Block copolymer libraries: modular versatility of the macromolecular Lego® system†

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The synthesis and characterization of a new 4 × 4 library of block copolymers based on polystyrene and poly(ethylene oxide) connected by an asymmetrical octahedral bis(terpyridine) ruthenium complex at the block junction are described, while initial studies on the thin film morphology of the components of the library are presented by the use of Atomic Force Microscopy, demonstrating the impact of a library approach to derive structure–property relationships.

Block copolymers of narrow polydispersity are ideal candidates as precursors for applications in nanotechnology,[1] since demixing of the polymer blocks leads to a well-defined microphase separation.[2] Current efforts are directed towards obtaining long-range order in phase-separated thin films with the main objective of gaining topological regularity.[3] In comparison with covalent block copolymers, block copolymers where the blocks are held together by non-covalent interactions offer the advantage of having reversible or switchable properties.[4] The morphology of these block copolymers may be more easily used as a template for the introduction of functionality by selectively removing one of the blocks. Reversible or switchable interactions at the block junction are therefore of key importance.[5] We have recently shown that metal–ligand coordination[6] can be employed to connect two different polymer blocks, more specifically by using asymmetrical bis(terpyridine) ruthenium(II) complexes.[7] The terpyridine-ligand can easily be introduced at the chain end of different polymers, thus giving rise to many possible combinations of different blocks.[8] Since the method for preparing block copolymers relies on the coupling of two polymer chains *via* a simple two-step synthesis using principles from coordination chemistry around a ruthenium metal ion,[7] it is straightforward to prepare a library of block copolymers. Block copolymers based on polystyrene and poly-(ethylene oxide) were selected as suitable first candidates. In this contribution we will present the preparation, characterization and the inital studies on the morphology of a new 4 × 4 library of polystyrene–poly(ethylene oxide) metallo-supramolecular diblock copolymers. The building blocks for the library have been prepared by polymer end group modification reactions[7] and nitroxide mediated controlled radical polymerization of styrene using a terpyridine functional initiator.[8] The terpyridine functionalized poly(ethylene oxide)s with molecular weights of 3000, 5000, 10 000 and 17 000 g mol⁻¹ (**17–20**) have been reacted with RuCl₃ to form the corresponding *mono*-complexes (**25–28**). In principle, polystyrene *mono*-complexes can be prepared and applied as well, again demonstrating the modular versatility of the approach. The poly(ethylene oxide) *mono*-complexes have been reacted under reducing conditions with the terpyridine functionalized polystyrenes with molecular weights of 2000, 7500, 21 000 and 25 000 g mol⁻¹ (**21–24**). The self-assembly process leads to octahedral bis(terpyridine) ruthenium complexes that serve as the asymmetrical metallo-supramolecular linker between the two blocks (Scheme 1).

Table 1 shows the theoretical molecular weights and their corresponding volume fractions of the polystyrene, the metal complex and the poly(ethylene oxide) of the block copolymers. The
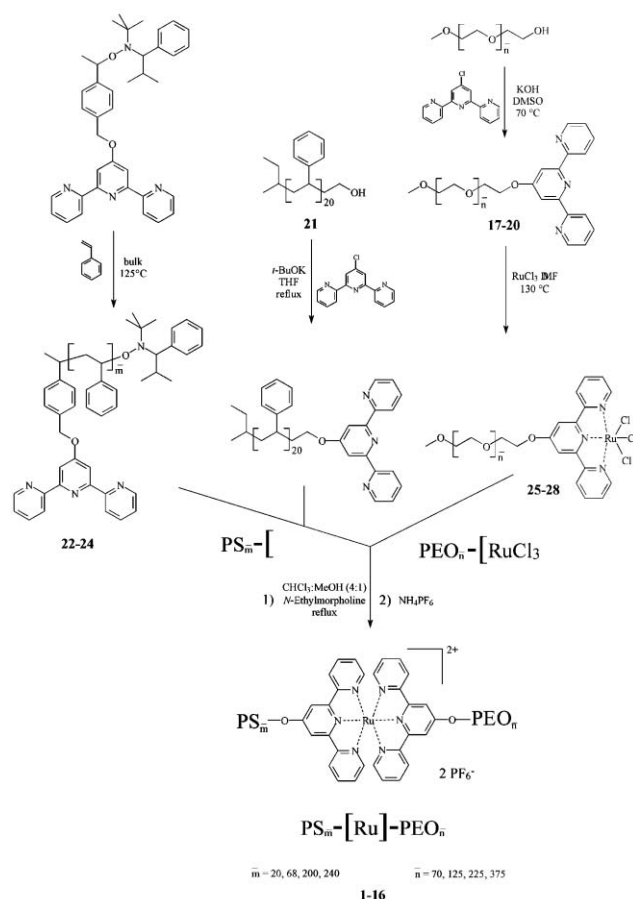
Scheme 1 Schematic representation of the synthetic route towards a library of PS$_m$-[Ru]-PEO$_n$ block copolymers, where m and n denote the degree of polymerization of PS and PEO respectively and where -[Ru]- represents the bis(terpyridine) ruthenium complex.

metal complex has been treated as the third block. All block copolymers have been purified by preparative size exclusion chromatography and column chromatography with isolated yields between 10 and 80%—the low yields are due to non-optimized purification procedures. The molecular weights and the purity of the block copolymers were measured by GPC using a photo-diode array detector. ¹H NMR spectra of each compound were recorded: integration of the signals gave the expected ratios for all components in the library as described in Table 1 within 10% error in each block.

The morphology of the library-components in a thin film obtained by spin-casting has been studied by means of Atomic Force Microscopy (AFM) and is shown in Fig. 1. At first glance, the different components of the library all show different phase behavior. Although trivial, this is an important observation: interpreting the phase behavior of these block copolymers by AFM is not straightforward. Complications involve phase attribution and the relationship between topology and morphology using this AFM technique.[9] In principle there are four individual contributors

Table 1 The block copolymers in the library are displayed in the table by name, by theoretical molecular weights and by the volume fractions of PS, -[Ru]- and PEO (annotated between brackets)

	PS$_{20}$-[	PS$_{70}$-[	PS$_{200}$-[	PS$_{240}$-[
PEO$_{70}$-[RuCl$_3$	PS$_{20}$-[Ru]-PEO$_{70}$ M_n = 6100 g mol^{-1} (35 : 16 : 49) **1**	PS$_{70}$-[Ru]-PEO$_{70}$ M_n = 11 400 g mol^{-1} (65 : 8 : 27) **2**	PS$_{200}$-[Ru]-PEO$_{70}$ M_n = 25 100 g mol^{-1} (84 : 4 : 12) **3**	PS$_{240}$-[Ru]-PEO$_{70}$ M_n = 29 300 g mol^{-1} (87 : 3 : 10) **4**
PEO$_{125}$-[RuCl$_3$	PS$_{20}$-[Ru]-PEO$_{125}$ M_n = 8400 g mol^{-1} (25 : 11 : 64) **5**	PS$_{70}$-[Ru]-PEO$_{125}$ M_n = 13 700 g mol^{-1} (54 : 7 : 39) **6**	PS$_{200}$-[Ru]-PEO$_{125}$ M_n = 27 400 g mol^{-1} (77 : 4 : 19) **7**	PS$_{240}$-[Ru]-PEO$_{125}$ M_n = 31 600 g mol^{-1} (80 : 3 : 17) **8**
PEO$_{225}$-[RuCl$_3$	PS$_{20}$-[Ru]-PEO$_{225}$ M_n = 12 800 g mol^{-1} (16 : 8 : 76) **9**	PS$_{70}$-[Ru]-PEO$_{225}$ M_n = 18 100 g mol^{-1} (41 : 5 : 54) **10**	PS$_{200}$-[Ru]-PEO$_{225}$ M_n = 31 800 g mol^{-1} (67 : 3 : 30) **11**	PS$_{240}$-[Ru]-PEO$_{225}$ M_n = 36 000 g mol^{-1} (71 : 3 : 26) **12**
PEO$_{375}$-[RuCl$_3$	PS$_{20}$-[Ru]-PEO$_{375}$ M_n = 19 400 g mol^{-1} (11 : 5 : 84) **13**	PS$_{70}$-[Ru]-PEO$_{375}$ M_n = 24 700 g mol^{-1} (31 : 4 : 65) **14**	PS$_{200}$-[Ru]-PEO$_{375}$ M_n = 38 400 g mol^{-1} (56 : 3 : 41) **15**	PS$_{240}$-[Ru]-PEO$_{375}$ M_n = 42 600 g mol^{-1} (60 : 2 : 38) **16**

to the phase contrast: amorphous PEO, crystalline PEO, the metal complex and amorphous polystyrene. The final morphology will be determined by competitions between self-organization, crystallization of the PEO-block and vitrification of the PS-block.[10] Moreover, the final morphology will be further complicated by competition between phase separation of the polymer blocks and association of polymer chains through ionic interactions.[11] These opposite driving forces give rise to a very rich phase behavior: annealing these thin films is therefore not straightforward, since the morphology continuously changes upon changing the temperature. We have therefore chosen to investigate the morphology after spin-casting without further annealing of the films, since this gave reproducible results. We assume that the metal complexes are located at the interfaces between the different phases and due to their minor content and small size ($\sim$1 nm), they will be impossible to visualize. Taking into account the volume fractions displayed in Table 1, block copolymers **3**, **4**, **8** and **13** are expected to give rise to a spherical morphology in the bulk. Indeed, spherical features can be observed for block copolymer **3**, **4** and **8** in the thin films, but **13** shows only crystalline PEO-domains. Block copolymers **2**, **7**, **9**, **11** and **12** are expected to give rise to a cylindrical morphology: **2**, **7**, **11** and **12** actually show features that could be explained by cylinders that are standing upright, oriented perpendicular to the silicon substrate and fully penetrating the block copolymer film. This phenomenon of spontaneous cylinder alignment has been observed and explained by Russell.[12] The remaining block copolymer morphologies are more difficult to understand without more

measurements. In the case of block copolymers **6**, **10** and **14** features appear that may be explained with lamellae which are expected on the basis of the volume fractions, albeit that **6** is the clearest. No preferential orientation of the lamellae is observed and roughly equal amounts of each block are visible at the surface. In the case of **10** and **14**, large domains of each single phase can be observed. Block copolymers **1** and **5** both contain the low molecular weight PS$_{20}$ and a relatively high amount of metal complex, which may lead to some mixing of the chains due to favorable electrostatic interactions between the chains. Block copolymers **15** and **16** are peculiar examples, both showing reproducibly this type of morphology with holes in the film. More measurements are definitely needed for understanding the origin of their phase behavior. The present approach demonstrates that block copolymer libraries using a coordination chemistry approach are ideally suited to study the influence of chain length and composition on the resulting morphologies avoiding complex multiple living polymerizations. The fact that the same batches of building blocks are used reduces the bias of small changes in molecular weight, composition (end group) and polydispersity normally obtained by traditional block copolymerization techniques. In the near future we will study further the morphology at different temperatures by isothermal crystallization of the thin films in order to increase our understanding of the morphology of all components in the library and the influence of the competition between self-organization, crystallization, vitrification and the association of the metal complexes on the morphology.
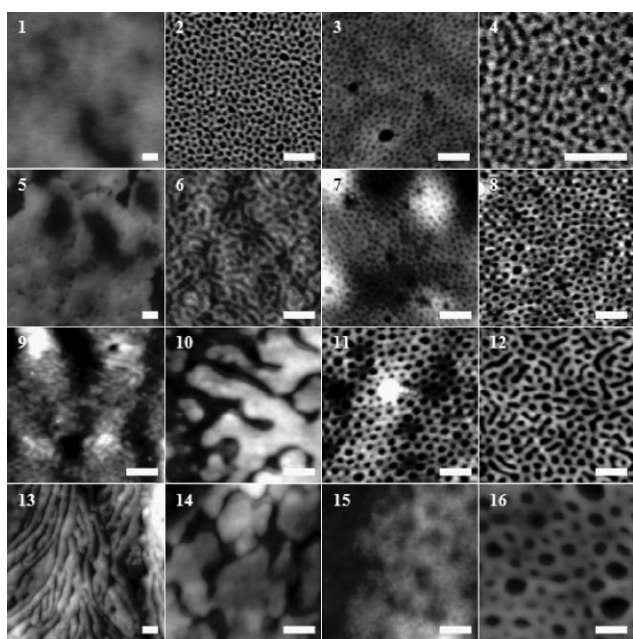

Fig. 1 AFM phase images of all block copolymers in the library after spin-casting from a 2 w/v % solution in toluene. No annealing has been performed. The scale bar represents 100 nm.

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