Chapman rearrangement in the synthesis of aromatic polyamides

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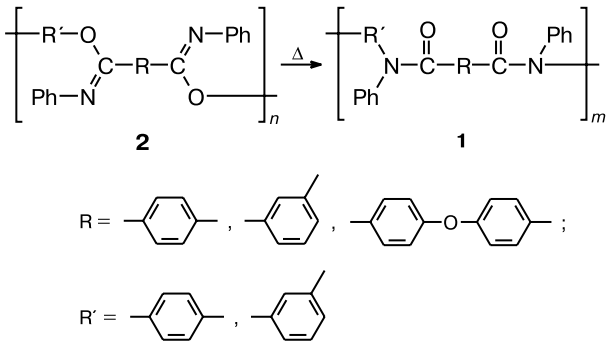
Aromatic *N*-phenylpolyamides are thermally more resistant and easier to process than their unsubstituted analogs.[1] We demonstrated that *N*-phenylpolyamides **1** can be synthesized from polyimidates **2** [2] *via* Chapman rearrangement[3] (Scheme 1).

Scheme 1



Such a rearrangement was carried out in melt (240—280 °C, 13—17 h), film (210—240 °C, 7—9 h), and a solution of diphenyl ether (230—250 °C, 8—11 h).

The structure of polymer **1** was confirmed by IR spectroscopic (KBr) data: the characteristic absorption bands of polyimidates (1651 cm^{-1} (C=N)) are shifted to 1657 cm^{-1} (C=O), while the band at 1210 cm^{-1} (C—O) is virtually absent. The most convincing evidence was obtained from ^{13}C NMR spectra (DMSO-d_6): the signal at δ 165.8 indicates the presence of a carbonyl C atom.

A comparison of the viscosity parameters of the starting and resulting polymers shows that the molecular mass remains virtually unchanged upon the rearrangement.

Like the corresponding polyimidates, the polyamides obtained are soluble in DMF, *N*,*N*-dimethylacetamide, DMSO, *m*-cresol, and pyridine, and, when heated, in $CHCl_3$ (no heating is required for the starting polymers).

The polyimidate—polyamide rearrangement insignificantly changes the heat resistance of the polymer: glass transition temperatures are 275—320 and 220—250 °C, respectively. The polyamides obtained are vastly superior to polyimidates in thermal stability. According to TGA data (5 °C min^{-1}, air), polyamides **1** lose 10% of their weight at 450—490 °C, the weight loss being much higher than that for the corresponding starting polyimidates (360—410 °C).

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