(13) Note added in proof: Experimental results pertinent to and supportive of the conclusions drawn here for poly(phenylmethylsilylene) are found in: (a) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 2037. (b) Harrah, L. A.; Zeigler, J. M. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987; p 482. Also, another conformational analysis of poly(phenylmethylsilylene) has recently been published: Sundararajan, P. R. *Macromolecules* **1988**, *21*, 1256.

Structure and Surface Energy Characteristics of a Series of Pseudo-Perfluoroalkyl Polysiloxanes

Marca M. Doeff*,[†] and Elek Lindner[‡]

Naval Ocean Systems Center, Code 521, San Diego, California 92152, and Computer Sciences Corporation, 4045 Hancock Street, San Diego, California 92110.

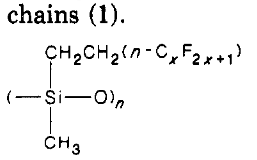
Received September 6, 1988; Revised Manuscript Received December 27, 1988

ABSTRACT: A series of pseudo-perfluoroalkyl-substituted polysiloxanes were synthesized and characterized by contact-angle measurements and polarization specular reflectance infrared spectroscopy. It was found that the dispersive surface energies for the siloxanes are comparable to the values found for carbon-based polymers such as poly(1*H*,1*H*-perfluorooctyl acrylate) and poly(1*H*,1*H*-perfluorooctyl methacrylate) and only slightly higher than that for adsorbed monolayers of perfluorolauric acid, the substance with the lowest known dispersion energy. This result as well as polarization specular reflectance infrared spectra indicates that the side chains in the siloxane polymers are oriented so that the perfluoroalkyl groups are approximately parallel to one another and normal to the substrate surface. Also, several of the free polymers have a fibrous appearance, and polarized light microscopy shows a high degree of orientation in some of the thicker fibers. However, X-ray diffraction does not indicate crystallinity. There is no straightforward variation of dispersive surface energy with the length of the perfluoroalkyl side chains in the polysiloxanes as there is in the carbon-based materials.

Introduction

Low surface energy polymer coatings have many characteristics that are useful industrially; for example, they may be used as mold release coatings in manufacturing processes. Poly(tetrafluoroethylene), widely used as a "nonstick" coating, has a dispersive surface energy of 18.5 dyn/cm.[1] Monolayers of perfluorolauric acid adsorbed onto platinum have an energy of about 10 dyn/cm,[2] the lowest value known. Various polymeric materials have been discovered that have dispersion energies nearly as low as that of the perfluoroacid monolayers. These polymers generally have a carbon-based backbone and long perfluoroalkyl side chains in a comblike arrangement. Extensive studies have been made on the effect of side-chain length, crystallizability, and type of backbone[3,4] upon the dispersion energy of these macromolecules. Less information is available for comb polymers that do not have a carbon-based backbone, although there have been a few reports on siloxanes.[5,6]

We are studying the variation of dispersive surface energy as a function of type of polymer backbone and length of perfluoroalkyl chain in "comb" polymers. The present paper concerns siloxane polymers substituted with pseudo-perfluoroalkyl chains (1).



$$\overset{\displaystyle CH_2CH_2(n\text{-}C_xF_{2x+1})}{\underset{\displaystyle CH_3}{(-Si-O)_n}}$$

1, x = 3, 6, 7, 8, 10

Experimental Section

The pseudo-perfluoroalkyl-substituted polysiloxanes were made by reacting poly(methylhydrosiloxane) (MW = 2270, Alfa Products, Danvers, MA) with the appropriate perfluoroalkyl-substituted 1-olefin in a modification of a method described by Rim et al.[7] In this procedure, weighed amounts of the polysiloxane starting material, the 1-olefin, and once-distilled toluene were added to a three-neck round-bottom flask fitted with a water-cooled condensor, an argon-gas purge, and a rubber septum cap. The amounts were chosen so that the olefin was in about 15% molar excess over poly(methylhydrosiloxane) and the total volume was about 20–30 mL. Argon gas was bubbled through the mixture at room temperature for 15 min to remove adventitious oxygen. The argon gas was then allowed to flow over the reaction mixture as it was heated to 60 °C and stirred. At this point, 2 mL of a solution of about 5 mg of H_2PtCl_6 in ethanol was added quickly by syringe to the reaction mixture. Larger amounts of catalyst did not give better results and caused difficulty in purification of product. After 3 days of reaction time, the mixture was filtered hot through a glass frit, and the toluene and excess olefin were distilled from the filtrate under vacuum. The resulting opaque white polymers were allowed to air dry for several days to remove remaining solvent. The complete absence of the Si–H stretch at 2171 cm^{-1} in the IR spectrum of these materials confirmed complete reaction of the material.

3,3,4,4,5,5,5-Heptafluoro-1-pentene used in the above synthesis was supplied by SCM (Gainesville, FL). The other 1-olefins were made by dehydro-iodination of the corresponding 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluoroalkanes, which were purchased from SCM or made by reacting ethylene gas with a perfluoroalkyl iodide obtained from SCM.[8]

Glass slides coated with the perfluoroalkyl-substituted polysiloxanes were used for the contact-angle measurements and for the FT-IR spectra. Duplicate samples were made for each polymer. The polymers were dissolved in mixtures of Freon 113 and hexane (approximately 1:100 w/w) and brushed onto clean glass slides. This process was repeated until coverage was complete, as judged by visual inspection. Then, slides were placed in an oven set at 60 °C for 24 h. After this time, most of the coatings had dried to a hard, translucent finish. Coating thicknesses are estimated to be about 4 μm, on the basis of the specular reflectance IR spectra.[9]

In addition to the samples coated with the perfluoroalkyl-substituted siloxanes, two slides were coated with poly(hydro-

---

[†] Computer Sciences Corp.

[‡] Naval Ocean Systems Center.

0024-9297/89/2222-2951$01.50/0

Table I
Surface Tensions (γ_L) of *n*-Alkanes Used To Calculate Dispersive Surface Energies of 1

n-alkane	surface tension,[a] dyn/cm	*n*-alkane	surface tension,[a] dyn/cm
decane	23.9	tetradecane	26.7
dodecane	25.4	hexadecane	27.6
tridecane	25.9		

[a] Values of γ_L correspond to γ_2 in Table III of ref 21. The anisotropic dispersion force contribution was included in all calculations used herein because of the anisotropy of the substituted polysiloxane system.

methylsiloxane). In these cases, neat liquid polymer was painted onto the slides, which were then placed in a 60 °C oven for 24 h. The coatings were clear and slightly soft but no longer liquid. The infrared spectra of the polymer-coated slides were qualitatively similar to that of the neat liquid polymer, indicating that no chemical reaction took place under this treatment.

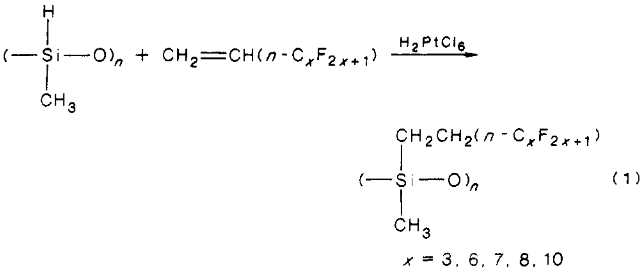
Contact-angle measurements were made on 10-μL sessile drops of *n*-decane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-hexadecane on the polymer-coated slides, by using a Rame-Hart Model A-100 contact-angle goniometer. Table I lists the surface energies of the *n*-alkanes used in this analysis. Measurements were made on three drops of each liquid, and the values averaged for use in calculations. Agreement was usually within 1° or 2°. Dispersion energies calculated from measurements for duplicate samples did not differ by more than 3% and in most cases varied less than that.

Fourier transform infrared spectra of the polymers coated on glass slides were obtained with a Bio-Rad FTS-60 Fourier transform infrared spectrophotometer, using a TGS detector. Spectra-Tech FT30 specular reflectance and FT80 specular reflectance units were used; the latter was equipped with a light polarizer consisting of an aluminum wire grid on a zinc selenide substrate. Ten scans with 8-cm^{-1} resolution were co-added for each sample spectrum in the transmittance mode. Background spectra were obtained from a silvered mirror. The reflection spectra were separated from the extinction coefficient spectra by applying the Bio-Rad Nk 1.10 software routine.[10] The resulting *k* or extinction coefficient spectra are in the absorbance mode and are similar in appearance to spectra taken by conventional nonreflectance techniques. Spectra were also taken of uncoated glass slides for comparison.

Polymers were visually inspected under a Zeiss polarized light microscope. Samples of poly(methyl(ethyleneperfluorodecyl)siloxane) and poly(methyl(ethyleneperfluorooctyl)siloxane) were coated with palladium metal, by using an Anatech Hummer Junior sputterer, and inspected under an ISI Super-IIIA electron microscope at magnifications ranging from 25 to 10 000. The X-ray diffraction experiment on poly(methyl(ethyleneperfluorooctyl)siloxane) was performed on a General Electric XRD5 instrument, using Cu Kα radiation. The samples were scanned at 4°/minute at 40 kV and 20 mA, with the beam slit at 1° and the detector slit at 0.2°. Both the solid polymer and coated glass slides were inspected.

Results and Discussion

The pseudo-perfluoroalkyl-substituted polysiloxanes were prepared by a hydrosilation reaction of a 1-olefin with poly(hydromethylsiloxane) (eq 1). The method of modifying a macromolecule under mild conditions rather than polymerizing an appropriate monomer ensures that backbone chain length remains constant within the series, so that any differences in properties may be attributed only to the change in side-chain length.



$$(\text{—}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{Si}}\text{—O})_n + CH_2{=}CH(n\text{-}C_xF_{2x+1}) \xrightarrow{H_2PtCl_6} (\text{—}\overset{\displaystyle CH_2CH_2(n\text{-}C_xF_{2x+1})}{\underset{\displaystyle CH_3}{Si}}\text{—O})_n \qquad (1)$$

$x = 3, 6, 7, 8, 10$

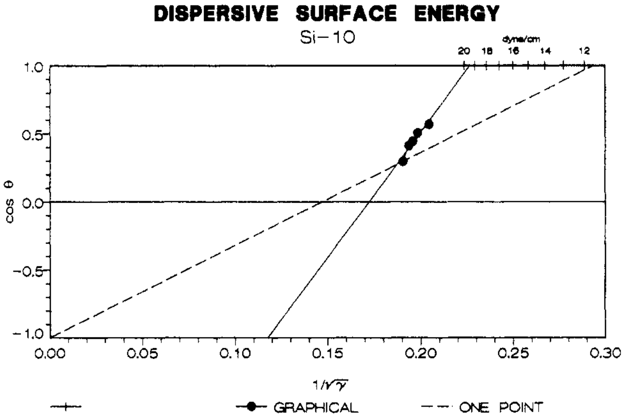


Figure 1. Contact-angle data for *n*-alkanes on a sample coated with **1**, $x = 10$ (poly(methyl(ethyleneperfluorodecyl)siloxane)). Equation 2 was used to analyze the data. The slope of the line is equal to $2(\gamma^D{}_s)^{1/2}$.

The dispersive surface energy measurements for the perfluoroalkyl-substituted polymers coated onto glass slides were obtained from contact-angle measurements made with a series of *n*-alkanes on the sample surfaces and used in the Girafalco–Good–Fowkes–Young equation[4,11-13] (eq 2).

$$\cos\theta = -1 + 2(\gamma^D{}_s)^{1/2}\gamma_L{}^{-1/2} \qquad (2)$$

θ = contact angle

$\gamma^D{}_s$ = dispersive surface energy of solid

γ_L = surface tension of test liquid

Both a graphical method, using several data points, and a single-point (hexadecane) method were used to analyze the data. Figure 1 shows an example of the analysis. The latter method probably gives more accurate dispersion energy values than the former, because surface solubility effects increase for smaller alkanes but are negligible for hexadecane,[4] causing an artifical steepening of the slope. This phenomenon explains the discrepancies illustrated in Figure 1. From this point on, we will refer to the values calculated from a single point only.

It is known that polysiloxanes generally have lower dispersive surface energies than similar carbon-based polymers (poly(dimethylsiloxane) = 24 dyn/cm,[14] poly(methyl methacrylate) = 31.3 dyn/cm).[1] It might seem to follow that a siloxane polymer with perfluoroalkyl side chains would have a lower surface energy than the corresponding carbon-based comb polymer. However, potential differences in degree of crystallinity[15] and orientation of the side chains, which are constrained by the polymer backbone, can be expected to affect the surface structure and the surface tension in a manner that is not easily predicted. The dispersion energy values for the polysiloxanes listed in Table II approach the values found for poly(1*H*,1*H*-perfluorooctylmethacrylate) (11.2 dyn/cm)[16,17] and perfluorolauric acid monolayers. Both types of polymers must have surfaces composed primarily of CF_3 groups, implying that the perfluoroalkyl groups are aligned nearly parallel to one another and perpendicular to the surface, as in the ideal case of the acid monolayers.[18]

It has been found that surface tension decreases as perfluoroalkyl chain length increases from C_4 to C_{12}, for a series of adsorbed perfluoro acid monolayers,[18] as well as in poly(1*H*,1*H*-perfluoroalkyl acrylates) and poly-

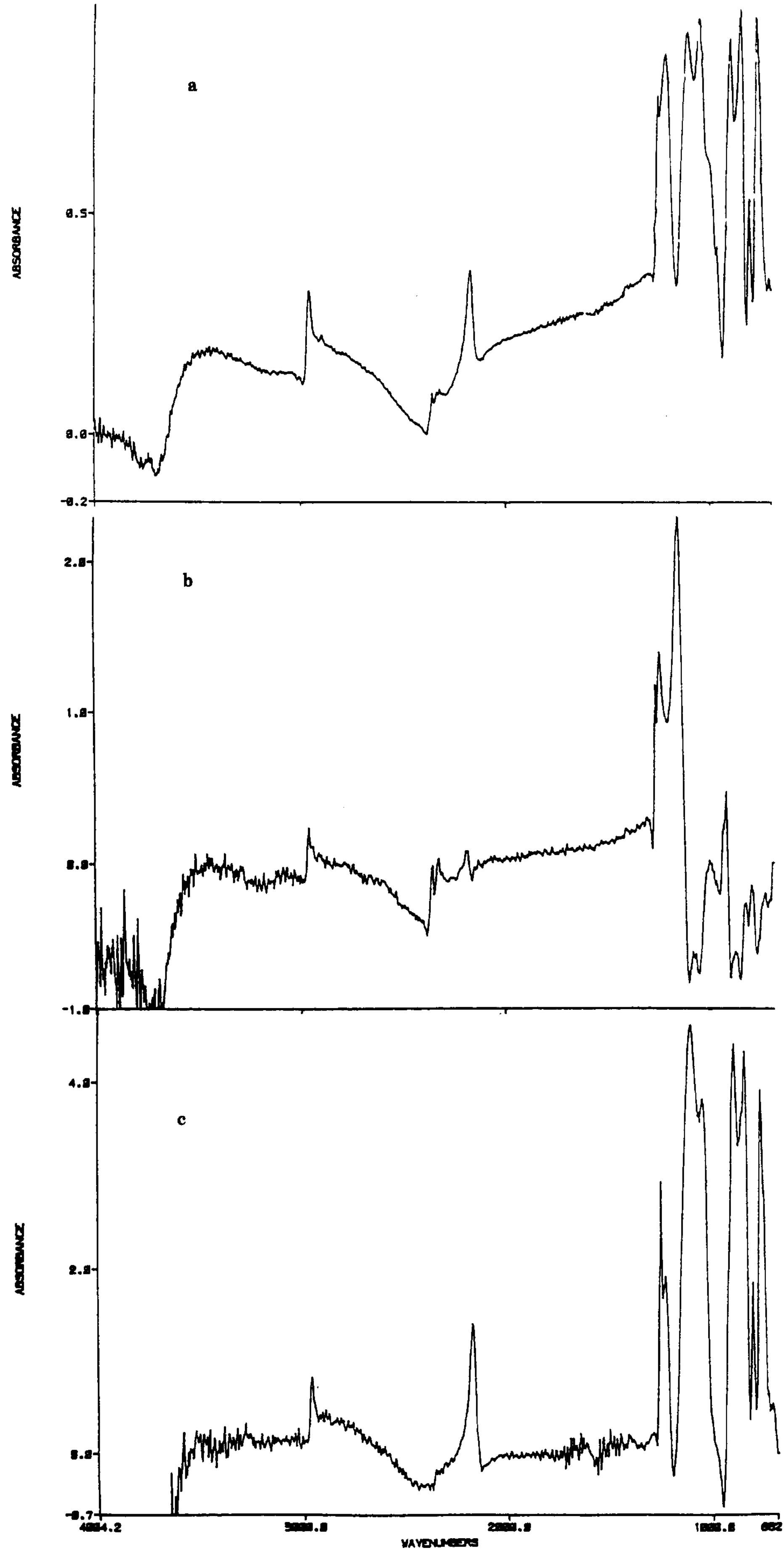


Figure 2. (a) Specular reflectance FT-IR spectrum of a glass slide coated with poly(hydromethylsiloxane), unpolarized light. Note the band at 2175 cm^{-1}, which is attributed to Si–H stretching. (b) Specular reflectance FT-IR spectrum of the same sample, light polarized at 0°. The band at 2175 cm^{-1} is nearly absent. (c) Specular reflectance FT-IR spectrum of the poly(hydromethylsiloxane) sample, light polarized at 90°. The band at 2175 cm^{-1} is now apparent.

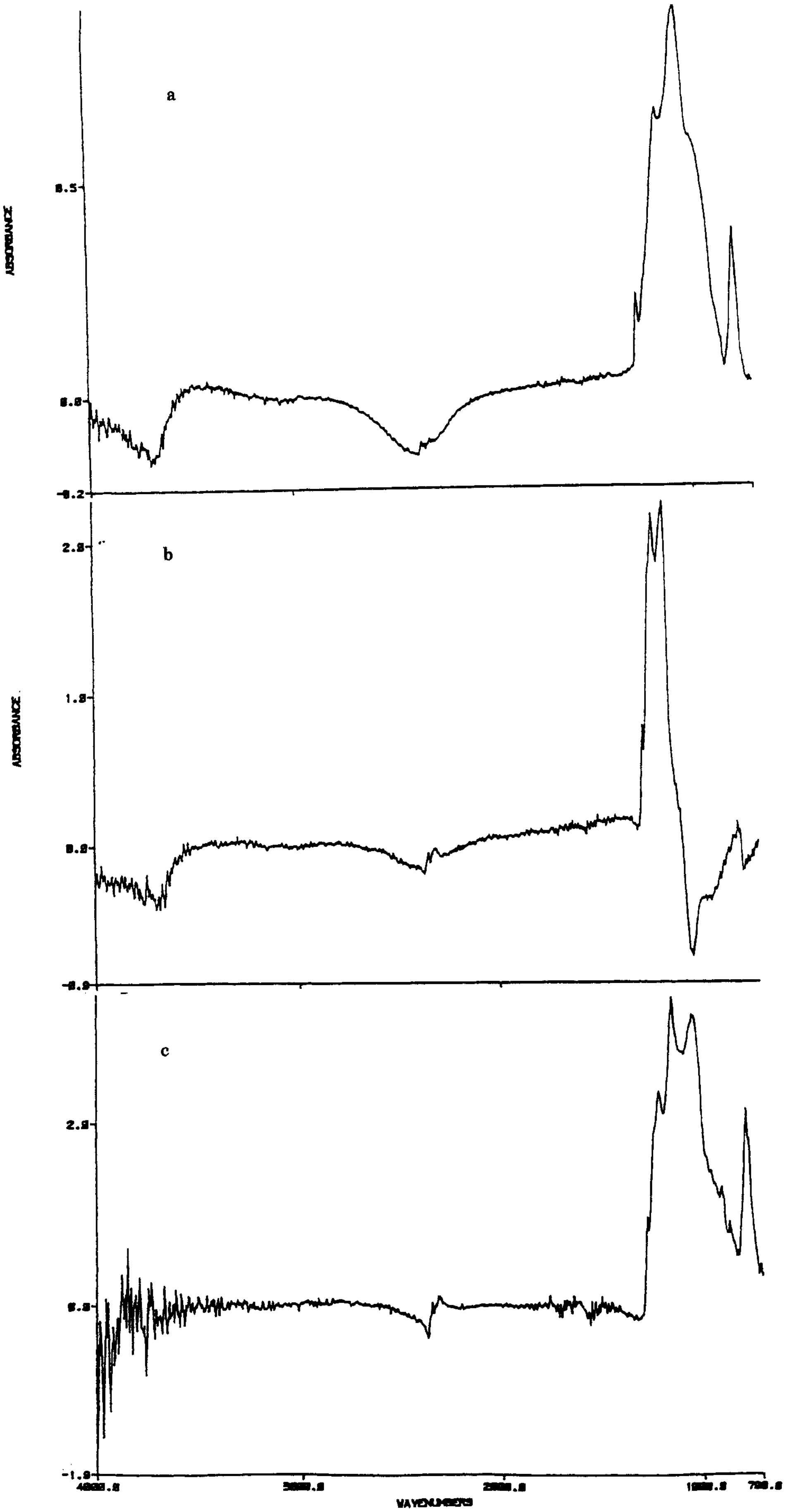


Figure 3. (a) Specular reflectance FT-IR spectrum of a glass slide coated with poly(methyl(ethyleneperfluorodecyl)siloxane), unpolarized light. (b) Specular reflectance FT-IR spectrum of the same sample, light polarized at 0°. (c) Specular reflectance spectrum of the poly(methyl(ethyleneperfluorodecyl)siloxane), light polarized at 90°. Note the differences in band shapes between b and c.

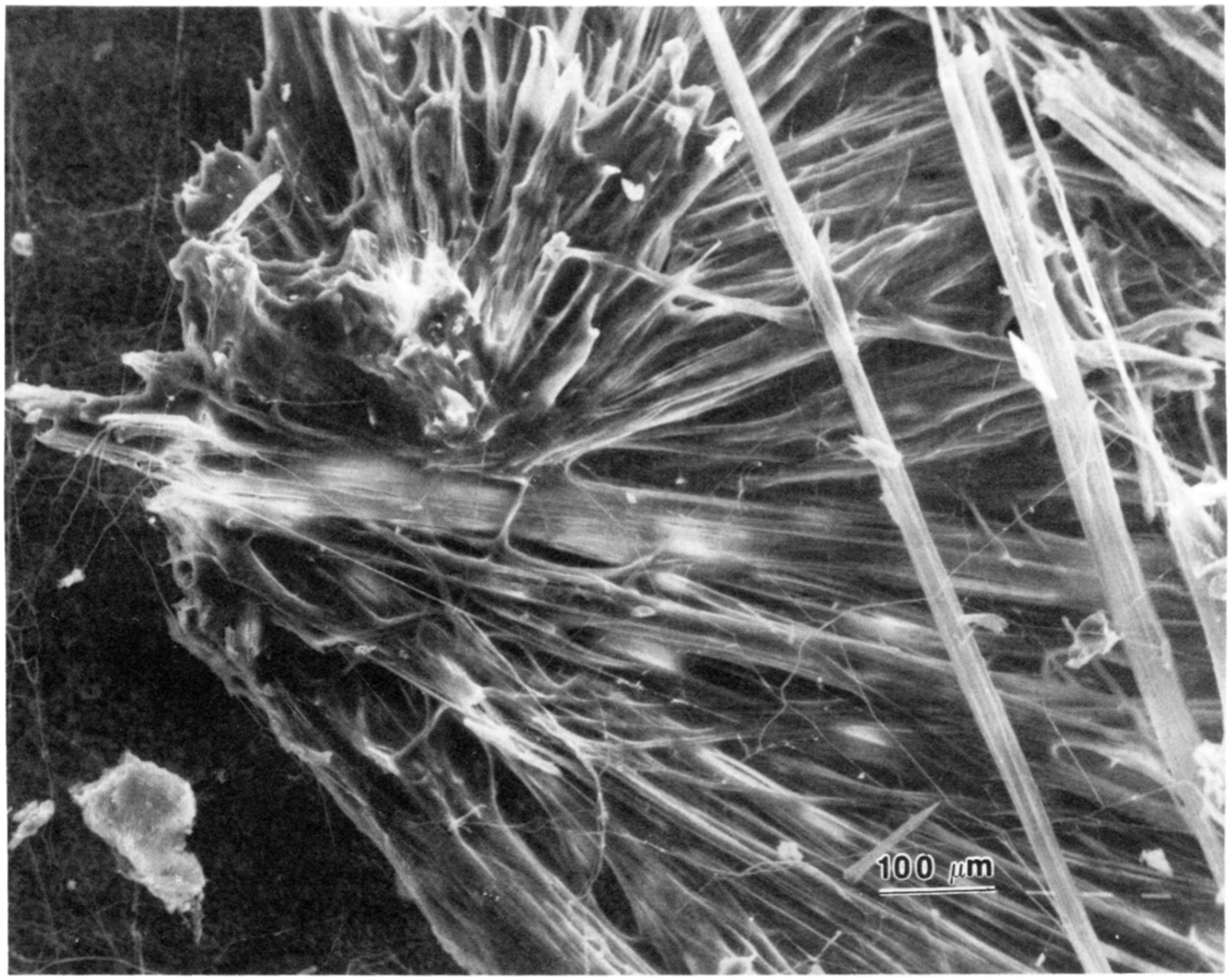


Figure 4. Electron microscopy photograph of poly(methyl(ethyleneperfluorooctyl)siloxane). Note the thick fibers (about 20 µm) on the right-hand side of the photograph, as well as much thinner fibers interspersed throughout the sample.

Table II
Dispersive Surface Energies of the Pseudo-Perfluoroalkyl-Substituted Polysiloxanes

compound	dispersive surface energies, dyn/cm single point	graphical
1, x =		
3	14.5	18.0
6	11.9	19.1
7	12.5	19.0
8	18.3	21.8
10	11.5	19.5
poly(hydromethylsiloxane)	22.6	23.8

(1*H*,1*H*-perfluoroalkyl methacrylates)[3,4] (C_4 and C_8). No trend is seen in the polysiloxanes. In the perfluoro acids, the longer chains pack more efficiently due to van der Waals forces,[3,18] leading to a lower surface energy. This may happen in the carbon-based polymers as well, although the backbone acts as a constraint upon the perfluoroalkyl groups, leading to an arrangement that falls short of the ideal. It is known that polysiloxanes have a more flexible backbone than carbon-based polymers.[7] This means that there is less constraint imposed upon the configuration of the side chains, leading to less dependence on chain length. The very short side chain in poly(methyl(ethyleneperfluoropropyl)siloxane) does not adequately shield the hydrocarbon portion from the surface, leading to a slightly higher surface tension measurement. We cannot easily explain the anomalously high measurement for the perfluorooctyl species.

The contact-angle measurements strongly suggest that the polysiloxane coatings are oriented on the surface of the slides so that the perfluoroalkyl chains are approximately parallel to one another. It should be noted here that no conscious attempt was made to orient the coatings when they were applied. To determine whether such orientation is indeed present, specular reflectance infrared spectra were taken of all the coated slides, both with unpolarized light and with light polarized at 0° (parallel to the sample surface) and 90° (normal to the sample surface). Typical spectra are shown in Figures 2 and 3. The substituted polysiloxanes gave nearly identical spectra. IR spectra taken by using this technique were qualitatively similar to the conventional IR spectra of the polymers. The primary feature in all cases is a broad band with many maxima centered at about 1160 cm^{-1}, which can be attributed to several vibrational modes, such as C–F stretching and Si–O–Si stretching.

When infrared light is polarized, the intensity of the absorption band is dependent upon the angle between the transition moment of the vibration and the electric field vector of the incident beam, as is shown in eq 3.[19] If a

$$A = \log I_0/I(\vec{M}\cdot\vec{E})^2 \qquad (3)$$

$\vec{M}$ = transition moment vector

$\vec{E}$ = electric field vector

polymer is completely randomly oriented on the surface of the sample, the infrared spectra with light polarized at

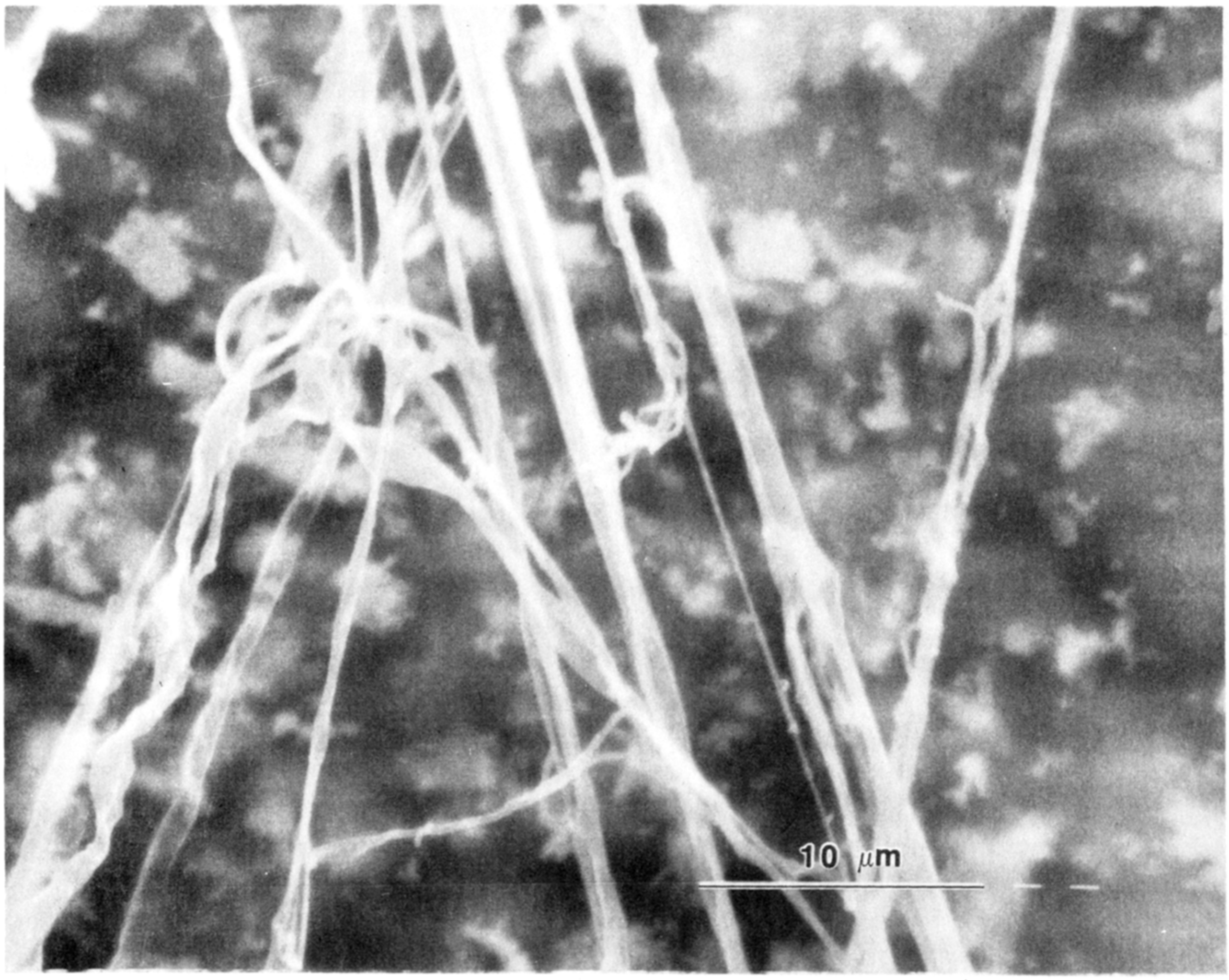


Figure 5. Electron microscopy photograph of poly(methyl(ethyleneperfluorodecyl)siloxane). Several long strands several micrometers in diameter are shown.

0° and 90° will be identical. If there is orientation, the intensity of some of the IR bands will differ when the angle of polarization is changed, and the degree of difference will depend upon the amount of order in the polymer and the angles at which the vibrations occur. All of the substituted polysiloxanes, as well as the adsorbed poly(hydromethylsiloxane) sample, have infrared spectra that are significantly different at 0° than at 90°. For adsorbed poly(hydromethylsiloxane) the Si–H band at 2175 cm^{-1} is strong in the 90° spectrum but nearly absent in the 0° case. This indicates that the Si–H bonds of this sample are oriented nearly normal to the surface. Due to the complexities of the substituted polysiloxane spectra, a detailed interpretation of the surface structure is not possible. However, the fact that significant changes in the band shape at 1175 cm^{-1} are seen in all of the cases, indicate strongly that there is orientation at the surface.

The free polysiloxanes with side chains of length 3 and 6 are translucent solids with an amorphous appearance. In contrast, the free polymers with side chains of length 7, 8, and 10 spontaneously form fibers so that they resemble glass wool when pure. To investigate this, the free perfluorooctyl- and perfluorodecylsiloxanes were inspected with an electron microscope and photographs taken. Figures 4 and 5 show typical results. Long fibers of various widths were seen at magnifications ranging from 25 to 10000, and the diameters could be estimated to range from 20 μm to less than 1 μm. Polarized light microscopy on the perfluorodecylsiloxane shows a high degree of orientation in some of the thicker fibers. However, X-ray diffraction experiments both on the free perfluorooctylsiloxane species and on coated glass slides do not indicate that this material is crystalline. The free polymers appear to be amorphous, and orientation in the coated samples does not result from crystallinity. In this regard, they are similar to poly(1*H*,1*H*-perfluorooctyl acrylate) and poly(1*H*,1*H*-perfluorooctyl methacrylate), which are also oriented when coated onto a surface but are not crystalline materials under normal conditions.[20]

Conclusions

It has been found that the perfluoroalkyl-substituted siloxanes have extremely low dispersive surface energies, comparable to those found for similar carbon-based polymers. Unlike the latter, however, the polysiloxanes show almost no dependence of surface energy upon side-chain length. Contact-angle measurements and polarization specular reflectance infrared spectra indicate that these polymers are at least partially oriented in such a way that the perfluoroalkyl side chains are approximately normal to the surface, and the surface is comprised of CF_3 groups. Some of the polysiloxanes spontaneously form long fibers of various widths when they are in a free state, appearing crystalline. Although polarized light microscopy shows a high degree of orientation in some of the thicker fibers, X-ray diffraction did not indicate crystallinity.

Acknowledgment. This work was funded by the FY 87-88 independent research program, Office of Chief of

Macromolecules 1989, *22*, 2957–2961 **2957**

Naval Research, NOSC Project No. 521-ZT75. We thank Carol Dooley for helpful discussion.

Registry No. Decane, 124-18-5; dodecane, 112-40-3; tridecane, 629-50-5; tetradecane, 629-59-4; hexadecane, 544-76-3.

References and Notes

(1) Dann, J. R. *J. Colloid Interface Sci.* **1970**, *32*, 302.
(2) See ref 1. Older references report this value as 6 dyn/cm but were calculated differently. For the sake of consistency the value obtained from the Girafalco–Good–Fowkes–Young equation is used here, as are all of the other surface energies reported herein.
(3) Pittman, A. G.; Sharp, D. L.; Ludwig, B. A. *J. Polym. Sci., Part A-1* **1968**, *6*, 1729.
(4) Johnson, R. E.; Dettre, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 48.
(5) Pittman, A. G.; Wasley, W. L. *Am. Dyest. Rep.* **1967**, *23*.
(6) Bascom, W. D. *NRL Report AD-683-661*, 1968.
(7) Rim, P. B.; Rasoul, H. A. A.; Hurley, S. M.; Orler, E. B.; Scholsky, K. M. *Macromolecules* **1987**, *20*, 208.
(8) Knell, M. U.S. Patent 4,058,873, 1977.
(9) Griffiths, W. *Fourier Transform Infrared Spectroscopy*; Wiley: New York, 1986; p 189.
(10) Krishnan, K. *FTS/IR Notes-BioRad, Digilab Division*, 1987, No. 51.
(11) Fowkes, F. M. *Adv. Chem. Ser.* **1964**, *43*, 99.
(12) Fowkes, F. M. *J. Phys. Chem.* **1962**, *66*, 382.
(13) Girafalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904.
(14) Lee, L.-H. *J. Adhes.* **1972**, *4*, 39.
(15) Roitman, J. N.; Pittman, A. G. *J. Polym. Sci., Polym. Lett.* **1972**, *10*, 499.
(16) Ramharack, R.; Nguyen, T. H. *J. Polym. Sci., Polym. Lett.* **1987**, *25*, 93.
(17) Bernett, M. K.; Zisman, W. A. *J. Phys. Chem.* **1962**, *68*, 1207.
(18) Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1954**, *58*, 236.
(19) Jasse, B.; Koenig, L. *J. Macromol. Sci.-Rev. Macromol. Chem.* **1979**, *C(17)1*, 61.
(20) Bovey, F. A.; Abere, J. F.; Rathmann, G. B.; Sandberg, C. L. *J. Polym. Sci.* **1955**, *15*, 520.
(21) Fowkes, F. M. *J. Phys. Chem.* **1980**, *84*, 510.

Formation of Hydroxyl Groups in Plasma-Polymerized *N*-Vinyl-2-pyrrolidone by Reduction with Sodium Borohydride

Dingsheng Yu[1] and Roger E. Marchant*

Department of Macromolecular Science and Department of Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 10, 1988*

ABSTRACT: Reduction of carbonyl to hydroxyl groups in plasma-polymerized *N*-vinyl-2-pyrrolidone (PPNVP) has been accomplished by using an aqueous sodium borohydride solution. Quantitative estimates of the hydroxyl content, determined from IR spectroscopy, indicated that the interfacial reduction of PPNVP films (approximately 1.5 μm thick) increased the hydroxyl content in the bulk polymer by up to 2.3 mmol/g. This was increased further by reducing PPNVP in the form of a suspension rather than as a film. The IR analysis, based on poly(vinyl alcohol) and 1-hexadecanol reference compounds, indicated that secondary alcohol was greater than 90% of the total hydroxyl in the reduced polymer films.

Introduction

The composition and structure of solid polymer surfaces dominate such properties as wettability,[2-4] adhesion,[3-5] friction,[3,4] permeability,[6] and biocompatibility.[7,8] Consequently, procedures for the surface modification of materials to improve interfacial properties are of considerable technological importance. One approach has been the use of plasma polymerization,[9,10] also referred to as glow discharge polymerization.

Plasma-polymerized films can be prepared with a wide range of compositions[10] and surface energies[10,11] through the choice of monomer and discharge reaction conditions. The deposition is largely independent of the substrate materials and is surface specific, so that a polymer (or other material) can be modified with little effect to its bulk properties. While plasma polymerization does have several attractive advantages over other methods of surface modification, there is a significant lack of chemical control over the polymer product. Reactions in the low-temperature plasmas are dominated by electron impact events such as ionization and dissociation, with active species reacting and recombining in the plasma and at the substrate surface. Because of the high energies involved in the process, this technique does not provide films with well-defined structures and specific functional groups.[12] Plasma-polymerized films prepared from monomers with oxygen or nitrogen functional groups invariably are polyfunctional, cross-linked, heterogeneous polymers.

Nevertheless, the objective of our studies has been to prepare plasma-polymerized films with a well-defined functional group that could serve as a reactive site for further modification. The common approaches for introducing specific functional groups into plasma polymers have been to vary the monomer and discharge conditions[13] or to use or include a gas such as CO$_2$[14] or NH$_3$,[15] which tend to increase carboxyl and amine groups, respectively. However, these reactions do not normally proceed to high yield with respect to a specific functional group. Nakayama et al.[15] have reported that primary amine in NH$_3$ plasma treated[16] polystyrene was 15–20% of total nitrogen content.

A novel alternative approach to functionalize a plasma-polymerized material is to take advantage of the functional group that is easily generated in the process: carbonyl groups. Plasma polymers derived from oxygen-containing monomers are invariably rich in carbonyl, regardless of the initial monomer structure. Thus, if a polymer or nonorganic was surface modified by plasma polymerization, carbonyl groups in the modified layer could then be derivitized to introduce a desired functional group. The major difficulty of this approach is associated with the very poor solubility of cross-linked plasma polymers in organic solvents. Derivitization has to be accom-

---

* To whom correspondence should be addressed.

0024-9297/89/2222-2957$01.50/0