Immobilization of Poly(ethylene Oxide) on Poly(ethylene Terephthalate) Using a Plasma Polymerization Process

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Synopsis

Poly(ethylene oxide) (PEO) has been covalently immobilized on poly(ethylene terephthalate) (PET) films using a radio frequency glow discharge polymer deposition process, followed by chemical coupling. Amino or hydroxyl groups were introduced onto the surface of the PET by exposing the films to allylamine and allyl alcohol plasmas. These functional groups were activated with cyanuric chloride, and then they were reacted with PEO. ESCA and water contact angle studies were used to characterize the surfaces of these films during the different stages of the reaction. The films containing the higher molecular weight PEO exhibited an increase in the —C—O— peak of the C_{1s} ESCA spectrum and an increase in oxygen content on the film surfaces. Increasing the molecular weight of the PEO attached to the PET also resulted in an increased wettability of the films.

INTRODUCTION

Poly(ethylene oxide) (PEO) is a synthetic, nontoxic water-soluble polymer used widely in the cosmetic, chemical, and biomedical industries.[1] In the last few years an increased interest has developed in the covalent attachment of PEO to different substrates. This interest is perhaps due to some of the unique properties that PEO-coated surfaces possess. PEO is both nonionic and hydrophilic. Coated PEO surfaces exhibit low degrees of protein adsorption and cell adhesion[2-14] and have the ability to chelate cations.[15] Some potential applications of PEO surfaces include improved biocompatibility,[2-14] antifouling coatings for biosensors, immunoassays, and affinity separation systems, improved electrophoresis and isoelectric focusing,[16] phase transfer catalysis,[17,18] and improvement in the hydrophilic and antistatic properties of synthetic, hydrophobic polymers.[19]

Several techniques have been used to covalently attach PEO to surfaces. These include graft copolymerization,[7-9,20] incorporation into polyether polyurethanes,[2-7] and the direct attachment of PEO molecules to a surface.[11-13,16] The direct attachment technique may lead to surfaces containing pendant PEO chains while the other methods contain PEO molecules which are either branches on a graft polymer backbone or which are segments in the backbone of a polymer. The direct attachment methods employ PEO molecules which have first been derivatized using a reactive coupling agent. The activated PEO then reacts with a functional group on the surface. Cyanuric chloride is one coupling agent that has been used to attach PEO to a quartz substrate

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containing aminopropyl groups.[16] The PEO in this previous study was first derivatized using cyanuric chloride[21] and then allowed to react with the amino groups on the glass. In this paper we describe a technique for attaching PEO directly to a cyanuric-chloride-activated PET surface.

The main research interests of our laboratory are in the field of polymeric biomaterials. PET is one such material which is currently used for a variety of artificial implants. Applications of PET biomaterials include vascular grafts, heart and major blood vessel patches, heart valve sewing rings, artificial ligaments, sutures, and backings of implants to permit tissue fixation. Despite the wide use of PET as a biomaterial, there is a need for improved biocompatibility of PET implants, particularly the blood-contacting materials. We are therefore immobilizing PEO on PET in an attempt to improve the blood compatibility of PET.

Amino or hydroxyl groups are first introduced on the PET surface by exposing the films to a radio frequency glow discharge (RFGD) of either allylamine or allyl alcohol. The functional groups are then activated with cyanuric chloride. Bisamino PEO, Jeffamines, and PEO-containing hydroxyl end groups then react with the cyanuric-chloride-activated PET. Electron spectroscopy for chemical analysis (ESCA) and water contact angle measurements were used to characterize these surfaces during the different stages of the PEO immobilization reaction.

EXPERIMENTAL

The PET substrates used in this study were 2.4 × 3.3 cm Lux Thermanox coverslips purchased from Miles Scientific Laboratories, Naperville, IL. In order to prevent oxidation of the PET surface, we asked the company not to expose the films to an oxygen plasma. This procedure is usually done to sterilize the films. The bisamino PEO samples of molecular weight 200, 400, 600, and 1000 were kindly provided as a gift from Toray Industries Inc., Kamakura, Japan. The Jeffamines were a gift from Texaco Chemical Company, Bellaire, TX. The hydroxyl-terminated PEO (Carbowax 1000 and 8000) was a gift from Union Carbide Corp., Danbury, CT. The bisamino PEO samples of molecular weight 3500 and 20,000 and the cyanuric chloride were purchased from Sigma Chemical Co., St. Louis, MO. The allyl alcohol was purchased from Alfa Products, Danvers, MA and the allylamine from Aldrich Chemical Co., Inc., Milwaukee, WI. All other reagents used were of analytical grade.

The molecular weight of the PEO samples was measured by gel permeation chromatography (GPC) on a Waters (Milford, MA) HPLC. The solvent delivery system was a Waters 6000A pump. A Waters U6K injector was used for sample injection, while the column effluent was run through a Waters R-401 differential refractometer. A Waters Ultrahydrogel 500 column was used with water as the solvent. The column was calibrated with PEO molecular weight standards purchased from Polysciences Inc., Warrington, PA.

The PET films were ultrasonically cleaned in four successive solutions of methylene chloride, acetone, deionized water, and acetone. Each wash took 15 min. After cleaning, the films were dried overnight in a vacuum desiccator. Dried films were placed horizontally in the middle of a 2.54 cm (i.d.) Pyrex reactor. The length of the reactor was 80 cm. The PET samples occupied the

middle 30 cm of this reactor. A 13.56 MHz RFGD system was used to create the plasmas. The power was coupled to the reactor through external moving copper capacitor plates, which were moved at a fixed, controlled speed along the reactor in the same direction as the monomer flow. A detailed description of the plasma polymerization reaction has been reported in a previous publication.[22]

Briefly, the PET was first etched with an argon plasma to further clean the surface. After the argon etch, the films were exposed to either the allyl alcohol or the allylamine plasma. Both plasmas were run at a power of 20 W, a pressure of 250 μHg and a plasma speed of 3.3 mm/s. Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR) and ESCA studies of the PET films exposed to these plasmas indicated that hydroxyl or amino groups were introduced onto the surface of the PET.[22]

The functionalized PET films were next activated in a 50 mg/mL cyanuric chloride solution in benzene by gentle shaking at 37°C for 20 h. This solution also contained 50 mg/mL of sodium carbonate which was added to remove any hydrogen ions that could displace a chlorine atom from the cyanuric chloride molecule. The benzene was stored over sodium for 24 h prior to use, and the cyanuric chloride was recrystallized from toluene. The hydroxyl-containing films were exposed to a 10% *n*-butyl lithium solution for 5 min prior to the cyanuric chloride activation to form the highly nucleophilic alkoxide ion. The solution was prepared by adding 1 mL of 1.6*M* butyl lithium in hexane to 9 mL of benzene.

After activation with cyanuric chloride, all films were rinsed for 5 min each in three benzene solutions. This was done to remove any excess cyanuric chloride from the PET. The cyanuric-chloride-activated films were then added to benzene solutions containing the different molecular weights of PEO or Jeffamine molecules. The concentrations of these PEO solutions ranged from 250 to 40 mg/mL, depending on the molecular weight of the PEO used. The PEO solutions also contained 50 mg/mL of sodium carbonate. The reaction was carried out for 27 h at 37°C with constant shaking. Figure 1 shows this overall reaction scheme.

Another technique was used to render the hydroxylated PEO molecules (Carbowax 1000 and 8000) more reactive toward the cyanuric-chloride-activated films. These molecules were first allowed to react with butyl lithium to form the alkoxide ion derivative.[21] This was done by adding 0.5 mL of 1.6*M* butyl lithium in hexane to 10 mL of benzene. The PEO-containing molecules were then added in excess, as determined by a titration technique. The indicator, 1,10-phenylanthroline, turned from bright orange to yellow when the end point was reached, indicating a slight excess of PEO. The cyanuric chloride activated films were then added to this solution containing the alkoxide derivative. The reaction was carried out for 27 h at 37°C with constant shaking. Upon completion of both reactions, the films were washed in benzene at room temperature for 30 min and then given six different water rinses over the next 2 h.

The samples were characterized during different steps of the PEO immobilization process by ESCA and water contact angle measurements. Water contact angle studies were done with a Ramé Hart Model A100 goniometer. A total of six advancing angles were measured from each sample. The angles

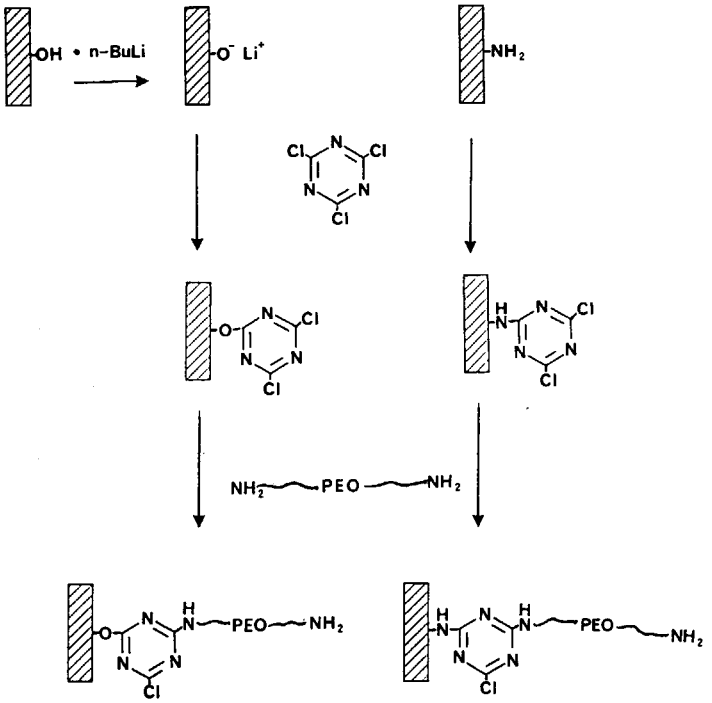

Fig. 1. Cyanuric chloride immobilization of bisamino PEO on PET films functionalized with hydroxyl or amino groups.

were measured within 20 s after the drop was applied to the film to eliminate artifacts due to evaporation. The ESCA studies were performed with a Surface Science Laboratories Model SSX-100 spectrometer at the National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO), University of Washington, Seattle, WA. Survey scans were done on all samples to determine the atomic composition of each surface. High resolution C_{1s} scans were also obtained from each sample. An angular dependent ESCA study was carried out on a PET film which was exposed to an allylamine plasma and then allowed to react with bisamino PEO-400. Using this technique, a depth profile of the surface was obtained.

RESULTS AND DISCUSSION

GPC Analysis of PEO Samples

A calibration curve was generated from the GPC analysis of the PEO standards, and all samples were compared to this curve. Most of the samples had narrow molecular weight distributions which agreed with the specifications supplied by the manufacturers. There were, however, a few samples which contained some unexpected lower molecular weight fractions. The Sigma bisamino PEO-20,000 contained both a 20,000 and a 1000 molecular weight fraction. The Jeffamine (ED6000) had a broader distribution ranging from molecular weights of 6500 down to 1500.

ESCA Analysis of Preliminary Screening Studies of Reaction Systems

Preliminary screening studies were carried out on PET surfaces exposed to allylamine and allyl alcohol plasmas and allowed to react with bisamino- and hydroxy-terminated PEO molecules. This screening allowed us to select the best reaction system for further study. Figure 2 shows the ESCA survey scan, and C_{1s} and O_{1s} spectra, during each stage of the PEO immobilization reaction on a PET film which was exposed to an allylamine plasma. Bisamino PEO-20,000 was used in this reaction at a concentration of 80 mg/mL. The survey scan of the PET shows only carbon and oxygen to be present on the films surface, as expected. The elemental composition of the PET predicted by ESCA is 72% carbon and 28% oxygen. These values are very close to the theoretical atomic composition for PET of 71% carbon and 29% oxygen. The C_{1s} spectrum of PET can be resolved into three distinct peaks which correspond to the three different carbon atomic environments. The O_{1s} spectrum can be resolved into two peaks which are indicative of the —C—O— and —C=O bonds of PET.

After the PET is exposed to the allylamine plasma, a nitrogen peak becomes evident in the survey spectrum, while the relative intensity of the oxygen peak decreases. Typical atomic compositions for this sample were 75% carbon, 4% oxygen, and 21% nitrogen. The oxygen could be coming from the underlying PET substrate and/or the post-reaction of free radicals on the PET film with atmospheric oxygen. When these films are stored in air for 2 weeks, the amount of oxygen increases up to about 7%. This increase in oxygen provides some evidence for the post-reaction of free radicals on the films' surface with oxygen. The C_{1s} spectrum of the PET film exposed to the allylamine plasma is quite different from that of PET, which, in combination with the nitrogen peak, indicates that a plasma-polymerized polymer of allylamine is covering the PET surface. The O_{1s} spectrum is still quite broad due to two different oxygen atomic environments.

The exact nature of the bond between the plasma-polymerized allyl alcohol or allylamine film and the underlying PET substrate is not known. In a plasma polymerization process, free radicals are created on both the substrate and in the plasma. These radicals can result in the covalent attachment of the plasma polymer to the substrate in addition to extensive crosslinking between the molecules in the plasma polymer itself. The amino and hydroxyl groups could therefore be attached to the PET substrate in several ways. Some of the functional groups may be covalently bonded directly to the PET (most likely to the nonaromatic hydrocarbon portion of the molecule, since these carbons will form free radicals more readily than the carbon atoms in the resonance stabilized benzene ring). Some of the groups could also be attached via a hydrocarbon arm to the PET. Finally the amino or hydroxyl groups could be attached to a plasma-polymerized film which is covering the PET in a highly crosslinked network. Ellipsometry studies of SiO_2 wafers exposed to an allylamine plasma showed that the resulting plasma polymerized film was between 150 and 300 Å thick.[22] We can probably assume that the allylamine film attached to the PET is of a similar thickness, since the same plasma reaction conditions were used. Thus, the amino groups which are subsequently

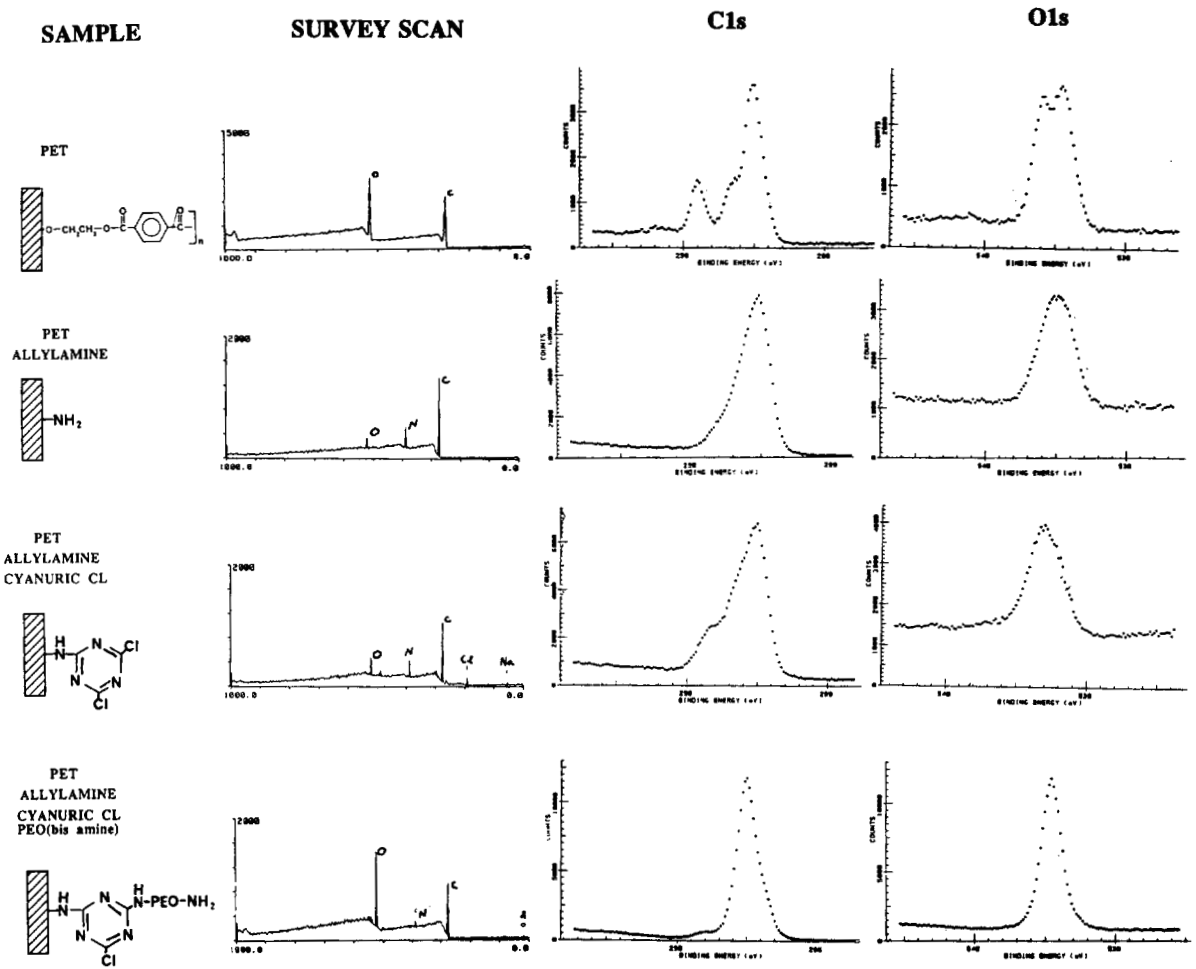

Fig. 2. ESCA survey scan, C_{1s} and O_{1s} spectra during each stage of the bisamino PEO immobilization reaction on a PET film exposed to an allylamine plasma and activated with cyanuric chloride.

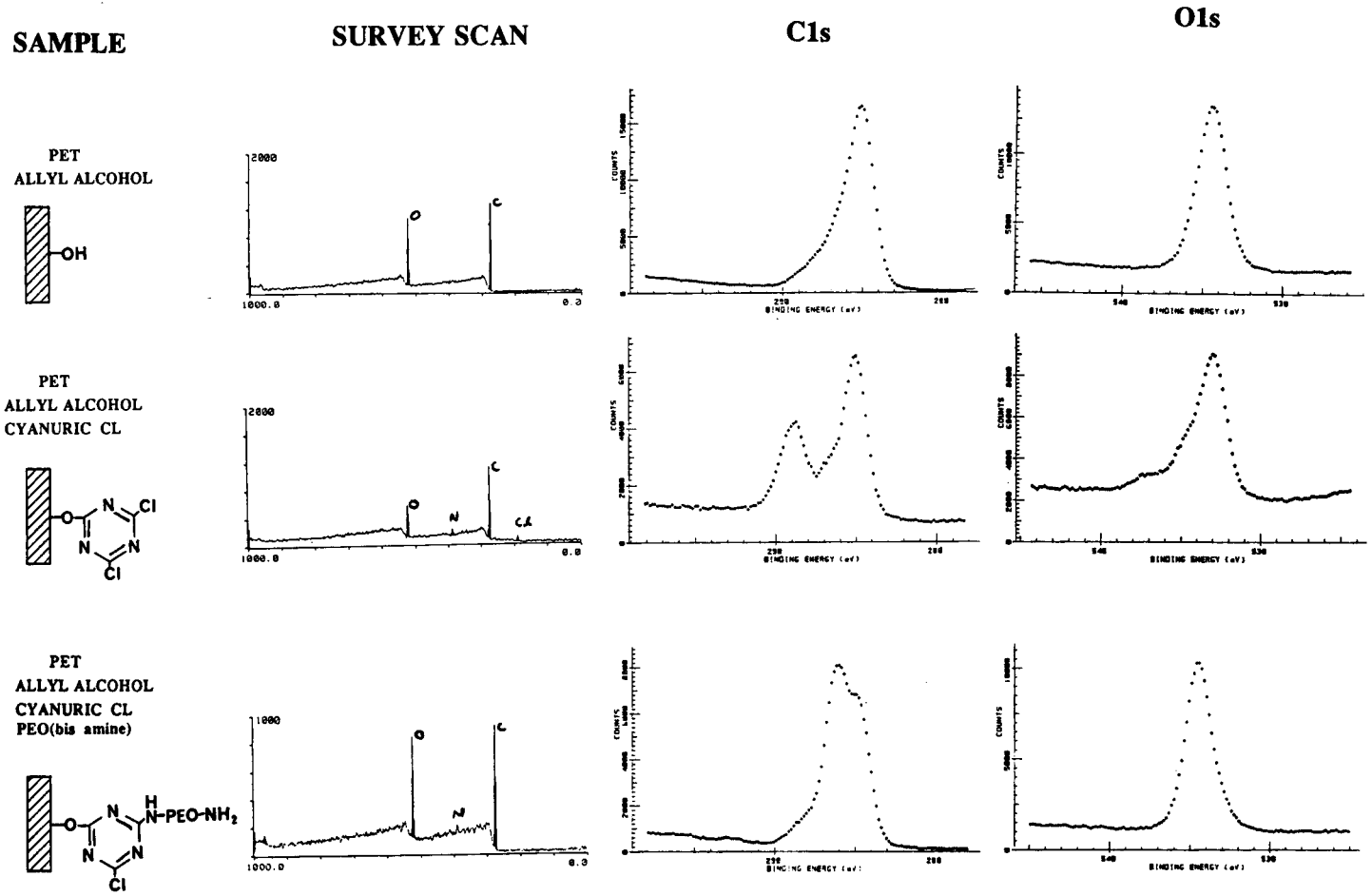

Fig. 3. ESCA survey scan, C_{1s} and O_{1s} spectra during each stage of the bisamino PEO immobilization reaction on a PET film exposed to an allyl alcohol plasma and activated with cyanuric chloride.

allowed to react with the cyanuric chloride are most likely incorporated in the plasma-polymerized polymer and not attached directly to the PET.

The reaction of the allylamine plasma-polymerized film with cyanuric chloride results in the incorporation of chlorine (~ 7%) and sodium (~ 5%) as seen in the ESCA survey scan (Fig. 2). The chlorine is due to immobilized cyanuric chloride which contains residual chlorine atoms. The sodium is most likely a contaminant in the benzene wash solution which was stored over sodium for 24 h. The C_{1s} spectrum of the cyanuric chloride activated film has a peak at about 287.5 eV. This peak position corresponds to the —C—N and —C—Cl bonds of the cyanuric chloride molecule. The O_{1s} spectrum is again quite broad and can be resolved into two peaks.

After the film reacts with bisamino PEO-20,000, the only peaks apparent in the survey scan spectrum are carbon (69%), oxygen (26%), and nitrogen (5%). The nitrogen signal can be attributed to the underlying allylamine polymer, the cyanuric chloride, and the amino groups on the ends of the PEO chains. The C_{1s} spectrum has also changed and is now dominated by a single peak, probably due to the —C—O— groups of the PEO. In addition, the O_{1s} peak is now very narrow, again due to the single ether oxygen of the immobilized PEO.

A similar trend in the ESCA spectra can be observed for the allyl alcohol plasma polymerized PET (Fig. 3). The C_{1s} spectrum of the cyanuric-chloride-activated film has a new peak present at 289 eV. This is in the same location as the —C=O peak of PET, but appears much larger in relative size when compared to the PET C_{1s} spectrum shown in Figure 2. One can also observe a peak at a slightly lower binding energy which is probably due to the —C—N and —C—Cl bonds of the cyanuric chloride. This peak has added to the —C=O peak to make it appear larger.

When the film reacts with bisamino PEO-20,000, the survey scan oxygen signal increases in intensity relative to the carbon peak. The C_{1s} spectrum now has a prominent —C—O— peak, although it does not dominate the entire spectrum. An additional peak at 285 eV is also present due to the —C—C— bond. Thus, bisamino PEO can be immobilized on PET films exposed to an allyl alcohol plasma and activated by cyanuric chloride. However, the reaction seems to be more efficient with the PET films exposed to an allylamine plasma, as indicated by the larger —C—O— peak in the C_{1s} spectrum.

We also attempted to immobilized hydroxy-terminated PEO on both the allylamine and allyl alcohol plasma-polymerized films, using the alkoxide derivatives of these molecules. They did not bind well to either type of surface. The ESCA C_{1s} spectra did have small polyether —C—O— peaks present, but they were usually dominated by the hydrocarbon peak at 285 eV. Based on the results of these preliminary reactions, we decided to confine our studies to the immobilization of bisamino PEO molecules on PET films exposed to an allylamine plasma.

Immobilization of Bisamino PEO on PET Exposed to an Allylamine Plasma

Six different molecular weight bisamino PEO molecules were immobilized on PET films exposed to an allylamine plasma. The molecular weights and

TABLE I
Bisamino PEO Samples and the Concentrations Used for Immobilization on Cyanuric Chloride Activated PET Film

Source	Nominal PEO MW	Reaction conc. (mg/mL)
Toray	200	143
Toray	400	115
Toray	600	240
Toray	1000	215
Sigma	3500	36
Sigma	20,000	40

concentrations of these samples are given in Table I. The 3500 and 20,000 molecular weight samples were used in much lower concentrations than the other PEO molecules, since higher concentrations resulted in very viscous solutions in which the films could not be stirred.

Figure 4 is a C_{1s} spectrum of a PET–allylamine-treated film which was allowed to react with bisamino PEO-400. The spectrum has been resolved into four different peaks. The tallest peak at 285 eV can be assigned to the hydrocarbon part of the sample. This includes —C—C— bonds from both the underlying PET substrate and the plasma-polymerized allylamine film. The next largest peak at 286.4 eV is due to the —C—O— bond. Contributions to this peak are from the ether groups in the immobilized PEO in addition to the —C—O— bonds in the PET. The chemical groups comprising the third largest peak at 287.5 eV cannot be identified without ambiguity, but it is likely that this peak is due in part to —C—N bonds in the plasma-polymerized allylamine film and the cyanuric chloride molecules. The

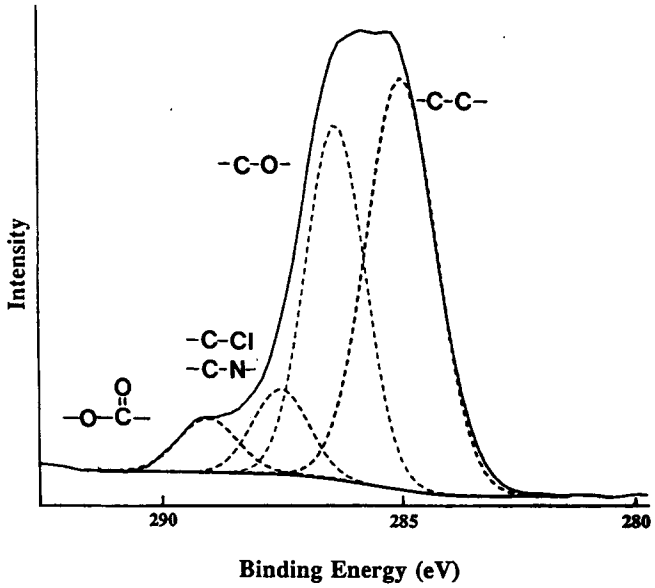

Fig. 4. ESCA C_{1s} spectrum of a PET film exposed to an allylamine plasma, activated with cyanuric chloride and allowed to react with bisamino PEO-400.

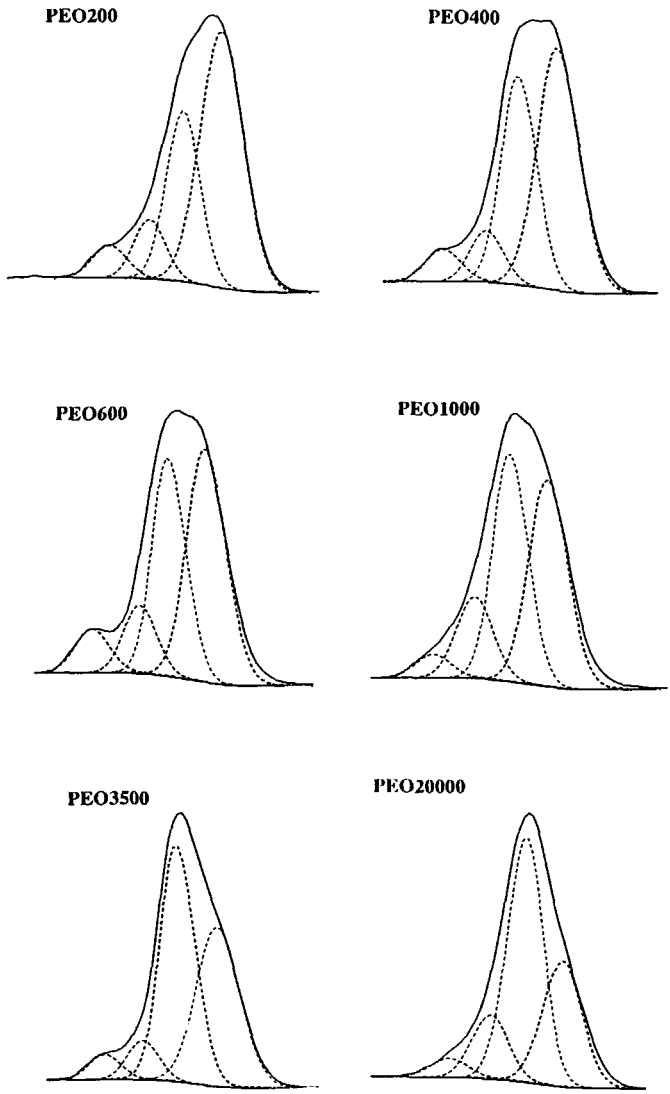

Fig. 5. ESCA C_{1s} spectra of PET films exposed to an allylamine plasma, activated with cyanuric chloride and allowed to react with different molecular weight bisamino PEO samples.

peak located at the highest binding energy (289 eV) can be attributed to ester carbon of the PET. The binding energies assigned to these peaks were based on values determined by Clark.[23]

Figure 5 shows the C_{1s} ESCA spectra of six allylamine-treated PET films which were allowed to react with different molecular weight bisamino PEO molecules. In each of these spectra, the hydrocarbon peak farthest to the right is at a binding energy of 285 eV. This peak undergoes a relative decrease in size as the molecular weight of the immobilized PEO increases. The —C—O— peak (286.4 eV), on the other hand, undergoes an increase in size with increasing PEO molecular weight. Figure 6 shows that the relative area of the —C—O— peak in the C_{1s} spectrum increases sharply at first and

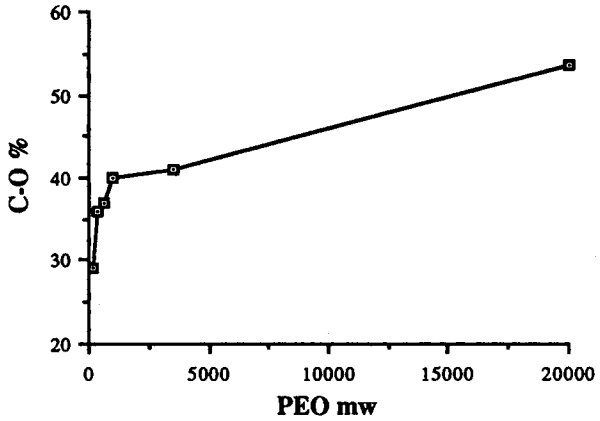

Fig. 6. The percent of —C—O— in the ESCA C_{1s} spectrum as a function of the molecular weight of immobilized bisamino PEO.

then much more gradually as the molecular weight of the attached PEO increases.

Figure 7 shows the atomic percents of carbon, oxygen and nitrogen on the surface of the samples as a function of PEO molecular weight. Chlorine, presumably from cyanuric chloride, was also present on all of the samples in concentrations of 1 or 2%. Several trends can be seen in this graph. The amount of nitrogen and carbon both decrease with increasing PEO molecular weight, while the amount of oxygen increases. The increase in oxygen is due to the increasing amount of ether oxygen on the surfaces containing the higher molecular weight PEO molecules. This trend agrees quite well with the increasing —C—O— content of the samples shown in Figure 6. The nitrogen probably decreases with increasing PEO molecular weight because the plasma-polymerized allylamine film is becoming covered by the PEO molecules. This is also the case for the hydrocarbon peak.

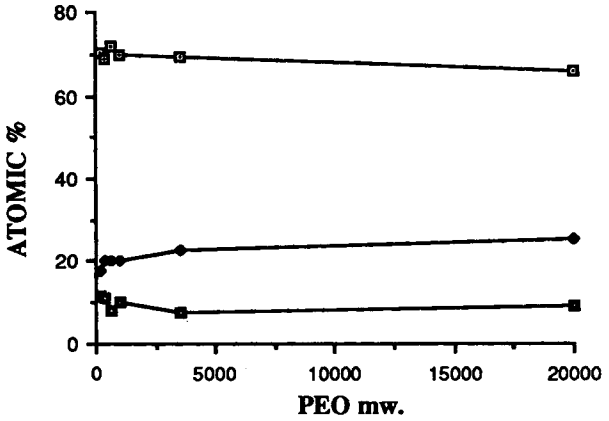

Fig. 7. Elemental composition as a function of the molecular weight of immobilized bisamino PEO: (⊡) C%; (◆) O%; (□) N%.

TABLE II
Jeffamine Samples, Their Approximate Molecular Weights, Molecular Weight of the PEO Portion of the Molecule, Concentrations Used for Immobilization on Cyanuric-Chloride-Activated PET, and Water Contact Angles of These Surfaces[a]

Jeffamine	Approx. MW	Approx. PEO MW	Reaction conc. (mg/mL)	Water contact angle ± SD
ED900	900	700	200	38.3 ± 0.7
ED2001	2000	1800	200	37.3 ± 0.6
ED4000	4000	3800	200	22.0 ± 0.5
ED6000	6000	5800	200	36.2 ± 0.8

[a] Each angle reported is the average of six contact angle measurements on each surface.

A series of Jeffamine molecules containing PEO (Table II) were also immobilized on PET films exposed to an allylamine plasma, using the same chemistry described for the bisamino PEO samples. These Jeffamines contained a small amount of poly(propylene oxide) (MW 145), in addition to PEO, according to the manufacturer. Well-defined —C—O— peaks were seen in the C_{1s} ESCA spectra of these samples. The size of this peak increased with increasing PEO molecular weight up to the ED4000 molecule. The C_{1s} spectrum of the ED6000 sample, however, was very similar to the ED4000. As previously mentioned, the GPC results indicated that the E6000 sample had a molecular weight distribution ranging from 6000 down to 1500. This would explain why the —C—O— contribution to the C_{1s} spectrum did not increase when compared to the ED4000 sample.

Angular-Dependent ESCA Study

Table III shows the atomic composition of a PET film exposed to an allylamine plasma and allowed to react with bisamino PEO-20,000, as a function of the ESCA take-off angle. A smaller take-off angle corresponds to an increasing sampling depth of the ESCA X-ray beam. The three different sampling depths of this surface have very similar atomic compositions. If one considers the sensitivity of the ESCA instrument (±5%), the numbers are essentially the same for each angle. The high resolution C_{1s} spectra at each take-off angle are also indentical. The relative sizes of the —C—O— peak from the PEO and the —C=O peak from the PET also remain the same.

This data leads us to believe that the PEO surface coverage is incomplete. The nitrogen signal remains constant at all sampling depths, indicating that there are patches of plasma-polymerized allylamine that are always exposed

TABLE III
Atomic Composition of a PET Film Exposed to an Allylamine Plasma and Allowed to React with Bisamino PEO-20,000 as a Function of Take-off Angle of the ESCA X-Ray Source

Take-off angle	%C	%O	%N
0°	70.8	22.4	6.8
55°	71.1	22.1	6.8
80°	71.1	21.5	7.4

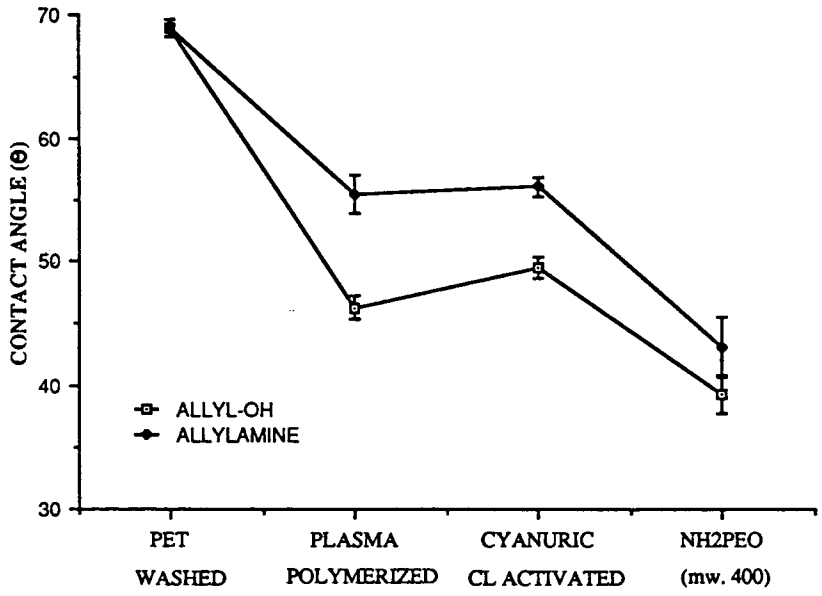

Fig. 8. Water contact angles during different stages of the bisamino PEO immobilization reaction to PET exposed to either an allylamine (◆) or an allyl alcohol (□) plasma.

to the ESCA X-ray beam. If the plasma-polymerized allylamine layer was completely covered with PEO, the nitrogen signal would decrease with decreasing sampling depth. In addition, the —C=O peak from the PET would decrease in size and the —C—O— peak from the PEO would increase in size as the sampling depth decreased.

Contact Angle Measurements

Water contact angle measurements were performed on the films at different stages of the immobilization reaction. These studies were done on PET films exposed to both allylamine and allyl alcohol plasmas, which were then allowed to react with bisamino PEO. Figure 8 shows the results of these contact angle studies using bisamino PEO-400. Exposure of the PET to both the allylamine and allyl alcohol plasmas resulted in an increased wettability of the films (as indicated by a decrease in contact angle). The allyl alcohol plasma produced a more wettable surface than the allylamine plasma, as expected. After the cyanuric chloride activation, both films decreased in wettability. This is also to be expected because the ring structure of the cyanuric chloride molecule is more hydrophobic than the —OH or $-NH_2$ groups. After the films were allowed to react with the bisamino PEO-400, both films exhibited the greatest degree of wettability due to the hydrophilic nature of PEO. Nevertheless, the contact angles are still high (around 40°) on each of these surfaces. A pure PEO surface would exhibit much lower water contact angles.

Figure 9 shows the water contact angles of PET films which were exposed to an allylamine plasma and then allowed to react with different molecular weight bisamino PEO molecules. The angle decreases rapidly between molecular weights of 200 and 1000. At higher PEO molecular weights the decrease

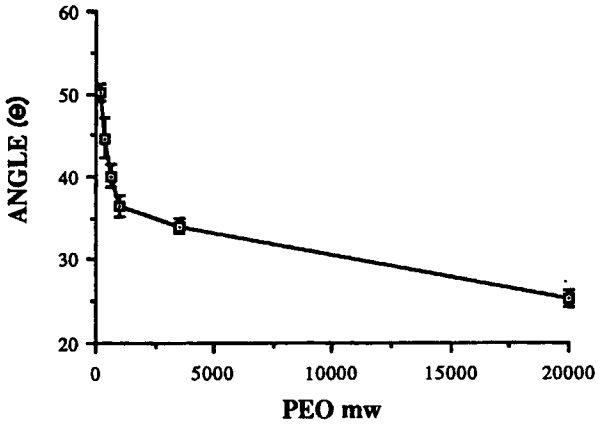

Fig. 9. Water contact angle as a function of the molecular weight of immobilized bisamino PEO on PET exposed to an allylamine plasma.

becomes more gradual. The relatively high water contact angles on the surfaces containing the lower molecular weight PEO can most likely be attributed to incomplete coverage of the plasma-polymerized allylamine film. The underlying hydrophobic layer may be exposed to the water drop, and could decrease the wettability of the surface. This is in agreement with the results obtained from the angular-dependent ESCA study. As the molecular weight of the attached PEO increases, the substrate becomes more completely covered with ether groups, as evidenced by the increasing —C—O— content shown in Figure 6 and the increase in wettability (Fig. 9). In the vacuum environment of the ESCA instrument, the dehydrated PEO molecules lie flat on the surface of the film. The higher molecular weight PEO covers more surface area than the lower molecular weight PEO, due to the increased length of the polymer chains. Figure 10 schematically depicts a high and a low molecular weight PEO surface in both the hydrated and dehydrated state. This diagram is based on the results of the ESCA and water contact angle studies. Thus, increasing the molecular weight of the immobilized PEO (from 200 to 1000) does not result in a thicker PEO film, but rather a more dense PEO film. A good analogy would be to imagine that the films are becoming covered with a finer meshed net of PEO, but still of the same thickness. The mesh size of the PEO net decreases rapidly between PEO molecular weights of 200 and 1000. As a result, the surfaces of the films undergo a rapid decrease in water contact angle and an increase in % —C—O—. Increases in total oxygen content and decreases in nitrogen content are also observed (Fig. 7).

As the molecular weight of the attached PEO is further increased (from 3500 to 20,000), the dehydrated polymer chains may now be long enough that they begin to overlap. As a result, the PEO layer on the film becomes thicker, but the surface chemisty remains very similar, as evidenced by a much smaller relative change in the % —C—O— (Fig. 6). The water contact angles still decrease, but this is again a much less dramatic change when compared to the decrease observed in going from PEO 200 to 1000 (Fig. 9).

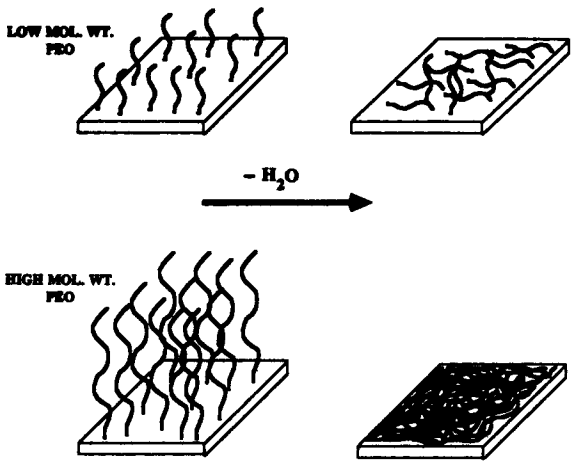

Fig. 10. A schematic representation of a PET surface covered with low and high molecular weight PEO molecules in the hydrated and dehydrated state.

Figure 11 shows the water contact angle as a function of the % —C—O— for films containing different molecular weight bisamino PEO. This graph was made by combining Figures 6 and 9. When a linear regression was performed on this data, we found a correlation coefficient of 0.97. Therefore, there is a strong relationship between the water contact angles and the —C—O— content of the PEO surfaces synthesized in this study.

Water contact angles were also measured on films which were allowed to react with the different Jeffamine molecules (Table II). The angle decreases as the molecular weight of PEO attached to the films is increased, except for the ED6000-treated sample. The higher contact angle can again be explained by the GPC results, which indicate that lower molecular weight compounds are present in this Jeffamine sample.

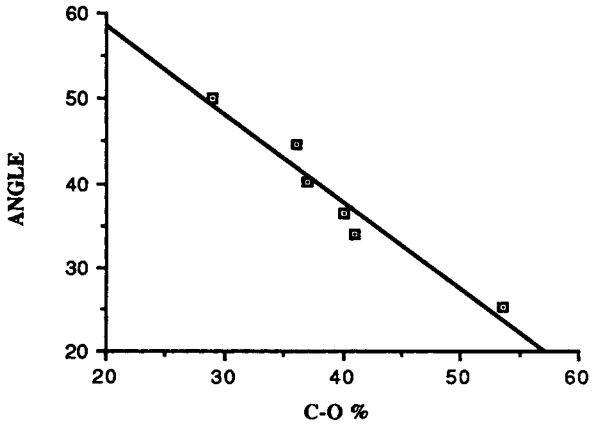

Fig. 11. Water contact angle as a function of % —C—O— for PET films exposed to an allylamine plasma and reacted with different molecular weight bis-amino PEO molecules.

CONCLUSIONS

This study has demonstrated that PEO can be covalently attached to PET films which have been functionalized by the plasma polymerization of allyl alcohol and allylamine and then activated with cyanuric chloride. PET films exposed to an allylamine plasma exhibit higher degrees of PEO attachment than the allyl-alcohol-treated PET. Bisamino PEO molecules react more efficiently than hydroxylated PEO molecules with the cyanuric-chloride-activated films.

ESCA is a valuable technique for following the different steps of the immobilization reaction. As the molecular weight of PEO on the surface increases, the —C—O— percent of the C_{1s} spectrum and the total oxygen content of the surface increases.

Water contact angles can also be used to demonstrate the PEO immobilization reaction. As the molecular weight of PEO on the surface increases, the water contact angle decreases, and there is a strong relationship between the water contact angle and the —C—O— content of these surfaces.

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