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Surface Modification of Ester-Containing Polymers with Anionic Derivatives of Amine-Terminated Oligomers

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The use of metalated derivatives of α,ω-diaminopoly(alkene oxide) oligomers as reagents to modify the surface of ester-containing polymers like poly(methyl methacrylate) and poly(ethylene terephthalate) with concomitant introduction of amino groups onto the surface of these films is described. Metalation significantly activates these amino-containing oligomers since the nonmetalated oligomers do not react to an appreciable extent under these conditions (60 °C, mixed ether–heptane solvent) with these ester-containing polymers. The modified surfaces have greatly enhanced hydrophilicity and contain predominantly α,ω-diaminopoly(alkene oxide) groups covalently bound through a terminal monoamido group based on ATR-IR and XPS spectroscopy. Cross-linking occurred but to only a limited extent. The unreacted amino groups of the α,ω-diaminopoly(alkene oxide) were chemically reactive and acted both as nucleophiles and bases in reactions with soluble reagents.

Introduction

Synthetic methodology affecting polymer surface chemistry has increased in importance in recent years. Such synthetic methodology can broaden the utility of polymers that already have desirable bulk properties.[1–3] The sorts of synthetic methods used vary depending on the substrate polymer. In many cases, chemically harsh methods are used. For example, surface modification of unreactive polymers like fluorinated polymers or hydrocarbon polymers generally require harsh reactions.[2,3] However, milder methods can be used with more reactive polymers.

The focus of this paper is on surface modification of more reactive polymers. Such surface modifications have been the subject of prior work. Oxidative processes like those used with unreactive polymers,[4–6] generation of nucleophilic centers on the polymer chain,[7] electrophilic modification of pendant groups,[8] and polymer modification using controlled aminolysis[9,10] or hydrolysis[11,12] are examples of chemistry that have been used with reactive polymer substrates. For example, recent work by Lee described the use of hydrolytic reactions to modify the outermost few thousand angstroms of polyimides to modify this polymer's adhesive properties,[11] and work by Baum has detailed the use of base to hydrolyze a polyimide surface to yield an ion exchangeable polyamic acid surface.[12] Examples of aminolyses include high-temperature aminolysis of poly(ethylene terephthalate) (PET) by a diaminopoly(ethylene glycol) to alter the hydrophilicity of a PET fiber[9] and modification of poly(methyl methacrylate) by ethylenediamine and its lithiated derivative.[10]

As part of a general program aimed at studying synthetic reactions at polymer–solution interfaces,[13–16] we have examined the utility of lithiated α,ω-diaminopoly(alkene oxide) oligomers for aminolysis of ester-containing polymers. Our interest in this chemistry stemmed from several considerations. First, the use of organometallic derivatives of polymers or oligomers for surface modification has relatively few precedents though similar solution-state chemistry is well established.[17,18] Second, the use of an α,ω-difunctional reagent for surface modification would be useful if reaction at both ends of the reagent could be avoided. In this case, this would allow us to generate a nucleophilic surface from an electrophilic one. Using lithiated derivatives of α,ω-diaminopoly(alkene oxide),[19] we have examined these questions in detail with polymer substrates that contain pendant ester groups or whose ester groups are part of the polymer chain. Poly(methyl methacrylate) was used as a substrate in the first instance. Poly(ethylene terephthalate) was used in the second instance. Our results show that readily available α,ω-diaminopolyethers can be easily activated by metalation and that they usefully modify the surface of these representative ester-containing polymers.

The polymer used in most of the chemistry below was poly(methyl methacrylate) (PMMA). Surface modifications of PMMA are of interest. For example, PMMAs use in biomedical applications is reportedly improved through surface modification using adsorption of poly(ethylene

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imine)[20] and hydrolysis is reportedly useful in modifying the surface and permeability of PMMA-containing gas separation membranes.[21] Poly(ethylene terephthalate) (PET) was the other polyester examined in the studies below. This polyester is easily processed into film and fiber. Modifications of its surface chemistry to increase its hydrophilicity have been reported using the general techniques described above.[5,6]

The α,ω-diaminopoly(alkene oxide) reagents used in our studies are commercially available and sold under the tradename Jeffamine.[19] They are derived from poly(ethylene oxide), poly(propylene oxide), and related α,ω-difunctional polyethers. Our studies mainly used the oligomer **1a** as a representative example of these materials. Similar diamines have also been tested in this chemistry though their products have not been as extensively studied:

$H_2NCHRCH_2(\text{-}OCH_2CHR')\text{-}_nOCH_2CHRNH_2$

1a: $R = R' = H$; $n = 1$
1b: $R = R' = H$; $n = 2$
1c: $R = CH_3$, $R' = H$; $n \approx 43$
1d: $R = CH_3$, $R' = CH_3$; $n \approx 2$
1e: $R = CH_3$, $R' = CH_3$; $n \approx 5$
1f: $R = CH_3$, $R' = CH_3$; $n \approx 32$

The ester groups in a polyester like PMMA can undergo reactions typical of ordinary organic esters although their reactivity is modified by their presence in a solid macromolecular environment. Carboxylic acid ester chemistry in homogeneous organic media usually involves substitution reactions at the carbonyl carbon. For example, aminolysis of esters is a feasible reaction in solution, though such aminolyses usually require an activated ester or harsh conditions. Aminolyses of solid ester-containing polymer also occur.[9,10] However, electrophilicity of an ester carbonyl in a solid polymer is less than that of a soluble ester because the ester groups are located in a polymer matrix. Furthermore, it is not feasible to activate a polymeric ester group. Thus, we reasoned that the use of an activated nucleophile would be appropriate.

Surface chemical modifications can invert the reactivity of a polyester. Polyesters are electrophilic. An inversion of these polymers' reactivity would occur if a product polymer were to incorporate nucleophilic functional groups. For example, decoration of the surface of a PMMA film with amines would introduce nucleophilic sites onto a PMMA film which could then be used in other functionalization or grafting chemistry.

Experimental Section

Materials. Poly(methyl methacrylate) powder and poly(ethylene terephthalate) pellets were purchased from Scientific Polymer Products Co. The PMMA powder was dissolved in chloroform to form a 20% (w/v) solution from which films were cast on polypropylene plates. The films obtained were smooth and transparent in appearance and were 0.05–0.1 mm thick. PET film (0.05 mm thick) was obtained from Du Pont. The PET pellets were made into PET powder by first dissolving them in refluxing nitrobenzene and then precipitating a powder by pouring the resulting solution into methanol at room temperature. α,ω-Diaminopoly(alkene oxide) oligomers were obtained from Texaco Chemical Co. and *n*-butyllithium (*n*-BuLi, 1.6 N in hexane) was purchased from the Aldrich Chemical Co. (Milwaukee, WI).

Representative Procedure for Aminolysis of an Ester-Containing Polymer Film. An α,ω-diaminopoly(alkene oxide) oligomer (1.48 g of **1a** (10 mmol)), 16 mL of anhydrous THF and 28 mL of anhydrous heptane were placed in a 200-mL Schlenk tube under nitrogen. Then, 3.5 mL (5.5 mmol) of *n*-BuLi was added dropwise with stirring using a syringe. After 10 min of stirring, 10 mL of this solution of **2a** was transferred by forced siphon using a cannula to a 20-mL septa-stoppered test tube containing 10 cm² of PMMA film. The aminolysis was carried out at 60 °C with shaking for varying periods of time. After quenching with methanol, the film was washed with 50% aqueous (v/v) methanol five times. The product film was then dried under vacuum overnight.

Analysis Procedures. ATR-IR spectra were recorded on a Mattson FT-IR Galaxy 4021 spectrometer at 1 cm^{-1} resolution using a Zn–Se 45° internal reflection element. Contact angle measurements were performed using a Ramê-Hart goniometer and doubly distilled water as the probe liquid. Dynamic contact angles were defined as advancing (θ_A) and receding angles (θ_R) which were determined as water was added and removed, respectively, from the drop with a Gilmont microsyringe. Contact angle values listed are the arithmetic average of 5–8 measurements on a film. Errors in measurement were estimated statistically as $\pm\sigma$.

Amine group loadings were determined using a literature method.[22] A modified PMMA film (2 cm²) was swollen in 10 mL of THF–heptane (4/7 v/v) for 5 min, treated with 10 mL of 5% (v/v) triethylamine in this same solvent mixture (twice for 3 min each time), washed with 10 mL of this mixed solvent (three times for 2 min each time), dyed with 10 mL of 0.1 M picric acid in this same mixed solvent for 6 min, and washed with 10 mL of the mixed solvent (five times for 2 min each time). The last two washes contained no picric acid by UV–visible spectroscopy. The ionically bound picrate on the film's surface was then removed using 2 mL of 5% triethylamine solution. The loading of $-NH_2$ groups on PMMA film's surface was calculated from the absorbance of the resulting solution at 345 nm using a measured molar extinction coefficient for triethylammonium picrate of 1.4×10^4 M^{-1} cm^{-1}.

Qualitative analyses of aminated PET films and powders were carried out using a mixed indicator solution. The indicator solution was prepared from 5 parts of 0.1% bromocresol green and 1 part of 0.1% methyl red in methanol. Free amine groups were indicated by formation of a blue color.

X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Perkin-Elmer (PHI) Model 5500 ESCA spectrometer (Mg Kα X-ray, 15 kV, 300 W). The incident angle was 45° except as noted. Atomic concentrations on film surfaces were calculated from integrated signal intensities from multiplex XPS spectra and atomic sensitivity factors.[23]

Results and Discussion

The strategy we have adopted to functionalize polyesters with amines is to use difunctional nucleophiles. We hoped to avoid cross-linking reactions by using a large molar excess of the difunctional nucleophile. This necessitated use of an inexpensive precursor which could be recycled. We also hoped to minimize reaction throughout the polymer's bulk by using a large diamine. We had earlier noted that a related chemistry using a smaller diamine like ethylenediamine led to degradation of polyesters.[10] Oligomeric α,ω-diaminopoly(alkene oxide)s **1a–f** met these conditions and were easily activated by metalation with *n*-butyllithium (*n*-BuLi) as discussed below.

The choice of solvent was problematic in PMMA functionalization. While we were not able to find a single, pure solvent that dissolved the lithiated α,ω-diaminopoly(alkene oxide) without damaging or dissolving the PMMA film, mixed alkane–ether solvents were suitable. We chose THF and heptane (4:7 v/v) as a mixed solvent for reactions of PMMA with **2a**. The product film retained its shape but lost some of its clarity when it was suspended in this solvent mixture.

Once a solvent mixture was chosen, an oligomer like **1a** was dissolved in a THF–heptane mixture. Lithiation was

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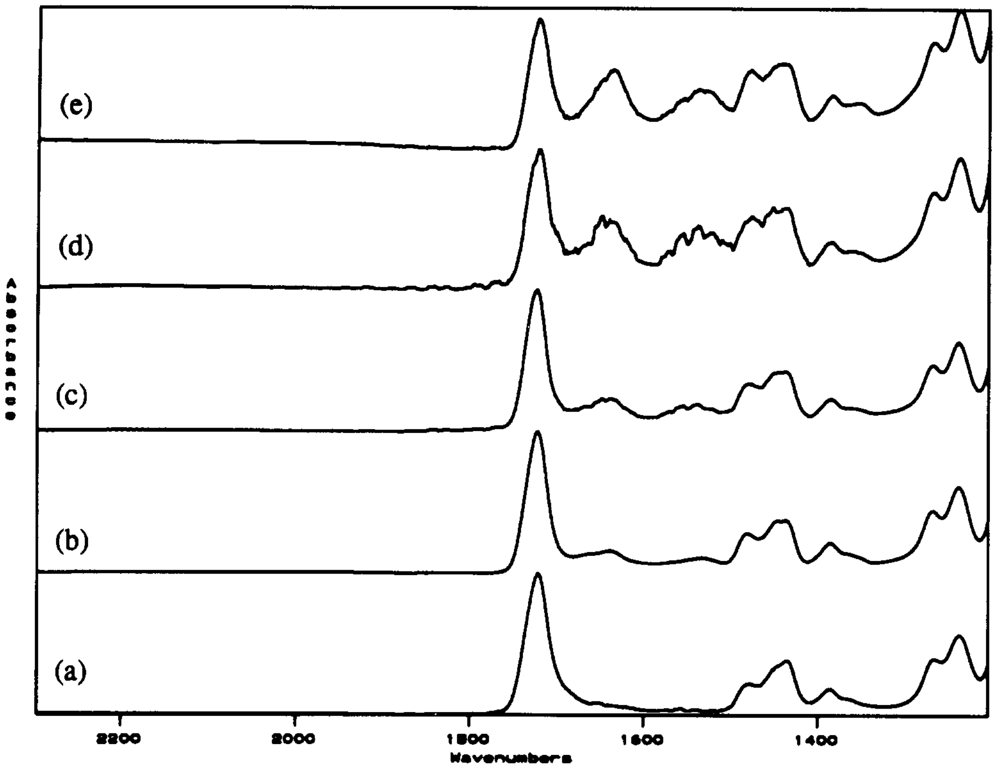
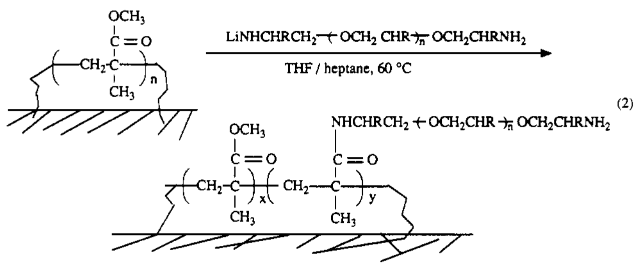


Figure 1. ATR-IR spectra of PMMA films reacted with lithiated α,ω-diaminopoly(alkene oxide) reagents for varying lengths of time at 60 °C: (a) initial PMMA film; (b) 10-min reaction time; (c) 20-min reaction time; (d) 30-min reaction time; (e) 60-min reaction time.

accomplished by addition of *n*-BuLi according to eq 1. The lithiated oligomer **2a** formed was then used to surface modify a PMMA film at 60 °C.

$$\underset{\textbf{1a-f}}{H_2NCHRCH_2(\text{-}OCHRCH_2)\text{-}_nOCH_2CHRNH_2} \xrightarrow{BuLi} \underset{\textbf{2a-f}}{H_2NCHRCH_2(\text{-}OCHRCH_2)\text{-}_nOCH_2CHRNHLi} \quad (1)$$

The course of the reaction (eq 2) was followed by several techniques including IR spectroscopy. An ATR-IR spectrum of the starting PMMA film is displayed in Figure 1a.



(2)

3a - 3f

An ATR-IR spectrum of the product amidated PMMA film is shown in Figure 1e. Comparison of these spectra shows that infrared absorptions at 1645 and 1544 cm^{-1} due to amide I and amide II bands appeared in the film after the film was allowed to react with **2a** at 60 °C for 60 min. These ATR-IR results indicate that the aminolysis reaction of PMMA film occurred as described in eq 2. To crudely examine the surface selectivity of this reaction, the modified PMMA film was ground into a powder and examined by transmission IR spectroscopy. A marked decrease in the IR absorbances at 1645 and 1544 cm^{-1} relative to the ester carbonyl was observed, indicating that the modification selectively happened at the PMMA film's surface. This suggests that reaction of **2a** with PMMA occurred within the outermost 2.5 μm of the film, based on the wavelength of IR radiation being used and the incidence angle (45°) of the ATR-IR spectroscopy.[24] A control reaction using **1a** instead of **2a** was also carried out. ATR-IR spectroscopy did not detect any amide formation when the PMMA film was treated with **1a** in this mixed solvent at 60 °C for 3 h. The product film's ATR-IR spectrum was the same as that of the starting film. This suggests that the α,ω-diaminopoly(alkene oxide) itself was not reactive enough to aminolyze the pendent ester groups on the PMMA surface under these conditions and that the lithiation activated the amine nucleophile as expected.

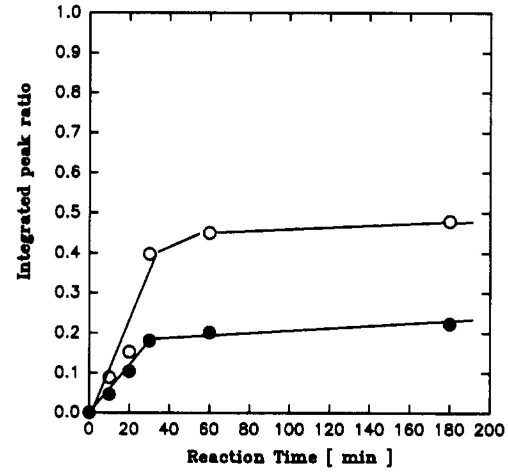


Figure 2. Plot of the A_{1645}/A_{1720} (○) and A_{1544}/A_{1720} (●) ratios from ATR-IR spectroscopy versus the reaction time in aminations carried out at 60 °C in THF–heptane solvent mixtures.

The rate of the appearance of the two amide bands at 1645 and 1544 cm^{-1} as a function of reaction time was examined by ATR-IR spectroscopy. A plot of the integrated IR absorbance intensity ratios of amide bands to the ester band at 1720 cm^{-1} (A_{1645}/A_{1720} and A_{1544}/A_{1720})

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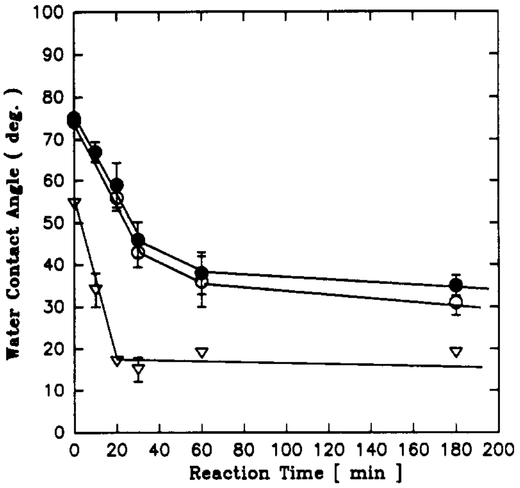

Figure 3. Plot of water contact angles versus the reaction time. Error bars represent one standard deviation for 5–8 contact angle measurements on the same film sample. Three angles were measured: advancing angle (●), Young's angle (○), and the receding angle (▽).

versus the reaction time is shown in Figure 2. This plot shows that the reaction was essentially finished in the ATR-IR surface region within 30 min.

Other surface properties of the PMMA film also changed in these reactions. Hydrophilicity is an important surface property that is a sensitive measure of the identity of functional groups in the outermost few angstroms of polymer films and self-assembled hydrocarbon monolayers.[25,26] Given the change in surface functionalization depicted in eq 2, we expected to see a detectable change in surface hydrophilicity. Figure 3 shows that the contact angle indeed decreased as the reaction time increased. These data indicate that the film's surface became significantly more hydrophilic after the Jeffamine was introduced on the film's surface through amide formation. The contact angle study also showed that the reaction was essentially complete in 20–30 min, in rough agreement with the result from the ATR-IR study (Figure 2).

Both the ATR-IR spectroscopy studies and contact angle measurements provided qualitative evidence for modification of a surface. Quantitative data about the modified PMMA films prepared according to eq 2 were obtained using reactive dyeing procedures. This was accomplished by using a picric acid method and UV–visible spectroscopy to estimate the amine group (–NH_2) loading on the PMMA film's surface.[22] Figure 4 shows that the amine group loading on a PMMA film's surface increased with the reaction time. In these experiments, film samples were carefully washed to ensure that the picric acid measured was ionically bound to a covalently modified PMMA film. Figure 4 shows that the density of amine groups on the surface was as high as 2.5 per Å^2.

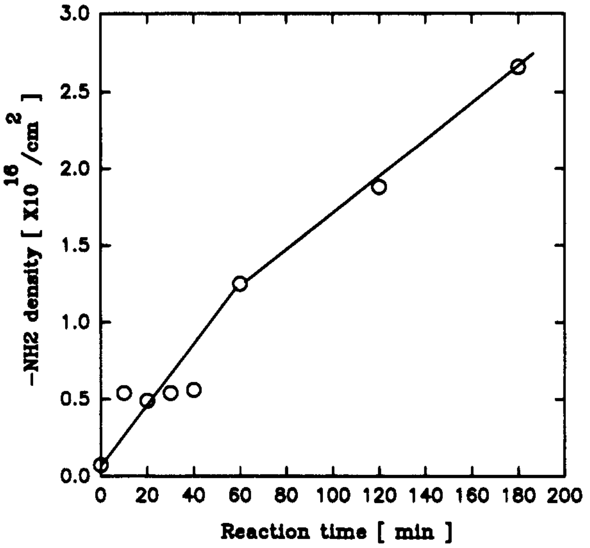

Figure 4. Plot of amine (–NH_2) loadings on PMMA films versus reaction time as measured from the amount of picric acid bound to free amine groups on the functionalized films.

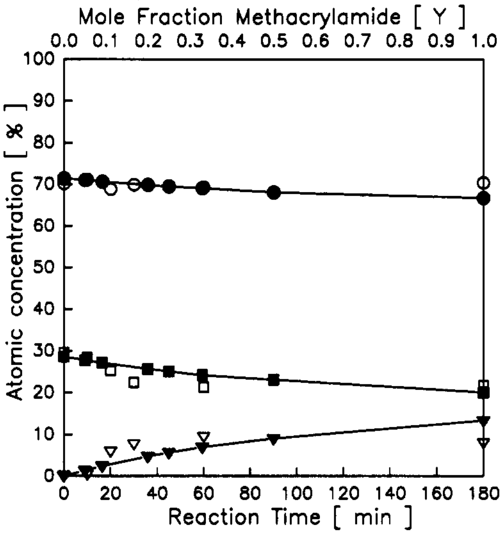

Figure 5. Atomic concentrations of carbon (circles), oxygen (squares), and nitrogen (triangles) on modified PMMA films as measured by XPS spectroscopy versus reaction time. Filled and open circles, squares, and triangles correspond to the calculated and measured atomic concentrations for a given Y value or a reaction time, respectively.

The density of amine groups measured by this reactive dyeing procedure exceeded what could be expected for a simple monolayer. The results suggest that the functionalization reaction produced an interface of amine functionality. This phenomenon is seen in other functionalizations and here is probably due to the presence of multilayers of amide-bonded poly(alkene oxide) amines and a microscopically roughened surface. In addition, Figure 4 shows that the amount of dyeable amine groups continued to increase as reaction time lengthened. Scanning electron micrographs showed that this was due to changes in the morphology of the surface with prolonged reaction time. These scanning electron micrographs showed that the surface of films both developed porosity and were roughened.

XPS spectroscopy was used to more fully characterize the surface of these modified PMMA films. A typical survey spectrum of the original PMMA film sample showed that the starting PMMA film did not have any nitrogen. However, after being modified by suspension in the THF–heptane solution of **2a** at 60 °C for 3 h, a survey spectrum showed that the film contained a nitrogen peak at a binding energy of about 400 eV. High-resolution spectra for the three major constituents (C, N, and O) were also recorded. As was true for the $\nu_{C=O}$ peak intensity (Figure 2), the intensity of nitrogen signal increased with the reaction time while the C_{1s} signal intensity was nearly constant. This is shown by the relative atomic concentrations of three major constituents which were calculated from the integrated intensities of the C_{1s}, N_{1s}, and O_{1s}

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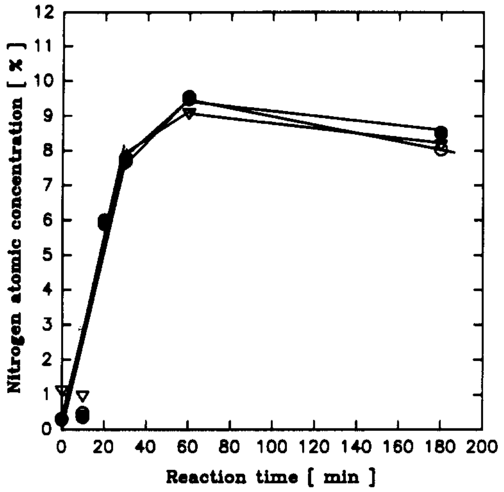
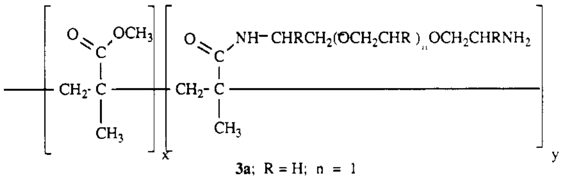


Figure 6. Plot of nitrogen atomic concentrations versus reaction time. Samples were examined at incident angles of 30(▽), 45(○), and 70(●) degrees by XPS spectroscopy.

peaks from these spectra (Figure 5). A graph of the atomic concentration of nitrogen versus reaction time shown in Figure 6 confirmed the approximate course of reaction seen in ATR-IR and contact angle studies. Homogeneity in the atomic composition of the outermost 50–100 Å of the modified films was confirmed using variable angle XPS spectroscopy (the incident angle was varied from 30° to 70°).

The elemental composition changes due to aminolysis can be calculated based on the generalized chemical structure **3a**. Figure 5 compares the calculated atomic

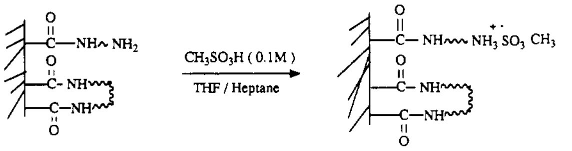


3a; R = H; n = 1

concentrations for various mole fractions of the methacrylamide ($Y = y/(x + y)$) with the measured atomic concentrations. This comparison shows that the mole fraction of methacrylamide at the surface reached a constant value after about 1 h. The highest atomic nitrogen concentration reached was ca. 9% which corresponds to a final mole fraction of methacrylamide of 0.5. This limiting value of 50% for the extent of functionalization is reasonable considering the steric effect of the reagent.

The other goal of our work was to exploit the difunctionality of the starting lithiated diamine to produce a reactive, nucleophilic chemically modified polyester. The principal problem in achieving this result was the potential of **1a** to act as a cross-linking agent. We hoped to maximize the amount of **1a** bound as a monoamide by using a large molar excess of **2a**. A large molar excess of the nucleophile in solution relative to the polymeric ester electrophile was expected to favor a monoamide derivative kinetically because of the bimolecular nature of the reaction between the soluble **2a** and the substrate polymer. In addition, formation of charged species at polymer surfaces is often less facile than similar chemistry in solution.[27] Thus, we expected it would be more difficult to form a second nucleophilic lithium amide anion at the polymer surface and that, consequently, it would be difficult to form a diamide since control experiments implied that activation of the amine was required.

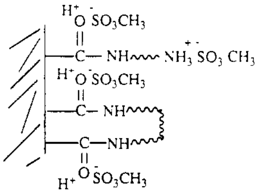
These expectations have largely been realized. The amine loading study (Figure 4) has proven that there are free amine groups at the surface after the reaction. However, the amount of **1a** bound as a mono- versus a diamide was not determined in these analyses. To better estimate the mode of binding of **1a** to the surface, an additional XPS study was conceived. In this labeling study, we sought to differentiate between surfaces containing mono- or diamide with methanesulfonic acid labeling. The putative labeling reaction is shown in eq 3.



(3)

According to eq 3, the ratio of sulfur to nitrogen (S/N) would be in the range 0–0.5 depending on the number of free amino groups. A value of 0.5 would mean that all of the diamine groups were attached to the PMMA surface through covalent bonds at only one end of the chain (a monoamide). If the ratio were zero, both ends of the starting diamine would have reacted to form covalent amide bonds (a diamide). An in-between ratio would represent a mixture of mono- and diamide for which the percentage of two types of binding could be calculated.

In the event, the methanesulfonic acid labeling was carried out in the same way as the picric acid dyeing. We were initially surprised to find an atomic ratio of S/N of 0.7. An S/N ratio greater than 0.5 suggests that there are basic species on the surface of this polymer other than the $-NH_2$ group of **3a**. Considering the acidity of methanesulfonic acid, protonation of amide groups seemed a likely alternative. In this case, the higher amount of sulfur might be accounted for by a protonated surface containing the methanesulfonates shown of **4**. In this case, the excess



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sulfur should be removable by treatment with a soluble amide. Indeed, when we washed samples of **3a** that had been treated with methanesulfonic acid with 10% (v/v) *N,N*-dimethylformamide (DMF) in the aforementioned mixture of THF and heptane 3 times for 3 min each time, this excess sulfur was removed. After being dried in vacuo overnight, these samples were examined by XPS spectroscopy. The results showed that the S/N ratio again leveled off after about 40 min but now the final S/N ratio was 0.36 ± 0.05. This suggests that about 70% of the bound **1a** is present as a monoamide.

The atomic composition of the product from the methanesulfonic acid labeling experiment and the original modified surface were the same after correction for the added atoms of the label. This reconfirmed that **1a** was covalently attached to the surface. It further shows that there were no substantial changes in the surface after CH_3SO_3H labeling and washing as a result of side reactions or surface reconstruction.

The use of higher homologs of **1a** was also successful in this chemistry as judged by XPS and by dyeing experiments of modified PMMA films using picric acid. Oli-

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gomeric α,ω-diaminepoly(alkene oxide)s ranging up to 2000 in molecular weight derived from both poly(ethylene oxide) and poly(propylene oxide) (**1b**–**f**) have been successfully attached to poly(methyl methacrylate).

Extension of this chemistry to polymers in which the ester group was part of the polymer chain was also successful. This was illustrated by the use of **2a** or **2b** to modify PET powders and films (4 h, 25 °C, THF suspension). In both cases, IR peaks at 1645 and 1540 cm^{-1} were detectable when an aminolysis analogous to reaction 2 was carried out. However, treatment of PET powder with **1a** at 25 °C for 4 h did not lead to any detectable amount of amide.

Confirmation of the presence of $-NH_2$ groups on modified PET powders and films was obtained from reactive dyeing experiments. First, a mixed indicator formed from a mixture of 0.1% methyl red and 0.1% bromocresol green in methanol was used to treat films or powders. Either films or powders treated with lithiated α,ω-diaminopoly(alkene oxide) oligomers were dyed blue by this indicator solution. Both an untreated PET film and an amide-containing poly(ϵ-caprolactam) film were unaffected by this indicator solution. To quantitatively measure the amount of $-NH_2$ loading, the picric acid method described previously was used. Using solutions of 0.5–15 g of **2a** in 40 mL of THF, amine loadings on the derivatized polymer powder varied from 0.02–0.17 mmol of $-NH_2$ groups/g. At the highest loading, this corresponds to PET chains with a molecular weight of about 6000 (assuming amine groups as a terminal group) and represents some degradation of the polymer as expected for a reaction involving chain scissive functionalization.

Comparison of aminolysis reactions using lithiated **1a**, **1b**, **1c**, and lithiated ethylenediamine was instructive. In the latter case, reaction for more than 30 min at 25 °C led to significant bulk modification of the starting polymer films. After 2 h, lithiated ethylenediamine completely destroyed the film. In contrast, reaction with the lithiated α,ω-diaminopoly(alkene oxide) oligomers left the PET films intact and transparent after a similar treatment.

Wettability of the PET films changed modestly during this chemistry. In the case of reactions using the smaller α,ω-diaminopoly(alkene oxide) oligomers as reagents, the product film had an advancing water contact angle of 64° versus a starting advancing water contact angle of 74°. Use of the larger α,ω-diaminopoly(alkene oxide) oligomers (**1c**) produced only a 5° change in advancing water contact angle.

In conclusion, the use of lithiated α,ω-diaminopoly(alkene oxide) oligomers as reagents for modification of polyesters via aminolysis reactions is a viable method to modify the surface of these polymers and to incorporate reactive amine groups. Lithiation of the starting reagents produces a more reactive reagent. The amount of free amine groups at the product film and powder surfaces can be quantitatively measured by UV–visible spectroscopy using reactive dyeing methods. XPS spectroscopy and contact angle measurements confirmed that the reactions were largely complete for PMMA films within 30 min at 60 °C. In addition, measurement of the atomic composition of the surface by XPS spectroscopy showed that the predominant species present were α,ω-diaminopoly(alkene oxide) oligomers attached via a single amide bond.

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Registry No. 1c (graft copolymer), 143837-92-7; (MMA)(oxirane) (graft copolymer), 112419-44-0; (MMA)(PPO) (graft copolymer), 125412-38-6.