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Double dynamers: molecular and supramolecular double dynamic polymers

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The formation of double dynamers, polymers that are dynamic on both the molecular and supramolecular levels, was achieved in solution and corroborated by electron microscopy; NMR and mass spectrometry studies confirm their double molecular and supramolecular nature.

The combination of polymer chemistry with supramolecular chemistry defines a supramolecular polymer chemistry.[1–3] It is by nature a dynamic chemistry in view of the lability of the non-covalent interactions linking the molecular components of a supramolecular entity.[3–5] Importing such dynamic character into molecular polymers may be achieved by introducing reversible covalent bonds into the polymeric chain, resulting in dynamic covalent polymers.[4–8] Particularly suitable are the imine type bonds, formed by reaction of amino-containing groups with carbonyl groups, so that polycondensation of difunctional monomers yields molecular dynamers, such as polyacylhydrazones.[8]

A further step consists in implementing dynamic character simultaneously on the molecular and supramolecular levels in the same system, thus achieving double dynamers, polymers incorporating both non-covalent and reversible covalent connections and combining polyassociation with polycondensation of components.

We now report such double dynamic supramolecular polymers (DDSPs), involving the use of: 1) high affinity sextuple hydrogen bond formation between a DAD–DAD (D = donor, A = acceptor) receptor and a cyanuric acid wedge;[10] 2) reversible acylhydrazone bond formation by condensation of hydrazides with aldehydes.[8,9]

In order to generate and study such DDSPs, the homoditopic receptors **1**,**2** have been synthesized and characterized (Fig. 1). Condensation of the functionally complementary monotopic building blocks **3** and **4** gave **1** and reaction of the dihydrazide **5** with **3** gave **2**. Depending on the bisreceptor (**1** or **2**), the corresponding supramolecular polymers SPI and SPII were generated by polyassociation with the complementary ditopic component **7**.[11]

SPI and SPII can be obtained in several ways using different combinations of constituents (Scheme 1). In the case of non-covalent polyassociation, the acylhydrazone bonds are formed first to give **1** or **2**, and the generation of supramolecular polymers proceeds on addition of **7** by hydrogen bonding between the components. Under covalent polycondensation, hydrogen bonding between **3** or **4** and **7** takes place first, and the formation of the acylhydrazone bonds as depicted in Scheme 1 yields the supramolecular polymeric entity.

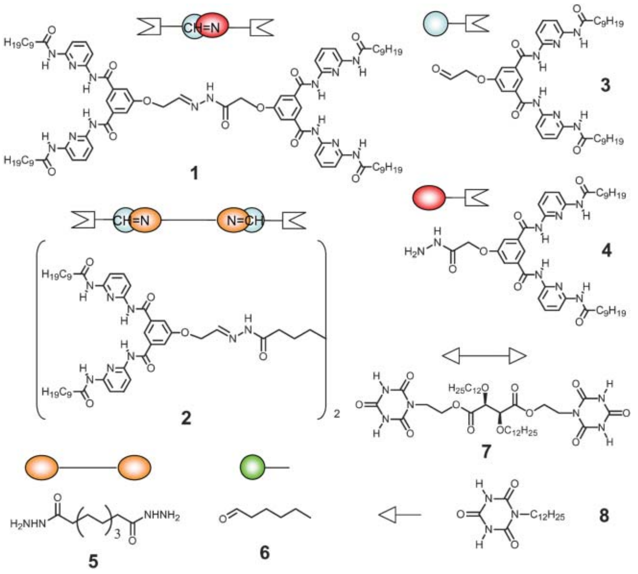

Fig. 1 Building blocks and corresponding molecular components of double dynamic supramolecular polymers.

The generation of SPI and SPII by both non-covalent polyassociation and covalent polycondensation was observed in solution. Fig. 2 displays ^1H NMR spectra for the preparation of SPII by these two methods. In all cases, the hydrazone condensation proceeded at room temperature without catalytic acid and could be followed by the progressive disappearance of the aldehyde proton signal around 9.9 ppm. The reference polymer of SPII was obtained from the separately prepared bisreceptor **2** by addition of the biswedge **7**.

The solution of SPI in decane gave an unstable gel, due probably to the low solubility of the polymer, resulting from the presence of the acylhydrazone functional group, as is the case for polyacylhydrazones.[8,12] This made it impossible to carry out viscometry measurements.

The formation of SPII was corroborated by electron microscopy studies, which showed extensive branched fibrous aggregates, a feature in agreement with the formation of polymer chains (Fig. 3).[13]

The double dynamic nature of these new DDSPs was revealed by covalent and non-covalent end-capping experiments. Under covalent end-capping conditions, excess hexanal **6** was added to SPI (5 mM in [D_2] tetrachloroethane) and its incorporation occurred on heating the sample in the absence of an acid catalyst,

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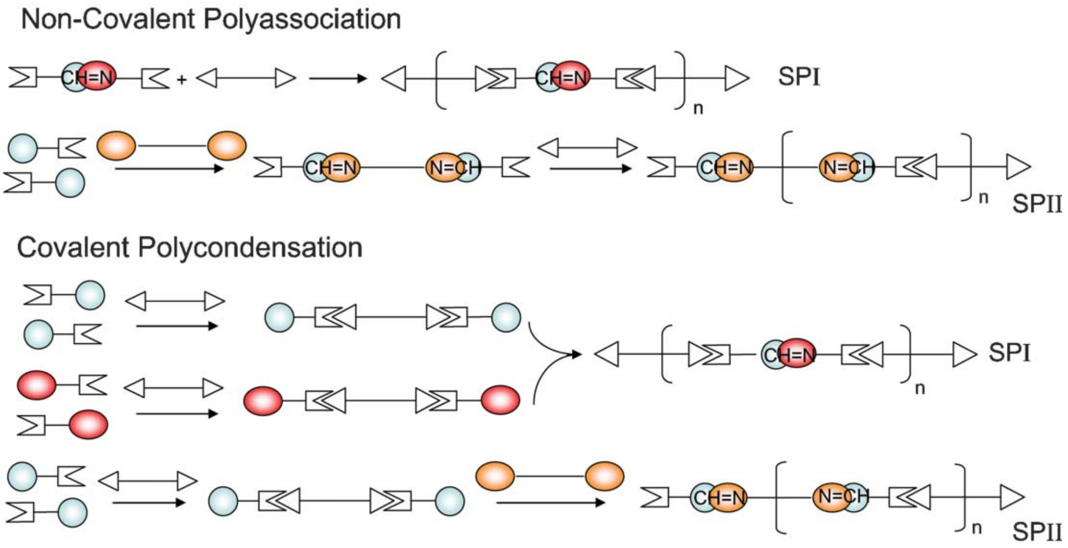

Scheme 1 Methods for the generation of the double dynamic supramolecular polymers SPI and SPII.

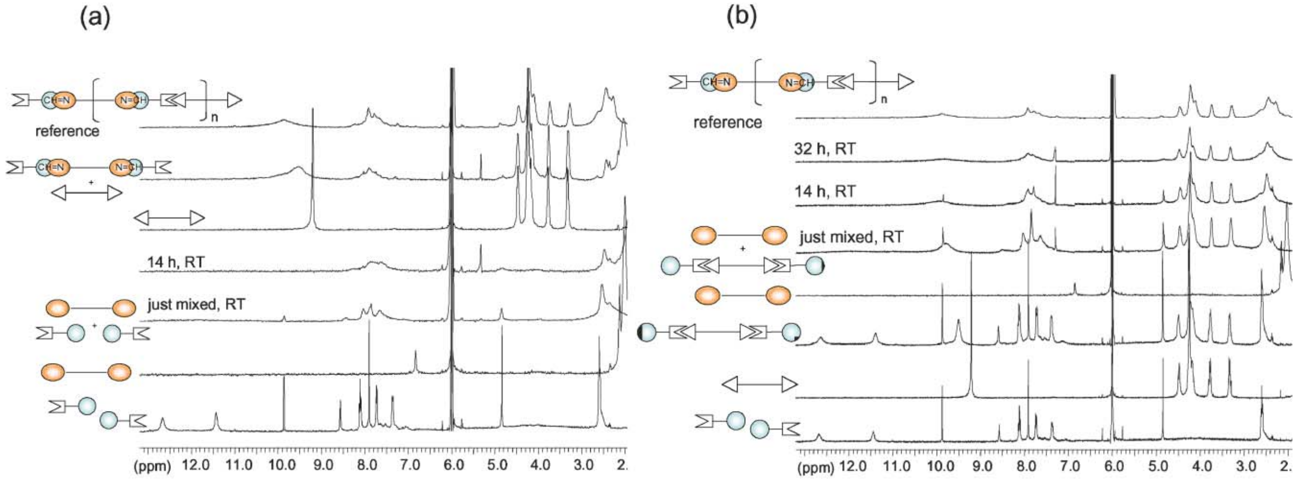

Fig. 2 ^{1}H NMR spectra for the generation of the SPII by (a) non-covalent polyassociation and (b) covalent polycondensation, at 25 °C and 5 mM of each component in [D$_2$] tetrachloroethane.

as indicated by a sharpening of the ^{1}H NMR signals corresponding to the generation of smaller species (Fig. 4). ES-MS confirmed the formation of a new acylhydrazone. In the case of non-covalent end-capping, cyanurate **8** was added portionwise to SPI (5 mM in [D$_2$] tetrachloroethane). This monotopic substrate competes with the ditopic cyanurate **7** for occupation of the receptor binding sites.

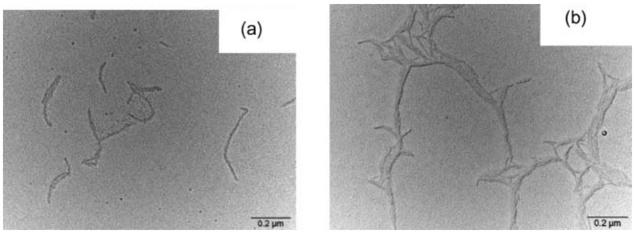

Fig. 3 Electron microscopy studies on the SPII generated by non-covalent polyassociation (a) and covalent polycondensation (b), following the sequences of addition of components shown in Scheme 1 and in Fig. 2; 5 mM in [D$_2$] tetrachloroethane in both cases.

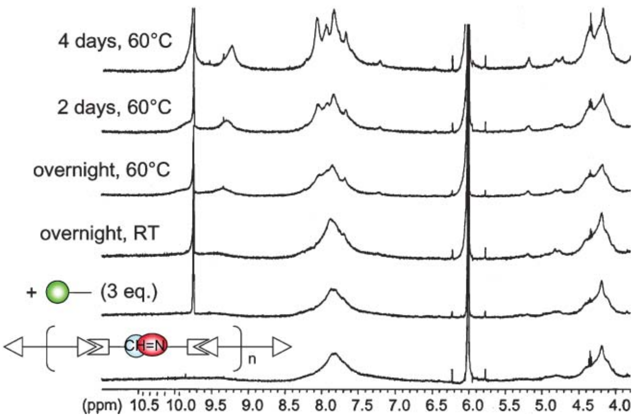

Fig. 4 Sequence of partial ^{1}H NMR spectra for covalent end-capping of the SPI (5 mM in [D$_2$] tetrachloroethane) by addition of **6**.

The result is a shortening of the polymeric chains with formation of smaller aggregates, leading to a significant sharpening of the ^{1}H

NMR spectra as increasing amounts of **8** are added (results not shown).

In conclusion, a novel type of supramolecular polymers was synthesized, where molecular components are connected through reversible covalent as well as non-covalent interactions. Component exchange in these DDSPs allows for the generation of dynamic constitutional diversity on both molecular and supramolecular levels. Because of their ability to undergo assembly, disassembly and exchange processes, they can be considered as constitutionally dynamic materials, capable in principle of selecting their constituents in response to external stimuli or environmental factors, thus behaving as adaptive materials.[3,4]

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12 A supramolecular polymer analogous to **1**, but with a trimethylene group as central spacer replacing the acylhydrazone containing unit, yields on addition of **7** a very stable, highly viscous organogel in decane; E. Kolomiets and J.-M. Lehn, work in progress.

13 The pictures obtained show more or less pronounced fiber formation, depending on the mode of generation of SPII (Fig. 3a and 3b). This may be due to either sample preparation or location of the area observed by TEM. In identical conditions one would expect to obtain the same type of fibres at equilibrium.