[26] The powder X-ray diffraction pattern was indexed (using the first 20 observable peaks) by the program ITO,[27] to give the unit cell: $a = 12.59$, $b = 10.20$, $c = 22.89$ Å, $\beta = 105.5°$. Systematic absences are consistent with the monoclinic space group $P2_1/n$. Density considerations suggest that there is one molecule in the asymmetric unit.

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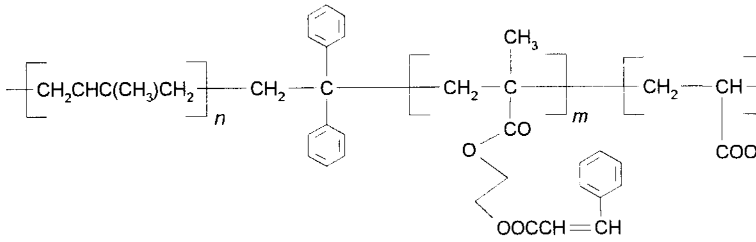
Preparation and Properties of Nanoporous Triblock Copolymer Membranes**

Guojun Liu,* Jianfu Ding, and Sean Stewart

A block copolymer is a linear macromolecule consisting of different monomers in long sequences. $(A)_n(B)_m(C)_l$, for example, denotes a triblock consisting of n units of monomer A, m units of B, and l units of C in sequence. The different blocks of most block copolymers are incompatible. They segregate in bulk, and each block forms domains with a specific shape. At block segregation equilibrium, the domain shape of a given block in a diblock copolymer, the simplest type of block copolymer, is determined by the composition of the diblock, and the domain shape/composition relation is well understood.[1] The morphologies of triblocks are, however, far more complex and less well understood because they are determined by two independent composition variables, the sequence of block linkage and the 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[2, 3] to cylinders,[3–9] dumbbells,[10] and layers.[2, 3, 6] The cylinders can be straight[3–6] or folded into loops[6, 7] or spirals.[7] The cylinders can also be tortuous and interconnected.[8, 9] The domain size of the minor component can be tuned by varying the molar mass of the block and has a very narrow distribution. The domains can be regularly packed. Because of these properties, films of block copolymers are ideal precursors for membranes with nanometer-sized channels or nanochannels. The nanochannels can be produced by full[11, 12] or partial decomposition[13, 14] of the cylindrical domains formed from one of the blocks, as was demonstrated for diblock films.[11–14]

Here we report the first preparation of thin films with nanochannels from a triblock copolymer, polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) or PI-*b*-PCEMA-*b*-P*t*BA **1**. The polymer consists of 3.7×10^2 units of isoprene, 4.2×10^2 units of CEMA, and 5.5×10^2 units of *t*BA. Ten weight portions of this triblock were mixed with one portion of a homopolymer P*t*BA (HP*t*BA) with approximately 1.0×10^2 units of *t*BA. At this mixing ratio, the P*t*BA block of the triblock and HP*t*BA form a seemingly novel continuous phase in the matrix of PI-*b*-PCEMA (Scheme 1). The PCEMA block was crosslinked by UV photolysis. Instead of generating nanochannels by the traditional block degradation method, we prepared membranes more conveniently in this study by extracting HP*t*BA out of the cast films with methylene chloride. Such extracted films had gas-permeability constants roughly 6 orders of magnitude higher than that of low-density polyethylene films. Membranes with even greater gas permeability were obtained by both extracting HP*t*BA and also removing the *tert*-butyl groups from the P*t*BA block by hydrolysis (see Scheme 1).



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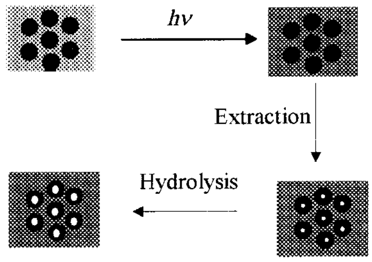

Scheme 1. Strategy for the preparation of nanoporous membranes. P*t*BA/HP*t*BA domains (black circles) do not form hexagonally packed cylinders in the system studied, and the cross-sectional view of hexagonally packed cylinders is shown here for convenience in drawing only. UV irradiation crosslinks the PCEMA domains in the PI-*b*-PCEMA matrix (gray rectangle). Extraction of HP*t*BA out of the P*t*BA/HP*t*BA domains yields membranes with nanochannels (white dots). Larger nanochannels (white circles) are produced by both extracting HP*t*BA and removing the *tert*-butyl groups in the P*t*BA block.

The polymer PI-*b*-P(TMS-HEMA)-*b*-P*t*BA (TMS = trimethylsilyl, HEMA = 2-hydroxyethyl methacrylate), the precursor to triblock **1**, was synthesized by combining procedures we used for the synthesis of PI-*b*-P(TMS-HEMA)[15, 16] and P(TMS-HEMA)-*b*-P*t*BA.[13, 14, 17] The exact reactions are outlined in Scheme 2. Isoprene polymerization was carried out in dry hexane at room temperature for two days with *sec*-butyllithium as the initiator. The other two blocks were

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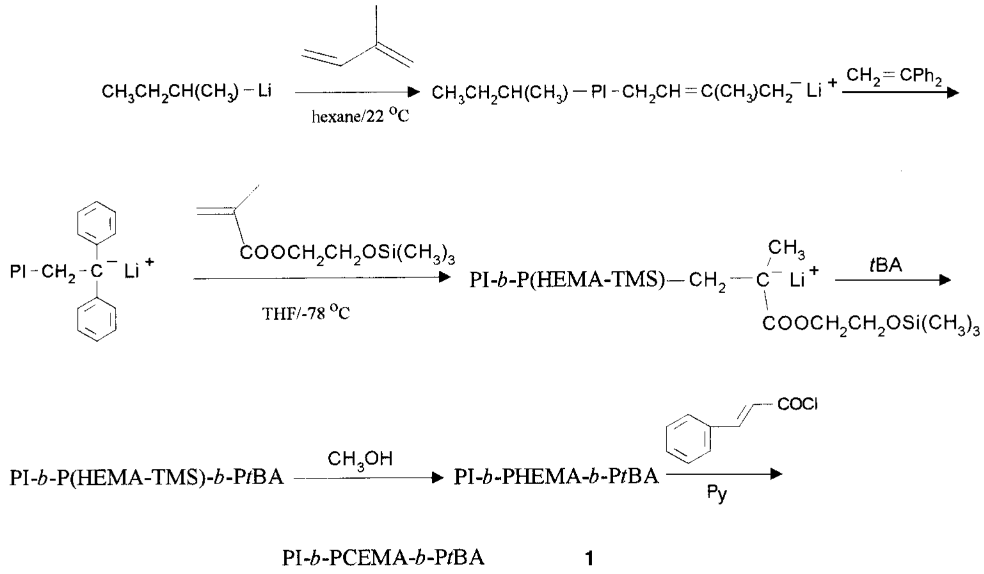


Scheme 2. Preparation of triblock **1**. Py = pyridine.

polymerized in sequence at −78 °C in THF/hexane. The polyisoprene anions were first converted into the sterically more hindered 1,1-diphenylethylene terminal anions to minimize side reactions between the polymer initiator and HEMA-TMS. The TMS groups were hydrolyzed by adding about 20 % methanol to the polymerization mixture to yield PI-*b*-PHEMA-*b*-P*t*BA. The cinnamoyl groups groups were attached by treating PI-*b*-PHEMA-P*t*BA with excess *trans*-cinnamoyl chloride in pyridine. The polydispersity indices of the isoprene block and the triblock were 1.05 and 1.16, respectively. The molar mass of the PI block was 2.5×10^4 g mol^{-1} as determined by light scattering, which yielded an isoprene repeat unit number of 3.7×10^2. The ratio of the isoprene, CEMA, and *t*BA repeat units as determined by NMR spectroscopy was 1.00/1.14/1.49. The CEMA and *t*BA repeat unit numbers are thus 4.2×10^2 and 5.5×10^2, respectively.

Films 20- to 50-μm thick were prepared by casting a solution of triblock **1** and HP*t*BA, 20 % by mass, in toluene on glass slides. The films were dried at room temperature for 2 h and at 70 °C for about 5 h, and were then annealed at 100 °C for 1 d. 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,[18] and P*t*BA[19] are 0.91, 1.25, and 1.00 g cm^{-3}, respectively, the volume fractions of PI, PCEMA, and P*t*BA/HP*t*BA in the triblock **1**/HP*t*BA mixture are 0.13, 0.43, and 0.44, respectively.

For transmission electron microscopic (TEM) studies, a small piece of such a film was embedded in an epoxy resin, and the epoxy resin was cured at 60 °C overnight. Slices, 50-nm thick, were obtained from the embedded film by microtomy. The thin slices were stained with OsO$_4$ vapor overnight before they were viewed under a Hitachi-7000 transmission electron microscope operated at 100 kV.

Figure 1 (top) shows the image of a typical slice cut approximately parallel to the plane of the bulk film. 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 P*t*BA/HP*t*BA domains. The image clearly shows that no macroscopic phase separation occurred for P*t*BA/HP*t*BA. The good mixing between HP*t*BA and the P*t*BA block is expected because the molar mass of HP*t*BA is much lower than that of P*t*BA.[1] The shape of the P*t*BA/HP*t*BA domains seems to change from location to location. The typical shapes of the P*t*BA 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 P*t*BA

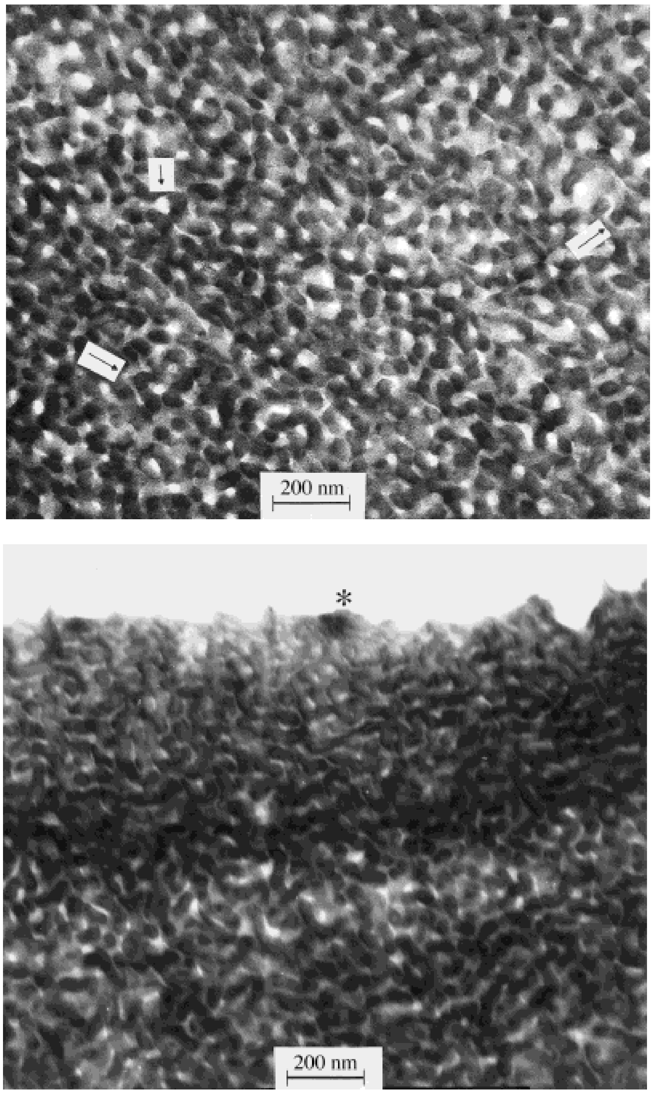


Figure 1. TEM images of 50-nm-thick films of triblock **1**/HP*t*BA stained with OsO$_4$. The thin sections were obtained by microtoming approximately parallel to the film plane (top; several P*t*BA domains are marked with arrows) and at an angle of roughly 30° to the film plane (bottom; air–polymer interface marked with an asterisk).

probably forms interconnected tortuous cylinders in the PI-*b*-PCEMA matrix. The tortuous cylinders may appear different depending on their different orientations relative to the electron beam.

Figure 1 (bottom) displays the image of a slice cut at an approximately 30° angle to the plane of the bulk film. Because of the different microtoming direction, more tortuous light stripes are seen. Also the morphology at the air–polymer interface (marked with an asterisk) seems to be fairly similar 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.[1] While the exact morphology of such a sample remains to be elucidated, the suggested continuity of the P*t*BA/HP*t*BA domain is, however, reasonable for the P*t*BA/HP*t*BA volume fraction of 0.44.

The bulk films were irradiated for 10 min on each side in a UV beam from a 500-W mercury lamp passed through a 310-nm cut-off filter. This caused crosslinking of roughly 40% of the PCEMA double bonds, as verified by FT-IR analysis. HP*t*BA was extracted out of the films by soaking them in CH_2Cl_2 for three days. The solvent was then gradually changed to methanol before the films were collected and dried at room temperature. The fact that the films did not disintegrate in CH_2Cl_2 suggests that PCEMA, at the volume fraction of 0.43, formed a continuous skeleton as well. The removal of HP*t*BA can be qualitatively judged from the fact that the extracted films appeared somewhat cloudy. More conclusive evidence for nanopore formation was obtained from TEM analysis of the microtomed slices of the extracted films.

Figure 2 shows a TEM image of nanochannels generated by both extracting HP*t*BA and removing the *tert*-butyl groups in the P*t*BA/HP*t*BA domains. The bright ovals must represent the 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 Figure 2 are bright tortuous stripes. This might be caused by the particular direction along which microtoming was performed to obtain this particular thin film, because bright tortuous stripes were seen in other images.

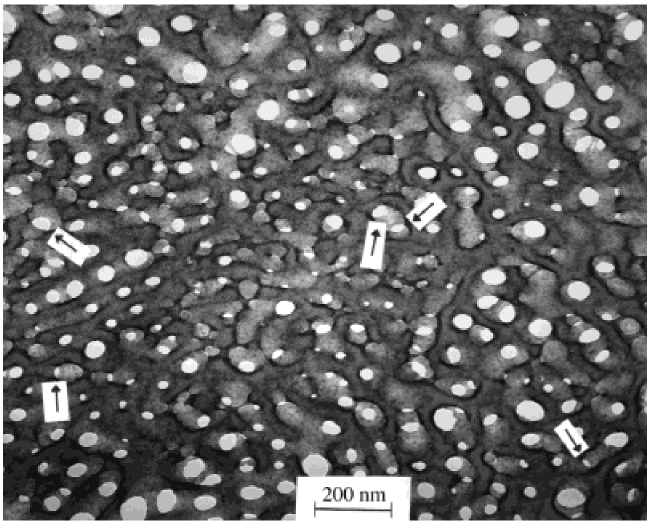
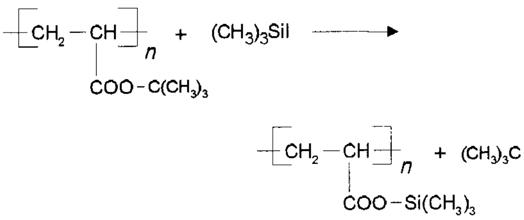


Figure 2. TEM image of a 50-nm-thick film of triblock **1**/HP*t*BA after extraction of HP*t*BA and removal of the *tert*-butyl groups. The sample was not stained. The bright circles must represent holes where polymer density is close to zero. Several tortuous channels are marked with arrows.

The simultaneous removal of HP*t*BA and the *tert*-butyl groups of the P*t*BA block was achieved by soaking the films in 0.10 M $(CH_3)_3SiI$ solution in dichloromethane for two weeks. The *tert*-butyl esters were transformed into TMS esters [Eq. (1)]. The TMS groups were then removed in methanol/water (95/5), yielding chains of poly(acrylic acid) (PAA) in the nanochannels.[13, 14] The quantitative cleavage of the *tert*-butyl groups was confirmed by comparing the FT-IR spectra of the films before and after the hydrolysis step.



$$-[CH_2-CH(COO-C(CH_3)_3)]_n- + (CH_3)_3SiI \longrightarrow -[CH_2-CH(COO-Si(CH_3)_3)]_n- + (CH_3)_3C{-}I \quad (1)$$

To test the gas permeability of this material, a membrane, typically 25- to 50-μm thick, was sandwiched at the interface between the arms of a U-tube. A gas pressure drop (Δp) of $\sim 1.96 \times 10^3$ Pa was applied across the membrane. After the thickness (l) and area (A) of the membrane and the gas permeation rate (F) had been determined (Table 1), Equation (2) was used to evaluate the gas-permeability constant (P). Plotted in Figure 3 are the variations in P as a function of the square root of the molar masses (M) of different gases for

$$P = \frac{F\,l}{A\Delta p} \quad (2)$$

the membranes from which HP*t*BA and both HP*t*BA and *tert*-butyl groups had been removed. The gas-permeability constants are on the order of 10^{-7} cm^{2}s^{-1}cm^{-1}Pa^{-1}, which is about 6 orders of magnitude higher than those found for low-density polyethylene.[20] The high gas permeability confirms the highly porous nature of the films.

Table 1. Permeation rates F [cm^{3}s^{-1}] of different gases across the two types of membranes measured at 22 °C.

H_2	N_2	O_2	Ar	CO_2
Membrane without HP*t*BA, $A = 0.071$ cm^2, $l = 2.0 \times 10^{-3}$ cm				
0.0350	0.0125	0.0112	0.0093	0.0076
Membrane without *tert*-butyl groups, $A = 0.049$ cm^2, $l = 2.5 \times 10^{-3}$ cm				
0.0248	0.0123	0.0111	0.0082	0.0135

We also tested water permeability across such membranes by filling the 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 HP*t*BA-free membranes was understandable, because the channels are hydrophobic and cannot be easily wetted by water. The lack of water permeability across the membranes without *tert*-butyl groups was more surprising, because the nanochannels with PAA chains are

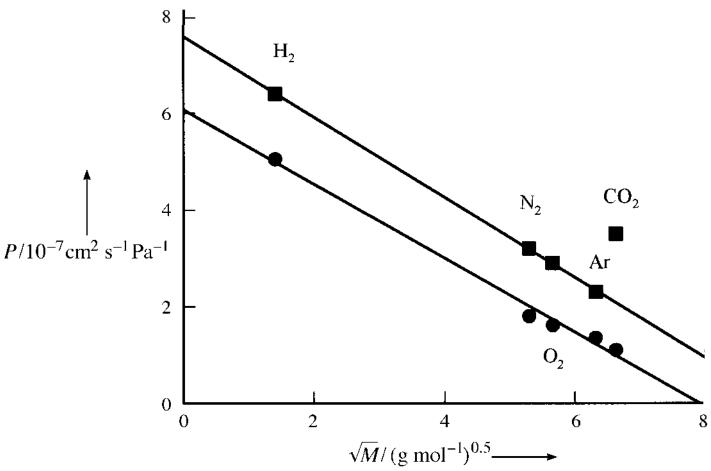


Figure 3. Plot of the permeability constants (P) of different gases across membranes from which HP*t*BA (●) and *tert*-butyl groups (■) have been removed as a function of the square root of the molar masses of the gases.

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. Such grain boundaries may be very narrow. While gas molecules can permeate through such boundaries with ease, water flow would be stopped there. This model is supported by the observation of water permeability across thinner films without *tert*-butyl groups, for instance 2-μm thick, obtained by microtoming a 50-μm-thick film.

The gas-permeability constants are higher for the membranes without *tert*-butyl groups. This is reasonable, because the channels and the pore volume fraction are supposed to be larger here owing to the removal of *tert*-butyl groups of the P*t*BA block. The linear decrease of P with increasing $\sqrt{M}$ indicates that the gas molecules permeate through the nanochannels due to Knudsen flow[21] and that the gas molecules have no specific interactions with the channel walls. The only exception to this is the permeation of CO_2 across these membranes. This abnormality is reproducible and suggests some specific interactions between the nanochannel walls and CO_2. The membranes without *tert*-butyl groups were not gas permeable immediately after their preparation. They became gas permeable after they were soaked in 0.10 M NaOH solution, rinsed in water, and dried. The treatment with base converts PAA to poly(sodium acrylate), and the electrostatic force between the different polyelectrolyte chains presumably pushes the channels open. While the exact mechanism for this specific interaction is not known, it must be between CO_2 and poly(sodium acrylate).

In summary, we have discovered a seemingly new morphology for triblock copolymers. A convenient method was demonstrated for preparing membranes that are gas- but not liquid-permeable. Such membranes may be permeable to water vapor as well and thus should behave similarly to Gore-Tex films, which reject liquid water because the channels cannot be wetted by water. The membranes without *tert*-butyl groups reject water probably due to channel discontinuity at grain boundaries. The methods proposed for membrane preparation are general and should be useful in many other systems. A detailed study aimed at examining the effect of varying the nanochannel size on gas permeability is under way.

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