Polyethylenes Bearing In-chain Amide Groups *via* Beckmann Rearrangement: Synthesis and Their Physical Properties

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The post-polymerization modification of polymer is a useful method to improve properties of commodity plastics. Insertion of atoms into polymer main chain is rather attractive, which would allow the significant change of physical properties of polymer. However, relatively less examples are known utilizing Schimidt rearrangement, Baeyer-Villiger oxidation, Claisen rearrangement, etc. Recently, Mecking *et al* and our group reported the polymerization of high density polyethylene (HDPE) bearing isolated in-chain carbonyls from ethylene and CO or $Fe_2(CO)_9$ as a CO source (**Figure 1**a).[1, 2] Furthermore, Mecking *et al* also reported the Baeyer-Villiger oxidation of polyethylene bearing in-chain carbonyls to polyethylene-ester, which demonstrates the potential of polyethylene-ketone as a substrate for main chain editing.[3]

In this work, polyethylenes bearing in-chain amide groups were synthesized by oxime-formation and Beckmann rearrangement of polyethylenes bearing in-chain carbonyl groups (**Figure 1**b). Despite the low solubility of the polymers, the use of DAST as a highly reactive promoter of Beckmann rearrangement allowed high conversion to amide functional group at room temperature with no remarkable decrease of molecular weight.[4] The new polymer showed similar thermal stability and melt property with polyethylene, however, the tensile test of the polymer revealed significantly increased strength compared to an unfunctionalized polyethylene bearing similar molecular weight, probably due to the hydrogen-bonding of amide groups.

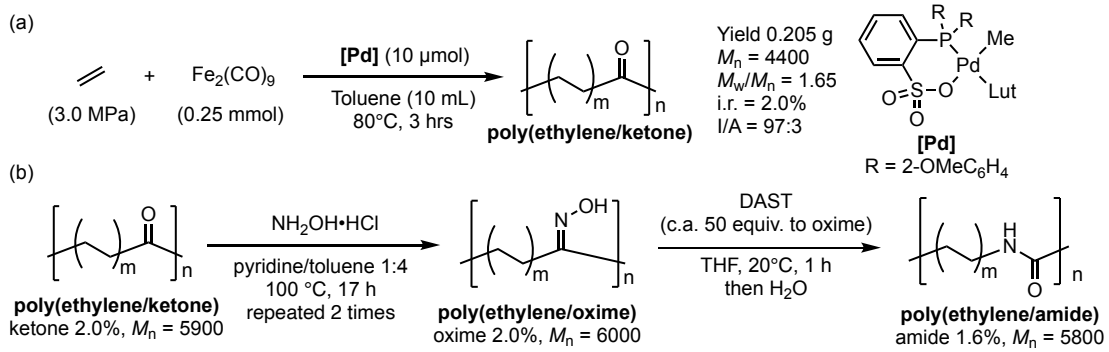

Figure 1. Post-polymerization modification of polyethylene bearing in-chain carbonyls

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