipitated bis-urea was filtered and dried. Recrystallization in ethyl acetate afforded 28.5 g of a white solid (90%), the purity of which was checked by thin-layer chromatography (TLC); mp, 185 °C (decomposition after melting). ¹H NMR (300 MHz, *d*₆-DMSO): δ (ppm) = 8.3/7.5 (s, 2H, Ar-NH), δ = 7.8 (s, 1H, Ar-H), δ = 7.1/6.9 (d, 2H, Ar-H), δ = 6.5/5.9 (t, 2H, CH₂-NH), δ = 3.0 (m, 4H, N-CH₂), δ = 2.1 (s, 3H, Ar-CH₃), δ = 1.3 (m, 18H, CH/CH₂), δ = 0.9 (t, 12H, CH₃). ¹³C NMR (75 MHz, *d*₆-DMSO): δ (ppm) = 155.4/155.3 (C=O), δ = 138.7/138.3/129.9/118.6/111.1/109.5 (Ar), δ = 41.5 (N-CH₂), δ = 39.3 (CH), δ = 30.5/28.5/23.7/22.5 (CH₂), δ = 17.2 (Ar-CH₃), δ = 14.0/10.6 (CH₃). Anal. calcd for C₂₅H₄₄N₄O₂: C, 69.40; H, 10.25; N, 12.95; O, 7.40. Found: C, 69.01; H, 10.31; N, 12.96; O, 7.72.

1-Butyl-1-methyl-3-[3-(3-butyl-3-methylureido)-4-methylphenyl]urea. To a stirred solution of 2,4-toluene diisocyanate (99%, Fluka, 12.37 g, 71 mmol) in 150 mL of dichloromethane (distilled over phosphorus pentoxide), *N*-methylbutylamine (Aldrich, 13.0 g, 149 mmol) in 250 mL of dichloromethane was added under nitrogen. After 20 h, the organic phase was washed with 200 mL of aqueous HCl (0.1 N) and then with water until neutral pH. After drying over magnesium sulfate, the crude product was purified by silica gel column chromatography with dichloromethane/ethyl acetate (30/70 v/v) as the eluent. Recrystallization in cyclohexane afforded 12.0 g of a solid (50%), the purity of which was checked by TLC; mp, 90 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) = 7.6 (s, 1H, Ar-H), δ = 7.4/7.0 (d, 2H, Ar-H), δ = 6.4/6.1 (s, 2H, Ar-NH), δ = 3.3 (q, 4H, N-CH₂), δ = 3.0 (d, 6H, N-CH₃), δ = 2.1 (s, 3H, Ar-CH₃), δ = 1.5 (m, 4H, N-CH₂-CH₂), δ = 1.3 (m, 4H, CH₃-CH₂), δ = 0.9 (m, 6H, CH₃-CH₂). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 155.6/155.5 (C=O), δ = 138.1/137.4/130.6/122.0/115.5/113.3 (Ar), δ = 49.0 (N-CH₂), δ = 34.7 (N-CH₃), δ = 30.3/20.3 (CH₂), δ = 17.2 (Ar-CH₃), δ = 14.0 (CH₃). Anal. calcd for C₁₉H₃₂N₄O₂: C, 65.49; H, 9.26; N, 16.08; O, 9.18. Found: C, 65.22; H, 9.11; N, 16.00; O, 9.67.

Bis-urea 2. The preparation was adapted from a literature procedure.¹⁴ In a three-necked round-bottom flask equipped with a condenser and a septum were placed 1-butyl-1-methyl-3-[3-(3-butyl-3-methylureido)-4-methylphenyl]urea (5.0 g, 14 mmol), toluene (50 mL, distilled over sodium), powdered sodium hydroxide (3.1 g, 77 mmol), anhydrous potassium carbonate (2.1 g, 15 mmol), and tetrabutylammoniumhydrogenosulfate (TBAH) (0.11 g, 0.32 mmol). The mixture was heated to 65–70 °C with mechanical stirring and under nitrogen for 1 h. Allyl bromide (3.75 g, 31 mmol) was then slowly added through the septum. After 2 h, the reaction mixture was cooled to room temperature and filtered. The filtrate was washed with 0.1 N aqueous HCl

Table 1. Geometrical Radius (*r*) and Linear Density (*m*_L) of the Wires, Obtained from ln(*qI*) vs *q*² Plots of SANS Data for Bis-urea 1 Solutions in *d*₈-Toluene

<i>c</i> (g/L)	<i>r</i> (Å)	<i>m</i> _L (Å ⁻¹)
0.89	13 ± 1	0.62 ± 0.18
2.0	13 ± 1	0.55 ± 0.12
4.9	13 ± 1	0.55 ± 0.12

(3 × 100 mL), followed by water (2 × 125 mL), and dried over magnesium sulfate. The crude product was purified by silica gel column chromatography with dichloromethane/ethyl acetate (40/60 v/v) as the eluent. A yellow oil (5.0 g, 83%) is recovered, the purity of which was checked by TLC. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.1/6.8 (d, 2H, Ar-H), δ = 6.7 (s, 1H, Ar-H), δ = 5.9 (m, 2H, CH=CH₂), δ = 5.0 (m, 4H, CH=CH₂), δ = 4.1/4.0 (d, 4H, N-CH₂-CH), δ = 3.1 (m, 4H, N-CH₂-CH₂), δ = 2.6/2.5 (s, 6H, N-CH₃), δ = 2.2 (s, 3H, Ar-CH₃), δ = 1.3 (m, 8H, CH₂), δ = 0.9 (t, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 161.7/161.2 (C=O), δ = 144.7/144.5/132.1/130.7/123.6/122.4 (Ar), δ = 135.4/134.9 (CH=CH₂), δ = 117.2/116.6 (CH=CH₂), δ = 54.8/54.3/50.1/49.9 (N-CH₂), δ = 36.2/35.7 (N-CH₃), δ = 29.7/20.3 (CH₂), δ = 17.7 (Ar-CH₃), δ = 14.1 (CH₃). Anal. calcd for C₂₅H₄₀N₄O₂: C, 70.06; H, 9.41; N, 13.07; O, 7.47. Found: C, 69.19; H, 9.44; N, 12.93; O, 8.45.

The synthesis of mono-urea **3** has been reported previously.⁷

Sample Preparation. The solutions were prepared at room temperature, under stirring for at least 1 night. The solvent (toluene, analytical grade) was used as received.

Capillary Viscosimetry. Measurements were performed at 25 ± 0.1 °C with a Cannon-Manning semimicro viscometer. Toluene solutions were not filtered, because of their high viscosity.

Rheology. Measurements were performed on a strain-controlled rheometer, a Rheometric RFSII equipped with cone and plate geometry (diameter, 50 mm; angle, 0.04 rad), at 25 °C. The samples were protected by a homemade cover to prevent solvent evaporation. Each measurement was repeated twice to ensure reproducibility (better than 5%). The mechanical history of the samples was the following: first, a strain sweep at fixed frequency (1 Hz) allowed determination of the linear viscoelastic regime. This measurement was stopped before reaching the early beginning of the nonlinear regime. Then the loss (*G*'') and elastic (*G*') moduli were measured in the linear viscoelastic regime (strain, γ = 10%) in a pulsation range from 0.1 to 100 rad/s.

IR Spectroscopy. Infrared spectra were recorded at 20 °C on a Nicolet FT-IR 320 spectrometer in KBr cells of 0.05–0.3 cm path lengths.

SANS. Measurements were made at the ILL (Grenoble, France) on the D11 instrument, at three distances to cover the 3 × 10⁻³ to 0.3 Å⁻¹ *q*-range, where the momentum transfer *q* is defined as usual for purely elastic scattering as *q* = (4π/λ) sin θ, and θ is half the scattering angle. Data were corrected for the empty beam signal, and a light water standard was used to normalize the scattered intensities. Standard programs were used for the transmission, background corrections, and radial averaging procedure of the 2-D scattering patterns. A uniform scattering length density profile (step function) was assumed for the fibrillar scatterers. The specific contrast ($\Delta\bar{b}$) of bis-urea **1** in *d*₈-toluene was calculated as $\Delta\bar{b} = b_2 - \rho_s v_2$, where *b*₂ is the calculated scattering length of bis-urea **1** (*b*₂ = 7.08 × 10⁹ cm g⁻¹), ρ_s is the calculated scattering length per unit volume of *d*₈-toluene ($\rho_s = 5.64 \times 10^{10}$ cm cm⁻³), and *v*₂ is the specific volume of bis-urea **1**, which was measured using a helium pressure densitometer Accupyc 1330 (Micromeritics) (*v*₂ = 0.942 cm³ g⁻¹ at 25 °C). The parameters given in Table 1 were determined by linear regression of the data in a ln(*qI*) versus *q*² plot.

Results and Discussion

Bis-urea **1** was synthesized in high yield (90% after recrystallization) by condensation of commercially available 2,4-toluenediisocyanate with 2-ethylhexylamine (Scheme 2). To compare the properties of bis-urea **1** to those of a nonassociating model compound, bis-urea **2** was synthesized in two steps (Scheme 3). Bis-urea **2** has

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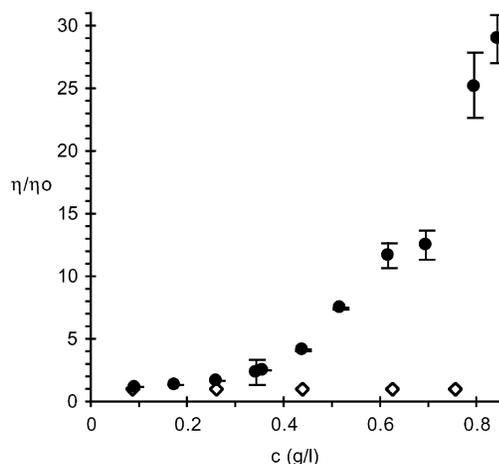
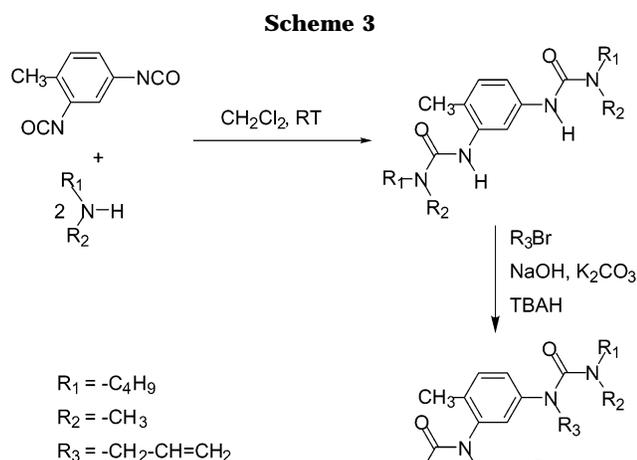


Figure 1. Reduced capillary viscosity versus concentration for solutions of bis-urea **1** (●) and bis-urea **2** (◇) in toluene, at 25 °C.



approximately the same molecular weight as **1** but cannot self-associate by hydrogen bonding because all the hydrogen atoms of the N–H groups have been replaced by aliphatic groups.

At low concentrations ($c \leq 1$ g/L), it is possible to measure the viscosity of solutions of **1** in toluene by capillary viscosimetry. Figure 1 shows that the relative viscosity increases steadily with concentration. At 0.8 g/L only, bis-urea **1** is responsible for a 30-fold increase of the viscosity of the solvent. By contrast, the increase in viscosity due to nonassociating bis-urea **2** is negligible. It is thus shown that the high viscosity of solutions of **1** is indeed due to intermolecular interactions.

The nature of the intermolecular interactions responsible for these remarkable rheological properties was examined by Fourier transform infrared (FTIR) spectroscopy. Figure 2a shows a part of the IR spectra of solutions of bis-urea **1** in toluene: the only feature is a large band centered at 3300 cm^{-1} , which can be assigned to hydrogen-bonded N–H groups. No significant band characteristic of free N–H groups can be detected down to a concentration of 0.2 g/L. This result confirms the fact that the high viscosity is due to intermolecular associations. Moreover, these spectra can be compared to those obtained under the same conditions, for solutions of mono-urea **3** (Chart 1). Figure 2b exhibits two main bands characteristic of hydrogen bonded N–H groups (3330 cm^{-1}) and free N–H groups (3430 cm^{-1}). At concentrations lower than 0.6 g/L

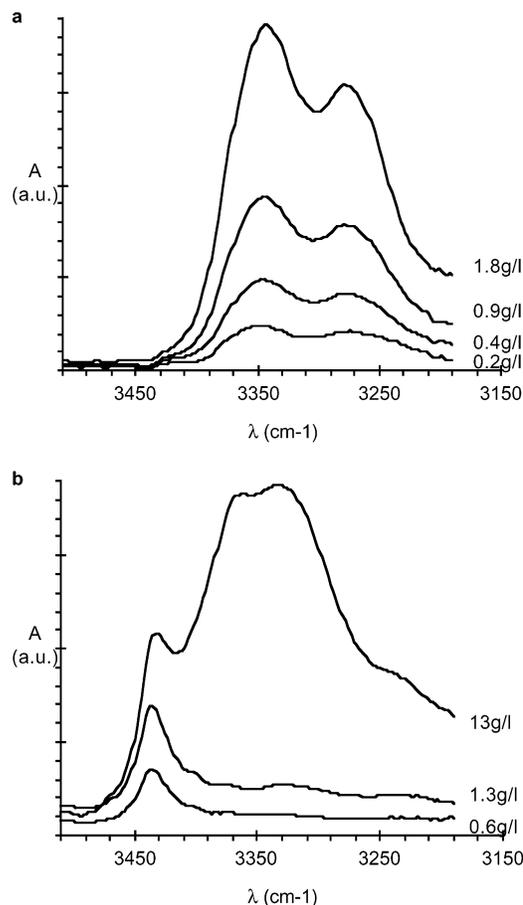
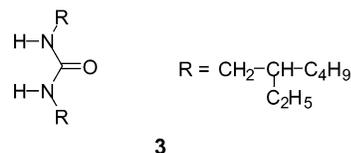


Figure 2. Part of the IR spectra of solutions of bis-urea **1** (a) and mono-urea **3** (b) in toluene, at 20 °C.

Chart 1



(2×10^{-3} mol/L), mono-urea **3** is totally dissociated, whereas at 0.2 g/L (10^{-3} mol/L of urea functions), bis-urea **1** is negligibly dissociated. This proves that the association of bis-urea **1** is highly cooperative, in the sense that the association of the first urea function of a bis-urea molecule favors the association of the second urea function of the same molecule. In other words, associations of the two urea functions of a bis-urea molecule are correlated, which rules out the formation of a random network reversibly cross-linked through the association of single urea functions.

Small-angle neutron scattering (SANS) is ideally suited to analyze the local structure of such jellies or gels.² Figure 3 shows the scattered intensity of solutions of bis-urea **1** at different concentrations in deuterated toluene. A specific qI versus q representation for fibrillar aggregates is used, where I is the intensity and q is the momentum transfer. At these concentrations ($0.9 \leq c \leq 5$ g/L), the scattered intensity is characterized at low angles by a q^{-1} dependence covering more than 1 decade. At larger angles, a sharp intensity decay can be seen, followed by the minimum of the first oscillation of the form factor. These scattering features are typical of long fibrillar scatterers. The characteristic dimensions of the scatterers can be deduced from a fit according to eqs 1 and 2, which are valid for long

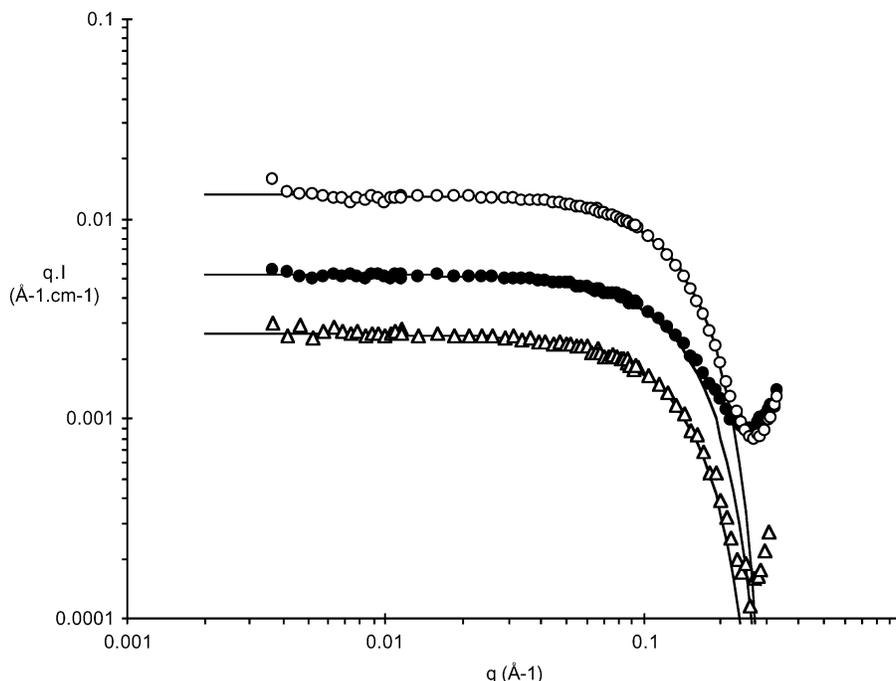


Figure 3. SANS curves of solutions of bis-ureas **1** in d_8 -toluene at 4.9 g/L (○), 2.0 g/L (●), and 0.89 g/L (△), at 22 °C. The curves correspond to eq 1; the parameter values are listed in Table 1.

and rigid isolated fibrillar species with a circular cross section and a uniform scattering length density profile.^{3c}

$$I = \frac{\pi c \overline{\Delta b^2} M_L}{q} \left[2 \frac{J_1(qr)}{qr} \right]^2 \quad (1)$$

$$(qI)_{q \rightarrow 0} = (qI)_0 \exp\left(-\frac{r^2 q^2}{4}\right) \quad (2)$$

c is the rod concentration (g cm^{-3}), M_L is the mass per unit length of the rod (g Å^{-1}), Δb is its specific contrast, r is the radius of the cross section, and J_1 is the Bessel function of first kind. The fit was performed at each concentration with M_L and r as adjustable parameters. Figure 3 shows the satisfying quality of the fit, which indicates that the geometrical model described by eqs 1 and 2 is relevant. The values of the fit parameters are given in Table 1. Over the concentration range under study, the cross section and the linear density n_L of the fibrillar species remain constant ($r = 13 \pm 1 \text{ Å}$, $n_L = M_L N_a / M_0 = 0.55 \pm 0.12 \text{ Å}^{-1}$, where M_0 is the molecular weight of bis-urea **1** and N_a is the Avogadro constant). To interpret these values, assumptions concerning the molecular packing have to be made. If the fibrillar species are more or less straight monomolecular wires (that is, if the cross section contains one molecule), then the value of the linear density means that the distance between two adjacent molecules is $d = 1/n_L = 1.8 \pm 0.5 \text{ Å}$. This extremely low value is unrealistic, which means that the wires cannot be straight and monomolecular. Moreover, a monomolecular helix wrapped around the rod axis would have a radius on the order of the overall length of bis-urea **1** (25 Å), which is twice as much as the measured radius of the wire (13 Å). Now, if the fibrillar species are bimolecular wires (that is, if the cross section contains two molecules), then the distance between two adjacent molecules is $d = 2/n_L = 3.6 \pm 1.1 \text{ Å}$. This value is more realistic and compares favorably with the measured distance between two hydrogen-bonded urea groups in 1,3-dimethylurea crystals

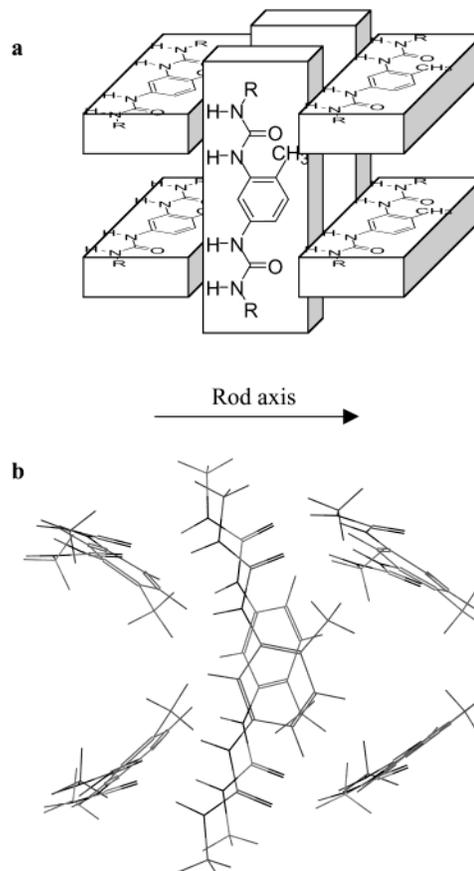


Figure 4. Tentative bimolecular wire structure proposed for bis-urea **1**. Schematic representation (a) and computer simulation performed with Insight II software (b). Ethylhexyl substituents are replaced by methyl groups for clarity.

(4.6 Å).¹⁵ If the fibrillar species are trimolecular wires, then the distance between two adjacent molecules is $d =$

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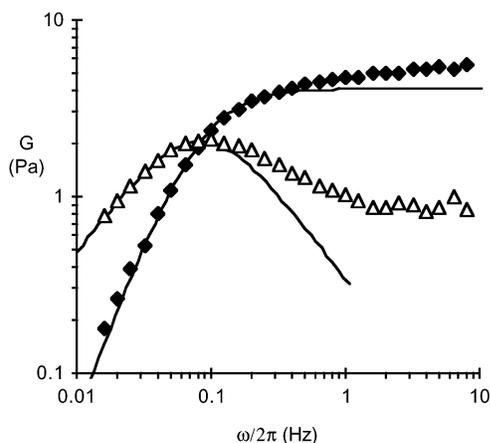


Figure 5. Storage modulus G' (\blacklozenge) and loss modulus G'' (\triangle) versus frequency of a 2 g/L solution of bis-urea **1** in toluene, at 25 °C. The curves correspond to fits according to the Maxwell model.

$3/n_L = 5.5 \pm 1.5 \text{ \AA}$, which is also possible. Finally, if the cross section contains four molecules, then the distance between two adjacent molecules is $d = 4/n_L = 7.3 \pm 2.0 \text{ \AA}$, which is very large and makes it difficult to imagine a corresponding hydrogen-bonded structure. Consequently, according to the SANS results, bis-urea **1** in toluene forms long and rigid fibrillar species which likely have a bimolecular or trimolecular cross section. Figure 4 shows a tentative bimolecular wire structure, which is compatible with the present results.

Then, the rheological properties of these fibrillar species were examined. Figure 5 shows the frequency dependencies of the storage (G') and loss (G'') moduli for a 2 g/L solution of **1** in toluene. At low frequencies, the mechanical response of the sample is dominated by the loss modulus. In this frequency range, $G' \sim \omega^2$ and $G'' \sim \omega$. This behavior is expected for liquidlike systems. At higher frequencies, G' is predominant and reaches a plateau value, whereas the frequency dependence of G'' passes through a minimum. The experimental data can partially be fitted with the so-called Maxwell model, which represents the behavior typical of a viscoelastic liquid presenting a single relaxation time, τ .

$$G'(\omega) = G_0 \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \quad (3)$$

$$G''(\omega) = G_0 \frac{\omega\tau}{1 + (\omega\tau)^2} \quad (4)$$

where G_0 is the plateau modulus. The solid lines in Figure

5 represent the best fits to eqs 3 and 4, where G_0 and τ have been used as adjustable parameters. The derived values are $G_0 = 4.1 \text{ Pa}$ and $t = 12 \text{ s}$. Since we know from SANS experiments that bis-urea **1** forms long wires in toluene solutions, the viscoelastic behavior could be due to reversible cross-links between the wires. These reversible cross-links could, for instance, result from a small amount of noncooperative hydrogen bond formation between wires. However, such reversible cross-links are not necessary to explain the rheological properties, which could simply be the result of entanglements of long and reversible wires. Indeed, the wires, which are formed by hydrogen bonding of small molecules and which have a small cross section, can be expected to be reversibly breakable. Moreover, Maxwellian behavior has been demonstrated and attributed to entanglements of long fibrillar species in the case of lecithin reverse micelles⁵ and wormlike surfactant micelles.¹⁶ The dynamics of such transient networks of entangled reversible polymers has also been theoretically studied.¹⁷ The deviation from the Maxwell model, observed at high frequencies for G'' , might be attributed to the contribution of Rouse modes to the overall dynamics of the system. Additional rheological experiments are necessary to test if the present system obeys all the characteristics of reversible polymers. However, the pseudo-Maxwellian behavior, the low value of the plateau modulus, and the regular increase of viscosity with concentration show that bis-urea **1** in toluene can be described as a jelly rather than as a gel, as defined in the Introduction.

Conclusion

Bis-urea **1** solutions in toluene present remarkable rheological properties at relatively low concentrations, which are unusual for low molecular weight solutes. The formation of these viscoelastic solutions is due to strong hydrogen bond interactions, which organize the bis-urea molecules into long and rigid fibrillar species. The cross section of these fibrillar species likely contains two or three molecules per axial repetition unit. The reversible association of the building blocks as well as the thin and linear wirelike structure of this supramolecular system makes it possible to call it a reversible polymer.¹⁸

Acknowledgment. ILL is acknowledged for providing access to the SANS experiment. Dr. M. Latroche is thanked for assistance with density measurements.

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