SYNTHESIS AND STRUCTURE OF REGIOREGULAR POLY(1,4-POLY-ARYLENE)

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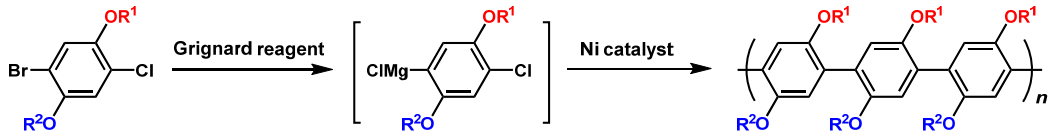
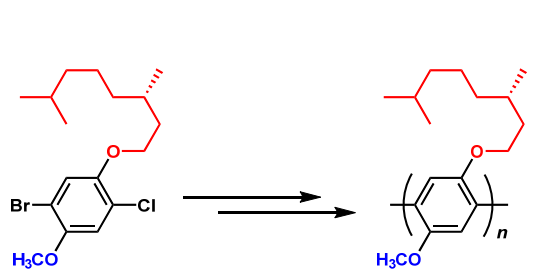
Herein we describe unprecedented synthesis of regioregular poly(1,4-arylene) bearing a different substituents at the 2- and 5-positions by polymerization of 1-bromo-4-chloroarylenes. Regioregular poly(1,4-arylene) bearing a chiral substituent was also synthesized suggesting chirality-induced higher order orientation of the polymer structure such as helix.

Polymerization of 1-bromo-4-chloroarylenes 2 was carried out with a Grignard reagent to undergo the carbon-bromine exchange followed by treatment with Ni catalyst to afford regioregular poly(1,4-arylene) 1. (Scheme1) Formation of the regioregular poly(1,4-arylene) was confirmed by the measurement of $^{13}C\{^{1}H\}$NMR spectrum, which showed remarkable difference from the related polymer with uncontrolled regioregularity. Measurement of the CD spectrum of obtained poly(1,4-arylene) 3 bearing a chiral substituent showed the Cotton effect at the wavelength corresponding to the λ_{max} of the (1,4-arylene) moiety of the polymer main chain. The Cotton effect was observed in a mixed solution 1,2-dichloroethane/methanol. (Scheme2)



2 1

Scheme 1.



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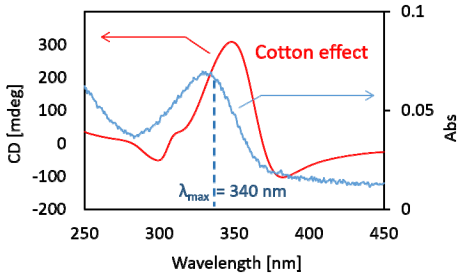
Scheme 2.



UV-vis and CD spectra
1,2-dichloroethane:methanol (7:3) solution