Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 4916–4924

polymer

www.elsevier.com/locate/polymer

Nylon surface modification. Part 1. Targeting the amide groups for selective introduction of reactive functionalities

Xinqiao Jia [a,*], Margarita Herrera-Alonso [b,1], Thomas J. McCarthy [b]

[a] Department of Materials Science and Engineering, University of Delaware, 201 DuPont Hall, Newark, DE 19716, USA
[b] Polymer Science and Engineering Department, Silvio O. Conte National Center for Polymer Research, University of Massachusetts, Amherst, MA 01003, USA

Received 23 January 2006; received in revised form 9 May 2006; accepted 16 May 2006
Available online 6 June 2006

Abstract

Nylon is a widely used synthetic polymer because it has a combination of strength, flexibility, toughness, and abrasion resistance. For a variety of applications, however, it is necessary to impart desired surface properties by introducing specific functional groups in specific locations and densities. Several chemical modification methods were developed for the introduction of functional groups to nylon surfaces using amide-selective reactions without cleaving the polymer chains. Activation of amides by reaction with potassium *tert*-butoxide (*t*-BuOK) facilitates the *N*-alkylation of surface amides. When 2-bromoethylamine hydrobromide (BEA–HBr) was employed as an alkylating agent, surfaces with a mixture of primary/secondary/tertiary amine groups were obtained. Alkylation with (3-glycidoxypropyl)triethoxysilane (GPTES) was utilized to prepare surfaces with silica-like reactivity. Chemical reduction with borane–THF complex (BH_3-THF) results in a 69% conversion of surface amide groups to the corresponding secondary amines. A kinetic study of this reaction for different types of nylon films revealed that the yield was dependent on the segmental mobility of the polymer. These surfaces are useful substrates for the fabrication of nylon-supported composite films.

Keywords: Nylon; Modification; Amide-selective

1. Introduction

Nylon was one of the first commercialized polymers and more than 3.25 billion pounds of nylon are produced annually in the United States, most of which is nylon 6/6 [1]. Nylon 6/6 is a semicrystalline material that has a combination of strength, flexibility, toughness, and abrasion resistance. It is also known for its dye-ability, low coefficient of friction (self-lubricating), low creep, and resistance to solvents, oils, bases, fungi, and body fluids [1,2]. The applications for nylon 6/6 include textile fibers, membranes, tapes, food packaging, electronics, and automotive parts. To further improve nylon's performance, it is necessary to introduce specific functional groups on its surface in pre-determined locations, densities, and patterns. For example, selective introduction of amine groups to nylon surfaces is likely to open up new possibilities for nylon because amine-enriched surfaces play an important role in processes such as the removal of heavy metal ions from aqueous solutions [3], for biofouling prevention [4], and for the covalent immobilization of biomolecules such as DNA and polysaccharides [5,6b]. On the other hand, when nylon films are used for food packaging, low gas permeability and a high barrier to water vapor are desirable properties. Since nylon readily absorbs water from air, we speculate that deposition of a dense silicon dioxide layer that is made hydrophobic by further silane chemistry may reduce the amount of water absorbed.

Nylon surfaces have been modified by physical and chemical methods. The first category includes activation of the surfaces through treatment with UV radiation [6], plasma activation [7] or plasma deposition [8]. While these methods are inherently clean, the disadvantages are that chemically well-defined surfaces cannot be designed and prepared and often, functionalization is accompanied by surface destruction [7c]. On the other hand, chemical surface modification of nylon surfaces has been accomplished by reaction at the terminal amine or carboxylic acid groups [9], or at the repeating amide group [10]. Since the concentration of terminal amine groups on the surface is low (0.011 amine ends/nm^2) [10a], high coverage is achieved only when the molecular size and the number of reactive sites of the grafted species are high.

---

[*] Corresponding author. Tel.: +1 302 831 6553; fax: +1 302 831 4545.
E-mail address: xjia@udel.edu (X. Jia).

[1] Present address: Department of Chemical Engineering, Engineering Quadrangle Princeton university, Princeton, NJ 08544, USA.

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.05.038

Problems associated with this modification method include inhomogeneous distribution of functional groups, uncertainty of chain orientation at the surface, and instability of the grafted layers. A more efficient modification approach is by reaction at the amide groups through hydrolysis, *O*-alkylation and *N*-alkylation. Partial hydrolysis of the amide results in an increased concentration of amine and carboxylic acid groups, which have been used for the immobilization of ligands and enzymes [10c]. Examples of N-alkylation include cross-linking of nylon 6/6 yarns by reaction with diisocyanates and diacid chlorides [10a], and activation of the amide with formaldehyde to generate hydroxyl groups that can further be used to immobilize polysaccharides [9b] or covalently bind biocidal moieties [10b].

In this report, we describe the chemical surface modification of nylon films. The reactions employed were targeted at the naturally abundant amide functionality rather than the more reactive amine end groups. Several modification methods were evaluated using nylon 6/6, with the goal of obtaining surfaces with enriched reactive functionalities. *N*-alkylation with 2-bromoethylamine hydrobromide (BEA–HBr) gave rise to surfaces with a mixture of primary/secondary/tertiary amine groups. Ethoxylation of the activated amides with (3-glycidoxypropyl)triethoxysilane (GPTES) were utilized to prepare surfaces with silica-like reactivity. Reduction with BH_3-THF complex proves to be a highly efficient method to introduce surface amine groups, and in-depth kinetics studies were carried out using different types of nylon films including nylon 6/6, nylon 4/6 and nylon 6/12. The surface modifications were monitored by contact angle, X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR-IR) and atomic force microscopy (AFM).

2. Experimental section

2.1. Materials

Nylon 6/6 films, Dartek® C-101 (100 μm), were obtained from DuPont Canada. Nylon 4/6 and nylon 6/12 were purchased from Aldrich as pellets. Sodium hydroxide and solvents used for washing (HPLC grade) were obtained from VWR Scientific. (3-glycidoxypropyl)triethoxysilane (GPTES) was obtained from Gelest. Borane–tetrahydrofuran complex solution (BH_3-THF, 1.0 M in THF), concentrated HCl, triethylamine (TEA, anhydrous), tetrahydrofuran (THF, anhydrous), potassium *tert*-butoxide (*t*-BuOK), dicyclohexyl-18-crown-6 (18-c-6), dimethyl sufoxide (DMSO, anhydrous), 2-bromoethylamine hydrobromide (BEA–HBr), and pentafluorobenzoyl chloride (PFB) were obtained from Aldrich and used as received. Air- or moisture-sensitive materials were stored in dry Schlenk tubes under dry nitrogen. House-purified (reverse osmosis) water was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange and filtration steps (18×10^6 Ω cm, Milli-Q water).

2.2. Characterization

X-ray photoelectron spectra (XPS) were recorded on a Perkin–Elmer-Physical Electronics 5100 spectrometer with Mg K_α excitation at 400 W and 15 kV. Depth profiling was achieved by collecting spectra at 15° and 75° take-off angles with respect to the plane of the sample surface; the analysis at 15° has a penetration depth of ~10 Å and that at 75° corresponds to a penetration depth of ~40 Å [11]. Each reported XPS datum is an average of at least two experimental data points with sample to sample variation of less than 2%. Contact angle measurements were performed using a Ramè-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat tipped needle. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. Contact angles reported are an average of at least three measurements taken at different locations on the sample; all values for each sample were in a range of ±3°. Attenuated total reflectance infrared (ATR-IR) spectra were recorded on a Bio-Rad 175C FT-IR spectrometer using a 45° germanium crystal as internal reflection element. Considering a refractive index value of 1.53 for nylon 6/6, the penetration depth observed by this technique, in the range from 4000 to 700 cm^{-1}, is 0.96–0.17 μm. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments 2100 DSC under nitrogen flow at a heating rate of 10 °C/min. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 microscope system (Digital Instruments, Inc.). Silicon cantilevers with a typical resonant frequency of 300 kHz and spring constant of 42 N/m were used to acquire images in TappingMode at room temperature under ambient conditions.

2.3. Pretreatment of nylon films

Commercial nylon 6/6 film contains a slip agent on one side of the film. The slip agent was removed with an acetone-soaked Kimwipe prior to any modification and only this side was in contact with the sample holder or any glassware during subsequent handling. Surface characterization was performed on the other side of the film. Films were cut into 1.5 cm × 1.5 cm samples and thoroughly rinsed with water, ethanol, isopropanol, acetone, THF, and hexane (in this order), and dried at 50 °C and 2.7 Pa for 24 h. Film samples were stored under vacuum before use.

Nylon 4/6 and 6/12 pellets were rinsed following the same sequence as described above for nylon 6/6 films and dried under reduced pressure (2.7 Pa, 50 °C, 12 h). The pellets were melt-pressed at 300 °C (nylon 4/6) and 190 °C (nylon 6/12) between a silicon wafer and a polyimide film to an approximate thickness of 200 μm. The side of the film that was in contact with the silicon wafer during melt-pressing was used for further analysis. Films were cut into 1.5 cm × 1.5 cm samples, rinsed, dried, and stored in the same manner as described above for nylon 6/6 films.

2.4. N-Alkylation with (3-glycidoxypropyl)triethoxysilane (GPTES) [12]

Potassium *tert*-butoxide (*t*-BuOK, 0.2244 g, 2 mmol) and dicyclohexyl-18-crown-6 (18-c-6, 0.0745 g, 0.2 mmol) were added to a Schlenk flask containing a stir bar and the nylon film samples in a dry box. The flask was then closed and removed from the dry box, and 25 mL of anhydrous THF were introduced via cannula. After stirring at room temperature for 1 h, the alkylating agent, GPTES, (4 mmol) was introduced via syringe, and the reaction mixture was maintained at 50 °C for 3 h. After removal of the solution, the film samples were washed with THF, ethanol, and then immersed in water overnight before drying (2.7 Pa, 50 °C, 24 h). The resulting surfaces are abbreviated as nylon–$Si(OH)_3$.

2.5. N-Alkylation with 2-bromoethylamine hydrobromide (BEA–HBr)

t-BuOK (0.2244 g, 2 mmol) was added to a Schlenk flask containing a stir bar and nylon film samples in a dry box. The flask was then closed and removed from the dry box, and 20 mL of anhydrous DMSO was introduced via cannula. After stirring at room temperature for 1 h, a 10 mL DMSO solution containing BEA–HBr (0.2049 g, 1 mmol) and *t*-BuOK (0.1122 g, 2 mmol), which was premixed and equilibrated at room temperature for 2 h, was introduced via cannula. The reaction mixture was maintained at room temperature for 12 h. Films were isolated and rinsed with DMSO, water, ethanol, THF, acetone, and hexane and dried for 24 h (50 °C, 2.7 Pa). The resulting surfaces are referred to as $^{\text{BEA–HBr}}$nylon–NH_2.

2.6. Reduction with borane–tetrahydrofuran (BH_3-THF) [13]

Twenty-five milliliters of anhydrous THF was added to a nitrogen-purged Schlenk tube containing nylon film samples and a stir bar. a solution of BH_3-THF (1.0 M, 4.0 mL) was introduced using a syringe. The temperature was maintained at 0 °C during the addition. After equilibration at room temperature for 1 h, the solution temperature was raised to 50 °C and maintained for 10 h. The film samples were removed from the reaction media, and thoroughly rinsed with THF, HCl (1.0 N), water, sodium hydroxide (1.0 N), water, THF, ethanol, acetone, and hexane. Samples were dried in a vacuum oven for 24 h (50 °C, 2.7 Pa) before further modification or characterization. The resulting surfaces are referred to as $^{BH_3\text{-THF}}$nylon–NH.

2.7. Labeling of amine groups for XPS characterization [14]

Nylon film samples that exhibit enriched amine groups were placed inside a Schlenk tube, which was then purged with nitrogen for 20 min. Anhydrous THF (25 mL) was added via cannula, followed by pentafluorobenzoyl chloride (PFB, 0.72 ml, 5 mmol) and triethylamine (TEA, 0.28 ml, 2 mmol). The reaction was carried out at room temperature for 4 h. The reaction solution was removed and the samples were washed with THF, ethanol, dichloromethane, acetone, and hexane and then dried (2.7 Pa, 50 °C, 24 h).

3. Results and discussion

Dartek® C-101 is a cast film made from nylon 6/6 for a wide range of industrial applications. One side of the film contains a slip agent (glass beads), and XPS analysis of this side indicates silicon atomic concentration of 3.79 and 1.13% at 15 and 75° take-off angles, respectively. The other side of the film, however, exhibits no contamination from the slip agent, and therefore, was used for XPS and contact angle analysis. Subsequent handling and modification was done ensuring that the slip agent-free side never contacted any glassware, and elimination of the slip agent was done following the procedure described in the Section 2. Since many of the modification reactions were done in anhydrous media, nylon 6/6 film samples were carefully dried under vacuum at high temperature (2.7 Pa, 50 °C) to remove absorbed water. Absorbed water dramatically plasticizes the polymer, leading to a reduced T_g (oven dry, $T_g = 66$–80 °C; 50% RH, $T_g = 35$ °C) [15]. Advancing and receding water contact angles for oven-dried virgin nylon are 69 and 20°, respectively. The crystallinity of the nylon 6/6 film was determined to be 27% by DSC. Surface atomic composition data of clean virgin nylon 6/6 is presented in Table 1 (first entry).

The primary goal of this study is to evaluate the efficacies of several chemical reactions that are applicable to the amide functionality on nylon surfaces. These reactions include *N*-alkylation and reduction. The reduction method was further investigated using different types of nylon films.

3.1. N-Alkylation

The first method employed to introduce functional groups on nylon 6/6 surfaces is *N*-alkylation using 2-bromoethylamine hydrobromide (BEA–HBr) and (3-glycidoxypropyl)triethoxysilane (GPTES) (Scheme 1). Amides are very weak bases, far too weak to attack alkylating agents. Therefore, they must first be converted to their conjugate bases. In the presence of *t*-BuOK, the amide groups can be attacked and partially ionized. In all cases, a large excess of *t*-BuOK (with respect to the amount of amides on nylon surface) were used to maximize the conversion of amide to its conjugate base form. Table 1 shows the XPS and contact angle analyses for *N*-alkylation reactions.

As discussed previously, the reduction of water uptake by nylon films that are used for food packaging may increase the shelf time of the packaged food. To this end, (3-glycidoxypropyl)triethoxysilane (GPTES) was employed as the agent to immoblize reactive silanols to nylon surfaces through *N*-alkylation. The surface activated amide groups are expected to initiate ring-opening polymerization of GPTES, and the presence of ethoxysilyl groups does not interfere with the polymerization. Propagation through the monoethoxylate anion proceeds without interference of the ethoxysilyl group during the anionic polymerization. Termination was achieved

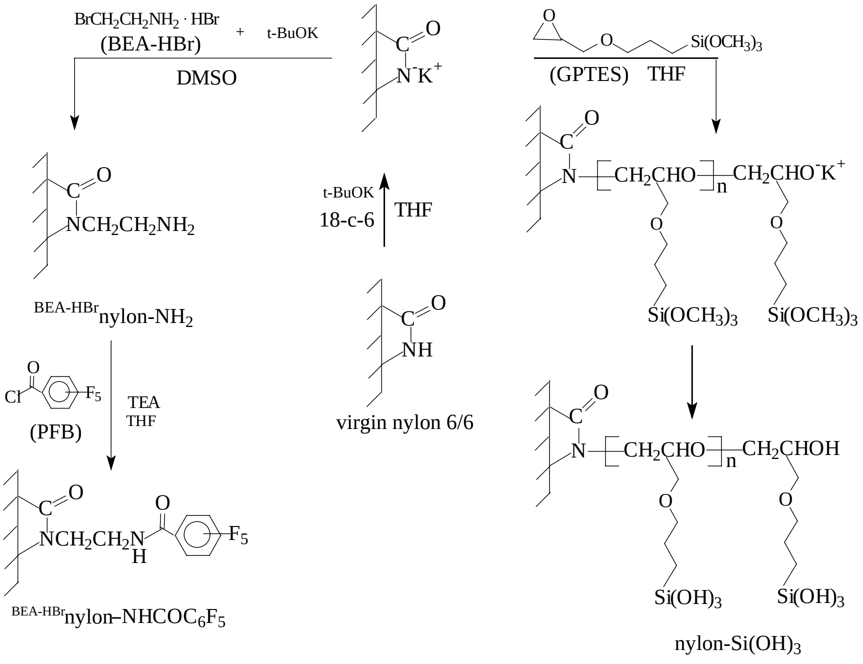
Table 1
XPS atomic composition and water contact angle data for *N*-alkylation reactions on nylon 6/6

Sample	XPS atomic composition (%)[a]				Contact angle (°)[b]	
	C	N	O	Other	θ_A	θ_R
Nylon 6/6[c]	76.09	10.07	13.84		69	20
	78.28	10.77	11.44			
Nylon–COC_6F_5[d]	74.61	8.86	12.35	4.63^F	72	17
	78.05	9.37	10.62	1.95^F		
Nylon–$Si(OH)_3$[e]	37.48	0.00	47.98	14.54^{Si}	51	10
	46.23	1.61	40.19	11.97^{Si}		
$^{BEA–HBr}$Nylon–NH_2[f]	78.12	9.64	12.24		74	10
	77.34	12.79	9.87			
$^{BEA–HBr}$Nylon–$NHCOC_6F_5$[g]	66.69	6.76	9.41	17.14^F	121	<10
	70.75	8.15	8.88	12.21^F		

[a] Upper rows are 15° take-off angle data and lower rows are 75° take-off angle data.
[b] Water contact angle of oven dried samples.
[c] Virgin nylon 6/6.
[d] Virgin nylon 6/6 reacted with pentafluorobenzoyl chloride (PFB).
[e] Nylon 6/6 modified with (3-glycidoxypropyl)triethoxysilane (GPTES).
[f] Nylon 6/6 modified with 2-bromoethylamine hydrobromide (BEA–HBr).
[g] $^{BEA–HBr}$Nylon–NH_2 labeled with pentafluorobenzoyl chloride (PFB).

by exposure to the washing solution whereas hydrolysis of the triethoxysilyl group was done by treatment in water for a prolonged period. The resulting sample is referred to as nylon–$Si(OH)_3$. The abbreviation is used for simplicity and consistency although we recognize that condensation of the silanols to siloxanes occurs to some extent and perhaps nylon–Si(O)OH represents the structure more accurately. The signals attributed to silicon observed in the XPS survey spectra (Si_{2s} at 153 eV and Si_{2p} at 103 eV) were indicative of the incorporation of GPTES functionality onto the surface, while the depth-dependent behavior of the N_{1s} signal suggested that the chemically anchored polymer layer has a thickness between 10 and 40 Å. The high-resolution C_{1s} spectrum (15° take-off angle) for nylon–$Si(OH)_3$ film sample is included in Fig. 1. Notice its strikingly different shape compared to virgin nylon 6/6. Further modification of nylon–$Si(OH)_3$ through chemical vapor deposition using tetrachlorosilane and water as precursors led to nylon-supported composite films that was made hydrophobic by reacting with a fluorinated silane reagent [16].

The fourth and fifth entries in Table 1 summarize the results for *N*-alkylation with BEA–HBr. The availability of primary amine groups in BEA makes it an attractive reagent for anchoring amine functionalities on nylon surfaces. Furthermore, previous study demonstrated that ethyleneimine groups could be introduced into poly(allylamine) by a simple in situ reaction of this polymer with 2-chloroethylamine hydrochloride, resulting in highly-effective polymeric chelating agents [17]. Due to the presence of HBr (1 mol



Scheme 1. Surface modification of nylon 6/6 by N-alkylation and subsequent reactive labeling.

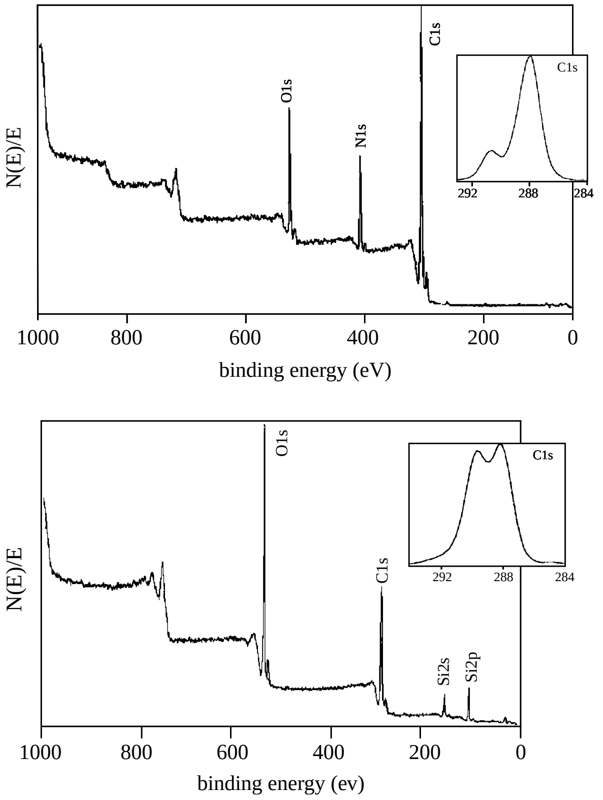
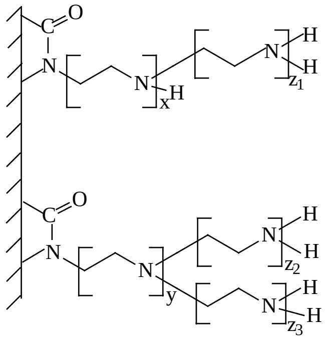


Fig. 1. XPS survey and C_{1s} high-resolution (15° take-off angle) spectra of virgin nylon 6/6 (a) and nylon–Si$(OH)_3$ (b).

equiv), a high yield was obtained when BEA–HBr was premixed with an equivalent amount of *t*-BuOK before introducing it to the reaction medium. The reaction of HBr with *t*-BuOK eliminated the likelihood of deactivation of amide ions by HBr during the subsequent reaction. The product, *tert*-butanol, which is the conjugate acid for *t*-BuOK, is not expected to have any effect on the alkylation reaction. To ensure a more homogeneous reaction medium, DMSO was employed as the solvent instead of THF. Because nylon 6/6 can dissolve in DMSO at high temperature (∼90 °C), the reaction temperature was maintained at ∼20 °C. A small change in the surface composition was observed upon modification with BEA–HBr (Table 1, fourth entry). Compared with virgin nylon 6/6, the advancing contact angle increases ($\theta_A = 74°$) while the receding contact angle decreases considerably ($\theta_R = 10°$), leading to an increase in contact angle hysteresis ($\theta_A - \theta_R = 64°$).

The amine functionalities were labeled by reaction of $^{\text{BEA–HBr}}$nylon–NH_2 with pentafluorobenzoyl chloride (PFB). Fluorine concentrations of 17.14 and 12.21% were obtained for 15 and 75° take-off angles, respectively, indicating surface enrichment with amine functionality. When virgin nylon 6/6 was subjected to the same treatment, a much lower fluorine concentration (4.63 and 1.95%) was detected both at 15 and 75° take-off angles (Table 1, second entry). Assuming no divergent growth, and 100% incorporation of BEA and a 100% labeling reaction, a 20.8% fluorine concentration is expected. The basic conditions employed in our reaction made it possible for in situ polymerization. However, due to steric hindrance, a high extent of dendritic growth is hard to achieve. The contact angle data upon PFB labeling are interesting in that θ_A as high as 121° was accompanied by θ_R of less than 10°. Notice that there is already an increase ($\theta_A/\theta_R = 74°/10°$ for $^{\text{BEA–HBr}}$nylon–NH_2 as compared to θ_A/θ_R of 69°/20° for virgin nylon) in contact angle hysteresis even before the labeling reaction. The extremely high hysteresis is attributed to the fact that the surface chemisorbed layer is thick and flexible. Water can penetrate more deeply into the film due to the favorable interaction of water with amines, causing a depressed receding contact angle. Based on these results, we speculate that a divergent growth is possible under the conditions employed, forming a branched oligomeric ethyleneimine layer that contains a mixture of primary, secondary, and tertiary amines (Scheme 2). The presence of diffuse layer with enriched amine groups also facilitate in situ generation of gold particles via electroless plating [16]. We refer to the modified surface as $^{\text{BEA–HBr}}$nylon–NH_2 for simplicity, realizing the presence of different functionalities on the surface.

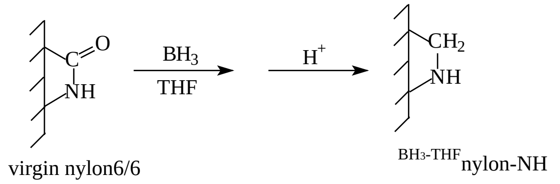


Scheme 2. Proposed surface structure for $^{\text{BEA–HBr}}$nylon–NH_2.

3.2. Reduction

Another interesting reaction suitable for nylon films is the selective reduction of amide repeating units that results in secondary amine groups. Here, we discuss chemical reduction using borane–tetrahydrofuran (BH_3-THF) complexes to produce amine-rich surfaces. The resulting surfaces are referred to as $^{BH_3\text{-THF}}$ nylon–NH (Scheme 3).

As presented in Table 2, contact angle measurements on (BH_3-THF)-reduced nylon 6/6 films reveal improved hydrophilicity ($\theta_A/\theta_R = 30°/15°$ compared to 69°/20° for virgin nylon 6/6), suggesting that a large percentage of surface amide groups were reduced to the corresponding secondary amines. The amine groups on $^{BH_3\text{-THF}}$nylon–NH surfaces can be readily protonated, giving rise to highly hydrophilic surfaces with



Scheme 3. Chemical reduction of nylon surfaces with borane complexes.

Table 2
XPS atomic composition and water contact angle data for reduction reactions on different types of nylon films

Sample	XPS atomic composition (%)[a]				Contact angle (°)[b]	
	C	N	O	Other	θ_A	θ_R
Nylon 6/6[c]	76.09	10.07	13.84		69	20
	78.28	10.77	11.44			
$^{BH_3\text{-}THF}$Nylon 6/6–NH[d]	83.6	10.4	5.5	0.5^{Cl}	30	15
	80.9	12.2	6.5	0.4^{Cl}		
$^{BH_3\text{-}THF}$Nylon 6/6–NHCOC$_6$F$_5$[e]	64.88	3.34	5.90	25.88^{F}	87	36
	65.51	4.84	5.30	24.35^{F}		
Nylon 4/6[f]	79.66	8.37	11.97		57	20
	74.00	13.18	12.82			
$^{BH_3\text{-}THF}$Nylon 4/6–NH[g]	90.27	3.76	5.55	0.43^{Cl}	28	16
	81.91	9.92	7.01	1.16^{Cl}		
Nylon 6/12[h]	86.83	6.48	6.69		78	13
	84.67	7.47	7.86			
$^{BH_3\text{-}THF}$Nylon 6/12–NH[i]	81.61	4.78	12.90	0.71^{Cl}	65	16
	83.41	6.50	8.89	1.11^{Cl}		

[a] Upper rows are 15° take-off angle data and lower rows are 75° take-off angle data.
[b] Water contact angle of oven dried samples.
[c] Virgin nylon 6/6.
[d] Nylon 6/6 reduced by BH_3-THF.
[e] $^{BH_3\text{-}THF}$Nylon 6/6–NH labeled with pentafluorobenzoyl chloride (PFB).
[f] Virgin nylon 4/6.
[g] Nylon 4/6 reduced by BH_3-THF.
[h] Virgin nylon 6/12.
[i] Nylon 6/12 reduced by BH_3-THF.

water contact angles of 20 and 5° for advancing and receding angles, respectively. XPS analysis also provided information regarding the reduction efficiency. Compared with virgin nylon 6/6, reduction with BH_3-THF led to a dramatic decrease of surface oxygen concentration (Table 2, second entry). High-resolution spectra of the C_{1s} region for virgin nylon 6/6 and $^{BH_3\text{-}THF}$nylon–NH are shown in Fig. 2. The C_{1s} region was curve-fitted with four peaks, with binding energies at 289.01 eV ($\mathit{C}H_2$), 289.49 eV ($\mathit{C}H_2C{=}O$), 290.08 eV ($\mathit{C}H_2NH$), and 292.01 eV ($CH_2\mathit{C}{=}O$) [18]. The higher binding energies of these signals compared to values previously reported are attributed to charging of the sample during analysis, however, curve-fitting was performed maintaining the differences in binding energies constant. It is clear that the reaction proceeded to a high extent, since the signals attributed to the amide group ($\mathit{C}H_2C{=}O$ at 289.49 eV and $CH_2\mathit{C}{=}O$ at 292.02 eV) almost disappear, in agreement with the water contact angle and atomic composition data. Because of its ease of identification, the signal characteristic of the carbonyl carbon was chosen to quantify the degree of reduction. Yields were estimated by comparing the area of this signal at a given time $(A^{C=O})_{to}$ referenced to its value for virgin nylon $(A^{C=O})_{to}$ as: yield (%) = $[(A^{C=O})_t-(A^{C=O})_{t_0}]/(A^{C=O})_{t_0}$. Based on this relationship, the yield of reduction after a 10 h reaction with BH_3-THF was 69%.

Reduced nylon 6/6 films were further derivatized by reaction with PFB and the results are presented in Table 2 (third entry). A much higher fluorine concentration was observed for surfaces treated with BH_3-THF as compared to the control sample (Table 1, second entry). To probe the penetration depth of the reduction with BH_3-THF, ATR-IR analysis was performed on the reduced samples. The resulting spectra (data not shown) are similar to virgin nylon, with no indication of secondary amines. This indicates a depth of reaction much less than the 0.17 μm sampling depth of ATR-IR. XPS, contact angle, and derivatization results suggest that upon reduction with BH_3-THF in THF, the solvent properties of the medium change with respect to the substrate, which at this point is present as the amine–borane complex, such that diffusion of the reagents into the film is possible

In-depth kinetics studies were carried out in order to gain insight into the reduction reaction. Samples were subjected to XPS analysis at predetermined times, and quantification was achieved by curve-fitting the C_{1s} region at different take-off angles. Fig. 3 shows the compositional change as a function of reaction time for nylon 6/6 films. With the increase of the reaction time, the relative percentages of the carbons associated with the carbonyl group ($\underline{C}H_2C{=}O$ and $CH_2\underline{C}{=}O$)

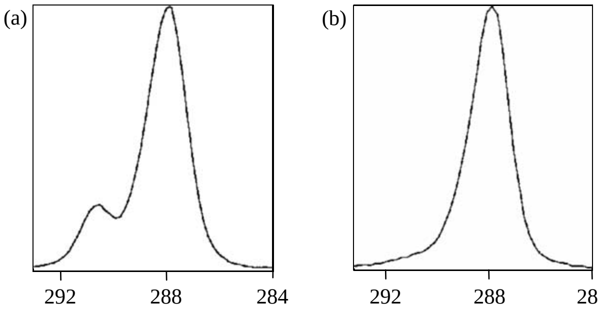


Fig. 2. High-resolution C_{1s} spectra (15° take-off angle) for virgin nylon 6/6 (a) and $^{BH_3\text{-}THF}$nylon–NH (b).

decrease, while those associated with amino group ($\underline{C}H_2$ and $\underline{C}H_2NH$) increase. Assuming a complete reduction of the amide group, the surface concentration of $\underline{C}H_2$ and $\underline{C}H_2NH$ species should correspond to 66.66 and 33.33%, respectively, while that of the $\underline{C}H_2C{=}O$ and $CH_2\underline{C}{=}O$ species should approach zero. If the reaction were confined to the surface, the take-off angle dependence should be such that a lower concentration of amide-related signals and a higher concentration of amine-related signals should be observed at lower take-off angles. The data presented in Fig. 3 show that this is not the case since no clear take-off angle dependent behavior is observed. This discrepancy suggests that the polymer chains at the solvent/film interface are relatively mobile during the reaction. As a result, a thicker modified layer with relatively homogeneous amine concentration is obtained. The experimental results, however, do approach the values theoretically predicted at long reaction times (24 h).

To evaluate the effect of chain mobility on the reaction, we studied three types of nylon that differ in their methylene ratios: nylon 4/6, nylon 6/6, and nylon 6/12. Nylon 4/6 and 6/12 pellets were melt-pressed into films of approximately 200 μm thickness, whereas nylon 6/6 films were obtained directly from DuPont with a thickness of 100 μm. The surface atomic compositions and water contact angles are included in Table 2. Fig. 4 summarizes the reaction kinetics for different types of nylon films, in terms of the yield as a function of reaction time and XPS sampling depth. It can be concluded that the yield is independent of the characteristics (T_g and crystallinity) of the nylon at the outermost surface layer (10 Å). Deeper into the film (40 Å from the surface), differences in segmental mobility and crystallinity begin to gain importance. The XPS data for nylon 6/6 and 6/12 indicate that the reaction occurs to comparable extents throughout the surface (Fig. 4(b) and (c)). This behavior contrasts that of nylon 4/6, for which stronger penetration-depth dependence was observed (Fig. 4(a)). These results can be explained in terms of the difference in segmental mobility and crystallinity of the nylon films during the reaction. The glass transition temperatures of the nylon films studied are 78 °C for nylon 4/6, 66–80 °C for nylon 6/6, and 50–60 °C for nylon 6/12. On the other hand, their crystallinity, as determined by DSC was 44, 27, and 18% for nylon 4/6, nylon 6/6 and nylon 6/12, respectively. The higher

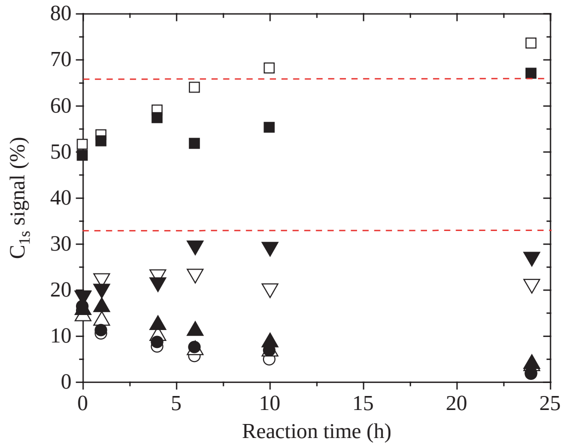


Fig. 3. XPS curve-fitting analysis of the C_{1s} region of $^{BH_3\text{-}THF}$nylon–NH as a function of reaction time. Closed and open signals correspond to data acquired at 15 and 75° take-off angles, respectively. $\underline{C}H_2$ (■, □); $\underline{C}H_2NH$ (▼, ▽); $\underline{C}H_2C{=}O$ (▲, △); $\underline{C}{=}O$ (●, ○). Dotted lines indicate the theoretical limits.

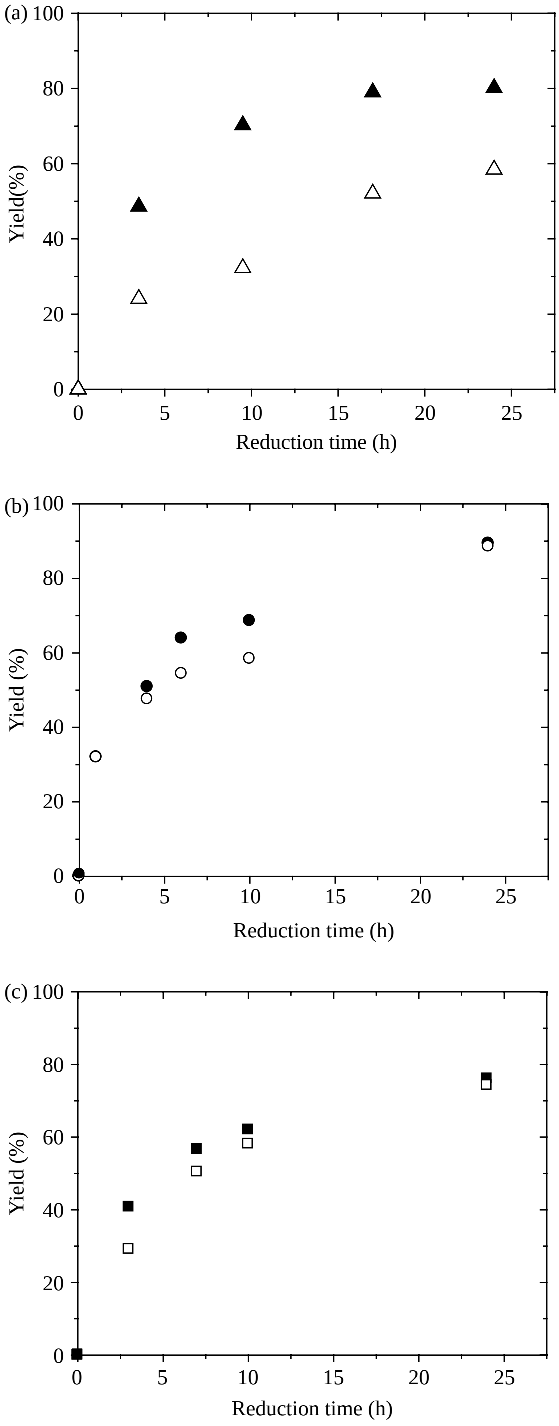


Fig. 4. Reduction kinetics determined by XPS at different take-off angles: (a) nylon 4/6 at 15° (▲) and 75° (△); (b) nylon 6/6 at 15° (●) and 75° (○); (c) nylon 6/12 at 15° (■) and 75° (□).

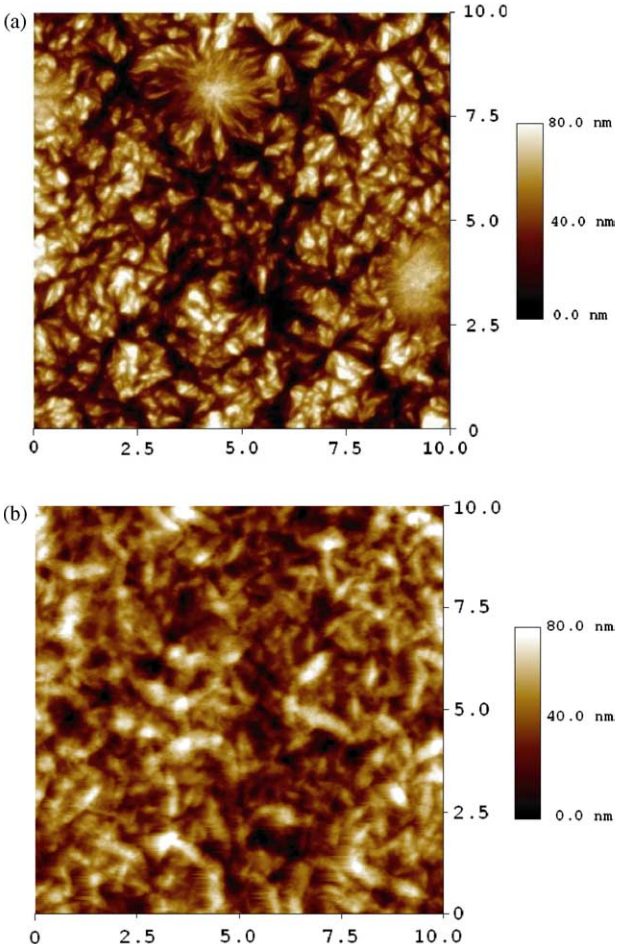


Fig. 5. TappingMode AFM images of $^{BH_3\text{-}THF}$nylon–NH films at different reduction times: 0 h (a) and 10 h (b). Images correspond to height plots of a 10 μm × 10 μm sampling area.

crystallinity for nylon 4/6 film limits the diffusion the reagents into the film, giving rise to its stronger depth dependence. Nylon 6/12 film exhibits the lowest T_g and crystallinity, therefore, the modified layer of this polymer is expected to be the thickest. However, XPS is a surface-sensitive technique that can only detect the ourtermost 40 Å surface layers, which may explain the similar penetration dependence behavior for nylon 6/6 and nylon 6/12.

Film morphology was examined by AFM. Height-image micrographs corresponding to the reduction of nylon 6/6 at different reaction times are presented in Fig. 5. The AFM images reveal that the original well-defined, spherulitic morphology of virgin nylon 6/6 is gradually lost upon reaction. After 10 h of reaction, the morphology has changed considerably. This can be explained in terms of the change in the solvent properties with respect to nylon. Although THF is neither a plasticizer nor a solvent for the nylon films studied here, the amine–borane complex anchored on the surface during the reaction is soluble in THF [19], resulting in increased chain mobility on the surface. The reorientation of the polymer chains on the surface inevitably leads to altered surface morphology.

4. Summary

Several techniques were developed to introduce reactive functional groups to nylon surfaces using reactions that target at the naturally abundant amide groups. Activation of amides with potassium *tert*-butoxide facilitates the *N*-alkylation of surface amides. When 2-bromoethylamine was employed as the alkylation reagent, surfaces with branched oligmeric ethyleneimine were obtained. Alkylation with (3-glycidoxypropyl) triethoxysilane generated surfaces that contain poly (ethylene glycol) with pendant silanols (nylon–Si(OH)$_3$). Reduction of surface amide groups by reaction with BH$_3$-THF complex produced surfaces enriched in secondary amine groups. This reaction occurred in high yields and was not confined to the outermost surface layers. Reaction yields depend on the segmental mobility of the polymer, which in turn, is determined by the glass transition and degree of crystallinity of the film. Surfaces with enriched functional groups were utilized as the ‘reactive handles’ for the fabrication of nylon-supported composite films [16].

Acknowledgements

We thank the Office of Naval Research and the NSF-sponsored Materials Research Science and Engineering Center at University of Massachusetts at Amherst for financial support.

References

[1] Odian G. Principles of polymerization. 3rd ed. New York, NY: Wiley; 1995.
[2] Brandrup J, Immergut EH, editors. Polymer handbook. New York, NY: Wiley; 1989.
[3] Deng S, Bai R, Chen JP. Langmuir 2003;19:5058.
[4] Dhamodharan R, McCarthy TJ. Macromolecules 1999;32:4106.
[5] (a) Morra M, Cassinelli C. Langmuir 1999;15:4658.
  (b) Zammateo N, Girardeacex C, Delforge D, Pireaux J, Remacle J. Anal Biochem 1996;236:85.
[6] (a) Shearer AEH, Paik JS, Hoover DG, Haynie SL, Kelley MJ. Biotechnol Bioeng 2000;67:141.
  (b) Ulbricht M. React Funct Polym 1996;31:165.
[7] (a) Foerch R, Hunter DH. J Polym Sci, Part A: Polym Chem 1992;30:279.
  (b) Tušek L, Nitschke M, Werner C, Stana-Kleinschek K, Ribitsch V. Colloids Surf, A 2001;196:81.
  (c) Lai JY, Shih CY, Tsai SM. J Appl Polym Sci 1991;43:1431.
[8] Weikart CM, Miyama M, Yasuda HK. J Colloid Interface Sci 1999;211:18.
[9] (a) Tobiesen FA, Michielsen S. J. Polym Sci, Part A: Polym Chem 2002; 40:719.
  (b) Beeskow T, Kroner KH, Anspach FB. J Colloid Interface Sci 1997; 196:278.
  (c) Michielsen S. J Appl Polym Sci 1999;73:129.
[10] (a) Perry E, Savory J. J Appl Polym Sci 1967;11:2473.
  (b) Lin J, Winkelman C, Worley SD, Broughton RM, Williams JF. J Appl Polym Sci 2001;81:943.
  (c) Bickerstaff GF. Methods in biotechnology. Immobilization of enzymes and cells, vol. 1. Totowa: Humana Press Inc.; 1997.
[11] Clark DT, Thomas HR. J Polym Sci, Polym Chem Ed 1977;15:2843.
[12] (a) Luh T-Y, Fung ST. Synth Commun 1979;9:757.
  (b) Feng Y, Billon L, Grassl B, Khoukh A, François J. Polymer 2002;43: 2055.
  (c) Dérand H, Jannasch P, Wesslén B. J Polym Sci, Part A: Polym Chem 1998;36:803.

[13] Brown HC, Heim P. J Org Chem 1973;38:912.
[14] Chapman TM, Benrashid R, Marra KG, Keener JP. Macromolecules 1995;28:331.
[15] Williams JCL. In: Kohan MI, editor. Nylon plastics handbook. New York, NY: Hansen Publishers; 1995. p. 294.
[16] Herrera-Alonso M, McCarthy TJ, Jia X. Langumir 2006;22:1646.
[17] Kuo P-L, Ghosh SK, Liang W-J, Hsieh Y-T. J Polym Sci, Part A: Polym Chem 2001;39:3018.
[18] Beamson G, Briggs D, editors. High resolution XPS of organic polymers: the scienta ESCA 300 database. New York, NY: Wiley; 1992.
[19] Perner T, Schultz RC. Br Polym J 1987;19:181.