Cyclopolymerization of Dimethyl Dipropargylmalonate in Supercritical Carbon Dioxide to Give a Regular Polyene Containing Predominantly Five-Membered Rings

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Recently, the literature reflected an intensive interest in metal-catalyzed olefin metathesis polymerization in supecritical CO_2 . Chemical interactions of supecritical CO_2 with substrates and/or catalysts offer an as yet largely unexplored potential for activity and selectivity control. 1,6-Heptadiyne containing appropriate substituents at the 4-position is a very interesting example of substituted acetylenes, which can be susceptible to the ring-forming polymerization to give a new type of conjugated polymer backbone system. It is a very important task to prepare cyclopolymers that have only one size ring. Herein, we report for the first time the cyclopolymerization of dimethyl diproparglymalonate by $MoCl_5$ catalysts (without using any well-defined alkylidene complexes as initiators) in supecritical CO_2 which encourage regioselective addition of the first triple bond to an alkylidene to give highly regular polyene containing one size rings in the polymer backbone as a consequence of chemical interaction of CO_2 with the transition metal catalysts.