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Linear Polyester Synthesized from Furfural-based Monomer by Photoreaction in Sunlight

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A novel linear polyester was synthesized from furfural-based monomer through solvent-free polymerization using sunlight. Furfural was first converted to 2-furanacrylic acid as a key photoreactive building block. The desired monomer was then prepared by linking two 2-furanacrylic acid molecules with 1,5-pentanediol, which can also be produced from furfural. An important photoreactive crystalline assembly of the monomer was characterized by powder and single crystal X-ray diffraction. The new linear polyester that contains 100% components from biomass-derived chemicals was synthesized by sunlight photoreaction of the pre-organized monomer in the solid state in 24 hours. The solvent-free sunlight photoreaction process was monitored by FT-IR and a key intermediate was confirmed by single crystal X-ray diffraction. Nanofiber of the linear polyester was observed under TEM. Similar to polyethylene terephthalate (PET) used in beverage bottles, the novel polyester contains alternating rigid and flexible moieties in the polymer chain.

Introduction

The world depends heavily on petroleum as its main source for chemicals.[1] The rapid growth of world population and irreversible consumption of fossil resources require the development of new materials from sustainable sources.[2-12] One of the most valued bio-based chemicals, furfural, is derived from a variety of agricultural byproducts such as wheat bran, corncobs, and sawdust.[13-14] Furfural provides renewable building blocks for the synthesis of new materials.[15] Designing new materials from furfural has recently attracted significant attention from academic and industrial researchers.[16-22]

Polyesters have been used in many fields. For example, polyethylene terephthalate (PET) is widely used in beverage bottles and other plastic containers.[23-25] The most popular thermoplastic materials are polyesters because of their impressive strength, thermal stability and transparency.[26-28] The polyester's light weight, low cost, and reusability also contribute to its popularity.[28] With limited fossil resources and an expanding polyester market, polyesters from sustainable resources are becoming attractive synthetic targets.[26-31] In fact, an increasing number of top companies have made the development of 100% bio-based polyesters a high priority.[32]

Recently, our research team has reported ladder[11] and two-dimensional[12] polyesters that can be synthesized from biomass-derived starting materials (64-84% biomass content) including sorbic acid, leaf aldehyde, malonic acid, and cinnamic acid. Herein, we demonstrate a 100% bio-based novel linear polyester that can be synthesized from furfural, 1,5-pentanediol (a derivative of furfural), and malonic acid, which exists in high concentrations in beetroot.[6,11] The new linear polyester was synthesized by using topochemcial photopolymerization of crystalline furfural-based monomer.[11-12, 33-37] To achieve topochemcial photopolymerization, the designed monomers first self-assembled in a crystalline solid by complementary π-π interaction so that their photoreactive centers were oriented toward each other. The oriented monomers then photopolymerized in its solid state. This locally confined polymerization process reduced the possibility of cross-linking and undesired side reactions, such as oxidation, and gave the novel linear polyester that would be otherwise difficult if not impossible to achieve. Moreover, because the polymerization step was solvent-free, its advantages included no waste, easy operation, and low energy consumption. The entire polymer synthesis process from commercially available, inexpensive starting materials was simple and no metal salts or other toxic chemicals were involved, which is particularly important for future applications in industry.

In this article, sunlight was proven to be a promising irradiation source to link the monomers into the linear polyester. Within green chemistry, the use of solar energy in reactions has been an attractive development.[38-41] Sunlight as a natural light resource is safer compared to more commonly-used ultraviolet (UV) lamps. Furthermore, sunlight is free, clean, and essentially inexhaustible, which makes this solvent-free polymerization process more environmentally friendly.

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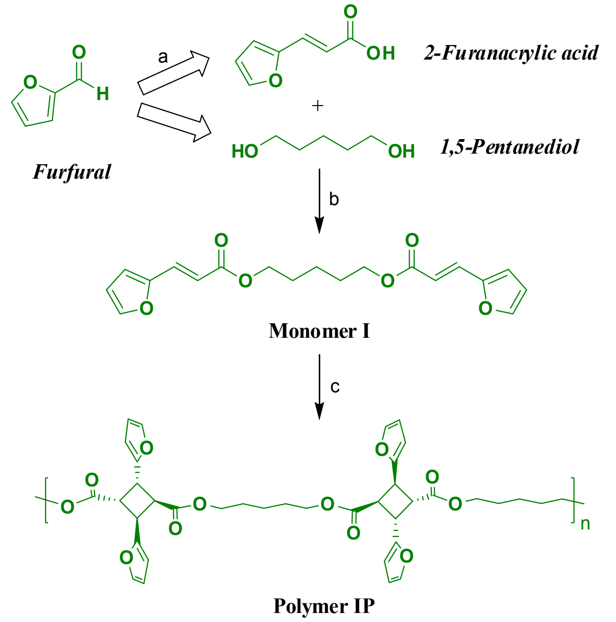
†Electronic Supplementary Information (ESI) available: Experimental details, characterization and properties of the synthesized linear polyester, photoreaction results, crystallographic data (CCDC: 1406681 and 1408218). See DOI: 10.1039/c000000x/

Results and discussion

The synthesis of monomer **I** starts with furfural (Scheme 1). The key building block of the monomer, 2-furanacrylic acid, was constructed by Knoevenagel condensation between furfural and malonic acid in a 2-methyltetrahydrofuran (2-MeTHF) solution, and subsequent decarboxylation. The newly-formed exocyclic carbon-carbon double bond (C=C) extended the branch of furfural and would be used for the solid-state [2 + 2] photoreaction. A photostable 1,5-pentanediol linker was then introduced to connect two 2-furanacrylic acid molecules together to form the monomer **I**. Specifically, the 2-furanacrylic acid was first activated by thionyl chloride. The monomer **I** was constructed in the following step within the same flask by connecting two 2-furanacrylic acid chloride molecules with 1,5-pentanediol via nucleophilic substitution. An important factor in the selection of 1,5-pentanediol as the linker and 2-MeTHF as the solvent was that both of them can be produced from furfural as well.[13, 42-43]



Scheme 1 The synthesis of monomer **I**: a) Malonic acid, pyridine, 2-MeTHF, reflux, 16 h; then HCl. b) $SOCl_2$, Et_3N, 2-MeTHF, reflux to r.t., 18 h. c) Topochemcial photopolymerization with 24 h sunlight.

The powder of monomer **I** polymerized under sunlight within 24 hours in the solid state.[44] To investigate the solvent-free polymerization, crystals of monomer **I** suitable for single-crystal X-ray diffraction (XRD) were obtained from DMSO/H_2O (3:1) at room temperature (see Figure S3 in the ESI†). Powder X-ray diffraction (P-XRD) was used for structural characterization of powder monomer **I**, which showed that the packing of monomer powder was the same as that of the single crystal structure (see Figure S6 in the ESI†). This indicated that the crystal structure of monomer **I** was suitable to analyze and interpret the solid state polymerization of both the crystal and powder forms. The crystal structure of monomer **I** reveals that the distance between the closest C=C bonds shown with same colors in Figure 1 (colors are introduced arbitrarily for clarity in discussion and ease of visualization) is around 3.68 Å. The distance between the closest C=C bonds with the different colors is around 4.14 Å. Because the adjacent C=C bonds with same colors are 12.5% closer than different colored double bonds in the crystal (3.68 *vs* 4.14 Å, Figure 1c), the [2 + 2] photoreaction between the C=C bonds of monomer **I** with the same colors is preferred.[45-46] Moreover, the π orbitals of adjacent C=C bonds with the same colors are directly pointing toward each other while the π orbitals of neighboring monomers with different colors are offset by more than 2 Å. This orbital overlap is critical for the locally confined reaction in the solid state, which proceeds with the minimum movement of atoms (Figure 1b-c). Therefore, the preorganization of the reactive centers in the self-assembly prefers that monomer **I** reacts with its two nearest same-colored neighbors to form the linear polyester as shown in Scheme 1.[37, 47]

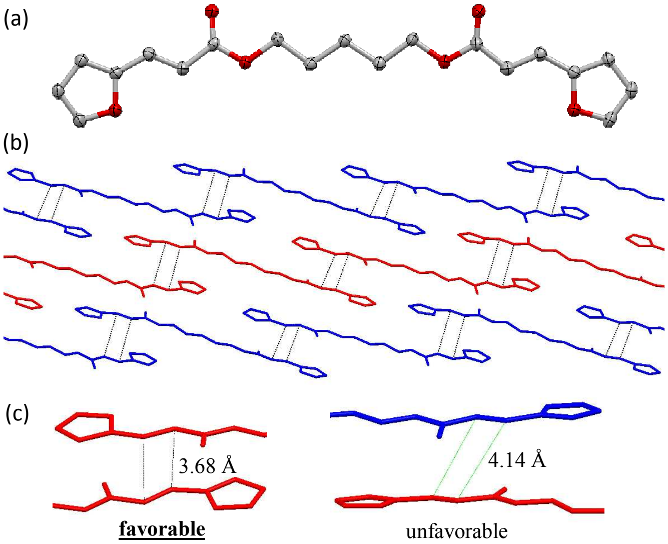


Fig. 1 Three views of the crystal structure of monomer **I** (Hydrogens are omitted for simplification and colors are introduced arbitrarily for clarity in discussion.): a) Oak Ridge Thermal Ellipsoid Plot (ORTEP) perspective at 50% electron density of the monomer **I** crystal structure. b) A side view of the crystal packing shown in capped sticks model. The closest C=C bonds are connected with dotted lines. c) The distances between C=C bonds in adjacent monomers. The dotted lines showing where the new C−C bonds could form.

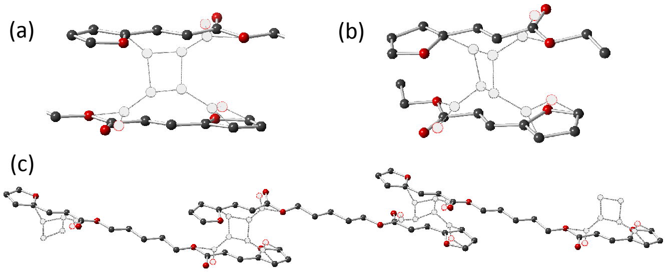


Fig. 2 The X-ray single crystal structure of intermediate **Ia** (The 15% of polymer is shown in grey and only part of the monomer/polymer is shown for simplicity.): a) Front view of the cyclobutane ring in the crystal. b) A different view of the cyclobutane showing the stereoregularity of the polymerization. c) Three monomers with the corresponding linear polymeric product.

The X-ray crystal structure with partial polymeric products was consistent with the above analysis of spatial approximation of the neighboring C=C bonds. Although the crystal **I** lost its crystallinity gradually under UV irradiation and became an amorphous solid, a single-crystal-to-single-crystal (SCSC) transformation was still observed in the beginning of the polymerization process. Figure 2 shows the partially polymerized crystal structure **Ia** with 15% of the C=C double bonds converted into cyclobutane rings. With the formation of the cyclobutane ring, the two carbonyl groups moved closer to adapt to the change of the structure in the solid state correspondingly. Meanwhile, the distance between the closest different-colored C=C bonds increased for about 0.03 Å. The partial SCSC transformation was readily repeatable. In the seven similar SCSC photopolymerization experiments, cyclobutane rings were only observed between the same-colored monomers and no cyclization was detected between the different-colored monomers. Such excellent selectivity can be ascribed to the formation of the cyclobutane ring between the two closest monomer arms, which causes a see-saw action whereby other monomer arms are made to react with monomers of the same color.

It is also noteworthy that SCSC experiments show that the monomer **I** underwent [2 + 2] photopolymerization in a known stereospecific manner.[12, 36, 48] Only one of the five possible stereoisomers of the [2 + 2] head-to-tail cyclobutane dimer was observed in all of the seven SCSC experiments (see Figure 2 and ESI† for X-ray single crystal structure of the formed stereospecific dimer and chemical structures of its four possible stereoisomers). This stereospecificity is because topochemical reaction normally proceeds with minimum movement of atoms. Stereoregularity is an essential property of polymers with stereocenters that directly affects the performance of the polymeric materials. Stereoregular polymers normally have many mechanical properties that are better than those of corresponding nonstereoregular polymers.[49]

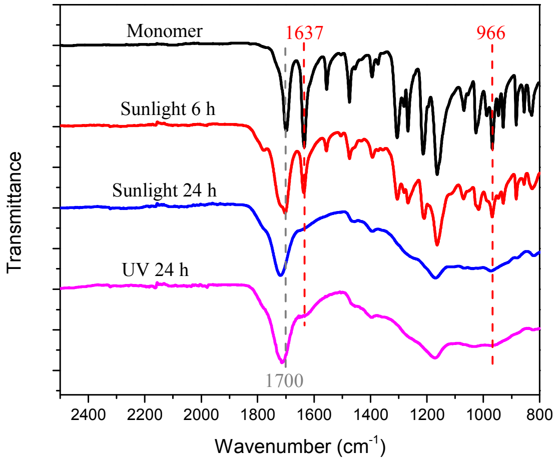


Fig. 3 The photopolymerization of monomer **I**: FT-IR spectra show that the photoreaction was completed in 24 h under sunlight and UV irradiation.

The photopolymerization process was monitored by FT-IR (Figure 3). The changes in FT-IR spectra shows the complete consumption of exocyclic C=C bonds, which is consistent with the formation of polyester **IP**. The IR spectrum of monomer **I** exhibited a strong band at 1700 cm^{-1} attributed to the stretching mode of the carbonyl groups. A new band appeared after irradiation, which indicated that the chemical environment of carbonyl groups was changing due to the de-conjugation (Scheme 1). The carbonyl band shifted from 1700 to 1723 cm^{-1} after 24 h irradiation, which signalled completion of the photoreaction. The accomplishment of the photopolymerization was also confirmed by the disappearance of bands at 1637 cm^{-1} and 966 cm^{-1} associated with the stretching of the exocyclic C=C double bond and the out-of-plane twist of the C-H single bonds in the *trans*-CH=CH unit, respectively. If a noteworthy amount of cross-linking had occurred (the [2 + 2] side photoreaction between monomers with different colors), a peak for the unreacted exocyclic C=C bond would have remained in the IR spectrum after the completion of the photoreaction.[12]

UV-Vis spectrum showed that monomer **I** had a broad absorption range from 250 to 370 nm in the solid state (see Figure S7b in the ESI†). The results of FT-IR indicate that the photopolymerization processes by sunlight and ultraviolet lamps were nearly identical (Figure 3). The photoreaction was so effective that even the small fraction of UV irradiation present in sunlight was sufficient to complete the reaction.

The polyester **IP** was found to be insoluble in common organic solvents (e.g., acetone, acetonitrile, ethyl acetate, toluene, DMF and DMSO) and acidic conditions (e.g., conc. HCl or 1M TFA), but decomposed in conc. KOH. TGA of the polyester **IP** showed nearly no weight loss below 150 °C (see Figure S8b in the ESI†). When the polymeric product was sonicated in water, nanofiber was observed under transmission electron microscopy (TEM, Figure 4).

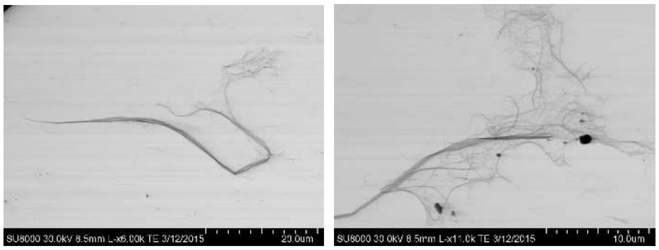


Fig. 4 TEM images of the linear polyester **IP** after exfoliation.

Similar to the design of PET, the novel polyester **IP** contains alternating rigid (the cyclobutane with two aromatic substituents) and flexible (the linear aliphatic linker) moieties in the polyester chain. Considering that the species $HO(CH_2)_nOH$ (n=2-4) can also be produced from biomass[13] and are commercially available, there is an opportunity to further tune the properties of the 100% bio-based polyesters according to future academic study or industrial production requirements. The scope of this topochemical photoreaction and the properties of the novel bio-based linear polyesters are currently under investigation.

Conclusions

A novel linear polyester was successfully synthesized from a furfural-based monomer through solvent-free photoreaction using sunlight or a UV lamp. The locally confined topochemcial polymerization process avoided cross-linking. The single crystal X-ray structures of the key photoreactive assembly and partially polymerized intermediate proved that the monomers underwent stereoregular [2 + 2] photopolymerization in the solid state. The newly formed cyclobutane rings connected monomers in one direction that resulted in the linear polyester. FT-IR spectra confirmed the completion of the ploymerization and showed sunlight was an efficient light source for the photoreaction. The polyester was formed from 100% biomass-derived chemicals via a green approach and showed promising chemical and thermal stability. The balance between the rigid and flexible moieties in the polyester chain may be fine-tuned using other commercially available bio-based diols. This research opens a new means for the construction of novel bio-based polyesters from furfural and its derivatives.

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A linear polyester was synthesized from furfural-based monomer through solvent-free polymerization using sunlight and the polymer structure was confirmed by a single crystal X-ray structure of a partially polymerized intermediate.