Solventless Attachment of Long-Chain Molecules to Poly(ethylene-*alt*-maleic anhydride) Copolymer Surfaces

### S. A. Evenson and J. P. S. Badyal*

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, England, U.K.

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Surface functionalization of poly(ethylene-*alt*-maleic anhydride) copolymer films with trifluoroethylamine and amine terminated polyethers (Jeffamines) to form amide linkages has been shown to proceed to high levels of conversion.

Introduction

Functionalized side chains bonded to polymer surfaces are important for a variety of industrial applications (e.g., adhesion, water repellency, lubrication, and biocompatability). Such attachment can be achieved by either surface grafting methods (sensitizers,[1] plasma treatment,[2] high-energy radiation,[3] etc.) or alternatively via direct chemical reaction with groups contained within the parent polymer backbone. A good example of the latter approach is the functionalization of anhydride groups present at the surface of poly(ethylene-*alt*-maleic anhydride) copolymer films. Anhydride group chemistry offers a whole range of possibilities including esterification and aminolysis reactions.[4] Direct surface functionalization reactions tend to be carried out in the solution phase.[5] Some of the major drawbacks associated with this type of method are reorientation of surface groups within the reaction medium and solvent extraction of product species.[5] Vapor-phase treatments can potentially alleviate these pitfalls.[6] In this article, the surface aminolysis of poly(ethylene-*alt*-maleic anhydride) copolymer using 2,2,2-trifluoroethylamine ($CF_3CH_2NH_2$) and a Jeffamine ($H_2N-CH(CH_3)-CH_2-[OCH_2CH(CH_3)]_n-NH_2$) are described.
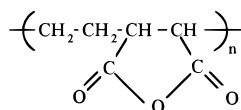
Poly(ethylene-*alt*-maleic anhydride) copolymer

Experimental Section

Poly(ethylene-*alt*-maleic anhydride) copolymer (Zeeland Chemicals, ∼100% purity) films were prepared by spin-coating from a 2 wt %/v acetone solution onto a glass substrate. Fourier transform (FT) infrared spectroscopy was used to check the purity of the polymeric film and the absence of anhydride group hydrolysis.[4] X-ray photoelectron spectroscopy (XPS) was used to confirm complete coverage of the substrate by the copolymer, as signified by the absence of any Si(2p) signals showing through from the underlying glass slide. Poly(ethylene-*alt*-maleic anhydride) copolymer surfaces were reacted with 2,2,2-trifluoroethylamine (Fluorochem, 99.5%) and poly(propylene glycol) bis(2-aminopropyl ether), also known as Jeffamine-D230 (Aldrich, average molecular weight $M_n = 230$).

The reaction procedure comprised placing the polymer coated substrate into a vapor-phase-labeling apparatus,[7] Figure 1,
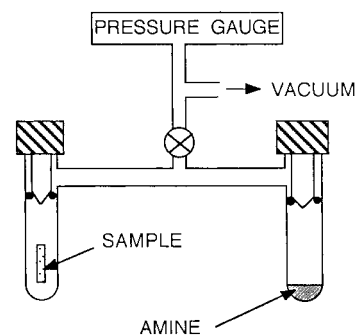
Figure 1. Vapor phase functionalization apparatus.

followed by evacuation to a pressure of better than 1×10^{-2} mbar using an Edwards double-stage mechanical rotary pump fitted with a liquid-nitrogen cold trap. The reaction cell was isolated from the pumping system, and amine vapor was allowed to fill and equilibrate into the empty volume (trifluoroethylamine, 68.5 mbar; Jeffamine, 10.6 mbar) at ambient temperature (∼25 °C). At this stage, timing of the surface functionalization reaction commenced. Upon termination of exposure, the amine reservoir was isolated, and the whole apparatus was pumped back down to its initial base pressure. Typical reaction profiles were compiled by varying the length of contact time between the copolymer surface and each amine, followed by XPS quantification of the extent of aminolysis.

XPS analysis was carried out using a Kratos ES300 electron spectrometer equipped with a Mg K$\alpha_{1,2}$ X-ray source (1253.6 eV) and a concentric hemispherical analyzer. Photoemitted electrons were collected at a take-off angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer. Instrumentally determined sensitivity factors using chemical standards were taken as C(1s):O(1s): F(1s):N(1s) equaling 1.00:0.55:0.67:0.74. FT−IR spectra of poly(ethylene-*alt*-maleic anhydride) copolymer thin films (spin coated onto preformed KBr disks) were acquired on a Mattson Polaris instrument at 4 cm^{-1} resolution in the range 400−4000 cm^{-1}.

Results

(a) Characterization of Poly(ethylene-*alt*-maleic anhydride) Copolymer Films. The C(1s) XPS envelope obtained for poly(ethylene-*alt*-maleic anhydride) copolymer could be fitted to equal amounts of the following carbon functionalities:[8]

Poly(ethylene-*alt*-maleic anhydride) Copolymer Surfaces
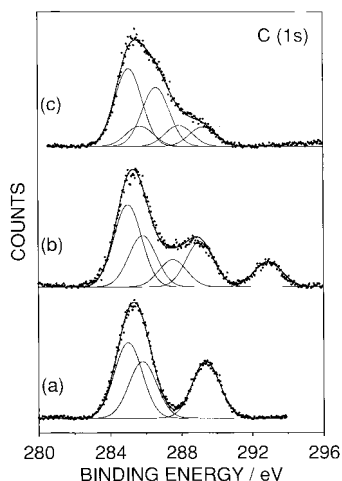
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Figure 2. C(1s) XPS spectra of (a) the untreated poly(ethylene-*alt*-maleic anhydride) copolymer, (b) the copolymer functionalized with trifluoroethylamine, and (c) the copolymer functionalized with Jeffamine D230.

hydrocarbon ($\underline{C}H_x \sim 285.0$ eV), carbon adjacent to an anhydride group ($\underline{C}-C-O(=O) \sim 285.8$ eV), and an anhydride group ($O=\underline{C}-O-C=O \sim 289.4$ eV), Figure 2a; this is in good agreement with the theoretically predicted 1:1:1 ratio. The surface O:C ratio was measured to be $1.00:2.33 \pm 0.02$, which is slightly lower than the expected theoretical value of 1.00: 2.00, and can be attributed to a number of possibilities: the orientation of the anhydride groups away from the near surface toward the bulk, to the presence of a small amount of hydrocarbon contamination, or to $-CH_2CH_2CH_2CH_2-$ residues contained within the copolymer backbone.

Infrared absorption spectroscopy of the copolymer displayed vibrational features at[4] 2947 cm^{-1} (CH_2 stretching), 1778 and 1713 cm^{-1} (C=O in cyclic anhydride), 1460−1370 cm^{-1} (CH_2 deformations), and 1224 cm^{-1} (C=O in anhydride). A very weak absorption band was noted at 725 cm^{-1} associated with skeletal vibrations of $-CH_2CH_2CH_2CH_2-$ residues[4] (this would account for the discrepancy between theoretically predicted and experimentally measured O:C XPS ratios).

(b) Functionalization of the Copolymer Surface with Trifluoroethylamine. The high-resolution C(1s) spectrum of poly(ethylene-*alt*-maleic anhydride) copolymer functionalized with trifluoroethylamine, Figure 2b, can be fitted to five different carbon functionalities:[8] hydrocarbon ($\underline{C}H_x \sim 285.0$ eV), carbon singly bonded to an amide/carboxylic acid group ($\underline{C}-C-NHR-(=O)/\underline{C}-C-OH(=O) \sim 285.7$ eV), carbon singly bonded to nitrogen and to a trifluoromethyl carbon ($N-\underline{C}-CF_3 \sim 287.3$ eV), amide/carboxylic acid group ($RHN-\underline{C}=O/O-\underline{C}=O \sim 289.1$ eV), and trifluoromethyl carbon ($-\underline{C}F_3 \sim 292.9$ eV). The presence of the trifluoromethyl C(1s) peak, as well as the contribution of the three trifluoromethyl fluorines[8] ($-C\underline{F}_3 \sim 687.7$ eV) to the F(1s) region, confirms that surface functionalization has indeed taken place.

The key reaction between polymeric derivatives of maleic anhydride and primary amines is aminolysis.[9] In the case of poly(ethylene-*alt*-maleic anhydride) copolymer and trifluoroethylamine, this leads to the formation of a half-amide, as shown in Scheme 1. Overall aminolysis efficiency can be calculated from the measured surface nitrogen concentration following functionalization.[10,11] For each anhydride group which undergoes reaction, there should be an overall increase by six in the number of atoms detected using XPS (since H is not measured by this technique), corresponding to two carbon, one nitrogen, and three fluorine atoms. Thus, by taking the conversion factor
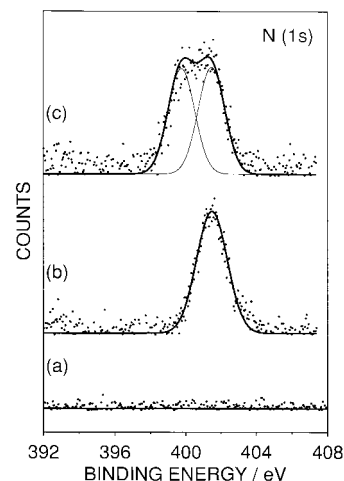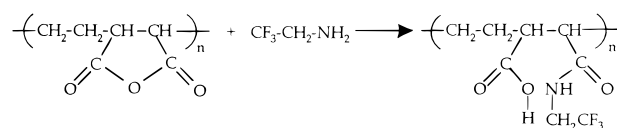

Figure 3. N(1s) XPS spectra of (a) the untreated poly(ethylene-*alt*-maleic anhydride) copolymer, (b) the copolymer functionalized with trifluoroethylamine, and (c) the copolymer functionalized with Jeffamine D230.

SCHEME 1: Reaction of the Copolymer with Trifluoroethylamine

of anhydride to half amide groups as being x (where $x = 0$ in the case of no reaction and $x = 1$ in the case of complete reaction) and by assuming that all elements are homogeneously distributed within the XPS sampling depth both before and after functionalization, the theoretical percentage concentration of surface nitrogen expected at conversion x can be predicted according to eq 1:

$$\%[N] = \frac{[O]_o(1 + x/3)}{[C]_o + [O]_o(1 + 2x)} \times (100) \qquad (1)$$

where $[O]_o$ and $[C]_o$ are the oxygen and carbon concentration levels present in poly(ethylene-*alt*-maleic anhydride) copolymer prior to functionalization (which were determined by experiment to be 30% and 70%, respectively). The actual nitrogen concentration at the surface of the functionalized copolymer can be measured from the area of the N(1s) XPS peak, Figure 3b, and can be assigned to amide nitrogen[8] ($RH\underline{N}-C=O \sim 401.9$ eV). Therefore, a graph of experimental conversion factor (x) vs reaction time can be plotted using the above equation, Figure 4a. This shows that the aminolysis reaction proceeds with an initial rate of reaction $= 0.078 \pm 0.02$ min^{-1} (calculated from the slope of the graph) and a limiting level of nitrogen incorporation occurring after a reaction time of approximately 20 min. Assuming that all of the oxygen atoms present at the surface of the unreacted copolymer are associated with the anhydride functionality, eq 1 yields a conversion factor of $x = 0.95 \pm 0.01$ following 100 min of reaction time.

(c) Functionalization of the Copolymer Surface with Jeffamine. The reaction of Jeffamine D230 with poly(ethylene-*alt*-maleic anhydride) copolymer is described in Scheme 2. The C(1s) spectrum of the copolymer surface following reaction, Figure 2c, could be fitted to five different functionalities:[8] hydrocarbon ($\underline{C}H_x \sim 285.0$ eV), carbon singly bonded to an amide/carboxylic acid group or an amine group ($\underline{C}-C-NHR-(=O)/\underline{C}-C-OH(=O)/\underline{C}-NH_2 \sim 285.7$ eV), carbon singly bonded
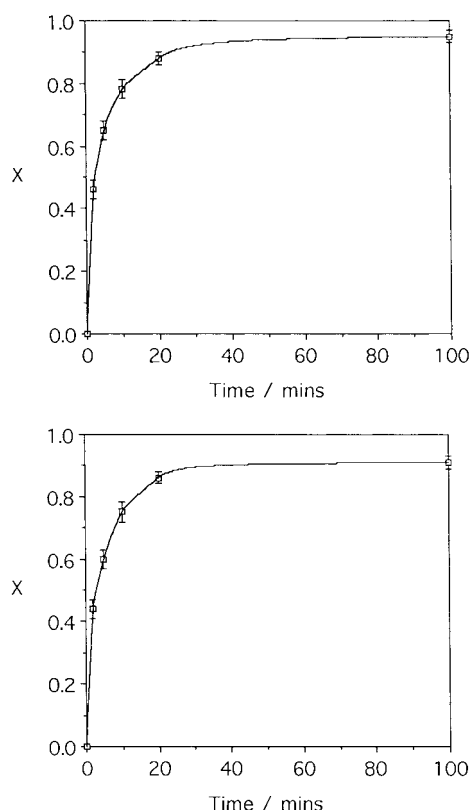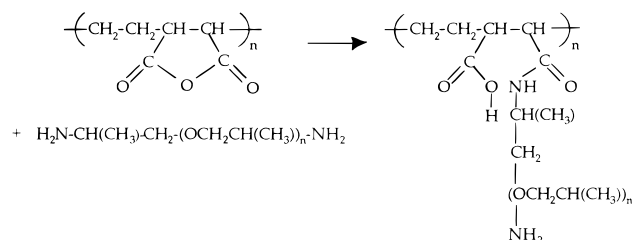
Figure 4. Experimental conversion factors as a function of reaction time for the copolymer functionalized with (a) trifluoroethylamine and (b) Jeffamine D230.

**SCHEME 2: Reaction of the Copolymer with Jeffamine D230**

to oxygen or singly bonded to an amide nitrogen ($-\underline{C}-$O/$\underline{C}-$NH$-$C=O $\sim$ 286.5 eV), amide group (RHN$-\underline{C}$=O $\sim$ 288.7 eV), and a carboxylic acid group (O$-\underline{C}$=O $\sim$ 289.3 eV). The N(1s) XPS region comprises two components arising from amide (RH$\underline{N}-$C=O $\sim$ 401.9 eV) and amine nitrogens (R$-\underline{N}$H$_2$ $\sim$ 399.9 eV) in approximately equal concentrations, Figure 3c, which is consistent with only one end of the Jeffamine molecule participating in the surface functionalization reaction.

The conversion factor was again calculated by measuring the area of the N(1s) XPS peak following surface reaction, Figure 3c. This extent of conversion was then plotted as a function of treatment time, Figure 4b. The initial rate of reaction ($x = 0.075 \pm 0.02$ min^{-1}) and overall conversion factor ($x = 0.91 \pm 0.02$ after 100 min of reaction) for the copolymer functionalized with Jeffamine was comparable to that obtained for trifluoroethylamine.

Discussion

The reaction of ammonia, primary, or secondary amines with anhydride groups is referred to as "Nucleophilic Acyl Substitution".[6] The tetrahedral intermediate, formed during nucleophilic attack on the anhydride group in the copolymer, expels one of

SCHEME 3: General Mechanism of the Nucleophilic Acyl Substitution Reaction of the Copolymer with an Amine to Yield a Half Amide
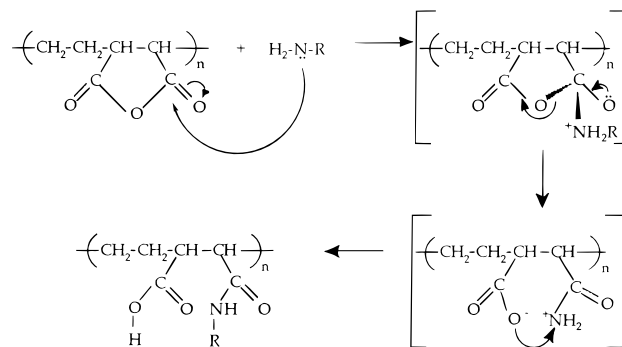
the substituents originally bonded to the anhydride carbon center resulting in the formation of a half-amide, Scheme 3. In the case of maleic anhydride, the half-amide derivative is named maleamic acid. Previous solution phase studies have shown that primary amines produce good to excellent yields of the *N*-alkylmaleamic acids, where the rate of reaction is found to rise with increasing basicity of the amine reagent.[4] The present surface functionalization results for poly(ethylene-*alt*-maleic anhydride) copolymer are consistent with this description. It is important to note that the initial rates of reaction and overall yields for both trifluoroethylamine and Jeffamine are much higher than those found in corresponding experiments concerning the reaction of alcohols with maleic anhydride copolymer surfaces.[12] This can be attributed to the greater nucleophilicity of amines compared to alcohols.[9] Therefore, it can be deduced that, in the general case, an amine of the type XCH$_2$NH$_2$ (where X could be a long alkyl chain, etc.) can be expected to undergo acylation at the maleic anhydride copolymer surface with high levels of conversion.

Conclusions

Vapor phase chemical functionalization of poly(ethylene-*alt*-maleic anhydride) copolymer surfaces with trifluoroethylamine and Jeffamine D230 produces a half-amide linkage, and is found to proceed to virtually 100% conversion. This methodology is a useful way for attaching amine terminated long-chain molecules to solid surfaces containing anhydride centers.

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