

Self-assembled Polymeric Materials via Breath Figure and Light

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The self-assembly of organic molecules has attracted much research interest and numerous organic molecules have been reported as low molecular-weight organogelators (LMOG) which form self-assembled fibrillar networks. However, the organogelators containing dendritic branches have been studied rather recently. Utilization of dendritic architectures in the self-assembly is highly attractive partly because of the interesting characteristics encoded in their molecular structures such as the cone-shape architecture, a large number of functional groups on the surface and easily tunable focal point. Also, the macromolecular nature with well-defined architecture is expected to fill the gap between polymeric and small molecules.

We synthesized bis-dendritic gelators consisting of aliphatic units containing a diacetylene group and benzamide units to achieve photopolymerizable self-assembled materials. The dendritic molecules showed a gelation behavior in many organic solvents. To make hierarchically structured polymeric materials with the organogelators, we combined the top-down and bottom-up approaches. The breath figure (BF) technique was applied to a photoresponsive organogelators containing diacetylene groups, causing it to self-assemble into supramolecular fibrillar networks and further a hierarchically ordered honeycomb structure. The resulting structure was then patterned by exposure to UV irradiation through a photomask, which induced selective chemical crosslinking in the exposed region. After developing, honeycomb lines were obtained at pre-defined locations. Not only the formation of highly ordered BFs with organogelator molecules, but also the programmed patterning of BFs by using lithographic techniques has been demonstrated. This process holds great promise for fabrication of “custom” honeycomb patterns, because it is simple, applicable to various substrates, and does not require additional photoresists or processes.

Evolution of supramolecular chirality from self-assembly of achiral compounds and control over its handedness is closely related to the evolution of life, and development of supramolecular materials with desired handedness has been a very challenging issue. We have demonstrated that the entire process of induction, control, and locking of supramolecular chirality can be manipulated by light. Combination of triphenylamine and diacetylene moieties in the molecular structure allowed photoinduced self-assembly of the molecule into helical aggregates in a chlorinated solvent by visible light and covalent fixation of the aggregate via photopolymerization by UV. By utilizing circular polarized light (CPL), we observed that supramolecular chirality of the resulting helical aggregates was selectively and reversibly controlled by the rotational direction of visible CPL, and the desired supramolecular chirality could be arrested by irradiation of circular polarized ultraviolet light. This methodology opens a route for the formation of chiral polymeric materials by self-assembly of achiral molecules.