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

Anja S. Goldmann[a], Daniela Pirner[a], Youyong Xu[a], Leonie Barner[b], Christopher Barner-Kowollik[c], Axel H.E. Müller[a]

[a] Macromolecular Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany; [b] Fraunhofer Institute for Chemical Technology, 76327 Pfinztal, Germany; [c] Preparative Macromolecular Chemistry Group, Institute for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

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-Ene Reaction. When a linear polymer is grafted with a large number of relatively short side-chains, cylindrical polymer brushes are formed.[1] 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 thiolene reaction. Scheme 1 displays the thiol-ene reaction of poly(para-*tert*-butoxystyrene)-*block*-polybutadiene(1,2) (ptSB) with thiol-endfunctionalized poly(N-isopropylacrylamide) (SH-pNIPAAm$_{45}$).
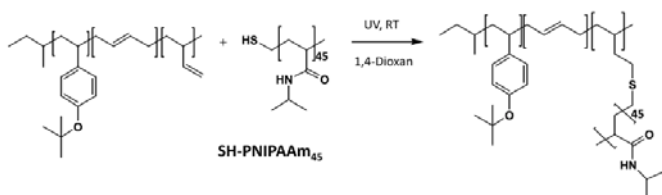

Scheme 1. Scheme for the grafting of a 1,2-polybutadiene block with thiol-endfunctional polyNIPAAm$_{45}$.
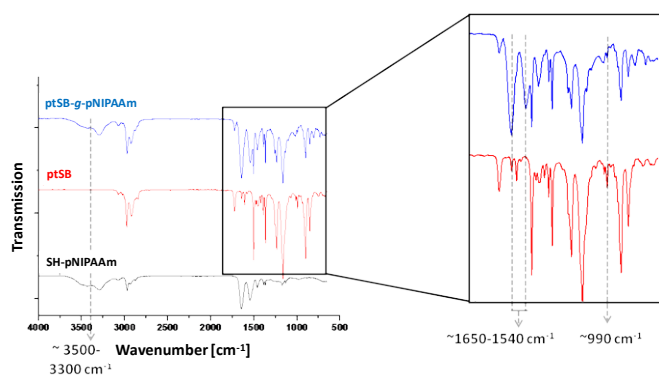
Figure 1. FTIR-spectra of ptSB-*g*-PNIPAAm$_{45}$ (blue), ptSB (red) and SH-pNIPAAm$_{45}$ (black) in THF. 3500-3300 cm^{-1} N-H-stretching vibration, 1650-1540 cm^{-1} N-H-deformation vibration, 990 cm^{-1} C=C-deformation vibration.

The IR spectrum of ptSB-*g*-PNIPAAm$_{45}$ (Figure 1) clearly shows the N-H stretching vibration (3500-3300 cm^{-1}) of the pNIPAAm$_{45}$ side chains. The magnified region stresses the N-H deformation vibration at 1650-1540 cm^{-1} of the pNIPAAm$_{45}$ 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.
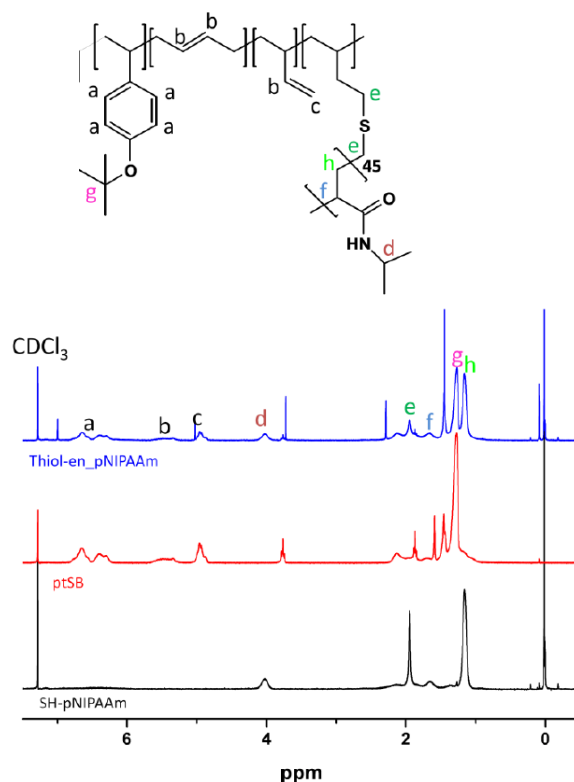
Figure 2. ^{1}H-NMR-Spectra in CDCl$_3$ of the thiol-ene-product (blue), ptSB (red) and SH-pNIPAAm (black)

The ^{1}H NMR (Figure 2) gives information about the grafting density of the thiol-ene reaction with SH-pNIPAAm$_{45}$. The assignment of the signals allows the successful thiol-ene reaction of pNIPAAm$_{45}$ chains. Calculations of the peak areas of the ptSB-*g*-pNIPAAm$_{45}$ compared to the precursor ptSB gives an average grafting density of 57%.

Furthermore, ptSB was also modified with SH-endgroup modified poly(ethylene glycol). Here, FT-IR and ^{1}H NMR also demonstrated the side-chain functionalization. The FT-IR spectrum of ptSB-*g*-PEG shows characteristic PEG bonds: 1100 cm^{-1} indicates the C-O-stretching vibration and the deformation vibration at 990 cm^{-1} of the double bonds which diminished nearly complete. From the decrease of the characteristic protons of the 1,2-polybutadiene grafting density of 79% can be calculated.

The synthesis of block-type Janus cylinder brushes is currently under investigation.

Surface Modification of Polydivinylbenzene Microspheres via the Thiol-Ene Reaction.[2] RAFT polymerization was carried out to synthesize SH-functional poly(*N*-isopropylacrylamide) (SH-pNIPAAm$_{45}$) 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$_{45}$ (Scheme 2).

**Scheme 2.** Thiol-ene modification of pDVB80 microspheres with SH-pNIPAAm$_{45}$ in a one-step approach.
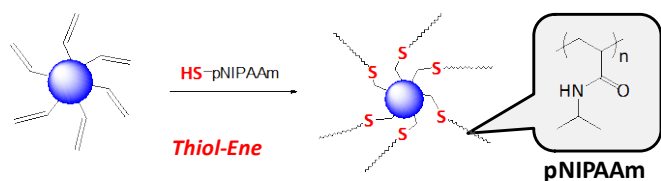
The surface-modified microspheres were characterized by elemental analysis, SEM, FTIR and XPS. The successful grafting was supported by a turbidimetric study from 20 °C to 70 °C. At room temperature the dispersion is turbid due to the micron-sized particles strongly scattering light. Above 40°C, which 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.
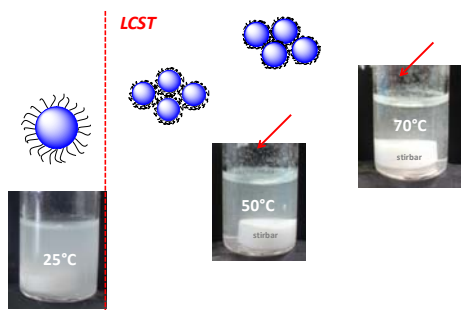
Figure 3. Temperature-dependent turbidity measurement of pDVB80-g-pNIPAAm$_{45}$ microspheres (20-70°C)).

Single-Molecular Hybrid Nanocylinders via Additon of Thiols to Oxirane Groups.[3] 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-bromoisobutyryloxy)-ethyl methacrylate) (PBIEM) via ATRP was first carried out. Gel permeation chromatography (GPC), ^{1}H 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.
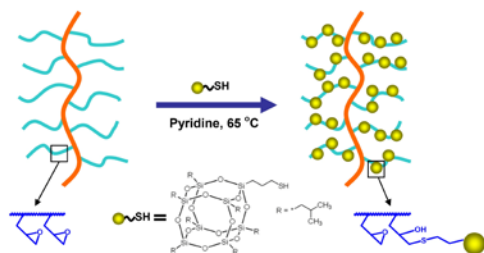
By reacting a monothiol-functionalized POSS with the glycidyl functions of the PGMA brushes, hybrid nano-cylinders were obtained. Scheme 1 shows the process. FTIR measurements of the solution-cast samples were performed. Almost no absorption is observed at around 3500 cm^{-1} for the precursor POSS-SH 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.

References
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