

Generation of Porous Polymer Surfaces by Solvent–Nonsolvent Treatment

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SYNOPSIS

A method to generate a porous region near the surface of a polymer is suggested. In this method the region near the surface is swollen by immersing the polymer for a short time in a solvent. Subsequently, the polymer is introduced in a nonsolvent (for the polymer) that is, however, miscible with the solvent. The formation of the porous region is a result of (1) the swelling accompanied by the disentanglement of the surface molecular chains, and the dissolution of some of them during the immersion in the solvent, and (2) the rapid extraction of the solvent from the swollen region by the nonsolvent. The porous surface provides a matrix into which a second incompatible monomer can be polymerized so that the two otherwise incompatible polymers can adhere to one another.

INTRODUCTION

Unlike other solid surfaces, the polymeric surface rearranges when its environment changes, by exposing additional polar moieties to a hydrophilic environment and nonpolar moieties to a hydrophobic environment.^{1–4} The rearrangement occurs in order to reduce the interfacial free energy between the polymer surface and its environment. As shown in previous experiments⁵ carried out with polyurethane, the kinetics of surface rearrangement can be accelerated by using a suitable solvent treatment before the substrate is immersed in water. When an amorphous polymer is treated with a solvent, the solvent softens, disentangles, and even dissolves some surface molecular chains. As a result, the mobility of the surface molecular chains is increased. A chemical infusion method for the formation of ultrasmooth polymer surfaces was reported by Duchane.⁶ In that process an ultrasmooth surface was generated by contacting the polymer with a mixture of two miscible compounds, one of them being a solvent for the polymer and the other a nonsolvent. The composition of the mixture was slowly changed in time by increasing the concentration of the non-

solvent. Initially, the polymer surface is swollen in the solvent, but, subsequently, with increasing concentration of the nonsolvent, the solvent is slowly extracted from the swollen surface.

In the present work a method for the generation of a porous region near the surface of the polymer is developed. In this method the polymer is first treated with a solvent and, subsequently, is rapidly introduced into a nonsolvent that is, however, miscible with the solvent. The two consecutive opposite effects generate a porous region in the neighborhood of the polymer surface; the inner core of the substrate remains, however, unmodified. The formation of the porous region is a result of (i) the swelling of the surface region and (ii) the rapid extraction of the solvent from the swollen region by the nonsolvent followed by the rapid partial reentanglement of the loosened molecular chains. The characteristics of the porous surface depend on the nature of the polymer and on the nonsolvent employed. Because of the surface rearrangements, a more polar nonsolvent can lead to a more hydrophilic porous surface, if the polymer has such groups, while a less polar to a less hydrophilic porous surface. It was also found that porous surfaces form only when the extraction rate of the solvent by the nonsolvent is sufficiently rapid.

Polymers with porous surfaces can be useful in a number of ways. In endothelial cell immobilization

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used to achieve biocompatible surfaces, substrates with a porous surface, such as knitted Dacron or expanded Teflon,⁷ are employed. The polymer with porous surface prepared by the solvent-nonsolvent method suggested here can be employed for cell immobilization. Such a material has the advantage that its bulk properties are those of the solid core, and only the surface region has a porous morphology. Another use of the polymer with a porous surface is in the adhesion of a second incompatible polymer to its surface. The porous surface provides a matrix into which the monomer of a second polymer can penetrate. Polymerizing the monomer, two otherwise incompatible polymers can adhere to one another through the porous region. This application is demonstrated later in this study.

EXPERIMENTAL

Chemicals and Instruments

PMMA [poly(methyl methacrylate)] sheets are commercially available (DuPont). The solvent for PMMA (chloroform) and the nonsolvents for PMMA (methanol, ethyl ether, and octane) were purchased from Aldrich. Angular-dependent electron spectroscopy for chemical analysis (ESCA) measurements were carried out with a Physical Electronics PHI 5100 ESCA instrument. Scanning electron microscopy (SEM) investigations were performed with a Hitachi S450 microscope.

Solvent-Nonsolvent Treatment of Polymers

In all the experiments a piece of PMMA ($0.5 \times 0.7 \times 0.09$ in.) was first immersed in chloroform for time periods ranging from 5 to 270 s. After the surface of PMMA was swollen in chloroform, the substrate was withdrawn from the solvent and immersed immediately in 10 mL of nonsolvent for 10 min. The nonsolvent that remained in the substrate was allowed to evaporate in the atmosphere.

Gravimetric Experiment

Since water is a polar liquid and octane is nonpolar, the amounts of liquids absorbed by the substrate can be used as indicators for the surface characteristics of the pores. The amounts of water or octane were determined gravimetrically, by imbibing the porous substrates with water or octane, which are nonsolvents for PMMA, for 15 min. Then, the substrate was slowly pulled out from the liquid and weighed carefully. The high boiling points of water

and octane constitute an advantage in these experiments.

RESULTS AND DISCUSSION

The Formation of a Porous Surface

When an amorphous polymer is treated with a solvent, its surface region can be viewed as a concentrated polymer solution, containing some dissolved polymer molecules as well as disentangled molecules attached to the surface. If subsequently the good solvent is replaced with a poor solvent, the disentangled polymer chains will associate with each other rather than with the nonsolvent molecules. If the replacement of the solvent containing some dissolved polymer molecules by the nonsolvent is slow, the disentangled chains of the attached polymers have time to associate in the most compact form, thus generating a smooth surface. If the replacement is rapid, the chains will associate in a loose fashion, thus generating a porous interfacial region. In this work PMMA, which is an amorphous polymer, is immersed in chloroform, which is a good solvent for PMMA. After a short period of immersion, PMMA is immersed in an excess amount of a nonsolvent (for the polymer)—methanol, ethyl ether, or octane—which is, however, miscible with chloroform. The solvent containing some dissolved polymer chains is extracted into the nonsolvent during this process. A white PMMA precipitate due to the molecules dissolved in the solvent is generated in the nonsolvent. The rapid replacement of chloroform with the nonsolvent forces the surface molecular chains to entangle again. This reentanglement being rapid generates a surface whose morphology is different from that of the untreated surface. The material treated in this manner has a white color. The morphology of the surface, examined with a scanning electron microscope, is presented in Figure 1. The pore size of the porous surface is in the range of submicrons.

The Effect of the Nonsolvent on the Characteristics of the Porous Surface

Two nonsolvents, methanol and ethyl ether, were selected to examine the formation of pores. Methanol is a polar solvent with a solubility parameter of 14.5, whereas ethyl ether is a less polar solvent with a solubility parameter of 7.4. Both are completely miscible with chloroform but are nonsolvents for PMMA. Therefore both are capable of extracting

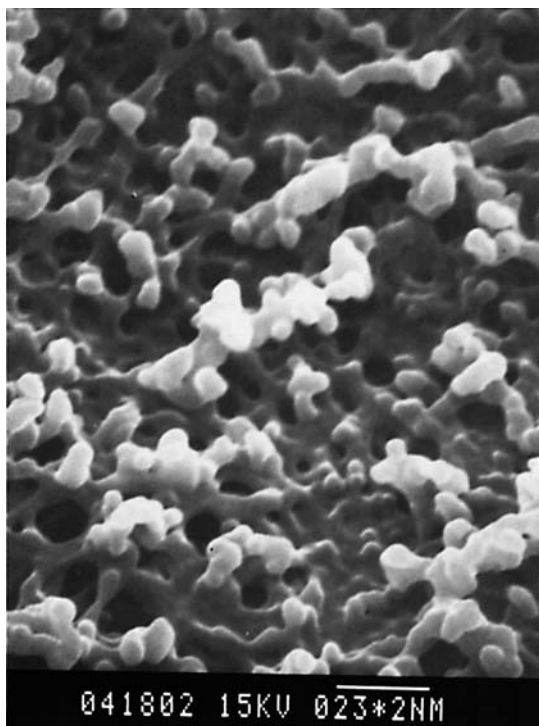


Figure 1 Porous surface. The substrate was first immersed in chloroform for 180 s and subsequently in ethyl ether for 10 min.

chloroform from the swollen polymer surface and hence can cause the reentanglement of the polymer chains. The nature of the nonsolvent is expected to affect the reentanglement. The characteristics of the pores were investigated by measuring the absorption of two different liquids: water, which is polar, and octane, which is nonpolar. The results are plotted in Figures 2 and 3. In Figure 2 the amounts of water and octane absorbed by the porous surface prepared with methanol as nonsolvent are plotted against the immersion time in chloroform. One can observe that the porous surface absorbs a slightly larger amount of water than octane. Figure 3 presents the amounts of water and octane absorbed when ethyl ether was the nonsolvent and shows that the amount of octane absorbed is significantly higher than the amount of water. The two different absorption behaviors indicate that the surface of the pores prepared with ethyl ether is more hydrophobic than that prepared with methanol. This can be ascribed to the more polar nature of methanol, which stimulates the rearrangement of the PMMA molecular chains by exposing some of their polar moieties to methanol. Figures 2 and 3 also show the effect of the immersion time in chloroform on the formation of the porous surface. One can note that, after a relatively short immersion time, the amounts of water or octane ab-

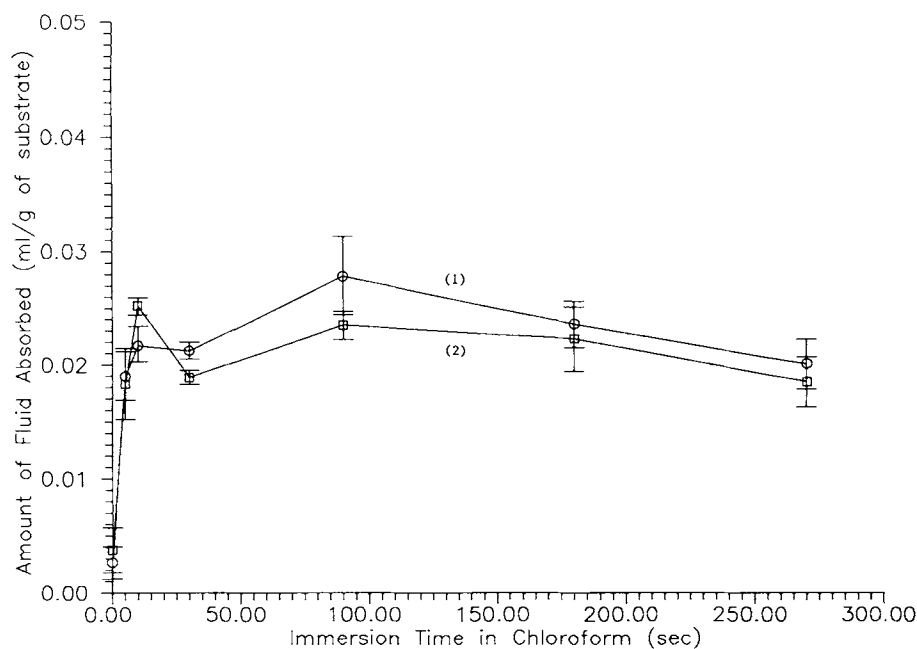


Figure 2 Absorptions of water and octane in the porous surface against immersion time in chloroform. The substrate was first immersed in chloroform and subsequently in 10 mL of methanol for 10 min. The treated substrates were imbibed with water and octane for 15 min before weighing. (1) Water. (2) Octane.

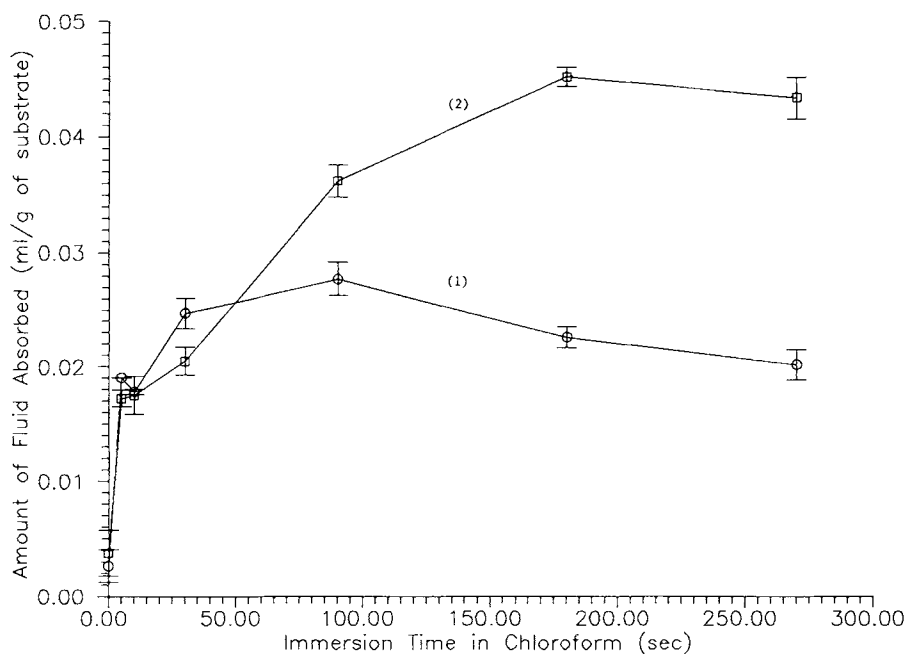


Figure 3 Absorptions of water and octane in the porous surface against immersion time in chloroform. The surface was first immersed in chloroform and subsequently in 10 mL of ethyl ether for 10 min. The treated substrates were imbibed with water and octane for 15 min before weighing. (1) Water. (2) Octane.

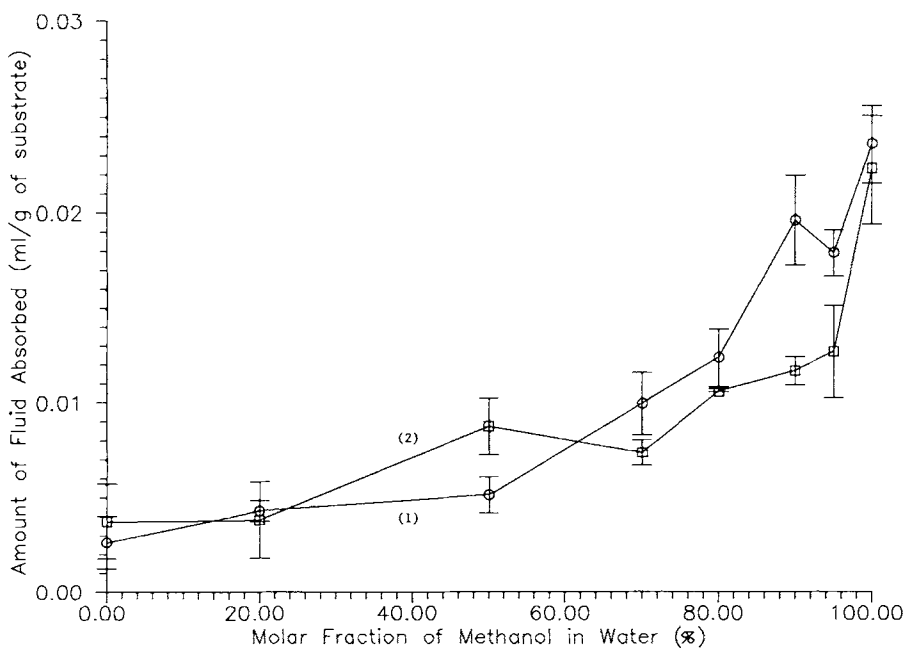
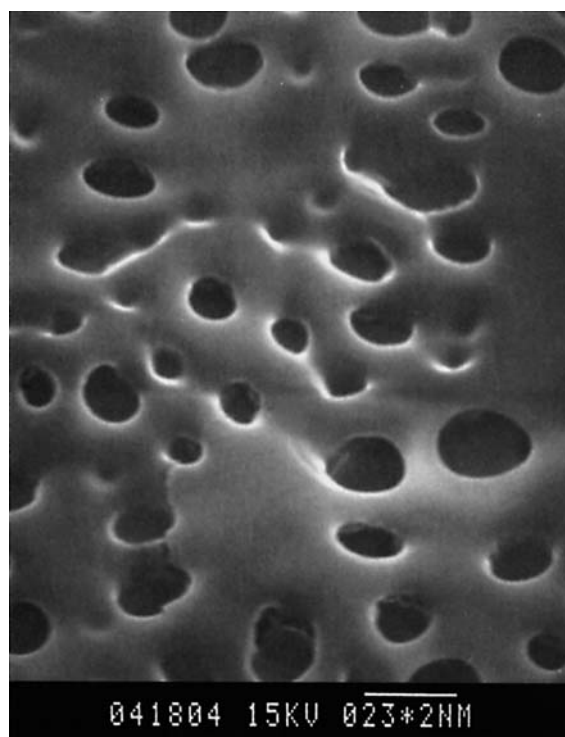


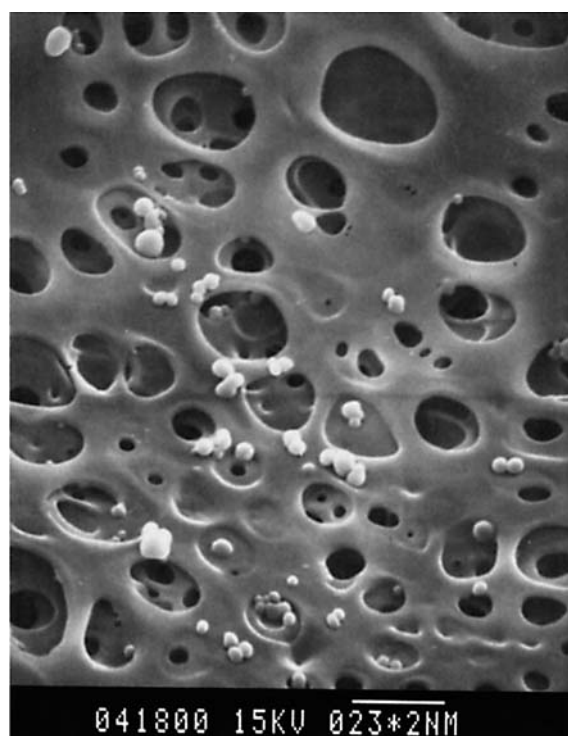
Figure 4 The effect of the water-methanol mixture on the absorptions of water and octane in the porous surface. The substrate was immersed in chloroform for 180 s and subsequently in a water-methanol mixture for 10 min. The substrates were imbibed with water and octane for 15 min before weighing. (1) Water. (2) Octane.



(a)



(b)



(c)

Figure 5 The morphology of surfaces prepared with water–methanol mixtures as non-solvents. All the substrates were immersed in chloroform for 180 s and subsequently in different water–methanol mixtures for 10 min. (a) 50 molar % of methanol. (b) 80 molar % of methanol. (c) 100% of methanol.

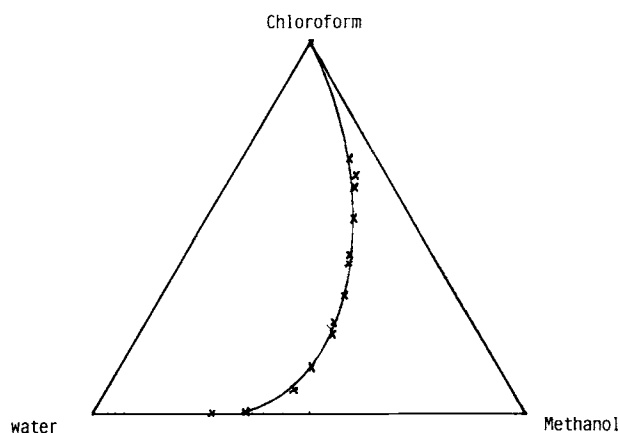


Figure 6 The phase diagram chloroform-methanol-water in mol%.

sorbed do not increase appreciably with increasing immersion time in chloroform. The penetration of the solvent is probably slowed down by its increased viscosity caused by the dissolution of polymer.

Rate Dependence of the Formation of a Porous Surface

As mentioned previously, relatively large pores form when the extraction of the polymer solution in chlo-

roform from the surface region is rapid and do not form at all when the extraction is sufficiently slow. The rate of extraction of the solvent (that contains some dissolved polymer molecules) by the nonsolvent is expected to play a major role in this respect. Two sets of experiments have been carried out to investigate this effect. Both involve the use of different nonsolvents in order to change the rate of extraction.

In the first set of experiments, a mixture of methanol-water solution, instead of pure methanol, was employed. Methanol is miscible with both water and chloroform, while water and chloroform are immiscible. It is therefore expected that the mixing of water with methanol will decrease the rate of extraction of chloroform from the swollen surface. The results are presented in Figure 4, which shows that the amounts of water and octane absorbed are low, when the mixture has a low content of methanol. The amounts absorbed increase when the fraction of methanol increases. Scanning electron microscopy pictures of substrates prepared with 50, 80, and 100 mol % methanol are presented in Figure 5. For 50% methanol the surface has no pores. The porosity increases with increasing content of methanol. It should be noted that 10 mL of 50 mol % methanol can dissolve up to about 3.4 g chloroform (Fig. 6). The small amount of chloroform retained by the

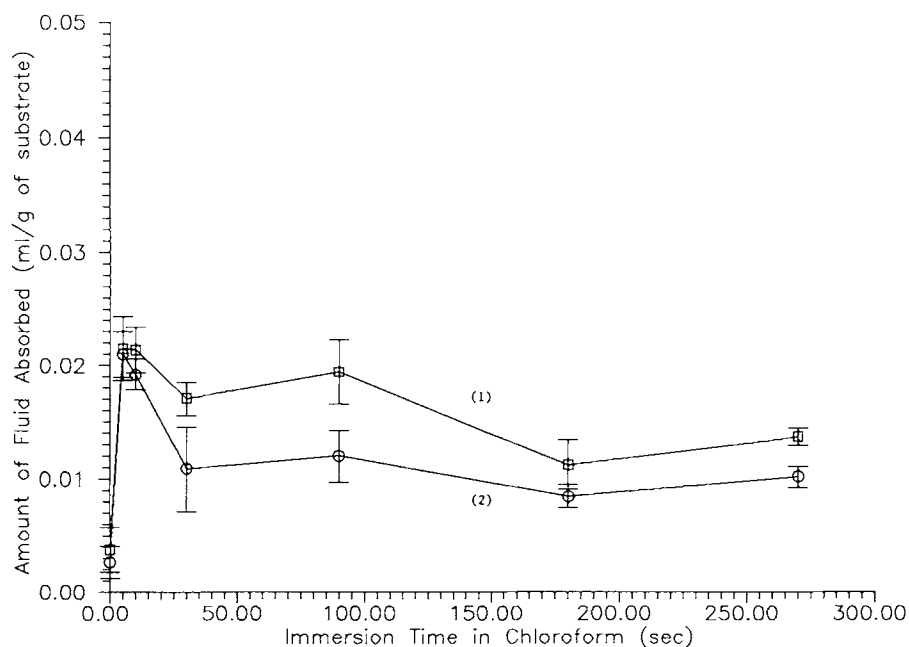
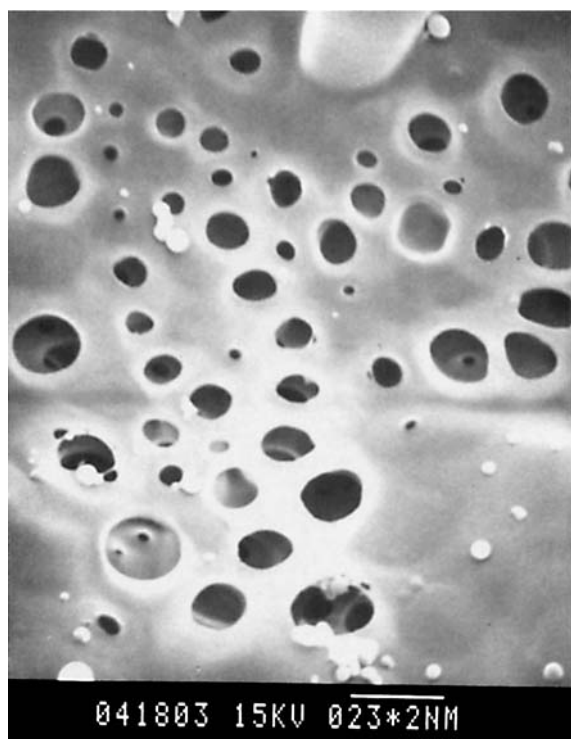
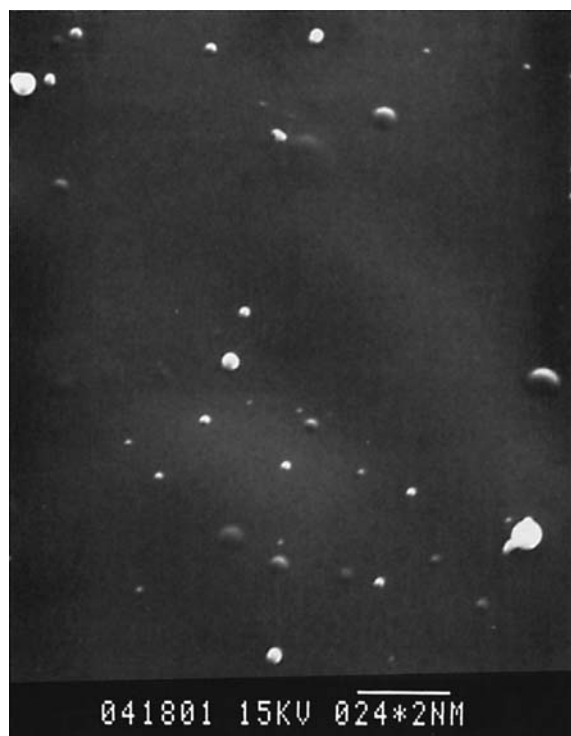


Figure 7 Absorptions of water and octane in the porous surface against immersion time in chloroform. The surface was first immersed in chloroform and subsequently in 10 mL of octane for 10 min. The substrates were imbibed with water and octane for 15 min before weighing. (1) Water. (2) Octane.



(a)



(b)

Figure 8 The surface morphology of a substrate prepared with octane as nonsolvent. (a) 10-s immersion in chloroform. (b) 180-s immersion in chloroform.

substrate after solvent treatment can be completely extracted by 10 mL of a 50 mol % methanol–water mixture. The fact that pores do not form when the substrate is prepared with 50 mol % methanol can be ascribed to the slow extraction rate of the chloroform (containing some dissolved polymer molecules) by the nonsolvent.

Another set of experiments was carried out by using a long-chain hydrocarbon, octane, as the nonsolvent. Figure 7 shows a somewhat different behavior than that observed with the other two nonsolvents. The absorptions of octane and water first increase but subsequently decrease with increasing immersion time in chloroform. For short immersion times (5–10 s), the substrates acquired a nontransparent white color similar to those obtained with ethyl ether or methanol. For longer immersion times, the surfaces became opaque. SEM investigations have shown that, when octane was the nonsolvent, porous surfaces formed [Fig. 8(a)] only for short immersion times (10 s) in chloroform; the surfaces remained, however, free of pores [Fig. 8(b)] for an immersion time of 180 s. As explained below, this behavior is a result of the slow extraction rate of the chloroform (which contains some dissolved polymer molecules) by octane.

The diffusion coefficient in the nonsolvent of the polymer molecules contained in the solvent is expected to be smaller when their sizes and the viscosity of the nonsolvent are larger. Some physical properties of the PMMA molecules, solvents, and nonsolvents are listed in Table I. The PMMA molecule is expected to be larger in a good solvent where it expands and smaller in a poor solvent where it contracts. Since the solubility parameters of octane and ethyl ether are approximately the same, the sizes of the PMMA molecules in octane and ethyl ether are expected to be comparable. From Table I one can see that the viscosity of ethyl ether is much smaller than that of octane. Hence, the diffusion

Table I

Materials	Density ^a	Viscosity ^a (cp)	$\delta^{a,b}$
Chloroform	1.492	0.542	9.3
Methanol	0.791	0.547	14.5
Ethyl ether	0.708	0.222	7.4
Octane	0.703	0.542	7.6
Water	1.000	1.000	23.4
PMMA	1.190	—	9.5

^a Ref. 9.

^b Solubility parameter (cal/cm³)^{1/2}.

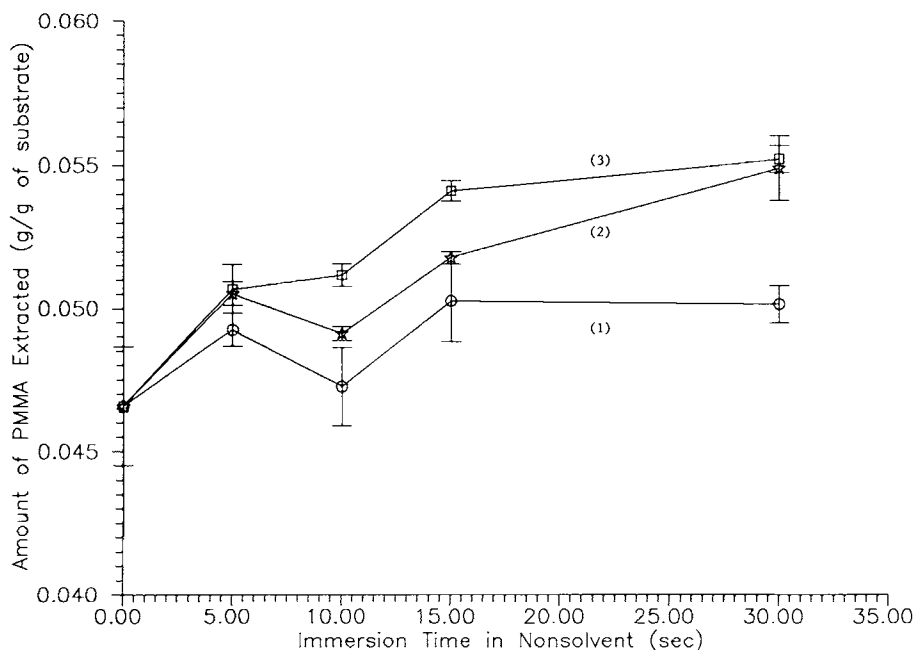


Figure 9 The extraction of PMMA molecules dissolved in chloroform by different nonsolvents. The PMMA substrates were treated with chloroform for 180 s. Subsequently, the substrates were immersed in different nonsolvents for various periods of time. (1) Octane. (2) Ethyl ether. (3) Methanol.

coefficient of PMMA molecules is expected to be larger in ethyl ether than in octane. Similar arguments can be adduced for the diffusion of PMMA molecules in methanol and octane. From Table I one can see that the viscosities of methanol and octane are comparable. The size of the PMMA molecule is, however, expected to be smaller in methanol than in octane because of a significant difference in

the solubility parameters of methanol and PMMA and a smaller difference for octane and PMMA. Consequently, the diffusion coefficient of PMMA molecules is higher in methanol than in octane. One can therefore conclude that the diffusion coefficient of the PMMA molecule in octane is the smallest among the three nonsolvents. This suggests that there is a slower extraction by octane of the chlo-

Table II Contact Angles of Air Bubbles and Octane Droplets on a Surface Immersed in Chloroform for 20 s and Subsequently in Methanol-Water Mixtures for 10 min

Methanol (mol %)	Contact Angle		Surface
	Air	Octane	
100	178.0 ± 2.0	172.0 ± 2.0	Porous
83.5	180 ^a	172.0 ± 2.0	Porous
80.8	180 ^a	168.0 ± 5.0	Porous
79.1	132.0 ± 2.0	96.0 ± 5.0	Nonporous
75.7	124.0 ± 1.5	91.0 ± 1.5	Nonporous
69.2	124.0 ± 4.5	88.0 ± 3.0	Nonporous
36.2	114.5 ± 1.5	88.0 ± 2.5	Nonporous
0	117.0 ± 2.0	90.0 ± 1.0	Nonporous
Untreated surface	119.0 ± 3.0	89.0 ± 3.0	Nonporous

^a The air bubbles cannot attach to the surface.

Table III Angular-Dependent ESCA*

Angle	15°		45°		90°	
	C	O	C	O	C	O
PMMA	72.82	27.18	71.42	28.58	71.64	28.36
Octane	72.83	27.17	71.73	28.17	71.34	28.66
Methanol	71.29	28.71	71.08	28.92	70.73	29.27
Ether	71.01	28.99	70.59	29.41	70.49	29.51

* All the substrates were treated as follows: immersion time in chloroform 180 s and immersion time in nonsolvent 15 min.

roform (containing some dissolved PMMA molecules) from the surface region. This conclusion was confirmed by measuring the weights of the substrates before and after the solvent-nonsolvent treatment followed by drying as a function of the immersion time in the nonsolvent. The results are presented in Figure 9, which shows that methanol and ethyl ether extract more PMMA than octane does.

Figures 2, 3, and 7 show that for short immersion times in chloroform there are no significant differences between the amounts of water and octane absorbed for any of the three nonsolvents employed, because the chloroform-swollen region in the neighborhood of the surface is thin and can be extracted rapidly. However, for long immersion times in chloroform, the slow migration of the PMMA-chloroform solution from the deeper regions can allow the more compact reentanglement of the PMMA chains during the immersion in the nonsolvent, and hence a porous surface will not be generated. This happens when octane is employed as the nonsolvent because the extraction is slow.

Wetting Angle Investigation

Contact angle measurements in a water environment, using octane and air as probe fluids,⁸ were carried out to obtain information regarding the surface properties of the porous surfaces. Table II lists the contact angles of air bubbles and octane droplets on surfaces prepared using different molar fractions of methanol-water mixtures as the nonsolvent. For low methanol content, the contact angles of air bubbles and octane droplets are near to those of the untreated PMMA surface. This indicates that the surface did not change significantly during the treatment. However, for a methanol content higher than 80 mol %, large contact angles of air bubbles and octane droplets were observed, indicating highly hydrophilic surfaces. This is because the pores are

filled with water. From a macroscopic point of view, the fine hydrophobic porous surface filled with water behaves like a hydrogel surface saturated with water. However, on the porous surfaces the angles of the probe fluids were not always stable.

ESCA Investigations

The surface composition of the porous surface was measured by the angular-dependent ESCA. The results are listed in Table III. It should be pointed out that for porous surfaces the angular-dependent ESCA provides only qualitative profiles of composition. For both methanol- and ethyl-ether-treated surfaces, the atomic concentrations of oxygen are higher than those of the untreated and octane-treated surface. This is due to the polar nature of methanol and ethyl ether, which stimulate the rearrangement of the surface molecular chains during immersion. The exposure of a greater number of polar moieties of the PMMA chains results in an increase in the atomic oxygen concentration. No significant differences in the composition profiles of methanol- and ethyl-ether-treated surfaces were detected by ESCA. The same surface composition profiles for both untreated and octane-treated PMMA provides another confirmation of the slow

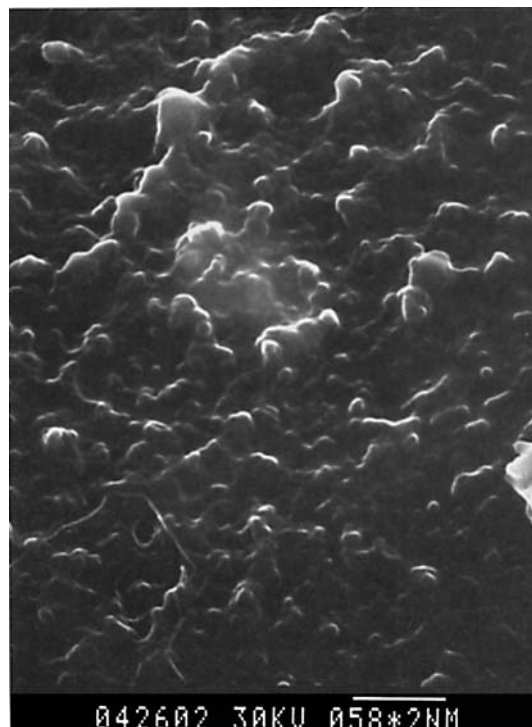


Figure 10 The incorporation of poly(acryl amide) in porous PMMA.

extraction rate outlined earlier. The slow migration of chloroform-PMMA solution allows the PMMA molecules to reentangle in their initial way.

The Incorporation of a Second Polymer in the Surface Region

One possible application of a material with a porous surface is the adhesion to a second incompatible polymer, which otherwise does not adhere to the smooth surface of the former. Acryl amide monomer (2.5 g) was dissolved in 5 g of water containing 0.2 g of $K_2S_2O_8$. The porous surface of a PMMA substrate, which is hydrophobic, was imbibed with the monomer solution for 30 min. Then, the system was subjected to polymerization in an oven at 45°C for 24 h. The final composite was examined by scanning electron microscopy, which showed that the polyacrylamide penetrates the matrix of the porous surface (Fig. 10). In contrast, the monomer solution, which is hydrophilic, does not spread over the untreated PMMA surface. A comparison between Figures 1 and 10 shows that the pores are largely covered with polyacrylamide.

CONCLUSIONS

1. A PMMA material with a porous surface was generated by first treating the substrate with a solvent (chloroform), followed by the rapid extraction of the solvent with a nonsolvent for the polymer (methanol, ethyl ether, or octane), which is miscible with the solvent. The formation of the porous surface is a result of two processes: (a) the swelling of the interface layer, associated with the disentanglement of the surface polymer chains and the dissolution of some of them, and (b) the extraction of the solvent containing some dissolved polymer molecules by the nonsolvent. When the extraction is rapid, a porous structure is generated; when the extraction

is slow, pores do not form because a compact reentanglement of the polymer chains can be achieved.

2. The surface properties of the pores depend on the nature of the nonsolvent. Surfaces treated with polar nonsolvents exhibit more hydrophilicity than those treated with nonpolar nonsolvents. This is due to the rearrangement of the surface molecular chains under the influence of the nonsolvent.
3. Pores do not form when octane is employed as the nonsolvent and the time of immersion in chloroform is sufficiently large.
4. A porous surface can be used to improve the adhesion between two incompatible polymers.

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