Synthesis, Properties, and Conformational Dynamics of Ladder Polymers Containing *N,N'*-Diacylated Diazacyclooctane Units in their Main Chains

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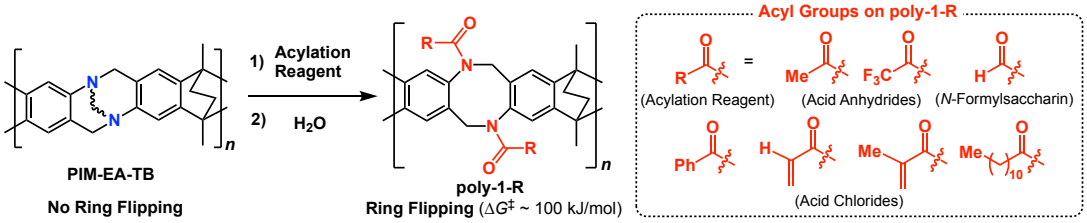
Ladder polymers are an interesting class of polymers having two or more than two bonds in their main chains and potentially exhibit superb properties, such as microporosity[1], over conventional non-ladder-type polymers. Although every previously reported ladder polymer consists of a rigid main chain, we recently reported the synthesis of conformationally flexible *N,N'*-dialkylated diazacyclooctane (DACO)-containing ladder polymers[2–4] by multi-step sequential post-polymerization reactions of a Tröger's base (TB)-containing ladder polymer (PIM-EA-TB[1]). In this work, we report a facile one-pot synthesis of *N,N'*-diacylated DACO-containing ladder polymers (poly-**1-R**) from PIM-EA-TB and their properties including the conformational dynamics and microporosity in the solid state. The reactions between PIM-EA-TB and acylation reagents, such as acid anhydrides, acid halides, and *N*-formylsaccharin, followed by addition of H_2O, successfully afforded *N,N'*-diacylated DACO-containing ladder polymers (poly-**1-R**) in quantitative conversions. The DFT calculations of the corresponding DACO monomer unit and the analysis of ^{1}H NMR spectra of the model compounds and polymers revealed that the *N,N'*-diacylated DACO ring undergoes ring flipping with an activation energy of ca. 100 kJ/mol in solution. Interestingly, despite their conformational flexibility, N_2 gas adsorption measurements at 77 K of the polymers showed that most of the *N,N'*-diacylated DACO-containing ladder polymers have microporosity in the solid state except for the polymers with phenyl groups or undecyl groups. In the presentation, we will detail the synthesis, properties, conformational dynamics, and gas adsorption properties of the *N,N'*-diacylated DACO-containing ladder polymers.



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