

NANOSTRUCTURES OF FUNCTIONAL BLOCK COPOLYMERS

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Abstract Nanostructure fabrication from block copolymers in my group normally involves polymer design, synthesis, self-assembly, selective domain crosslinking, and sometimes selective domain removal. Preparation of thin films with nanochannels was used to illustrate the strategy we took. In this particular case, a linear triblock copolymer polyisoprene-*block*-poly(2-cinnamoyl ethyl methacrylate)-*block*-poly(*t*-butyl acrylate), PI-*b*-PCEMA-*b*-PtBA, was used. Films, 25 to 50 μm thick, were prepared from casting on glass slides a toluene solution of PI-*b*-PCEMA-*b*-PtBA and PtBA homopolymer, *h*PtBA, where *h*PtBA is shorter than the PtBA block. At the *h*PtBA mass fraction of 20% relative to the triblock or the total PtBA (*h*PtBA and PtBA block) volume fraction of 0.44, *h*PtBA and PtBA formed a seemingly continuous phase in the matrix of PCEMA and PI. Such a block segregation pattern was locked in by photocrosslinking the PCEMA domain. Nanochannels were formed by extracting out *h*PtBA with solvent. Alternatively, larger channels were obtained from extracting out *h*PtBA and hydrolyzing the *t*-butyl groups of the PtBA block. Such membranes were not liquid permeable but had gas permeability constants ~ 6 orders of magnitude higher than that of low-density polyethylene films.

Keywords Nanostructures, Block copolymers, Nanochannel generation, Self-Assembly, Polyisoprene-*b*-poly(2-cinnamoyl ethyl methacrylate)-*b*-poly(*t*-butyl acrylate)

INTRODUCTION

The preparation of nanometer-sized structures with well defined shape and narrow size distribution, *i.e.* nanostructures, has attracted much attention recently mainly to meet the demand for smaller electronic devices^[1]. Nanostructures are also useful in the preparation of high-strength nanocomposites or sensors that may imitate enzymes in molecular recognition. Nanostructures were previously prepared mainly from inorganic or organic precursors.

Synthetic polymers are widely used as a versatile modern material. Unfortunately, they were not taken full advantage of in the preparation of nanostructures of different shapes other than nanospheres^[2]. Research development in the past few years has changed this situation^[3, 4]. Reviewed in this paper are the strategies used in my group for polymeric nanostructure fabrication from block copolymers^[3].

Nanostructure preparation by chemists normally involves molecular design, synthesis, and self-assembly. The same procedure can be used for nanostructure fabrication from polymer precursors. In our case, the "building blocks" for nanostructure fabrication are block copolymers. The simplest block copolymers are diblocks $(A)_n(B)_m$, which consist of linear A and B chains with n and m units, respectively, joined head-to-tail. Block copolymers self-assemble in both bulk and block-selective solvents. Block copolymers self-assemble in bulk due to block incompatibility. The block segregation patterns are diversified, as reviewed by Hasegawa and Hashimoto^[5] for diblocks and by Bates and Fredrickson^[6] for triblocks. The patterns vary with block copolymer structure, block copolymer composition, temperature, and block connection sequence for triblocks such as $(A)_n(B)_m(C)_l$, where $(C)_l$ denote a C chain with l repeat units. In a block-selective solvent that does not solubilize

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all the blocks of a block copolymer, the block copolymer forms micelles of various shapes. In a micelle, the soluble block or blocks stretch into the solvent phase and the insoluble block or blocks of different chains aggregate to form a polymer-rich phase to minimize the insoluble block/solvent contact. For diblocks, the micelles can be spherical^[7], cylindrical^[8], vesicular^[9, 10] or donut-shaped^[10].

Nanostructures such as block copolymer micelles prepared from the three-step approach as described above are held together by van der Waals forces. They are stable under their preparation conditions but disintegrate or mutate when the environment changes. Prochazka *et al.*^[11], Wilson *et al.*^[12], and Ishizu *et al.*^[13] circumvented this spherical micelle stability problem by crosslinking them. In an attempt to prepare stable porous solids, Lee *et al.*^[14] crosslinked one and degraded another block of block-segregated diblock solids. The vast potential of chemical modification of pre-assembled mesophasic structures of block copolymers for the preparation of other types of nanostructures, however, remained to be demonstrated by us^[3], Wooley and coworkers^[15, 16], Armes and coworkers^[17], and Bates and coworkers^[18]. Using a fourth “locking in” step, i.e. nanostructure crosslinking, and sometimes a fifth step, i.e. nanostructure “sculpturing” or the selective removal or degradation of a domain or domains in a nanostructure, we prepared many new sophisticated stable functional nanostructures. Examples include nanospheres^[19–24], crosslinked polymer brushes (diblock monolayers)^[25], nanofibers^[26], nanotubes^[27], and nanochannels in polymer thin films^[28, 29]. The nanospheres, as illustrated in Fig. 1, can then be hairy^[19], magnetic^[20], shaved^[21], porous^[22], hollow^[23] or with crosslinked shells^[24]. In this paper, I will use the preparation of nanochannels in polymer thin films^[29] to illustrate the approach we took. Since the choice of system has been made based on novelty, more characterization is unavoidably required. Also, the potential of the membranes prepared from this methodology remains to be explored.



Fig. 1 Structure of different nanospheres

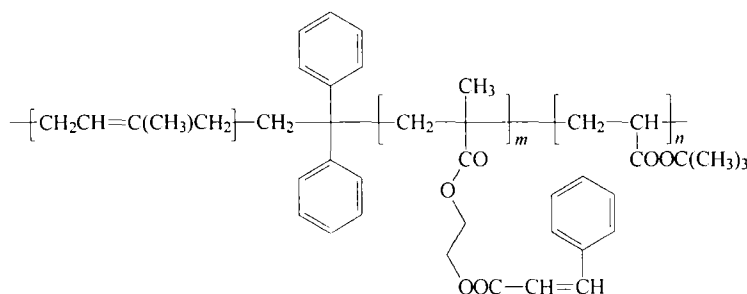
Illustrated in order are hairy nanospheres, shaved nanospheres, porous nanospheres, hollow nanosphere S, hollow nanosphere D, surface-shaved hollow nanospheres, shaved hollow nanospheres and nanospheres with crosslinked shell.

METHODOLOGY

Self-assembly of a linear triblock copolymer in bulk was taken advantage of in the preparation of nanochannels in thin films. At block segregation equilibrium, each block of $(A)_n(B)_m(C)_l$ forms domains with a specific shape. The morphologies of $(A)_n(B)_m(C)_l$ are determined by the volume fractions of the blocks, the sequence of block linkage, and interfacial tensions between the different blocks. The domain shape of the minor component, which exists in the least amount in a triblock, ranges from spheres^[30] to cylinders^[31], dumbbells^[32] or layers^[30, 31d]. The cylinders can be straight^[31a–d] or folded into loops^[31d–e] or spirals^[31e]. The cylinders can also be tortuous and inter-connected^[31f–g]. Our strategy was to control the volume fraction of C so that C forms inter-connected cylinders or gyroids inside the matrix of A and B. After crosslinking the A and B matrices, C is then removed or degraded or partially removed or degraded to generate nanochannels. While the most straightforward method for changing the volume fraction of C is to vary the number of repeat units of each block or n , m , and l , an alternative approach we took was to incorporate homopolymer C into the triblock to increase the C volume fraction. This was possible because the molar mass of homopolymer C was less than that of the C block of the triblock and the homopolymer was thus completely miscible with the C block^[5]. After crosslinking the A and B matrix, one method for preparing membranes was to extract the homopolymer out of the C domains.

Polymer Used

The specific polymer used was polyisoprene-*block*-poly(2-cinnamoyl ethyl methacrylate)-*block*-poly(*t*-butyl acrylate) or PI-*b*-PCEMA-*b*-PtBA, where $n = 370$, $m = 420$, and $l = 550$. The precursor to this triblock was prepared by anionic polymerization. The polydispersity of the triblock, as estimated from gel permeation chromatography in terms of polystyrene standards, was 1.16. The molar mass of the PI block was determined from light scattering. The values of $n/m/l$ were determined from NMR. The PtBA homopolymer or *h*PtBA used had ~ 100 repeat units.



PI-*b*-PCEMA-*b*-PtBA

Membrane Preparation and Evaluation

Films, 20–50 μm thick, were prepared by casting a triblock/*h*PtBA (wt/wt = 80/20) solution, $\sim 15\%$ polymer by mass, in toluene on glass slides. The films were dried at room temperature for 2 h, at 70°C for ~ 5 h, and then annealed at 100°C for 1 day. The colorless films were softened by soaking in methanol for 20 min before they were peeled off the glass slides with the help of a razor. Since the densities of PI, PCEMA^[28c], and PtBA^[33] are 0.91, 1.25, and 1.00 g/cm³, the volume fractions of PI, PCEMA, and PtBA/*h*PtBA in the triblock/*h*PtBA mixture are 0.13, 0.43 and 0.44, respectively.

The bulk films were irradiated for 10 min on each side in an UV beam, from a 500-W mercury lamp, that passed through a 310 nm cut-off filter. This caused $\sim 40\%$ of the PCEMA double bonds to crosslink, as verified by FTIR analysis. Homopolymer *h*PtBA was extracted out of the films by soaking in CH₂Cl₂ for three days. The solvent was then gradually changed to methanol before the films were picked up and dried at room temperature.

For testing water permeation, a PS-*b*-PAA film was sandwiched between two polyethylene films (30 μm thick) with paraffin linings (~ 10 μm thick), where both the polyethylene films and linings had a 1-mm hole in the center. The softer paraffin linings were used to ensure sealing between polyethylene films and the membrane. After the membrane was sandwiched, the composite film was lightly pressed between two glass plates and mounted between two arms of a U-tube with a ground interface and a circular opening with a diameter of ~ 1.5 mm. The two sides were held together by a clamp. Water flowed from one arm of a U-tube to the other due to height difference h between the two arms.

For gas permeability test, the same U-tube technique was used except that no liquid was introduced into the tubes. A gas pressure drop, ΔP , of $\sim 1.96 \times 10^3$ Pa was applied across the membrane. The amount of gas permeated through a membrane was determined by a gas buret^[34]. The thickness of membranes was measured using a micrometer.

Transmission Electron Microscopy Study

For transmission electron microscopic (TEM) studies, a small piece of a bulk film was embedded in an epoxy resin and the epoxy resin was cured at 60°C overnight. 50 nm thick slices were obtained from microtoming the embedded film and were viewed under a Hitachi-7000 microscope operated at 100 kV.

RESULTS AND DISCUSSION

Morphology of PI-*b*-PCEMA-*b*-PtBA/*h*PtBA

Illustrated in Fig. 2a) is a TEM image of a typical slice cut approximately parallel to the plane of a film that was ~ 50 μm thick. Since OsO_4 was used to stain the sample, the dark and gray domains represent the locations of PI and PCEMA, which are not differentiated well here. The light regions must correspond to the locations of PtBA/*h*PtBA. The image clearly shows the absence of macroscopic phase separation for *h*PtBA. The good mixing between *h*PtBA and the PtBA block is expected because the molar mass of *h*PtBA is much lower than that of PtBA and the system is in the wet-brush regime^[5]. The shape of the PtBA/*h*PtBA domains seems to change from location to location. The typical shapes of the PtBA domains as revealed by TEM are circles (one is marked by a short arrow) and tortuous stripes (two are marked by long arrows). This suggests that PtBA probably forms inter-connected tortuous cylinders in the PI-*b*-PCEMA matrix. The tortuous cylinders may appear different due to their different orientation relative to the electron beam. Illustrated in Fig. 2b) is the image of a slice cut along a direction forming an angle of $\sim 30^\circ$ with the bulk film plane. Because of the different microtoming direction, more tortuous light stripes are seen. Also the morphology at the air and polymer interface (marked by P/A Interface) seems to be fairly close to that in bulk. The TEM image patterns shown here do not resemble any found for triblock copolymers but bear resemblance to those known for the gyroid morphology of diblocks^[5]. While the exact morphology of such a sample remains to be elucidated, the suggested continuity of the PtBA/*h*PtBA domain is, however, reasonable for the PtBA/*h*PtBA volume fraction of 0.44.

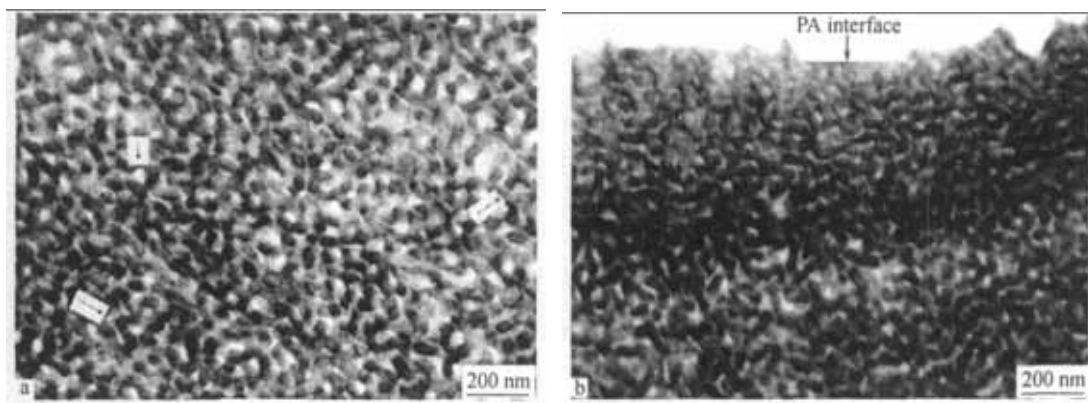


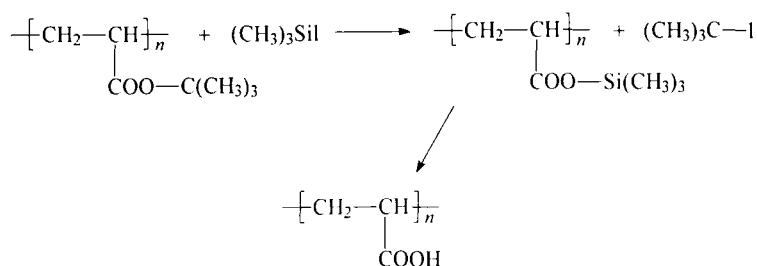
Fig. 2 TEM images of 50 nm thick PI-*b*-PCEMA-*b*-PtBA/*h*PtBA films stained with OsO_4 . The thin sections were obtained by microtoming a) approximately parallel to the film plane and b) along a direction $\sim 30^\circ$ off the film plane.

Membrane Formation

PCEMA crosslinks because of dimerization between CEMA groups of different chains in the PCEMA domain. The degree of PCEMA crosslinking was established by following the decrease in the intensity of the double bond absorption peak at 1635 cm^{-1} ^[19c]. PCEMA crosslinking was also demonstrated by the fact that the films did not disintegrate in CH_2Cl_2 . In addition, the film stability in CH_2Cl_2 suggested the formation of a continuous skeleton by PCEMA at a volume fraction of 0.43.

Homopolymer *h*PtBA was extracted out of the films by soaking in CH_2Cl_2 for three days. The removal of *h*PtBA was qualitatively judged from the fact that the extracted films appeared somewhat cloudy. More conclusive evidence for nanopore formation was obtained from FTIR and TEM analysis.

The removal of the *t*-butyl groups from the PtBA block was achieved by soaking PCEMA-crosslinked films in 0.10 mol/L $(\text{CH}_3)_3\text{SiI}$ solution in methylene chloride for two weeks. This, as confirmed by a FTIR measurement, led to the replacement of the *t*-butyl group by a trimethylsilyl group^[28c, 35].



The $(\text{CH}_3)_3\text{Si}$ group was removed by hydrolysis in methanol/water (95/5) for one day.

Illustrated in Fig. 3 is a TEM image of nanochannels generated by combining the *hPtBA* extraction and *t*-butyl group removal. Since the contrast of the TEM image was obtained without resorting to chemical staining, the bright ovals must represent the locations of channels. Some of the channels (marked by arrows) are obviously not normal to the film plane but tortuous as judged from the contrast variations surrounding the bright ovals. Not seen in Fig. 3 are bright tortuous stripes. This might be caused by the particular direction along which microtoming was performed to obtain the thin film imaged, as bright tortuous stripes were seen in other images. The quantitative cleavage of the *t*-butyl group was confirmed by comparing the FTIR spectra of the films before and after the hydrolysis step.

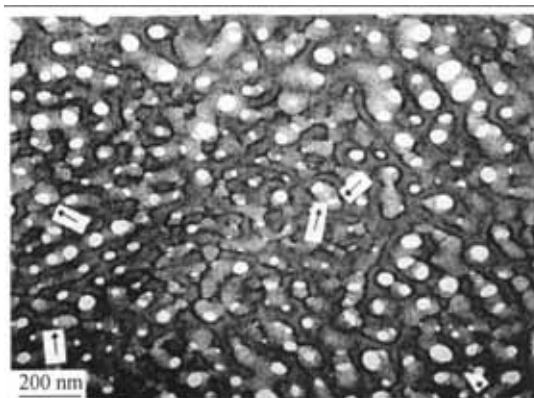


Fig. 3 TEM image of a 50 nm thick film after *hPtBA* extraction and *t*-butyl group removal
The sample was not stained, the bright circles must represent holes where polymer density is close to zero.

Membrane Performance

For gas permeability test, a membrane, typically 25–50 μm thick, was sandwiched at the interface between the two arms of a U-tube. After the thickness, l , and area, A , of a membrane and the gas permeation rate, F , were determined (Table 1), the equation

$$P = \frac{Fl}{A\Delta p} \quad (1)$$

was used to evaluate the gas permeability constants, P . Plotted in Fig. 4 are the variations in P as a function of the square root of the molar masses, m , of different gases for the *hPtBA*-removed and *t*-butyl-removed (*hPtBA* was removed as well) membranes. The gas permeability constants are of the order of $10^{-7} \text{ cm}^3 \cdot \text{cm} \cdot \text{s}^{-1} \cdot \text{cm}^{-2} \cdot \text{Pa}^{-1}$, which is ~ 6 orders of magnitude higher than those found for low-density polyethylene^[36]. The high gas permeability confirms the highly porous nature of the films.

The gas permeability constants are higher for the *t*-butyl-removed membranes. This is reasonable, because the channels and the pore volume fraction are supposed to be larger here due to the removal of *t*-butyl groups of the *PtBA* block. The linear decrease of P with increasing $\sqrt{m}$ indicates that the gas molecules permeated

through the nanochannels due to Knudsen flow^[37] and the gas molecules have no specific interactions with the channel walls. The only exception to this is the permeation of CO₂ across the *t*-butyl-removed membranes. This abnormality is reproducible and suggests some specific interactions between the nanochannel walls and CO₂. The *t*-butyl-removed membranes were not gas permeable immediately after their preparation. They became gas permeable after they were soaked in 0.10 mol/L NaOH solution, rinsed in water, and dried. The base treatment converted PAA to poly(sodium acrylate) and the electrostatic force between the different polyelectrolyte chains presumably pushed the channels open. The permeability of CO₂ was abnormally high probably because of the increased solubility of CO₂ in the poly(sodium acrylate) layer. It is well known that the permeability constant of a permanent is a product of its solubility and diffusivity in a membrane^[38].

Table 1 Permeation rates, F in the units of cm³/s of different gases across the two types of membranes measured at 22 °C

H ₂	N ₂	O ₂	Ar	CO ₂
HPtBA-removed membrane, $A = 0.071 \text{ cm}^2$, $l = 2.0 \times 10^{-3} \text{ cm}$				
0.0350	0.0125	0.0112	0.0093	0.0076
<i>t</i> -butyl-removed membrane, $A = 0.049 \text{ cm}^2$, $l = 2.5 \times 10^{-3} \text{ cm}$				
0.0248	0.0123	0.0111	0.0082	0.0135

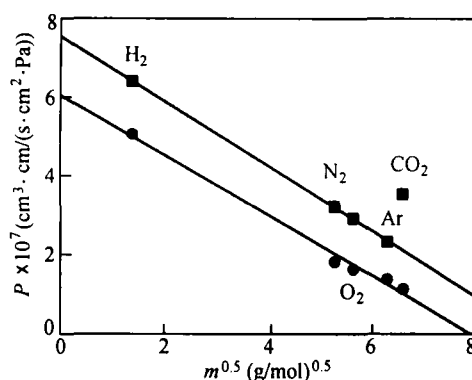


Fig. 4 Plot of the permeability constants P of different gases across HPtBA-removed (●) and *t*-butyl-removed membranes (■) as a function of the square root of the molar masses of the gases

We also tested water permeability across membranes with the thickness between 20 and 50 μm by filling the two arms of a U-tube with water to different heights. Regardless of the ionic strengths or pH of the aqueous medium, no water permeation was noticed. The lack of water permeability across the hPtBA-extracted membranes was understandable, because the channels were hydrophobic and were not wetted by water. The lack of water permeability across the *t*-butyl-removed membranes was more surprising, because the nanochannels with PAA chains were hydrophilic. The lack of water permeability and high gas permeability suggest that the PAA nanochannels are probably continuous in a grain, which may be of the size of several micrometers, and are discontinued at the boundaries between different grains. A grain here would be similar to a single crystal in which the different polymer domains are packed with order and the same orientation. From grain to grain, the domain orientations may change and the channels may be discontinued. Such grain boundaries may be very thin. While gas molecules can permeate through such thin boundaries, water flow would be stopped there. This model is supported by the observation of water permeability across thinner *t*-butyl-removed films, e.g. 2 μm thick, derived from microtoming a 50 μm thick film.

CONCLUSION

The strategy we adopted to prepare stable block copolymer nanostructures generally involves block copolymer design, synthesis, self-assembly, selective domain crosslinking, and sometimes selective domain removal. The use of five such steps was clearly exemplified in the preparation of thin films with nanochannels. After the five

steps, the nanochannels generated in films of a triblock copolymer with thickness between 20 and 50 μm were gas- but not liquid-permeable. Such membranes may be permeable to water vapor as well and thus should behave similarly as the Gore-Tex[®] films. A marvelous feature of this membrane preparation method is its convenience. The membrane precursor films were obtained from solution casting rather than from microtoming bulk solid as was used previously^[28]. Then, this method is convenient because only physical extraction of a homopolymer out of the matrix rather than chemical domain degradation was required for nanochannel generation.

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