

Poly(substituted Methylene) Synthesis: Construction of C–C Main Chain from One Carbon Unit

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Abstract This review describes recent progress in the preparation of C–C main chain polymers, where the main chain is constructed from one carbon unit. The first example for this strategy is polymerization of diazoalkanes and aryldiazomethanes, which were extensively explored in the period 1950–1970, despite the high explosiveness of the monomers. The metal surface-catalyzed polymerization of diazoalkanes has recently attracted much attention, as an efficient method for coating the surface with nanometer-scale polymethylene thin films, which can be regarded as a useful substitute for polyethylene films. Diazocarbonyl compounds such as diazoacetates, diazoketones, and diazoacetamides with a variety of substituents have been polymerized by Pd-complexes to give poly(substituted methylene)s with polar functional groups. Rh(diene) complexes polymerize ethyl diazoacetate in a stereospecific manner, giving high molecular weight polymers (M_n up to 270,000). Organoborane-initiated living polymerization of sulfoxonium methylides is remarkably effective as a method for preparing polymethylenes with a controlled chain length and a well-defined polymer architecture. Some polymerizations related to the above examples are also described.

Keywords Diazoalkane · Diazocarbonyl compound · Metal surface · Organoborane · Poly(substituted methylene) synthesis · Pd complex · Rh complex · Sulfoxonium ylide

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