Two-Dimensional Oligomers and Polymers: Design and Template-Free Synthesis

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Design principle. This project involves the development of a strategy for realizing two-dimensional polymerization method that involves only the structures and bond-formation of the basic building blocks without relying on any 2D template and/or confinement. As shown in Figure 1, the bond-formation reaction involves the reaction of monomers carrying 1,2-diketone and aromatic o-diamine that result in the highly efficient (nearly quantitative) formation of a

Figure 1. Basic coupling reaction for solution-phase 2D polymerization.

pyrazine moiety. This reaction is highly favorable because it is driven by an aromaticzation process. The pyrazine ring serves as an extremely stable and rigid planar linkage that, upon being formed, prohibits bond rotation that enforces co-planarity on the now connected structural units.

Synthesis of monomeric building blocks and model reaction. During the last year, we synthesized essential building blocks, tetraketones **K1**, **K2**, **K3a**, and **K3b** (Figure 2a), by starting from the commercially available cyclic diketone **1** based on a new synthetic route we designed. The availability of these tetraketones allows our proposed 2D polymerization strategy to be tested. A model reaction was first performed by refluxing

Figure 2. (a) Synthesis of tetraketones **K1**, **K2**, **K3a**, and **K3b**. (b) A model reaction.

tetraketone **K1** with two equivalents of diamine **2** in acetic acid (Figure 2b). Product **3**, being characterized with ^1H and ^{13}C NMR and ESI-MS, was obtained in quantitative yield. The quantitative formation of compound **3** suggest that the coupling steps in a 2D polymerization based on this reaction will ensure the connection of the monomeric units in a way that is the same as that of 1D polymerizations.

Solution-phase, confinement-free 2D polymerization. The tetraketones were then treated with hexamine **A1**, which was synthesized based on reported procedures (*J. Org. Chem.* **2007**, *72*, 8683). As shown in Figure a, three reactions were performed.

Upon refluxing tetraketone **K1** and hexamine **A1** in acetic acid, a yellow precipitate, **polymer-1**, crashed out of the solution (Figure 3a). The product was collected by simple filtration and was washed with water, methanol, and dried in oven. However, attempts to dissolve **polymer-1** had failed with all solvents including the highly polar and powerfully solvating DMSO and DMF, which implies that **polymer-1** very likely has a planar rigid that strongly promote aggregation, a feature typical of many planar 2D structures.
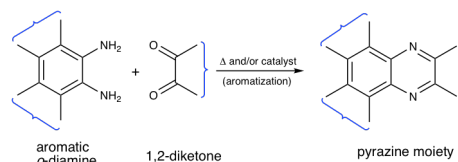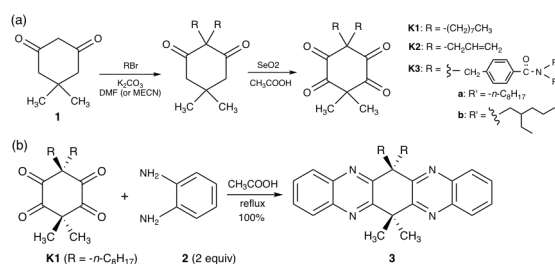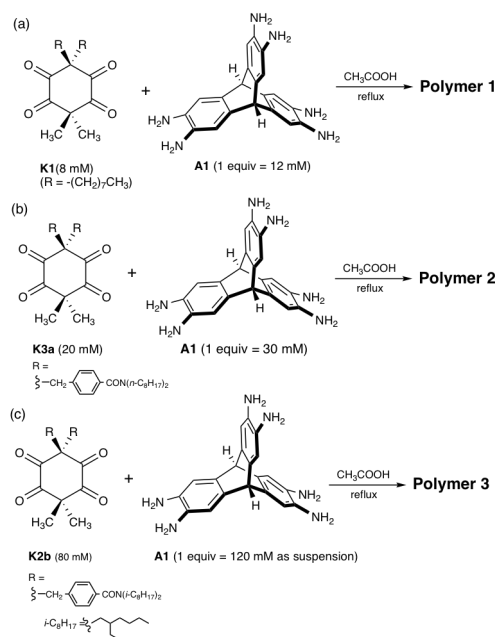

Figure 3. Solution-phase 2D polymerization reactions.

To improve the solubility of the 2D polymer product, tetraketone **K3a** was reacted with hexamine **A1** by refluxing in acetic acid (Figure 3b). The product, a light yellow solid (**polymer-2**), has a very limited solubility in chloroform that allowed ^{1}H NMR spectrum with poorly resolved peaks to be recorded. Gel permeation chromatography revealed molecular weight of over 30K.

To further improve the solubility of the polymer product, tetraketone **K3b** was reacted with hexamine **A1** by refluxing in acetic acid (Figure 3c). The precipitated product (**polymer-3**), a light yellow solid, was found to have good solubilities in chloroform, THF, DMF, DMSO, and acetic acid. Solution in THF cannot be filtered through a filter of 0.45-мm pores, implying the presence of rather large structures or particles.

Attempted characterization of 2D polymers. **Polymer-2** and **polymer-3**, the putative 2D polymers, were first examined with IR spectroscopy. The C=O stretching frequency of tetraketones **K1**, **K2a,** and **K2b** at 1708 cm^{-1} is absent in the IR spectra of compound **3** from the model reaction, and **polymer-2** and **polymer-3**, suggesting that the reaction did happen and the tetraketone reactants were consumed. New stretching bands at 1614 cm^{-1} (for **3**), 1631 cm^{-1} (**polymer-2**), and 1632 cm^{-1} (for **polymer-3**) appear in the IR spectra, indicating the formation of new C=N bonds. The ^{1}H NMR spectra of **polymer-3** in CDCl$_3$ and DMSO-d_6 peaks that can be attributed to the resonances of protons a and d that belong to the hexamine **A1** and protons b, c, and e that are from tetraketone **K3b**. The severely broadened ^{1}H NMR are consistent with the polymeric nature of the product (Figure 4). The fact that the ^{1}H NMR spectra of **polymer-3** gives the similar

Figure 4. ^{1}H NMR spectra of **polymer-3** in CDCl$_3$ (bottom) and DMSO-d_6 (top).

broadened peaks further indicate that that line-broadening is unlikely caused by aggregation but is due to the structure of the polymer itself. Attempt to image polymer-3 with AFM has not succeeded. Efforts are being made to reveal the expected honeycomb structure of **polymer-3** with STM.
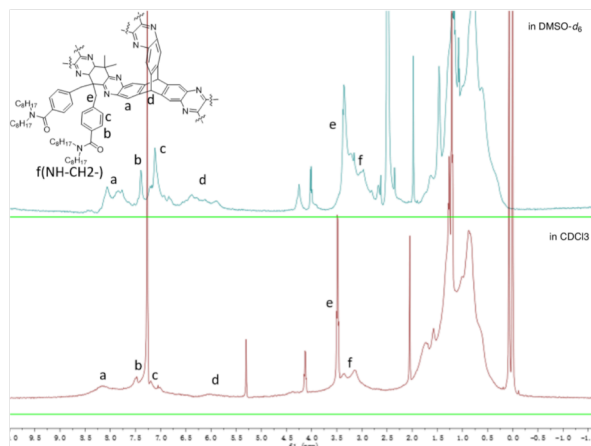
Molecular modeling of the 2D polymers. The structures of polymer-2 and polymer-3 were probed by molecular modeling. It was found that due to the rigidity of 2D polymer backbone, the modeled structure is very well defined, allowing accurate estimate of the pore size in the 2D network. Figure 5 shows the energy-minimized structure of one hexagon unit, which gives a pore of ~2.5 nm across, of the honeycomb 2D network of **polymer-2** or **polymer-3**. The side chains (replaced with methyl groups) all extend above and below the plane of the 2D network, which should help improve the solubility of the 2D polymer and thus address a major challenge in the synthesis and characterization of 2D polymers.
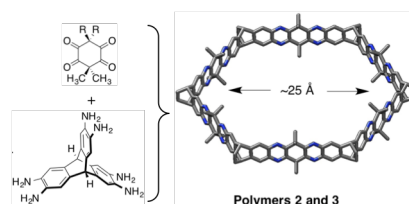

Figure 5. Energy-minimized structure of the basic hexagon unit of the honeycomb network of **polymer-2** or **polymer-3**.

Impact of the research. By performing this project, the PI and his students have had the opportunity to experience concepts and analytical techniques that are new to the group. These include the adoption of reaction conditions that are unique for forming polymeric structures, and analytical techniques such as GPC, mass spectrometry for detecting very high molecular weights, high-resolution AFM and STM, that had rarely been encountered by us before. Previous research by many other has suggested that the structural confirmation of 2D polymers represents one of the most daunting challenges toward realizing real 2D polymerization, a conclusion we also realized. However, the successful synthesis of the well soluble **polymer-3** has provided us with a unique platform for exploring all possible analytical tools to tackle this problem. We expect to obtain a host of soluble 2D polymers and to confirm the identities of at lease some of these 2D polymers at the end of the second year of this project.