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Isophthalic Acid−Pyridine H-Bonding: Simplicity in the Design of Mechanically Robust Phase-Segregated Supramolecular Polymers

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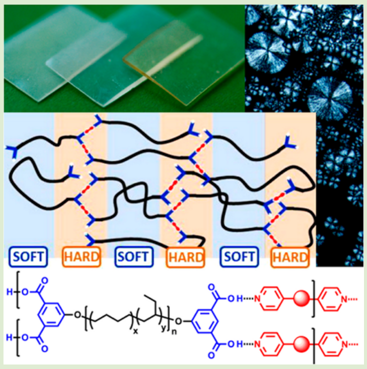
Supporting Information

ABSTRACT: We report a new series of supramolecular polymeric networks based on the isophthalic acid−pyridine (IPA−Py) H-bonding motif. The IPA units were attached as end-groups to telechelic poly(ethylene-*co*-butylene) to create a tetrafunctional macromonomer, which was cross-linked by the addition of various bispyridines. Some of the supramolecular polymer networks thus made display surprisingly good mechanical characteristics. We show that their structure and properties are strongly influenced by the nature of the bispyridine motif and by the fact that some of the IPA−Py motifs aggregate into particularly well-defined hard phases.



Supramolecular polymers consist of macromolecules that are assembled from lower-molecular-weight building blocks through noncovalent interactions such as H-bonding, $\pi-\pi$ stacking, or ligand−metal complexation.[1] The strength of useful noncovalent bonds varies over a wide range, and their reversible and in many cases dynamic nature bestows supramolecular polymers with stimuli-responsive properties.[2−6] Supramolecular polymers based on highly dynamic bonds, however, often exhibit low resistance to mechanical stress, which limits their usefulness in applications where high strength and stiffness are required. This problem can to a certain extent be overcome by kinetically trapping dynamic bonds by means of physical phenomena such as crystallization, the formation of a glass, or gelation.[1,7] The design of H-bonded supramolecular polymers that undergo phase segregation has been shown useful to improve mechanical properties. Representative examples of such materials include telechelics with terminal H-bonding motifs, which microphase segregate into a hard phase that serves to physically cross-link the soft phase formed by the telechelic cores, thereby increasing strength and stiffness. This strategy has been widely exploited in connection with strong H-bonding units (association constant $K_a = 10^4-10^7$ M^{-1}), for example, by Meijer and Sijbesma et al., who pioneered the use of ureidopyrimidone (Upy) and ureidotriazine units,[8−10] by Binder et al., who utilized the Hamilton wedge,[11] and by Wilson and co-workers who employed ureidoimidazole−amidoisocytosine heterodimers as the binding motif.[12] Interestingly, supramolecular polymers based on telechelics bearing structurally simple, weakly H-bonding end groups have received much less attention, perhaps because it proved difficult to impart mechanical robustness to these materials. Following early work by Stadler et al. on phase segregation effects in poly(butadiene)s functionalized with phenylurazole units,[13−15] several groups explored other telechelic cores and H-bonding units, including telechelic poly(tetrahydrofuran) terminated with benzoic acid,[16] nucleobase- and barbituric acid-terminated poly(isobutylene),[11,17] and thymine-functionailzed telechelic poly(propylene oxide).[18] Rowan, Mackay, and co-workers introduced supramolecular materials based on nucleobase-terminated telechelic poly(tetrahydrofuran).[4] The latter are rare examples of supramolecular polymers based on a weak H-bonding motif ($K_a < 5$ M^{-1}), where the formation of self-standing flexible films was observed; the work also highlights the importance of phase segregation to impart this behavior.

We herein report a new series of supramolecular polymers based on the isophthalic acid−pyridine (IPA−Py) H-bonding motif and demonstrate that it is possible to create supramolecular polymers with high stiffness and strength on the basis of simple hydrogen-bonding motifs. The related benzoic acid−pyridine pair ($K_a \sim 500$ M^{-1}) has been widely used to create supramolecular liquid crystalline (LC) polymers,[1] including the main-chain[19] and side-chain[20−22] LC supramolecular polymers reported by Kato and Fréchet, as well as the LC supramolecular networks prepared by Wiegel and co-workers[23−25] and Lin and Hendrianto.[26] While these studies demonstrate strikingly that simple H-bonding motifs permit the construction of sophisticated supramolecular architectures, their low association constant and the absence of suitable phase segregation effects afforded materials with very limited mechanical properties. This behavior may be the reason for the fact that

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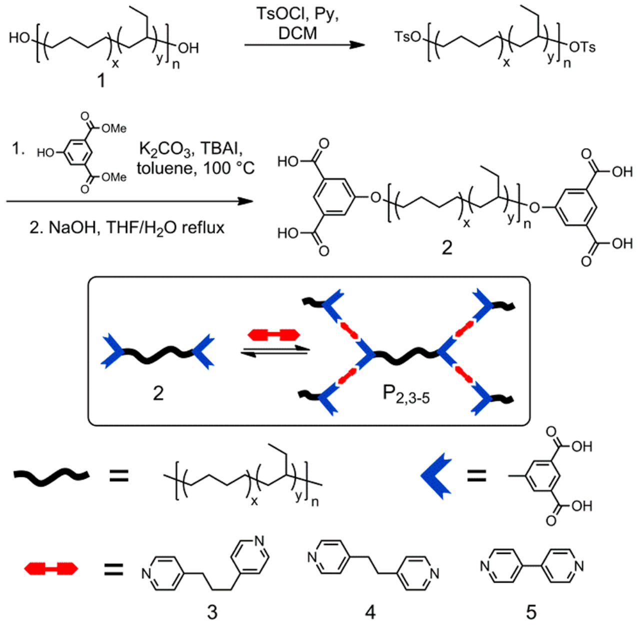
supramolecular polymers solely based on isophthalic acid−pyridine (IPA−Py) H-bonding have thus far remained unexplored. However, based on work by Jones and co-workers,[27] who reported that isophthalic acid cocrystallizes with 4,4′-bipyridyl to afford zigzag tapes, which further arrange into supramolecular sheets through intertape H-bonding, we surmised that hydrophobic telechelics equipped with isophthalic end-groups should assemble into robust phase-segregated supramolecular polymers with highly ordered hard phases when combined with bispyridines. To confirm this hypothesis, we derivatized telechelic poly(ethylene-*co*-butylene) (**1**, number-average molecular weight M_n = 3100 g/mol) with isophthalic acid units at the two termini (**2**, Scheme 1). As shown in many studies, the hydrophobic character, low glass transition temperature, and amorphous nature of the resulting soft phase render **1** highly suitable as a basis for phase-segregated supramolecular polymers.[6,10,28−30]

Scheme 1. Synthesis of IPA-Terminated Poly(ethylene-*co*-butylene) 2 and Schematic Representation of Supramolecular Networks Formed by the Assembly of 2 and Various Bispyridines



The new supramolecular building block **2** was prepared from the hydroxyl-terminated poly(ethylene-*co*-butylene) **1** in three steps. Instead of the customary functionalization based on Mitsunobu coupling,[6,29] we opted to tosylate **1**, subject the resulting intermediate to nucleophilic substitution with dimethyl 5-hydroxyisophthalate, and deprotect the ester groups. This approach resulted in complete end-group conversion and permitted us to prepare **2** of a molecular weight of 5000 g/mol (determined by ^{1}H NMR end group integration) on a 5 g scale without the need for chromatographic purification.

While the starting material **1** is liquid at room temperature, the IPA-functionalized telechelic **2** is a sticky, highly viscous material, on account of some H-bonding between the terminal IPA units. To create a supramolecular polymer network, a THF solution of **2** was combined with 4,4′-trimethylenedipyridine (**3**) in a 1:2 molar ratio, and films were prepared by solution-casting. After exhaustive vacuum drying, a transparent, homogeneous, robust film (**P$_{2,3}$**) was obtained (Figure 1, inset), which could be reprocessed by dissolution in THF and recasting or melt-processing upon heating to ∼50 °C. By contrast, the combination of **2** and **3** in a 1:1 ratio afforded a viscous material with an appearance similar to that of **2**. This suggests that the properties of **P$_{2,3}$** are associated with the formation of a supramolecular network in which each pyridine unit forms one H-bond with one carboxylic acid. The ^{1}H NMR spectrum of **P$_{2,3}$** (Supporting Information, Figure S3) shows a low-field shift of the aromatic protons of **3** as a result of the established H-bond and a IPA:Py 1:2 ratio confirming the targeted composition.

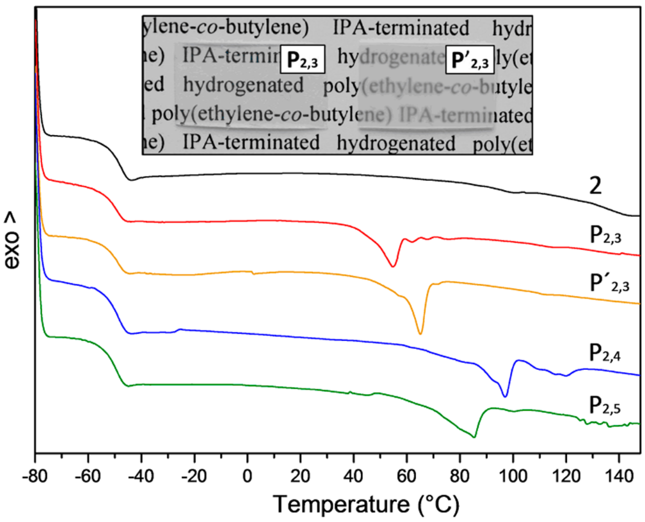


Figure 1. DSC traces of IPA-terminated poly(ethylene-*co*-butylene) **2** and the supramolecular polymers **P$_{2,3}$**, **P′$_{2,3}$**, **P$_{2,4}$**, and **P$_{2,5}$**. The inset shows photographs of films of **P$_{2,3}$** and an annealed sample **P′$_{2,3}$**.

To demonstrate that the properties of the new two-component supramolecular system can readily be tuned by variation of the bispyridine component, we extended our study to two other bispyridines, i.e., 1,2-bis(4-pyridyl)ethane **4** and 4,4′-bipyridyl **5**. Thus, **P$_{2,4}$** and **P$_{2,5}$** were prepared in the same manner as **P$_{2,3}$**, i.e., by casting THF solutions of **2** and either **4** or **5** in a 1:2 ratio, and also these supramolecular polymers formed robust, transparent films.

The thermal properties of the new materials were probed by means of dynamic scanning calorimetry (DSC). The DSC traces of **P$_{2,3}$**, **P$_{2,4}$**, and **P$_{2,5}$** (Figure 1 and Supporting Information, Table S1) all display a glass transition at −49 °C, which corresponds to the soft phase formed by the poly(ethylene-*co*-butylene) segments and is also observed in the DSC trace of the parent telechelic **2**. The DSC scans further display endothermic peaks in the range of 55−97 °C, which can be ascribed to phase transitions of the hard phases formed by the H-bonded IPA−Py motifs. Considering the similar structures of bispyridines **3**−**5**, the remarkable differences between the transition temperatures of **P$_{2,3}$** (55 °C), **P$_{2,4}$** (97 °C), and **P$_{2,5}$** (85 °C) cannot be explained solely on the basis of H-bond dissociation energies. Instead, it appears that the extent and structure of the resulting crystalline domains seem to have a dominant influence on the thermal and mechanical properties of these materials. This hypothesis was qualitatively confirmed by combining **2** with an equimolar mixture of bispyridines **3**, **4**, and **5** while keeping the overall ratio of **2** and (**3** + **4** + **5**) fixed at 1:2. The resulting material has an appearance that is similar to that of neat **2**, and it does not form self-standing films. This result is consistent with lacking hard-phase formation, on account of using a mixture of bipyridines. The melting temperatures of the hard phases of $\mathbf{P}_{2,3}$−$\mathbf{P}_{2,5}$ correlate well with the melting points of neat bispyridines **3** (60 °C), **4** (111 °C), and **5** (110 °C). The lower-than-expected transition temperature of $\mathbf{P}_{2,5}$ may be related to the limited conformational flexibility of **5**, which may stifle an efficient packing of the polymer's hard phase. The transitions observed by DSC can therefore be primarily related to the melting of crystalline IPA−Py assemblies and to a lesser extent to H-bond dissociation.

To maximize the extent of phase segregation and the crystallinity of the hard phase, we performed annealing experiments and studied the effect on the properties of the new supramolecular polymers. Thus, films of $\mathbf{P}_{2,3}$, $\mathbf{P}_{2,4}$, and $\mathbf{P}_{2,5}$ were annealed for 24 h at different temperatures below the hard phase transition temperature. In the case of $\mathbf{P}_{2,3}$ annealing at 42 °C caused an increase of the hard phase transition temperature by 10 °C from 55°C to 65 °C (Figure 1, the annealed sample is referred to as $\mathbf{P'}_{2,3}$) as well as a change in the appearance of the film, which became more turbid (Figure 1, inset). Despite the low hard phase content (11 mol %), polarized optical microscopy images of $\mathbf{P'}_{2,3}$ reveal the presence of spherulites with clear maltese crosses (Figure 2, inset), a phenomenon that has also been observed in similar supramolecular systems with hard phase contents as low as 14 mol %.[18] Annealing experiments of $\mathbf{P}_{2,5}$ in the range of 50−80 °C (Supporting Information, Figure S4) resulted, in the best case, in a 6 °C increase of the transition temperature (Supporting Information, Figure S4) that was not accompanied by any change in its visual aspect under crossed polarizers. As for $\mathbf{P}_{2,4}$, annealing experiments in the same temperature range (Supporting Information, Figure S4) resulted in the disappearance of some minor endotherms in the range of 110−120 °C but did not affect the main transition temperature nor its macroscopic appearance (Supporting Information, Figure S4).

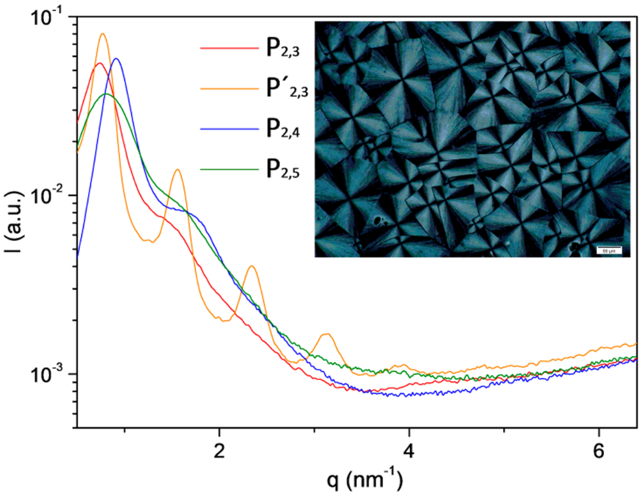


Figure 2. Azimuthally integrated small-angle X-ray scattering (SAXS) spectra of supramolecular polymers $\mathbf{P}_{2,3}$, $\mathbf{P'}_{2,3}$, $\mathbf{P}_{2,4}$, and $\mathbf{P}_{2,5}$. The inset shows an optical micrograph of $\mathbf{P'}_{2,3}$ between crossed polarizers (scale bar = 50 μm).

Small-angle X-ray scattering (SAXS) experiments performed on ca. 300 μm thin films of polymers $\mathbf{P}_{2,3}$, $\mathbf{P}_{2,4}$, and $\mathbf{P}_{2,5}$ confirm the formation of phase-segregated structures with a characteristic length scale on the order of 8−9 nm (Figure 2). While the scattering peaks are feeble in the case of the as-prepared samples, the SAXS analysis of annealed $\mathbf{P'}_{2,3}$ shows equidistant Bragg diffraction peaks up to the fifth order, which confirm the formation of a well-defined lamellar morphology. On the other hand, no differences were observed in the annealed samples of $\mathbf{P}_{2,4}$, and $\mathbf{P}_{2,5}$ (Supporting Information, Figure S5)

The mechanical properties of the new materials were elucidated by means of dynamic mechanical analysis (DMA) and tensile testing. A plot of the storage moduli as a function of temperature (Figure 3 and Supporting Information Table S1) shows that the as-prepared materials show a rubbery plateau with storage moduli between 17 ± 2 MPa ($\mathbf{P}_{2,5}$) and 34 ± 1 MPa ($\mathbf{P'}_{2,3}$) at 25 °C. It is noteworthy that the annealing of $\mathbf{P}_{2,3}$ (23 ± 2 MPa) resulted in a modulus increase of about 50% and that these materials showed higher storage moduli than previously reported UPy-urethane terminated poly(ethylene-*co*-butylene) (5 MPa).[10] In all cases, the DMA traces show a sharp decrease of the storage modulus upon increasing the temperature above the hard phase dissociation temperature established by DSC. A comparison of the DMA traces of $\mathbf{P}_{2,3}$ and $\mathbf{P'}_{2,3}$ confirms again that the annealing process indeed increased the dissociation temperature; the stepwise decrease of the storage modulus of $\mathbf{P}_{2,3}$ suggests crystallization while the sample was tested. The same effect, although somewhat less pronounced, was observed with annealed sample $\mathbf{P'}_{2,5}$, where the storage moduli increased to 26 ± 2 MPa, but no changes were observed with the annealed sample $\mathbf{P'}_{2,4}$ (Supporting Information Figure S8 and Table S1).

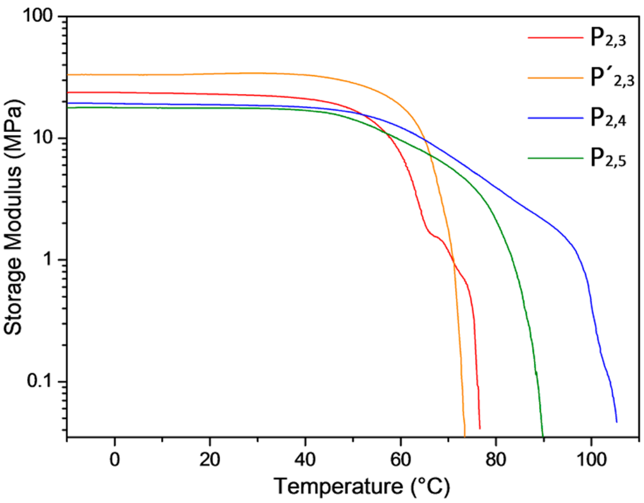


Figure 3. Storage modulus as a function of temperature for supramolecular polymers $\mathbf{P}_{2,3}$, $\mathbf{P'}_{2,3}$, $\mathbf{P}_{2,4}$, and $\mathbf{P}_{2,5}$ (representative curves are shown, and the storage moduli provided in the text are average values of three independent measurements).

Tensile tests (Supporting Information Figure S9 and Table S1) reveal Young's moduli of 4−18 MPa and tensile strengths of 0.1−0.4 MPa, and the trends seen in the data mirror the DMA results. The materials all showed a rather low strain at break (4−7%) that may be related to the low dissociation constant of the IPA−Py motif and a high propensity for chain pull-out of the hard phase at higher strains. Our initial observations are in agreement with systematic investigations by Sijbesma and Meijer on similar telechelic poly(ethylene-*co*-butylene)s functionalized with end-to-end and/or lateral quadruple H-bonding units.[10] Remarkably, $\mathbf{P'}_{2,3}$ exhibits a

Young's modulus (18.0 ± 1.5 MPa) that matches that of Upy-terminated poly(ethylene-*co*-butylene) supported by additional urea groups (17 MPa), although the Upy-bonded supramolecular polymer showed a much higher strain at break (>30 viz a viz 4−7%).[10] While the thermal treatment of $\mathbf{P}_{2,4}$ did not affect its tensile properties, the annealing of sample $\mathbf{P}_{2,5}$ afforded a stiffer material ($\mathbf{P'}_{2,5}$) with an increase of 6 MPa in the Young modulus (10.3 ± 2.2 MPa). The variations observed in the mechanical properties of these polymers upon thermal annealing may be ascribed to the presence of secondary crystalline domains in the as-prepared polymers and highlight the dynamic nature of these supramolecular networks.

In summary, we have introduced a new family of supramolecular networks based on a simple H-bonding motif, which so far appears to have been overlooked in the context of supramolecular polymerization. The materials based on the IPA−Py motif display mechanical properties that compare well with those of more complex, albeit linear, systems comprising H-bonding motifs with much higher association constants. Our data suggest that the properties of these phase-segregated supramolecular polymers are largely dictated by the ability of the IPA−Py motif to pack into highly ordered crystalline domains. This is consistent with our work on supramolecular metallopolymers, which suggest that the mechanical properties of the materials in question are much more influenced by the extent of phase separation than the degree of cross-linking. The "two-component approach" pursued here, where a difunctional IPA-terminated building block is combined with a bispyridine, offers an additional degree of design freedom compared to self-complementary H-bonding motifs, as simple variation of either the donor or (as shown here) acceptor component permits variation of the resulting materials structure and properties. Overall, our findings suggest that other supramolecular materials based on simple binding motifs may be worth exploration.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data including ^{1}H NMR, size exclusion chromatography (SEC), stress−strain tests, and additional DSC analyses. 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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