

SUPPORTING INFORMATION

Solvent-free reactive extrusion as an innovative and efficient process for the synthesis of polyimides

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Characterization of the reagents and expected products by ^{13}C NMR
(Table S1)

Table S1: ^{13}C NMR shifts for BTDA, Jeffamine D-230, the corresponding poly(amic acid) and polyimide^{35–37}

| Atom | δ (ppm) | | | |
|----------|----------------|----------------|---|-------------|
| | BTDA | Jeffamine | Poly(amic acid) | Polyimide |
| a | 193.9 | - | 195.1 | 193.7 |
| b | 163.0 | - | 167.7 - 167.2 | 167.5 |
| c1 | 138.3 | - | 142.9 | 141.8 |
| c4 | 137.7 | - | 139-138.5 (amide) 137.5/137.4 (acid) | 135.0 |
| c3 | 132.7 | - | | 132.1 |
| c6 | 132.6 | - | 135.6 | 136.1 |
| c2 | 130.1 | - | 133.8 – 128.7 | 123.9 |
| c5 | 129.1 | - | | |
| d1/d2/d3 | - | 78.5 – 72.1 | 75.4 – 70.0 | 75.3 – 68.7 |
| d4 | - | 46.9/46.7/46.5 | 45.9 – 44.9 | 47.4 – 46.5 |
| e1 | - | 17.6 | 17.8 – 17.3 | 17.7 – 17.1 |
| e2 | - | 20.6 | 17.5 – 17.4 | 15.1 |

Imidization kinetics by ^{13}C NMR (Table S2) and by DSC (Table S3)

Table S2: Imidization rate determined by ^{13}C NMR according to equation (1).

| System | | BTDA/D230 | | |
|-----------------------------|---------|-----------|-----|-----|
| T ($^{\circ}\text{C}$) | | 180 | 200 | 225 |
| Imidization rate (mol %) | 0 min | 10 | 10 | 10 |
| | 0.5 min | 57 | 72 | 85 |
| | 1 min | 77 | 86 | 90 |
| | 1.5 min | 82 | 88 | 95 |
| | 2 min | 87 | 91 | 95 |
| | 2.5 min | - | - | - |
| | 3 min | 89 | 93 | 97 |
| | 4 min | 90 | 95 | 98 |
| | 5 min | 93 | 96 | 98 |

Table S3: Imidization enthalpy and molar conversion values measured by DSC for the system BTDA/D-230

| System | | BTDA/D-230 | | |
|-------------------------------------|---------|------------|------|-----|
| T (°C) | | 180 | 200 | 225 |
| Enthalpy (kJ.mol ⁻¹) | 0 min | 149 | | |
| | 0.5 min | 37.1 | 32.9 | 7.2 |
| | 2.5 min | 17.1 | 4.2 | 3.2 |
| | 4 min | 10.2 | 3.9 | 3 |
| | 0 min | 0 | 0 | 0 |
| Conversion (mol%) | 0.5 min | 75 | 78 | 95 |
| | 2.5 min | 89 | >95 | >95 |
| | 4 min | 93 | >95 | >95 |