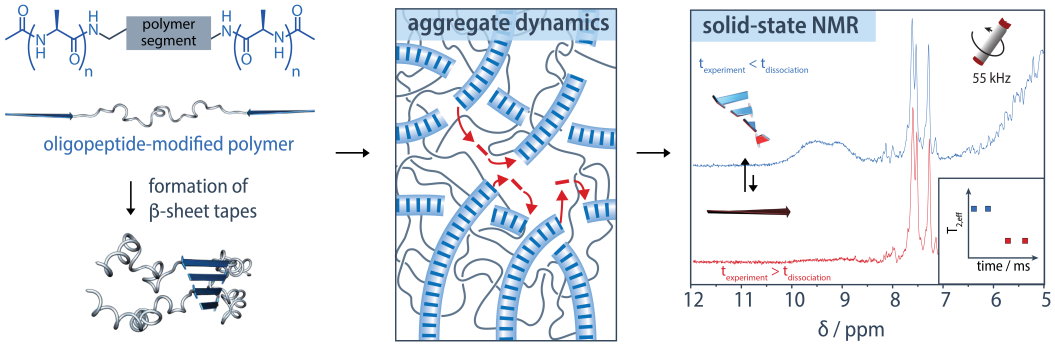
Insights into the Dynamics of Supramolecular Materials from Semicrystalline Polyesters by Solid State NMR

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Supramolecular network materials exhibit broadly tailorable thermomechanical properties which is important to adjust the processability, final product performance, or recyclability of contemporary polymer materials. These materials are typically based on the thermoreversible formation of well-defined aggregate structures from self-complementary hydrogen-bonding ligands that serve as physical crosslinks to the polymer matrix. The intrinsic dynamic behavior of these aggregates often gives further rise to self-healing properties, shape-memory effects, or stimuli-responsiveness. This dynamic behavior arises from the scission-reaggregation events of the ligands at the molecular level, the timescale of which directly influences their macroscopic behavior. Site-specific studies on the dynamic kinetics of supramolecular crosslinks on a molecular scale are limited to dilute solution states, leaving a fundamental gap in our understanding of structure-dynamics-property relationships in technologically relevant solid-state polymer materials.



In this study, we investigate the aggregation-scission dynamics of helical one-dimensional network junctions from β-sheet forming oligopeptide end groups of a telechelic polyester using solid-state NMR for the first time. By employing Carr-Purcell-Meiboom-Gill relaxation dispersion experiments, we monitor the dissociation events over time and at different temperatures, including room temperature when the polymer matrix is semi-crystalline. Our results reveal that the amide dissociation in the crystallized polymer matrix occurs between 0.15–0.45 ms, and is accelerated to a range of 0.08–0.15 ms in the polymer melt at 60 °C. This methodology eliminates the need for additional chemical modifications, can site-specifically detect dissociation events down to 1 wt% of supramolecular linker content, and is applicable at variable temperatures, even in semi-crystalline polymer states. Our approach therefore holds promise for advancing the understanding of supramolecular network dynamics and for accelerating the development of next-generation functional materials.

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