THIOL-ENE AND THIOL-OXIRANE CHEMISTRIES FOR THE SYNTHESIS AND MODIFICATION OF CYLINDRICAL POLYMER BRUSHES AND SURFACE MODIFICATION OF MICROSPHERES

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Introduction

Among the various click chemistry methods, the radical addition of thiols to double bonds is – under certain conditions – a highly efficient method used for polymerizations, curing reactions, grafting reactions and for the modification of polymers. However, the addition of thiols to epoxides also provides an excellent opportunity to attach functional groups to polymers. We report three different applications in the synthesis of polymer brushes, hybrid nanocylinders and surface modification.

Results and Discussion

Cylindrical Polymer Brushes via Thiol-En reaction.

When a linear polymer is grafted with a large number of relatively short side-chains, cylindrical polymer brushes are formed. Due to their anisotropic nature in topology, they have attracted more and more research interest in their synthesis, bulk, or solution properties, as well as in the applications of such polymers. They are also denoted as “bottle brushes” or “molecular brushes”. Cylindrical brushes with a linear backbone and grafted side-chains were made via thiol-ene reaction. Scheme 1 displays the thiol-ene reaction of poly(para-tert-butoxy styrene)-block-polybutadiene (ptSB) with thiol-endfunctional poly(N-isopropylacrylamide) (SH-pNIPAAm).

Figure 1. FTIR-spectra of ptSB-g-pNIPAAm (blue), ptSB (red) and SH-pNIPAAm (black) in THF. 3500-3300 cm\(^{-1}\) N-H-stretching vibration, 1650-1540 cm\(^{-1}\) N-H-deformation vibration, 990 cm\(^{-1}\) C=C-deformation vibration.

The IR spectrum of ptSB-g-pNIPAAm (Figure 1) clearly shows the N-H stretching vibration (3500-3300 cm\(^{-1}\)) of the pNIPAAm side chains. The magnified region stresses the N-H deformation vibration at 1650-1540 cm\(^{-1}\) of the pNIPAAm units. Furthermore the reduction of the deformation vibration of 1,2-polybutadiene units (990 cm\(^{-1}\)) indicates the successful thiol-ene reaction. The polymer brushes were further analyzed by \(^1\)H NMR and DLS measurements.

Surface Modification of Polydivinylbenzene Microspheres via the Thiol-En reaction.

RAFT polymerization was carried out to synthesize SH-functional poly(N-isopropylacrylamide) (SH-pNIPAAm) and utilized to generate pNIPAAm surface-modified microspheres. The accessible double bonds on the surface of the microspheres allow the direct coupling with SH-pNIPAAm (Scheme 2).
Scheme 2. Thiol-ene modification of pDVB80 microspheres with SH-pNIPAAm45 in a one-step approach.

The surface-modified microspheres were characterized by elemental analysis, SEM, FTIR and XPS. The successful grafting was supported by a turbidimetric study from 20 °C to 70 °C. At room temperature the dispersion is turbid due to the micron-sized particles strongly scattering light. Above 40°C, which is slightly higher than the LCST of pNIPAAm (34 °C), a strong increase of the transmission is observed (Figure 3). Above the LCST the pNIPAAm chains collapse, inducing a more hydrophobic environment and therefore decreasing the dispersibility of the microspheres. At this transition point, the microspheres aggregate and move to the water surface leading to a more transparent solution.

Figure 3. Temperature-dependent turbidity measurement of pDVB80-g-pNIPAAm45 microspheres (20-70°C)).

Single-Molecular Hybrid Nanocylinders via Addition of Thiols to Oxirane Groups.

Novel single-molecular hybrid nano-cylinders by covalently attaching a monothiol-functionalized polyhedral silsesquioxane (POSS-SH) to poly(glycidyl methacrylate) (PGMA) cylindrical brushes were prepared. Grafting of GMA from a long poly-initiator poly(2-(2-bromoisobutyloxy)-ethyl methacrylate) (PBIEM) via ATRP was first carried out. Gel permeation chromatography (GPC), 1H NMR, dynamic light scattering (DLS), static light scattering (SLS) and atomic force microscopy (AFM) measurements confirmed the well-defined worm-like structures of the PGMA brushes. Then POSS-SH was covalently linked to PGMA brushes by reaction with about 19% of the epoxy groups.

Scheme 3. Procedure for the preparation of nano-hybrid PGMA-POSS brush.

By reacting a monothiol-functionalized POSS with the glycidyl functions of the PGMA brushes, hybrid nano-cylinders were obtained. Scheme 1 shows the process. FTIR measurements of the solution-cast samples were performed. Almost no absorption is observed at around 3500 cm⁻¹ for the precursor POSS-SH and PGMA brush, indicating absence of hydroxyl groups. In contrast, a strong and broad peak around 3500 cm⁻¹ was clearly seen for the hybrid material PGMA-POSS, indicating the abundance of hydroxyl groups in this brush. The spectrum of PGMA-POSS also shows the coexistence of the strong peaks attributed to the ester groups (around 1720 cm⁻¹) from the PGMA precursor and Si-O (around 1100 cm⁻¹), demonstrating the success of the fabrication of the hybrid materials.

Figure 4. Non-stained TEM image of PGMA-POSS hybrid brushes on a carbon-coated TEM grid and TGA measurements of PGMA brush, POSS-SH and PGMA-POSS in air.

In the non-stained TEM image of PGMA-POSS (Figure 4) clear nano-cylinders can be observed and their lengths are around 150 nm, which is somewhat higher than that of precursor PGMA brushes on mica surface, likely caused by the stretching effect of the attached POSS-SH. The increase of the contrast in the TEM measurements provides another proof that the high-contrast POSS nanoparticles have been attached to the brushes. The degradation temperature of PGMA-POSS hybrid is somewhat lower than those of the precursor PGMA and POSS-SH, probably a result of the epoxy groups’ ring-opening and formation of large number of hydroxyl groups.

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References