

Polymer Helix Formation on Irradiation with Circularly Polarized Light

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Interactions between substances and light play important roles in life. One of the most important aspects is photosynthesis by plants and other organisms. In photosynthesis, sugars and molecular oxygen are produced from carbon dioxide and water where photon energy drives the reaction. Moreover, in artificial chemical synthesis, light promotes various reactions that are not driven by thermal energy. Further, in reactions where chiral compounds are produced, non-racemic products can be obtained using circularly polarized light (CPL). We recently reported that a preferred-handed helical conformation is induced for a linear polyfluorene derivative (poly(9,9-dioctylfluorene-2,7-diyl [PDOF])) in the solid state when the polymer is irradiated with CPL (Scheme 1) [1,2]. The mechanism of this chirality induction involves a twisted-coplanar transition (TCT) of an aromatic–aromatic junction in the polymer where one of the enantiomeric, right- and left-handed twists is preferentially excited into the coplanar conformation. TCT through photo excitation was first predicted for biphenyl through theoretical calculations [4].

In the CPL-driven helix formation of the linear polyfluorene derivative, strong inter-chain interactions were important in effectively induce chirality, which in turn implicates that polymers with weak inter-chain interactions cannot be subjected to the CPL method. This weak point of the CPL method was over come via using aid molecules which reinforce or simulate inter-chain interaction. This method was realized for a star-shaped fluorene oligomer which had been designed to have only weak inter-chain interactions [3]. The applicability of the CPL method was thus largely extended.

A series of work was initiated by the finding of photo racemization of a preferred-handed helical polyacrylate where side-chain biphenyl moiety in the polymer underwent “twist-coplanar transition” on photo excitation with non-polarized light.^{2,3} This work was extended to CPL-driven helix formation of poly(9,9-di-n-octylfluorene-2,7-diyl) in a thin film form where 5/1-helix is reversibly formed by CPL irradiation.⁴⁻⁶ This methodology has been extended to other polymer chains.

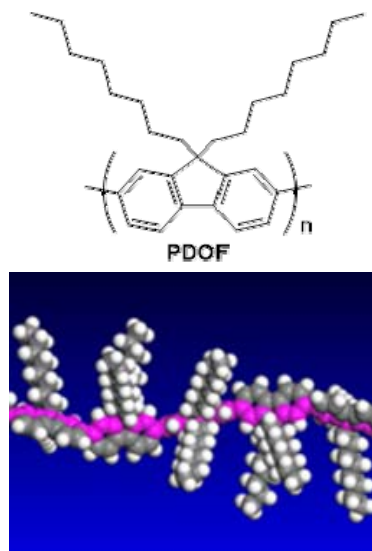


Fig.1 Chemical structure (top) and 5/1-helical conformation (bottom) of PDOF.

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