Cross-Linked Polymer Brushes. II. Formation and Properties of Poly(isobutyl vinyl ether)-*b*-Poly[2-(vinyloxy)ethyl cinnamate] Brushes

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SYNOPSIS

A diblock copolymer, i.e., poly(isobutyl vinyl ether)-*b*-poly[2-(vinyloxy)ethyl cinnamate] (PIBVE-*b*-PVEC), has been shown to form polymer brushes quickly on the surface of solid substrates by deposition from a solvent selectively poor for PVEC. The resultant brush could be cross-linked photochemically by initiating the dimerization between VEC groups of different polymer chains and the cross-linking was extremely efficient. Cross-linked polymer brushes, as expected, were resistant to organic solvent, such as chloroform, and nitric acid attacks. Important industrial applications are expected of cross-linked brushes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A diblock copolymer, i.e., $(A)_n-(B)_m$, can deposit spontaneously from a block-selective solvent onto a solid substrate to form a self-assembled polymeric monolayer called a polymer brush.[1-4] Polymer brushes play an important role in the stabilization of surfactant particles[5-7] and in the modification of surface properties of solid objects.[8,9]

In the first article in this series,[10] we discussed the feasibility of fixing polymer brushes on a solid substrate by cross-linking the anchoring block of a brush and proposed some applications for cross-linked brushes. Among those, a cross-linked brush on the inner wall of a capillary column may function as the stationary phase for capillary gas chromatography. Silica gel particles coated with cross-linked polymer brushes may be used as reverse-phase HPLC column packing.

We then reported the design and synthesis of a photo-cross-linkable diblock copolymer, i.e., poly(isobutyl vinyl ether)-*b*-poly[2-(vinyloxy)ethyl cinnamate] (PIBVE-*b*-PVEC):
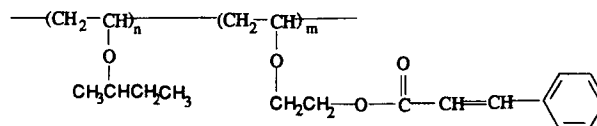
To produce a cross-linked polymer brush from such a polymer, two essential steps, i.e., brush formation and cross-linking, should be invoked. In this article, we examine, from an application point of view, the efficiency of those steps. Also examined is the stability of cross-linked PIBVE-*b*-PVEC brushes against chloroform and nitric acid attacks.

The kinetics of brush formation, i.e., diblock copolymer adsorption on a solid substrate from a coating solution, has been previously studied by techniques such as scintillation counting,[11-13] X-ray photoelectron spectroscopy,[11,12] surface plasmon spectroscopy,[14] and internal reflection interferometry.[11,15] The use of those techniques provides information about the amount of polymers adsorbed over a time period. Since such instruments were not of easy access to us and also our intention at this stage was to assess the feasibility of commercializing such processes for glass or silica surface property modification, the kinetics of polymer brush formation was thus carried out by monitoring the interfacial tension change of a dried coated glass plate or silica capillary tube as a function of its soaking time in a polymer coating solution. These results

provide a guideline as to how a coating experiment should be done for surface property modification of glass or silica. They, however, do not indicate the rate of polymer deposition in terms of the amount of polymers absorbed in unit time.

The interfacial tension measurement method has been widely used for characterizing the rate of monolayer formation from small surfactant molecules such as stearic acid.[16,17] It has also been used for studying the layered structure of polymer brushes.[15] Ruckenstein and co-workers used the method to follow the restructuring of a polymeric surface in contact with a hydrophobic or hydrophilic liquid[18] and to verify that a deposited block copolymer was not extracted during long exposures to an aqueous medium.[19]

The kinetics of the PVEC double-bond disappearance due to cross-linking on quartz or glass plates could, in principle, be monitored using techniques such as surface-enhanced Raman spectroscopy,[20] attenuated total reflection spectroscopy,[16] or grazing angle spectroscopy.[16] As far as industrial applications are concerned, we need only to determine the minimal radiation dosage required for producing a solvent-resistant brush. For this purpose, we coated a series of glass plates and irradiated them for different periods of times. The irradiated plates were then soaked in chloroform, a good solvent for both blocks. A not well cross-linked brush will dissolve in chloroform. Upon drying, the water contact angle on such a plate will decrease. From the change in water contact angles on irradiated and chloroform-treated glass plates, we can determine the minimal dosage required for producing an insoluble brush.

EXPERIMENTAL

GPC Molar Mass Determination

The determination of GPC molar masses of polymers were carried out in ethyl acetate on a Varian Model 5000 HPLC instrument using Styragel HR 4 (Waters) and Zorbax PSM 60-S (Chromatography Specialties) columns in series. The columns were calibrated with polystyrene standards (PolySciences). Due to the use of polystyrene standards, the determined molar masses may be in error.

Materials

Two polymers were mainly used for solid substrate coating. One of the polymers (Polymer I) was synthesized by polymerizing VEC first, using CF_3COOH and $ZnCl_2$ as the initiator at 0°C in toluene for 25 h, and then IBVE using living PVEC cations for another 15 h.[10] The other sample (Polymer II) was prepared by polymerizing IBVE first, using 1-(isobutoxy)ethyl acetate and $EtAlCl_2$ as the initiator, and then VEC using living cations of PIBVE.[10] The characterization results of the two polymers are summarized in Table I.

As discussed before,[10] $ZnCl_2$ is a weaker Lewis acid than $EtAlCl_2$ and cannot react with impurities in VEC to polymerize VEC. Polymer I was, thus, strictly a diblock copolymer with a negligible amount of homopolymers either in the form of PIBVE or PVEC. The numbers of repeat units m and n of VEC and IBVE in this polymer as determined by GPC approached those calculated using [VEC]/[CF_3COOH] and [IBVE]/[CF_3COOH] ratios. Polymer II, unfortunately, had a small amount of PVEC homopolymer, because impurities in VEC reacted with $EtAlCl_2$ to polymerize VEC after its addition.[10] This small amount of PVEC impurity showed up as a shoulder peak overlapping with the PIBVE-b-PVEC peak. In evaluating the GPC $\bar{M}_n$ value of the diblock copolymer, the shoulder peak from the PVEC homopolymer was not excluded, which largely accounts for the apparently low GPC $\bar{M}_n$ for the diblock copolymer as shown in Table I.

The n/m ratio determined from GPC $\bar{M}_n$ values for Polymer II was significantly larger than that determined from ratioing the ^{1}H-NMR peaks of PVEC

Table I Characteristics of Diblock Copolymers Used for Solid Substrate Coating

Sample	Molar Masses of the First Block ($\times 10^4$ g/Mol)			Molar Masses of Block Copolymer ($\times 10^4$ g/Mol)			$\left(\dfrac{n}{m}\right)^a$ Determined from	
	$\bar{M}_p$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_p$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	GPC	NMR
Polymer I	3.9	3.1	1.18	4.8	3.5	1.20	0.35	0.29
Polymer II	1.30	1.06	1.05	3.3	2.3	1.35	1.82	1.00

^{a} The ratio of the number of repeat units of IBVE to that of VEC.

to PIBVE. This is so partially because the GPC $\bar{M}_n$ value of the diblock copolymer is in error and the m value calculated using

$$m = \frac{\bar{M}_n(\text{diblock}) - \bar{M}_n(\text{PIPVE})}{218} \quad (1)$$

is erroneously small, where 218 g/mol is the molar mass of VEC. The other reason is that the n/m value determined from NMR peak ratioing can be erroneously small, because the peak intensity of PVEC contains contributions both from homopolymer PVEC and from the PVEC block in the diblock copolymer. The true n/m value for the diblock copolymer should be between 1.82 and 1.00. The n/m value calculated from the peak molar masses, Mp, of PIBVE and the diblock copolymer using eq. (1) is 1.43, which may be very close to the real value.

Other polymers used in this study were synthesized using a procedure similar to that for Polymer I synthesis.[10] Their characteristics are given in Table II.

Preparation of Polymer Coating Solutions

A polymer coating solution was prepared by first dissolving a diblock copolymer in ethyl acetate, a good solvent for both the PIBVE and PVEC blocks. Hexanes, a poor solvent for the PVEC block, was then added to the solution dropwise to turn it just cloudy. All final coating solutions were controlled at a concentration $\sim$ 20 g/L. The mixture was filtered through a 0.45 μm hydrophobic filter (Millipore) before being used for coating.

Coating Glass Slides

Microscope glass slides were boiled in concentrated nitric acid for 3 h, rinsed with distilled water, and vacuum-dried. They were coated by immersing in a polymer coating solution to allow the deposition of a self-assembled polymeric monolayer on their surface. After a period of time, the glass slide was removed and rinsed for $\sim$ 20 s in a solvent mixture consisting of the same ratio of ethyl acetate/hexanes as used in preparing the coating solution. Coated slides were then dried *in vacuo* for 2 h before any interfacial tension measurement or cross-linking reactions were carried out.

Coating Capillary Tubes

Undeactivated fused-silica capillary tubes with internal diameters of either 0.32 or 0.25 mm (Chromatography Specialties) were burned using a low-

Table II   Characteristics of Polymers Used for Constructing Figure 1

| | Molar Masses ($\times 10^4$ g/Mol) | | | $\left(\dfrac{n}{m}\right)^a$ Determined from |
| | | | | |
Sample	$\bar{M}_p$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	NMR
III	2.11	1.81	1.16	0.51
IV	2.12	1.50	1.22	1.32
V	4.20	3.55	1.13	2.33
VI	2.94	2.49	1.15	3.85
VII	2.94	2.33	1.21	5.56

^{a} The ratio of the number of repeat units of IBVE to that of VEC.

temperature flame to strip off the polyimide protective coating on their outside wall. The inner wall (also the outer wall) of a capillary tube was then coated by immersing it in a polymer coating solution for a certain period of time. Coated capillary tubes were rinsed by filling them with solvent and emptying them three to four times.

Cross-linking Polymer Brushes

Polymer brushes on microscope slides and capillary walls were cross-linked using a UV beam passing through a 260 nm cutoff filter from a 1000 W mercury lamp (Oriel Corp.).

Water Contact Angle θ Measurement

The contact angle θ of distilled water on a coated or uncoated glass plate was determined using a customer-built liquid-tight cylindrical cell, ca. 4.0 cm in inner diameter and ca. 8.0 cm in length. At the two ends of the cell are two mountable glass windows. Inside the cell is a support for a glass plate. Distilled water can be dispensed onto a glass plate, fixed by the support, through a syringe needle that reaches in through penetrating a silicone rubber septum mounted on the top wall of the cylindrical cell. For the θ measurement, a small amount of water was first added to the cell. Placed against the wall were some wetted filter papers to maintain a saturated water-vapor pressure inside the cell. A glass plate was then mounted on the support. A fixed aliquot, ca. 0.02 mL, of water was dispensed onto the glass plate using the syringe and 5 or 15 min were allowed for the water drop to reach equilibrium with its surroundings. By then, a picture was taken of the droplet. The shape of the droplet was approxi-

mated as a spherical cap. The value of θ was calculated using the determined height and width using required geometric relations.[21]

Water Rising Level in a Capillary Tube

The bottom of a small beaker was covered with a thin layer ($\sim$ 0.1 mm) of distilled water. Capillary tubes were then placed in to stand vertically against the beaker wall for either 1 min or a sufficiently long period of time so that equilibrium water rising level had been reached. The water column length was read by placing a capillary against a ruler. Due to the thinness of the water layer in the beaker, the water column length in a capillary was taken as the water rising level without subtracting the height of water in the beaker.

RESULTS AND DISCUSSION

Polymer Coating Solutions

A polymer coating solution was prepared by adding enough hexanes, a selective solvent for PIBVE, to an ethyl acetate solution of a diblock copolymer to turn it just cloudy. At this solvent composition, we believe that the polymer is very close to its critical micellar concentration (cmc). In such a solution, most polymer chains exist as unimers,[3] i.e., single chain micelles in which the poorly solvated PVEC block clusters together and the soluble PIBVE block assumes random-coil conformation.

Preparing a coating solution this way has two advantages: One is that the solvent composition can be controlled so that the solution is always close to or below the polymer's cmc. A solution above the polymer's cmc is not suitable for coating, because polymeric micelles have been found to deposit on surfaces above cmc.[11–15] The incorporation of micelles into a polymer brush disrupts the monolayer feature and thus affects the quality of a polymer film. However, the content of the block-selective solvent, i.e., hexanes in this case, in a polymer coating solution should be as high as possible. This ensures that the quality of the solvent mixture is sufficiently poor for the anchoring block so that enough driving force is provided for the diblock copolymer to deposit out from a solution to form a polymer brush.

The other advantage of using a solvent mixture for preparing a coating solution is that the cmc of a polymer can be made artificially high by adding less block-selective solvent. A concentrated solution, still close to the polymer's cmc, for coating is ad-

vantageous, because previous kinetic studies have demonstrated that the rate of polymer adsorption increases with polymer concentration.[11–15] Also, the equilibrium surface covering density increases with the polymer solution concentration. In our experiment, the coating solution was controlled at $\sim$ 20 g/L.

The disadvantage of using a solvent mixture is that the property of a solvent mixture is sometimes difficult to predict. A classical example is that both ethanol and water are poor solvents for poly(methyl methacrylate) (PMMA). A 10/90 v/v mixture of water/ethanol, however, dissolves PMMA.[22] This abnormality obviously does not occur here according to our data on the amount of hexanes required to turn a PIBVE-b-PVEC ethyl acetate solution just cloudy. We have prepared ethyl acetate solutions of a series of PIBVE-b-PVEC samples with different IBVE to VEC molar ratios; the amount of hexanes required to turn a solution just cloudy increases as the [IBVE]/[VEC] ratio increases, where IBVE is the soluble block. This trend is shown in Figure 1. The characteristics of the polymers used for constructing this figure are shown in Tables I and II with the exception of a PVEC homopolymer, of which the GPC $\bar{M}_n$ is 1.78×10^4 g/mol, and the polydispersity, 1.13. For obtaining the data, the initial concentrations of the polymers were so controlled that at the cloudy point the polymer concentrations were always $\sim$ 20 g/L.

Incompatibility of the PIBVE and PVEC Blocks

For polymer brush formation, the two blocks of a diblock copolymer should be incompatible. This is obviously the case for the polymer studied. Dissolving PIBVE and PVEC homopolymers in ethyl ac-
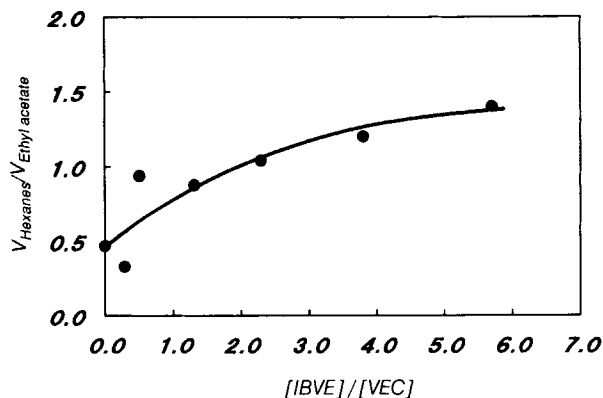
Figure 1 Plot of the cloudy-point solvent composition $V_{hexanes}/V_{Ethyl\ acetate}$ vs. the composition [IBVE]/[VEC] of diblock copolymers PIBVE-b-PVEC.

etate followed by solvent evaporation led to phase-separated cloudy films.

Monolayer Films Due to Brush Formation

Polymer brush formation is a well-documented phenomenon and has been studied extensively both theoretically and experimentally. Many diblock copolymers have been shown to form brushes. The layered structure of polymer brushes, i.e., the insoluble block anchors on the solid substrate and the soluble block tops the insoluble block, has been verified using techniques such as X-ray photoelectron spectroscopy,[23] surface-enhanced Raman spectroscopy,[20] and interfacial tension measurement.[15] Our diblock copolymer, without exception, should form brushes under the experimental conditions employed.

Interfacial tension measurement has clearly indicated the existence of a polymer layer on either the wall of a capillary or the surface of a glass microscope slide after our coating procedure. The question is whether this layer is indeed due to brush formation or due to polymer left on a surface upon solvent evaporation. To differentiate, we coated five capillaries using Polymer **II** by immersing them in our coating solution for 1 h. The capillaries were then rinsed with the solvent mixture used for preparing the coating solution. The rinsing was done by filling a capillary with the solvent and then emptying it by contacting the tip of the capillary with a kimwipe. The procedure was repeated two, four, six, eight, and ten times for five capillaries, respectively. Regardless of the number of times the capillaries were rinsed, after drying, a reproducible water rising level, i.e., $\sim$ 0.2 mm, was obtained within experimental error for all capillaries. On the other hand, if the experiment was done by making use of a coating solution prepared from a PIBVE homopolymer, the water rising level in the dried capillary tubes was found to increase with rinsing times. The comparison between the two cases is illustrated in Table III. The film obtained from diblock copolymer adsorption is resistant to washing.

This is a feature expected of a polymer brush. Polymer brushes form because the insoluble block wants to minimize its contact with the solvent and this process is thermodynamically favored. Desorption, the reverse of the thermodynamically favored adsorption process, should have a relatively high activation energy barrier and thus be slower. This has been shown to be true from more sophisticated theoretic analyses[3,24,25] and the "washing time" for brushes can be as long as 5.5×10^7 s, depending on the binding energy between the surface and the an-

Table III   Comparison of the Effect of Solvent Rinsing of Capillaries Coated by Immersion in Polymer II and PIBVE Coating Solutions[a]

Times Rinsed	Water Rising Level[a] (mm)	
	PIBVE-*b*-PVEC	PIBVE
2	0.2	0.9
4	0.3	48.5
6	0.3	55.8
8	0.2	58.5
10	0.2	52.5

[a] The water rising height in an uncoated capillary was 85 mm.

choring block as well as on the molar mass of the soluble block.

The next concern is directed to the use of Polymer **II** in performing the coating experiments. This polymer contains PVEC impurities and was used because we did not have better polymers when the experiments were performed. The homopolymer PVEC in Polymer **II** might preferentially adsorb onto a solid surface relative to PIBVE-*b*-PVEC and the resultant polymer film on a solid substrate might consist mainly of PVEC. To examine the extent of interference from PVEC on the coating results, we prepared a critical or a just cloudy solution of pure PVEC (GPC $\bar{M}_n = 1.78 \times 10^4$ g/mol) at a concentration $\sim$ 20 g/L by adding hexanes to its ethyl acetate solution. Glass plates were then coated by immersing them in such a PVEC solution overnight. Without rinsing after the withdrawal of a glass plate from this coating solution, θ, determined after plate drying, was 65 ± 3 degrees. Rinsing a plate, after its withdrawal from the coating solution, in a hexane/ethyl acetate solvent mixture used for preparing the PVEC coating solution for 20 s reduced the θ value to $39°$, which is the same as the θ value on an uncoated glass plate. Since θ on a plate coated with Polymer **II** was much larger, i.e., $80° \pm 3°$, and was unchanged by a short time rinsing of the plate in a solvent mixture, the effect of the PVEC impurity on properties of Polymer **II** films, if there is any, should be small.

Layered Structure of PIBVE-*b*-PVEC Brushes

Since PIBVE-*b*-PVEC deposits out from a solvent that is selectively poor for the PVEC block, the anchoring block should be PVEC and the top layer, i.e., the layer exposed to the solvent and later to the atmosphere in the dried state, should consist mainly

of PIBVE. This structure has been confirmed by results of interfacial tension measurement. We spin-coated quartz disks with homopolymers PIBVE and PVEC. The water contact angle measured on PIBVE films was 87° ± 3°, whereas that on PVEC films was 76° ± 3°. The θ averaged from 14 runs on films formed from Polymer I was 84° ± 3°, which is, within experimental error, the same as the water contact angle for PIBVE films.

The average θ on polymer brushes prepared from Polymer II was 80° ± 3°, which was 4° smaller than that on Polymer I brushes. This discrepancy was due to different conditions used for θ measurement. The θ on Polymer II brushes were determined 15 min after water droplets were dispensed on them, whereas the θ on Polymer I brushes or on homopolymer PVEC or PIBVE films were determined 5 min after water droplets were dispensed on them. That the contact angle of a liquid droplet on a solid substrate decreases with time has been well documented[21] and our experimental results have also confirmed this.

Rate of Brush Formation

We used the change in the interfacial tension of a solid substrate and water as an indication of the rate of brush formation. The change in θ with plate coating time in Polymers I and II solutions is illustrated in Figure 2. The rapid increase in the water contact angle from 39° to 77° after soaking a glass plate in a Polymer II solution for 10 min suggests that polymer brush formation was fast and could be used as a method for modifying surface properties of a solid substrate from an industrial viewpoint.
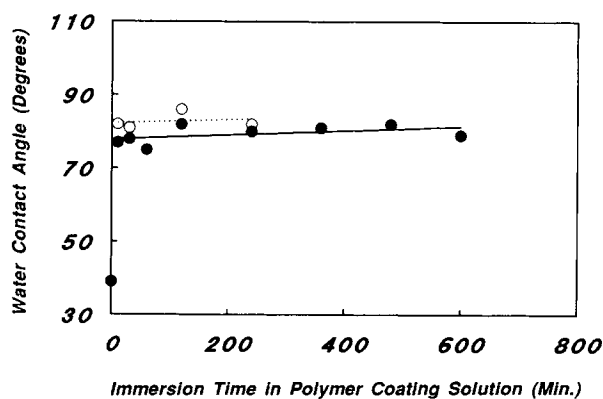
Figure 2 Plot of the change in water contact angles on coated and dried glass plates as a function of their soaking time in polymer coating solutions: results for glass plates coated with (○) Polymer I and (●) Polymer II.
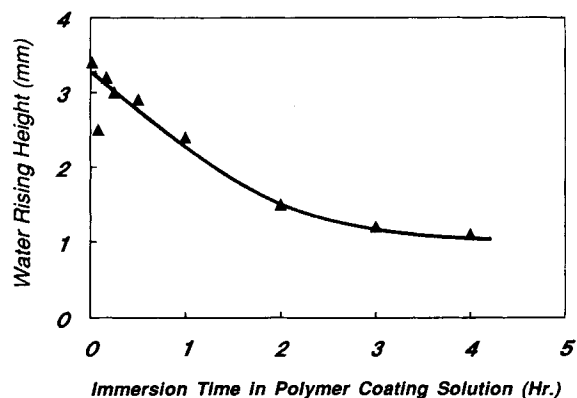
Figure 3 Plot of the change in water rising heights in coated and dried capillary tubes as a function of their soaking time in a Polymer II coating solution. The inner diameter of the capillary was 0.32 mm and the water rising height in the uncoated capillary was 58 mm. Reported water rising heights are the equilibrium values.

Within experimental error, the θ values did not increase with glass plate immersion time t in a coating solution if t was larger than 10 min. Thus, the water contact angle measurement results suggest that the adsorption equilibrium of diblock copolymers was established very quickly. This conclusion seems to contradict the theoretical predictions.[22,23] According to different theories, brush formation occurs in two stages: In the initial stage, the surface is relatively clean of adsorbed chains and unimers deposit at a diffusion-controlled rate. In this stage, the adsorbed chains are away from one another and each adsorbed chain exists as an "island." The process is fast (finished in fractions of a second) and finishes when adsorbed chains begin to overlap. In the second stage, adsorbed polymer chains begin to overlap and the structure of a brush appears. New chains now need to penetrate the brush formed by already-adsorbed chains to be incorporated and the process of reaching the equilibrium surface-covering density is slow.

This apparent contradiction can be explained by the insensitivity of this technique to minor changes in surface-covering densities. We coated capillaries using Polymer II. The water rising level in such capillaries, after rinsing and drying, as a function of their soaking time is illustrated in Figure 3. The soaking of a capillary in a Polymer II solution for 1 min reduced the water rising height from 58 to 3.4 mm. This fast decrease in the water rising level was then followed by a slower decrease in the water rising height as a function of their immersion time, as expected from theoretical predictions.[24,25] The capillary experimental results suggest that an immersion time
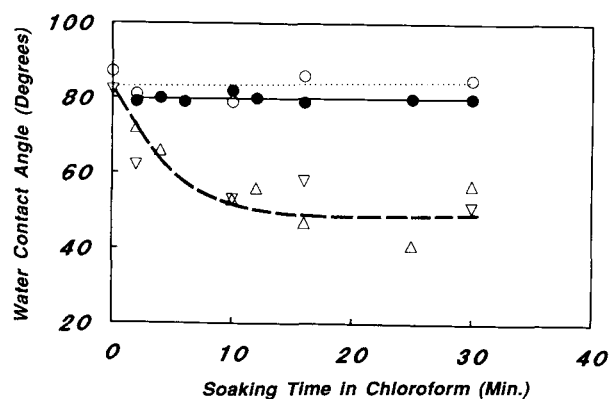
of 3 h is required for the establishment of the ad-
sorption equilibrium.

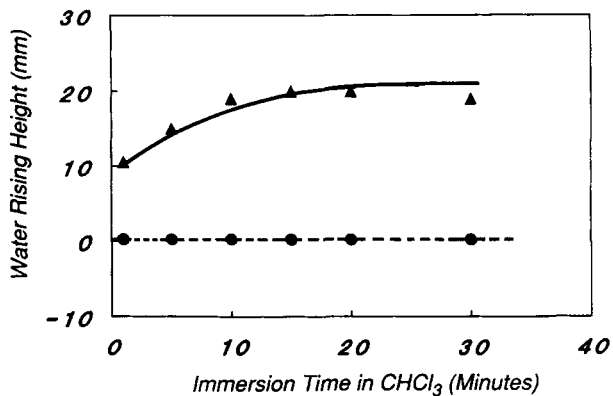## Chloroform Resistance of Photocured Polymer Brushes

The major anticipated advantage to cross-linked
polymer brushes is that they should withstand sol-
vent attacks. To test that, glass plates or capillaries
were coated with Polymers **I** and **II**. Those plates
or capillaries were then divided into two groups: ir-
radiated and nonirradiated. Soaking the radiated
plates or capillaries in chloroform did not change
the θ or water rising heights at all, as shown in Fig-
ures 4 and 5. Soaking the nonirradiated plates and
capillaries in chloroform did reduce θ and raise the
water rising heights. Since a gradual decrease in θ
or increase in the water rising height indicates the
gradual removal of polymers from a substrate, we
thus conclude that non-cross-linked brushes are
removed by chloroform and the cross-linked ones
are not.

Efficiency of Photo-cross-linking

Not highly cross-linked films can be removed by
chloroform. How efficiently PIBVE-*b*-PVEC cross-
links on a glass substrate was tested by measuring
the contact angles of water on coated glass plates
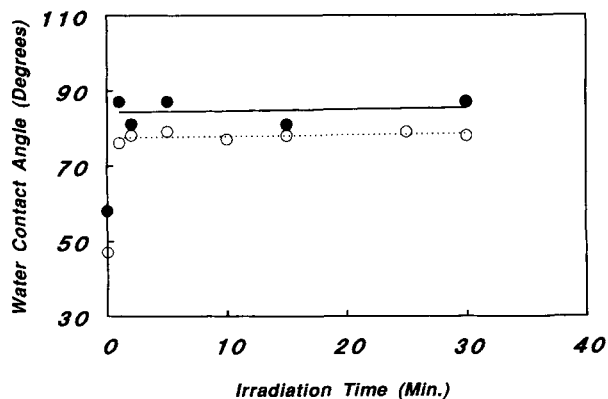that have been irradiated for different periods of

Figure 5 Plot of the change in water rising heights in
coated capillary tubes as a function of their soaking time
in chloroform. The capillary tubes were coated by soaking
them in a Polymer **II** coating solution for 4 h. Cross-linking
was achieved by irradiating the capillaries on one side for
15 min, rotating them by 180°, and then irradiating for
another 15 min. The water rising heights were recorded
1 min after the tips of capillaries were inserted into water.
The cross-linked polymer brushes (●) showed no sign of
polymer dissolution.

time and then soaked in CHCl$_3$ for 15 min. Results
of Figure 6 indicate that the cross-linking is highly
efficient, because 1 min of radiation is sufficient for
producing an insoluble film. The high cross-linking
efficiency also suggests that chains of the PVEC
block interpenetrate with one another and the sur-
face covering density is high.

Figure 4 Plot of the change in water contact angles of
coated glass plates as a function of their soaking time in
chloroform. Polymer **I** brushes, (○) cross-linked and (▽)
non-cross-linked, were prepared by soaking the glass plates
in a coating solution for 4 h. Polymer **II** brushes, (●)
cross-linked and (△) uncross-linked, were prepared by
soaking the glass plates in a coating solution for 2 h. The
cross-linking was achieved by irradiating coated glass
plates for 0.5 h.

Figure 6 Plot of the change in water contact angles of
chloroform-treated glass plates as a function of their ir-
radiation time. (○) Polymer **I** brushes were obtained by
immersing the glass plates in a Polymer **I** coating solution
for 4 h. (●) Polymer **II** brushes were obtained by im-
mersing the glass plates in a Polymer **II** coating solution
for 2 h. After UV irradiation, all plates were soaked in
chloroform for 15 min.

Nitric Acid Resistance of Photocured Brushes

Photocured and noncured PIBVE-b-PVEC brushes were tested for their resistance to 5% (w/w) nitric acid. Nitric acid does not dissolve the block copolymer. Upon reaching the glass and polymer interface, nitric acid may cause film delamination. A partially delaminated film looked cloudy at the delamination points, because after the removal of nitric acid by evacuation, air voids were left at those spots and the air voids scattered light. Thus, the measurement of the change in the light transmission efficiency of an acid-soaked film may allow the monitoring of the delamination process. Also, it was hoped that film delamination might cause the interfacial tension of water and a coated glass substrate to change and thus allow an alternative method for monitoring the delamination process.

Results of the water contact angle measurement for glass plates coated with cross-linked Polymer **II** brushes are shown in Figure 7. The θ values were unaffected by the immersion of the glass plates in the acid. This was also confirmed by the unchanged light transmission efficiency of these glass plates with their soaking time in nitric acid. On the other hand, the immersion of glass plates coated with non-cross-linked polymer brushes in nitric acid for ca. 20 min caused certain areas, ca. 10% of the total area, of a glass plate to turn cloudy. Due to the non-uniform distribution of the cloudy domains, accurate determination of the light transmission efficiency of those plates was difficult, so was the θ measurement. For a given sample, the contact angle measured depended on the region in which the water drop was
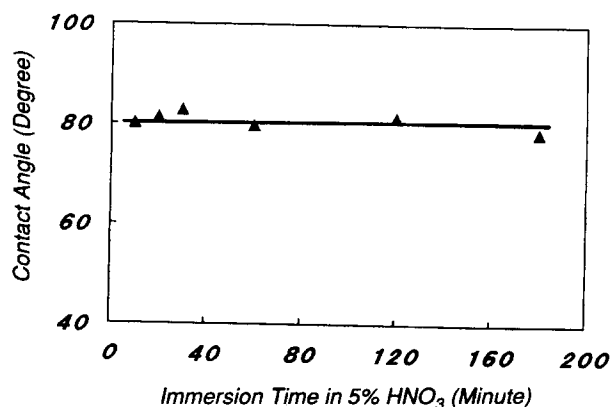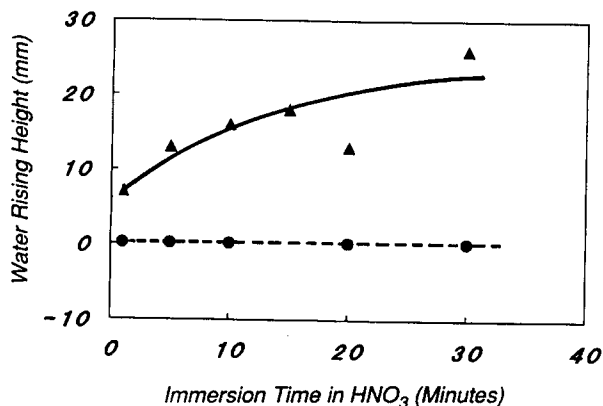
Figure 8 Plot of the change in water rising heights of coated capillary tubes as a function of their soaking time in 5% nitric acid. Although (●) cross-linked films were not delaminated by the acid treatment and the water rising height remains constant, film delamination occurred with non-cross-linked films.

dispensed. For the glass plate that was immersed in nitric acid for 2 h, the contact angle measured varied, e.g., from 56° to 77° in four measurements. The light transmission efficiency of the glass plate at 595 nm varied from 81.2 to 88.6% in four measurements, again depending on where on the plate the measurement was carried out.

In Figure 8 are shown the results of nitric acid-resistance experiments performed using capillaries. Although soaking capillary tubes coated with cross-linked films in nitric acid did not lead to any change in the water-rising level, soaking those coated with non-cross-linked films caused the water rising level to increase gradually, an indication of film delamination.

CONCLUSIONS

A diblock copolymer, i.e., poly(isobutyl vinyl ether)-b-poly[2-(vinyloxy)ethyl cinnamate] (PIBVE-b-PVEC), was shown to form polymer brushes on the surface of glass and silica by deposition from a hexane/ethyl acetate mixture. The layered structure of polymer brushes has been verified by water contact angle measurement. The process of brush formation has been shown to be fast and only a 10 min soaking was required of a solid substrate in a polymer coating solution to change its surface properties completely. The resultant brush could be cross-linked photochemically by initiating the dimerization between VEC groups of different polymer chains and the cross-linking reaction was extremely efficient. Cross-

Figure 7 Plot of the change in water contact angle of glass plates coated with cross-linked polymer brushes as a function of their soaking time in 5% nitric acid. The plates were coated by soaking in a Polymer **II** coating solution for 2 h and cross-linked by irradiating for 30 min.

linked polymer brushes, as expected, were resistant to organic solvent, such as chloroform, and nitric acid attacks. Important industrial applications one expected of cross-linked brushes.

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