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Surface selective modification of poly(vinyl chloride) film with lithiated α,ω-diaminopoly(alkene oxide)s

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Procedures that lead to surface selective modification of preformed poly(vinyl chloride) (PVC) films are detailed. Using X-ray photoelectron spectroscoy (X.p.s.), ultra-violet (u.v.)–visible spectroscopy and attenuated total reflectance infra-red spectroscopy, we followed the changes induced in PVC films by dehydrochlorination with lithiated α,ω-diaminopoly(alkene oxide)s. By controlling the temperature of the reaction, we could control the depth and extent of reaction. After about 20–30 min at −78°C, −42°C or 0°C, the depth of the polyunsaturated layer was about 60 Å, 500 Å or 2000 Å (1 Å = 0.1 nm), respectively, as estimated by u.v.–visible analysis. Further modification at that point occurred at a slower rate. X.p.s. analysis of the changes in the Cl_{2p} and C_{1s} signals indicated that about 60% of the vinyl chloride subunits had been consumed by the lithiated amide base in 1 h at −78°C. Subsequent modifications of the unsaturated surfaces produced by dehydrochlorination are also described. Nucleophilic substitution led to surfaces grafted by poly(alkene oxide)s or poly(ethylene imine)s. Hydroboration–oxidation or hydroboration–grafting led to surfaces containing hydroxy groups or poly(methyl methacrylate) grafts. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: poly(vinyl chloride); dehydrochlorination; surface modification)

INTRODUCTION

Surface and interface properties are important in polymer processes that involve adhesion, blending and printing. Generally, physical and chemical properties on polymer surfaces can be modified using various chemical treatments[1–5]. Such chemistry includes both wet chemistry methods and gas phase treatments. As part of a broader programme to study polymer surfaces in contact with organic solvents and reagents, we have been exploring methods that could be used to control reactions in wet chemical treatments of common polymers[6–11]. Much of this work has focused on polyalkenes like polyethylene. However, we recently described some of our first studies using lithiated oligomers to alter the intrinsic reactivity of polyester. In this chemistry, a lithiated α,ω-diaminopoly(alkene oxide) was allowed to react with the electrophilic carbonyls of a polyester like poly(ethylene terephthalate) or poly(methyl methacrylate) to generate a nucleophilic aminated surface[8]. Here we describe the effects of these same lithiated α,ω-diaminopoly(alkene oxide)s on surfaces of solvent-cast poly(vinyl chloride) films.

Poly(vinyl chloride) (PVC) is an important and widely used thermoplastic material. This surface character can be a limitation in some areas like adhesion where surface and interface interactions are important. It is thus not surprising that chemical modification of PVC either in the bulk or at the surface has been an interest both in industry and in academic circles[12–16].

Lithiated α,ω-diaminopoly(alkene oxide)s are strong bases. The expected product of their initial reaction with PVC is a dehydrochlorinated product containing a carbon–carbon double bond. Subsequent chemistry could involve either further dehydrochlorination leading to conjugated carbon–carbon double bonds or nucleophilic substitution of allylic chloride groups. In the results described below, both types of chemistry are seen. Our results show that these reagents initially generate a polyunsaturated surface layer. Our studies show that these reagents can be used to control the depth of the dehydrochlorination reaction on a PVC film surface. These studies also show how the carbon–carbon unsaturation produced in this chemistry can be used subsequently to introduce other functional groups.

To our knowledge, no attempt has been made so far to surface modify PVC by this type of approach using very strong bases like these metallated diamino oligomers. However, there are several reports that are related to this study. These reports include studies of anionic grafting of PVC material in homogeneous solution[17–19] and the heterogeneous surface modification of halogenated polyalkenes such as poly(chlorotrifluoroethylene)[20] and poly(vinylidene fluoride)[21,22].

EXPERIMENTAL

Materials

Poly(vinyl chloride) powder was obtained from Vista Chemical Corporation (Austin, TX). The PVC powder was dissolved in tetrahydrofuran (THF) to form a 15% (w/v) solution. PVC films with a nominal thickness of 0.02 mm were then cast from this solution by pouring

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the solution into a glass plate. α,ω-Diaminopoly(alkene oxide)s were obtained from Texaco Chemical Co. All other reagents were obtained from Aldrich Chemical Co. Where necessary, anhydrous and oxygen-free solvents were obtained by distillation from solutions or suspensions of sodium–benzophenone. The methyl methacrylate monomer used in grafting studies was simply dried over molecular sieves prior to use.

Representative procedure for the dehydrochlorination of poly(vinyl chloride)

An α,ω-diaminopoly(alkene oxide) (10 mmol) was dissolved in a 4 : 7 (v/v) mixture (ca. 50 ml) of anhydrous THF and heptane in a 200 ml Schlenk tube. Addition of 2 ml of 1.6 N BuLi (3.2 mequiv.) by syringe produced a solution of the lithiated diamine. After 10 min of stirring, 10 ml of this solution was transferred by forced siphoning using a cannula to a 20 ml, septum-stoppered test tube containing a 10 cm^2 piece of PVC film. The dehydrochlorination was then conducted at 0°C (or some other temperature) for a set time period. Occasional agitation by shaking or with a mechanical shaker was used to ensure good contact of the reagent solution and the substrate PVC film. The reaction was then terminated by addition of methanol. The final product film was washed with argon-purged ethanol at 0°C five times for 10 min each time and finally vacuum dried.

Hydroboration and oxidation of dehydrochlorinated PVC films

To a 20 ml flask containing 5 cm^2 of a sample dehydrochlorinated PVC film (PVC-[C]) was added 10 ml of diethyl ether. Then 1 ml of neat borane–dimethyl sulfide was added by syringe. After 6 h at ambient temperature the yellowish colour on the PVC-[C] film had obviously discharged. After the ether solution of borane was removed, 5 ml of a 3 M NaOH solution was added followed by 5 ml of 30% aqueous H_2O_2 at 0°C. After 6 h, the film was again washed with ethanol (10 times, 5 min each time) and dried for 2 days *in vacuo.*

Preparation of poly(vinyl chloride)-g-poly(methyl methacrylate)

Graft copolymerizations were carried out using an alkylborane derivative of a PVC film as an initiator as described previously[11].

Analytical procedures

Ultra-violet (u.v.)–visible spectra of dehydrochlorinated films were recorded over the range 240–700 nm using a Perkin–Elmer model 554 u.v.–visible spectrometer. A pure PVC film of the film thickness was used first to run a background spectrum. X-ray photoelectron spectroscopy (X.p.s.) was carried out using a PHI ESCA model 5500 spectrometer (MgKα X-rays, 15 kV, 400 W). X.p.s. analyses usually required 10 min for each sample. In cases where two sequential runs of the same PVC sample were carried out under these conditions, the atomic concentrations of chlorine and carbon were unchanged from run to run, indicating that no significant dechlorination occurred in the X.p.s. analysis. Attenuated total reflectance (ATR) or transmission infra-red (i.r.) spectra were recorded on a Matteson Galaxy model 4021 spectrometer at 1 cm^{-1} resolution. ATR i.r. spectra were obtained using a zinc selenide 45° internal reflection element. Contact angle measurements were obtained using a Ramè–Hart goniometer with doubly distilled water as the probe liquid. Advancing and receding contact angles were taken when water was added to and removed from the film, respectively, using a Gilmont microsyringe. Errors in contact angle measurements were estimated as ±2°.

RESULTS AND DISCUSSION

Dehydrochlorination

Initial formation of a lithiated α,ω-diaminopoly(alkene oxide) was accomplished using the chemistry shown in equation (1). This is the same chemistry as used in our earlier study of the modification of polyesters[8]. However, unlike the results seen with polyesters, the products **2a–2f**: from this reaction behave principally as bases rather than as nucleophiles in their reaction with PVC.

$$\mathrm{H_2NCH_2CHR(OCH_2CHR)_{\mathit{n}}OCH_2CHR'NH_2} \quad \mathbf{1a-1f}$$

$$\xrightarrow[\text{THF–heptane}]{\text{BuLi}}$$

$$\mathrm{LiHNCH_2CHR(OCH_2CHR)_{\mathit{n}}OCH_2CHR'NH_2} \quad \mathbf{2a-f}$$

1a: $R = R' = H;\ n = 1$

1b: $R = R' = H;\ n = 2$

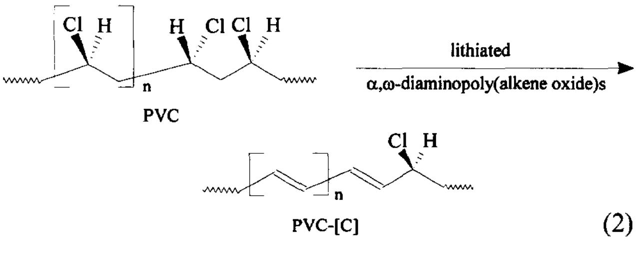
1c: $R = Me,\ R' = H;\ n \approx 43$

1d: $R = R' = Me;\ n \approx 2$

1e: $R = R' = Me;\ n \approx 5$

1f: $R = R' = Me;\ n \approx 32$ (1)

The main reaction we observed on treatment of PVC with lithiated α,ω-diaminopoly(alkene oxide)s was dehydrochlorination. The reaction (equation (2) produced a pale yellow film with short reaction times or low temperature treatment and a brownish film after longer reaction times or at higher temperature. Essentially similar chemistry was seen with oligomers **2a–2f**. The bulk of the studies below have therefore focused on the chemistry of a single example of a lithiated α,ω-diaminopoly(alkene oxide), namely **2a**. *Figure 1* shows the u.v.–visible spectra of the transparent product films formed from reaction of **2a** with PVC at various temperatures. It can be seen that the absorbance band produced varied in intensity and width, extending from 240 nm to 520 nm. Prior work on conjugated polyene systems has shown that this broad peak consists of absorbance bands from polyenes with different conjugation lengths *i*. Similar results have also been seen in dehydrochlorination of solutions of PVC where dehydrochlorination occurred in a zipper-like manner to produce conjugated polyenes[12].



(2)

These u.v.–visible spectra also allowed us to follow the change in depth of functionalization of PVC by analysis of the amount of polyene produced. Using absorption coefficients from prior studies of homogeneous dehydrochlorinated PVC and assigning appropriate conjugation numbers to the polyenes formed here based on the observed λ_{max} values, the observed intensities and the film density[17,18] we can calculate approximately the thickness (h) of the unsaturated surface layer in the dehydrochlorinated PVC films from

$$h = \frac{10^4 C M_{CH_2}CHCl}{2d(1000)} \mu m \qquad (3)$$

and

$$C = \sum_{i=2}^{14} iA_i/\epsilon_i \qquad (4)$$

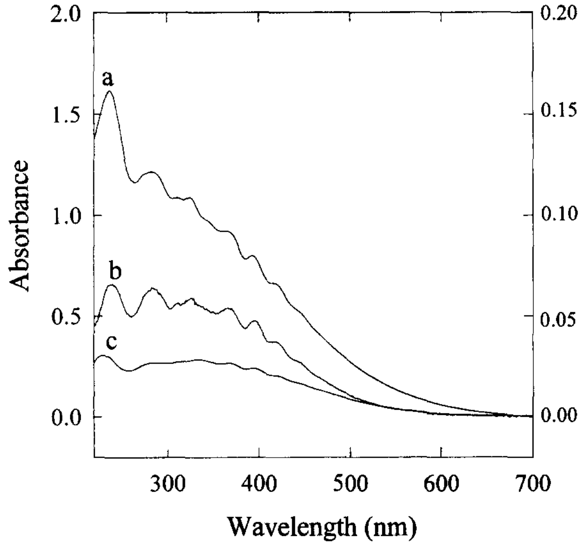


Figure 1 U.v.–visible spectra of PVC films allowed to react with **2a** for 30 min at (a) 0°C, (b) −78°C and (c) −42°C. The −78°C spectrum is actually less intense than the spectrum for the −42°C reaction but is amplified 10-fold to illustrate the presence of fine structure

In these equations, the maximum u.v.–visible absorbance and absorption coefficient are A_i and ϵ_i for a polyene with i conjugated double bonds. C is the summation of all the unsaturated carbon–carbon double bonds, M_{CH_2CHCl} is the formula weight of the repeat unit and d is the density of the resin. The factor 2 in the denominator of equation (3) is present because both sides of the film sample reacted. In these calculations, polyenes containing from two to 14 units absorb u.v.–visible light in the wavelength range 240–520 nm. The results of these calculations showed that the depth of the modified layer increased with reaction time. In addition, the rate at which more unsaturation was introduced decreased after about 20–30 min. Calculations showed that reactions at 0°C, −42°C and −78°C led to unsaturated layers that were approximately 2000 Å, 500 Å and 60 Å (1 Å = 0.1 nm) deep, respectively. This indicated that the depth of the modified layer is controllable through variation of either temperature or reaction time.

X.p.s. analysis

X.p.s. was also effective at following the chemical

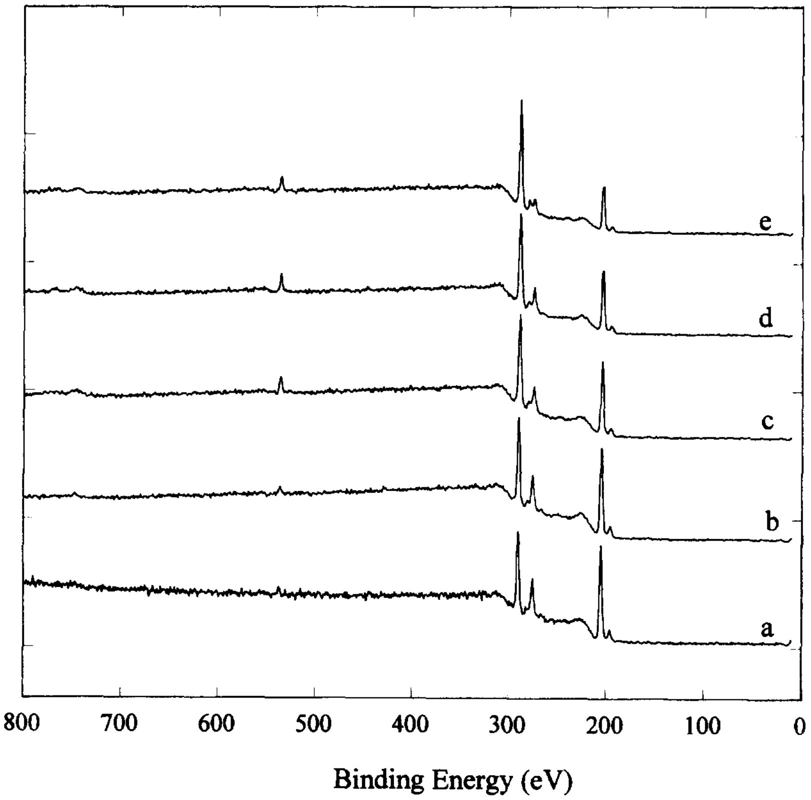


Figure 2 X.p.s. survey spectra of PVC films allowed to react with **2a** for varying lengths of time at −78°C: (a) starting pure PVC film; (b) a 10 min reaction time; (c) a 30 min reaction time; (d) a 60 min reaction time (PVC-[C]); (e) a 270 min reaction time

changes occurring at the PVC film surface in the reaction of equation (2). These studies were all carried out with films that had been dehydrochlorinated by **2a–2f** at −78°C. As can be seen in the survey spectra in *Figure 2*, the Cl_{2p} peak at 200 eV decreased with reaction time, dropping from 29 at% to 12 at% after 1 h of treatment. The survey spectra also contain a small oxygen peak. This is probably due to adventitious oxidation of the dehydrochlorinated material. Similar oxidation has been seen in studies of the elimination products of other halogenated polyalkenes[20–23] and was more pronounced in our case for films that had been dehydrochlorinated at ambient temperature.

High resolution C_{1s} X.p.s. traces helped to substantiate the chemical changes deduced from the survey spectra. Specifically, the traces in *Figure 3* show an initial C_{1s} signal for virgin PVC due to equal amounts of two types of carbon. The carbons with a binding energy of 286.6 eV are probably carbons attached to chlorine. The peak at 284.6 eV was assigned to the CH_2 carbons. An approximate measure of the relative amounts of the two types of carbon was ascertained by peak fitting the X.p.s. data using commercial software. As can be seen in the peak-fitting curves shown, the intensity of the peak assigned to carbons attached to chlorine gradually decreased to about 40% of the original, in rough agreement with the decrease in the Cl_{2p} signal seen in the survey spectra.

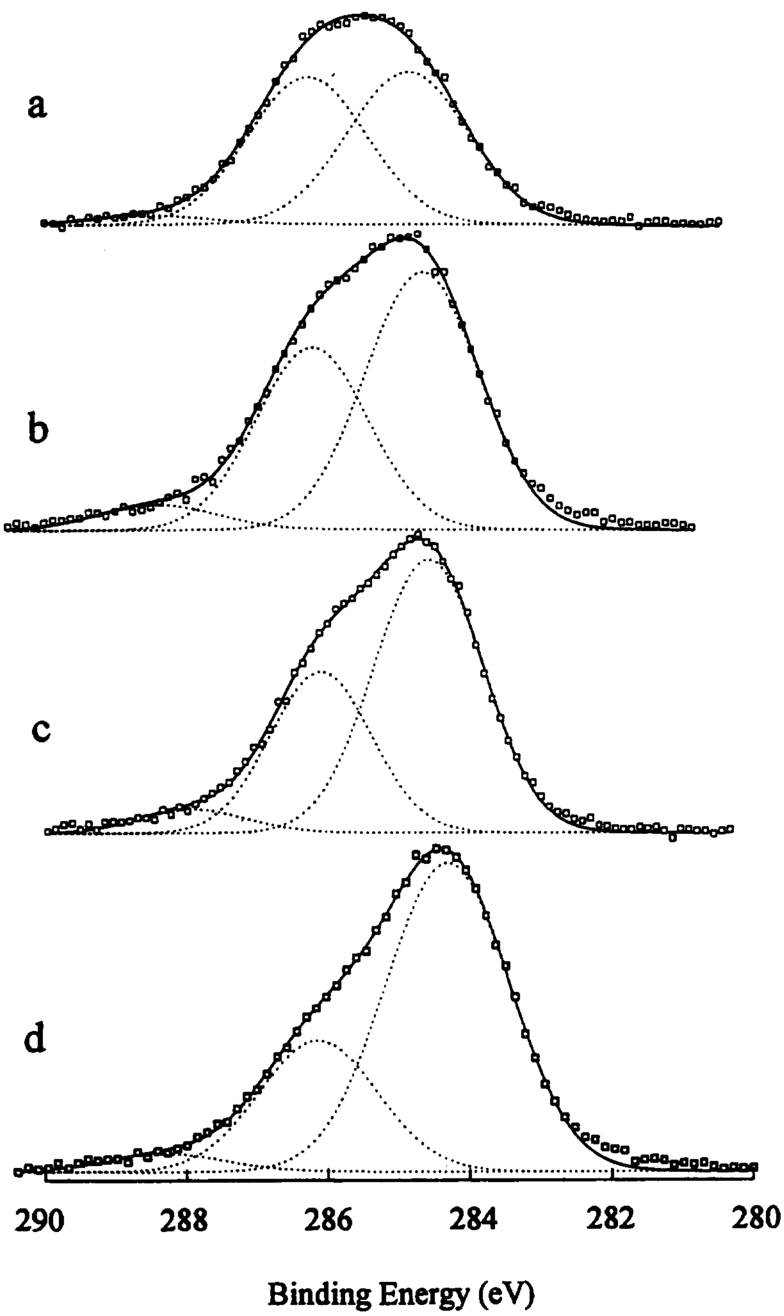


Figure 3 High resolution X.p.s. traces (C_{1s} region) of PVC films allowed to react with **2a** at −78°C for (a) 0 min, (b) 30 min, (c) 60 min and (d) 270 min. The open squares are the original spectrum and the solid line is a simulated spectrum produced by curve fitting. The two major resolved peaks (dashed line) are the major carbon components corresponding to carbon with two hydrogens (CH_2) and carbon attached to chlorine (CHCl) at ca. 284.6 eV and 286.6 eV, respectively

ATR i.r. analysis

ATR i.r. spectra of these dehydrochlorinated PVC films also show evidence for C=C bond formation. When PVC was dehydrochlorinated at 0°C for 1 h, its ATR i.r. spectrum (*Figure 4b*) had an absorbance band at 3015 cm^{-1} ($\nu_{\mathrm{H-C=}}$) and a broad absorbance band at 1630 cm^{-1} ($\nu_{\mathrm{C=C}}$). However, these peaks do not appear in the spectrum of PVC film dehydrochlorinated with **2a** at −78°C for 1 h (*Figure 4a*). There is also an obvious difference between *Figure 4b* and *Figure 4a*. The intensity of i.r. absorbance around 2900 cm^{-1} ($\nu_{\mathrm{C-H}}$) on *Figure 4b* is obviously lower than that on *Figure 4a*. The absorbance bands around 2900 cm^{-1}, 1427 cm^{-1} and 606 cm^{-1} are ascribed to $\nu_{\mathrm{C-H}}$ (stretching), $\delta_{\mathrm{C-H}}$ (bending) and $\nu_{\mathrm{C-Cl}}$ (stretching), respectively[24]. In the ATR i.r. spectra, sampling depth (d_p) varies with wavelength according to

$$d_p = \frac{\lambda}{2\pi n_1[\sin^2\alpha - (n_2/n_1^2)]^{1/2}} \tag{5}$$

where λ is the wavelength of the i.r. radiation in micrometre, d_p is the depth of penetration of the i.r. radiation, n_1 is the refractive index of the ATR crystal, n_2 is the refractive index of the polymer film and α^2 is the angle of incidence of the i.r. beam on the ATR crystal. At 2900 cm^{-1}, 1427 cm^{-1} and 606 cm^{-1}, the calculated sampling depths will be 0.7 μm, 1.4 μm and 3.3 μm, respectively. If the reaction is surface selective and the depth of the modified layer on the surface can be controlled by the reaction temperature, the ratios of the absorbance intensities of these absorbance bands at these wavenumbers will be different at different reaction temperatures. The intensity at 2900 cm^{-1} is expected to decrease faster than that at 1427 cm^{-1} and 606 cm^{-1} with an increase of the reaction temperature because that area of the spectrum is most surface selective. Since the peak at 606 cm^{-1} has the largest sampling depth (3.3 μm), its intensity should be the least sensitive to the surface modification in these three wavelength areas, and it is reasonable to take it as an internal reference. *Figure 5* shows the ratios (I_{2900}/I_{606}, $I_{1427}I_{606}$) of the integrated intensities of the i.r. absorbances changing with the reaction temperature. Here, all the samples were treated with **2a** for 1 h. It can be seen that the intensity at 2900 cm^{-1} decreased faster in the higher temperature region (from −42°C to 0°C) than in the lower temperature region (from −78°C to −42°C). The intensity of the absorbance band at 1427 cm^{-1} decreased more slowly with changes in the reaction temperature owing to the greater sampling depth of ATR i.r. spectroscopy at this frequency, which results in lower surface selectivity. This ATR i.r. spectroscopic study shows that the dehydrochlorination reaction occurred through an interfacial depth of several tenths of a micrometre at 0°C. This result largely agrees with results described above based on u.v.-visible spectroscopy. Any differences that are seen are probably due to problems in achieving good physical contact between the film surface and the ATR i.r. crystal surface, which may cause some deviation in

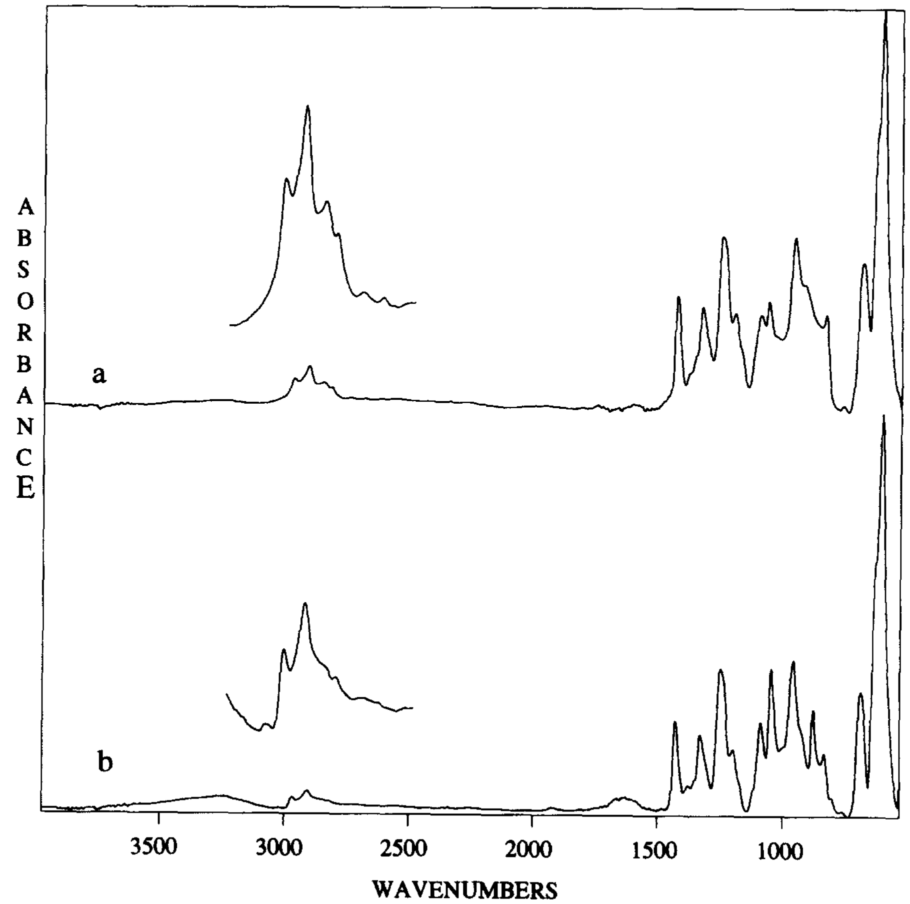


Figure 4 ATR i.r. spectra of PVC films dehydrochlorinated with **2a** for 1 h at (a) −78°C and (b) 0°C

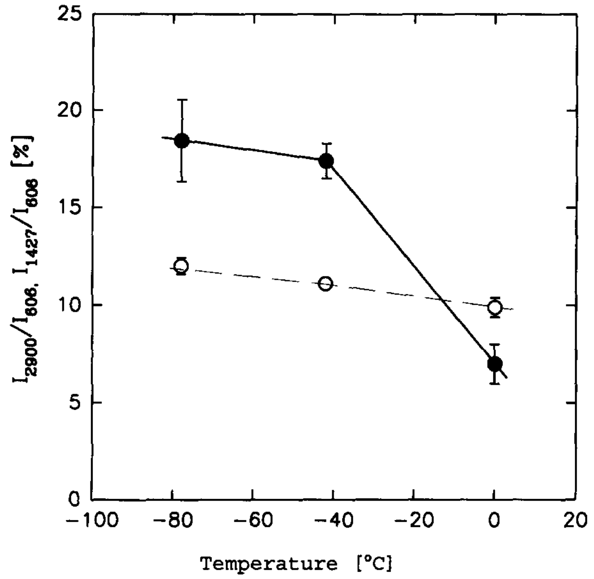


Figure 5 Intensity ratios of ATR i.r. absorbances versus reaction temperature: (—) I_{2900}/I_{606}; (---) I_{1427}/I_{606}

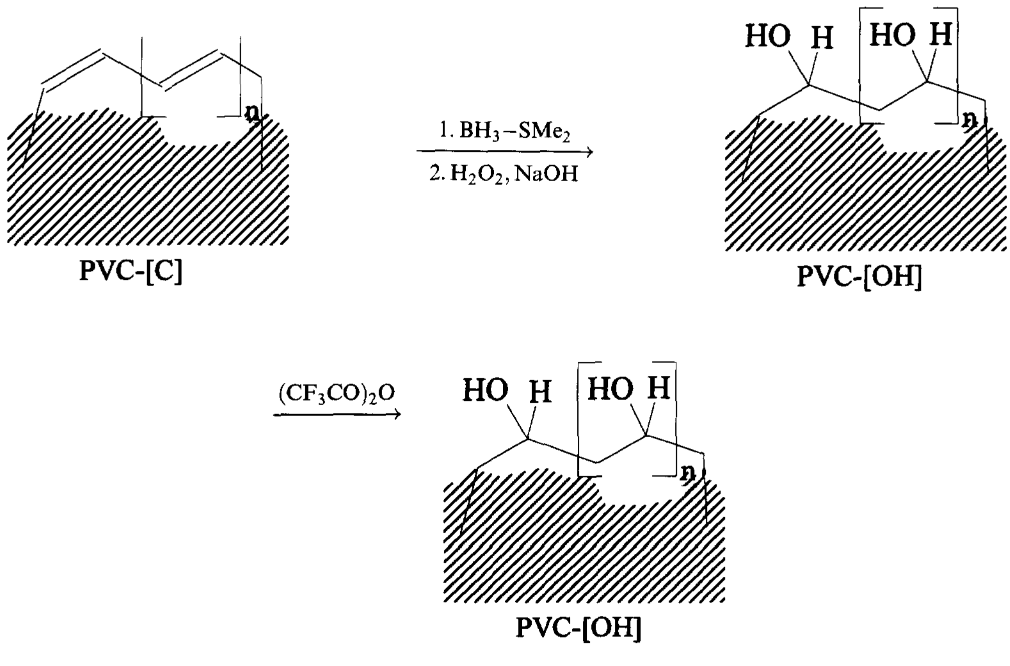
the interphase depth measured[14,25]. The error bars for each point in *Figure 5* represent standard deviations for the measurements.

Further functionalization of the dehydrochlorinated PVC surface

We had originally hoped that the reaction of the lithiated α,ω-diaminopoly(alkene oxide) with PVC would yield products due to both the basicity and nucleophilicity of the lithiated α,ω-diaminopoly(alkene oxide)[8]. Specifically, we had speculated that the initial product of dehydrochlorination would be an allylic chloride that would have enhanced reactivity as a substrate for nucleophilic attack by unreacted lithiated α,ω-diaminopoly(alkene oxide). Indeed, we did observe as much as 3–4 at% of nitrogen by x.p.s. for PVC films treated with **2a** at 0°C. However, at elevated temperature, dehydrochlorination was evidently too fast and the main derivatized product was due to some unknown oxidation process (up to 18 at% of oxygen was present) that occurred during work-up. This oxidation was less of a problem with surfaces generated by treatment of PVC with **2a** at −78°C. However, at −78°C nucleophilic substitution was also decreased (up to 0.5 at% of nitrogen). Separating the elimination and substitution into two separate steps at least partially solved this problem. For example, when a PVC film that had been dehydrochlorinated at −78°C was subsequently treated with poly(ethylene imine) at room temperature, a surface containing 6.9 at% of nitrogen and only a small amount of oxygen was produced.

The two-step dehydrochlorination–modification procedure was most successful when the second step was an addition reaction. Using hydroboration followed by alkaline hydrogen peroxide oxidation, we generated a PVC-[OH] film as schematically shown in equation (6). In this case, the yellowish colour and the u.v.–visible spectrum characteristic of the PVC-[C] film were absent for the hydroborated oxidized film, suggesting that much of the unsaturation was consumed. Advancing and receding water contact angles on pure PVC, PVC-[C] and PVC-[OH] were 91°/72°, 92°/52° and 80°/36°, respectively. These wettability changes are in accord with the premise that a more polar, hydroxylated surface was produced in this chemistry. Further evidence for the presence of OH groups on the PVC-[OH] film was obtained from reaction with $(CF_3CO)_2O$, the product of which had a $\nu_{C=O}$ peak at 1780 cm^{-1} and water contact angles of 89°/50°. X.p.s. traces (*Figure 6*) showed clear and unambiguous evidence for the formation of a surface layer of trifluoroacetoxy groups based on the increases in the F_{1s} and O_{1s} signals. No carbonyl peak and no F_{1s} signal appeared for PVC that had merely been treated with $(CF_3CO)_2O$, supporting our belief that these signals are the result of hydroxy groups being introduced onto the PVC surface by the two-step elimination–hydroboration synthetic sequence.

The most successful derivatization procedure we found



(6)

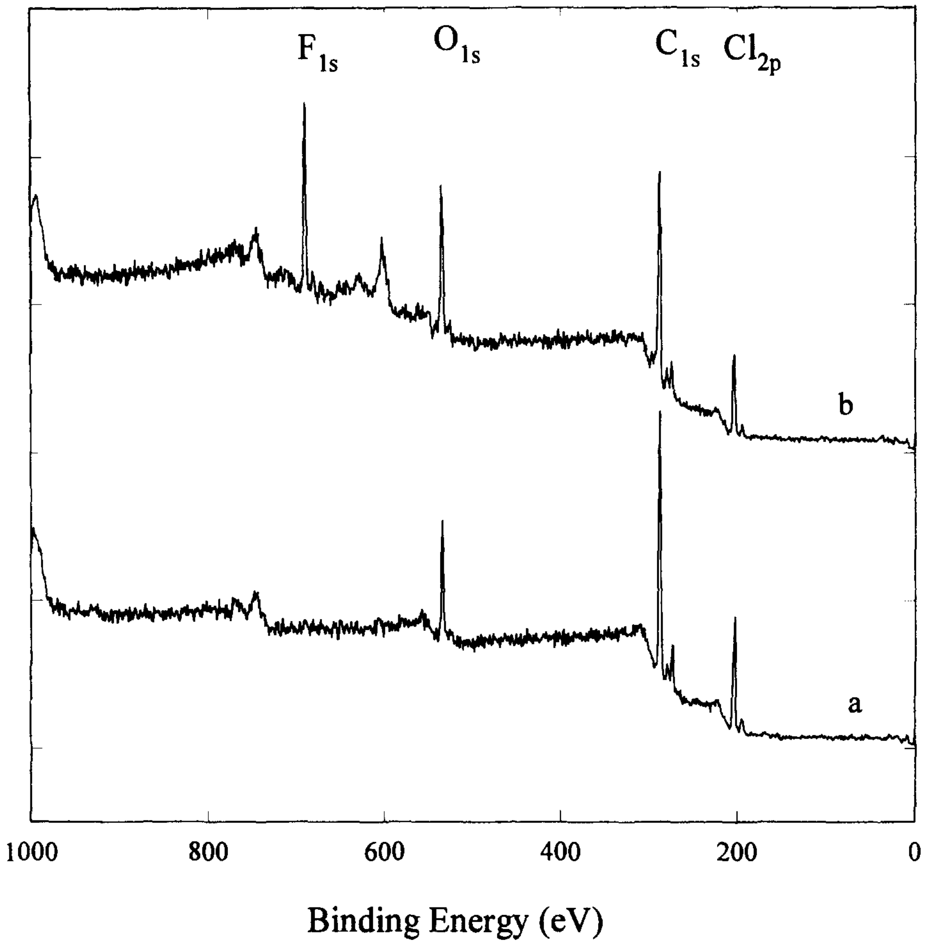


Figure 6 X.p.s. traces of (a) hydroxylated PVC-[C] film (PVC-[OH]) and (b) PVC-[OCOCF$_3$] film formed by esterification of the hydroxylated film with trifluoroacetic anhydride

for the dehydrochlorinated surfaces of these PVC films was hydroboration followed by grafting. Grafting using alkylboranes as graft initiators is an old reaction that has received recent interest owing to the efforts of Chung and coworkers[26,30]. In an earlier publication, we reported that this same chemistry was suitable for heterogeneous grafting onto polyalkenes or PVC using what residual unsaturation is present in either of these substrate polymers[11]. It is thus not surprising that such grafting is also successful on the dehydrochlorinated polymers produced here.

CONCLUSIONS

In summary, dehydrochlorination of PVC films by the lithiated α,ω-diaminopoly(alkene oxide)s **2a–2f** can lead in a controlled manner to chemically modified PVC film surfaces that contain variable amounts of unsaturated groups. The depth of this chemistry can be varied by controlling the reaction temperature. The unsaturated surfaces so formed can be further modified by additional nucleophilic substitution reactions or simple alkene chemistry.

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