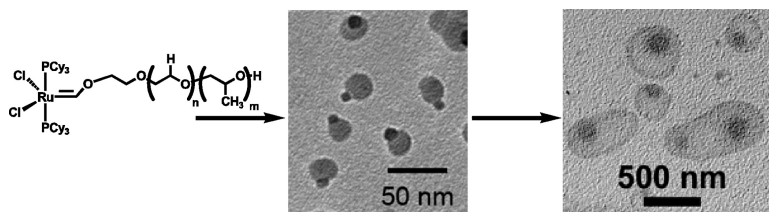


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## Janus Micelles Induced by Olefin Metathesis

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Supramolecular polymeric structures are frequently visualized using transmission electron microscopy (TEM). The differentiation between individual compartments or constituents of the supramolecular assembly can be difficult or even impossible due to lack of contrast. Often, heavy metal staining agents are employed to increase the image contrast between areas of different chemical composition.<sup>1</sup> The most common examples are osmium tetroxide which has been widely employed as a stain for unsaturated polymers,<sup>1</sup> ruthenium tetroxide for saturated and unsaturated polymers,<sup>1</sup> or phosphotungstic acid which is especially useful for polyamide staining.<sup>1</sup>

To our surprise, the commercially available ruthenium carbene catalysts developed by Grubbs et al.<sup>2</sup> have to date not been employed in TEM staining of polymers. One advantage this catalyst might offer is its ability to covalently bind to the polymeric substrate in a regioselective and irreversible manner, forming a so-called Fischer carbene. Due to the catalyst's large size and hydrophobicity, we were particularly interested in the effects of covalent catalyst attachment on solution self-assembly of block copolymers.

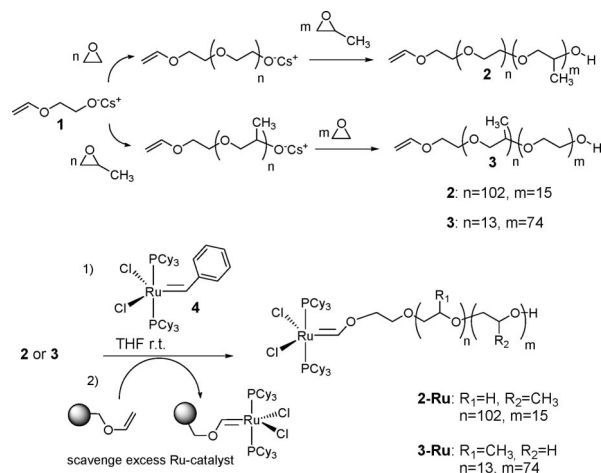
Here we report a facile one-step method allowing regio-specific covalent binding of Grubbs' first generation catalyst (Scheme 1, compound **4**) to polymeric architectures.

As proof of principle, we synthesized poly(ethylene oxide)-*block*-poly(propylene oxide) (PEO-PPO) block copolymers which are known to form micelles in aqueous solution and for which the solution structures have been well investigated.<sup>3</sup> In order to be able to attach Grubbs' first generation catalyst to the diblock copolymer, we initiated the ring opening polymerization of ethylene oxide or propylene oxide using the cesium salt of 2-(vinylxy)ethanol (**1**, Scheme 1). This approach allowed us to prepare two PEO-PPO diblock copolymers with the vinyl ether moiety attached to either the hydrophilic (**2**, PEO<sub>102</sub>-PPO<sub>15</sub>,  $M_n(\text{THF}) = 5300 \text{ g mol}^{-1}$ , PDI = 1.06) or the hydrophobic (**3**, PPO<sub>13</sub>-PEO<sub>74</sub>,  $M_n(\text{THF}) = 4200 \text{ g mol}^{-1}$ , PDI = 1.05) chain end.

Addition of an excess of **4** to the THF solutions of **2** and **3** initiated an olefin metathesis reaction at the vinylic chain ends of the block copolymers. This resulted in the formation of a Fischer-type carbene, covalently bound to the block copolymer chain end. The formation of the Fischer-type carbene, and thus polymers **2-Ru** and **3-Ru**, could be followed by additional <sup>1</sup>H NMR kinetic studies, which were carried out in dichloromethane-*d*<sub>2</sub>.

After a reaction time of 2.5 h at room temperature, 80% of all polymer chains carried catalyst **4** covalently bound as a Fischer carbene. Excess **4** was removed by immobilization using a specially developed scavenger resin carrying vinyl ethers (Scheme 1). This technique removed virtually all catalyst **4** that was not covalently bound to the polymer, as could be shown by <sup>1</sup>H NMR spectroscopy. The scavenging of excess catalyst **4**

Scheme 1<sup>a</sup>



<sup>a</sup> Top: Synthesis of amphiphilic PEO-PPO diblock copolymers carrying the vinyl ether moiety at the hydrophilic (**2**) or the hydrophobic (**3**) chain end. Bottom: Attachment of Grubbs' 1st generation ruthenium catalyst **4** to the chain ends of polymers **2** and **3**. A newly developed scavenger resin was employed to remove excess **4** from polymers **2-Ru** and **3-Ru**.

could also be followed with the naked eye, as the resin turned markedly darker over the reaction time.

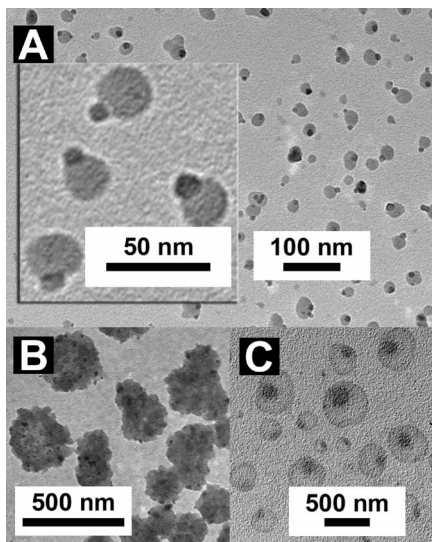
After removal of the resin by filtration, the THF solutions of **2-Ru** and **3-Ru** were diluted with water ( $V_{\text{THF}}/V_{\text{water}} = 1:50$ ) to induce micellation. After 0.5 and 3 h of equilibration time, TEM images were recorded by drop casting the THF/water solutions onto carbon-coated copper grids.

Polymer **3-Ru**, where the metathesis reaction occurred at the hydrophobic end of the copolymer, only showed dark spherical "classical" micelles. We believe that due to slower phase separation processes the Ru complex is most likely kinetically trapped in the micellar PPO core. Detailed investigations are part of ongoing studies.

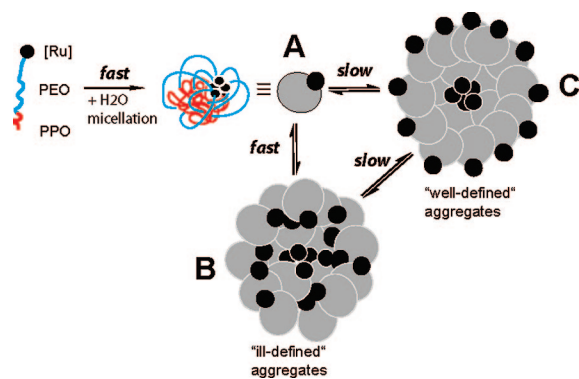
Interestingly, the TEM images recorded of polymer **2-Ru** after 0.5 h of equilibration time showed micellar objects which closely resembled the so-called Janus micelles reported by Nie et al. and others (Figure 1A).<sup>4</sup> Similar to previously reported observations, these small micelles ( $\varnothing_{\text{av.}} = 35 \text{ nm}$ ) coexist with their supramolecular aggregates ( $\varnothing_{\text{av.}} > 200 \text{ nm}$ , Figure 1B).<sup>4</sup>

Such unusual polymeric solution structures, particularly, nonspherical micelles, have received increased attention over the past decade.<sup>5-7</sup> Since the first mention of Janus micelles,<sup>8,4</sup> Janus discs<sup>9</sup> and Janus cylinders<sup>10</sup> have also been reported and raised broad academic interest.<sup>11</sup>

Upon increasing the equilibration time from 0.5 to 3 h before preparation of the TEM sample, much larger assemblies could be observed ( $\varnothing_{\text{av.}} = 30-500 \text{ nm}$ , Figure 1C). We believe that addition of water to the THF solution of **2-Ru** induces formation



**Figure 1.** Transmission electron microscopy (TEM) images of block copolymer **2-Ru** drop cast from THF/water solution ( $c = 1 \text{ mg mL}^{-1}$ ). (A) Janus micelles are observed after 0.5 h of equilibration time. (B) Ill-defined aggregates of Janus micelles are observed after 0.5 h of equilibration time. (C) After 3 h of equilibration time, large well-defined assemblies (super-micelles) of the Janus micelles can be observed.



**Figure 2.** Cartoon representation showing the formation of Janus-type micelles from block copolymer **2-Ru** and their assembly into larger aggregates depending on equilibration time.

of micelles in which the two hydrophobic segments, that is, the Fischer carbene end group and the PPO block, are phase-separated. This gives rise to the peculiar anisotropic shape of the micelles (Figure 2) and allows for a high contrast differentiation when using electron microscopy. These Janus micelles can further aggregate and, depending on the equilibration time in solution, can be visualized as ill-defined clusters (Figure 1B and Figure 2B) or well-defined aggregates (Figure 1C and Figure 2C) for short and extended equilibration times, respectively.

The formation of Janus micelles (Figure 1A and Figure 2A), that is, the first stage of the hierarchical self-assembly, yields objects with a very narrow size distribution and an average diameter ( $\varnothing_{\text{av.}} = 35 \text{ nm}$ ) which is in good agreement with the molecular constitution of the copolymer **2-Ru**. As has been described earlier,<sup>4</sup> these Janus micelles can self-assemble into larger “ill-defined” clusters giving rise to an overall enhanced contrast in TEM (Figure 1B and Figure 2B). These aggregates then equilibrate into well-defined “super-micelles” as shown in Figure 2C and Figure 1C. Such a self-assembly of Janus micelles

into super particles has recently been proposed based on calculations.<sup>12</sup> The “super-micelles” and the constituting Janus micelles are self-similar. However, the super-micelles show a broad range of different sizes. A statistical analysis in which the diameter of the darker (ruthenium-containing) core of the well-defined super-micelles was plotted against the diameter of the entire super-micelle gave a linear relationship (see Supporting Information). This is in good agreement with our model that the larger super-micelles are built from smaller well-defined building blocks, such as the Janus micelles.

In conclusion, we have demonstrated that commercially available Grubbs first generation ruthenium catalyst offers a facile synthetic route for hydrophobic modification and TEM image contrast enhancements of block copolymers. Formation of a Fischer-type carbene allows the covalent attachment of the ruthenium complex to predefined sites on the polymer chain. The formation of Janus micelles in the case of the examined PEO–PPO block copolymers as well as their self-assembly into higher well-defined aggregates could be shown.

This new technique of regioselective hydrophobic modification of polymers in combination with a newly developed scavenger resin for ruthenium carbene complexes adds a valuable new instrument to the visualization toolkit for supramolecular polymeric architectures.

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**Supporting Information Available:** Experimental procedures, compound analyses, and more electron microscopy images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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