



## Supporting Information

for

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# Entropically-driven Ring-opening Metathesis Polymerisation of Macrocyclic Olefins with from 21- to 84-Ring Atoms

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The Supplementary Information given here consists of four examples of gel permeation chromatograms (GPC's) and an example of a matrix assisted laser desorption ionisation time of flight mass spectrum (MALDI TOF MS). It should be noted that the manner in which the GPC's are plotted means that the hydrodynamic volumes of the components **decreases** from left to right. The low molecular weight markers, indicated on traces by "M" and is in most cases *n*-dodecane, appear at the extreme right. Finally, details of the conditions used to obtain the GPC's and the MALDI TOF MS are given.

**Figure 1** shows the GPC of the cyclic monomer **4** obtained after purification by column chromatography. The GPC was obtained using the "oligomers" instrument.

**Figure 2** shows the GPC of the mixture of cyclic oligomers **15** obtained by the cyclo-depolymerisation of polymer **12**. The GPC was obtained using the "oligomers" instrument.

**Figure 3** shows the GPC of the product obtained by the ring-opening polymerisation of the mixture of cyclic oligomers **15**: see Table 1, entry 7. The GPC was obtained using the "polymers" instrument.

**Figure 4** shows the MALDI TOF MS of the mixture of cyclic oligomers **15** obtained by the cyclo-depolymerisation of polymer **12**. There are clear signals due from the cyclic monomer **5** up to the cyclic pentamer. The signals correspond to the series  $[M + Na]^+$

**Figure 5** shows the series of GPC's for the experiments summarised in Table 2 of the paper. In the experiments the cyclic monomer **4**, either neat or at various concentrations in

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dichlormethane, was equilibrated for 12 hrs at 40°C using 1 mol% of “second generation” catalyst **2**. The GPC’s were obtained using the “polymers” instrument. Trace (a) is that obtained from the experiment carried out with neat monomer **4**; Trace (b) is that obtained using a 50% w/v solution; Trace (c) is that obtained using a 2% w/v solution; and Trace (d) is that obtained using a 0.5 % w/v solution.

### *Experimental Details*

Two GPC instruments were used. One was equipped with columns best suited to the analysis of “oligomers” and the other with columns best suited to the analysis of “polymers”.

The GPC instrument for “oligomers” was an in-house-assembled instrument equipped with a Waters M45 pump operating at a flow rate of 1 cm<sup>3</sup> per minute through a Waters Styragel HR1, 2 and 3 three-column set followed by a Gilson 132 Differential Refractometer for detection with tetrahydrofuran as eluant. The data was collected and analysed using software developed in the Manchester Polymer Group from Lab VIEW software (National Instruments).

The GPC instrument for “polymers” was an in-house-assembled instrument equipped with a Knauer 64 pump operating at a flow rate of 1 cm<sup>3</sup> per minute through a PL Gel 30 cm 10 μ Mixed-B (x 2) and 500A (x 1) three-column set followed by a Gilson 132 Differential Refractometer for detection with tetrahydrofuran as eluant. The system was calibrated using a series of polystyrene standards, each with a narrow polydispersity. The data was again collected and analysed using software developed in the Manchester Polymer Group from Lab VIEW software (National Instruments).

The MALDI-ToF MS was obtained using a Micromass ToF Spec 2E mass spectrometer equipped with a Nitrogen Laser operating at 337nm with a 4 ns pulse width. The matrix employed was dithranol doped with sodium bromide.

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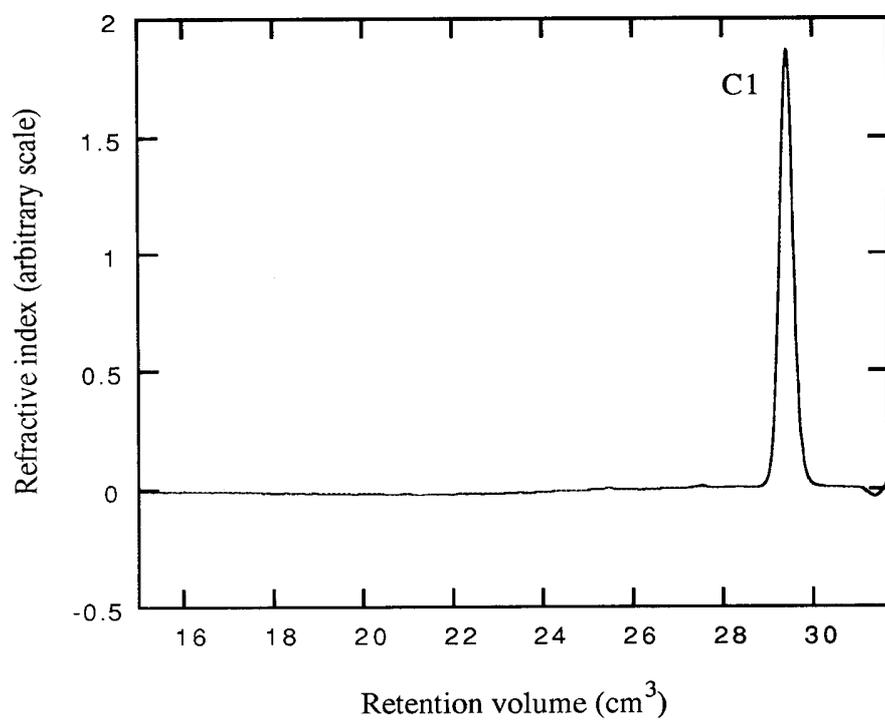


Figure 1

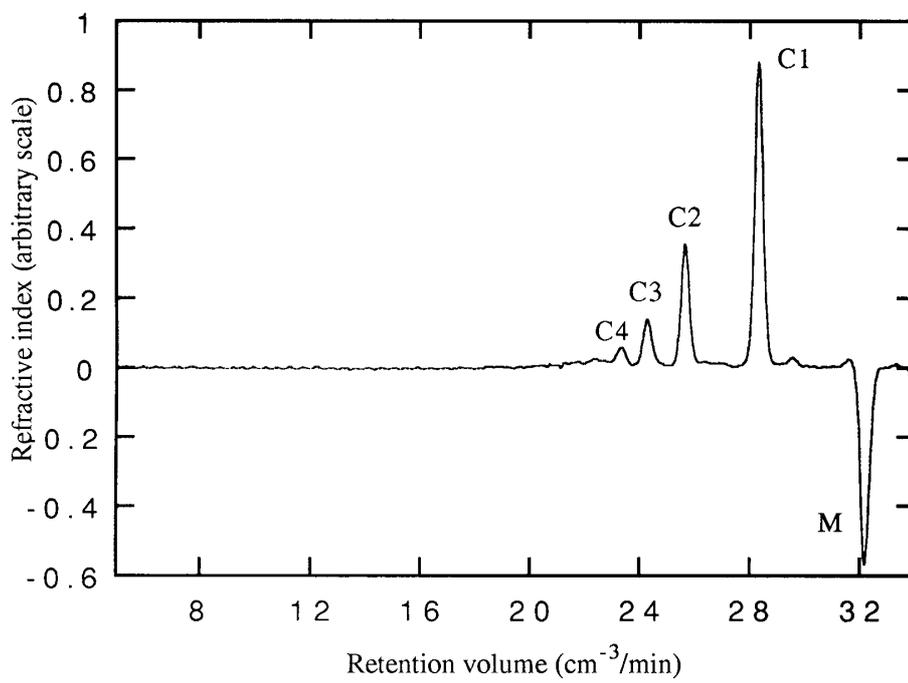


Figure 2

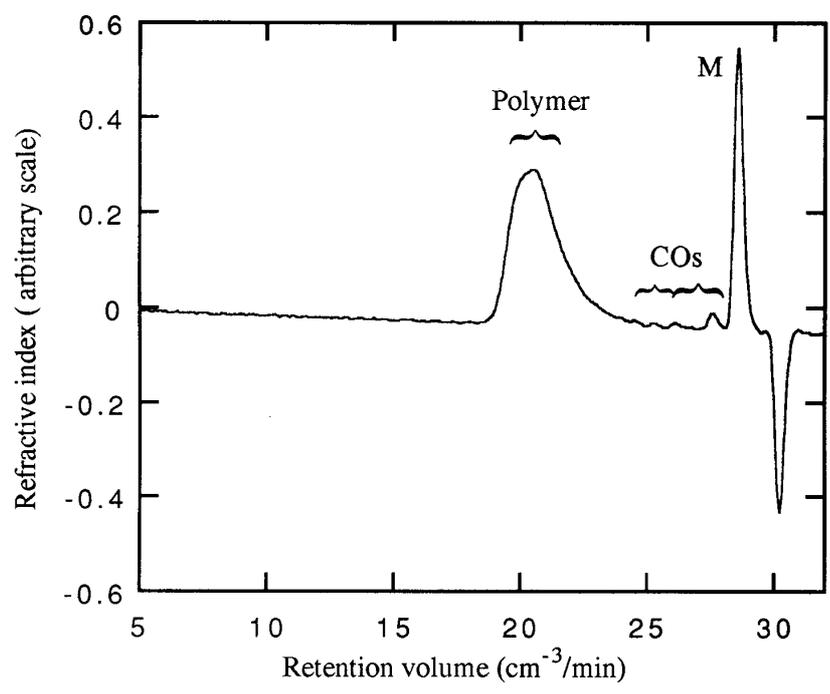


Figure 3

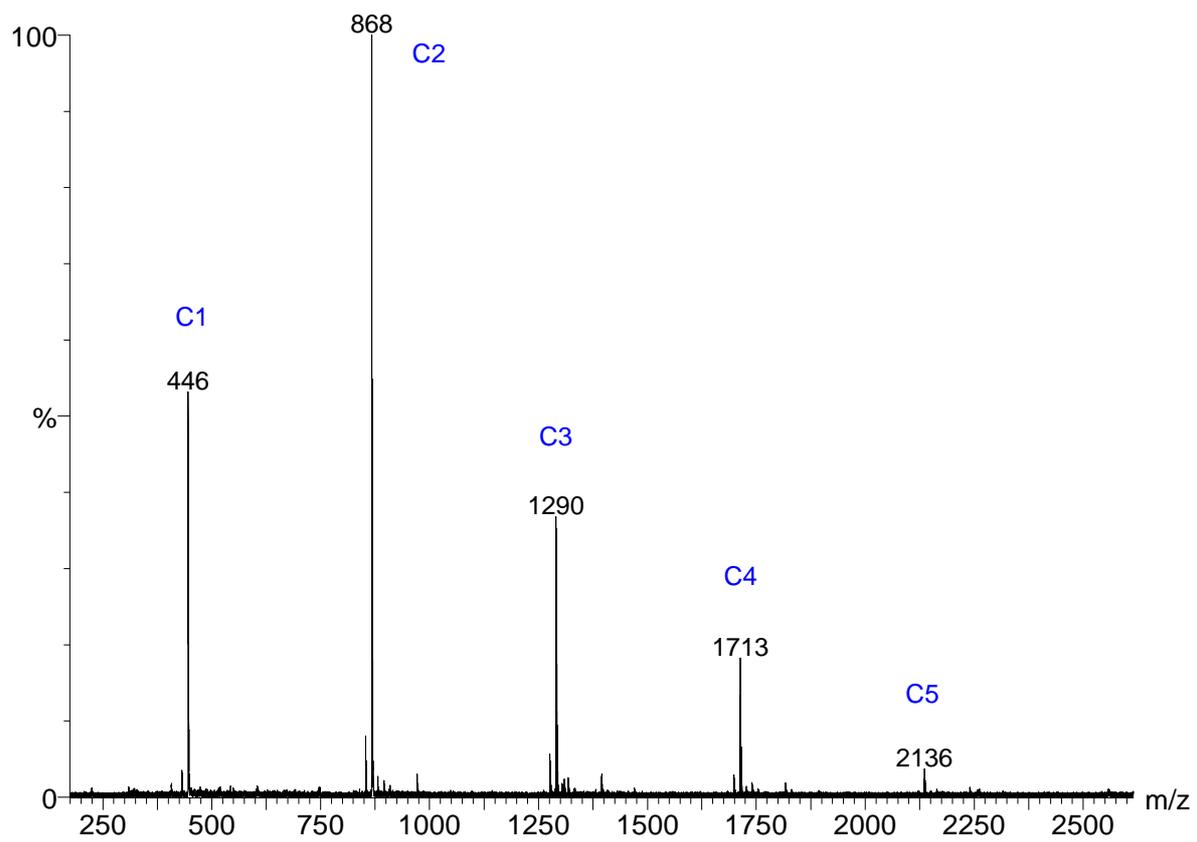


Figure 4

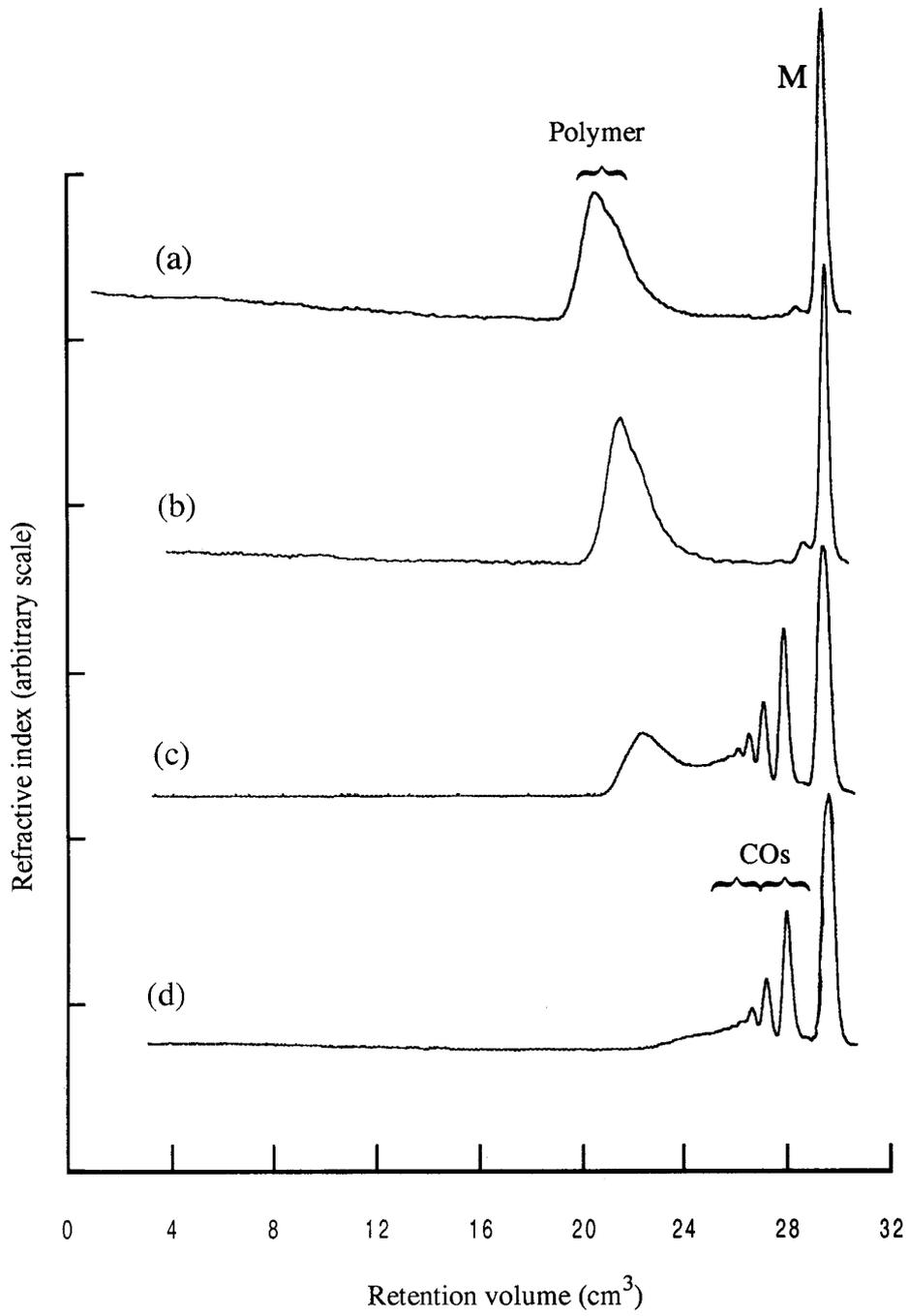


Figure 5

