

Communication: A minimalist furan-maleimide AB-type monomer and its thermally reversible Diels-Alder polymerization

Talita M. Lacerda, Antonio J. F. Carvalho, Alessandro Gandini*

SUPPORTING INFORMATION

Experimental

Materials

Furan ($\geq 99\%$, Sigma-Aldrich), maleic anhydride (99%, Sigma-Aldrich), 2-furfurylamine ($\geq 99\%$, Sigma-Aldrich) and all solvents were used without any additional purification.

Characterization Methods

FTIR spectra were taken with a Perkin Elmer Spectrum 100, working in an attenuated total reflection (ATR) mode.

$^1\text{H-NMR}$ spectra were run with a Bruker spectrometer operating at 9,4 Tesla (400 MHz). The samples were dissolved in deuterated chloroform (CDCl_3), 1,1,2,2-tetrachloroethane (TCE-d_2) and dimethyl sulfoxide (DMSO-d_6), depending on the respective sample solubility. The chemical shifts (δ) are reported in ppm relative to TMS.

Differential scanning calorimetry (DSC) thermograms were obtained using a Perkin Elmer Pyris DSC 8000 calorimeter operating under a nitrogen atmosphere.

The heating rate used for the analysis of PolyAB **4** was of 70 °C min⁻¹, from room temperature to 150 °C, with a sample mass of approximately 5 mg. In the case of ABMon **5**, a heating rate of 50 °C × min⁻¹ was used, from room temperature to 150 °C. These high heating rates were applied to minimize the interference from the rDA depolymerisation in the case of **4** and from the DA polymerization in the case of **5**. The thermogravimetric analyses (TGA) of PolyAB **4** were conducted using a Perkin Elmer Pyris-1 operating under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹, from room temperature to 700 °C.

X-ray diffraction analyses were carried out with a Panalytical MRD-XL equipment (X'Pert Pro), with 2θ ranging from 5 to 120°.

Procedures / Results

*a. General procedure for the synthesis of exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride **2** (furan/maleic anhydride adduct)*

9.81 g of maleic anhydride (0.1 mol) were stirred with 60 mL of diethyl ether, at room temperature, until complete solubilisation. 6.81 g of furan (0.1 mol) were added and the solution kept under constant stirring in a stoppered round bottom flask, until the formation of white crystals, indicating the successful formation of the adduct. The crystals were isolated by filtration, and stirred with diethyl ether to remove any unreacted maleic anhydride, 95% yield.

¹H-NMR (DMSO-d₆, 400 MHz) δ / ppm: 6.58 (t, J = 1.2 Hz, 2H, -HC=CH-), 5.34 (t, J = 0.9 Hz, 2H, -HC-CH-O-), 3.31 (s, 2H, -HC-CH-C=O).

FTIR: 3100, 3090, 3067, 3032, 3002, 2990, 1859, 1786, 1310, 1283, 1233, 1210, 1147, 1083, 1019, 951, 924, 906, 879, 847, 819, 792, 733, 693, 670.

b. General procedure for the synthesis of ProtAB 3

In a round bottom flask equipped with a water circulation condenser, 4.8 g of furfurylamine (0.05 mol) were mixed with 8.4 g of *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride **2** (furan/maleic anhydride adduct, 0.05 mol) and 150 mL of dry methanol. The reaction was conducted for three days at 56 °C under magnetic stirring. Thereafter, the flask was kept at -20 °C for another three days, and the precipitated product isolated by filtration as a yellowish solid in 89% yield.

¹H-NMR (CDCl₃, 400 MHz) δ / ppm (see Figure 2): 7.33 (t, J = 1.3 Hz, 1H, furan H5), 6.52 (s, 2H, adduct CH=CH), 6.30 (s, 2H, furan H3 and H4), 5.30 (t, J = 0.8 Hz, 2H, -HC-CH-O-), 4.66 (s, 2H, Fu-CH₂-N), 2.88 (s, 2H, -CH-CH-C=O).

FTIR (cm⁻¹, see Figure 1): 3454, 3151, 3132, 3096, 3084, 3018, 2985, 2946, 1775, 1699, 1503, 1430, 1389, 1358, 1316, 1282, 1272, 1234, 1216, 1199, 1168, 1151, 1137, 1085, 1054, 1016, 1003, 955, 948, 930, 913, 875, 851, 830, 796, 754, 720, 703, 668.

c. General procedure for the deprotection/polymerization of ProtAB 3/synthesis of PolyAB 4

For the deprotection of ProtAB **3**, 1.23 g (5 mmol) were stirred with 10 mL of 1,1,2,2-tetrachloroethane (TCE) in a round bottom flask equipped with a water circulation condenser at 110 °C for 5h. The polymerization consisted of a second reaction step, where the temperature was reduced to 60 °C. The medium was then left under magnetic stirring for 3 days, and the polymer (PolyAB **4**) precipitated into an excess of cold petroleum ether with a yield of 92%, based on complete deprotection, viz 100% yield of monomer **5**.

¹H-NMR (CDCl₃, 400 MHz) δ / ppm (see Figure 2): 6.63–6.16 (m, 2H, -HC=CH-),

5.23 (m, 2H, -HC-CH-O-), 4.48–3.99 (m, 2H, -CH₂-N-), 2.94 (m, 2H, -HC-CH-C=O).

FTIR (cm⁻¹, see Figure 1): 3095, 3004, 2953, 1774, 1700, 1420, 1397, 1347, 1313, 1287, 1247, 1223, 1187, 1150, 1110, 1067, 1027, 967, 950, 913, 887, 867, 833, 803, 736, 716, 693.

d. General procedure for the isolation of ABMon 5 (2-furfurylmaleimide)

ABMon 5 (2-furfurylmaleimide) was isolated by heating polymer 4 at 150 °C for 6 h in a high-vacuum flask equipped with a liquid nitrogen cold finger. The rDA depolymerization reaction released ABMon 5, whose sublimate was collected on the cold finger in 78% yield, as high-purity white crystals.

¹H-NMR (CDCl₃, 400 MHz) δ / ppm (see Figure 2): 7.33 (t, J = 1.4 Hz, 1H, furan H5), 6.73 (s, 2H, maleimide -HC=CH-), 6.31 (d, J = 1.6 Hz, 2H, furan H3 and H4), 4.70 (s, 2H, fu-CH₂-N).

FTIR (cm⁻¹, see Figure 1): 3455, 3165, 3145, 3124, 3104, 3091, 1774, 1696, 1502, 1427, 1400, 1344, 1322, 1236, 1194, 1134, 1075, 1004, 970, 948, 929, 884, 869, 843, 764, 745, 689.