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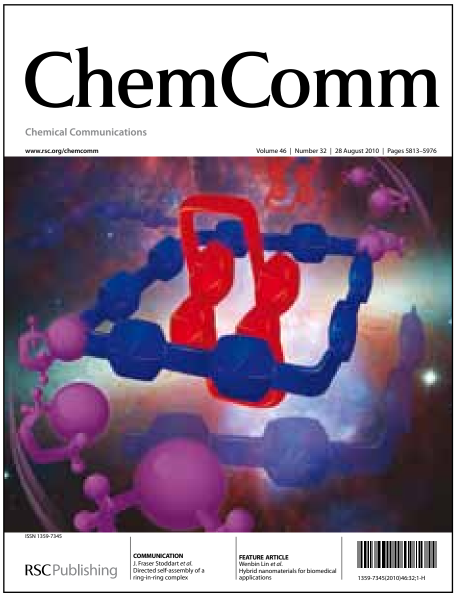

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ARTICLE TYPE

Synthesis of Polymeric Ladders by Topochemical Polymerization

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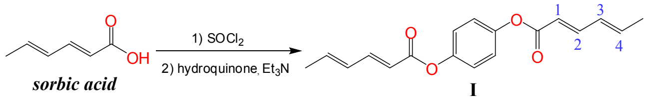
Two polymeric ladders were synthesized by topochemical polymerization. The critical assemblies with multiple reactive centers were characterized by single crystal X-ray diffraction. Approximately 64% and 70% of the mass of the two polymeric ladders can be derived from biomass, respectively.

Polymeric ladders are a high value synthetic target and are predicted to have high thermal/chemical stability because the chains do not automatically fall apart if one covalent bond is broken.[1,2] Polymeric ladders are constructed with monomers containing more than two reactive centers. The challenge lies in synthesizing a polymeric ladder by the classical one-pot approach because of the potential for cross linking between the monomers. Herein, we report two polymeric ladders synthesized by using topochemical polymerization [3-8]

A monomer used in this study is compound **I** with two reactive diene groups connected by an unreactive 1,4-phenylene diester linker (Scheme 1). Facile synthesis of monomer **I** was accomplished in 90% yield by activating sorbic acid with thionyl chloride and then coupling with hydroquinone.

A variety of physical properties were studied to determine if compound **I** is a viable candidate for polymerization. It was found to be a reactive white powder with melting point of 178-180 °C. The differential scanning calorimetry curve (DSC, Fig. 1) showed an endothermic peak at around 179 °C corresponding to its melting point. The exothermic peak to the right of the endothermic peak was consistent with an exothermic polymerization event. The featureless curves of first cooling and second heating were also consistent with the completion of the polymerization. The polymerization could be reproduced under conventional conditions in near quantitative yield by heating monomer **I** at 150 °C for a week. UV-Vis spectra showed that the monomer **I** absorbed irradiation between 260 nm and 300 nm in a chloroform solution and between 240 nm and 340 nm in the solid state (Fig. 1). The powder of monomer **I** polymerized slowly at room temperature under UV irradiation using a high-pressure Hg lamp. The reaction can be accelerated and was finished in 95% yield within 8 h by UV irradiation at 120 °C, well below the melting point of monomer **I**. Raising the temperature increased thermal vibration of the monomer in the solid state; therefore heating sped up the topochemical polymerization.[3-8] FT-IR spectra of monomer **I** compared with its polymers showed a shift of C=O stretching vibration from 1717 cm^{-1} to 1740 cm^{-1} (see ESI). The anti-symmetric stretching of C-C at 1008 cm^{-1} shifted to a higher wavenumber 1014 cm^{-1} and the relative intensity of the peak for the isolated trans C=C at 970 cm^{-1} increased after polymerization. These changes showed that the polymerization broke the conjugation between the carbonyl and diene in the monomer **I**.



Scheme 1 Synthesis of the monomer **I** from sorbic acid.

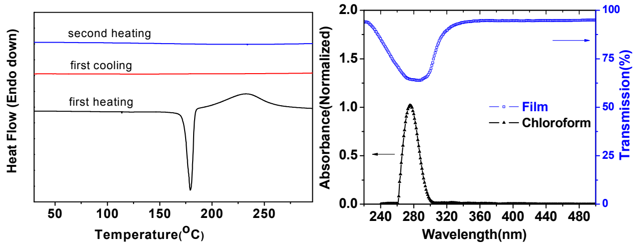


Fig. 1: left) DSC curves of monomer **I**; right) UV-Vis spectra of **I**.

To further investigate the solid state polymerization, high quality crystals of monomer **I** were obtained by slowly cooling a saturated DMSO or acetone solution. The structure was determined by single crystal X-ray diffraction. The monomer **I** self-assembled into columnar complexes based on π-π stacking as shown in Fig. 2. Within the assembly, the closest reactive atoms are the 1st diene carbon and 4th diene carbon in the nearest neighboring monomer as marked in Scheme 1 and Fig. 2a. These two adjacent reactive sp^2 hybridized carbons are only separated from each other by 3.66 Å and their π orbitals are well overlapping each other. The distance and orientation are ideal to form a new carbon-carbon bond in the solid state upon UV irradiation or heating.[9-11] The powder XRD pattern of the synthesized monomer **I** without further processing was nearly identical to that of the calculated one from the single crystals (see ESI) making this crystal structure suitable to analyze and interpret the solid state polymerization for both crystals and powder. After the photopolymerization, the polymer maintained its crystallinity. The powder XRD pattern of the polymer was similar to that of the monomer **I**; therefore consistent with the theory that the soild-state polymerization was a topochemical reaction involving minimum movements of the atoms.

Due to the preorganization of the reactive centers in the self-assembly, the monomer **I** is photoreactive allowing each monomer in close enough proximity to react with its two nearest

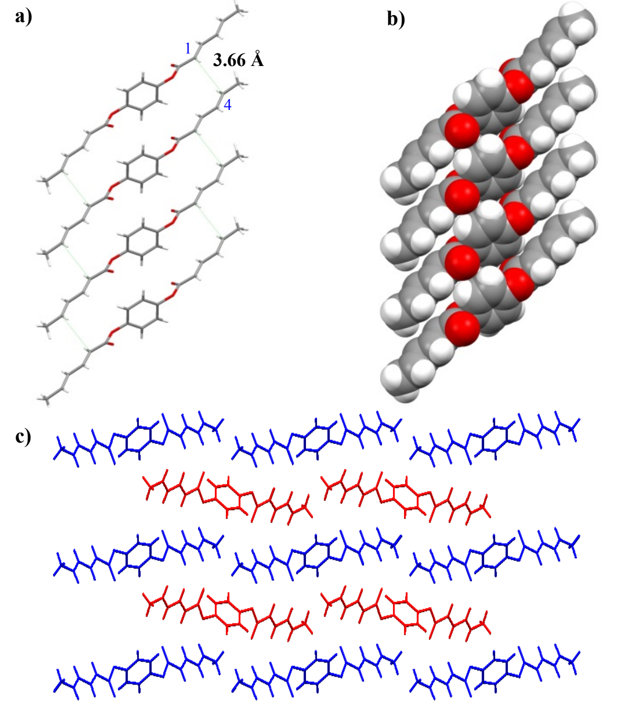


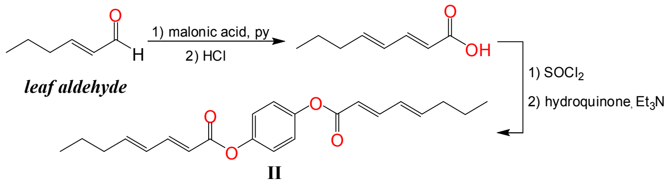
Fig. 2 The crystal structure of the reactive monomer **I**: a) side view of a π-π stacking column showing the reactive centers; (Only five molecules are shown for simplicity.) b) side view of the π-π stacking column in space filling style; c) top view of 13 π-π stacking columns in capped stick style. (Colors are introduced to illustrate the packing of these supramolecular columns.)

neighbors. UV irradiation and heating of the self-assemblies furnished polymeric products. As outlined in the graphic abstract, the 1,4-photopolymerization is proposed.[2a, 4a] Essentially, this process occurs via an intra-assembly reaction. The reactive alkene sp^2 carbons between self-assemblies are too distant for polymerization and their π orbitals are not overlapping (Fig. 3c, top view of 13 self-assemblies based on π-π interaction). The formation of the polymeric ladder was confirmed by solid state ^{13}C NMR, which showed the disappearance of two sp^2 hybridized carbons of the diene concurrent with the appearance of two sp^3 hybridized carbons around 43.6 and 56.4 ppm. Hydrolysis of the polymeric product of **I** yielded hydroquinone and no unreacted monomer was observed by NMR (see ESI). The result of product hydrolysis further supports completion of the topochemical reaction and the formation of the molecular ladder.

To explore the scope of the reaction, monomer **II** was synthesized (Scheme 2). Specifically, a Knoevenagel condensation between leaf aldehyde and malonic acid followed by a decarboxylation at 60 °C yielded the (2*E*,4*E*)-octa-2,4-dienoic acid. This dienoic acid was then activated by thionyl chloride and coupled with hydroquinone to offer the desired monomer **II**.

Due to the presence of the two three-carbon alkyl chains, the above monomer **II** has improved solubility in many organic solvents such as acetone, acetonitrile and ethyl acetate when compared with monomer **I**. X-ray quality crystals of monomer **II** were obtained by slow evaporation of an acetone solution. The structure determined by single crystal X-ray diffraction is shown in Fig. 3. The critical π-π stacking of the monomer remained in this crystal structure. The distances between the centroids of the aromatic rings shown in the π-π stacking columns in Fig. 2b and 3b are 5.60 and 5.49 Å, respectively. The 1st diene carbon and 4th diene carbon in the adjacent monomers are only 3.62 Å from each other. The closest reactive sp^2 carbons between self-assemblies are more than 5 Å away, so the alkenes between self-assemblies are unlikely to react (Fig. 3c). Although the packing of these π-π assemblies of **II** is different from that of the monomer **I** (Fig. 2c and 3c), the solid-state reactivity of monomer **II** is comparable to that of the monomer **I**. The topochemical UV polymerization of monomer **II** was finished in the solid state within 64 h at 70 °C, below its melting point 107-108 °C.

Topochemical reactions offer a unique opportunity to synthesize molecules and macromolecules with regio- and stereo-specificity.[9-13] Because the topochemical polymerization proceeds with minimum movement of atoms, stereoregular polymeric ladders are proposed as products (Fig. 4). The four carbon-carbon bonds that each monomer forms with its two adjacent neighbors all involve chiral centers that are generated stereo-specifically. Besides their stereoregularity, the two polymeric ladders have shown excellent chemical stability, which is also important for future applications. They are insoluble in all the common organic solvents. The ladders can tolerate strong acids such as concentrated HCl and TFA, and organic bases such as Et_3N (even when refluxed overnight). However, these ladder polymers are degradable in aqueous potassium hydroxide and can be oxidized by concentrated sulfuric acid.



Scheme 2 Synthesis of the monomer **II** from leaf aldehyde.

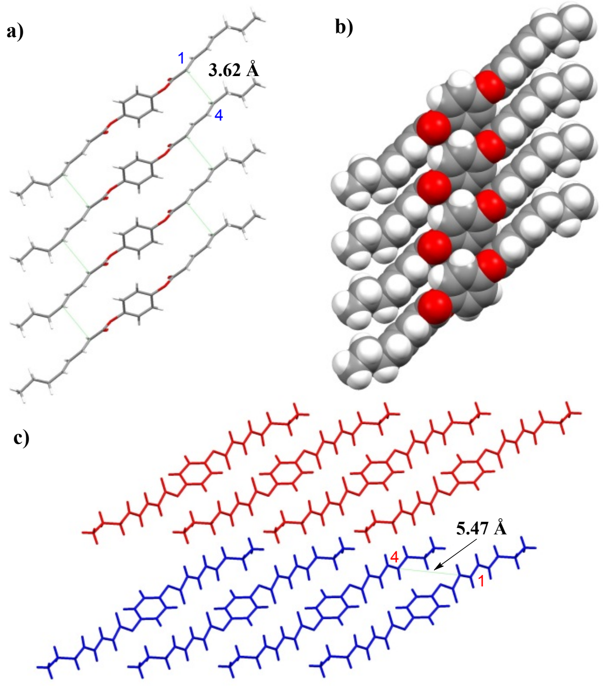


Fig. 3 The crystal structure of the reactive monomer **II**: a) side view of a π-π stacking column showing the reactive centers; (Only five molecules are shown for simplicity.) b) side view of the π-π stacking column in space filling style; c) top view of 8 π-π stacking columns in capped stick style. (Colors are introduced to illustrate the packing of these supramolecular columns.)

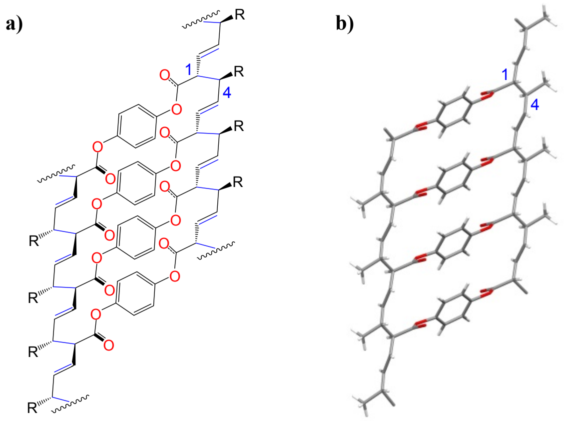


Fig. 4 Stereochemical structure of the polymeric ladders: a) a structural formula showing the chiral centers; b) a model of the polymeric ladder built from the crystal structure of monomer **I** to illustrate the stereochemistry. (Only four repeating units are shown for simplicity.)

Another significant characteristic of the polymeric ladders is their partial environmentally friendly origin.[14] The polymeric ladder **I** is approximately 64% by mass from the renewable starting material sorbic acid. Sorbic acid is commercially available and can be produced from triacetic acid lactone, which is a versatile biorenewable molecule with potential to be a platform chemical for the production of commercially valuable chemical intermediates and end products.[15] The polymeric ladder **II** is approximately 70% by mass renewable but synthesized from leaf aldehyde and malonic acid. Both chemicals are commercially available and malonic acid can be made from 3-hydroxypropionic acid, which is one of the top sugar-derived building blocks.[16]

In summary, two stereoregular polymeric ladders were synthesized from plant-derived materials. Other starting materials and reagents or their preparations were also readily available and inexpensive. The monomer powder **I** directly obtained from synthesis was not an amorphous solid, but was indeed microcrystals, which were suitable for topochemical polymerization. The above characters show possibility to scale up the synthesis. The two ladders in this communication align well with a known supramolecular ladder, which was synthesized from a two-dimensional *p*-xylylenediammonium discorbate, showing that the topochemical 1,4-polymerization of diene could be a useful reaction to make interesting targets with potential applications.[2a] Furthermore, the polymeric ladders exemplified herein will provide an access to other covalently bonded ladder materials, and allow researchers to further explore their unique properties such as mechanical strength.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure, full characterization and spectra, and crystallographic data. See DOI: 10.1039/b000000x/

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