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Synthesis of a Two-Dimensional Array of Organic Functional Groups: Surface-Selective Modification of Poly(vinylidene fluoride)

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ABSTRACT: An autoinhibitive surface modification reaction of poly(vinylidene fluoride) has been developed and assayed for surface selectivity. Phase-transfer-catalyzed dehydrofluorination using aqueous sodium hydroxide and tetrabutylammonium bromide produces an eliminated surface. Contact angle, ESCA, ATR IR, gravimetric, UV–vis, and SEM analyses indicate a mild, surface-selective reaction. Estimates of reaction depth are ~10 Å or less. The basis for the surface selectivity of this reaction is the product inhibition of the phase transport step.

Introduction

The chemical environment of reactive portions of organic molecules (functional groups) is markedly affected by the state of the organic material. Functional group environments in gases, liquids, and solids have obvious differences. In solution (the condition under which most organic reactions are carried out), functional groups are surrounded by solvent molecules. Forces due to solvation are often responsible for the outcomes and rates of chemical reactions. Solution organic chemistry has developed to an advanced stage.

The extent to which this body of knowledge can be applied to functional groups on polymer surfaces is not obvious. The chemical environment of surface functional groups is certainly different: if the solid polymer is placed in a nonswelling liquid, the environment of the surface functional groups is that of a solid in one direction and that of a solution in the other. Forces due to solvation are attenuated. If the solid is placed in contact with a vapor, its environment is half solid-like, half gas-like. Geometrical constraints on functional groups confined to two dimensions should inhibit reactivity: organic chemistry requires three dimensions. Surface physics should perturb reactivity as well: polymers tend to concentrate nonpolar functionality at their surfaces to minimize surface energy;[1-4] hence surface reactions with polar transition states may have especially high activation barriers.

To study the organic chemistry of surface-confined polymer functional groups, particularly with regard to how their two-dimensional environment affects reactivity, refined methods for the introduction of polar functionality onto chemically resistant nonpolar solid organic polymers must be developed. The requisite substrate for approaching this objective is a two-dimensional array of versatile organic functional groups covalently attached to a polymer which is not swollen by a variety of solvents and is inert to the reaction conditions for a variety of functional group transformations. Presently available techniques for polymer surface modification are not appropriate for preparation of this substrate: oxidation,[4-6] reduction,[7] flame treatment,[8] and corona discharge treatment[9] all involve severe conditions and products of these reactions are less inert than the unmodified polymer; hence autocatalysis and pitting ensue (Figure 1). The cascade of secondary reactions makes control of surface functionality difficult if not impossible.

Here we report an *autoinhibitive* surface modification reaction of poly(vinylidene fluoride) (PVDF) which, as expected from the modification kinetics allows surface-selective functional group introduction. The depth of reaction is estimated by several techniques.

Experimental Section

Materials. Poly(vinylidene fluoride) films were 5-mil Pennwalt Kynar obtained from Westlake Plastics. The samples were uniformly 1.27×10^{-2} cm thick and had a density of 1.74 g/cm^3. Films were extracted in refluxing dichloromethane (30 min) and dried in a vacuum oven (14 h, 50 °C, 0.05 mm) to constant mass. This procedure consistently produced films which were free from contaminants that interfere with surface characterization. All water was distilled twice. Sodium hydroxide solution (8 N) was stored in polypropylene screw-cap bottles to restrict silicate presence. Bromine in carbon tetrachloride (0.2 N) was kept in an amber-colored bottle in a refrigerator. Dimethylformamide was distilled from barium oxide at 39 mm (76 °C) and stored under nitrogen.

Methods. Advancing and receding contact angles were obtained by using water distilled from potassium permanganate, a Rame–Hart telescopic goniometer, and a Gilmont syringe. The reported data are the mean of at least six measurements and their

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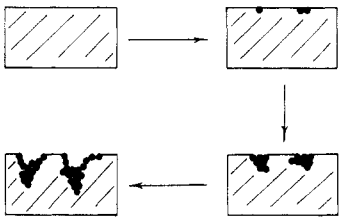


Figure 1. Autocatalysis and pitting in modification reaction of chemically resistant polymer.

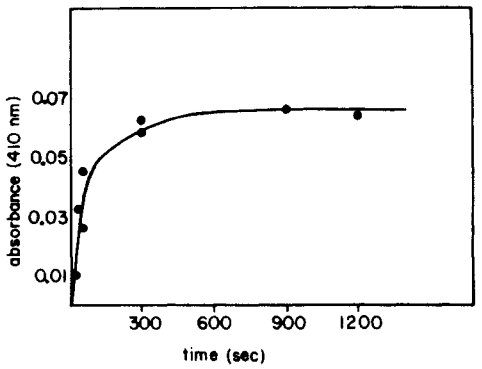


Figure 2. Absorbance vs. time plot of dehydrofluorination of poly(vinylidene fluoride).

standard deviation. UV–vis spectra were obtained directly from the films by placing them in film holders. Gravimetric analyses were performed with a Cahn electrobalance using films totaling 9-cm^2 surface area (two 1.5 cm × 1.5 cm films (both sides)). Attenuated total reflectance infrared spectra were recorded with a Perkin-Elmer 283 (germanium, 45°). Scanning electron micrographs of gold sputter-coated samples were obtained with a JEOL 100CX. ESCA spectra were obtained by using a Mg Kα source with a Kratos XSAM 800 spectrometer. No attempt was made to protect films from oxidation prior to recording spectra. Quantitative measurements were made by using peak areas (cut and weighed), literature photoelectric cross sections, and a sampling depth of 100 Å.

Elimination. A solution of 0.1 g of tetrabutylammonium bromide in 150 mL of 8 N NaOH was prepared and stirred at room temperature for 15 min. A PVDF film sample (of size appropriate for analytical method) was submersed in the solution for the selected time, removed with a forceps, and washed repeatedly in water (5 × 100 mL) by stirring the water with the film and then likewise in ethanol (3 × 100 mL) before drying at 0.05 mm for 24 h. The control was treated identically excluding the tetrabutylammonium bromide.

Bromination of Eliminated PVDF. Eliminated film samples (two 1.5 cm × 1.5 cm) were placed in a screw-cap vial containing 10 mL of 0.2 N Br_2/CCl_4 at 0 °C for 15 min. The films were removed from the bromine solution, washed with carbon tetrachloride (three fresh 10-mL portions) and then likewise with dichloromethane, and dried at 0.05 mm for 24 h. Controls (from the elimination procedure) were treated identically.

Beer's Law Justification. Elimination produces an extended-conjugated surface with a broad UV–vis absorbance with a λ_{max} = 410 nm. The absorbance at this wavelength exhibits a linear relationship with concentration over at least 3 orders of magnitude concentration (ϵ_{410} = 7.81 × 10^4 mL/g^{-1}/cm^{-1}). A DMF solution of PVDF (0.2 g of PVDF/30 mL of DMF) was prepared under dry nitrogen. Potassium *tert*-butoxide dissolved in DMF (1 equiv, i.e., 1 mol per mol of monomer CH_2=CF_2) was added and allowed to react for 24 h. Titration with 0.100 N HCl indicated that the base was completely consumed at or before this time. The resulting reaction mixture was centrifuged to remove precipitated polymer and potassium fluoride. The supernatant was diluted in serial fashion and used to establish the Beer's law relation. The diluted solution concentrations were measured by evaporating a known solution volume and weighing the remaining polymer. Residual ash mass was established by combustion and subtracted from the polymer mass. The analytical expression

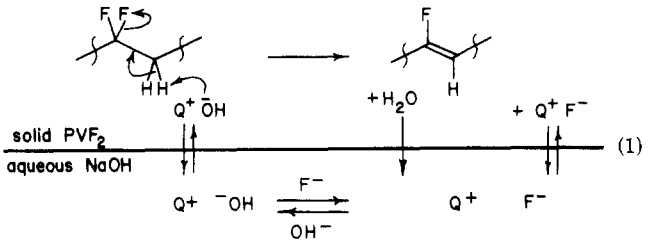
Table I
Advancing and Receding Water Contact Angle Data

	Θ_A, deg	Θ_R, deg
PVF_2	88.0 ± 1.0	66.0 ± 1.0
$PVF_2 \xrightarrow[TBAB]{NaOH}$	83.5 ± 0.5	40.5 ± 0.5
$PVF_2 \xrightarrow{NaOH}$	88.0 ± 1.0	62.0 ± 1.0
$PVF_2 \xrightarrow[TBAB]{NaOH} \xrightarrow[(2)\ H_2O]{(1)\ H_2SO_4}$	71.5 ± 0.5	18.5 ± 0.5
$PVF_2 \xrightarrow{NaOH} \xrightarrow[(2)\ H_2O]{(1)\ H_2SO_4}$	85 ± 2	59 ± 2

obtained from linear regression is concentration = (abs + 2.83 × 10^{-4})/7.81 × 10^4.

Results and Discussion

When PVDF film is submersed in 8 N sodium hydroxide solution containing a catalytic amount of tetrabutylammonium bromide for 60 s at room temperature, rinsed with water and then ethanol, and dried at reduced pressure, contact angles, ESCA, gravimetry, and UV–vis and ATR IR spectroscopy indicate that a surface-sensitive dehydrofluorination is effected (eq 1). In the absence of



tetrabutylammonium bromide, the reaction proceeds at a rate at least 2 orders of magnitude slower. The basis for the surface selectivity of this reaction is the autoinhibitive nature of the phase transport step of this phase-transfer-catalyzed reaction. Applying phase-transfer catalysis[10,11] to surface modification of PVDF, the outer few angstroms of the solid organic polymer is regarded as the organic phase; hydroxide ion is transported from an aqueous phase in contact with the polymer to this "organic phase" where dehydrofluorination is effected. The nonmolecular terminology "wetting" may be appropriate here: water and PVDF in contact with one another define a sharp interface; that is, water neither dissolves nor swells the polymer. Hydroxide ion (in the absence of phase-transfer catalysts) does not induce dehydrofluorination because the basic solution does not "wet" the film. Tetrabutylammonium ion transports hydroxide ion across this interface (serves as a "wetting agent") where it can react to form poly(fluoroacetylene). The eliminated surface is impenetrable under these conditions; hence elimination is confined to the surface. Figure 2 shows a plot of absorbance (at 410 nm) vs. time for this reaction; autoinhibition is apparent. More extensive modification reactions of poly(vinylidene fluoride)[12] and poly(vinyl chloride)[13,14] based on phase-transfer catalysis have been reported.

Advancing and receding water contact angles (Table I) indicate that elimination (60 s) followed by hydration (treatment with concentrated H_2SO_4 and then water) introduces polar functionality. The decrease in contact angles upon elimination is probably due to partial oxidation of the conjugated surface. The data indicate that the uncatalyzed reaction proceeds to a negligible extent under these conditions. Contact angle data for short reaction times suggest that elimination produces a homogeneously modified surface at the level of this analysis:[15] Scatter in

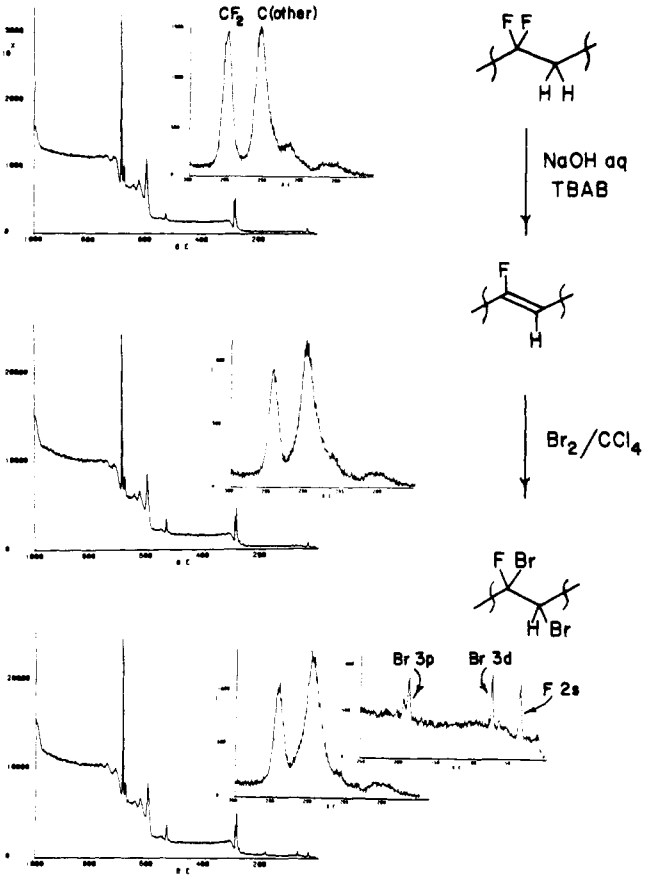


Figure 3. ESCA spectra of eliminated and eliminated/brominated poly(vinylidene fluoride).

contact angles is greater than 2° for reaction times less than 30 s. For longer reaction times, the scatter is less than 0.5°. This indicates that the surface is heterogeneous at reaction times less than 30 s but becomes homogeneous thereafter.

Attenuated total reflectance infrared spectra indicate that the depth of elimination is shallow with respect to the sampling depth of this technique: there is no discernible difference between spectra. The sampling depth at 1580 cm^{-1} using the conditions of this experiment is about 1 μm. Scanning electron micrographs of samples before and after elimination exhibit no change in microtopography at a resolution of 60 Å.

Three independent estimates of the depth of the elimination reaction were made. Figure 3 exhibits ESCA spectra for the elimination and bromination reactions. The increase in oxygen upon elimination is likely due to oxidation of regions of extended conjugation. By cutting and weighing the appropriate peaks and factoring photoelectric cross sections, three estimates of reaction depth were obtained. The ESCA sampling depth used for calculations was 100 Å. Comparison of the ratio of the CF_2 peak area to the other carbon peak area, before and after elimination, yields an estimate of 12.1 Å. Comparisons of bromine $3d_{3/2}$ + $3d_{5/2}$ and the bromine $3p_{1/2}$ + $3p_{3/2}$ peaks with the fluorine 2s signal give values of 2.6 and 2.2 Å, respectively. This technique cannot be considered quantitative; the three values depict its poor precision. There are many sources of error: the estimated sampling depth, the assumption that the material's composition is homogeneous throughout the sampling depth (which we know to be false), and the error associated with taking ratios of numbers with small differences. The data do, however, suggest that a small portion of the ESCA sampling depth has been modified and is consistent with more precise estimates: The UV–vis absorbance of a film eliminated for 60 s corresponds to a depth of reaction of 8.5 Å. Dissolution of the film in DMF followed by solution analysis yields a reaction depth of 8.1 Å. These estimates assume that the elimination performed in solution gives rise to the same products as the surface elimination. Gravimetric analysis has proved to be the most precise method for determining reaction depth. Films with surface areas of 9 cm^2 gain ~6 μg upon elimination (60 s) and bromination, which corresponds to a reaction depth of 10.6 ± 0.8 Å (95% confidence based on seven measurements).

In summary, phase-transfer-catalyzed dehydrofluorination of poly(vinylidene fluoride) is a mild, controllable, and rational method for introducing unsaturation to the surface of a nonpolar, chemically resistant polymer. This unsaturation is a "handle" upon which further chemistry can be effected. We have hydrolyzed (H_2SO_4/H_2O) and oxidized (*m*-chloroperbenzoic acid) the eliminated products and obtained highly wettable surfaces but have not further characterized them. Estimates of reaction depth are ~10 Å or less.

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