Electronic Supplementary Material (ESI) for Soft Matter. This journal is © The Royal Society of Chemistry 2016

Supporting Information

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1. Synthesis of surface-attached hydrogel films



The schematic of the synthesis of surface-attached hydrogel films is shown. The ene-functionalized polymer is spin-coated on thiol-modified substrate with dithiol crosslinkers. Thiol-ene click reaction allows simultaneously the cross-linking and the surface attachment of polymer chains.

2. Synthesis of ene-functionalized poly(NIPAM) and poly(DMA)



The schematic of the synthesis of ene-functionalized poly(NIPAM) in water in two steps is shown. The principle is the same for ene-functionalized poly(DMA). First, poly(NIPAM-co-AA) copolymers are synthesized by free radical polymerization in water using (NH₄)₂S₂O₈/Na₂S₂O₅ redox couple initiators. The copolymerization reaction is achieved at 10 wt% under nitrogen at ambient temperature during 24 hours. Second, ene-functionalization of poly(NIPAM-co-AA) copolymers is achieved by amide formation using allylamine in water with EDC/NHS coupling. EDC is the dehydration agent and NHS the addition agent used to increase yields and decrease side reactions. Both radical polymerization and amide formation are advantageously performed in water as all the chemicals used are water-soluble. They are carried out at ambient temperature below the LCST of poly(NIPAM). The ene-functionalized polymer can be easily purified by dialysis against water and recovered by freeze-drying to be stored and characterized by Size Exclusion Chromatography and NMR spectroscopy.

Polymers	Mw (kg/mol)	PDI*	Ratio of ene-groups
Poly(NIPAM)	337	1.5	3.0 %
Poly(DMA)	320	2.2	2.5 %

The chemical characteristics of ene-functionalized polymers are shown in the table: the molecular weight M_w and the polymer dispersity index PDI (defined as Mw/Mn ratio) which are determined by SEC chromatography, and the ratio of ene-groups measured by ¹H NMR spectroscopy.

From ellipsometry measurements carried out in water using thin (less than 1 μ m) films, the swelling ratios of the poly(NIPAM) and poly(DMA) films were found to lie in the ranges 3-3.3 and 2.8-3.1, respectively.

3. Synthesis of ene-functionalized poly(PEGMA)



The schematic of the synthesis of ene-functionalized poly(PEGMA) is shown. Poly(PEGMA-co-AMA) copolymers are synthesized by free radical polymerization in organic solvent using AIBN as thermal initiators. The copolymerization reaction is achieved at 20 wt% in toluene under nitrogen at 70°C. The polymer solution can be used as it is for the fabrication of surface-attached hydrogel films by spin-coating.

From ellipsometry measurements carried out in water using thin (less than 1 μ m) films, the swelling ratio of the poly(PEGMA) films was found to lie in the range 2.5-2.8.