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Grafting of end-functionalized poly(*tert*-butyl acrylate) to poly(ethylene-*co*-acrylic acid) film

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Abstract

Poly(*tert*-butyl acrylate) (P*t*BA) was grafted to the surface of poly(ethylene-*co*-acrylic acid) (EAA) film and the pendant groups of the tethered P*t*BA were modified to create chemically tailored surface modifying layers. The carboxylic acid groups in the copolymer film served as the grafting sites for the covalent tethering of end-functionalized P*t*BA. The progression of these reactions was monitored using attenuated total reflectance (ATR)-FTIR and X-ray photoelectron (XPS) spectroscopies along with static contact angle measurements. By controlling the reaction conditions, the chemical functionality of the grafted layer ranged from *tert*-butyl ester (EAA-*g*-P*t*BA) to carboxylic acid (EAA-*g*-PAA) and was demonstrated by corresponding changes in wettability. The choice of P*t*BA as the tethered polymer allows for the subsequent substitution of the *tert*-butyl ester groups. To demonstrate, a novel procedure was used to replace the *tert*-butyl ester with *N*,*N*-dimethylethylenediamine (DMEDA) to form EAA-*g*-PDMEDA. These reaction schemes can be used to create tunable surface-grafted layers with various pendant group chemistries.

Keywords: Polymer surface grafting; Ethylene–acrylic acid copolymer; Poly(*tert*-butyl acrylate)

1. Introduction

There has been a significant amount of research on tethered polymers. Theoretical work has looked at chain conformations and surface concentration profiles [1–6]. A limited number of experimental studies deal with the grafting of end-functionalized polymers, and only a few of these examine the grafting of end-functionalized polymers to polymeric substrates [7–9]. Our interest lies in using a copolymer film as the substrate, particularly poly(ethylene-*co*-acrylic acid) (EAA) where the acid groups serve as surface-grafting sites. EAA is useful because it is commercially available with a variety of acrylic acid contents, chemically resistant to many organic solvents, and commonly used in film and coating applications.

In this research, the grafted layer was formed from carboxyl-terminated poly(*tert*-butyl acrylate) (P*t*BA), which is commercially available in various molecular weights with a narrow molecular weight distribution. The P*t*BA was selected because the pendant *tert*-butyl esters are considered to be good leaving groups and can be replaced with other functional groups as desired. For example, Boyes et al. polymerized block copolymers from silicon wafers using atom transfer radical polymerization, with one block being P*t*BA [10]. The *tert*-butyl esters subsequently were converted to acids and then to silver salts. Yang et al. performed an analogous study on C_{60} end-capped P*t*BA–polystyrene block copolymers in solution [11]. Lee et al. attached an azobenzene alkanethiol to gold to form a brush terminated with *tert*-butyl ester groups [12]. Those terminal groups were then converted to acids using chemical and photochemical methods. In this work, our goal was to investigate the efficacy of converting the *tert*-butyl ester pendant groups of P*t*BA that was grafted onto EAA copolymer film.

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To our knowledge, neither the grafting of P*t*BA to EAA nor the conversion of *tert*-butyl ester groups to amines on surface-grafted P*t*BA has been reported previously.

2. Experimental section

The polymer substrate used in this study was an ethylene–acrylic acid (EAA) random copolymer film. The film (nominal thickness of 75 μm) was extruded at the Cryovac Division of Sealed Air Corporation (Duncan, SC) using EAA resin from Dow Chemical Company (PRIMACOR 1410, 9.7 wt% acrylic acid content, $M_n = 19.9$ kDa, $M_w = 83.6$ kDa). The EAA contained 500 ppm of antioxidant (IRGANOX 1010). Because of its hydrophobicity and relatively high molecular weight (~1200 Da), IRGANOX 1010 does not readily migrate to the surface of polyolefinic films. It has no reactive groups or nitrogen-containing groups that would interfere with the surface chemistry or XPS analyses described later.

The following chemicals were used as received: dichloromethane (Burdick and Jackson, 99.9+%), ethylenediamine (Aldrich, 99%), phosphorous pentachloride (Aldrich, 95%), and *N*,*N*-dimethylethylenediamine (TCI, 99%). Poly(*tert*-butyl acrylate) (P*t*BA) ($M_w = 7500$ Da, $M_w/M_n = 1.07$) and carboxylic acid-terminated poly(*tert*-butyl acrylate) (P*t*BA–COOH) ($M_w = 7000$ Da, $M_w/M_n = 1.08$, fraction of chains with acid end-groups = 0.98) were purchased from Polymer Source, Inc. and used as received. The molecular weight, molecular weight distribution, and end-group concentration of the P*t*BA and P*t*BA–COOH were characterized by the manufacturer using GPC and acid–base titration.

Prior to grafting the end-functionalized polymer to the copolymer surface, both the P*t*BA–COOH and the EAA film were chemically modified. Fig. 1 shows these reactions steps (all at room temperature), which are described below.

2.1. EAA surface chemistry

The carboxylic acid groups that are present in the EAA film were used as the reaction sites for the grafting reactions. To facilitate the grafting process, the acid groups were first converted to acid chlorides (reaction I; Fig. 1) by immersion in a solution of PCl_5/CH_2Cl_2 (0.03 g/mL) for up to 30 min with sonication [reaction product denoted as EAA–Cl]. The next step involved the conversion of the acid chloride groups to primary amines (reaction II; Fig. 1) using a solution of ethylenediamine/H_2O (0.0025 g/mL). This step was also performed with sonication and the reaction was complete after 4 h [EAA–NH_2].

2.2. End-group modification of PtBA–COOH

The carboxylic acid of the end-functionalized P*t*BA was converted to acid chloride (reaction III; Fig. 1) in preparation for the grafting reaction. To a solution of P*t*BA–COOH in CH_2Cl_2 a stoichiometric excess of PCl_5 was added. This reaction proceeded with sonication to form the acid chloride end-functionalized P*t*BA [P*t*BA–COCl].

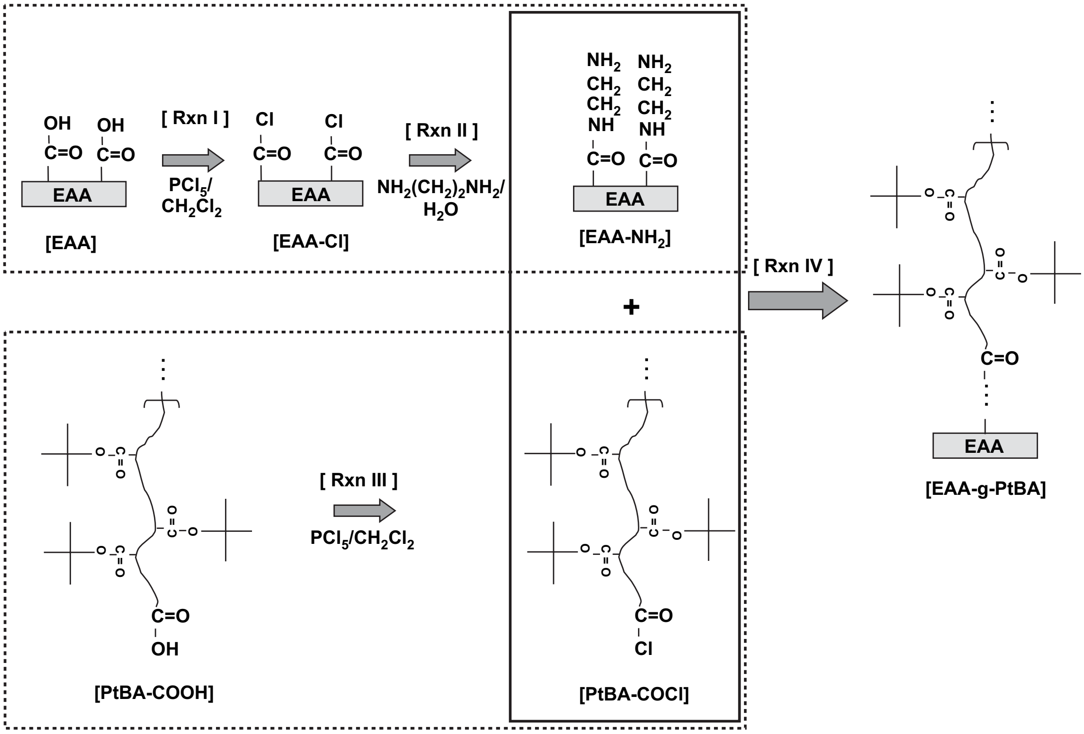

Fig. 1. Overall reaction scheme for grafting P*t*BA–COOH to EAA copolymer film. The process involved conversion of EAA to EAA–Cl (reaction I) then to EAA–NH_2 (reaction II) and the conversion of P*t*BA–COOH to P*t*BA–COCl (reaction III). The end product shown in this scheme is poly(*tert*-butyl acrylate) (P*t*BA) grafted onto EAA copolymer film (EAA-*g*-P*t*BA) (reaction IV). All reactions were performed at room temperature.

2.3. Grafting reaction

The amine-reacted EAA films [EAA–NH_2] were then placed into the PtBA–COCl/PCl_5/CH_2Cl_2 solution (from reaction III) and allowed to react with sonication to graft the PtBA to the EAA film (reaction IV; Fig. 1) [EAA-*g*-PtBA].

2.4. tert-Butyl ester substitution

Once a layer of P*t*BA was grafted to the EAA surface [EAA-*g*-P*t*BA] using the scheme described above, the pendant *tert*-butyl ester groups were replaced by dimethyl amine functionality. We have combined the chemistry from several previous studies to develop a new reaction scheme to convert the *tert*-butyl ester groups to an amine/amide functionality [13–16]. As discussed later, the grafted polymer had a mixture of *tert*-butyl ester and carboxylic acid groups. Using our reaction schemes, both functionalities were converted either via the carboxylic acid route or directly from the *tert*-butyl ester.

In this process, the EAA-*g*-P*t*BA samples were added to a stirred, saturated $ZnBr_2$/CH_2Cl_2 solution that had been prepared a minimum of 24 h in advance. The EAA-*g*-P*t*BA samples were allowed to complex with the $ZnBr_2$ a minimum of 12 h with continuous stirring. *N*,*N*-Dimethylethylenediamine was then added to the solution (0.0035 g/mL) and the reaction was allowed to proceed with stirring for 5 h. The samples were then rinsed and sonicated repeatedly in clean CH_2Cl_2 to remove any physisorbed material.

2.5. Characterization

2.5.1. IR spectroscopy measurements

The progression of the various reaction steps was monitored using attenuated total reflectance (ATR)-FTIR spectroscopy. For the polymer film samples, a flat ATR crystal was used with a constant clamping load to achieve reproducible contact between the films and the crystal [17]. For the conversion of the terminal carboxylic acid group of end-functionalized poly(*tert*-butyl acrylate) (P*t*BA–COOH) to an acid chloride (P*t*BA–COCl), two accessories were used. *In situ* ATR was conducted using a nitrogen purged ReactIR accessory with a diamond probe to monitor the progress of the reaction with time. However, the signal-to-noise ratio was too low to achieve quantitative results and these results are not shown in this work. Subsequently, an ATR trough plate was used by placing an aliquot of the solution in the trough and allowing the solvent to evaporate before the scans were collected. For measurements using the trough and flat-plate configurations, a Nicolet Avatar 360 with a horizontal multibounce accessory was used with a germanium crystal at a 45° incidence angle that allowed for a penetration depth of approximately 0.4 μm [18]. All ATR-FTIR characterizations were conducted in a nitrogen purged chamber at room temperature (~25 °C).

2.5.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were obtained using a Kratos AXIS 165 XPS spectrometer equipped with a monochromated Al Kα (1486.6 eV) X-ray source and hemispherical analyzer. The X-ray source was operated at 15 kV (45 W) using a take-off angle of 90° to the sample surface to yield an analysis depth of approximately 10 nm. The diameter of the analysis area was maintained at roughly 200 μm. Elemental identification and quantification were done with a survey spectrum over the 0–1200 eV binding energy range, using a pass energy of 40 eV. High-resolution spectra of the C 1s, O 1s, and N 1s core levels were also collected. Spectral analysis was done with CasaXPS software using atomic sensitivity factors. The binding energies were corrected by referencing the C 1s binding energy to 284.5 eV. Peak shifts for the carbon and nitrogen functionalities were taken from the literature.

2.5.3. Contact angle

Static contact angle measurements were used to assess the changes in wettability. The sessile drop method was used with a Krüss DSA10-Mk2 instrument and digital photo analysis software. With a syringe, a water drop (volume ≈ 1.3 μL) was carefully placed onto the specimen of interest. The contact angle values reported are averages of a minimum of nine drops for each sample along with 95% confidence intervals.

3. Results and discussion

The primary goal of this work was to investigate a method for grafting P*t*BA polymer to the surface of a copolymer film. Chemical reactions on both the EAA copolymer film substrate and the grafted P*t*BA were monitored. Included in this work is also the conversion of the pendant *tert*-butyl ester and acid functionalities of the grafted polymer layer to an amine/amide pendant group. The efficacy of the chemistries involved was characterized along with the changes in surface functionality and wettability. This characterization was done using a combination of FTIR and XPS spectroscopies and static contact angle measurements and is discussed in detail below.

3.1. FTIR results

3.1.1. Poly(ethylene-co-acrylic acid) surface chemistry (reaction I)

For neat EAA, the peak corresponding to the carbonyl stretch of the carboxylic acid is present at ~1705 cm^{-1}. As the carboxylic acid groups were converted to acid chlorides, the carbonyl peak shifted to ~1803 cm^{-1} as shown by the ATR-FTIR results in Fig. 2. This reaction was carried out using sonication with excess PCl_5 (0.03 g/mL) and progressed quickly with complete conversion in less than 5 min as evidenced by the disappearance of the 1705 cm^{-1} peak. Since the penetration depth for our ATR-FTIR configuration is ~0.4 μm, these results indicate that even sub-surface carboxylic acid groups were converted to acid chlorides. The ability for small molecules to penetrate and react with the interior of a polymer film has been shown previously by other researchers [19,20]. It should be noted that there was no visible negative

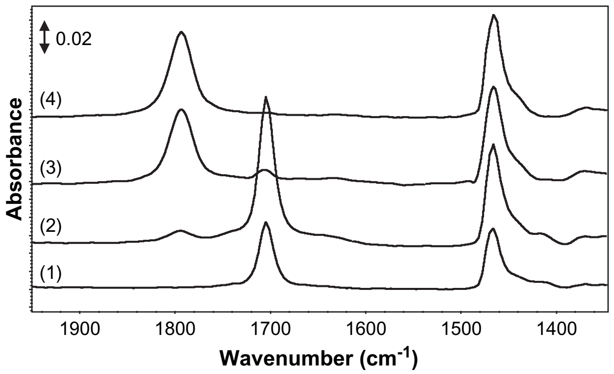

Fig. 2. Representative ATR-FTIR spectra for the conversion of the COOH groups present in the EAA film substrate to COCl groups (reaction I; Fig. 1). Reaction times: (1) 0 min, (2) 0.5 min, (3) 1 min, and (4) 5 min. PCl_5 concentration = 0.03 g/mL.

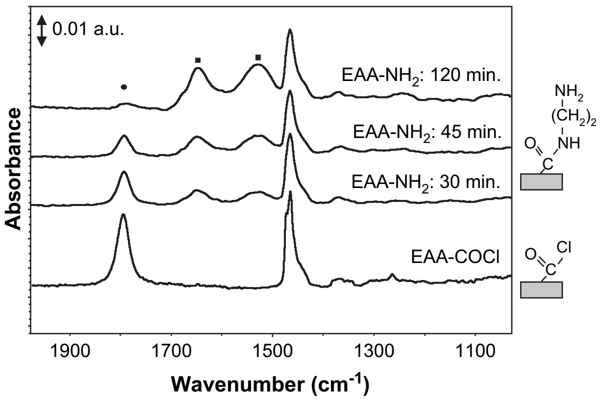

Fig. 4. Representative ATR-FTIR spectra for the conversion of EAA–Cl to EAA–NH_2 (reaction II; Fig. 1). As the reaction progressed, the acid chloride peak (●) decreased while the amide peaks (■) increased.

effect on the appearance of the copolymer film from the PCl_5 treatment.

Peak area ratios of COOH/CH_2 (1705 cm^{-1}/1465 cm^{-1}) and COCl/CH_2 (1803 cm^{-1}/1465 cm^{-1}) are plotted with respect to PCl_5 solution concentration for a reaction time of 30 min in Fig. 3. The 1465 cm^{-1} peak corresponds to C–H bending from methylene groups and was used as an internal standard. Both the reduction of COOH and the increase in COCl detected in the EAA film during this reaction follow expected trends as the carboxylic acid groups were converted to acid chlorides. Based on the peak area ratios achieved, a concentration of 0.03 g/mL PCl_5 and a 30 min reaction time were used for subsequent conversions of EAA to EAA–Cl.

3.1.2. *Poly(ethylene-co-acrylic acid) surface chemistry (reaction II)*

Reaction of EAA–Cl with ethylenediamine (EDA) provides a terminal primary amine at the film surface [EAA–NH_2] that will be used for the subsequent grafting of P*t*BA. In addition to the primary amine, the reaction of EAA–Cl and EDA also forms a secondary amide. This is indicated by the development of two peaks at ~1647 and ~1531 cm^{-1} in the ATR-FTIR spectra shown in Fig. 4. As the reaction proceeded, the acid chloride peak decreased and the amide peaks increased. These changes were quantified using peak area ratios of amide I/CH_2 (1647 cm^{-1}/1465 cm^{-1}), amide II/CH_2 (1531 cm^{-1}/1465 cm^{-1}), and COCl/CH_2 (1803 cm^{-1}/1465 cm^{-1}). Minimal error can be expected using the 1465 cm^{-1} peak as the normalizing peak since the EDA adds a very small amount of CH_2 groups compared to the aliphatic CH_2 content from the EAA within the ~0.4 μm penetration depth for ATR-FTIR.

The peak area ratios are plotted as a function of reaction time in Fig. 5, and reaction II appeared to be complete in ~130–150 min. As with the conversion of carboxylic acid to acid chloride in the EAA film, ATR monitored the functional group changes on the surface as well as in the sub-surface region. It is apparent from the reduction in the acid chloride peak (Figs. 4 and 5) that the EDA was able to penetrate at least 0.4 μm and react with sub-surface acid chloride groups. Therefore, it is expected that the reaction with functional groups on only the surface of the EAA film was occurring much faster than the 130–150 min time indicated from the ATR results.

The reaction of the amines of EDA with separate acid chlorides has the potential to form cyclic structures. However, we believe that cyclic group formation is unlikely with the system we are using. The EAA had only ~4 mol% acrylic acid

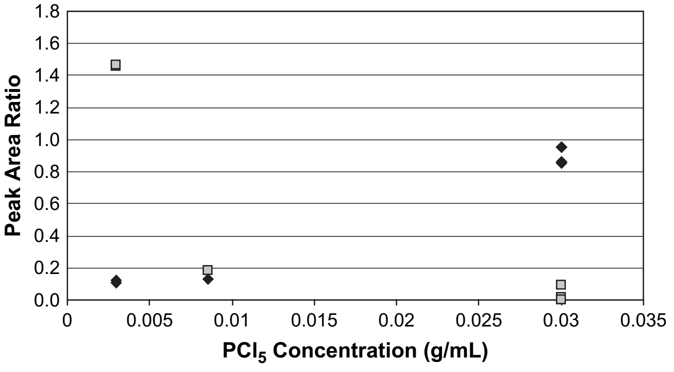

Fig. 3. Peak area ratios determined from ATR-FTIR spectral analyses for the conversion of COOH to COCl in EAA film (reaction I; Fig. 1); (▨) COOH/CH_2, (◆) COCl/CH_2. The multiple symbols at a given condition represent replicate experiments. Reaction time = 30 min.

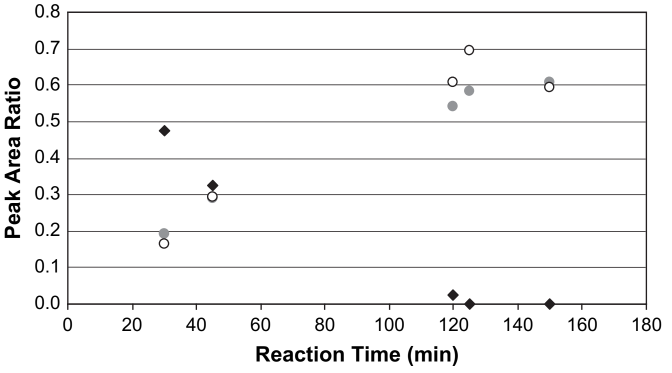

Fig. 5. Peak area ratios as a function of reaction time determined from ATR-FTIR spectral analyses for reaction of EAA–Cl to EAA–NH_2 (reaction II; Fig. 1); (●) amide I/CH_2, (○) amide II/CH_2, (◆) COCl/CH_2. EDA concentration ≈ 0.009 g/mL.

content (i.e., 1 acrylic acid for every 24 ethylene repeat units) and these are randomly distributed. In addition, EDA is relatively short, which would make it extremely difficult to form a cyclic structure. To investigate this point, closer examination of the FTIR spectra does not show a corresponding shift in the C−H stretching or bending bands upon reaction with EDA that would be seen in a cyclic structure. Demonstration that there are primary amines present in addition to the secondary amides is difficult with FTIR since the majority of the bands overlap. However, peaks seen in the EAA−NH$_2$ samples at ~1368 cm^{-1}, 1051 cm^{-1}, and 979 cm^{-1} (not shown in detail) were identified as corresponding to the C−N stretch of amines (and not amides) [21–23]. Moreover, the subsequent grafting of the polymer (P*t*BA−COCl) to the EAA−NH$_2$ (described below) indicates that primary amines were still present on the EDA-modified film.

3.1.3. End-group modification of PtBA−COOH (reaction III)

The conversion of the carboxylic acid end-group of P*t*BA−COOH to an acid chloride [P*t*BA−COCl] is a difficult step to observe with FTIR due to the relatively small number of COOH groups, the dilute solution conditions, and the close wavenumber proximity of the acid carbonyl peak to the prominent ester carbonyl peak. However, shown in Fig. 6 are the spectra corresponding to progressing reaction times of P*t*BA−COOH with PCl$_5$ collected using an *ex situ* trough plate method in which an aliquot of reaction solution was placed in a Germanium crystal trough. The solvent was then allowed to evaporate and the residual sample analyzed with ATR-FTIR spectroscopy. The acid chloride peak at ~1803 cm^{-1} increased with reaction time up to 6 h. The uppermost spectrum in Fig. 6, which was subjected to 12 h of additional reaction time without sonication showed that the ester peak (~1730 cm^{-1}) broadened significantly to encompass peaks corresponding to carboxylic acid (~1710 cm^{-1}) and the carboxylate anion (~1630 cm^{-1}) due to hydrolysis of the esters. Also note that the CH$_3$ peak at 1480 cm^{-1} (present due to the high CH$_3$ content from the pendant *tert*-butyl ester groups) was present for reaction times ≤ 6 h yet absent in the uppermost spectrum representing a reaction time of 18 h, supporting the hypothesis of *tert*-butyl ester conversion to the carboxylic acid and anion. The goal of this reaction was the conversion of only the end-group. However, the *tert*-butyl ester groups are easily hydrolyzed. By controlling the reaction time for reaction III, the chemistry of the grafted layer can be tuned from poly(*tert*-butyl acrylate) to a mixture of *tert*-butyl ester and acrylic acid groups to poly(acrylic acid). To minimize hydrolysis of the *tert*-butyl groups, a reaction time of 30 min was used in all subsequent P*t*BA−COOH to P*t*BA−COCl reactions.

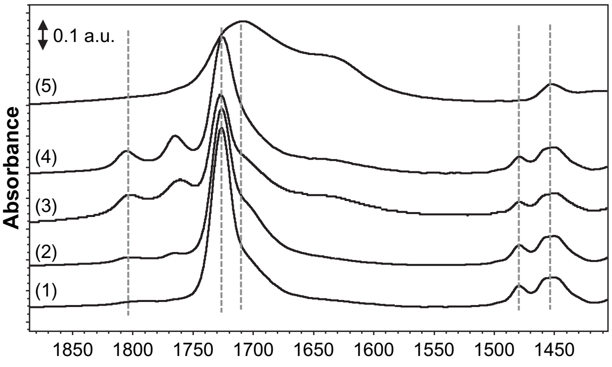

Fig. 6. Conversion of P*t*BA−COOH to P*t*BA−COCl (reaction III; Fig. 1) using 0.0025 g/mL P*t*BA−COOH and 0.03 g/mL PCl$_5$ in CH$_2$Cl$_2$. Reaction times using sonication: (1) 15 min, (2) 45 min, (3) 3 h, (4) 6 h, and (5) 6 h + 12 h without sonication.

3.1.4. Grafting reaction (reaction IV)

EAA−NH$_2$ films were added to the solution containing P*t*BA−COCl and PCl$_5$ in CH$_2$Cl$_2$ to form EAA-*g*-P*t*BA. As shown in Fig. 7, peaks corresponding to both the ester and acid (see Section 3.1.3) functionalities were observed at short reaction times. As the reaction progressed, the ester content was converted to carboxylic acid and the corresponding anion. Therefore, the grafted layer produced may have varying amounts of *tert*-butyl ester and carboxylic acid pendant groups. This pendant group chemistry can be controlled using the combined reaction times for reaction steps III and IV. The ability to control the pendant group functionality not only allows for control over the surface properties of this material, but also affects further pendant group substitution.

3.1.5. tert-Butyl ester substitution

The FTIR results presented thus far demonstrate that the primary goal of grafting P*t*BA to EAA copolymer substrate was accomplished. A secondary goal of this work was the substitution of the pendant groups in the grafted polymer layer with amide/amine functionality. A demonstration of this type of chemical conversion is shown here for the replacement of the *tert*-butyl ester groups with *N*,*N*-dimethylethylenediamine (DMEDA) to give tertiary amine pendant groups. Fig. 8 shows ATR-FTIR results for this reaction. Comparing the EAA-*g*-P*t*BA and EAA-*g*-PDMEDA spectra, the ester and acid peaks at ~1730 cm^{-1} and 1705 cm^{-1} disappeared and were replaced

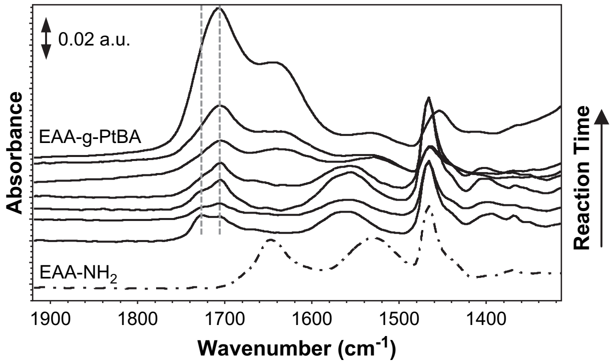

Fig. 7. ATR-FTIR spectra for EAA−NH$_2$ (dashed line) and the subsequent grafting reaction (reaction IV; Fig. 1) to produce EAA-*g*-P*t*BA (solid line). While initially both ester and acid groups were present in the grafted layer (see Section 3.1.4), the pendant groups were progressively converted to acid groups (and the corresponding anion) as the reaction time increased.

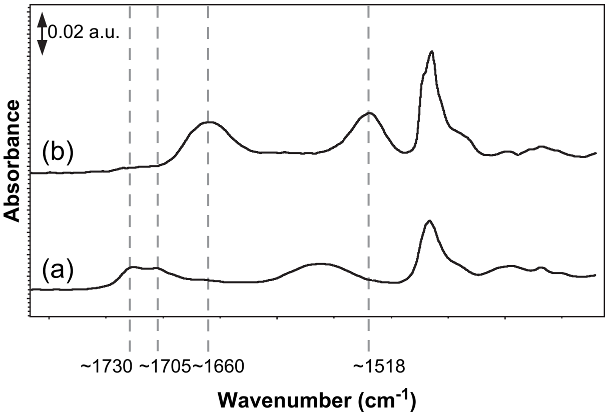

Fig. 8. Representative ATR-FTIR spectra showing the conversion of the ester (~1730 cm^{-1}) and acid (~1705 cm^{-1}) functionalities present in (a) EAA-*g*-P*t*BA to amides (~1660 cm^{-1} and 1518 cm^{-1}) and in (b) EAA-*g*-PDMEDA.

by strong amide peaks at ~1660 cm^{-1} and 1518 cm^{-1}, which confirm that the *tert*-butyl ester and acid groups were replaced by the dimethylethylenediamine functionality [14,21–23].

3.2. XPS results

Survey and high-resolution X-ray photoelectron spectroscopy (XPS) scans were obtained for modified and unmodified EAA samples. The survey scans allowed the atomic composition within the uppermost 10 nm of the samples to be determined after each reaction step (Table 1). Neat (unmodified) EAA film showed ~4.5% oxygen content, which is in good agreement with the expected value of 4.9% for EAA with 9.7 wt% acrylic acid content. When the carboxylic acid groups in EAA were converted to acid chlorides and then reacted with ethylenediamine (EDA), the oxygen content decreased and nitrogen was detected at ~3.6% as the carboxylic acid was converted to an amide. Considering the probe depth of XPS, the 3.6% nitrogen content is much greater than expected if the EDA reaction was confined to the film surface. It is highly probable that the EDA migrated into the film and reacted with sub-surface acid chlorides and is supported by the ATR-FTIR results shown in Figs. 4 and 5. In fact, if we assume that the reaction occurs uniformly within the XPS probe depth, the 3.6% nitrogen content agrees well with the theoretical prediction of 4.0%.

After the P*t*BA was grafted, the oxygen content increased significantly to ~25% (theoretical oxygen content of P*t*BA is 27.5%). A large standard deviation in the oxygen content measurements was expected since the samples examined cover a range of reaction times resulting in a range of mixtures of *tert*-butyl ester and carboxylic acid groups (from hydrolysis). The theoretical oxygen content of P*t*BA is 27.5% and would increase to 47% for fully hydrolyzed P*t*BA (yielding polyacrylic acid). Note that the nitrogen content of EAA-*g*-P*t*BA film did not change from EAA–NH$_2$. After the diamine reaction to yield EAA-*g*-PDMEDA, the oxygen content decreased to ~16% and the nitrogen content increased to ~11%. The theoretical compositions for the (*N*,*N*-dimethylamino)ethylacrylamide polymer are ~12.5% oxygen and ~21.9% nitrogen. For both EAA-*g*-P*t*BA and EAA-*g*-PDMEDA, it is not straightforward to compare the experimental and theoretical contents because the theoretical values (listed above) are based on the structures of only the grafted layers, but experimentally XPS is probing the grafted layer and a portion of the EAA substrate. Even if the relative probe depths of the grafted layer and the substrate were known, the calculation would be further hindered by the fact that the grafting density is unknown. Because of these complicating factors, it is also difficult to determine from these data the extent to which the *tert*-butyl ester groups were replaced with diamines. High-resolution XPS was performed to address this issue.

High-resolution C 1s scans of the modified and unmodified EAA samples were taken and the results are shown in Fig. 9. The binding energies were referenced to the CH$_x$ peak at 284.5 eV. The carboxylic acid [(*C*=O)OH] peak in neat EAA film was seen at ~289.0 eV [24–26] (Fig. 9a). After the reaction of EAA with ethylenediamine, the carboxylic acid peak disappeared and peaks developed for the amide [(*C*=O)N] at ~287.5 eV and for the *C*–N at ~285.1 eV [25,27–29] (Fig. 9b). When P*t*BA was grafted to EAA–NH$_2$, a peak for the ester [(*C*=O)OC] was seen at ~288.9 eV [24,25,28,29] along with a peak at ~285.5 eV corresponding to the combination of the *C*–N (~ +0.6 eV), *C*(C=O)N (~ +0.8 eV), *C*–(C=O)O (~ +0.8 eV), (C=O)O*C* (~ +1.2 eV), and *C*(CH$_3$)$_3$ (*tert*-butyl) (~ +1.7 eV) functionalities [30] (Fig. 9c). Fig. 9d shows the high-resolution spectrum obtained from neat P*t*BA showing the ester peak at 288.6 eV and the *tert*-butyl ester peak at ~286.3 eV. After conversion of the pendant *tert*-butyl ester groups to the dimethylamino terminal group, peaks at ~285.4 eV for C–N and at ~287.2 eV for amide can been seen in the C 1s spectrum (Fig. 9e). The lack of a distinctive ester or acid [(*C*=O)O] peak at ~289 eV suggests that the diamine reaction was complete (or nearly so). Therefore, the survey and high-resolution XPS results confirmed that the P*t*BA was grafted as a surface

Table 1
Atomic oxygen and nitrogen compositions in EAA samples

Sample	Oxygen content (%)				Nitrogen content (%)			
	Avg.	Std. Dev.	Max.	Min.	Avg.	Std. Dev.	Max.	Min.
EAA (neat)	4.5	0.3	5.9	3.5	–	–	–	–
EAA–NH$_2$	3.3	0.1	3.9	2.7	3.6	0.5	4.3	3.1
EAA-*g*-P*t*BA	25.2	7.1	32.2	11.1	3.5	0.5	5.3	2.4
EAA-*g*-PDMEDA	16.2	2.1	17.7	14.7	10.7	1.8	12.0	9.5

Each average is from a minimum of two samples with each sample being scanned in two different spots.

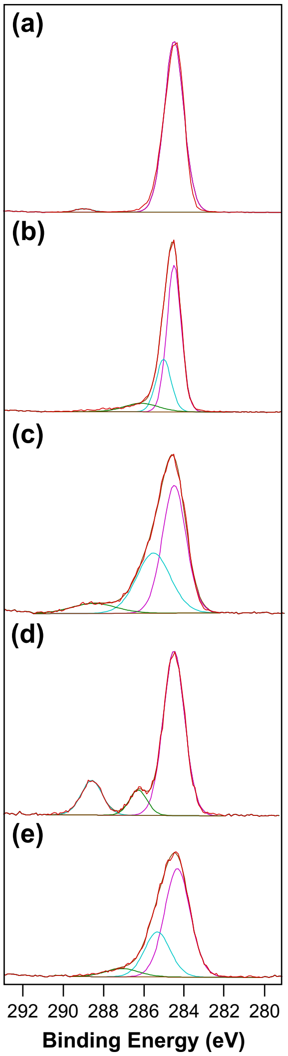

Fig. 9. High-resolution C 1s XPS spectra for (a) neat EAA, (b) EAA–NH_2, (c) EAA-*g*-P*t*BA, (d) neat P*t*BA, and (e) P*t*BA-*g*-PDMEDA.

layer and that the *tert*-butyl ester groups were converted to yield tertiary amine functionality.

3.3. Contact angle results

The static water contact angles measured after various reaction steps are shown in Table 2. The contact angle for neat (unmodified) EAA film was 95°. The contact angle measured for EAA-*g*-P*t*BA at short reaction times (<10 h for reaction III) was 85°, which correlates well to the experimentally measured (Table 2) and the literature values for neat P*t*BA of 88° [31] and for *tert*-butyl ester terminated self-assembled monolayers of 89° [12]. Samples reacted for longer times had a contact angle of 51°. This result is consistent with the FTIR results that show partial conversion of the *tert*-butyl ester groups to carboxylic acid and carboxylate groups with sustained reaction with PCl_5. After reaction with *N*,*N*-dimethylethylenediamine to form EAA grafted with poly(*N*,*N*-dimethylamino)ethylacrylamide (EAA-*g*-PDMEDA), the contact angle was 74°. This contact angle matches literature values for a polymer surface partially grafted with pendant dimethyl amine groups [32,33]. The fact that the contact angle of EAA-*g*-PDMEDA was much greater than that expected for polyacrylic acid (~40–50°) is further the supporting evidence that the *tert*-butyl ester groups were converted to diamines rather than acids.

Table 2
Static water contact angle results with 95% confidence intervals

Sample	Water contact angle (degrees)
EAA (neat)	95 ± 1.6
P*t*BA[a]	88 ± 2.6
EAA-*g*-P*t*BA[b]	85 ± 2.2
EAA-*g*-P*t*BA[c]	51 ± 1.9
EAA-*g*-PDMEDA	74 ± 2.9

[a] Neat polymer; non-end functionalized.
[b] Time of reaction III ≈ 6 h.
[c] Time of reaction III ≈ 18 h.

4. Conclusions

In this work, an original approach for producing surface-grafted layers with tunable properties was developed. The carboxylic acid functionality present in EAA film was converted to acid chloride and then to primary amine to allow for the grafting of a layer of end-functionalized P*t*BA. These chemistries involving PCl_5 and EDA were shown to occur not only at the EAA film surface, but also within the near-surface region of the film. P*t*BA polymer layer was then grafted to the modified EAA surface. It was shown that the reaction conditions could be controlled to allow for the hydrolysis of the pendant *tert*-butyl ester groups of the grafted P*t*BA to form PAA. Regardless of the pendant groups' functionality (*tert*-butyl ester versus carboxylic acid) of the grafted layer, the pendant groups were converted using a novel technique involving $ZnBr_2$ in CH_2Cl_2 to yield a grafted layer of poly(dimethylethylenediamine) (PDMEDA). The chemical modification of the EAA film, grafting of P*t*BA, and subsequent pendant group conversion reaction were confirmed using ATR-FTIR and XPS spectroscopies. The chemical functionality incorporated into the grafted layer significantly changed the wettability of the EAA copolymer film as demonstrated by static water contact angle measurements.

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