

Supramolecular Thermoplastic with 0.5 Pa·s Melt Viscosity

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S Supporting Information

ABSTRACT: Design of materials with polymer-like properties at service temperature but able to flow like simple liquids when heated remains one of the important challenges of supramolecular chemistry. Combining these antagonistic properties is highly desirable to provide durability, processability, and recyclability of materials. Here, we explore a new strategy based on polycondensation reactions to design supramolecular polymer materials with stress at break above 10 MPa and melt viscosity lower than 1 Pa·s. We report the synthesis and rheological and mechanical properties (uniaxial tensile tests) of supramolecular polymers based on a multiblock polyamide architecture. The flexibility of polycondensation reactions made it possible to control the molecular size distribution, the strength of hydrogen bonds, and the crystallization of middle and end groups and to achieve targeted properties.

Unlike amorphous plastics, semicrystalline polymers maintain high levels of mechanical resistance above their glass transition temperature thanks to their morphology consisting of crystalline clusters connected to each other by molecular bridges. Semicrystalline polymers can be molten, solubilized, processed, and even recycled.¹ Yet, to attain good mechanical properties, entanglements in the amorphous phase are necessary to bring additional connectivity. Thus, as a rule, semicrystalline thermoplastics are relatively high molecular weight compounds with the disadvantage of high melt viscosities, typically in the 10²–10⁴ Pa·s range at low shear rates.²

To design thermoplastics with enhanced processability, supramolecular chemistry can be employed.³ Noncovalent bonds are reversible, and their dynamics depends on the chemical and physical environment. It should be then possible to tune the mechanical and rheological properties of materials comprising such interactions.⁴ For example, advantages of easier processing and recyclability brought by thermoreversibility of the H-bonding supramolecular links have been demonstrated for amorphous systems by the group of Meijer.⁵ Their systems display elongations at break around 6 MPa and viscosities in the 20–30 Pa·s range.⁶ For semicrystalline systems, the group of T. Long obtained impressive results by attaching 2-ureido-4[1H]-pyrimidone at the ends of low molecular weight poly(butylene terephthalate). The presence of multiple hydrogen bonding groups imparted high tensile and impact strength while keeping viscosity lower than 30 Pa·s at 235 °C.⁷ Gaymans and co-workers obtained high melting point semicrystalline materials by using segmented copolymers made of monodisperse crystallizable H-bonding fragments linked to each other by soft spacers.⁸

However, relatively high molecular weights of components yield melt viscosities well above 30 Pa·s.

To reach viscosities below the target value of 10 Pa·s, which is highly desirable, for example, in hot-melt technologies, our group designed bicomponent materials made of polyamide ($M_n \approx 20$ kg/mol) blended with 10–50% of a semicrystalline supramolecular polymer⁹ ($M_n \approx 800$ g/mol). The latter brings high elastic modulus and low melt viscosity, whereas the former affords strain resistance and toughness. In this approach, the miscibility of the components and the crystallization of H-bonding groups are key parameters that can be controlled by design.¹⁰

In parallel studies, we also demonstrated that supramolecular polymers made of highly associative groups separated by a linear oligomeric chain are analogous to triblock copolymers for which microphase separation has more influence on mechanical properties than the efficiency of directional interactions.¹¹

This analogy suggests numerous possibilities of morphologies control¹² and efficient strategies to tailor mechanical properties.¹³ An example is the use of multiblock architectures; the group of Bates demonstrated that lamellar ABA triblock mixed with only 15% of ABABA pentablock copolymers show a much enhanced crack resistance due to the possibility of molecular bridgings and knotted loopings.¹⁴

Here, we show the utility of controlling phase separation, bridging, connectivity, and polydispersity to design supramolecular materials combining a high melting point, a very low viscosity in the melt, and mechanical properties approaching those of industrial hot melt adhesives and thermoplastics. The materials we investigate are based on condensation oligomers of the A—A + B—B type terminated at both ends by strongly associating H-bonding groups. We distinguish two different situations: When A—A and B—B fragments are both amorphous and chemically similar to each other (Figure 1b), supramolecular polymers thereby obtained will not differ fundamentally from those based on soft telechelic homopolymers such as poly(propylene glycol) derivatives¹¹ where molecular recognition and end group crystallization into separate subdomains determine self-assembling and solidlike properties. However, when the sequence is an alternation of soft (amorphous) and stiff (crystallizable) fragments as depicted in Figure 1a, the final structure may become more ordered and the material can obtain additional connectivity through microphase separation and crystallization of the midblocks. Moreover, it will be shown that the overall connectivity in this case is much less sensitive to

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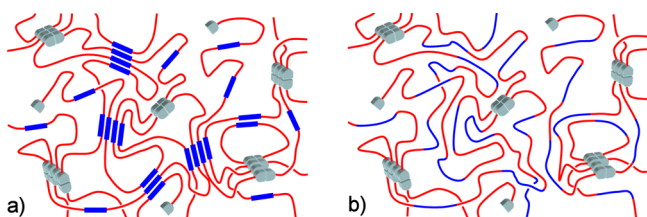


Figure 1. Expected self-assembly of multiblock oligomers (a) with segregation of alternating rigid (blue rectangles), soft (red wavy lines) segments, and terminal H-bonding groups (in gray) and (b) without rigid midsegments.

incomplete conversion, which is the common situation when polycondensation reactions are involved.

The molecular design of the series **a1–a4** is presented in Figure 2a. H-bonding end groups (in gray) are inspired by our previous works on supramolecular self-healing materials,^{15,16} but here the aminoethyl-imidazolidone fragment is connected through a diamide spacer, which affords high melting point and crystallinity. Diamide spacers (in blue) are also present in the main chain and behave as rigid blocks. They present additional ability to self-organize and crystallize. The rest of the molecule (in red), derived from vegetable oil chemistry, is actually a complex mixture of C36 isomers. It is basically noncrystallizable and forms the soft segments. Using the same procedure, control samples **b2–b4**, with the same H-bonding end groups but without rigid blocks in the main chain, have been also prepared.

Compounds **a1–a4** are obtained by the melt polycondensation reaction shown in Figure 2 involving three components: $(1 - x)$ equivalents of a diacid (adipic acid), 1 equiv of a diamine (Priamine 1074), and x equivalents of the monofunctional molecule UDETA-C6; the average number of repeat units in the target oligomers should be $n = (1 - x)/x$ at 100% conversion. Control samples **b2–b4** with the same feed ratios but a noncrystallizable diacid (Pripol 1009) instead of adipic acid were also prepared. Pripol 1009, another biobased material, has the

same hydrocarbon skeleton as Priamine 1074 (see Supporting Information). NMR analyses performed after 4 h at 160 °C indicate conversions of more than 95% and the formation of amide bridges (see Supporting Information); integration of the signals gives an estimate of the number-average value of n (Figure 2b). The molecular weight distributions predicted through Stockmayer equations¹⁷ for such a conversion are displayed in Supporting Information, and M_w and M_w/M_n obtained by the same calculation are presented in Figure 2b.

Four different stoichiometries have been prepared. Compound **a1** ($x = 1$) is targeted to be a single component at full conversion, and therefore, a narrow distribution is expected, whereas compounds **a2**, **b2** ($x = 0.5$), **a3**, **b3** ($x = 0.33$), and **a4**, **b4** ($x = 0.25$) are mixtures of oligomers of different sizes and should display a broader molecular weight distribution. These expectations are confirmed by size exclusion chromatography (SEC) (Supplementary Figures S6–S7). Although we do not have calibration for this new class of oligomers, this technique provides, on the basis of a PMMA calibration, molecular weights close to the expected values (Figure 2b). SEC also confirms that the stoichiometry of monomers according to the chain stopper UDETA-C6 provides control over chain size. In the perspective of a scale-up, we wondered how the multiblock architecture would be affected if a lower conversion is achieved. Indeed, low conversion means that a number of oligomers are generated with less than two crystallizable blocks per chain. We anticipated that such oligomers are unable to form bridges inside the material. Their weight fraction is plotted in Figure 2c for compound **a4** and for its counterpart **b4**, which has crystallizable blocks only at the ends (see also Supplementary Figures S4 and S5). It is evident that in the latter case nonbridging monomers rapidly become the majority at low conversions. In contrast, their fraction remains low in compounds **a2–a4**, which bodes well for the robustness of the process when crystallizable midsegments are present.

At the end of the process, the compounds are collected through the bottom valve of the reactor (Figure 3a). The typical

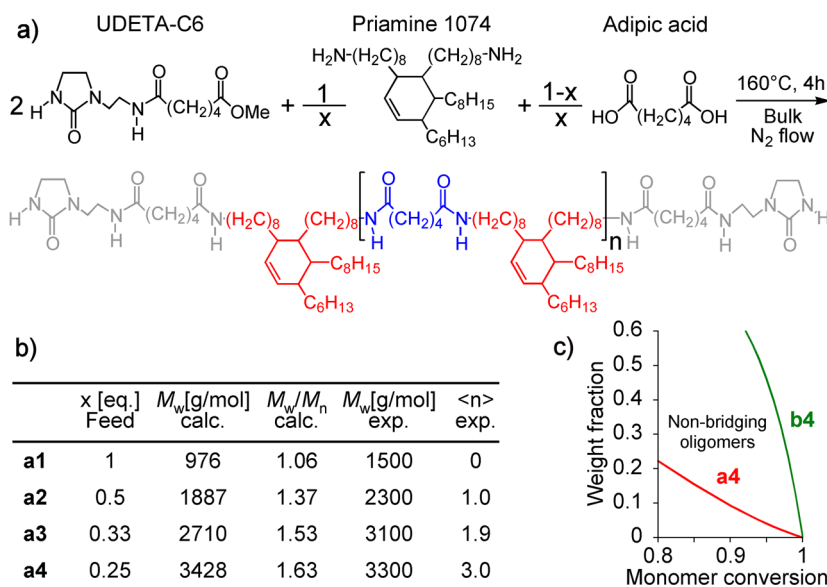


Figure 2. (a) Bulk one-pot synthesis of semiflexible oligomers **a1–a4** terminated at both ends by UDETA-C6 H-bonding groups. (b) Target composition of compounds **a1–a4** predicted by Stockmayer equations according to the feed ratio $x = [\text{COOMe}]/[\text{COOH}]$ and assuming a conversion of 0.95; SEC measurements of molecular weights (relative to PMMA standards) and average value of n given by NMR. (c) Predicted weight fraction of oligomers containing less than two crystallizable blocks per chain for different monomer conversions.

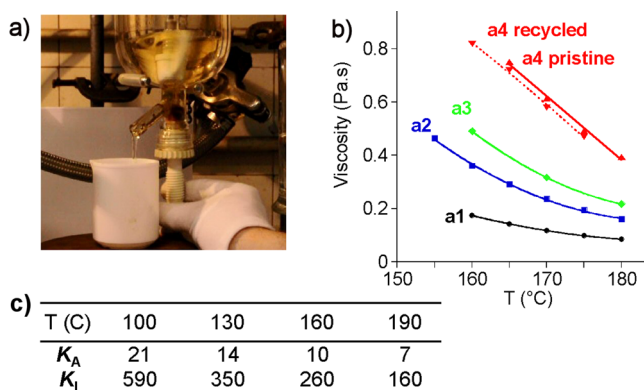


Figure 3. (a) Casting through the bottom valve of the reactor at the end of the synthesis. (b) Temperature dependence of viscosity of compounds **a1**–**a4**. (c) Association constants of amide, K_A , and of imidazolidone, K_I , functions.

yield for a 23 g batch is 90%. Thermal data of the materials are presented in Table 1. All compounds have a melting temperature

Table 1. Glass Transition (T_g), Melting Point (T_m), and Crystallization (T_c) Temperatures and Melting Enthalpy (ΔH_m)

compd	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)
a1	1	164	137	39
a2	6	147	132	27
a3	9	147	124	21
a4	–5	149	118	12
b2	–9	159	132	12
b3	–17	156	124	6
b4	–18	153	118	3

higher than 140 °C. Evidently, the melting enthalpy and glass transition temperature values are higher in **a2**–**a4** than in their **b2**–**b4** counterparts, consistent with the higher number of crystalline clusters.

The temperature dependence of viscosities was measured by rheometry above the melting point for the whole series (Figure 3b). Compounds **a2**–**a4** and **b2**–**b4** show very similar profiles (see Supplementary Figure S9); all compounds have a viscosity of less than 1 Pa·s above their melting point. This low value is due to the presence of a large fraction of short oligomers and low level of intermolecular H-bond association, as reflected by the modest value of the association constants at these temperatures (Figure 3c).

Pictures of tensile test specimens placed between crossed polarizers are shown in Figure 4. Before stretching, samples are weakly birefringent. On stretching, the mechanical birefringence appears, but there is a difference between both series. In **a2**–**a4**, the birefringence color is quite uniform throughout the sample until the fracture, whereas in **b2**–**b4** samples there is evidence of shear banding and necking before break, characteristic of plastic deformation.¹⁸ Compounds **a2**–**a4** have interesting mechanical properties; in particular, the stress at break comprised between 5 and 12 MPa. Thus, sample **a4**, in absence of annealing, has an elongation at break of 24% and a stress at break of 7.5 MPa. This value jumps to 11.5 MPa after annealing 1 h at 100 °C (Figure 4c). Its counterpart **b4** without crystallizable stiff spacers has a stress at break of 1.8 MPa but a larger ductile range. The same observations apply for the whole **b2**–**b4** series (see Supporting Information) with stress at break between 1 and 5 MPa and

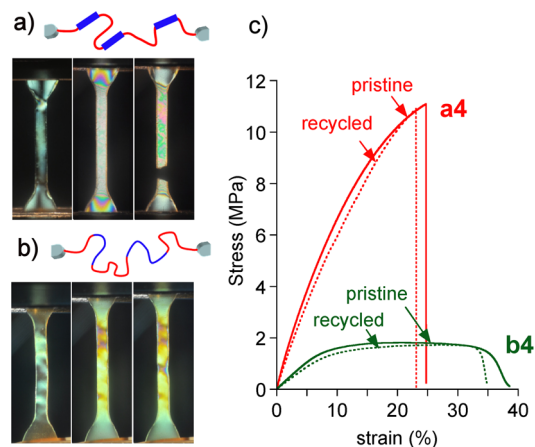


Figure 4. Stress profiles of samples **a4** (a) and **b4** (b). Samples were annealed for 1 h at 100 °C before measurements. (c) Corresponding stress–strain curves.

strains at break between 29% and 38%. In both series, broken samples may be molten and reprocessed without significant change of mechanical and flow properties (Figures 4c and 3b).

In Figure 5, we present the X-ray scattering data of compounds **b4**, **a4**, and **a5**. Compound **a5** was obtained from **a4** by removing

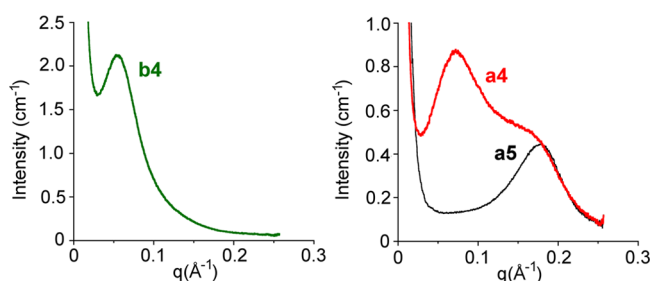


Figure 5. X-ray scattering spectra of compounds **b4**, **a4**, and **a5** (room temperature, annealed samples). Compound **a5**, containing a low amount of crystallizable end groups, shows a single diffraction event. Compound **a4**, containing high concentrations of crystallizable end groups and bridging groups, shows an additional diffraction peak. Compound **b4**, without crystallizable bridging groups, shows a single diffraction peak at low q .

the low molecular weight fraction by solvent extraction. Compound **a5** has a viscosity of 1.3 Pa·s at 175 °C and by NMR an average value of $n \approx 6$. In **b4**, a single maximum is detected at $q \approx 0.05 \text{ \AA}^{-1}$. This diffraction peak corresponds to a spacing of 125 Å, comparable with the size of the oligomers (100–200 Å). It reveals the microphase separation of flexible cores and crystallizable end groups.¹¹ The diffraction event at $q \approx 0.17 \text{ \AA}^{-1}$ that is evident in compounds **a4** and **a5** corresponds to a spacing of 37 Å, commensurate with the length of the repeat unit in the oligomers. It may be attributed to the mean distance between clusters of crystallized adipic diamide fragments. The other diffraction peak at $q \approx 0.07 \text{ \AA}^{-1}$, present only in **a4**, corresponds to a distance of 89 Å. It may be attributed to the mean distance between another type of clusters, made of crystallized end groups. Such clusters are not detected in **a5**, owing to the very low concentration of end groups. Thus, in the **a2**–**a4** series, two types of crystalline links contribute to the mechanical toughness of the material.

We demonstrated that the flexibility of polycondensation reactions can be employed to fix the molecular architecture and

obtain an efficiently bridged semicrystalline structure even though the chains are short. Starting from ingredients all available at the industrial scale, we synthesized oligoamides showing melting temperatures of about 150–160 °C and interesting mechanical strength, in the typical range for a polyamide hot-melt but with a 10^2 times lower viscosity.⁹ The important concept is to incorporate between associating end groups an alternation of soft (amorphous) and stiff (crystallizable) fragments; soft fragments based on renewable fatty acid derivatives were used to produce the desired structure. Such architecture, as in classical polyurethanes, yields crystalline domains linked together by a number of flexible bridges. With this design, even when conversion of polycondensation is not 100%, the overall connectivity of domains is not critically affected.

The presented strategy could lead to the development of materials allowing for substantial energy savings when processed or recycled, and their very low viscosity is also an asset for efficient wetting of fibers. We thus anticipate that supramolecular multiblock oligomers could find applications in composites and open new perspectives in adhesives.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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