Synthesis and Characterization of Methoxybenzene-Linked Polyimides by 1,4-Addition to Bismaleimides

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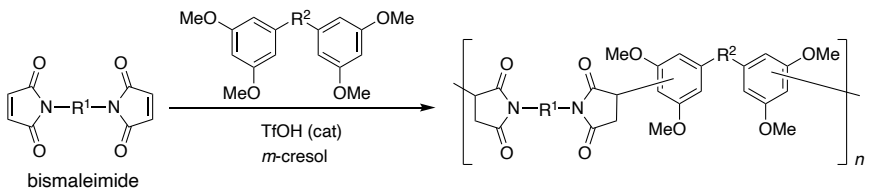
Bismaleimides have been employed in polymer synthesis by Diels−Alder, ene, and 1,4-addition (Michael addition) reactions.[1] Focusing on the 1,4-addition reactions, commercial Kerimid 601 and Compimide 200, which have been employed as advanced composites with high thermal stability, were prepared from bis(4-aminophenyl)methane and 4,4'-bismaleimidodiphenylmethane. In 1,4-addition reactions, three types of nucleophiles such as diamines, dithiols, and *glycerol* have been reported to react with bismaleimides to give various polyimides.[2] We envisioned that 1,4-addition of nucleophilic monomers having two alkoxybenzenes to bismaleimides would afford a new series of polyimides.[3]

Reaction of 1,3-bis(3,5-dimethoxyphenoxy)propane and 4,4'-bismaleimidodiphenylmethane with a catalytic amount of trifluromethanesulfonic acid (TfOH) in *m*-cresol yielded a polyimide with a number average molecular weight (M_n) of 8000 and a molar-mass dispersity ($Đ_M$) of 2.2. Characterization of the polymer by ^{1}H NMR and MALDI-TOF MS measurements suggested that it was formed via 1,4-addition. Both linear and cyclic polymers were formed with a mixture of regioisomers on the benzene rings. The use of different bismaleimides provided polyimides having M_n values of 9500 and 15000 with $Đ_M$ values of 2.1 and 3.9, respectively. On the other hand, polymerization with 5,5'-oxybis(1,3-dimethoxybenzene) as a nucleophilic monomer provided polyimides with M_n values of less than 4000.

The synthesized polyimides showed good thermostability as judged by 10% weight loss temperatures more than 400 °C. Their glass transition temperatures were around 200 °C. These polymers were well soluble in organic solvents such as *m*-cresol and DMF, but not in hexane, benzene, toluene, and methanol.



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