

Microfabrication of high-performance aromatic polymers as nanotubes or fibrils by *in situ* ring-opening polymerisation of macrocyclic precursors

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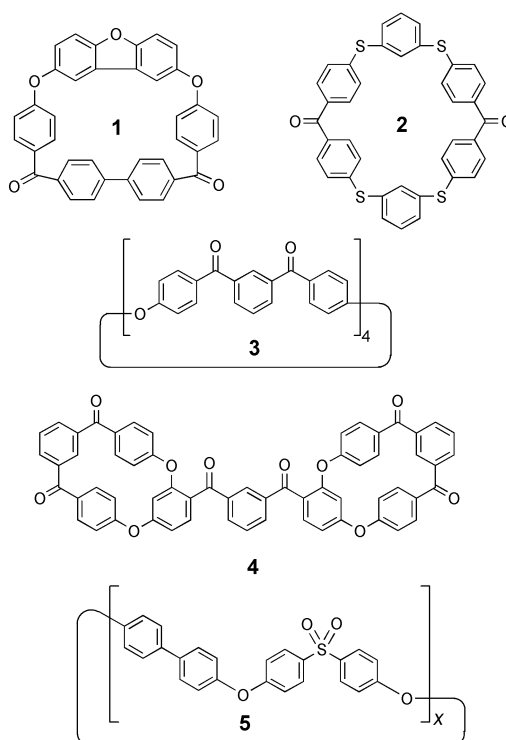
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Melt-phase nucleophilic ring-opening polymerisation of macrocyclic aromatic ethers and thioethers at high temperatures within the cylindrical pores of an anodic-alumina membrane, followed by dissolution of the template, enables replication of the membrane's internal pore structure and so affords high-performance aromatic polymers with well-defined fibrillar or tubular morphologies.

In view of the very high melt viscosities of commercially available high-performance aromatic polymers such as the polyimides,¹ polysulfones,² and polyketones,³ their potential applications in microscale fabrication are severely limited. However, no such restriction should, in principle, hold for reactive processing of macrocyclic homologues of such materials, since oligomers of this type have extremely low melt viscosities and readily undergo nucleophilic ring-opening polymerisation, *via* ether interchange, at high temperatures.^{4,5} Successful replication of the internal pore structure of an alumina microfiltration membrane is generally regarded as an excellent test of a material's potential value in micro-fabrication applications.⁶ Using this technique, we now demonstrate microfabrication of high-performance polymers on a length scale of 200–400 nm *via* melt-phase ring-opening polymerisation.

The known polymer precursors, **1** and **2**,^{4b,5d} and two novel macrocycles, **3** and **4**, were chosen for this investigation, together with the polymerisable macrocyclic ether-sulfone fraction **5** ($x = 2-10$).^{5g} All these precursors melt below 360 °C and are thus potentially capable of being processed in the melt without interference from thermal decomposition. Macrocycle **3** was synthesised by base-promoted cyclocondensation of 1,3-bis(4-fluorobenzoyl)benzene with 1,3-bis(4-hydroxybenzoyl)benzene under pseudo-high dilution conditions. It was isolated chromatographically in 10% yield from a mixture of macrocyclic products and was characterised both spectroscopically and by single crystal X-ray analysis (Fig. 1).[†] The novel bicyclic oligomer **4**,[‡] designed to undergo cross-linking ring-opening polymerisation, was obtained in high yield by Friedel-Crafts condensation of isophthaloyl chloride with two equivalents of a known resorcinol-derived macrocycle.⁷



Two alternative approaches to microfabrication *via in situ* polymerisation were investigated. In the first, an intimate mixture of nucleophilic initiator (a fluoride or phenoxide salt) and macrocycle was compressed to form a thin (*ca.* 0.2 mm) disc, which was placed in direct contact with the surface of the membrane (Whatman Anodisc, limiting pore diameter 0.1 μm) in a DSC crucible. The sample was then heated, under nitrogen, to a temperature at which it was envisaged the macrocycle would melt and be drawn rapidly into the pores by capillary action before polymerising. After a short time (5–10 min) at the polymerisation temperature (typically 350–380 °C) the sample was cooled, removed from the DSC crucible and immersed in 3 M sodium hydroxide overnight to dissolve the templating alumina membrane. The structure of the polymeric residue was



Fig. 1 X-Ray structure of the macrocyclic ether-ketone precursor 3.

then examined by scanning electron microscopy. A micrograph of the polyetherketone resulting from ring-opening polymerisation of macrocycle 3 is shown in Fig. 2. The fibrillar microstructure provides strong evidence that the membrane pores were completely filled by molten macrocycle, and the obvious flexibility of the resulting fibrils suggests that they do indeed comprise high molar mass polymer. This was confirmed by GPC analysis of the fibrillar material produced by ring-opening polymerisation of macrocyclic fraction 5, which gave values for M_w and M_n of 44700 and 24200 respectively. A sharply defined transition zone between fibrillar material produced within the membrane and solid polymer formed from excess macrocycle remaining on the surface is clearly evident at the lower left of Fig. 2. Careful measurements of the fibrils produced in this and other polymerisations gave diameters of between 200 and 400 nm, in contrast to the nominal membrane pore diameter of 0.1 μm . The latter value however relates to the separation properties of the membrane, not specifically to its internal pore dimensions. Electron microscopy in fact shows a significant degree of membrane asymmetry, such that the internal pore diameter is greater than the nominal figure.

A second approach to reactive microfabrication involved prior impregnation of the membrane with caesium fluoride initiator. Alumina-supported fluoride ion is known to be highly reactive,⁸ and polymerisation should, in these circumstances, occur only within the membrane pores. The technique was designed specifically to enable fabrication of the highly strained macrocycle 1 which is known to undergo nucleophilic polymerisation only a few degrees above its melting point.^{4b} By locating the initiator *within* the membrane, premature

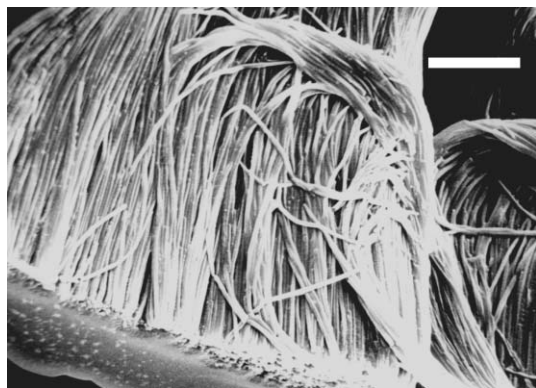


Fig. 2 Fibrillar morphology of the polyetherketone fabricated by membrane-templated ring-opening polymerisation of macrocycle 3, initiated by caesium fluoride added to the macrocycle. Scale bar: 10 μm .

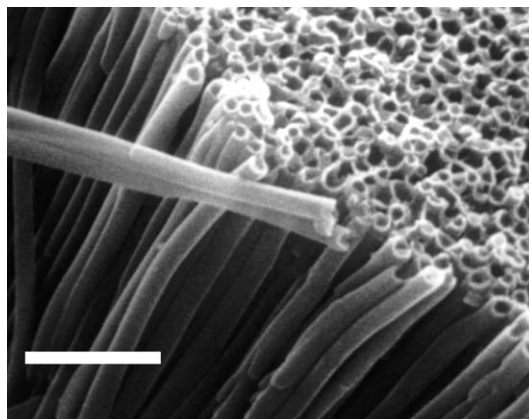


Fig. 3 Tubular morphology of a cross-linked polyetherketone formed by ring-opening polymerisation of macrobicyclic 4, initiated by the potassium salt of 4-hydroxybenzophenone. Scale bar: 2 μm .

polymerisation was avoided, again giving a material with a well defined fibrillar morphology.

In a number of cases (specifically with precursors 4 and 5), *tubular* rather than fibrillar polymer morphologies were identified (see for example Fig. 3). Analogous tubular morphologies have been observed in materials formed by solution-polymerisation of acrylonitrile within anodic alumina membranes,⁹ and also by melt-impregnation of polystyrene and other polymers into these and other related types of membrane.^{6d} Tubule formation was there explained in terms of preferential adsorption of material on the pore walls, and the same effect (assuming a deficit of precursor relative to the available pore volume) would account for tubule formation in the present work.

In conclusion, we have demonstrated that *in situ* ring-opening polymerisation of a wide range of low-viscosity macrocyclic aromatic oligomers enables fabrication of high-performance polymers at length scales well below 1 μm , successfully replicating the internal pore structure of an anodic alumina membrane with both linear and cross-linked polymers.

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Notes and references

† Characterisation data for 3: M.p. 337 °C (DSC); MS (MALDI-TOF, dithranol matrix) $m/z = 1200$ (100%, $[M + H]^+$); $^1\text{H NMR}$ (CDCl_3) δ (ppm) 8.08, (t, $J = 1.6$ Hz, 4H), 7.96 (dd, $J = 7.8$ and 1.6 Hz, 8H), 7.80 (d, $J = 7.9$ Hz, 16 H), 7.60 (t, $J = 7.8$ Hz), 7.07 (d, $J = 7.9$ Hz, 16H); Anal. Calc. for $\text{C}_{80}\text{H}_{48}\text{O}_{12}$: C, 79.99; H 4.03. Found: C, 79.26; H 4.01%. Crystal data: $\text{C}_{80}\text{H}_{48}\text{O}_{12} \cdot 2\text{CH}_2\text{Cl}_2$, triclinic, space group $P\bar{1}$, $a = 9.699(1)$, $b = 12.532(1)$, $c = 14.642(2)$ Å, $\alpha = 77.94(1)$, $\beta = 88.10(1)$, $\gamma = 71.15(1)^\circ$, $V = 1645.9(3)$ Å³, $M = 1371.04$, $T = 293(2)$ K, $Z = 1$, $D_c = 1.383$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 2.188$ mm⁻¹, $F(000) = 708$, $R_1 = 0.0509$, $wR_2 = 0.1347$ for 3852 independent observed reflections, $R_{\text{int}} = 0.032$ [$I > 2\sigma(I)$]. CCDC reference number 208055. See <http://www.rsc.org/suppdata/jm/b3/b303948j/> for crystallographic data in CIF or other electronic format.

‡ Characterisation data for 4: M.p. 332 °C (DSC); MS (MALDI-TOF, dithranol matrix, CF_3COONa) $m/z = 938$ (100%, $[M + \text{Na}]^+$); IR (Nujol) ν_{max} 1664, 1593 cm⁻¹; $^1\text{H NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$) δ (ppm) 8.38 (t, $J = 1.4$ Hz, 1H), 8.24 (dd, $J = 7.7$ and 1.5 Hz, 4H), 7.98 (dd, $J = 7.7$ and 1.4 Hz, 2H), 7.68 (t, $J = 7.7$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 4H), 7.48 (t, $J = 7.7$ Hz, H), 7.36 (d, $J = 8.7$ Hz, 4H), 7.09 (d, $J = 8.7$ Hz, 4H), 7.03 (t, $J = 1.5$ Hz, 2H), 6.96 (dd, $J = 8.5$ and 2.2 Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 4H) and 5.77 (d,

$J = 2.2$ Hz, 2H). Anal. Calc. for $C_{60}H_{34}O_{10} \cdot 0.25CH_2Cl_2$: C 77.30%, H 3.71%; Found C 77.70%, H 3.79%.

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