

Reversible polymers from self-complementary monomers, using quadruple hydrogen bonding

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**Reversible Polymers Formed from Self-Complementary Monomers Using
Quadruple Hydrogen Bonding**



Rint P. Sijbesma; Felix H. Beijer; Luc Brunsveld; Brigitte J. B. Folmer; J. J. K. Ky
Hirschberg; Ronald F. M. Lange; Jimmy K. L. Lowe; E. W. Meijer

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blocked and zonal flows in atmospheric observations. The absence of baroclinic instabilities in our annulus [compare with (18), for instance], and the greater stability of the experimental zonal flow (12) is presumably the cause of this discrepancy.

We conjecture that in the experiment, there are two basins of attraction, zonal and blocked (12, 15), connected by heteroclinic orbits. Similar switches between flow regimes—characterized there by distinct wavenumbers—have been observed in the thermally driven annulus, even in the absence of topography (28). Chaotic itinerancy (16, 29) provides a plausible scenario for such sporadic transitions; confirmation of such a scenario is left for further experiments and numerical simulations (30).

In the intermediate regime of Fig. 4, the fraction of time spent in one state varied as a function of the Rossby number (Fig. 5B). Similarly, as the pole-to-equator temperature gradient changes—from season to season or year to year in the same season (8, 12, 15, 16, 26, 27)—the relative prevalence of zonal- or blocked-flow episodes can change. Our results and idealized barotropic models (12) agree in that the frequency of blocking events increased when approaching the parameter range where blocking is the stable regime [see also (15)]. The seasonal and interannual variability of persistent nonzonal flow patterns, such as blocking, in the atmosphere is subtler and has been documented to some extent in the Pacific–North American sector, for both observations and general circulation models (31).

Our results provide new criteria by which topographic effects on low-frequency atmospheric, oceanic, and laboratory flows can be distinguished from thermal- and eddy-forcing effects.

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Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding

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Units of 2-ureido-4-pyrimidone that dimerize strongly in a self-complementary array of four cooperative hydrogen bonds were used as the associating end group in reversible self-assembling polymer systems. The unidirectional design of the binding sites prevents uncontrolled multidirectional association or gelation. Linear polymers and reversible networks were formed from monomers with two and three binding sites, respectively. The thermal and environmental control over lifetime and bond strength makes many properties, such as viscosity, chain length, and composition, tunable in a way not accessible to traditional polymers. Hence, polymer networks with thermodynamically controlled architectures can be formed, for use in, for example, coatings and hot melts, where a reversible, strongly temperature-dependent rheology is highly advantageous.

Noncovalent interactions are increasingly being used in the molecular self-assembly of well-defined supramolecular structures and materials. Such interactions are important in polymer science, where hydrogen bonding and other weak reversible interactions are important in determining polymer prop-

erties and in the design of new polymer architectures (1, 2). However, the interactions used always rely on the cooperative phenomenon of many weak interactions, which lack directionality, giving rise to microphase-separated structures or gelation due to network formation (3). For linear supramolecular polymers (4), it is a prerequisite to have strong and highly directional, reversible interactions in order to construct materials that include a reversible alternative for the covalent bond. This concept has been known for years (5–13), but polymers with appreciable degrees of polymerization in the amorphous state or even in

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dilute solution have not been obtained because it was not known how to incorporate such sufficiently strong, but still reversible, interactions. Efforts to use highly directional multiple hydrogen bonds have been hampered mainly by the insufficient stability of single (6–9), double (10, 11), or triple (12, 13) hydrogen bonds and the difficult preparation of the strongest couples (14), and coordination of metal ions has limited reversibility and tunability (5).

Our recent finding (15) that derivatives of 2-ureido-4-pyrimidone **1** (Fig. 1A) are easy to synthesize and dimerize strongly (dimerization

constant $K_{\text{dim}} > 10^6 \text{ M}^{-1}$ in CHCl_3), by means of a self-complementary DDAA (donor-donor-acceptor-acceptor) array of four hydrogen bonds, prompted us to use this functionality as the associating end group in reversible self-assembling polymer systems (Fig. 1B). Compounds **2a** and **2b**, synthesized as shown in Fig. 2, form viscous solutions in CHCl_3 ; the viscosity is highly concentration- and temperature-dependent. A plot of the logarithm of the specific viscosity (η_{sp}) against the logarithm of the concentration is linear for **2a** with a slope of 3.76 (Fig. 3A). The constant high slope of the plot suggests

that, over the concentration range studied, the viscosity of **2a** follows Cates's model for reversibly breakable polymers above the overlap concentration (16). The closely related **2b**, however, displays viscosity with a completely different concentration dependence (Fig. 3A). At low concentrations, the viscosity is low and the plot has a slope of approximately 1. Above $100 \text{ g} \cdot \text{liter}^{-1}$, the plot curves upward to a slope of more than 6. In static light-scattering experiments of $32 \text{ g} \cdot \text{liter}^{-1}$ solutions of **2a** and **2b** in CHCl_3 , the Rayleigh ratio at a scattering angle of 90° (R_{90}) for **2a** is 3.5 times higher than for **2b**. Proton nuclear magnetic resonance (^1H

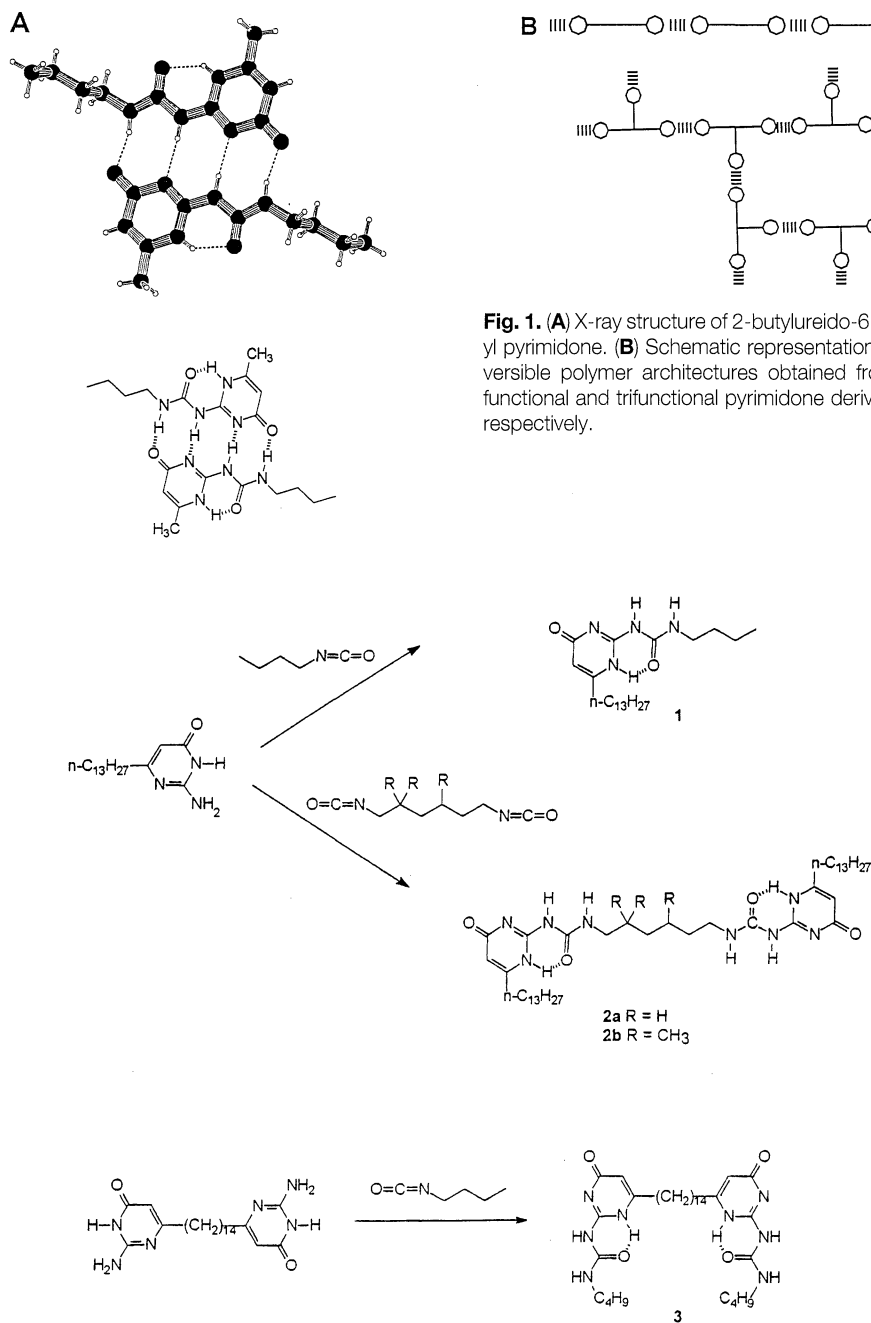
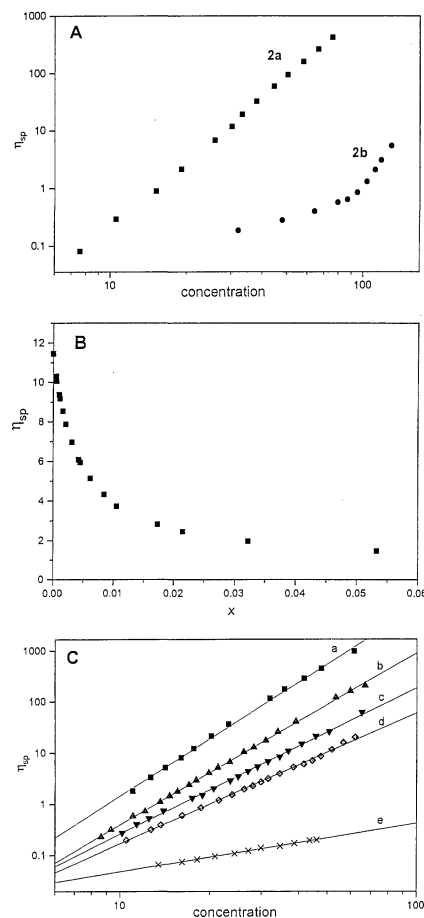


Fig. 2. Synthesis of monofunctional 2-ureido-pyrimidone **1**, bifunctional derivatives **2a**, **2b** (prepared with a commercial mixture of 2,2,4- and 2,4,4- trimethylhexanediiisocyanate isomers), and **3**.



NMR) studies in CDCl_3 show that at concentrations below $100 \text{ g} \cdot \text{liter}^{-1}$, multiple sets of signals are present for **2b**, whereas one set of signals predominates for higher concentrations of **2b** and concentrations down to $5 \text{ g} \cdot \text{liter}^{-1}$ for **2a**. These results are in agreement with the proposal of an equilibrium between linear polymeric and oligomeric cyclic structures. Because of restricted conformational freedom, **2b** is more prone to the formation of rings than **2a**.

We confirmed the unidirectionality of the hydrogen bonding by adding monofunctional compound **1**, which can act as a chain stopper, to solutions of **2**. A dramatic drop in viscosity was observed when very small amounts of **1** were added to **2a** (Fig. 3B). Compound **1** (mole fraction x) limits the number-average degree of polymerization (DP) to at most $\text{DP}_{\text{max}} = 2/x$. Fitting (17) of the data presented in Fig. 3B affords an estimate for the DP of **2a** of 7×10^2 at 40 mM, which corresponds to an average molar mass of $\sim 5 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$. This observation shows that the association process is reversible and that no uncontrolled multidirectional gelation occurs.

We combined the concentration-dependent viscosity of the self-assembled polymers and the use of chain stoppers, such as **1**, in studying the solution properties of **3**, in which the association units are linked at the 6-posi-

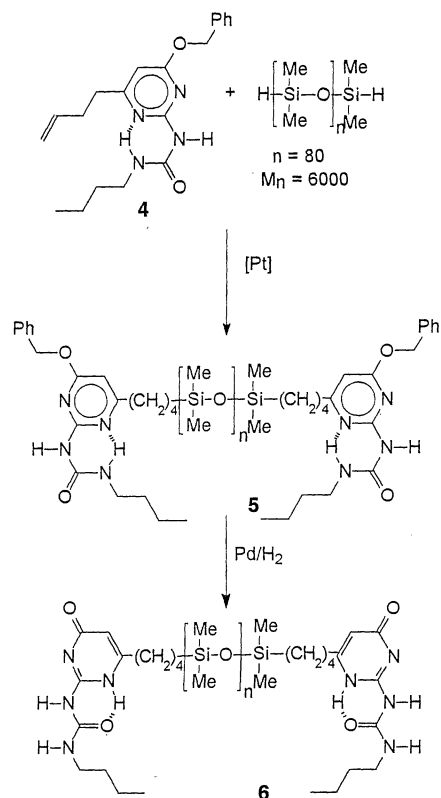


Fig. 4. Synthesis of bifunctional compounds **5** and **6** from precursor **4**; Ph, phenyl; Me, methyl; M_n , number-average molecular weight.

tion of the isocytosine ring (Fig. 2). Remarkably, the plots are linear for all ratios of monofunctional to bifunctional molecules, whereas the slope of the plots gradually decreases with increasing amount of chain stopper (Fig. 3C).

The results presented above are in full agreement with concepts worked out by Flory for condensation polymers (18), but these structures have a reversible nature because of the limited lifetime of their bonding. The chain stopper experiment is completely anal-

ogous to the way the molar mass of a condensation polymer is limited by the addition of monofunctional compounds, and the ratio of cyclic versus linear species is controlled by the structure of the monomer and the concentration. On the other hand, the molar masses of these polymers are very high compared to the values for normal condensation polymers, as a result of the self-complementarity, the lack of reaction products in polymer formation, and the high dimerization constants. Because of

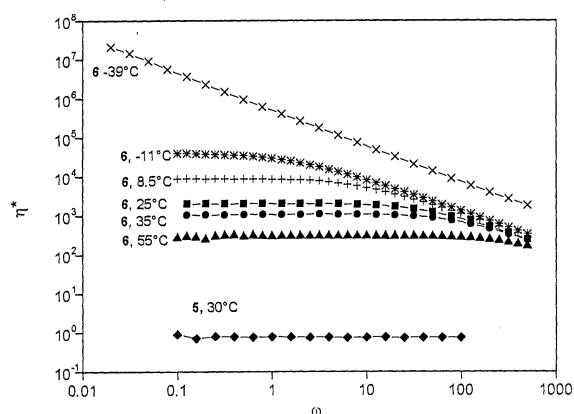


Fig. 5. Complex viscosity η^* (pascal · seconds) of compounds **5** and **6** versus frequency ω (radians per second) of applied strain at different temperatures. Data were collected in small oscillatory deformation experiments.

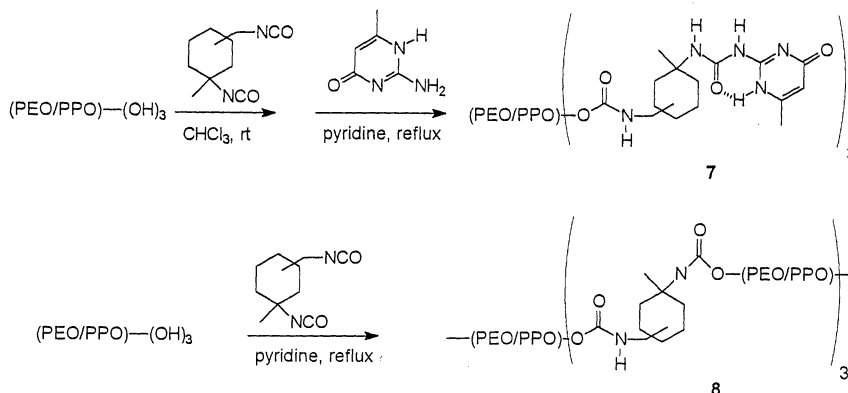


Fig. 6. Synthesis of compounds **7** and **8**; rt, room temperature; $(\text{PEO}/\text{PPO})-(\text{OH})_3$ is a block copolymer of poly(ethylene oxide) and poly(propylene oxide) with three hydroxyl end groups and a molecular weight of $6 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$. This polymer, the diisocyanate, and methylisocytosine are commercially available materials.

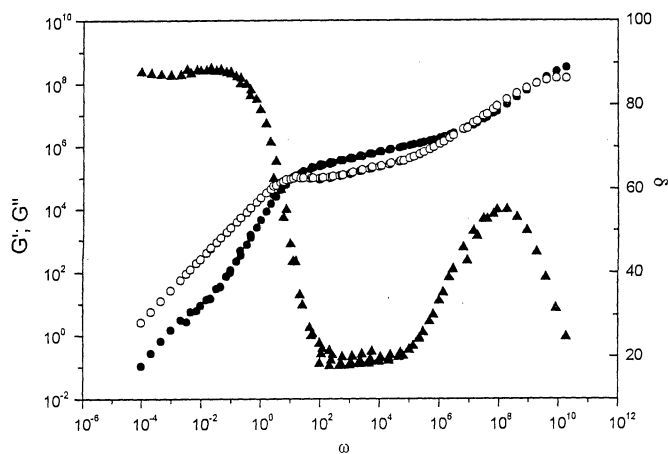


Fig. 7. Mechanical spectra of compound **7**. Master curves of the storage modulus G' (●) (pascals), the loss modulus G'' (○) (pascals), and phase angle δ (▲) (degrees) versus frequency ω (radians per second) of applied strain, obtained by the superposition of curves obtained at different temperatures. Reference temperature is 30°C . Data were collected with small oscillatory deformation experiments.

the limited and tunable lifetime of the hydrogen bonds, the material is always in its thermodynamically most favorable configuration and the reversibility of the bonding permits the material to immediately adjust its configuration to external stimuli.

The bulk viscoelastic properties of reversible polymers of the kind described above are of interest for possible applications as materials. For compounds **2a**, **2b**, and **3**, however, these properties were difficult to study because of the history-dependent phase behavior and the tendency of these compounds to crystallize. Therefore, we investigated the properties of compound **6** with siloxane spacers (Fig. 4). The synthesis makes use of a protected compound **4**, which is regarded as a useful synthon for a large number of structures.

Neat compound **6** (number-average molecular weight M_n of the monomer is 8×10^3) shows shear thinning and polymer-like viscoelastic behavior, whereas its synthetic precursor **5** behaves in a purely Newtonian fashion (Fig. 5). The zero shear viscosity of **6** at 30°C is 1000 times the viscosity of **5** and is comparable to the value for unfunctionalized poly(dimethylsiloxane) with $M_n = 3 \times 10^5$. The strong temperature dependence of the viscosity of **6** is ascribed to an increased rate of chain-breaking as well as to increasing the dissociation at higher temperatures. To our knowledge, the thermoplastic behavior of **6** is unprecedented for self-assembled structures.

We extended our study to reversible networks that are always in their thermodynamically determined architecture. Reversible polymer networks were obtained from trifunctional copolymers of propylene oxide and ethylene oxide by functionalization with (isocyanatomethyl) methylcyclohexylisocyanate, followed by reaction with methylisocytosine (Fig. 6). Compound **7** has a plateau modulus of 5×10^5 Pa (Fig. 7), six times the plateau modulus of covalently cross-linked copolymer **8**. The phase angle of **7** shows a frequency-dependent transition from purely viscous to viscoelastic behavior (Fig. 7), whereas **8** is viscoelastic across the whole frequency range. If we may assume that the relaxation of **7** is described by a pure Maxwell element, the relaxation time at 30°C, determined at a phase angle of 45°, is estimated to be 0.1 s. This value agrees with NMR experiments of the lifetime of dimers of **1** and the mechanical properties of linear polymers **6**.

The higher plateau modulus of **7** compared to **8** and the frequency dependence of **7** shows that the reversible cross-links in **7** behave like entanglements in an ordinary linear polymer. The reversibility of the hydrogen bonds allows the molecules of **7** to assemble into a more dense, thermodynamically determined network, whereas the cross-links in **8** are irreversibly formed to yield a kinetically determined network.

The polymers assembled by well-defined dimerization of the quadruple hydrogen-bonded ureido-pyrimidone functionality have unique features that distinguish them from existing systems. Because of the high association constant, the linear polymers **2a** and **3** have DPs far exceeding those of existing self-assembled systems based on less than four hydrogen bonds. Polymer-like behavior is thus observed even in semidilute solution. At the same time, the directionality of the interaction prevents microphase separation through crystallization in the bulk material or gel formation in solution. Particularly in the reversible networks, the absence of unspecific aggregation means that a high level of control over the network architecture is possible, because the degree of association, the degree of branching, and the distance between cross-links can all be tuned through chemical modification of the spacers and by variation of the hydrogen-bonding functionality. As a result, polymer networks can be developed with thermodynamically controlled architectures, for use in hot melts and coatings, where a reversible, strongly temperature-dependent rheology is highly desirable.

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17. Assuming that the association constant of functional groups is independent of DP, we derived the following equation:

$$DP = \frac{2 \cdot ([2] + [1])}{[1] - \frac{1}{4K_{dim}} \left[1 - \sqrt{1 + 8K_{dim}([1] + 2 \cdot [2])} \right]}$$

where the brackets denote concentration. When an exponential relation between η_{sp} and DP is assumed, the values of K_{dim} and the exponent in DP that give the best fit to the data are $\eta_{sp} \approx (DP)^{0.78}$ and $K_{dim} = 2.2 \times 10^6$.

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19. We thank J. Palmen and M. van Gorp (DSM Research) for performing mechanical measurements. The x-ray structure determination of 2-butylureido-6-methyl pyrimidone was performed by H. Kooijman and A. L. Spek (Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University).

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Two-Dimensional Melting of an Anisotropic Crystal Observed at the Molecular Level

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A distinctive two-dimensional (2D) melting transition occurring at nearly 100 degrees Celsius (°C) has been observed in Langmuir-Blodgett films by in situ atomic force microscopy (AFM). A 2D orthorhombic crystal phase melted to a 2D smectic phase at about 91°C. The smectic phase was characterized by 1D molecular periodicity with short-range correlations (about 40 angstroms). At 95°C, the smectic order melted to form a hexatic phase. Infrared spectroscopy measurements were consistent with the AFM observations. These observations support the dislocation-mediated melting scenario for an anisotropic 2D crystal predicted by Ostlund and Halperin. A longer wavelength height modulation was also observed in the smectic and hexatic phases.

In the late 1970s, Halperin, Nelson, and Young (1) built upon the ideas of Kosterlitz and Thouless (2) to describe melting in two dimensions. Before melting to an isotropic

liquid, a hexagonal crystal was predicted to pass through an intermediate "hexatic" phase that retained the sixfold orientational order of the crystal without long-range translational order. The proposed mechanism for the crystal-to-hexatic transition was the unbinding of pairs of lattice dislocations with opposite Burger's vec-

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