ized while spatial proximity to the quaternary aliphatic group is minimized. This picture is a greatly simplified representation and the proposed order is also localized. However, the spatial criteria for the placement of the DBP carbonyl derived from spin diffusion lead to a location of this functional group near the carbonate of BPA-PC. This is consistent with the presence of a specific interaction between the antiplasticizer and the polymer as postulated in some of the classic models of antiplasticization.[3,4,7]

At higher concentrations of DBP structurally selective spin diffusion is not observed and plasticization behavior commences. This indicates a loss of specific relative spatial positioning, and, in our view, this corresponds to the presence of DBP molecules near BPA-PC units that are not at a specific relative position and are not interacting with a particular functional group of the BPA-PC unit in question. The presence of nonspecifically interacting diluent is the cause of the onset of plasticization behavior, again in agreement with the premise of certain of the antiplasticizer–plasticizer models.[3,4,7]

In this report we have qualitatively connected structurally selective spin diffusion with preferential disposition of diluent molecules relative to the polymer chain in an antiplasticized glass. Currently a more quantitative approach involving numerical analysis of the decay curves based on coupled differential equations describing the concurrent contributions of spin–lattice relaxation and spin diffusion[11] in conjunction with a lattice model to count diluent–polymer contacts is under development. At this stage, carbon-13 spin diffusion appears to be at least capable of identifying local structure in multicomponent amorphous glasses. The method holds promise for the determination of intermolecular structure in other amorphous systems such as polymer blends where local interactions are presumed[15] but only identified in special cases such as hydrogen bonding.[16] More detailed models of intermolecular structure could result from a quantitative analysis of spin diffusion and from studies involving labeling several chemical positions of a given component.

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Registry No. BPA-PC (SRU), 24936-68-3; BPA-PC (copolymer), 25037-45-0; DBP, 84-74-2.

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Poly(chlorotrifluoroethylene)-Containing Surface-Confined Hydroxyl Groups: A Chemically Versatile, Model Hydroxylated Surface

The chemistry of surface-confined hydroxyl groups is central to a wide range of adhesives technologies. Glass, mineral, and most metal (in the ambient) surfaces contain hydroxyl groups that are routinely exploited with coupling agents to prepare composite materials,[1,2] modified electrodes,[3] and chromatography supports.[4] For the purpose of studying hydroxylated-surface chemistry, these inorganic surfaces are often not suitable substrates: Their high surface energies cause spontaneous hydration and adsorption of atmospheric contaminants. These materials are opaque in much of the spectrum lucid to hydroxyl group chemistry, and transmission spectroscopies are not useful analytical techniques. They can dissolve in acidic and basic solution (the metal–oxygen bonds are labile); thus the surfaces are not stable to the reaction conditions of many hydroxyl group transformations. The density of hydroxyl groups (number of hydroxyl groups per cubic centimeter of surface area) on these surfaces cannot be controlled. These problems do not prevent practical applications of chemistry at these surfaces; however they do impede its fundamental study. We have been studying surface modification of chemically resistant polymers[5-7] with the objective of preparing materials with a reactive surface functionality and inert bulk. These materials obviate the problems of inorganic surfaces; their advantages as surface chemistry substrates have been discussed.[7]

We have reported[8] the independent introductions of carboxylic acid, aldehyde, and alcohol functional groups to the surface of poly(chlorotrifluoroethylene) (PCTFE) film using two step modification sequences: Lithium reagents containing the protected functional groups react with PCTFE film surfaces via a reduction–addition–elimination sequence; deprotection of the functional groups renders PCTFE–COOH, PCTFE–CHO and PCTFE–OH. Equation 1 summarizes the synthesis of PCTFE–OH; the

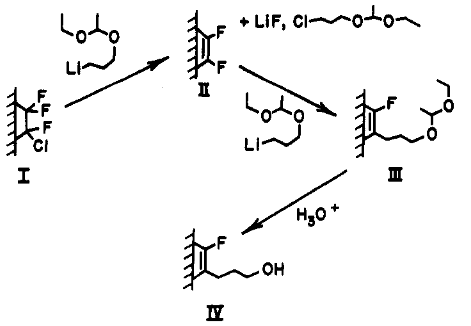

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Table I
Elemental Analyses Obtained from XPS Spectra[15]

	calcd						obsd					
surface	C	F	O	Cl	S	Si	C	F	O	Cl	S	Si
1	33	50		17			34	51	<1	15		
3	73	12	15				73	12	15			
4	69	19	13				69	16	15			
5	69	8	17		6		67	10	18		5	
6	69	19		12			69	18	3	10		
7	54	11	14	21			54	11	15	19		
8	71	13	8			8	68	13	11			8
9	61	17	17		6		59	16	20	<1	5	
10	71	12	17				69	13	18	<1		

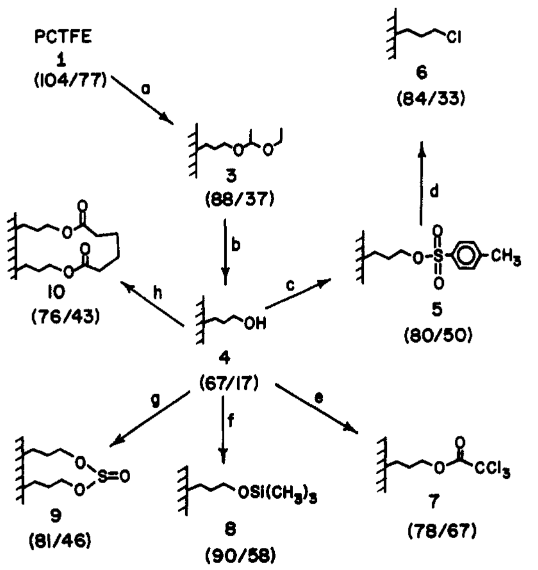

Figure 1. Summary of surface hydroxyl group transformations and contact angle data:[10] (a) acetaldehyde 3-lithiopropyl ethyl acetal, THF/heptane, −15 °C, 30 min; (b) HCl, water/methanol, reflux, 3 h; (c) TsCl, pyridine, −20 °C, 40 h; (d) Bu_4NCl, methanol, reflux, 24 h; (e) trichloroacetyl chloride, THF, 0 °C, 20 h; (f) Me_3SiCl, THF, 0 °C, 18 h; (g) $SOCl_2$, THF, room temperature, 24 h; (h) adipoyl chloride, THF, room temperature; 40 h. The concentration of reagents were, in all cases, in the range 0.1–0.4 M. Reaction conditions were roughly optimized to have complete conversion in the minimum reaction time.

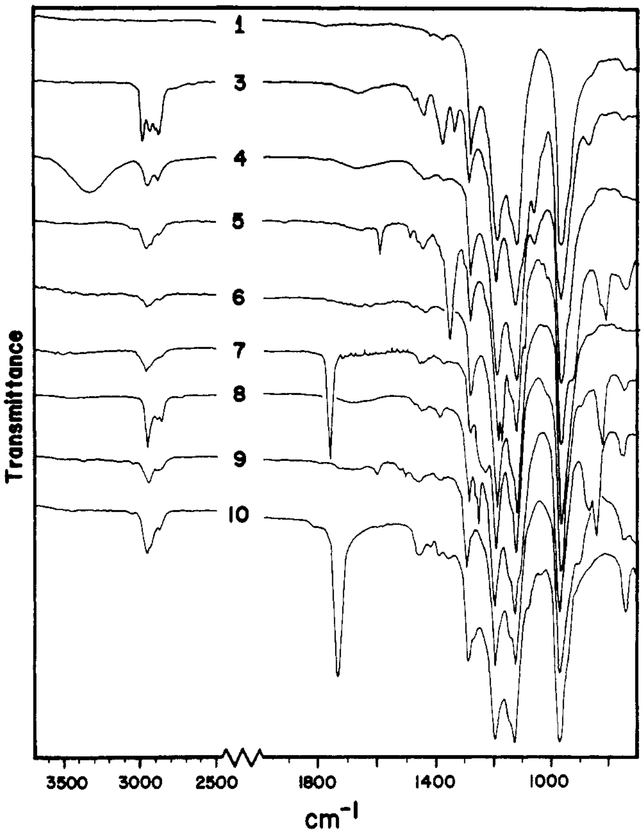

Figure 2. ATR IR spectra[12] for surfaces described in Figure 1.

depth of the reactions with acetaldehyde lithiopropyl ethyl acetal (LiPEAA) (which controls the density of hydroxyl groups in PCTFE–OH) is extremely temperature-sensitive and we have estimated[8] that reactions for 60 min at −78, −20, and 0 °C give modified layers of 50-, 1150-, and 1600-Å thickness, respectively. The reactions described in eq 1 are not quantitative, and we estimate that the product of the reaction of PCTFE with LiPEAA consists of 80% III and 20% II. This indicates that PCTFE–OH contains four hydroxyl groups per five PCTFE repeat units. We are studying the chemistry of PCTFE–OH, find it to be a versatile and easy-to-study substrate, and report our preliminary results in this Communication.[9] A range of modification reactions has been carried out; surface functionality undergoes both nucleophilic and electrophilic reactions. Each of the modified surfaces has been characterized by attenuated total reflectance infrared spectroscopy (ATR IR), X-ray photoelectron spectroscopy (XPS), and contact angle analysis.

Figure 1 is a summary of the reactions reported here along with contact angle data for each surface.[10] The contact angle data give neither quantitative nor qualitative information concerning functional groups but do indicate that reactions, consistent with the expected changes in hydrophilicity, have occurred. The PCTFE–OH film samples used for all experiments discussed here were prepared as described in eq 1 at −15 °C for 30 min, giving a modified layer approximately 1500 Å thick. These samples have a high enough density of hydroxyl groups that ATR IR spectra give lucid information on the reactions.[11] Figure 2 shows ATR IR spectra[12] of each of the surfaces depicted in Figure 1. Four strong absorbances (1287, 1194, 1125, and 968 cm^{-1}) are present in each of the spectra and are due to bulk PCTFE. Surface 3 exhibits the same C–H stretching and deformation modes as does $BrCH_2CH_2CH_2OCH(CH_3)OCH_2CH_3$, indicating the presence of the acetaldehyde propyl ethyl acetal group. PCTFE–OH (4) shows a broad hydrogen-bonded O–H band (3335 cm^{-1}), a C–O stretching band (1063 cm^{-1}), and methylene peaks (2946 and 2878 cm^{-1}). Formation of the *p*-toluenesulfonate 5 is indicated by the disappearance of the O–H band (3335 cm^{-1}) and appearance of SO_2 stretching (1358 and 1177 cm^{-1}), S–O–C stretching (932 cm^{-1}), and aromatic absorbances (1599 and 816 cm^{-1}). The *p*-toluenesulfonate can be displaced with chloride to yield 6. The peaks corresponding to the *p*-toluenesulfonate have disappeared, but the methylene bands are still present. The C–Cl stretching band is obscured by PCTFE. Reaction of PCTFE–OH with trichloroacetyl chloride yields the expected ester 7: The O–H band is replaced by C=O

(1767 cm^{-1}), C–O–C (1235 cm^{-1}), and C–Cl (828 cm^{-1}) stretching bands. The trimethylsilyl ether **8** can be prepared: The O–H band is replaced by the expected $OSi(CH_3)_3$ bands (2957, 1252, 868, and 841 cm^{-1}). Reaction of PCTFE–OH with thionyl chloride does not yield the expected chloride. Instead, the sulfite **9** is formed is evidenced by the OS(O)O band (907 cm^{-1}). Another expected absorbance due to OS(O)O overlaps the PCTFE peak at 1194 cm^{-1}. This reaction does not follow the typical pathway of solution alcohol–thionyl chloride reactions.[13] The chlorosulfite intermediate is trapped by a surface hydroxyl group to yield **9** faster than SO_2 is eliminated to form the chloride **6**. Treatment of PCTFE–OH with adipoyl chloride renders the diester **10** and a negligible amount[14] of the half ester/half acid chloride. A single carbonyl stretching band (1734 cm^{-1}) appears in the ATR IR spectrum.

It was possible to obtain elemental analyses of the modified surfaces by XPS, which were consistent with the chemistry detailed in Figure 1.[15] Table I summarizes this data. Elemental analysis of surface **3** indicates that its actual structure is 80% III and 20% II. Calculated values for surfaces **4**–**10** are based on this structure, that is, four functional groups per five PCTFE repeat units. These data complement the ATR IR spectra, confirming ambiguous intepretations, particularly for surfaces **6**, **9**, and **10**.

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(9) There is a large body of work on the surface modification of polymers containing hydroxyl groups, e.g., poly(vinyl alcohol) and cellulose. For examples, see ref 16–19. These materials are not appropriate for surface studies of the type reported here. They interact extensively with polar solvents (swell and dissolve) and are not chemically resistant, and the derivatized materials contain unreacted hydroxyl groups, which make analyses difficult. We found[19] that it is difficult to control the extent of these reactions.

(10) The numerators of the fractions appearing below the structures in Figure 1 are the advancing contact angles; the denominators are the receding contact angles. Doubly distilled (Gilmont still) water was the probe fluid and a Rame-Hart telescopic goniometer was used to perform analyses. Advancing contact angles were determined by measuring the tangent normal to the drop at the drop–surface intersection as water was added to the drop (using a Gilmont syringe) and the drop advanced. Receding contact angles were measured as water was removed from the drop and the drop receded.

(11) We have carried out several of these reactions on PCTFE–OH samples with 50-Å-thick modified layers and the contact angle and X-ray photoelectron spectroscopy indicate that identical reactions occur; however, ATR IR spectra provide little information.

(12) ATR IR spectra were obtained with an IBM 38 FTIR at 4-cm^{-1} resolution and a germanium 45° internal reflection element.

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(14) XPS indicates that chlorine is less than 1% of the atomic composition. Treatment of **10** with water removes all chlorine and decreases the contact angles slightly (indicating the presence of COCl, which hydrolyzes to form COOH groups).

(15) XPS spectra were obtained with a Perkin Elmer-Physical Electronics 5100 with Mg $K\alpha$ excitation. Spectra were recorded at a 75° (from the surface) takeoff angle and indicate the composition of the outer 40 Å. Variable-angle analyses indicate that the samples are homogeneous throughout the outer 40 Å.

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Comment on "A Calculation of Thermal Degradation Initiated by Random Scission. 1. Steady-State Radical Concentration"

Inaba and Kashiwagi[1] recently presented calculations concerning the effects of the initial polydispersity of molecular weight in a specialization of the general chain mechanism of thermal degradation formulated by Simha, Wall, and Blatz[2] to chain scission initiation. As the description by Inaba and Kashiwagi of the previous literature dealing with this problem was inaccurate and incomplete, we take this opportunity to describe some of the highlights related to it. In addition we point out an inadequacy in a simplification used by them. Gordon[3] showed that the rate equations could be solved for the special case of end-group initiation and no chain transfer if the initial molecular weight distribution were "most probable" (actually the "exponential" approximation to it). He found equations connecting the evolution of sample weight and molecular weight and showed that explicit separate expressions for the average molecular weight and sample weight vs. time in terms of the rate constants could be found under the above circumstances. Simha[4] found that equations connecting sample weight and molecular weight could be obtained under the more general circumstances of the complete mechanism that includes scission initiation and chain transfer and under arbitrary initial distribution. Boyd[5] showed that the complete general mechanism rate equations could be solved and explicit separate molecular weight and sample weight equations found under the circumstance of an initial "most probable" distribution. It is important to realize that the results of Gordon and Boyd showing that the *form* of the "most probable" distribution is preserved if present initially are a consequence of the mechanism and not an assumption. The sample weight can be considered to be the first moment of the molecular weight distribution and the number-average molecular weight to be the ratio of the first to zeroth moment. Thus the equations connecting molecular weight and sample weight evolution referred to above are equations connecting the zeroth and first moments of the molecular weight distribution. Boyd and Lin[6,7] showed that, in general, equations connecting the n-th and $(n + 1)$-th moments (end-group initiation) or n-th, $(n + 1)$-th, and $(n + 2)$-th moments (scission initiation) can be derived. This summarizes the situation with respect to exact results;

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