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Versatile One-Pot Synthesis of Supramolecular Plastics and Self-Healing Rubbers

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One of the most fascinating aspects of supramolecular chemistry is the diversity of materials that can be simply obtained by self-assembling molecules through noncovalent bonds. In particular, careful control of the chemistry of the hydrogen-bonding functional units can lead to a wide range of well-defined assemblies: crystals,[1,2] liquid crystals,[3,4] supramolecular linear[5] and star-shaped[6] polymers, supramolecular networks,[7] and block copolymers.[8,9]

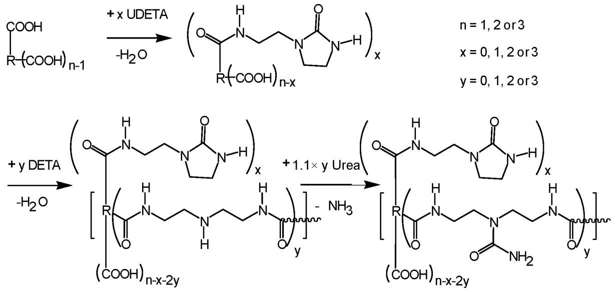
In bulk, such assemblies can exhibit properties usually associated with macromolecular systems and behave like amorphous or semicrystalline thermoplastics,[10,11] viscoelastic liquids,[12] or thermoplastic elastomers[13] but, in addition, show unique properties such as easy processability or abilities to self-repair.[14,15] In an alternative route, high molecular weight polymers are grafted with H-bonding units to form supramolecular networks with interesting thermoplastic and elastomeric properties.[16−18]

Up to now, the design strategy was mainly focused on grafting H-bonding moieties onto previously synthesized appropriate backbones (telechelic, star shaped, or multifunctional polymer).[19,20] Here, our aim is to show that by combining and controlling the backbone building, with the grafting of the functional groups, all the aforementioned variety of materials can be obtained from a same one-pot reaction by merely varying the stoichiometry of the reactants.

We illustrate this strategy by using oligocondensation of a mixture of fatty mono-, di-, and triacids (see Materials in Supporting Informations (SI) for a detailed description) with diethylenetriamine (DETA). We control and adjust the molecular weight and the degree of branching of the backbones by selection of the ratio of di- and triacids and by end-capping before the condensation reaction some acid groups with 2-aminoethylimidazolidone (UDETA) which plays the role of a self-complementary hydrogen bonding moiety. Additional complementary H-bonding units are introduced by grafting urea onto all secondary amines of DETA. Analogous synthetic routes with different H-bonding moieties or building blocks of branched backbones can of course be envisaged.

The reaction is conducted in three steps without the need of solvent (see Scheme 1). First, we graft UDETA onto fatty acids. Then, we add DETA. Urea is finally reacted on the secondary amines of DETA, giving rise to 1,1-dialkylureas. The stoichiometries of DETA and UDETA to fatty acids grant, at the same time, control of molecular weight of the molecules formed, their degree of branching, and the number of H-bonding moieties per molecule. Dotted lines in Figure 1 illustrate how the weight average polymerization index N_w varies with stoichiometry.

Scheme 1. Synthesis of Supramolecular Plastics in Three Steps[a]



[a] Fatty acids: $n_{avg} = 2.03$ + (1°) aminoethyl imidazolidone (UDETA), (2°) diethylenetriamine (DETA), (3°) urea. Branching is shown in parentheses; brackets indicate polymerization.

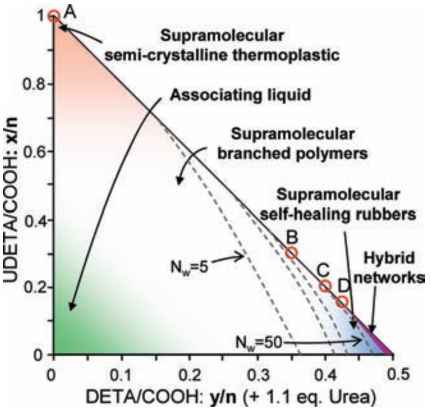


Figure 1. Materials obtained by varying the ratio of UDETA/COOH and DETA/COOH. Dotted lines: $N_w = 5$, 10, 20, and 50 (weight average number of H-bonding moieties per molecule) calculated from simulations based on Flory−Stockmayer theory.[21,22] **A (x/n = 1, y/n = 0)**, **B (x/n = 0.3, y/n = 0.35)**, **C (x/n = 0.2, y/n = 0.4)**, and **D (x/n = 0.15, y/n = 0.425)**: syntheses discussed below.

Four different classes of materials have been observed (see Figure 1). For low amounts of DETA and UDETA, we obtain a low viscosity associating liquid. When high amounts of UDETA (>80%) are grafted, the material behaves like a semicrystalline plastic. The crystallinity gradually decreases when the proportion of functional end-capping moieties (UDETA) is decreased. By increasing the fraction of DETA used in the second step of reaction, both the average molecular weight of backbones and the molecular disorder (polydispersity and branching) are increased. For samples containing less than 30% of UDETA, crystallization is not detected, and the materials are amorphous with a glass transition temperature (T_g) between 10 and 20 °C. At room temperature, they behave like viscoelastic melts. The highest molecular weight materials, where the mechanical relaxation time is particularly long, behave like supramolecular self-healing rubbers: they can be reversibly extended several times their initial size with little creep under stress, and

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when cut and put together, they self-repair. For still lower content of UDETA (below 12%), the covalent gel point is crossed and the system is then a hybrid network covalently cross-linked but still able to form reversible physical cross-links via H-bond association.

We discuss in more detail four examples with different UDETA/DETA compositions (see Scheme 1): **A, x/n = 1 y/n = 0; B, x/n = 0.3 y/n = 0.35; C, x/n = 0.2 y/n = 0.4** and **D, x/n = 0.15 y/n = 0.425**. Synthetic procedures as well as spectroscopic characterization (FT-IR, ^{1}H NMR) and DSC measurements can be found in the SI.

Figure 2 clearly illustrates both the increase of the average molecular weight and the width of the size distribution when the degree of covalent cross-linking increases (**A** < **B** < **C** < **D**). In accordance with theoretical models of condensation,[21,22] the quantity of noncondensated species is not negligible and the presence can be seen in SEC experiments (peak at elution volume 30 mL).

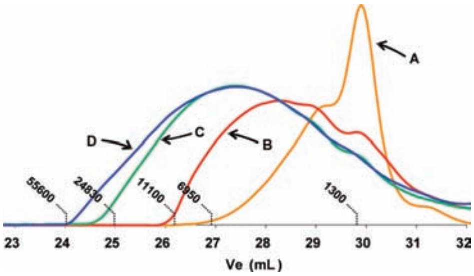

Figure 2. Viscosimetric SEC traces of materials A (yellow), B (red), C (green), and D (blue) in benzyl alcohol (130 °C, 0.5 wt %). Elution volumes of PMMA standards (M in g/mol) are shown for comparison.

To quantify the different relaxation dynamics, creep measurements were conducted at 30 °C (see Figure 3a). Below its melting point, material **A** behaves like a solid: when a 3 kPa stress is applied, the deformation is ~0.1% after 70 min. Material **B** is viscoelastic: the creep experiment induces 180% strain after 20 min. Materials **C** and **D** show much slower relaxations, with creep-induced strains of, respectively, 21% and 10% after 6 h.

The increase of relaxation time with the molecular weight shown by materials **B**, **C**, and **D** is a trend expected from theoretical models of dynamics of associating polymers.[23−25] For materials **C** and **D**, this relaxation time is particularly long and elastic behavior dominates. Tensile curves of material **C** show an extensibility of more than 750% at 50 °C (see Figure S1 in the SI), and after a 40% strain step for 3 h at 40 °C, the material recovers more than 88% of deformation. Material **D** resembles even more a cross-linked elastomer: after the 40% strain step, the strain recovery is greater than 94%. The tensile curve shows a lower strain at break than material **C** and a higher modulus.

The unique feature of supramolecular polymers is their ease of processability. At higher temperatures, the relaxation times decrease considerably. Materials **A** and **B** flow like liquids above 90 °C. Creep experiments carried out at different temperatures on material **C** show two regimes (see Figure 3b): from 30 to 90 °C, the creep-induced strain rate stays below 4%/h. Above 110 °C, the strain rate can increase as fast as 22%/h. This change of behavior is related to both the decrease in the number of associated functional groups with increasing temperature and the decrease of diffusion-controlled associating time-life. In practice, **C** as well as **D** can be processed at 130 °C.

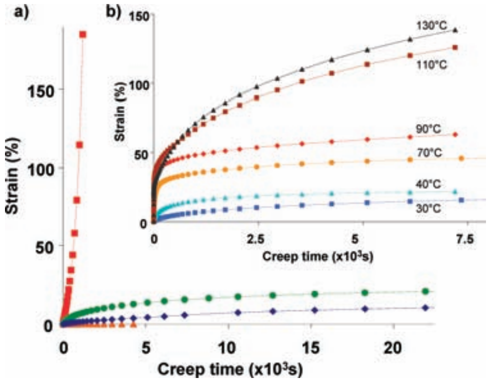

Figure 3. Creep-induced strain curves with 3 kPa nominal stress: (a) 30 °C, **A**: yellow; **B**: red; **C**: green and **D**: blue. (b) **C** from 30 to 130 °C.

This synthetic strategy allows for not only the synthesis of new classes of materials but also, for supramolecular rubbers, a much easier control of molecular structure than the method previously described.[14,15] The latter method achieved control of structure by using an excess of reagents that implied complex and costly extractions.

In summary, we proposed here a strategy to obtain a large variety of organized solid and viscoelastic supramolecular materials which relies on simultaneous controlled synthesis of covalently branched molecules and their functionalization with self-complementary and complementary hydrogen bonds. The proposed strategy can be generalized to various other condensation schemes and other functional groups.

Supporting Information Available: Detailed synthetic procedures, characterization. Simulations of molecular distributions. Tensile measurements, DSC procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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