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Amphiphilic Networks. 9. Surface Characterization[†]

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ABSTRACT: Amphiphilic networks consisting of hydrophobic polyisobutylene and a hydrophilic polymer, such as poly(2-hydroxyethyl methacrylate) (PHEMA) or poly(*N,N*-dimethylacrylamide) (PDMAAm), were prepared and their surfaces characterized by various techniques. According to X-ray photoelectron spectroscopy (XPS) C_{1s} spectra, the atomic ratios O/C and N/C were considerably lower at the outermost surface (ca. 20–100 Å) than in the bulk of the networks. The surface morphologies of amphiphilic networks of various compositions were investigated by atomic force microscopy (AFM). The surface microroughness greatly increased by swelling in water or *n*-heptane which suggests surface heterogeneity. According to surface energetics studies by dynamic contact angle (DCA) measurements of dry and wet samples, the surfaces of the networks are heterogeneous and highly mobile; specifically, dry surfaces rapidly rearrange upon exposure to water.

Introduction

Amphiphilic networks are cross-linked random assemblages of hydrophilic and hydrophobic polymer segments. Recently, Kennedy and co-workers[1–3] have synthesized a series of amphiphilic networks by simultaneous copolymerization/cross-linking of hydrophobic methacryloyl-capped polyisobutylene (MA–PIB–MA) with hydrophilic comonomers such as 2-hydroxyethyl methacrylate (HEMA) or *N,N*-dimethylacrylamide (DMAAm). Interest in these amphiphilic networks, particularly for biomedical applications, warrants further surface characterization of these networks, since the surface composition and morphology are dominant factors for blood compatibility.[4] It has been found that amphiphilic networks with around 50/50 wt % hydrophilic/hydrophobic moieties exhibit excellent biocompatibility and biostability *in vivo* in rats.[5] Furthermore, PHEMA–l–PIB and PDMAAm–l–PIB (for brevity H and A networks, respectively) with 50 wt % of PIB exhibited reduced protein adsorption in human plasma protein adsorption tests and reduced cell adhesion in human monocyte adhesion tests, suggesting hemocompatibility.[6]

This work, which supplements our brief previous report,[7] concerns the surface chemical composition of amphiphilic networks by XPS and surface microstructure by AFM. Unswollen networks and networks swollen in water or *n*-heptane were also compared. The dynamic contact angles of both dry and wet networks were also investigated.

Experimental Section

Materials. The preparation of the networks has been described.[1–3] The number-average molecular weight (M_n) of PIB was 4300 for XPS and AFM studies and 4500 or 10 000 for contact angle measurements. We assumed that the M_n of the PIB and its M_c, i.e., the M_n between cross-linking sites, are the same. In our abbreviation symbolism the first number (e.g., 4.3) is the number-average molecular weight of PIB used in thousands, and the second number (e.g., 50) is the weight precent of PIB in the network. The samples for AFM and XPS experiments were sheets about 2 mm thick. Only the upper

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[†] For paper 8 in this series, see: Lindhout, T.; Keszler, B.; Kennedy, J. P. *Polym. Bull.*, *34*, 101 (1955).

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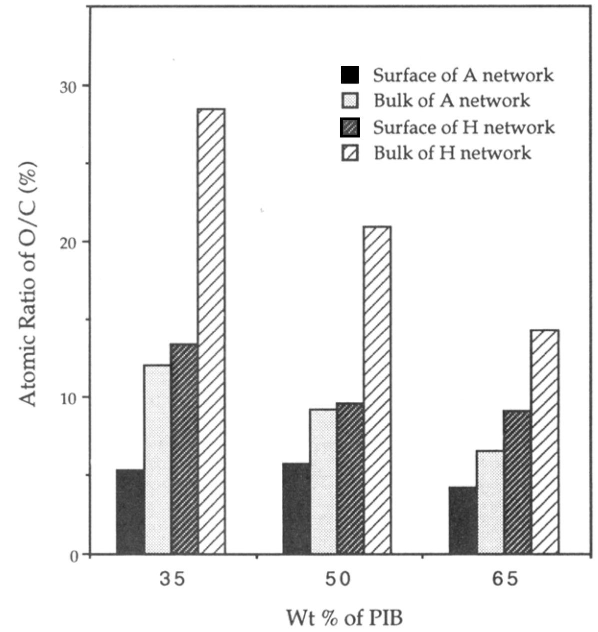


Figure 1. Comparison of O/C ratios between surface and bulk for different compositions of amphiphilic networks.

sides of the samples which were in contact only with air were investigated. Swollen samples were prepared by placing the networks in H_2O or *n*-heptane at 23 ± 3 °C for 7 days to reach equilibrium swelling. The swollen samples were scanned in an AFM liquid cell filled with the same solvent used for the swelling.

XPS Experiments. XPS spectra were obtained with a Surface Science Instruments (SSI) X-probe ESCA instrument utilizing an Al Kα 1,2-monochromatized X-ray source. This instrument permits the analysis of the outermost 20−100 Å of a sample in an elliptical area whose short axis can be adjusted from 150 to 1000 μm. The energy of the emitted electrons was measured with a hemispherical energy analyzer at pass energies ranging from 25 (resolution 1) to 150 eV (resolution 4). Lower pass energies provide higher spectral resolution. The higher pass energies permit more rapid data acquisition and more accurate quantitative analysis. SSI data analysis software was used to calculate the elemental compositions from the peak areas and to peak fit the high-resolution spectra. An electron flood gun operating at 5 eV was used to minimize surface charging. The binding energy scale was referenced by setting the CH_x peak maximum in the C_{1s} spectrum to 285.0 eV. Typical pressures in the analysis chamber during spectral acquisition were 10^{-9} Torr.

Depth profile spectra were collected with the wide-angle acceptance lens. The sample was rotated about an axis perpendicular to the analyzer lens axis and in the plane of the X-ray beam. The spectra were collected with the analyzer at 80°, 68°, 55°, 39°, and 0° with respect to the surface normal of the sample. The angular-dependent studies are described in more detail in a recent publication.[7]

AFM Experiments. A Nanoscope II (Digital Instruments, Inc.) equipped with an atomic force head D of 15 × 15 μm^2 scan range was used. Constant force mode was employed, and the force constant of the microlever was 0.21 N/m. The microlever (Park Scientific Instruments) had an integrated pyramidal tip (Si_3N_4) and was of 100 μm (*L*) × 13 μm (*W*) × 0.6 μm (*T*) dimensions. The average surface roughness was obtained from at least nine different areas of measurements; the observed area was 2.5 × 2.5 μm^2.

Dynamic Contact Angle Measurements. Dynamic contact angle measurements were made with dry and wet samples by using a Cahn DCA-312 instrument and double-distilled water as the test liquid. The samples were dried in vacuum for a week at 110 °C or equilibrated in double-distilled water before measurement. Both advancing and receding angles were obtained at a platform speed of 0.12 mm/s. Immersion depth was 15 mm. Averages of five measurements are reported.

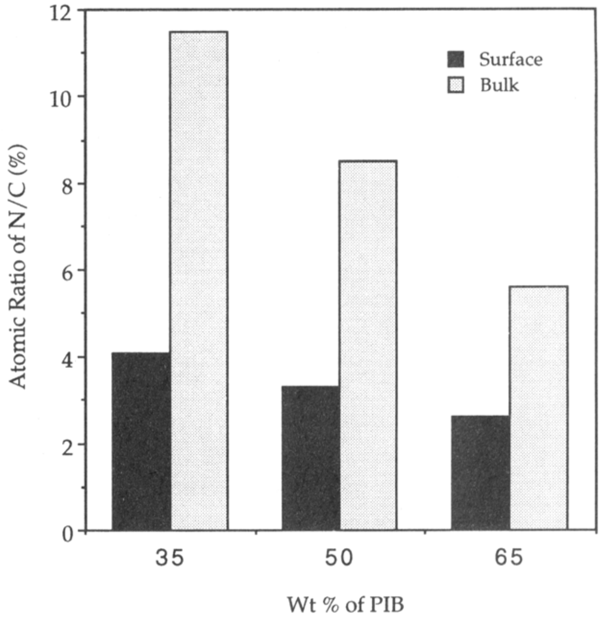


Figure 2. Comparison of N/C ratios between surface and bulk for different compositions of A networks.

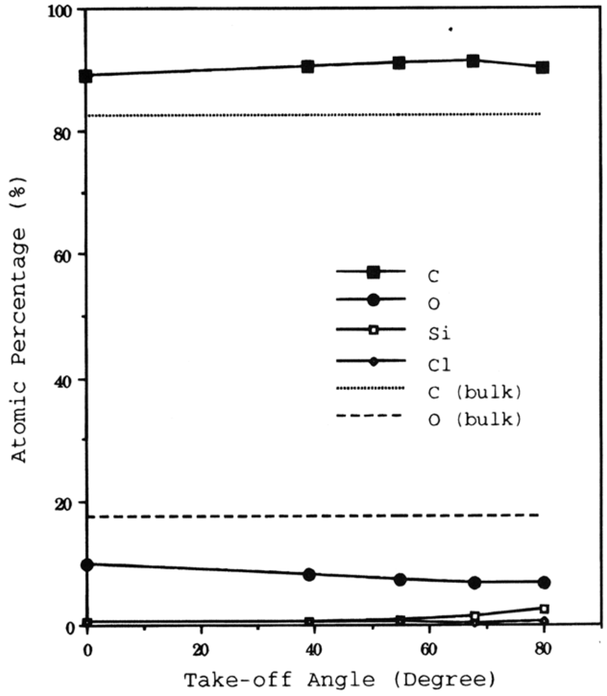
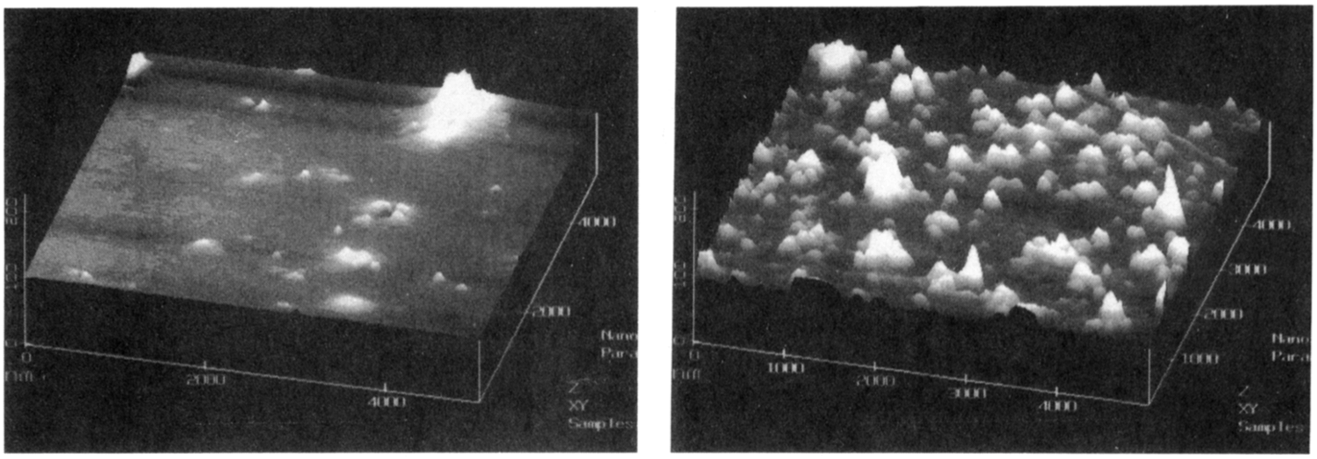


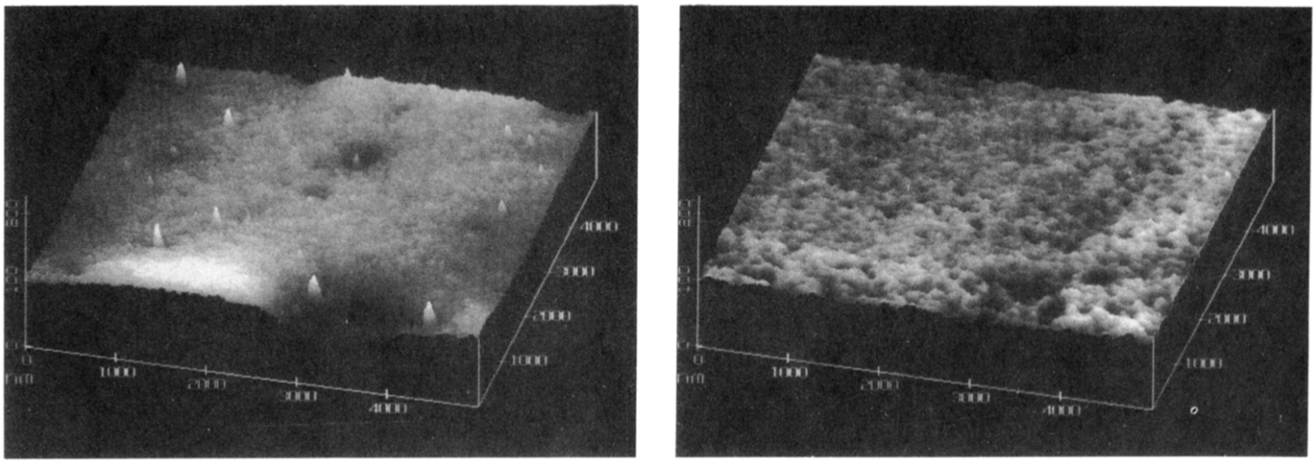
Figure 3. Surface composition of H-4.3-50 as a function of take-off angle.

Results and Discussion

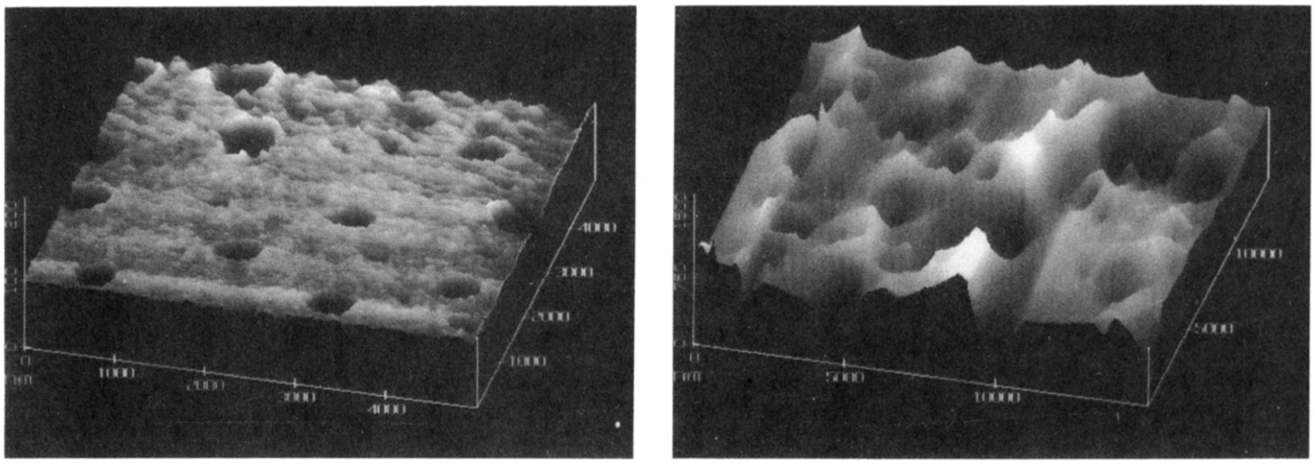
The surface composition of amphiphilic networks was obtained from XPS C_{1s} core level spectra. A binding energy (BE) of 285 eV in XPS C_{1s} spectra represents the hydrophobic hydrocarbon segments. We cannot be absolutely sure that the 285.0 eV peak is only due to the polymer; however, these polymer networks have been thoroughly extracted and therefore are initially relatively clean. The extent of contamination is very low because the driving force to deposit a hydrocarbon on a hydrocarbon surface is low (no significant decrease in interfacial energy occurs by such an adsorption). The low extent of contamination is illustrated by the high



(a) PHEMA (b) H-4.3-15



(c) H-4.3-35 (d) H-4.3-50



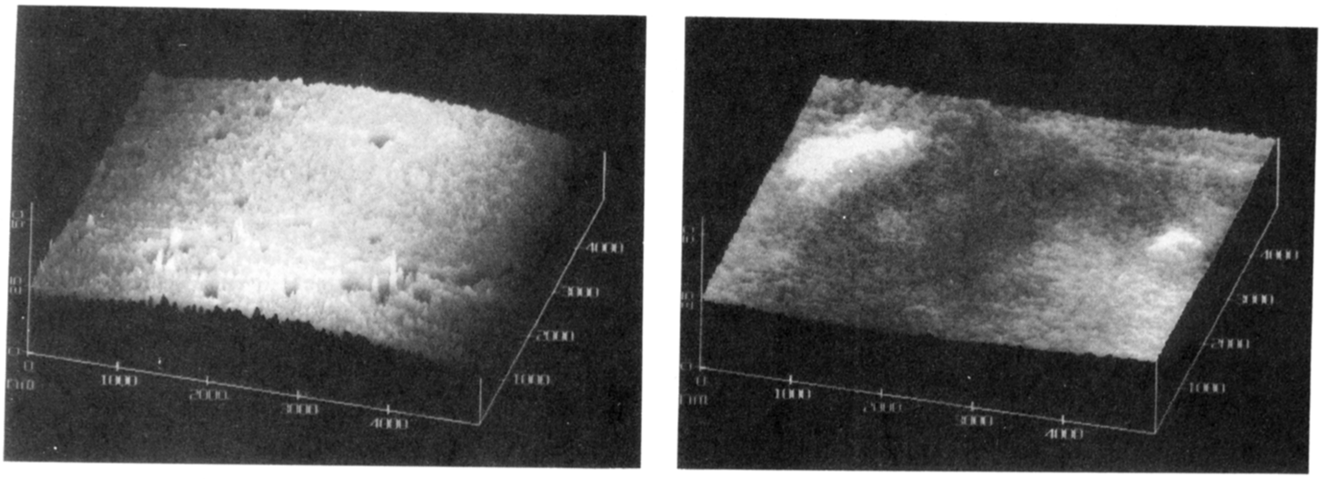
(e) H-4.3-65 (f) H-4.3-85

Figure 4. AFM images of the surfaces for different compositions of H networks.

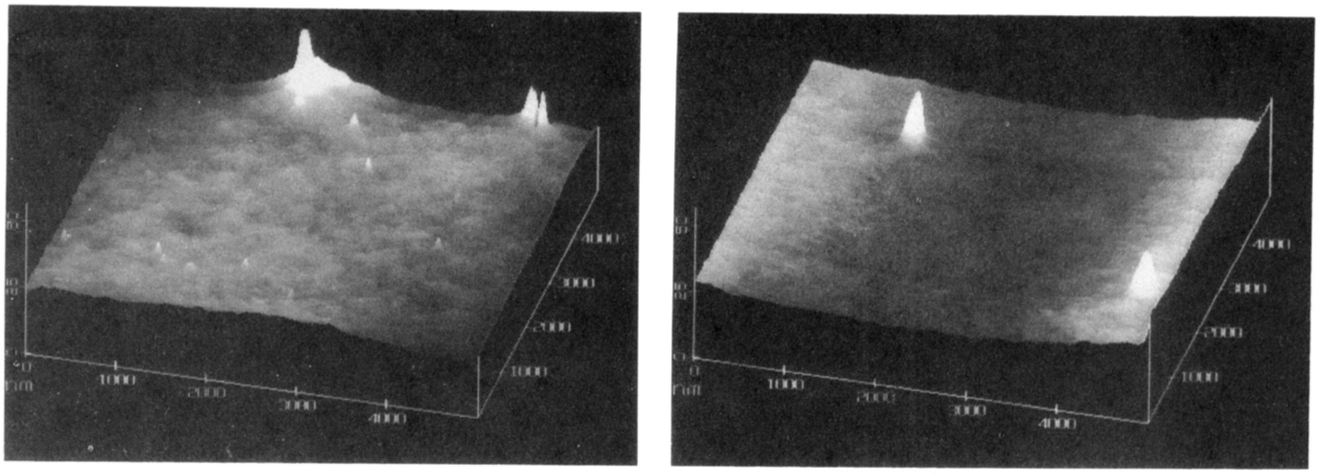
accuracy of the data for poly(tetrafluoroethylene) (PTFE) and poly(ethylene glycol) (PEG). Additionally, BE's of 286.2, 286.7, 287.8, and 289.3 eV correspond to the hydrophilic groups C−N (A network), C−O (H network), C=O (A network), and OC=O (H network), respectively. From these C_{1s} peak areas, the atomic percentage of the surface was calculated.

Figures 1 and 2 show the O/C and N/C atomic ratios of the surfaces of different H and A networks. The O/C and N/C ratios at the surfaces are considerably lower than those in the bulk. This is presumably because, when the surface of the sample is exposed to vacuum or air (both of which are highly hydrophobic), the hydrophobic hydrocarbon segments will move toward the surface, whereas the hydrophilic segments will become buried in the bulk.

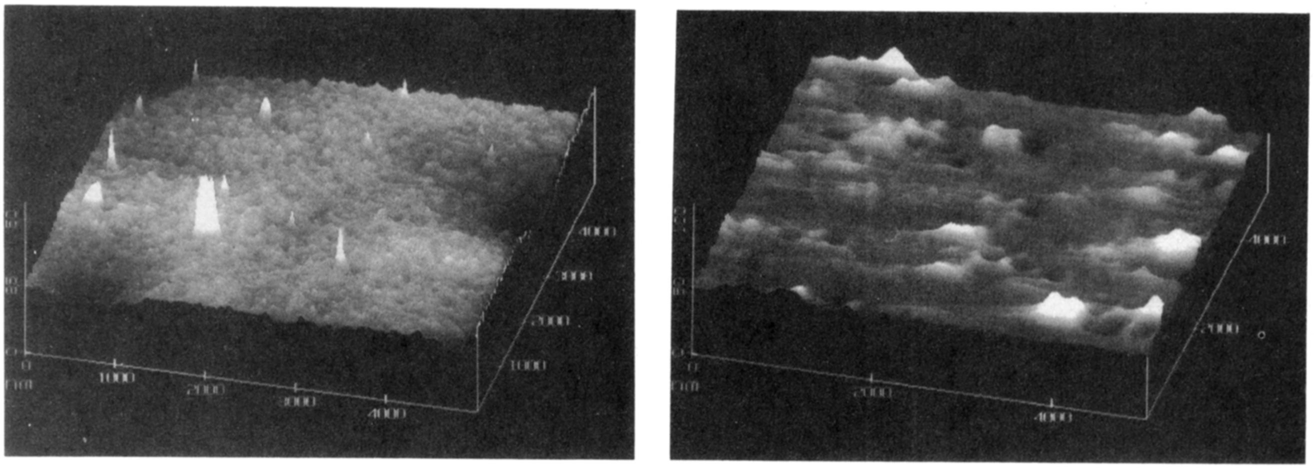
It is worthwhile investigating the vertical gradient of atomic composition of the surface. The surface



(a) PDMAAm (b) A-4.3-15



(c) A-4.3-35 (d) A-4.3-50



(e) A-4.3-65 (f) A-4.3-85

Figure 5. AFM images of the surfaces for different compositions of A networks.

chemistry varies depending on sampling depth, given as the distance normal to the surface from which 95% of the photoemission has taken place. The sampling depth of XPS by conventional X-ray sources is 0–80 Å.[8] The information from the outermost ~80 Å of a surface is converted into a depth profile by using data acquired in an angular-dependent XPS experiment.[9] The effective sampling depth decreases by a factor of cos θ, where θ is a take-off angle normal to the surface. Figure 3 shows the angular-dependent surface depth profile in atomic composition for the H network H-4.3-50. The percentage of carbon, which reflects hydrophobicity, increases as the take-off angle increases (i.e., as sampling depth decreases), whereas the percentage of surface oxygen, which reflects hydrophilicity, decreases with increasing take-off angle. However, the percentage of carbon decreases at the take-off angle of 80° (sampling depth = ca. 14 Å) because of Si and Cl contamination

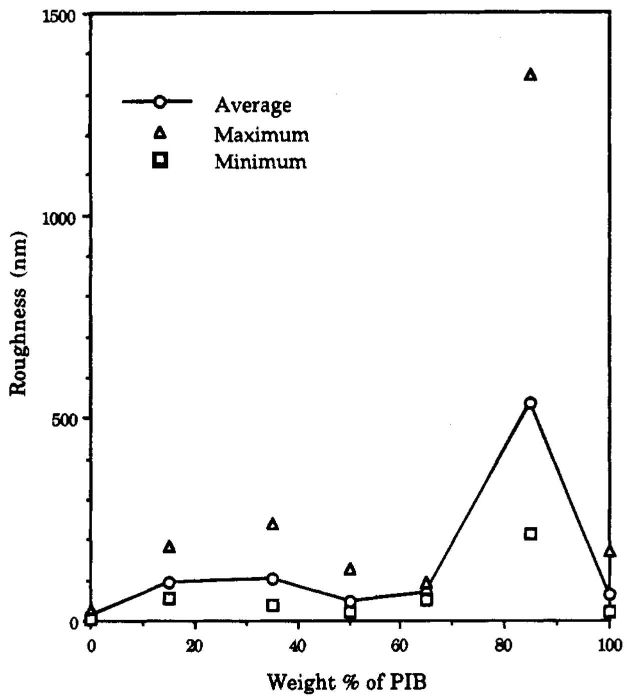


Figure 6. Surface roughness of H networks determined by AFM; observed area = 2.5 × 2.5 μm^2.

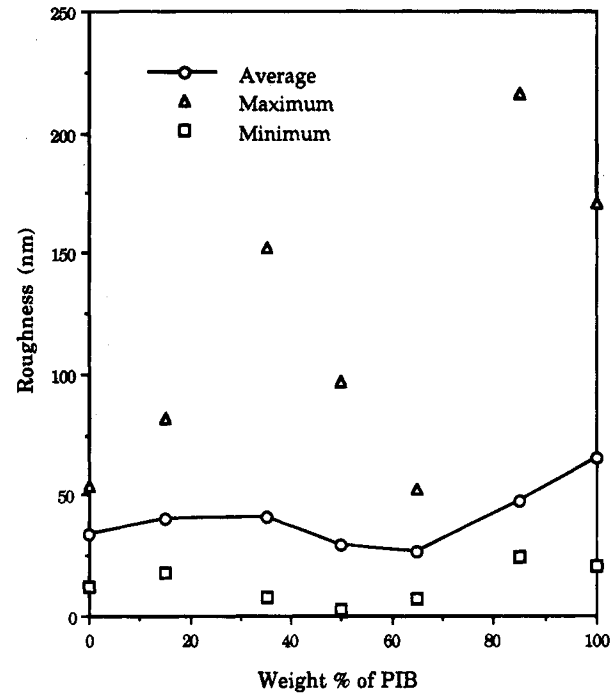


Figure 7. Surface roughness of A networks measured from AFM; observed area = 2.5 × 2.5 μm^2.

Table 1. Dynamic Contact Angles of H and A Networks

	dry		wet	
sample	θ_A/θ_R	$\Delta\theta$	θ_A/θ_R	$\Delta\theta$
H-4.5-35	98.9/36.1	62.8	78.4/28.1	50.3
H-4.5-50	101.6/40.5	61.1	84.5/30.7	53.8
H-4.5-65	104.3/42.2	62.1	87.8/33.5	54.3
H-10-36	102.8/32.6	70.2	81.8/30.4	51.4
H-10-51	103.4/33.4	70.0	81.9/31.3	50.6
H-10-65	109.1/37.2	71.9	89.2/32.6	56.6
A-4.5-35	106.4/16.8	89.6	88.4/22.1	66.3
A-4.5-50	110.1/20.2	89.9	95.2/23.7	71.5
A-4.5-65	115.8/23.7	92.1	99.6/23.9	75.7
A-10-44	110.8/17.1	93.7	91.9/20.5	71.4
A-10-57	116.2/22.1	94.1	94.1/22.0	72.1
A-10-70	117.6/24.4	93.2	100.8/23.1	77.7

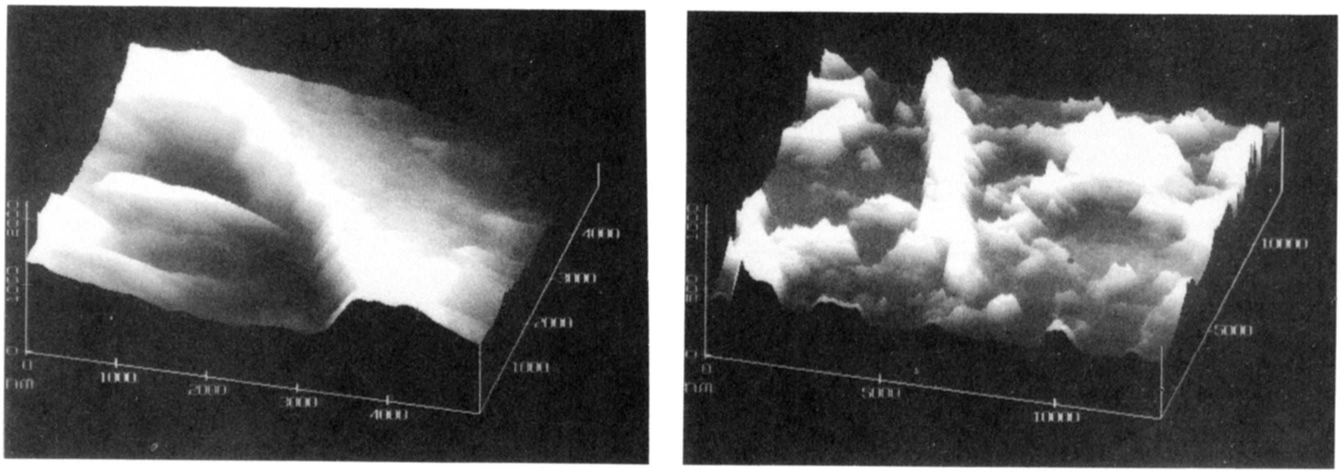
on the outermost surface.

The changes in XPS atomic ratios in some cases appear to be quite small both going from surface to bulk in the surface depth profile. However, where reasonably high levels of various elements are present at the surface of a specimen (as is the case here), the accuracy and reproducibility of the XPS data are very good. Consider the numbers: For PEG samples (n = 12), XPS atomic percent values of % O were 33.8 ± 0.4 (theory = 33.3%). XPS atomic percent values of % C were 66.2 ± 0.4 (theory = 66.6%). For PTFE samples (n = 22), XPS atomic percent values of % C were 32.6 ± 0.5 (theory = 33.3%). XPS atomic percent values of % F were 67.1 ± 0.4 (theory = 66.6%).

Organic silicone is a common contaminant of laboratory air. The source of the Cl contamination is unknown. The angular-dependent analysis may distinctly show the presence of surface silicone through the carbon signal because of the large difference in carbon contents of silicone (50 atomic %) and network H-4.3-50 (82.7 atomic %), that is, a difference of 32.7 atomic %. Comparing the silicone O to the network O, silicone (poly(dimethylsiloxane)) contains 25% O, while the network has approximately 17.3% O. The difference (7.7 atomic %) may simply not be great enough to see, particularly when so may effects may contribute to the angular dependence of the data set.

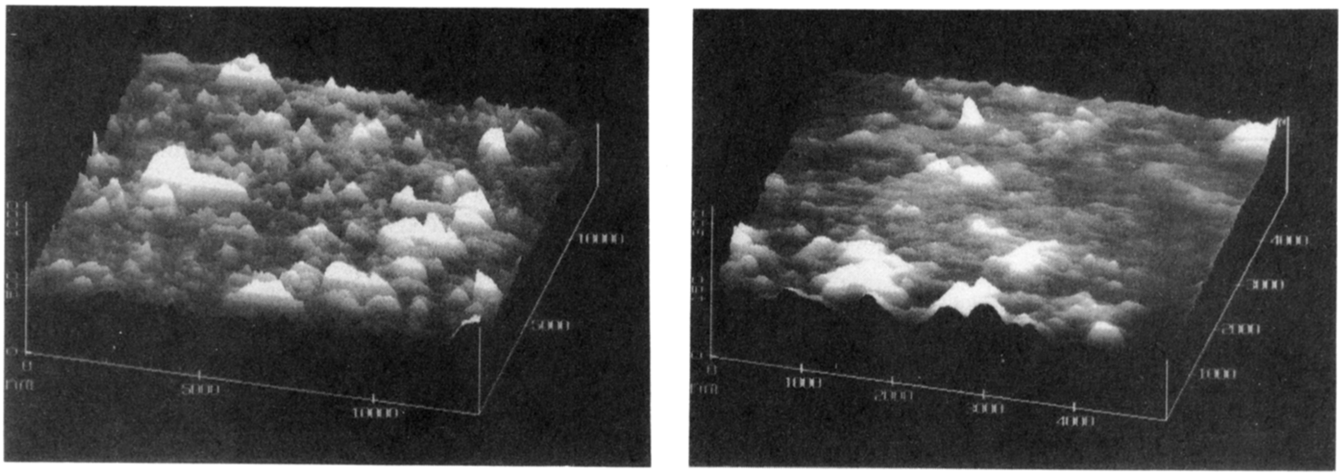
It is generally accepted that the smoother the surface of a polymer, the less thrombogenic it is.[4] Physical defects on the surface, such as small pinholes and grooves, may trap microemboli and perturb the laminar flow of blood, resulting in thrombus formation.[4] Figure 4 shows AFM images of different H networks. Network H-4.3-65 shows may small holes, which probably were formed when the solvent (THF) was evaporated during drying. The actual depth of the hole is not as great as it appears if we consider that the scale of height (200 nm) of the AFM images is much lower than that of the lateral scale (5000 nm); the depth and diameter are ca. 64 and ca. 1000 nm, respectively. Similarly, the cone-shaped structure in H-4.3-35 are not as tall as they appear in the figure; they are in fact spherical "bumps". There are more such bumps in H-4.3-15. The bumps on the surfaces are probably not due to purely hydrophobic domains caused by the hydrophobicity of the air with which the surface was in contact but to regions containing both hydrophilic and hydrophobic segments (the number and size of these bumps do not increase with increasing PIB content, and the sizes of the bumps are much larger than the average long spacing measured by small-angle X-ray scattering).[10] The effect of these surface defects on biocompatibility is unknown. However, all H networks except H-4.3-85, whose surface is very rough and contains many big holes, show very smooth surfaces. According to this evidence PHEMA is the smoothest and should be the most biocompatible; however, this is not the case; H-4.3-50 exhibits the highest biocompatibility. Biocompatibility cannot be determined only be roughness. By human blood monocyte adhesion tests, A-4.5-50 showed lower cell adhesion than that of H-4.5-50, while in protein adsorption tests these samples gave comparable results.[6] Biocompatibility is determined by a great variety of factors in a complicated way, which have not yet been fully elucidated.

A networks exhibited smoother surfaces than H networks, as shown in Figure 5 (the height dimensions



(a) H-4.3-35

(b) H-4.3-50



(c) H-4.3-65

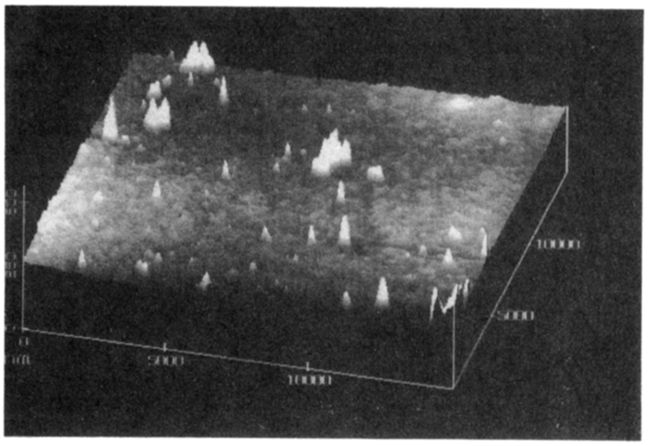
(d) A-4.3-50

Figure 8. AFM images of the surface of amphiphilic networks which are swollen in water.

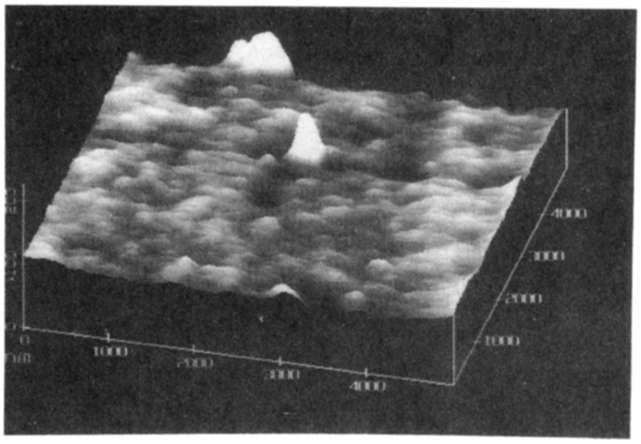
are more magnified than in Figure 4). Holes were not found for compositions up to 50 wt % PIB. At 65 wt % and 85 wt % of PIB (Figure 5e,f) holes can be seen which probably formed during solvent evaporation. The surface of A-4.3-85 is quite rough but not more so than that of H-4.3-85. Figures 6 and 7 show plots of surface roughness for different H and A networks. Evidently surface roughness varies depending on composition. However, sample preparation conditions (drying, extraction procedure, etc.) might also affect surface morphology. Network A-4.3-50 shows low surface roughness in both the unswollen and water-swollen states. The excellent biocompatibility, low protein adsorption, and low cell adhesion of A-4.3-50[6] may be due to low surface roughness.

Figures 8 and 9 show AFM images of H and A networks swollen in water or *n*-heptane. Care should be exercised when comparing these pictures because the height scales are not the same; by increasing the magnification of the swollen sample to 50 nm or by reducing the magnification of the dry sample to 1000 nm (i.e., changing the magnifications by the same factor), featureless images are obtained. The roughness of the surfaces of both H and A networks increases considerably by swelling in both water and *n*-heptane.

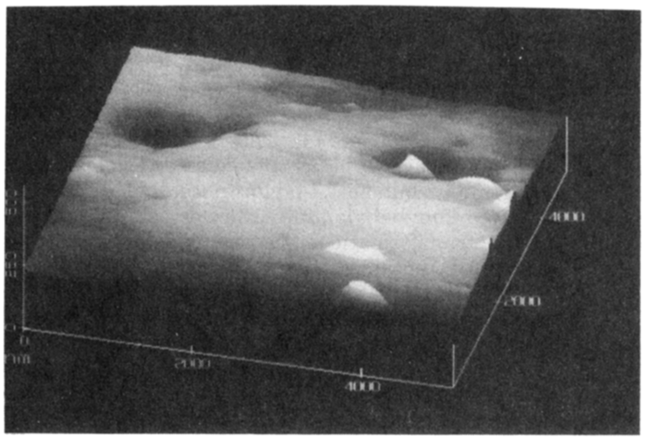
Dynamic contact angle data are shown in Table 1. Both advancing (θ_A) and receding (θ_R) contact angles decrease with increasing polyacrylate content in the networks. This observation is in good agreement with the increasing hydrophilic nature of the networks. θ_A's measured on wet samples are considerably lower than those measured on dry samples. The large contact angle hysteresis ($\Delta\theta = \theta_A - \theta_R$) suggests rapid surface reorganization with changing surface environment or surface heterogeneity. The large θ_A is due to hydrophobic, low surface free energy PIB domains on the surface in air, whereas θ_R reflects a large contribution from the high surface free energy of polyacrylic domains.[11] θ_A's are higher for the networks with higher molecular weight PIB at the same composition. Higher molecular weight PIB is expected to produce larger mesh sizes and consequently more mobile structures. Higher surface mobility enhances domain segregation and therefore the segregation of a nonpolar PIB chain at the surface which further increases θ_A. The contact angle data suggest that the surfaces of these amphiphilic networks are highly mobile, specifically that dry surfaces can rapidly reorganize upon exposure to water. These networks are able to adopt different surface conformations in different environments, so as



(a) A-4.3-35



(b) A-4.3-35



(c) H-4.3-50

Figure 9. AFM images of the surface of amphiphilic networks which are swollen in *n*-heptane.

to increase surface accommodation with the milieu and thereby minimize the total free energy of the system.

Conclusions

According to XPS C_{1s} spectra, hydrophobic segments preferentially exist on the surface rather than in the bulk of amphiphilic networks in vacuum or air; the O/C and N/C ratios were lower at the outer surfaces than in the bulk of the networks. The surface morphologies of amphiphilic networks of different compositions were investigated by AFM. The surface microroughness of A networks was lower than that of H networks at the same PIB content, suggesting superior antithrombogenic surfaces of the former. Surface roughness is greatly enhanced by swelling in both water or *n*-heptane, indicating surface heterogeneity. According to DCA measurements, dry predominantly hydrophobic surfaces rapidly rearrange to hydrophilic surfaces when immersed into water. The XPS data support the DCA data and suggest conformational reorganization at the surfaces.

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