

Organic Base Triggered Living Supramolecular Polymerization (LSP) and Pathway Selectivity of a Carboxylic acid Appended Naphthalene-diimide (NDI) Derivative

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ABSTRACT: Living supramolecular polymerization (LSP), initiated by an externally added seed, has emerged as an attractive methodology to synthesize well-defined controlled supramolecular polymers. However, the initiator seed, unfortunately, is ill-defined fragments of a preformed aggregate which may not be desirable for achieving a high-level structural precision. To address such issues, in a conceptually new strategy, we have recently explored ^[1] a molecule triggered LSP of a naphthalene-diimide based carboxylic acid, NDI-1 (Figure 1). NDI-1 spontaneously forms entangled fibrillar aggregate (NDI-1_{agg}) in decane, but by fine-tuning the sample preparation condition, a kinetically trapped monomeric form (NDI-1_{mono}) can be produced in which the carboxylic acid group remains intramolecularly H-bonded with the adjacent imide carbonyl of the NDI chromophore. NDI-1_{mono} exhibits LSP in presence of a catalytic amount of organic base such as 4-Dimethylaminopyridine (DMAP), producing an ultra-thin 2D nano-sheet (NDI-1_{poly}), in sharp contrast to NDI-1_{agg}. By a detail mechanistic investigation, it becomes evident that the DMAP helps in the ring-opening of the intramolecularly H-bonded monomer and in situ breeds the free acid, which, beyond a critical concentration, initiates the LSP via a chain-growth route. Initially formed NDI-1_{poly} acts as a macro-initiator and can polymerize a fresh batch of NDI-1_{mono} (tested up to three cycles). Recently we have demonstrated ^[2] another

interesting possibility to regulate the pathway of supramolecular polymerization by such specific acid-base interaction. NDI-3 with three methylene spacers (instead one) between the NDI ring and the carboxylic acid group, cannot be trapped in the intra-molecularly H-bonded state. Instead, its spontaneous assembly produces irregular spherical morphology. But in presence of one equivalent DMAP, the NDI-DMAP complex is formed which adopts a well-defined cooperative supramolecular polymerization pathway, driven by the dipole-dipole interaction and π -stacking, producing J-aggregated 1D fibrillar morphology and gel in decane. With just 10 % DMAP, similar nucleation occurs but propagation occurs by an open chain H-bonding (head-to-tail arrangement) with the remaining free monomer. However further reducing the DMAP amount to 2.5 % and by slow cooling, a different supramolecular polymerization pathway was recognized. It involves nucleation by the H-bonding in the head-to-head fashion between the free carbonyl oxygen atom of the NDI-DMAP complex and free COOH of NDI-3 and propagation by H-bonding in similar fashion, leading to the formation of 2D sheet, the thermodynamically controlled product, previously achieved by LSP.^[1] This presentation will describe these recent results on such molecular recognition driven living supramolecular polymerization and pathway selectivity.

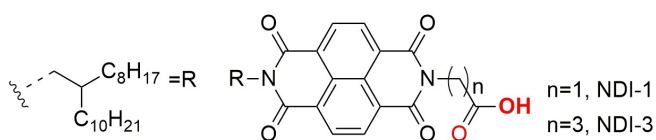


Figure 1: Chemical structures of NDI-1, NDI-3

KEY WORDS: Kinetic and thermodynamic control • 2D assembly • Hydrogen-bonding •, Ring opening polymerization • Externally regulated nucleation-elongation

References:

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