Blue-Light Emitting Polymer Films

Nano- and Micro-Engineering of Ordered Porous Blue-Light-Emitting Films by Templating Well-Defined Organic Polymers Around Condensing Water Droplets**

Christopher Barner-Kowollik, Helen Dalton, Thomas P. Davis,* and Martina H. Stenzel**

Recent advances in the field of living free-radical polymerization techniques, such as the reversible addition fragmentation chain transfer (RAFT) process,[1–5] atom-transfer radical polymerization (ATRP),[6–8] and nitroxide-mediated polymerization (NMP),[9] have enabled the synthesis of polymers with well-defined and in some cases complex macromolecular architectures. These novel architectures include block copolymers, comb polymers, and star-shaped macromolecules.[1,10] Star, block, microgel, and comb polymers have been successfully cast into (self-assembling) porous films of regular structure and pore size.[1,11–15] Self-assembling macromolecular structures such as those reported herein may be used in a wide range of applications, such as molecular electronics, optoelectronics, and phototonics, as well as in biological applications such as microarrays and as potential substrates for studying cell growth.[12,14–20] Analogous structures based on the assembly of colloidal particles have also been reported as inverse opal substrates.[21] In a recent study Lu and Jenekhe generated blue-light-emitting polystyrene by a simple modification of polystyrene to poly(vinyldiphenylquinoline).[22] Herein we report on the application of the above-mentioned modification procedure to linear and six-arm, star-shaped polystyrene generated by the RAFT process. In addition, we utilized ATRP to synthesize poly(ethylene glycol)–styrene block copolymers, prior to chemical modification to poly(vinyldiphenylquinoline). The resulting (blue-light-emitting) modified polymers were then cast into self-assembling porous films with regular pore sizes. Confocal and scanning electron microscopy (SEM) techniques were subsequently applied as analytical tools to probe the porous structures.

The star polymers were synthesized either by copper-mediated ATRP or by RAFT polymerization.[7,23] A multifunctional initiator was employed, from which arm growth occurs. The preparation of the six-arm star-shaped polystyrene by the RAFT process utilized hexakis(thiobenzoylthiomethyl)benzene as an initiator.[23] Similar five-arm, star-shaped polymers can also be generated by ATRP using a functionlized glucose initiator.[7,8] The synthetic strategies used are given in Table 1.

An extensive discussion of these syntheses is not required as both approaches have been detailed in previous publications.[7,8,23] In addition to the star-shaped architectures, two linear architectures were prepared. Linear polystyrene with a narrow polydispersity was prepared by using the RAFT process with cumyl dithiobenzoate as the RAFT agent. A poly(ethylene glycol)–styrene block copolymer was prepared by converting the end hydroxy group of poly(ethylene glycol) methyl ether into a brominated ATRP initiator, which was subsequently chain-extended with styrene. These approaches are also detailed in Table 1.

All of the polymers generated by living radical polymerization were subsequently modified by using a two-step approach to convert the styrene groups into vinyldiphenylquinoline units.[22] The reaction was monitored by ^{1}H NMR spectroscopy and in all cases functionalization was close to 100% (see Experimental Section). A (typical) significant change in the molecular weight distribution was indicated by gel permeation chromatography analyses of the linear polystyrene (generated by RAFT; Figure 1).

All of the above architectures (those based on polystyrene as well as those modified to poly(vinyldiphenylquinoline)) were utilized in the preparation of honeycomb films (or inverse opal substrates). The films were cast on a glass slide from a solution of the polymer in carbon disulfide under humid conditions. A typical example of the morphologies we attained from films cast from the linear poly(vinyldiphenylquinoline) and star-shaped poly(vinyldiphenylquinoline) is shown in Figure 2. Whilst pores were generated in the case of

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[*] Dr. C. Barner-Kowollik, Prof. Dr. T. P. Davis, Dr. M. H. Stenzel
Centre for Advanced Macromolecular Design
School of Chemical Engineering and Industrial Chemistry
The University of New South Wales
Sydney, NSW 2052 (Australia)
Fax: (+61) 2-9385-6250
E-mail: camd@unsw.edu.au
Dr. H. Dalton
School of Biotechnology and Biomolecular Sciences
The University of New South Wales
Sydney, NSW 2052 (Australia)

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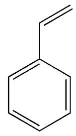
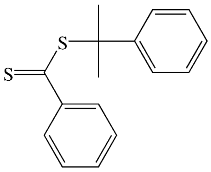
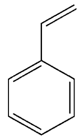
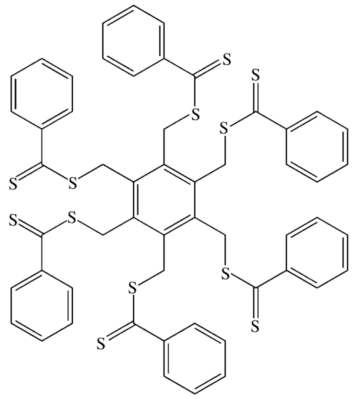
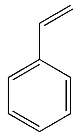
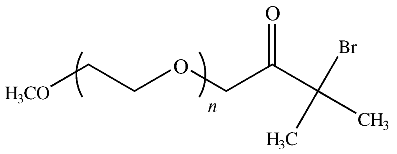
Table 1: Synthetic strategies for the generation of light-emitting polymer material based on linear and star-shaped architectures.[a]

Synthetic approach	Reactants		Molecular architecture obtained	M_n	PDI
RAFT, 60 °C, AIBN			linear	45 000	1.15
RAFT, 60 °C, AIBN			six-arm star	72 500	1.20
ATRP, 80 °C			linear block copolymer	4600	1.22

[a] The polymers were obtained by the RAFT process and poly(ethylene glycol)-*block*-styrene polymer by ATRP. M_n: the number average molecular weights, PDI: polydispersities of the prepared architectures, AIBN: 2,2-azobisisobutyronitrile.

a the linear architectures (Figure 2b), there is clearly a lack of order, thus confirming our earlier observations[11,12] that either complex architectures or some level of amphiphilicity (sometimes supplied by the end group) are generally required to get hexagonal close packing and a narrow pore-size distribution. The ability of star-shaped polymers to generate films with a higher degree of ordering is linked to their ability to precipitate instantaneously at the solution/water interface. Experimental evidence underpins this notion by showing that linear polystyrene precipitates to a lower extent at the interface, while polystyrene stars immediately form a solid layer.[19]

Not surprisingly, some improvement in film ordering was noted with the star-shaped architecture (namely, on going from Figure 2b to 2a).[11] The cast films based on star-shaped polymer material displayed areas of hexagonal close-packed pores, however, a number of grain boundaries were observed that disrupted the overall film regularity. A significant observation is that pores were generated with diameters as low as 150 nm (Figure 2). We believe that these are the smallest pores reported to date for this simple casting process. A similar result was observed for the poly(ethylene glycol)-*block*-poly(vinyldiphenylquinoline) copolymers, with pore sizes close to 150 nm and a similar degree of ordering as in the case of the linear polystyrene. As our intention was to study the blue-light emission and porous structure using confocal microscopy, we recast the films using a very low air flow. This procedure gives the condensing water droplets time to grow prior to encapsulation with the polymer, thus forming larger pores suitable for image analysis. The resultant films, now with pores on the micron scale, displayed high levels of order. Typical confocal microscopy images of the cast star-shaped poly(vinyldiphenylquinoline) prepared by the RAFT process are shown in Figure 3.

The honeycomb structure of the film with a pore size of approximately 1 μm can clearly be observed when recording the emission between 500 and 600 nm (Figure 3a), while the emission between 640 and 740 nm seems to be generated rather irregularly throughout the film (Figure 3b). Distinct locations of the emission between 640 and 740 nm can be detected by combining both fluorescence micrographs (Figure 3c).

This emission has a maximum intensity when emitted from the polymer bridging/separating two adjacent pores, while the emission between 500 and 600 nm is most intensely emitted from the polymer bridging/separating three adjacent pores. The fluorescence spectrum recorded by confocal microscopy is given in Figure 3d. The micrographs clearly indicate that in addition to the porous patterning on the micron scale, another pattern of organization is also imposed (as revealed by the fluorescence measurements). To our knowledge this is the first time that such an observation has

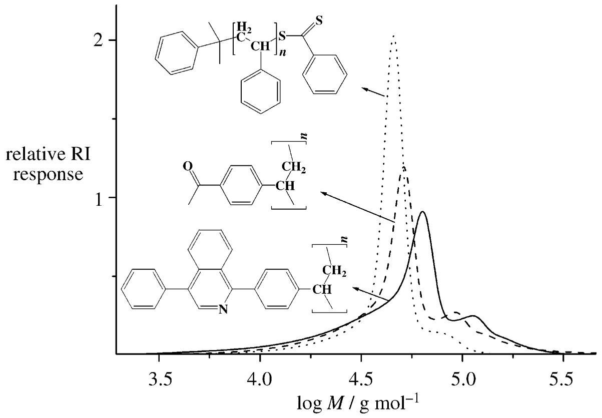


Figure 1. Sequential change in the molecular-weight distributions during the step-by-step modification of polystyryl dithiobenzoate to (light-emitting) linear poly(vinyldiphenylquinoline). RI = refractive index.

been made. The origin of the fluorescence patterning can be attributed to the enveloping of the polymer around condensing water droplets, which results in specific orientation of the polymer chains at the interface. As the water evaporates, this orientation is frozen into the final material. However, the precise molecular interactions that lead to the complex spectra remains a subject of conjecture and further analyses are currently underway.

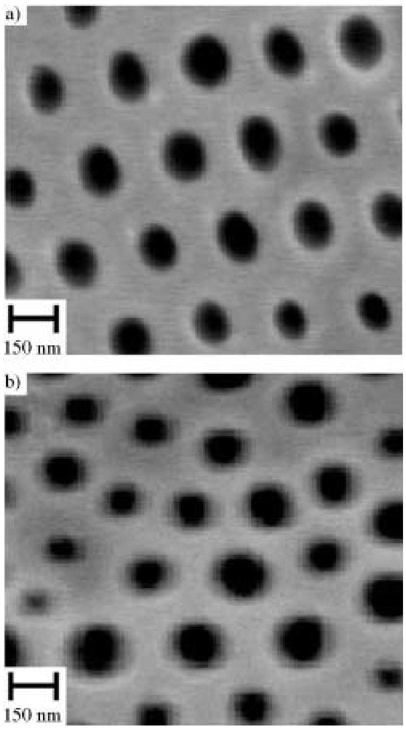


Figure 2. SEM images of porous films made from star (a) and linear (b) poly(vinyldiphenylquinoline) prepared by modification of macromolecular architectures generated by the RAFT process (see text).

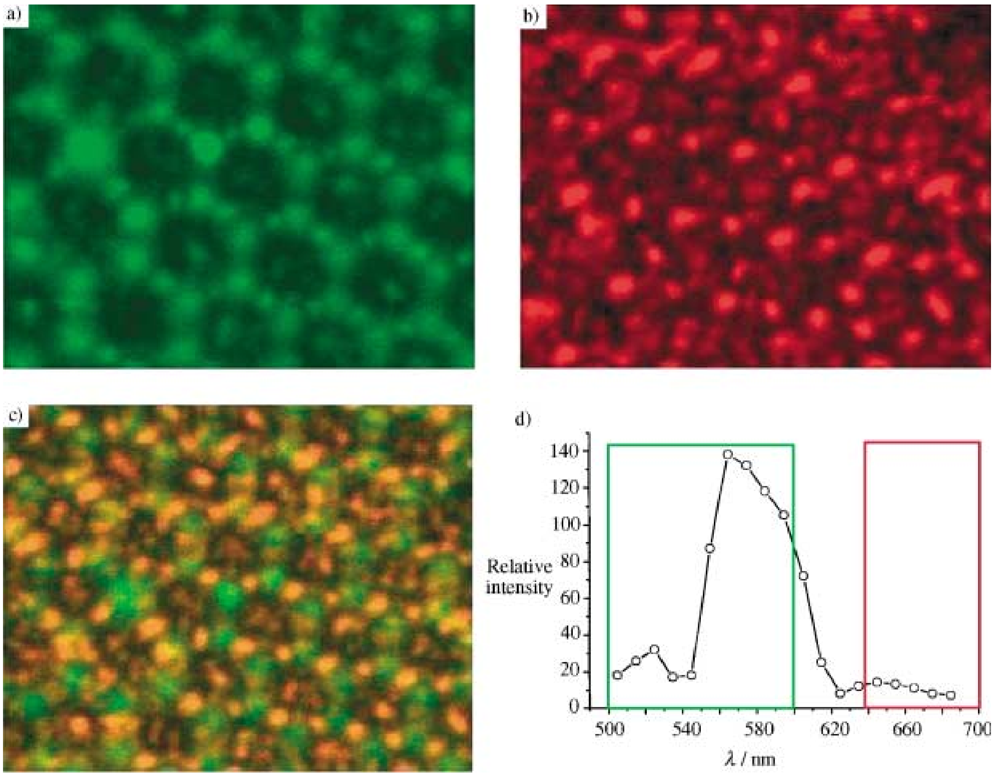


Figure 3. Confocal fluorescence microscopy images of a honeycomb-structured film prepared with poly(vinyldiphenylquinoline) star material prepared by RAFT (see Figure 1) showing the emission of the fluorescing films between 500 and 600 nm (a) and 640 and 740 nm (b). The excitation wavelength was 488 nm. Also shown is the combination of both images indicating two distinct regions for both emissions (c). Fluorescence spectrum (d) as recorded with the confocal microscope. The boxes in the red and the green regions of the spectrum indicate the emission range where the images (a, green) and (a, red) were taken, respectively. Relative intensity is given in arbitrary units.

In conclusion, we have demonstrated the versatility of the water-droplet templating process. Blue-light-emitting films were cast and the pore sizes of the films were engineered from the nano- to the microrange by simply manipulating the casting conditions. The confocal microscopy images demonstrate highly fluorescent organized porous materials with additional ordering within the polymer phase of the films. It is envisaged that the self-assembly of macromolecular material containing light-emitting functionalities on the nano- and microscale will find potential applications in the fabrication of molecular electronic devices[24] as well as photonic and band-gap materials.[25,26]

Experimental Section

Synthesis and modification of the linear polystyrene RAFT agent: The linear polystyrene RAFT agent was synthesized by the cumyl dithiobenzoate (CDB) mediated free-radical polymerization of styrene (Aldrich, 99%, purified by passing over a column of basic alumina) at 60°C. The initial CDB concentration was close to 3.8×10^{-3} mol L^{-1}. Cumyl dithiobenzoate was prepared by a literature method, using *n*-hexane as the solvent.[27] The purity of the RAFT agent was close to 97% as verified by ^{1}H NMR analysis. The concentration of the initiator (AIBN; Aldrich, 99%, recrystallized twice from ethanol) was close to 3.5×10^{-3} mol L^{-1}. The reaction mixture was thoroughly degassed by purging with nitrogen prior to reaction. The polymeric RAFT agent ($M_w = 45000$ g mol^{-1}) was isolated from the reaction mixture after 24 h by precipitation into an excess of methanol. The polymer was subsequently dissolved in THF (Aldrich, analytical grade) and precipitated again. The resulting powdery pink polymer was dried for 2 days at 30°C under vacuum. The subsequent two-step polymer modification procedure[22] gives poly(vinyldiphenylquinoline) as an off-white powder. The polymer modification consists of a Friedel–Crafts acylation (step I) and a subsequent condensation reaction with 2-aminobenzophenone (step II). Each of the individual reaction steps were checked for completeness by ^{1}H NMR spectroscopy. Similar ^{1}H NMR data regarding the transformation of the linear polystyrene to poly(vinyldiphenylquinoline) can be found in ref. [22] In addition, the acylation product (modification step I) and the final product (poly(vinyldiphenylquinoline) were both subjected to molecular-weight analysis. The molecular-weight distributions associated with each reaction step are given in the text.

Synthesis and modification of the star-shaped polystyrene RAFT agent: The synthesis of star-shaped poly(vinyldiphenylquinoline) proceeded by the same reaction sequence as indicated above for the linear poly(vinyldiphenylquinoline). The star-shaped polystyrene RAFT agent was generated by the hexakis(thiobenzoylthiomethyl)-benzene-mediated free-radical bulk polymerization of styrene at 60°C. Hexakis(thiobenzoylthiomethyl)benzene was synthesized according to a literature method[23] and its purity (99%) was confirmed by ^{1}H NMR spectroscopy. The subsequent two-step polymer-modification procedure was identical to the procedure given above for linear polyRAFT agents.

Synthesis of PEG–STY block copolymers by ATRP: Poly(ethylene glycol) methyl ether (Aldrich, $M_n = 550$ g mol^{-1}; 20 g) and triethylamine (8.4 mL) were dissolved in anhydrous THF (500 mL). 2-Bromo-2-methylpropionyl bromide (7.2 mL) was then added dropwise under an atmosphere of dry nitrogen. After 48 h at room temperature, the reaction mixture was added to dichloromethane (200 mL) and subsequently washed repeatedly with saturated, aqueous sodium hydrogen carbonate (3×200 mL). The resulting organic phase was dried over anhydrous magnesium sulphate. The structure and purity was confirmed by ^{1}H NMR spectroscopy and elemental analysis.

Copper-mediated ATRP: An *N*-(*n*-propyl)-2-pyridylmethanimine ligand was used. The PEG chain was successfully extended with styrene and a styrene block of $M_n = 4600$ g mol^{-1} was estimated by ^{1}H NMR spectroscopy. The final polydispersity of the PEG–STY chain was 1.22 as estimated by gel-permeation chromatography using linear polystyrene standards in THF.

Molecular-weight analysis: Molecular-weight distributions were measured by SEC on a Shimadzu modular system, comprising an auto injector, a 5.0-μm bead-size guard column (50×7.5 mm, Polymer Laboratories), followed by three linear columns (10^5, 10^4, and 10^3 Å; Polymer Laboratories) and a differential refractive index detector. The eluent was THF at 40°C with a flow rate of 1 mL min^{-1}. The system was calibrated using polystyrene standards ranging from 500 to 10^6 g mol^{-1}.

Film casting: The films were prepared from carbon disulfide solutions with a concentration of 10 g L^{-1}. The films were cast on a glass support and dried with a flow of humid air at 22°C. The casting process was carried out in a custom designed box at a constant humidity level of 85%. The air flow was controlled using a flow meter to ensure reproducible conditions.

Confocal microscopy and SEM: The fluorescence micrographs were taken with a Leica confocal microscope TCS SP2 AOBS with a water lens (63.0×1.20 W CORR UV). The excitation was set at 488 nm, while the emission was measured at different wavelengths as indicated in the main text. The SEM images of chromium-coated samples were recorded on a Hitachi S900 scanning electron microscope.

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