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Potential Skin Layers for Membranes with Tunable Nanochannels

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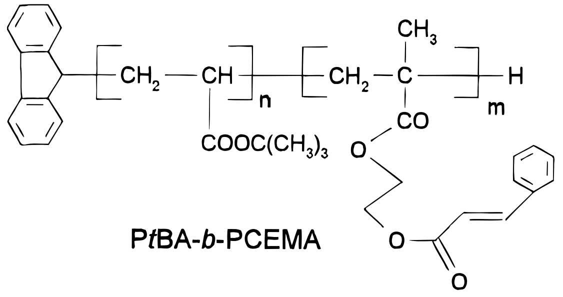
Membranes from synthetic and semisynthetic polymers have found applications in a wide range of industrial processes such as reverse osmosis, ultrafiltration, pervaporation, electrolysis etc.[1] More recently, membranes with uniform pore sizes have been used as templates for nanomaterial fabrication.[2−4] For all applications, the pore sizes and size distribution determine the ultimate performance of a membrane. In this communication, we report a process for producing potential skin layers for membranes with nanochannels tunable both in functional groups and in channel sizes.

The strategy we utilized involved the preparation of polymer films from poly(*tert*-butyl acrylate)-*block*-poly(2-cinnamoylethyl methacrylate) with the PCEMA block photo-cross-linkable and the *tert*-butyl groups of the P*t*BA block cleavable by hydrolysis. The samples we used had *n* and *m* values equal to 2.3×10^2 and 3.7×10^2 for polymer **I** and 3.8×10^2 and 6.4×10^2 for polymer **II**. Like conventional diblocks in bulk,[5] these polymers with a P*t*BA weight fraction of ~25% formed thermodynamically stable ordered phases, in which cylindrical microdomains of P*t*BA were uniformly distributed in the matrix of PCEMA. Thin films, e.g., ~2 μm thick, of these polymers were obtained by ultramicrotomy of the bulk films. Subsequent UV irradiation caused the PCEMA phase to cross-link. Treatment of these cross-linked films with $(CH_3)_3SiI$ followed by hydrolysis cleaved the *tert*-butyl groups of the P*t*BA domains to produce nanometer-sized channels partially filled with poly(acrylic acid) (PAA), spanning the whole thickness of the films.



P*t*BA-*b*-PCEMA

A literature search revealed that Lee et al. also attempted similar research.[6] In their case, the PVPDMPS block in bulk films, ~20 μm thick, of poly[(4-vinylphenyl)dimethyl-(2-oxopropyl)silane]-*block*-polyisoprene (PVPDMPS-*b*-PI) was cross-linked by acid-catalyzed condensation polymerization. The PI backbone was cleaved by ozonolysis. Their research was directed at bulk porous materials rather than at the preparation of potential skin layers for membranes.

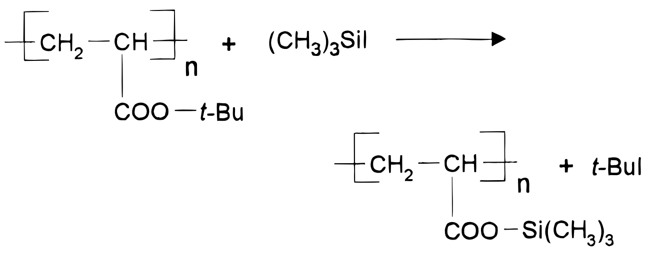
The precursor polymer, P*t*BA-*b*-P(TMS-HEMA), to P*t*BA-*b*-PCEMA was synthesized by sequential anionic polymerization of *t*BA and 2-(trimethylsilyl)ethyl methacrylate (TMS-HEMA) using fluorenyllithium as the initiator. The TMS group was then removed by hydrolysis in a THF/methanol mixture with ~20% methanol. The cinnamoyl group was attached by reacting P*t*BA-*b*-PHEMA with excess *trans*-cinnamoyl chloride in pyridine.[8−10] The polydispersity indexes of **I** and **II** determined by GPC against PS standards were 1.10 and 1.18. The *t*BA-to-CEMA repeat unit ratios determined by NMR were 0.62 and 0.59, and the weight-average molar masses determined by light scattering in chloroform according to the Zimm method were 1.27×10^5 and 2.21×10^5 g/mol, respectively. The molar masses determined were approximate, as they were not corrected for the different scattering powers of the constituent blocks.[11]

Transmission electron microscopy (TEM) was used to demonstrate cylindrical phase formation from the P*t*BA block. P*t*BA-*b*-PCEMA, 0.20 g dissolved in 2.0 mL of toluene, was added to polyethylene capsules. The samples were dried at room temperature for 3 days and at 60 °C under 30 cmHg pressure for 3 days and then were annealed at 110 °C under argon for 2 weeks. The annealed sample was sectioned by ultramicrotomy (Ultracut-E, Reichert-Jung) to slices of thickness between 25 and 50 nm. The microtomed samples were stained by OsO_4 vapor overnight and viewed with a Hitachi-7000 electron microscope operated at 100 kV.

Illustrated in Figure 1 is the TEM image of such a sectioned sample of **I**. The hexagonally packed lighter circles represent P*t*BA cylinders pointing outward. The continuous phase is darker, as the aliphatic double bonds of PCEMA selectively reacted with OsO_4 to get “stained”. The diameter of the cylinders is ~10 nm. A similar morphology was observed for **II** with the diameter of ~15 nm. Thus, the size of the P*t*BA phase increased with its molar mass as expected.[5] Changing the molar mass of the P*t*BA block thus offers a convenient method for tuning the size of the final nanochannels.

Sectioned films were then irradiated with UV light which had passed through a 260-nm cutoff filter from a 500-W Hg lamp for 8 s to cause the PCEMA phase to cross-link.[8,12] UV absorption analysis of the films at 274 nm indicated that ~35% of the aliphatic double bonds of PCEMA disappeared with this treatment.

The irradiated films were then soaked in a trimethylsilyl iodide solution, 0.050 M in dichloromethane, for 2−3 days. This triggered the following reaction:[13]



$$-\!\!\left[CH_2-\underset{\displaystyle COO-t\text{-}Bu}{CH}\right]_n- + (CH_3)_3SiI \longrightarrow -\!\!\left[CH_2-\underset{\displaystyle COO-Si(CH_3)_3}{CH}\right]_n- + t\text{-}BuI$$

After such a film was rinsed in methylene chloride briefly, it was immediately mounted on the sample stage of the TEM and viewed. A TEM image for such a film without OsO_4 staining is illustrated in Figure 2. The PCEMA phase now appears light, and the cylindrical domains are dark. This is in agreement with the

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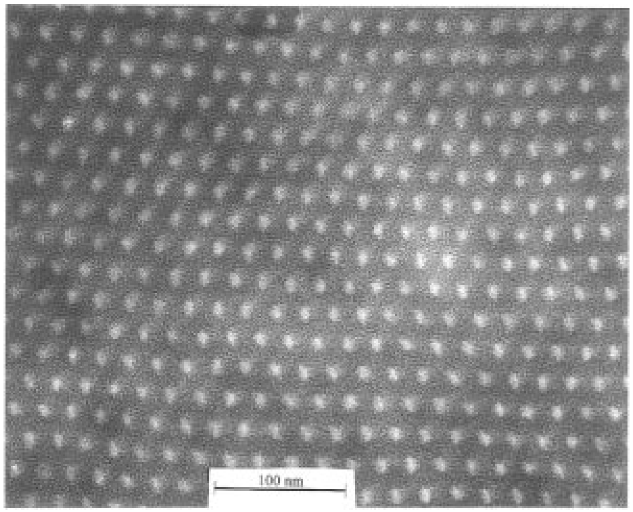

Figure 1. TEM image of an OsO_4-stained cross-linked polymer **I** film.

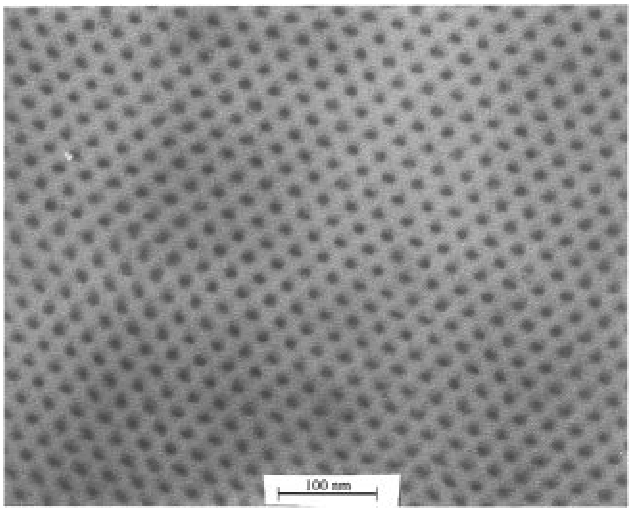

Figure 2. TEM image of a $(CH_3)_3SiI$-soaked polymer **I** film. The film was not stained.

anticipation that trimethylsilyl iodide reacted only with P*t*BA. The P*t*BA domains are dark, as silicon is a more effective electron scatterer than carbon, hydrogen, and oxygen atoms found in PCEMA.

That the reaction illustrated above did occur was further confirmed by our experiments performed using a Zeiss 902 microscope equipped with an energy loss spectrometer. When the microscope was operated at 100 kV and a small area of a $(CH_3)_3SiI$-treated polymer **II** film was imaged using electrons with the energy of 100 keV−110 eV, Figure 3 was obtained. The cylindrical domains now appear bright, as more electrons with the energy of 100 keV−110 eV emerged out of the cylindrical domains than from the continuous phase. This was the case because the binding energy of the L-shell electrons of silicon was ~110 eV.[14] The transfer of ~110 eV from some of the incident electrons to silicon should have produced a richer population of electrons with the energy of 100 keV−110 eV emerging from the silicon-rich cylindrical domains.

Close examination of Figure 2 reveals that the average diameter of the dark cylinders is ~13 nm. The diameter of the white cylinders in Figure 3 is ~15 nm. The diameters of 13 and 15 nm for trimethylsilyl-substituted P*t*BA domains are the same, within the

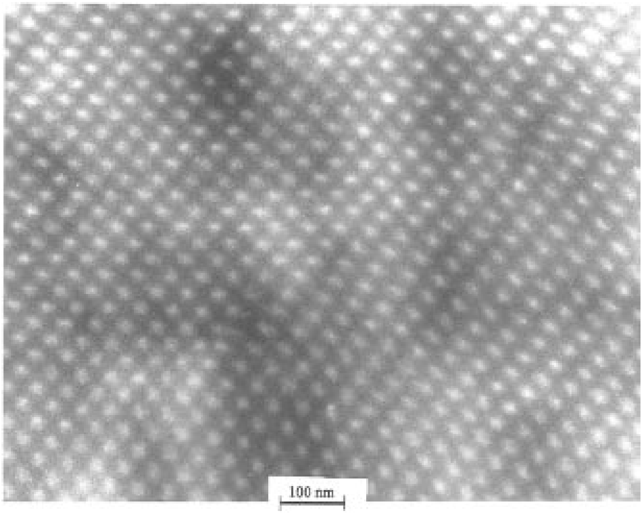

Figure 3. Silicon-specific image of a $(CH_3)_3SiI$-soaked polymer **I** film. The light and dark patches in the figure were probably due to the fact that the film was not rinsed in methylene chloride after being taken out of the trimethylsilyl iodide solution.

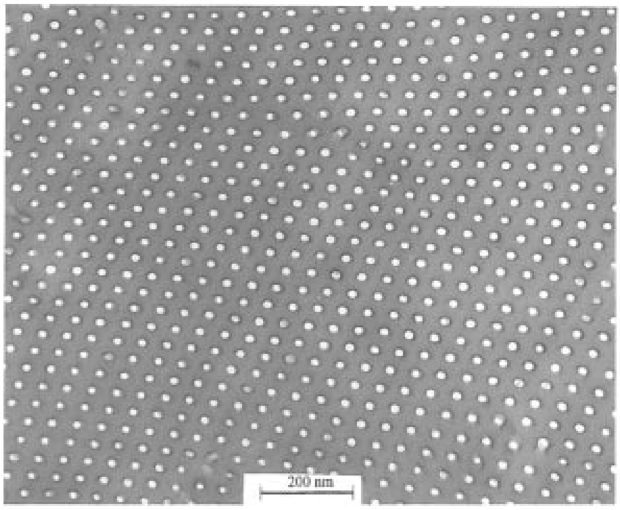

Figure 4. TEM image of a completely hydrolyzed polymer **II** film. The film was not stained.

error of visual diameter measurement, as 10 and 15 nm, the diameters of P*t*BA cylinders of **I** and **II**.

Experiments aimed at quantifying the degree of replacement of *tert*-butyl groups of P*t*BA by trimethylsilyl groups are currently being performed using the Zeiss 902 microscope. We expect this reaction to be close to quantitative, at least for thin films where the reagent transfer rate should be sufficiently high, as the reaction was approximately quantitative in solution phase.[7,13]

Silicon-specific imaging experiments demonstrated that the removal of trimethylsilyl groups attached to PAA was fast and could be achieved quantitatively by soaking the $(CH_3)_3SiI$-treated polymer films in methanol/water (95/5 by volume) mixtures for several minutes. This fast hydrolysis reaction for the trimethylsilyl groups explained why the image shown in Figure 3 was obtained without rinsing the film in methylene chloride. After the removal of trimethylsilyl groups, images with silicon-specific contrast could not be obtained anymore. Illustrated in Figure 4 is an image of a polymer **II** film after removal of the trimethylsilyl groups, obtained using the Hitachi instrument. The contrast between the light cylindrical regions and the dark PCEMA phase is now very sharp. The contrast was obtained without resorting to chemical staining; this suggests that the materials in the cylindrical regions were not as dense as those in the continuous phase.

Close examination of Figure 4 reveals that the brightness level is not uniform across the white circles denoting the cylindrical domains. Slightly dark inner circles seem to exist in the center of some of the white circles. The nonuniform brightness level in the cylindrical domains suggests that they are not empty. This is in agreement with our expectation that only the *tert*-butyl part of P*t*BA was hydrolyzed to create partially filled cylindrical domains. Further experiments to confirm the presence of PAA in the white domains using the Zeiss microscope are being performed.

The diameter of the cylinders in Figure 4 was ∼17 nm, which was the same, within diameter measurement error, as the 15 nm value found for the P*t*BA cylinders of **II**.

In conclusion, selectively locking in one phase and cleaving the other of a diblock copolymer film represents an effective method for producing thin films with regularly packed and uniformly sized nanochannels. Since the diameter of the P*t*BA cylinders was controlled by the molar mass of the P*t*BA, varying the molar mass of P*t*BA block offers a convenient method for tuning the size of the final channels. The channel size can also be further tuned by derivatizing the PAA block, e.g., by methylating or partially methylating PAA in the channels. Similarly, the functional groups in the channels can be changed by PAA derivatization. Films prepared this way may serve as the skin layers for membranes with channels tunable both in size and in functional groups.

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