Temperature-Responsive Glycopolymer Brushes Synthesized via RAFT Polymerization Using the Z-group Approach

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1. NMR of Monomer

2. Synthesis of brushes

Grafting of PAGA

Grafting of AGA was performed using a treated silicon wafer with immobilized RAFT agent immersed in a solution of AGA (0.715 mol.L⁻¹), 4,4’-(azobis(cyanopentanoic acid) (7.14×10⁻⁴ mol.L⁻¹), and 1,2-dichloroethane (15 mL).
mol.L\(^{-1}\)) as the initiator and the trithiocarbonate agent (I) as RAFT agent (3.57 \(10^{-3}\) mol.L\(^{-1}\)) in deionized water-ethanol mixture (5:1 v/v).

Typically, the aqueous monomer solution (2.5mL, 2.14 \(10^{-3}\) mol) was mixed with a 0.5 mL ethanol solution of ACPA (0.6mg, 2.14\(\times\)10\(^{-6}\) mol) and I (2.91mg, 1.073\(\times\)10\(^{-5}\) mol) and transferred to Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw cycles. The solution was then transferred into a deoxygenated vial containing one piece of silicon wafer. A sufficient amount of solution was added to ensure that the silicon wafer was thoroughly covered with solution. The vials were then placed in a constant temperature water bath at 60°C. The samples were removed at regular intervals and subsequently plunged into iced water. The wavers were washed with excess water and ultrasonication in water followed by ethanol. The solvent of the reaction solution was left to evaporate to obtain the polymer-monomer mixture. The crude mixture was finally characterized (1H NMR, gel permeation chromatography).

The conversions were determined by \(^1\)H-NMR in D\(_2\)O by relative integration of vinyl (non-reacted AGA, \(\delta=5.67-6.24\)) and CH\(_2\)-CH glycopolymer backbone protons (\(\delta=1.3-2.5\)). A conversion of 65% was achieved after a reaction time of 6 hours.

NMR of monomer/polymer mixture for conversion determination

\[
\text{conversion} = \frac{I(1.3-2.5)}{I(1.3-2.5) + I(5.67-6.24)}
\]

alternatively: \(\text{conversion} = 1 - \frac{I(5.67-6.27)/3}{I(3.3-3.8)/5}\)
Grafting of NIPAAm and formation of PGA-PNIPAAm block brushes

Grafting of NIPAAm onto a wafer or the chain extension of PAGA brushes were performed using a treated silicon wafer with immobilized RAFT agent or a silicon wafer with PGA brushes immersed in a solution of NIPAAm (1.82 g, 0.8 mol.L⁻¹), 4,4’-(azobis(cyanopentanoic acid) (4.0 mg, 7.14 × 10⁻⁴ mol.L⁻¹) as the initiator and the trithiocarbonate agent (I) as RAFT agent (10.7 mg, 1.96 × 10⁻³ mol.L⁻¹) in deionized water-DMSO mixture (1:1 v/v). The procedure was similar to the grafting of AGA. The samples were washed with ethanol using ultrasound and dried. After a reaction time of 4 hours a conversion of 70% was obtained.

The conversion of NIPAAm was determined by ¹H NMR (DMSO-d6).

The brushes were dried under high vacuum and kept in a dry environment prior to further analysis to avoid the swelling of the brushes.

3. Time-conversion plot of homopolymerization
Conversion vs time of “free” polymer in solution of PAGA (squares) and PNIPAAm (circles) homopolymer. Open symbol and crossed symbol represent two independent experiments.

(PAGA brushes: \([\text{AGA}] = 0.71 \text{ mol.L}^{-1}, [\text{ACPA}] = 7.1 \times 10^{-4} \text{ mol.L}^{-1}, [I] = 3.5 \times 10^{-3} \text{ mol.L}^{-1}\) in water/ethanol (5:1 v/v);
PNIPAAm brush: \([\text{NIPAAm}] = 0.8 \text{ mol.L}^{-1}, [\text{ACPA}] = 7.1 \times 10^{-4} \text{ mol.L}^{-1}, [I] = 1.96 \times 10^{-3} \text{ mol.L}^{-1}\) in water/DMSO (1:1 v/v))