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Functionalization of the Surface of Poly[bis(trifluoroethoxy)phosphazene] by Reactions with Alkoxide Nucleophiles

Harry R. Allcock* and Richard J. Fitzpatrick

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

Lawrence Salvati

Physical Electronics, Perkin-Elmer, Edison, New Jersey 08820

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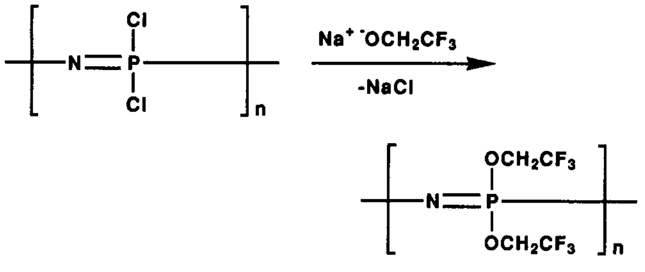
Films of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)]_n$, underwent surface reactions when treated with solutions of sodium alkoxides such as $Na^{+-}(OCH_2CH_2)_xOH$, where $x = 1$, 2, or 4; $Na^{+}\,{}^{-}(OCH_2CH_2)_xNH_2$, where $x = 1$ or 2; and $Na^{+-}OCH_2CH_2CN$. The nucleophiles replaced trifluoroethoxy groups at the polymer surface without detectable side reactions. The modified surfaces were more hydrophilic than the starting material. The presence of the new surface groups was confirmed by contact-angle measurements, SEM, XPS, TEM, and ATR-IR methods. The accessibility of the surface hydroxyl and amino groups to further functionalization was confirmed by the reaction of these groups with phenyl isocyanate.

Introduction

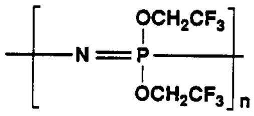
Fluorinated polymers have many interesting and useful properties, including hydrophobic surface character (low surface energy)[1-3] and, in some cases, bulk elasticity or flexibility. This combination of properties is valuable for the utilization of fluoropolymers as inert biomaterials, as well as in general areas of advanced technology. However, such materials generally have limitations with respect to fine tuning the surface character or the use of the surface for the covalent binding of, for example, bioactive molecules. With classical organic fluoropolymers attempts have been made to modify the surfaces by treatment with a variety of reagents,[4-6] and some success has been achieved, for example, in enhancing their adhesive character.

A fluoropolymer with a number of interesting characteristics is poly[bis(trifluoroethoxy)phosphazene] (1), prepared by the chemistry shown in eq 1.[7,8] This polymer is a semicrystalline thermoplastic that is soluble in common organic solvents such as tetrahydrofuran (THF) or acetone. Films of this polymer are flexible and are extremely hydrophobic. The polymer shows a high resistance to ultraviolet light and γ-rays and to a variety of aggressive media. It also exhibits impressive inert biocompatibility.[9,10] However, its utilization in biomedicine has been limited by the lack of a method for fine tuning its surface properties, for example, to allow the covalent linkage of bioactive agents, such as enzymes, nonthrombogenic proteins, or antigens to the surface.



1

Commercial poly[(fluoroalkoxy)phosphazene] elastomers (2) possess a chemical structure similar to that of 1 but contain both trifluoroethoxy and longer chain fluoroalkoxy side groups.[11,12] These elastomers are used both in advanced engineering and in biomedical applications.[10,13] Thus, the modification of 2 to alter its surface properties is also important, since the control of surface character is critical to the optimization of biocompatibility.



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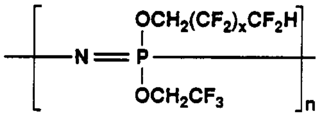

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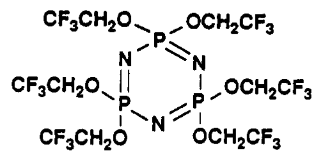

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In an earlier article,[14] we demonstrated that the surface of 1 can be altered by a controlled reaction with aqueous sodium hydroxide solution in the presence of a phase-

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(14) Allcock, H. R.; Rutt, S. J.; Fitzpatrick, R. J. *Chem. of Mater.*, previous paper in this issue.

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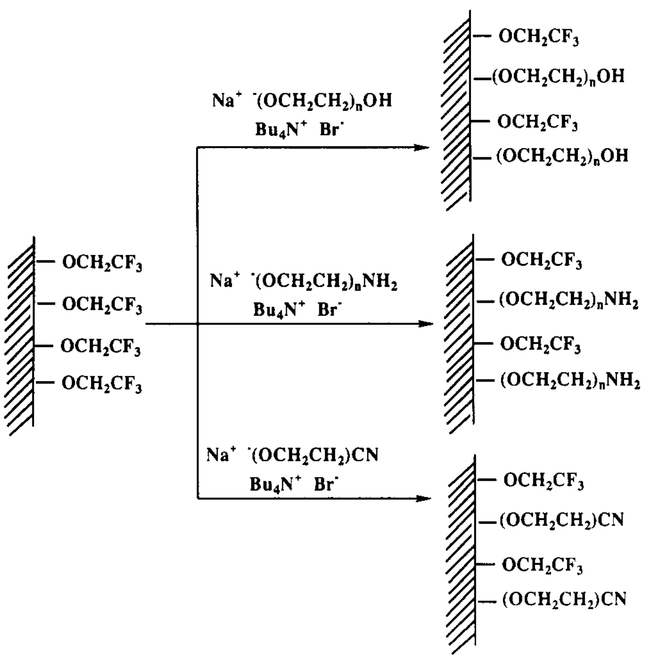
Scheme I



transfer agent (Bu_4NBr). The reaction involves the replacement of surface $-OCH_2CF_3$ groups by $-O^{-+}NBu_4$ groups. The treated surfaces were more hydrophilic and adhesive than the untreated surfaces of 1. Moreover, in an earlier paper[15] it was demonstrated that fluoroalkoxy-substituted polyphosphazenes *in solution* will undergo side-group exchange when treated with fluoroalkoxide nucleophiles. Thus, it appeared possible that related reactions might be feasible at the surface of a solid fluoroalkoxy-substituted polyphosphazene.

Results and Discussion

Reactions with Alkoxide Anions. Here we report that films of poly[bis(trifluoroethoxy)phosphazene] (1) undergo reactions with solutions of sodium alkoxides in the presence of tetra-*n*-butylammonium bromide (Bu_4NBr) as a phase-transfer agent to yield functionalized surfaces (Scheme I). The difunctional alkoxides Na^+ $^-OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$ (a), Na^+ $^-OCH_2CH_2OCH_2CH_2OH$ (b), $Na^{+-}OCH_2CH_2OH$ (c), $Na^{+-}OCH_2CH_2OCH_2CH_2NH_2$ (d), $Na^{+-}OCH_2CH_2NH_2$ (e), and $Na^{+-}OCH_2CH_2CN$ (f) replaced trifluoroethoxy groups at the surface via nucleophilic substitution reactions.

Synthesis and Characterization of 1. Polymer 1 was prepared as described earlier.[7,8,14] Smooth opalescent films of 1, 140 μm thick, were prepared on glass plates by solution-casting-methods. Scanning electron microscopic (SEM) analyses showed that the untreated films were smooth on both the glass and air sides. The films were washed with hexane before use. The ^{13}C NMR *solution* spectrum of unreacted 1 consisted of a quartet centered at 63 ppm for the methylene carbon of the trifluoroethoxy group and a quartet centered at 120 ppm from the CF_3 carbon of the trifluoroethoxy group. The ^{31}P NMR solution spectrum of 1 in acetone before reaction consists of a singlet at −4 ppm. Polymer 1 had a $M_w = 2 \times 10^6$.

Qualitative Aspects of the Surface Reaction. The sodium alkoxide solutions were prepared by reaction of an excess of the alcohol with sodium (see the Experiment Section). The large excess of alcohol favored the formation of the monosodium salts only of a–c, so that the second hydroxyl group of the reagent would be available for subsequent surface reactions.

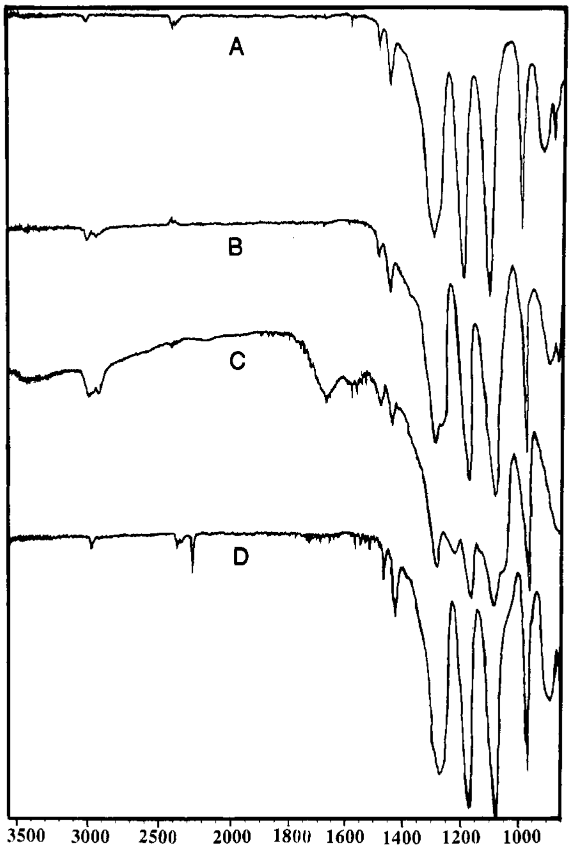


Figure 1. ATR-IR spectra of (A) the surface of untreated polymer 1, (B) after treatment with $NaOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, (C) with $NaOCH_2CH_2NH_2$, and (D) with $NaOCH_2CH_2CN$.

The surface reactions of 1 with reagents a–c were carried out at 100 °C, and those with d–f were at 70 °C. Reasons for the choice of these temperatures are as follows: The alcohols used as precursors for reagents a–f did not distort or dissolve films of 1 at room temperature. Alcohol precursors for a–c did not affect the films even after 24 h at 100 °C. However, films of 1 dissolved in the dialcohols of d–f at 100 °C. Thus, the surface reactions with d–f were carried out at 70 °C. Reactions with all six reagents at higher temperature (120 °C) brought about a distortion of the films, probably a consequence of penetration by the alcohol into the polymer. *No increase in adhesive character was detected after the surfaces were modified by reactions with reagents a–f.*

The surface interactions with the alkoxide anions required longer reaction times and higher temperatures than did the previously studied reaction with sodium hydroxide.[14] This may be due to the larger size and lower reactivity of the alkoxide anions compared with the hydroxide ion.

ATR-IR and XPS Analysis of Alkoxide-Modified Surfaces. ATR-IR spectra of the surfaces after reaction were significantly different from those of the starting polymer (Figure 1). An appreciable increase had occurred in the intensity of the aliphatic C–H stretch at 3000–2850 cm^{-1}. Etheric C–O–C stretches appeared at 1120 cm^{-1} when a, b, and d were the nucleophiles. The N–H stretches appeared as low broad peaks between 3350 and 3000 cm^{-1} when the surfaces of 1 were exposed to d or e. No obvious resonances could be assigned to the O–H stretches of side groups derived from a–c, but other workers have also reported the difficulty of detection of O–H stretching peaks

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(15) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1972**, *5*, 231.

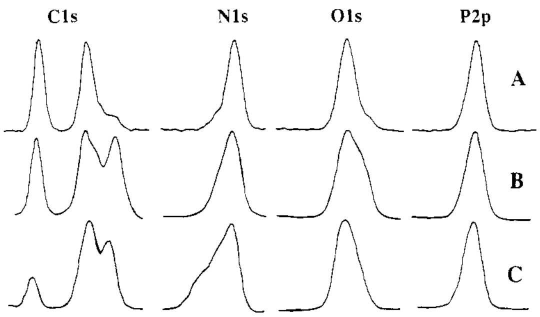

Figure 2. X-ray photoelectron spectra of (A) polymer 1, (B) the same polymer after surface reaction with $NaOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, and (C) after surface treatment with $NaOCH_2CH_2OCH_2CH_2NH_2$.

in ATR-IR spectra. When f was used to modify the surfaces of 1, a new resonance at 2255 cm^{-1} appeared, which corresponded to the CN stretch of the cyano group.

A new C 1s peak at 285.5 eV (Figure 2) was present in the XPS spectra of the modified films. This peak corresponds to the carbon atoms in the alkylene units of a–f. When d and f were the nucleophiles, a shoulder appeared at 400.2 eV on the N 1s peak. This new N 1s peak corresponds to the terminal amino group of the new side unit. No obvious changes occurred for the O 1s, F 1s, or P 2p peaks. However, the atomic composition of the surfaces had changed. The atomic percentage of carbon at the surface increased, while the fluorine content decreased. On the basis of the XPS data, the modified surfaces of 1 contained 19% of units from a, 30% from b, 28% from c, 54% from d, 39% from e, and 28% from f.

In theory, an alternative surface reaction that might have occurred could involve dehydrofluorination followed by the addition of the alcohols or amines across the resultant double bond. However, no sites of this type were detected in the ATR-IR spectra of any of the modified films.

Contact-Angle Measurements of Alkoxide-Modified Surfaces. Contact angles provide an exceedingly sensitive measure of surface changes. In this system the reduced contact angles appeared to be a function of the number of ethylenoxy units in the newly introduced side groups. In addition, the extent of reaction, the pH of the applied liquid, and the acidity/basicity of the functional groups had an influence on the contact angle.

The contact angles to aqueous media decreased following all the surface reactions. The longer the aliphatic ether chain linked to the surface, the lower was the contact angle. Thus, surfaces with groups b showed a contact angle of 95°, and with groups c a value of 100°. The surface modified with a had a lower contact angle (80°), and this was attributed to the longer, more hydrophilic structure of the newly introduced surface groups.

Surfaces with groups d or e had pH-sensitive contact angles. With acidic solutions, the amino groups are quaternized to give polar hydrophilic species. These surfaces had lower contact angles (43° for d and 48° for e). When the liquid applied to the surface was basic, the amino groups were less hydrophilic and yielded a higher contact angle (65° for d and 71° for e). The other modified surfaces were not pH sensitive, presumably because no strongly acidic or basic functional groups were present.

Depth of the Surface Reactions. By SEM analysis, the reacted films of 1 differed little from the starting material. TEM analysis of film cross sections stained with lead indicated that the depth of modification was consistently <1 μm. Exact measurements were difficult to obtain because of problems with the microtoming of the embedded films. However, the results clearly indicate that the reactions were restricted to the surface.

Solution Characterization of Alkoxide-Modified Sites. The polymers were still soluble in organic media after the surface treatment. GPC elution traces of the modified polymers were essentially identical with those of the starting polymer. This is in contrast to the basic hydrolysis of 1, in which an obvious decrease in molecular weight was detected.[14] In the basic hydrolysis, a hydroxy group first replaces a trifluoroethoxy group. Phosphazenes with P–OH side units can undergo migration of the hydroxyl group proton to a backbone nitrogen atom, and this results in the formation of a hydrolytically unstable phosphazane site. Surface modification with alkoxides a–f involves the replacement of one alkoxy group by another, and apparently this does not result in polymer chain cleavage at the surface.

When 1 was treated *in solution* with an excess of d, an adhesive, methanol-soluble polymer was formed. The ^1H NMR spectrum of this product had resonances at 4.6 and 3.0–4.0 ppm, which corresponded to the trifluoroethoxy methylene, the ethylene units from d, and the amino protons from d. The ^{13}C NMR spectrum contained resonances at 77.5, 70.8, 69.5, 64.9, 63.0, and 57.7 ppm, which correspond to the carbon atoms of the trifluoroethoxy groups and groups derived from d. The ^{31}P NMR spectrum was a broad singlet at −7.2 ppm. A *film* of 1 that had been treated for an extended time with nucleophile d dissolved in THF and gave NMR resonances identical with those of the *solution*-modified sample.

A similar solution-state side-group replacement occurred for model compound trimer 3. When solutions of 3 were treated with reagent d, a completely water-soluble product was formed. The product was a mixture of various species of formula $N_3P_3(OCH_2CF_3)_{6-x}(OCH_2CH_2OCH_2CH_2NH_2)_x$, where $x = 4$, 5, or 6. This provides a facile method for the preparation of functionalized phosphazene cyclic oligomers.

Role of Bu_4NBr in the Surface Chemistry. The use of a phase-transfer agent in heterophase polymer reactions is well known.[16] The phase-transfer agent allows the active reagent to more readily cross the polymer/liquid interface and react with the surface. The agent can increase the rate of a surface reaction in three possible ways: First, it creates a naked anion that is more reactive than the original ion. Second, the resultant cation may be more soluble in the polymer than is the original cation. And finally, the phase-transfer agent may act as a sufactant and induce more effective wetting of the polymer surface.

The role of the Bu_4NBr as a surfactant appears to be important for the surface *hydrolysis* of 1 by aqueous sodium hydroxide solution.[14] No surface modification occurred without it. However, the reaction of reagents a–f with the surface of 1 did not require the presence of a phase-transfer agent, although they proceeded faster when one was present. Solutions of a–f generated lower contact angles on the surface of 1 than did an NaOH solution, and the presence of the Bu_4NBr in the solutions of a–f did not lower the contact angle. For example, the alcohol precursors to a–f gave the following contact angles on 1 (the first angle shown in each case is for the pure alcohol or water, and the second value is for the same medium with 2% Bu_4NBr): a 90°, 90°; b 92°, 90°; c 98°, 98°; d 62°, 61°; e 65°, 66°; f 90°, 87°; H_2O 108°, 86°. Thus, the Bu_4NBr does not influence the reactions of a–f as a surfactant. Although the Bu_4NBr was not absolutely necessary, lower reaction temperatures and times could be employed when

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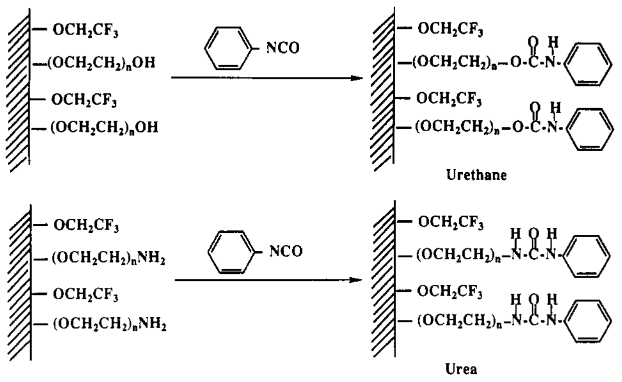
Scheme II



it was used, probably because of the greater reactivity of the naked anion, and the greater solubility of the anion and its associated phase-transfer cation in the polymer.

Surface Treatment of Other Phosphazene Polymers. Films of the hydrophobic (aryloxy)phosphazene polymers, poly(diphenoxyphosphazene) (**4**), poly[bis(*p*-bromophenoxy)phosphazene] (**5**), and poly[bis(2-phenoxyethoxy)phosphazene] (**6**) were immersed in the reagent solutions, but no surface reaction was detected visually or by ATR-IR analyses. In addition, these polymers did not react with the alkoxide in refluxing THF solution. Thus, the trifluoroethoxy side group provides a unique opportunity for surface reactions with polyphosphazenes. This is a consequence of its high reactivity as a leaving group.

Reconstruction of the Modified Surface. Polymer surfaces may reorganize in different environments or at different temperatures.[17] The T_g of **1** is −66 °C, and at room temperature the polymer backbone can undergo facile torsional motions that could facilitate surface reorganization. Reconstruction should also be favored by heating the polymer to temperatures above the phase transition at 80 °C.

The modified polymer surfaces shown in Scheme III are potentially amphiphilic, because both polar hydroxyl, amino, or cyano side groups and hydrophobic trifluoroethoxy side groups are present. Thus, heat treatment or exposure of the polymer to a nonpolar environment may allow low-surface-energy trifluoroethoxy groups to replace hydrophilic groups at the film surface.

The treated films were soaked in warm hexane. The XPS spectra of the modified films were now identical with those of the untreated surface of polymer **1**. No C 1s peaks corresponding to the nonfluorinated groups were present in the spectra. This provides evidence that the more hydrophilic groups had retreated from the surface. The hydrophilic groups were still detectable by ATR-IR analysis, but this technique analyzes to a greater depth (1 μm) than does XPS (50 Å).

Reactivity of the Hydroxyl and Amino Groups. The hydroxyl and amino groups at the modified surfaces were allowed to react with phenyl isocyanate to form urethane and urea units, respectively (Scheme II). The products yielded ATR-IR spectra with carbonyl C=O stretching peaks at 1740 cm^{-1}, an indication that the functionalized surfaces of **1** had reacted with phenyl isocyanate. No carbonyl peak was detected in the ATR-IR spectra when unreacted **1** was treated with phenyl isocyanate as a control. Thus, the functional groups at the modified surfaces are accessible for the covalent binding of bioactive and other species to the surface.

Conclusions

The functionalization of poly[bis(trifluoroethoxy)phosphazene] surfaces by treatment with alkoxides provides a facile and versatile method for the preparation of hydrophilic, reactive surfaces while leaving the internal properties of the polymer intact. The experimental parameters, reaction time and temperature, determine the degree of surface modification that occurs.

It is significant that the reactions that occur at the surface of **1** appear to be very similar to those that take place in solution. Thus, at least for polymer **1**, the solution reactions constitute a "model" for the analogous surface interactions.

This work suggests that flexible films or fibers of poly[bis(trifluoroethoxy)phosphazene] or mixed-substituent (fluoroalkoxy)phosphazene elastomers can form the starting point for the preparation of new materials with uses as immobilization substrates for bioactive compounds as well as surface-tailored polymers for utilization as inert biomaterials.

Experimental Section

Equipment. The surface and solution characterization equipment and protocols for the NMR, FTIR, ATR-IR, GPC, contact angle, and XPS measurements were the same as those reported in an earlier publication.[14] X-ray photoelectron spectra (XPS) were recorded at the Perkin-Elmer Physical Electronics Laboratory (Edison, NJ) on a Perkin-Elmer Physical Electronics 5000 LS spectrometer. Transmission electron microscopy (TEM) analysis was carried out at the electron microscope facility of the Department Molecular and Cell Biology at The Pennsylvania State University.

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was recrystallized several times from hexane before use. Poly(dichlorophosphazene) was obtained by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[8] Tetra-*n*-butylammonium bromide (Aldrich) and phenyl isocyanate (Aldrich) were used as received. Tetraethylene glycol (Aldrich), diethylene glycol (Aldrich), ethylene glycol (Aldrich), 2-(2-aminoethoxy)ethanol (Aldrich), 2-aminoethanol (Aldrich), 2-cyanoethanol (Aldrich), and dimethylformamide (DMF, Aldrich) were all vacuum distilled and then stored over 4-Å molecular sieves. Sodium was stored and weighed in a glovebox. Distilled water was passed through a Millipore ion-exchange resin before use. Tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under a nitrogen atmosphere.

Preparation of Phosphazenes 1–5. The synthesis and characterization of polymer **1** has been described elsewhere.[7,8,18] Compounds **3**–**5** were also prepared by methods described previously.[19–21]

Preparation of Polymer 6. Poly(dichlorophosphazene) (5.0 g) was dissolved in warm dioxane (250 mL). To a suspension of sodium (6.05 g) in dioxane (250 mL) was added 2-phenoxyethanol (46 g). The reaction mixture was stirred and heated for 24 h until all the sodium had reacted. The salt solution was then added via a double-tipped syringe to the polymer solution. The reaction mixture was then stirred and heated for 48 h. The cooled reaction mixture was concentrated on a rotary evaporator, and the viscous solution was precipitated into deionized water. The polymer was then reprecipitated from THF into deionized water (four times) and hexane (three times). The product was isolated as a tough, white solid. Characterization data: ^{1}H NMR 6.9–7.4 and 3.5 ppm; ^{31}P NMR −7.8 ppm; ^{13}C NMR 158.6, 129.4, 120.6, 114.5, 67.0, and 64.6 ppm; $M_w = 4.6 \times 10^6$; $T_g = -7$ °C. Elem Anal. Calcd: C

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(21) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.

60.18, H 5.68, N 4.39. Obsd: C 59.99, H 5.82, N 4.19.

Preparation of Films. Polymer 1 was dissolved in a solution of acetone/THF (1:1). The solution was filtered and then cast on a clean level glass surface in a dust-free drybox. The solution was then covered to slow the rate of solvent evaporation. After 48 h, the films were removed from the glass and were vacuum dried for 24 h. The films were soaked and sonicated in deionized water, ethanol, and then hexane before storage in a sealed bottle.

Surface Reactions of 1. Solutions of reagents a-f were prepared by cooling the undiluted alcohol (30 mL) in an ice bath and adding sodium (0.8 g). The reaction mixture was stirred for 24 h or until all the sodium had reacted. Bu_4NBr (1.0 g) was then added. Films of 1 were immersed in the solutions of a-c for 12 h at 100 °C, and in solutions d-f for 3 h at 70 °C. The films were removed from the reaction medium and were rinsed and then soaked in deionized water.

Solution Reactions. Polymer 1 (1.0 g) was dissolved in dry THF (50 mL). Sodium (0.25 g) was added to undiluted 2-(2-aminoethoxy)ethanol at 0 °C. The reaction mixture was stirred overnight at room temperature or until all the sodium had reacted. n-Bu_4NBr (0.5 g) was then added to the salt solution. The alkoxide solution was added slowly to the polymer solution, and the mixture was stirred for 24 h at 70 °C. The reaction mixture was concentrated on the rotary evaporator and then dialysized (M_w cutoff = 10000-12000) against deionized water for 4 days and against methanol for 3 days. The polymer was isolated by evaporation of the contents of the dialysis tube.

Treatment of the Modified Surfaces with Phenyl Isocyanate. Untreated and reacted films of 1 were immersed in 10 mL of a 4% (v/v) solution of phenyl isocyanate in ether at room temperature for 2 h. The films were removed and were washed with and soaked in diethyl ether for 4 h. They were then rinsed and soaked in ethanol and deionized water. Finally, the films were vacuum dried for 24 h.

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Photoconductor Fatigue. 1. Photochemistry of Hydrazone-Based Hole-Transport Molecules in Organic Layered Photoconductors: Spectroscopic Characterization and Effect on Electrical Properties

J. Pacansky,* R. J. Waltman, R. Grygier, and R. Cox

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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The hole transport molecule p-(diethylamino)benzaldehyde diphenylhydrazone (DEH) undergoes a photochemical reaction to an indazole derivative when exposed to light with $\lambda \leq \sim 480$ nm. When contained in the hole-transport layer of an organic photoconductor formulation, a clear and direct relation is found between the DEH photochemistry and an increase in the residual surface voltage during light decay of the organic photoconductor. Spectroscopic data and electrical properties measurements with DEH and its derivatives firmly establish this correlation. The increase in residual surface voltage is attributed to the trapping of holes in the charge-transport layer during light decay.

Introduction

Electrophotography is the process by which an electrostatic image, formed on the surface of a photoconductor, is transferred and developed on paper by using a toner containing, for example, carbon black.[1] A typical electrophotographic process used in commercial copiers and printers is illustrated in Figure 1. A layered organic photoconductor (to be described below) is wrapped around a drum and, at step (a) in the dark, the photoconductor is charged by a negative corona to about 900 V; this latter quantity is referred to as the dark voltage. During the time required for the photoconductor drum to move from the charging station (a) to the discharge station (b) the electrical conductivity of the photoconductor must be low enough so that the surface potential changes negligibly with time; this decrease in dark voltage with time is commonly labeled dark decay. At step (b) areas of the charged photoconductor are selectively exposed to light and in these exposed regions the photoinduced current ultimately erases the surface charges, leaving on the surface of the photoconductor a latent electrostatic image; the drop in voltage, referred to as light decay, must be rapid and must return as close as possible to zero. The residual voltage after exposure is often called the white voltage. At the center of Figure 1 the relevant changes in electrical properties that the photoconductor exhibits are plotted as a function of time from station to station. This, of course, is the photoinduced discharge curve and represents ideal photoconductor behavior.

The electrostatic image is developed into a real image on paper by using negatively charged carbon black particles; this development process is shown in Figure 1c, where the toner (containing charged carbon particles) is brought into contact with the photoconductor by using magnetic carrier beads that are charged positively. During the development stage the negatively charged carbon black toner particles move to the exposed regions of the photoconductor due to the lower surface potential. At Figure 1d the carbon black is transferred to paper and heated to fuse the image. The process is now complete and the drum returns to (a) to repeat the process, all of which occurs several times or more a second; the cycle occurs about 10^3-10^6 during the lifetime of the photoconductor.

It is clear from Figure 1 that the photoconductor is subjected to light and corona discharges. Additional environmental stresses that the photoconductor is subjected to that are not obvious from Figure 1 are heat (primarily generated by the heat required to fuse toner to paper), and light from fluorescent lights in the work environment (room light). Although, the accumulative incident dose

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[1] Carlson, C. *Xerography and Related Processes*: Dessauer, J. H., Clark, H., Eds.; The Focal Press: New York, 1965; pp 15-49.

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