Annealing and Reorganization of Sulfonated Polyethylene Films To Produce Surface-Modified Films of Varying Hydrophilicity

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Received December 3, 1990

The modification of organic polymer surfaces is a subject of theoretical and practical importance.[1-3] Recent studies have focused attention on factors responsible for and kinetics of reorganization of functional groups at the surface of oxidized hydrocarbon polymers and halogenated polymers.[4-6] These results and many prior studies of functionalized polymers indicate that annealing and reorganization lead to lower energy surfaces.[7] Often such studies have used a surface's water wettability as a probe of such effects. Here we describe studies of sulfonated polyethylenes which, in contrast, show an increase in water wettability on thermal reconstruction.

The general trend of functionalized polymers to reorganize to produce less polar surfaces reflects several factors as has been discussed by Whitesides.[4] The energetically favorable change to a lower surface free energy at a vacuum/polymer interface is the dominant factor responsible for reconstruction of high energy functionalized polymer surfaces. However, other factors such as the nature of the substrate polymer, entropic factors, and the identity of the reorganizing functional groups could affect the overall energy change and the outcome of any annealing experiment. The work described here shows that sulfonated polyethylene films reorganize at rates comparable to those of carboxyl-containing polyethylene films but in a manner such that a *more hydrophilic* surface is produced after annealing. This result is seen for a range of polyethylenes with varying amounts of sulfonation. It is not due to a detectable increase in the amount of sulfonic acid groups accessible to an azo dye titrant. Dyeing experiments and ESCA analysis show that annealing reduces the concentration of surface sulfonic acid groups. Conversion of these sulfonic acid groups into alkylammonium salts provided a means to control the eventual hydrophilicity of the product polymer.

Sulfonation of polyethylene films was accomplished by using various fuming sulfuric acid mixtures as sulfonating agents.[8,9] The free SO_3 concentration was estimated from density measurements and a standard table.[10] The presence of sulfonic acid groups in the product films was verified by ATR FT-IR spectroscopy. The extent of sulfonation varied with sulfonation time and with the nature of the polyethylene film. The extent of sulfonation was measured on the basis of the amount of para-methyl red which was attached to the surface by reactive dyeing. Contact angle measurements of the sulfonated polymers also showed lower contact angles with increasing sulfonation time (Table I). In a typical procedure the sulfonated film was prepared by immersing a polyethylene film[11] (ca. 3 × 3 cm) in 15% fuming sulfuric acid for 5 min at ca. 25 °C. The product film was then washed in a series of baths (5% SO_3/H_2SO_4; concentrated H_2SO_4, 50% H_2SO_4; water; and finally acetone) and dried in a vacuum at 25 °C. The product film from this procedure typically had a θ_a of ca. 63° (θ_Y of 58°) and contained ca. 5×10^{14} SO_3H groups/cm^2.[11] Contact angles were measured by using a Ramē-Hart goniometer equipped with an environmental chamber at 100% relative humidity. They were the average of 8–10 measurements on the same film and have an error of ±3°. Concentrations of SO_3H groups were measured by dyeing the film with an excess of para-methyl red for 12 h. Rinsing followed by exchange with excess Et_3N in ethanol produced a solution of methyl red that was analyzed as its protonated form by UV–visible spectroscopy. Films with lesser, varying amounts of SO_3H groups were prepared by reducing the sulfonation time (Table I).

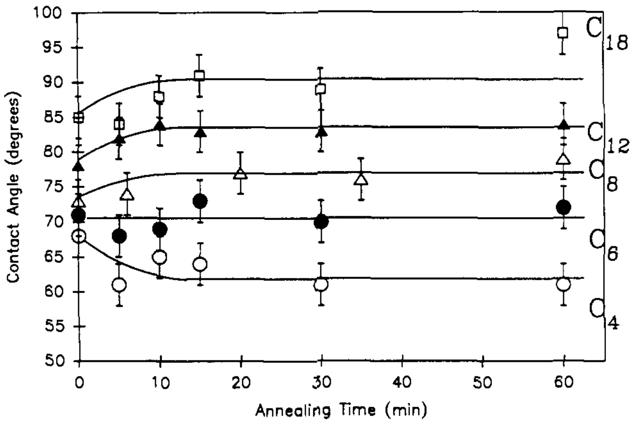

Figure 1. Reconstruction of PE-[$SO_3^-NH_3R^+$] at 70 °C in vacuum at various times with various R groups as measured by advancing water contact angles.

Heating any of the sulfonated films in a vacuum oven at 70 °C produced an annealed film, the hydrophilicity of which varied with annealing time. A typical variation in hydrophilicity would be a change in θ_a from 63° to 49° over a 1-h period. While separate sulfonation experiments yielded films whose initial θ_a and final θ_a varied by as much as 5°, every sulfonated film annealed to produce a more hydrophilic surface. More lightly sulfonated films had a higher initial and final θ_a. In contrast, the θ_a for a carboxylated film changed from 74° to 100° under the same conditions in accord with earlier reports.[2,3] The rate of change of θ_a with annealing time was similar for the PE-[SO_3H] or PE-[CO_2H] samples. Suspension of PE-[SO_3H] or PE-[CO_2H] films in refluxing 2-propanol also led to surface hydrophilicity changes in these films. In this case, the limiting value of θ_a for PE-[CO_2H] was 82° while the limiting value of θ_a for PE-[SO_3H] was 56°.

Substitution of other groups for H^+ in the sulfonated film showed that the hydrophilicity of the annealed film could be controlled. This was accomplished by treating the sulfonated polymer with an organic or aqueous solution of a primary amine. The products of this exchange had contact angles that varied depending on the alkyl group of the amine. In general, the value for θ_a increased as the alkyl group of the ammonium salt increased

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(11) The polyethylene used (Fortiflex J36-25-142) was obtained from Soltex Corp. and had a density of 0.936 g/cm^3 and a melt index of 0.25 g/10 min. Samples were washed in a Soxhlet apparatus for 24 h with hexane and then for 24 h with THF to remove processing additives or antioxidants. After washing in this way, the polyethylene had an advancing water contact angle θ_a of 111° (θ_r = 79°). The crystallinity of the sulfonated polyethylene as measured by IR spectroscopy (determined from A_{1472}/A_{1462} and A_{730}/A_{720} to be 59% and 48%, respectively) was the same before and after annealing) (ref 12). Carboxylated surfaces used in comparisons were derived from the same polymer films by using procedures describes in detail in the literature (ref 6).

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0002-7863/91/1513-1447$02.50/0

Table I. Hydrophilicity and Accessible Sulfonic Acid Groups in Sulfonated Polyethylene Films before and after Annealing[a]

sulfonation time,[b] min	annealing time, min: 0 $[SO_3H]$[c]	θ_a[d]	θ_r[d]	15 $[SO_3H]$[c]	θ_a[d]	θ_r[d]	60 $[SO_3H]$[c]	θ_a[d]	θ_r[d]
0.5	1.38×10^{14}	77	15	1.37×10^{14}	67	6	0.78×10^{14}	69	7
3.0	4.17×10^{14}	71	12	2.26×10^{14}	56	12	1.36×10^{14}	58	10
5.0	5.67×10^{14}	61	7	4.24×10^{14}	54	7	2.51×10^{14}	54	4

[a] Annealing was carried out in vacuum at 70 °C for 15-min or 60-min periods at a pressure of ca. 0.1 Torr. Annealing in air gave essentially the same results, but vacuum annealing was used to minimize the risk of autooxidation. Hydrophilicity was measured by using advancing water contact angles using doubly distilled water. [b] Sulfonations were carried out on commercial polyethylene films (cf. ref 11) according to the procedures described in the text. [c] Number of SO_3H groups/cm^2. [d] Degrees.

in size. More interesting was the behavior of films containing ammonium salts on annealing (Figure 1). As can be seen from these plots of θ_a versus annealing time, films with ammonium salts having longer organic groups annealed to form polyethylene-like surfaces while those having shorter chain alkylammonium salts annealed to form more hydrophilic surfaces.

Exchange of one alkylammonium salt for another indicated that these effects are reversible. For example, treatment of the octadecylammonium-containing film ($\theta_a = 81°$) with butylamine in ethanol for 1 h at 25 °C produced a film whose advancing contact angle after annealing in vacuum at 70 °C was 58° while treatment of a butylammonium film ($\theta_a = 62°$) with octadecylamine in ethanol for 1 h at 25 °C produced a film with $\theta_a = 85°$ after annealing.

There are a variety of possible explanations for the observed changes in hydrophilicity seen in the above experiments. First, it seems reasonable that the initial extent of sulfonation and advancing water contact angle both result from increasing amounts of surface sulfonation. Similarly, introduction of ammonium salts onto unannealed films produces a series of films whose contact angle varies in accord with the hydrophobicity of the introduced alkylammonium group. However, the explanation for the changes seen on annealing is less clear. Our experiments do however exclude some explanations. SEM and FT-IR measurements[11] before and after annealing show no change in the polymer's morphology though the SEM photographs showed that the surfaces were etched. The hysteresis seen in the contact angles (Table I) results, in part, because we are not dealing with smooth surfaces. All SO_3H-containing polymers had a decreased θ_a (water) after annealing. Receding contact angles were always low. The change in water contact angle roughly paralleled a decrease in the number of titratable SO_3H groups. The conclusion from the dyeing experiments that the $[SO_3H]_{surface}$ is diminished on annealing was confirmed by ESCA. ESCA showed that the area ratio for S/O/C was 0.19/1.34/1.00 initially and 0.10/0.45/1.00 after 60 min of annealing for a 5-min-sulfonated film. The change in the S/C ratio was approximately the same as noted in the dyeing experiment. The presence of sulfonated oligomers and the presence of other impurities seem unlikely explanations for the observed effects since similar changes were seen in vacuum and in refluxing solvent. Products of oxidative chain cleavage or other impurities should have been extracted by refluxing 2-propanol. An explanation for the decrease in θ_a invoking migration of SO_3H groups to the surface is also precluded by the *decrease* in $[SO_3H]$. One possible explanation for the observed *increase* in water wettability and the *decrease* in amount of sulfonic acid groups would be a morphological change in which the two-dimensional distribution of groups was altered. A broader distribution of sulfonic acid groups would plausibly produce a more hydrophilic surface even if the total number of sulfonic acid groups decreased. Such a change could occur if the initial sulfonated product contained areas with extensive sulfonation and areas with little sulfonation. Annealing could then have redistributed groups laterally in addition to redistribution of SO_3H groups into the subsurface. In qualitative agreement with this notion, a set of more heavily sulfonated films from one sulfonation experiment (2-, 3-, or 5-min sulfonation) all annealed in 1 h to form films with similar θ_a (56°, 58°, and 54°) and similar $[SO_3H]$ (0.9, 1.6, and 1.9 $\times 10^{14}$ groups/cm^2).

In conclusion, introduction of very polar sulfonic acid groups and salts onto surfaces of medium-density polyethylene films produces surfaces that do not thermally reorganize to a more hydrophobic surface unless they have been modified so as to contain a long-chain hydrocarbon group. Instead, these surfaces' hydrophilicity is retained or actually increased. This might be due to a change in the uniformity of distribution of sulfonic acid groups. Regardless of the explanation, these studies show that a judicious choice of functional groups and substrate polymer can be used to produce functionalized polymer films whose hydrophilicity can be controlled through synthesis.

Acknowledgment. Support of this research by the National Science Foundation (DMR 8917810) and the Texas Advanced Technology Program is gratefully acknowledged.

Nitrogen-15-Labeled Oligodeoxynucleotides. 2. Solvent Isotope Effects on the Chemical Shift of the Adenine N1 in an A·T Base Pair

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Received August 20, 1990

The ^{15}N chemical shift potentially is a valuable monitor of the H-bonding involved in nucleic acid–nucleic acid, protein–nucleic acid, and drug–nucleic acid interactions.[1,2] Experiments at both the monomer and polymer levels have succeeded in demonstrating chemical shift changes consistent with H-bonding between the nucleic acid bases.[3-7] There is, however, no direct evidence that H-bonding is the cause of the observed changes. In ^1H NMR studies using uniformly ^{15}N enriched tRNA, the low-field (H-bonded) ^{15}N–H resonances were observed as doublets only; there was no evidence of additional coupling to the ^{15}N acceptor in the partner base.[5] Similarly, in a hexameric DNA fragment containing a [1-^{15}N]adenine residue, d[CGT($^{15}N^1$)ACG], we observed an upfield ^{15}N chemical shift change of ~2.6 ppm in the duplex, but nevertheless could not detect coupling between the adenine $^{15}N1$ and the thymine H3 in either the ^{15}N or ^1H NMR.[7] We now report, using this same molecule in mixtures of D_2O and H_2O, evidence of a through-space interaction between these atoms.

A comparison of the ^{15}N NMR spectra of d[CGT($^{15}N^1$)ACG] in H_2O (95%) versus D_2O, using either broad-band or selective

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