

Formation of Nanoporous Materials via Mild Retro-Diels-Alder Chemistry

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Materials: Benzylpyridin-2-yldithioformate (BPDF) was synthesized according to the literature^[1]. Styrene (Merck) was passed through a column of basic alumina (Acros) to remove inhibitor and stored at -19 °C. 2,2'-Azobisisobutyronitrile (AIBN, Sigma-Aldrich) was recrystallised twice from methanol and stored at -19 °C. THF (extra dry, over molecular sieves, Acros), poly(ethylene oxide) 5000 monomethyl ether (Sigma-Aldrich), *p*-toluenesulfonyl chloride (Acros), nickelocene (NiCp_2 , 99 %, Strem Chemicals), sodium iodide (≥ 99 %, Fluka), triphenylphosphine (Merck) and trifluoroacetic acid (TFA, Sigma-Aldrich) were used as received.

*Synthesis of thermally cleavable PS-*b*-PEO*

α -Methoxy- ω -toluenesulfonyl-PEO NaOH (1.4 g) was dissolved in 7.5 mL of H₂O. A solution of poly(ethylene oxide) monomethyl ether (10.0 g, 2.0 mmol) in 12 mL THF was subsequently added. The resulting mixture was cooled in an ice bath. To this a solution of *p*-toluenesulfonyl chloride (4.3 g, 23 mmol) in 6 mL THF was added. The mixture was stirred overnight at ambient temperature. The mixture was extracted with CH₂Cl₂ and the organic phases were combined and washed three times with water. The organic phase was dried over MgSO₄, filtered, and concentrated in vacuo. Precipitation in cold diethyl ether yielded a white solid (9.41 g, 91 %). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 2.45 (s, CH₃-C₆H₅), 3.38 (s, CH₃-O), 4.15 (t, CH₂-CH₂-OTs), 7.36 (m, arom), 7.81 (m, arom).

α -methoxy- ω -cyclopentadienyl-PEO (1) A solution of α -methoxy- ω -toluenesulfonyl-PEO (1.8 mmol), triphenylphosphine (3.6 mmol, 2 eq.) and sodium iodide (10.8 mmol, 6 eq) in anhydrous THF (20 mL) was prepared under a nitrogen atmosphere. Separately, a stock solution of NiCp_2 in anhydrous THF (0.36 mol·L⁻¹) was prepared under a nitrogen atmosphere. The NiCp_2 solution (10 mL, 4 eq.) was subsequently added to the polymer solution and allowed to stir 70 h at 40 °C. The mixture was extracted with CH₂Cl₂ and the

CH_2Cl_2 phase was washed three times with water. The organic phase was dried over MgSO_4 , filtered, and concentrated. PEO (**1**) was isolated by repeated precipitations in cold diethyl ether (yield 76 %). ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 2.71 (m, $\text{CH}_2\text{-C}_5\text{H}_5$), 2.95 (m, bridge head), 3.38 (s, $\text{H}_3\text{C-O-}$), 6.47–6.08 (m, C_5H_5 , vinylic).

Poly(styrene) (2a,b**)** A solution of BPDF (14.6 $\text{mmol}\cdot\text{L}^{-1}$) and AIBN (2.4 $\text{mmol}\cdot\text{L}^{-1}$) in styrene (30 mL) was deoxygenated by purging with nitrogen for 30 min. The polymerization reactions were performed at 60 °C for 10 h (**2a**) and 20 h (**2b**), respectively. The reactions were stopped by chilling in an ice bath and exposure to oxygen. The resulting poly(styrene)s were isolated by two-fold precipitation in cold methanol. **2a**: $M_{n,\text{GPC}} = 10600 \text{ g}\cdot\text{mol}^{-1}$, $PDI_{\text{GPC}} = 1.14$; **2b**: $M_{n,\text{GPC}} = 18500 \text{ g}\cdot\text{mol}^{-1}$, $PDI_{\text{GPC}} = 1.12$

PS-*b*-PEO (3a,b**)** Cyclopentadienyl terminated PEO (**1**) (50 μmol) and dithioester capped PS (**2a,b**) (50 μmol) were dissolved in 10 mL CHCl_3 . After the addition of 1.5 equiv TFA, the mixture was stirred for 2 h at ambient temperature. The reaction mixture was washed with saturated NaHCO_3 solution, dried over MgSO_4 and the solvent removed in vacuo. The solid residue was extracted with diethyl ether to remove any residual homo-PS, redissolved in CHCl_3 and precipitated in cold methanol to give PS-*b*-PEO (**3a,b**) as light brown solid. **3a**: $M_{n,\text{GPC}} = 16900 \text{ g}\cdot\text{mol}^{-1}$, $PDI_{\text{GPC}} = 1.6$; $M_n(\text{PS})/M_n(\text{PEO}) = 1.9$ calculated by $^1\text{H-NMR}$ integration. **3b**: $M_{n,\text{GPC}} = 24100 \text{ g}\cdot\text{mol}^{-1}$, $PDI_{\text{GPC}} = 1.11$, $M_n(\text{PS})/M_n(\text{PEO}) = 3.2$ calculated by $^1\text{H-NMR}$ integration.

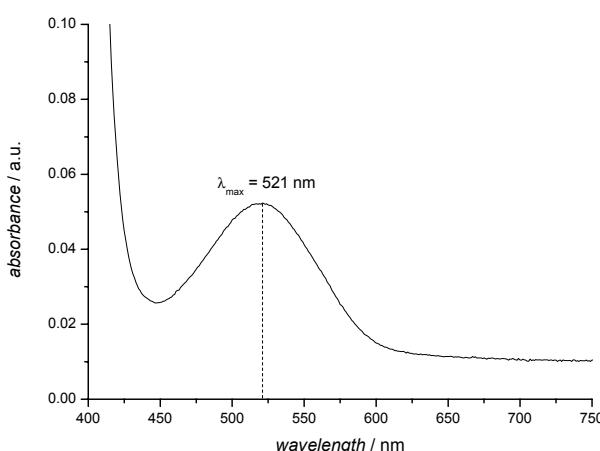


Fig. S1 UV-Vis spectrum of the pure dithioester capped PS (**2b**). The absorbance reaches its maximum at 521 nm.

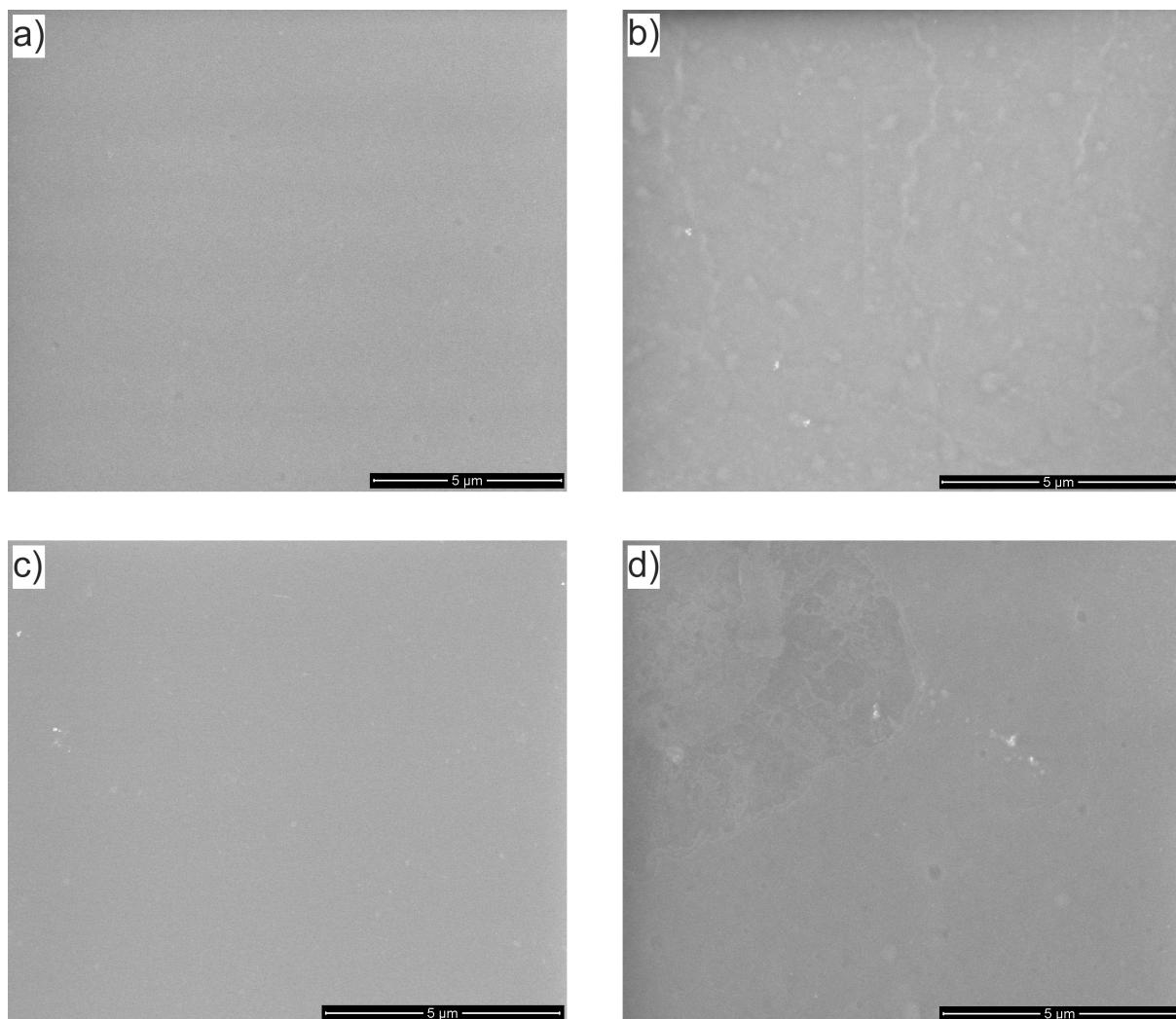


Fig. S2 SEM images of blind film samples. a) PS-*b*-PEO **3b** before heating and washing; b) PS-*b*-PEO **3a** before heating and washing; c) PS **2b** after heating and washing; d) PS-*b*-PEO **3b** after washing with water (without heating).

[1] A. Alberti, M. Benaglia, M. Guerra, M. Gulea, P. Hapiot, M. Laus, D. Macciantelli, S. Masson, A. Postma, K. Sparmacci, *Macromolecules* **2005**, *38*, 7610.