Photo-induced depolymerization of reversible supramolecular polymers

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The degree of polymerization of supramolecular polymers based on quadruple hydrogen bonding of 2-ureido-4-pyrimidone units is decreased upon the photochemical formation of reversibly interfering end-caps.

Photo-induced processes to control the molecular weight of polymers are well-known and used in many advanced applications, like coatings and photolithography.[1–3] In all of these processes, the photochemical event changes the molecular structure by either polymerization of monomers, the cross-linking of polymers, the depolymerization of polymers or the side-chain modifications of polymers by, for example, the photo-induced formation of initiators or catalysts. The changes in the chemical composition of the material and, hence, in properties like solubility or viscosity, are the result of the breaking or making of covalent bonds of the polymer.

Recently, we introduced the concept of using quadruple hydrogen bonding to prepare reversible supramolecular polymers.[4] Linear polymers **1** (Fig. 1) are formed by the self-assembly of two 2-ureido-4-pyrimidone units, which dimerize strongly in solvents like $CHCl_3$ and in the solid state with dimerization constants (K_{dim}) exceeding 10^6 M^{-1}. The polymers obtained exhibit true polymer properties illustrated by high solution viscosities, shear thinning in the melt and viscoelastic properties of the neat materials. The reversibility of the supramolecular polymers, with degrees of polymerization (DP) of more than 500, is demonstrated by experiments where monofunctional 2-ureido-4-pyrimidone **2** is added as a chain stopper to polymer **1**. A rapid exchange controls the DP, leading to a strong decrease in viscosity upon addition of **2** to **1**. This control of DP resembles the way the DP of condensation polymers is tuned,[5] but now in an unprecedented rapid way under ambient conditions.

Here we report on the photo-induced generation of chain stopper **2**, and how the viscosity of the solution of supramolecular polymer **1** is triggered by a photochemical process (Scheme 1). We designed precursor **3**, being the *o*-nitrobenzyl ether protected derivative of chain stopper **2**. This protecting group is well-known for its clean cleavage upon UV irradiation,[6] by which compound **3** is converted into chain stopper **2** (Scheme 2).

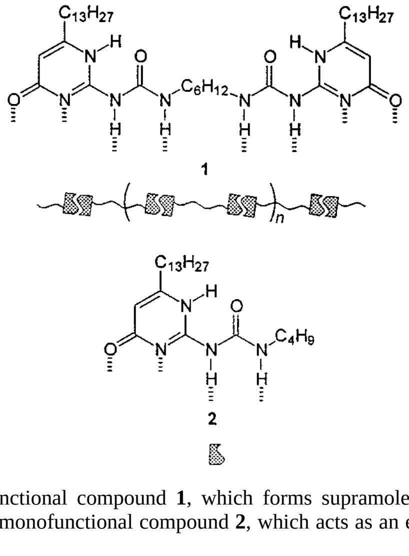
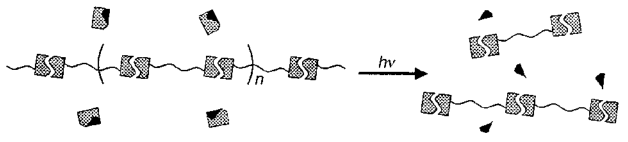


Fig. 1 Difunctional compound **1**, which forms supramolecular polymer chains, and monofunctional compound **2**, which acts as an end-cap



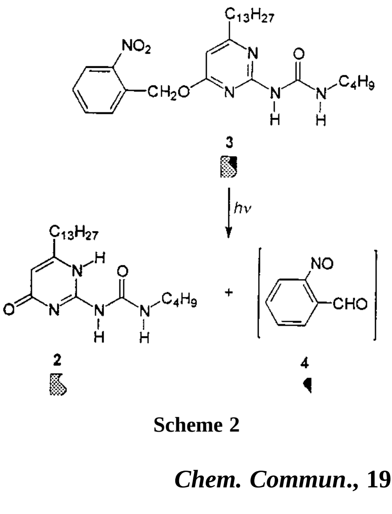
Scheme 1

Compound **3** was prepared by the reaction of *o*-nitrobenzyl chloride with **2**, that in turn was made by the reaction of butyl isocyanate with the corresponding isocytosine. Bifunctional compound **1** was prepared by the reaction of the same isocytosine and hexane-1,6-diyl diisocyanate following a procedure published previously.[4] When **1** is more than 99.9% pure, a DP of around 700 is obtained and a 40 mM solution of **1** in $CHCl_3$ exhibits a η_{rel} of 13.16.

The photolability of **3** was investigated by UV irradiation of a 9.9 mM solution of **3** in $CDCl_3$.‡ The progress of the deprotection was readily monitored *via* ^1H NMR spectroscopy; the H-5 signal of pyrimidine **3** at δ 6.25 decreased in intensity as the upfield H-5 signal of pyrimidone **2** at δ 5.81 increased. Also the characteristic NH signals of **2**, downfield in comparison to the NH signals of **1** due to dimerization, appear upon formation of **2**.

The photogeneration of **2** (0.1 equiv.) in the presence of polymer **1** was monitored *via* viscosity measurements (η_{rel} in $CDCl_3$), as presented in Fig. 2. The addition of 0.1 equiv. of precursor **3** produced a small decrease in the viscosity (η_{rel} went from 13.16 to 10.79) *versus* the enormous drop in viscosity (η_{rel} went from 13.16 to 1.92) upon the addition of 0.1 equiv. of chain stopper **2**. After 2 h irradiation of the mixture of **1** and **3**, the η_{rel} is similar to the η_{rel} of a solution of **1** and 0.1 equiv. of chain stopper **2**. The shape of the plot of the decrease in η_{rel} with time is consistent with the monoexponential formation of **2** from **3** and the way **2** directly affects the DP of **1**.

In order to check for artefacts in the approach used, we have performed a number of reference experiments. A decrease in



Scheme 2

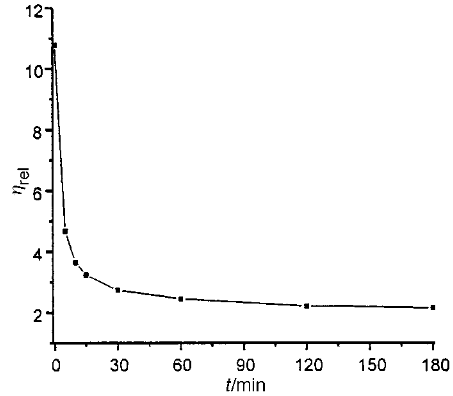


Fig. 2 Relative viscosity of a 40 mM solution of **1** with 0.1 equiv. of **3** in $CHCl_3$ upon UV irradiation

η_{rel} from 13.16 to 12.83 was found after 4 h irradiation of **1** without end-caps. The addition of 0.1 equiv. of *o*-nitrobenzyl ether protected phenol to a solution of **1** in $CDCl_3$ followed by UV irradiation for 3 h resulted in a decrease in η_{rel} from 13.16 to 8.46, while the addition of 0.1 equiv. of phenol to a 40 mM solution **1** in $CDCl_3$, resulted in a relative viscosity of 11.00. Hence, the large decrease in viscosity of the photoactive system is mainly caused by the formation of chain stopper **2**.

In conclusion, we have demonstrated the triggering of the DP of a reversible supramolecular polymer. These experiments also confirm the selectivity and specificity of polymer formation by quadruple hydrogen bonding.

Part of this investigation was supported by The Netherlands Foundation for Chemical Research (SON), with financial aid from The Netherlands Organization for Scientific Research (NWO). E. C. acknowledges the EU for an Erasmus grant.

Notes and References

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‡ The equipment used for the deprotection was a 15 W Cosmolux fluorescent UV lamp, and the solution was irradiated in a quartz cuvette at a distance of 10 cm.

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Received in Bath, UK, 20th June 1998; 8/04797I