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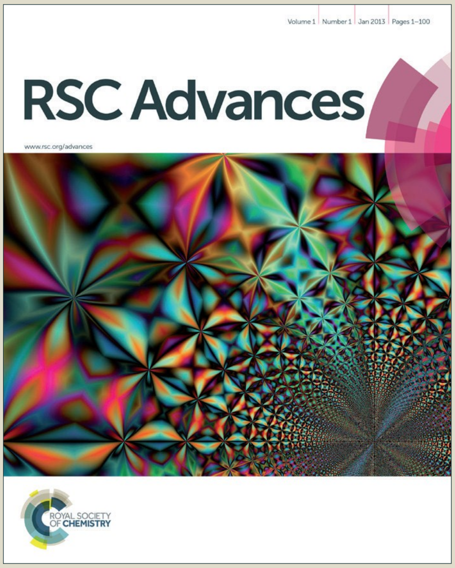

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ARTICLE

Stable Nanoporous Thin Films through One-Step UV Treatment of Block Copolymer Precursor

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Nanoporous structures derived from self-assembled block copolymers (BCP) are facile template for the nanofabrications. In order to enhance the stability of the nanoporous structures toward collapse, which is of crucial importance for the practical applications, cross-link of the matrix is an essential process. Most of the BCP precursors undergo separated processes of degradation and cross-link. Here, we provided one-step fabrication of stable nanoporous film from BCP precursor by UV treatment, eliminating multistep processing. The BCP contains ortho-nitrobenzyl (ONB) group as UV degradable juncture and coumarin group as UV cross-linkable component. After UV exposure, the ordered nanoporous thin film was achieved, with carboxyl groups in situ generated. The tolerance of solvents was highly enhanced. This facile strategy provides promising applications in stable nanoporous scaffolds.

Introduction

Nanostructural materials derived from self-assembled block copolymer (BCP) have been attracted great attention as templates in naonofabrications. There are various nanostructures, such as lamella, hexagonally packed cylinders (HPC), body centered cubic spheres, etc.[1-7] Nanoporous films are formed by removal of the minor component from the BCP precursors.[8-13] Successful examples of nanoporous films are obtained by using technologies, such as chemical etching[14-16], ozonolysis,[17, 18] and UV degradation,[19, 20] dissolution of additives,[21-23] and so on. The nanoporous films are promising applications as scaffolds for separation, catalysts, microelectronic devices,[24-27] etc.

The stability of the nanoporous structures toward collapse from the solvents, heat, or internal surface pressure is of crucial importance for the practical applications. The matrix must be stabilized to preserve the porosity. Many methods have been developed to immobilize the matrix. Incorporating cross-linkable groups into the matrix block is the widely used. For example, thermally cross-linkable groups (benzocyclobutene),[28] chemical cross-linking of PS by using RuO_4,[29] photoacid generator to promote cross-linking of poly(4-hydroxystyrene),[30] radical induced cross-linking of polyisoprene.[31, 32] All the methods include the separated procedures of the degradation and the cross-link of the BCP precursors. One-step procedure of simultaneous degradation and the cross-link is seldom reported.

In this contribution, we provide one-step fabrication of stable nanoporous film from BCP precursor by UV treatment, eliminating multistep processing. The BCP has a UV cleavable juncture between the blocks and UV cross-linkable groups in the major block. When the functional groups are both sensitive to the same conditions of UV light, cleaving and cross-linking will occur simultaneously. Here, we introduced an ortho-nitrobenzyl (ONB) group and coumarin group into one block (see Scheme 1). By this way, stable nanoporous film can be obtained in one-step upon UV exposure.

Results and discussion

Scheme 1 shows the molecular design concept of the BCP. ONB group is chosen as the connection between the blocks. The ONB groups have been widely used as the UV sensitive groups for degradation. Meanwhile, coumarin groups are also UV sensitive, on the contrary, for cross-link in many studies.[33] Therefore, by introducing both the groups into one polymer chains, degradation and cross-link will occur simultaneously. The consideration of choosing PEO as the sacrificial block is that the PEO can be dissolved in most of common solvents after degradation. PS is used as the other block for the consideration of the similar polymerization kinetics with the coumarin monomer, as well as the low cost. Another remarkable feature is that, after UV cleavable of ONB, in situ carboxyl groups remain in the cross-linked nanoporous structures. The carboxyl groups are potential functional sites for the future application.

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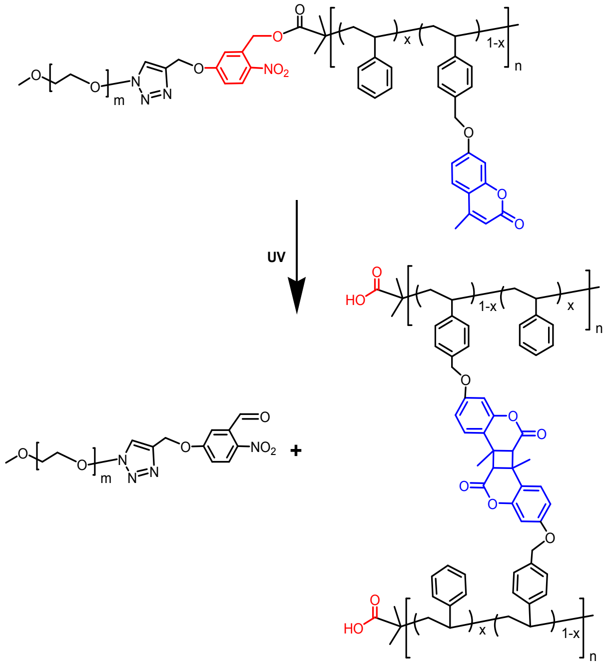

Scheme 1. Scheme of BCP PEO-*hv*-PScs with UV-degradable linker between the blocks and UV cross-linkable courmarin groups in one block. The BCP is degraded upon UV exposure into two parts. One is soluble PEO block, while the other is simultaneously cross-linked PScs matrix bearing carboxylic groups.

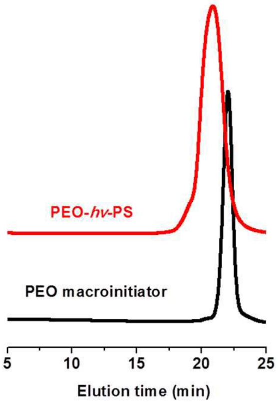

Fig. 1. GPC traces of PEO macroinitiator and BCP PEO-*hv*-PS.

We synthesize the BCPs from PEO macroinitiator by ATRP. Coumarin containing monomer and styrene are randomly polymerized. From the GPC result (Fig. 1), the curve of BCP is unimodal shift to higher MW, compared to the curve of PEO macroinitiator. The polymerization is well controlled. The molecular weight and molecular distribution is 18000 and 1.21, respectively.

^{1}H NMR measurement confirms the structures (Fig. 2). The successful introduction of UV cleavable ONB groups is evidenced by the appearance of the characteristic peak at δ=5.22. The successful introduction of UV cross-linkable coumarin groups is confirmed by the appearance of the characteristic peaks at δ=2.38, attributing to the methylene protons in the coumarin group, δ= 5.11, arising from the benzyl protons, and δ= 6.14, corresponding to the proton of double bond close to carbonyl group. The total weight percent of PEO is around 20.1%, and the weight content of coumarin groups in PS is about 6.3% by weight.

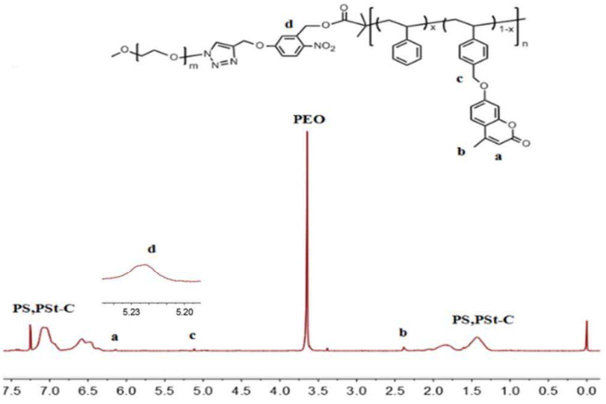

Fig. 2. ^{1}H NMR of BCP PEO-*hv*-PScs, indicating the successful introduction of the UV cleavable and cross-linkable groups (CDCl$_3$, 400 MHz).

The next step was to demonstrate the UV-cleavage and cross-link of the BCP. The ONB groups and coumarin units are all sensitive to UV light. Fig. 3 shows the UV-vis absorption spectroscopy of the BCP after UV irradiation under >300 nm for various times. The intensity of the band at around 290 nm, related with the nitro-aromatic linker, decreases obviously as the irradiation time increases. It indicates the successive cleavage of the ONB group.[9] Under the same UV irradiation condition, the photodimerization of the coumarin groups occur simultaneously, which is confirmed by the intensity decreases of the peak at around 320 nm.[34-36]

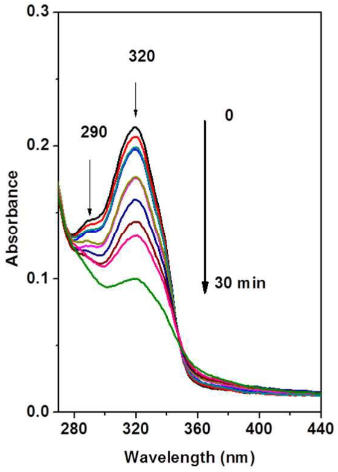

Fig. 3. UV-vis absorption spectroscopy of the BCP after various UV exposure times. The irradiation times are 0, 1, 2, 3, 5, 7, 10, 15, 20, and 30 min. The decrease of the peaks at 290 nm and 320 nm indicates that degradation and cross-link occur simultaneously.

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The successful removal of PEO and cross-link of coumarin groups via UV treatment are further demonstrated by FTIR spectroscopy measurements. In the original BCP sample, the peaks at the wavenumber of 1108 and 943 cm^{-1} are assigned to the C–O–C stretching and CH_2 rocking modes in PEO, respectively. The both peaks decrease obviously after removal of PEO. The carboxyl groups are by default generated after ONB group cleavage, evidenced by the appearance of broad peak at the 3333 cm^{-1}. The photo-crosslink of the coumarin units was reflected by the peaks decrease at the wavenumber of 1602 cm^{-1}, corresponding to C=C ring stretch. As the dimerization reaction proceeds, the double bond forms the cyclobutane ring.

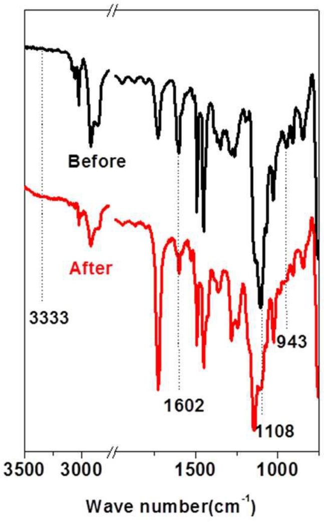

Fig. 4. FTIR spectra of the BCP before and after UV treatment.

As the BCP is successfully degraded and cross-linked, the BCP may also be suitable for the generation of stable nanoporous thin films. As mention above, The weight percent of PEO is around 20.1%. The self assemblied structure was detected by small angle X-ray scattering (SAXS), and HPC structure was observed. From SAXS curve in Fig. 5a, a primary peak can be found around a scattering vector q value corresponding to a d-spacing of 16 nm. Higher order reflections are also seen at scattering vector positions of $3^{1/2}$, $4^{1/2}$ of the first-order maximum, indicating of a hexagonal packing. The HPC structures are also confirmed by TEM. The self-assembled structure of the BCP is shown in Fig. 5b. Contrast to PS matrix, PEO domains are selectively stained by RuO_4. The image gives direct evidence of ordered microphase separation structures. The distance between the PEO domains is approximately 18 nm, which is in accordance with the SASX data.

When the self-assemble nanostructures are treated with UV irradiation, nanoporous film retains the long-range ordering throughout the UV-treatment. Thin film of the BCP was spin coated onto silicon wafers, and annealed in a saturated toluene vapor for phase separation and morphology development. After that, the film was exposed to UV light, and washed with methanol to remove the PEO chains. The hexagonally packed nanopores are seen in the height image, as shown in Fig. 7. Also, obvious contract is shown in the phase image, indicating successful removal of PEO from ordered BCP precursor.

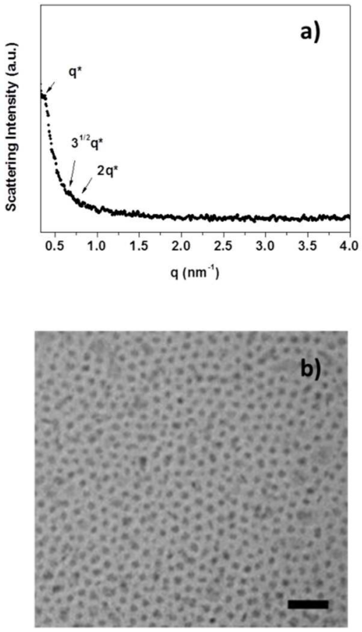

Fig. 5. SAXS curve (a) of the BCP sample and TEM image of BCP thin film(b), indicating hexagonally packed cylinderical structures (PEO was selectively stained by RuO_4,scale bar: 100 nm).

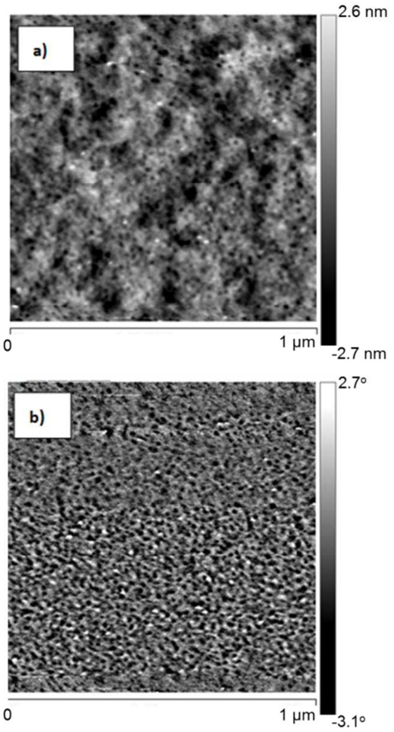

Fig. 6. AFM image of nanoporous thin film from BCP precursor, height (a) and phase (b) image, exhibiting nanopores formation after UV treatment.

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Since the coumarin units are cross-linked after UV irradiation so that the solvent durability of the nanoporous film is dramatically enhanced. As shown in Fig. 7, the thin film of the BCP before UV treatment is destroyed by acetone. However, after the sample was exposed under UV light, the film was stable when contacted with acetone, as well as other solvents, such as methylene chloride, chloroform, THF, etc.

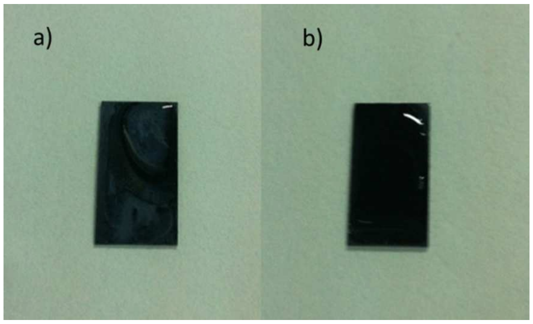

Fig. 7. Digital photographs of BCP thin film immersed in acetone (a) and of nanoporous thin film (b) after UV treatment, indicating that the solvent durability of the film after UV treatment is highly enhanced.

As mentioned above, carboxyl groups are left on the PS terminals where ONB groups are degraded after UV irradiation. The carboxyl groups on the inner surface of the nanopores are important for the future applications, for example, functional modification. The appearance of carboxyl groups on the nanoporous surface can be proved by zeta potential measurement. Fig. 8 shows the zeta potential tendency on the surface with various pH values. The zeta potentials are negative at pH>6, and the absolute value increase with the pH values increase, due to the deprotonation of the carboxyl groups. As the pH decreases, the carboxyl groups get protonation. Thus, the zeta potentials increase to near zero, and the surface is slightly positive. The tendency of the zeta potentials as the function of pH is characteristic of a weakly acidic surface.

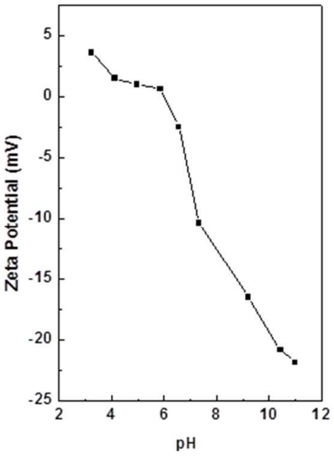

Fig. 8. Zeta potentials-pH curve of nanporous thin film after UV treatment, indicating that carboxyl groups are generated on the wall surface.

Experimental

Materials

Chlorobenzene (Analytical purity, Beijing Chemical Reagents Co.) was distilled with CaH_2 before use. Toluene and THF (Analytical purity, Beijing Chemical Reagents Co.) were distilled with Na/benzophenone. CuBr was synthesized from $CuBr_2$. 7-hydroxyl-4-methylcoumarin (Analytical purity, Beijing Chemical Reagents Co.), PMDETA (99.5%, TCI), 1-(chloromethyl)-4-vinylbenzene (97%, Aldrich) were used as received. Styrene (Analytical purity, Beijing Chemical Reagents Co.) was distilled prior to use. Copper grid was purchased from KYKY, China. Silicon wafer was purchased from Zhejiang Silicon material Company).

Synthetic Procedures

UV-cross-linkable momoner coumarin-derived styrene (CS) was synthesized by coupling of coumarin and 1-(chloromethyl)-4-vinylbenzene. Synthesis of macroinitiator PEO-Br was synthesized elsewhere.

Synthesis of BCP 1.05 g PEO-Br macroinitiator ($M_{n,\ GPC}$ =5.0 k, PDI =1. 09, 0.50 mmol) was dissolved in 5.10 g of chlorobenzene. And then 3.67 g of styrene (35.3 mmol), 0.50 g of St-C (1.7 mmol), 0.10 mg of CuBr (0.69 mmol), 0.10 mg of PMDETA (0.58 mmol) were added. The mixture was degassed by three freeze-pump-thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 90 ^{o}C for 8 h. The reaction was quenched by dipping the reaction tube in ice/water before the tube was broken. The mixture was diluted with CH_2Cl_2, passed through a basic Al_2O_3 column, and precipitated into methanol. The block copolymers were filtered and dried in vacuo. White powder was obtained.

UV treatment of the sample. On a quartz plate, 5 wt% THF solution of PEO-*hv*-PScs was spin-coated. After removal the solvent in oven, the sample was exposed under UV light (365 nm) with different times. And the UV-cleavage and cross-linking of the film was in situ monitored by UV-vis absorption spectra (300 to 450 nm).

FTIR experiment (Nicolet iN10MX) was carried out to confirm the cleavage and cross-linking of the PEO-*hv*-PScs after exposure to UV light for 4 h. the UV-treated sample was washed with methanol to dissolve the PEO block.

Zeta potential experiments were carried out by using an Anton Paar SurPASS. Two nanoporous films on silicone wafer (1×2 cm) after UV treatment were loaded into the clamping cell. The plates were separated by a spacer, providing a channel for electrolyte flow. The test electrolyte was 0.1 mol/L KCl solution, of which pH values was manually adjusted from 11 to 3, by using 1 mol/L NaOH and 1 mol/L HCl solution.

TEM sample preparation. On a copper grid, copolymer was dip-coated from 1 wt% toluene solution. In order to obtain cylindrical PEO domains oriented the film from bottom to top, the film was placed in vacuum drying oven under 140 ^{o}C for 2 hours. After thermal annealing, the film was dropped to room temperature. Last, the sample was measured by TEM. In order to enhance the contrast between two phase, RuO_4 was used to stain the PEO phase for 1 min. TEM experiments were done by using JEOL-2100F.

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AFM sample preparation. On a mica plate, copolymer was spin-coated from 1wt% toluene solution in glove box, with the spin speed of 1000 rpm and time 110 s. Then, the film was placed in vacuum drying oven under 140 °C for 2 hours. After thermal annealing, the film was dropped to room temperature. The film thickness is around 1 μm), determined by SEM observation of the film cross section. In order to remove the PEO domain, the film was exposed under UV light (λ=365nm) for 3 hours under ambient condition. After that, the PEO cylinder was degraded and the PS matrix was cross-linked. And the sample was immersed and washed with methanol. Last, the sample was measured by Dimension Icon.

Conclusions

A kind of UV-crosslinkable and degraded BCP PEO-*hv*-PScs is successfully synthesized by ATRP with the coumarin units and ONB groups. After thermal annealing, the block copolymer self-assembled into ordered PEO structures in the PS matrix. Because of the exist of coumarin units and ONB groups, the thin film were cross-linked and degraded under UV irradiation. We obtained successfully the stable nanoprous structures. The one-step strategy facilitate the process of nanoporous structure fabrication. For example, a mechanically-strong anti-reflection film could be generated by this method, which brings air voids/pockets into the film matrix.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No. 21204002, 51272010, 51472018), Beijing Nova Program (No. XX2013009), Pre-research Project of China Aerospace Medical Engineering (2012SY54A1106, CWS11J176).

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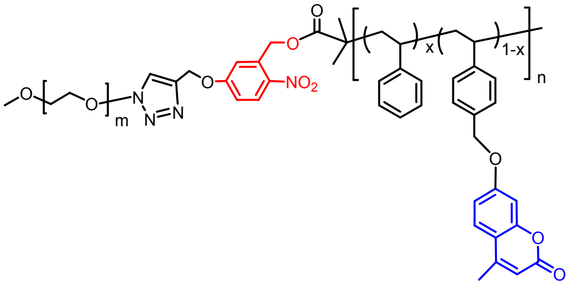
Stable Nanoporous Thin Films through One-Step UV Treatment of Block Copolymer Precursor

Xia Ma,[a] Xin Sui,[b] Zhenyu Zhang,[c] Naifu Zhang,[b] Chao Li,[b] Aihua Chen,[a]* Qiong Xie[d] and Longcheng Gao[b,]*

Stable nanoporous structures was fabricated from a self-assembled block copolymer precursor by one-step UV treatment.



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