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Synthesis and Characterization of Hexadecaniline-Grafted Comb-like Poly(maleic acid-*alt*-1-octadecene)

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*Highly soluble hexadecaniline (A₁₆)-grafted polyolefin derivatives poly(maleic acid-hexadecanilinamide-*alt*-1-octadecene) (PMAO-A₁₆) in a comb-like configuration with alternate linear hexadecane and A₁₆ side-chains were synthesized and characterized. The structure of PMAO-A₁₆ was substantiated by infrared and UV-Vis spectra showing high intensity of characteristic absorption peaks corresponding to a high degree of A₁₆ attachments. Covalent grafting of hexadecanilines onto the polymer backbone of PMAO was confirmed by the detection of a new amide [-(C=O)-NH-] absorption band appearing at 1661 cm⁻¹ accompanied with the full disappearance of anhydride carbonyl absorptions. Based on the comparison between TGA profiles of PMAO-A₁₆ and hexadecaniline, a 12.5% wt loss at 365–600°C was accounted for full elimination of aliphatic side-chains that matches approximately with the weight percentage of total hexadecane arms (12.7%). The data revealed a nearly quantitative yield of A₁₆ grafting on anhydride subunits leading to complete conversion of PMAO into PMAO-A₁₆. Furthermore, preliminary ¹H-NMR study of PMAO-A₁₆ indicated its capability to undergo molecular self-assembly in DMSO where A₁₆s were dispersed in the solvent phase with hexadecane side-chains located in a phase-separated domain.*

Keywords hexadecaniline, tetraaniline, conductive comb-like polymer, poly(maleic anhydride-*alt*-1-octadecene)

Introduction

Chemically and electrochemically synthesized polyaniline (PAni) and substituted polyanilines became one class of primary materials used for the fabrication of electroactive polymer actuators (1–9). Actuation action often associated with doping effect on highly conducting stretchable polyaniline films and fibers with HCl, organic acids, ionic liquids, and solid electrolytes at low *pH* values with different oxidation levels (10, 11). That induced the change of electronic and ionic charges and the number of protons along

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the polymer chain. Balance of charge numbers in response to protonation/deprotonation actions on either benzenoid or quinonoid moieties to effect addition or removal of electronic charge from the polymer backbone forced corresponding counter anions to be relocated and transferred into or out of, respectively, the PANi film to maintain charge neutrality. Ion transport at the polymer and aqueous solution interface resulted in the change of the film volume. The most effective *pH* ranges for protonation of insulating leucoemeraldine, conducting emeraldine base, and insulating pernigraniline forms of PANi were evaluated to be 0.0–1.0, ~3.0, and 0.0, respectively, based on their pK_a values (12, 13). For example, PANi in its emeraldine base form may contract upon immersion into a basic solution or a solution of *pH* much higher than 3.0. Alternatively, the polymer film of PANi also contracts upon the decrease of the oxidation state from emeraldine base form to its leucoemeraldine form at *pH* 1.0–3.0 due to anion exclusion or mass decrease (14, 15). In the reverse cycle going from leucoemeraldine form to emeraldine base form by oxidation, polyaniline film expands by anion insertion at the same *pH* range.

It is desirable to select a flexible substrate or polymer blends, such as dielectric acrylic and silicone elastomers, for the electro-responsive film fabrication to facilitate the mechanical movement of the actuator (16). Our approach involved incorporation of molecular self-assembly of well-defined oligoanilines in the flexible polymer matrix to control the morphology of electroactive components during thin film fabrication. Specifically, we grafted polar oligoanilines onto the side-chain of soft polymer backbone containing secondary comb-like hydrophobic long alkyl side-arms. In this macromolecular structure, incompatibility among polar oligoaniline brushes and hydrophobic long alkyl comb-branches induces self-assembly of each component within polymer domains following phase-separation processes during a slow film formation step. Covalent grafting of oligoanilines on a linear polyolefin resembles pre-aligned PANi segment pendants that may increase the degree of local ordering of active conductive conjugates within the polymer without formation of many random and disordered long-range aggregations as irregular phase-separated domains. Accordingly, improved homogeneity of oligoaniline distribution is expected. In the present study, we reported facile synthesis and characterization of highly soluble poly(maleic acid-hexadecanilnamide-*alt*-1-octadecene) (PMAO-A₁₆) as a comb-like amphipolar polymer consisting of a polyolefin backbone and alternate hydrophobic hexadecane and polar hexadecaniline side-chains. This structural model can be applied for the design of actuator materials.

Experimental

General

Poly(maleic anhydride-*alt*-1-octadecene) (M_n 30,000–50,000), *N*-phenyl-1,4-phenylene diamine (98%), ferric chloride hexahydrate (FeCl₃·6H₂O, 99%), hydrochloric acid (HCl, 37%), diethylether (99%), *N,N*-dimethylformamide (DMF, 99%), ammonium hydroxide (NH₄OH, 30%), petroleum ether (35–60°C), tetrahydrofuran (THF, 99%), 10-camphorsulfonic acid (98%) and pyridine (99.9%) were purchased from Aldrich Chemicals and used as received.

Infrared spectrum was recorded on a Nicolet 750 series FT-IR spectrometer as a KBr pellet using pre-dried samples under vacuum for 12 h at ambient temperature. UV-Vis spectrum was recorded on a Perkin-Elmer UV-VIS-NIR Lambda 9 series spectrometer.

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Spectrospin-250 spectrometer.

Synthesis of Tetraaniline (A₄)

A solution of *N*-phenyl-1,4-phenylene diamine (4.1 g, 0.25 mol) in water (400 mL) was added conc. HCl (7.5 mL) and stirred for a period of 12 h. The reaction mixture was filtered to remove insoluble materials. An additional dil. HCl (2.5 mL, 0.1 N) was added. The green colored solution obtained was cooled to 0°C and added FeCl₃·6H₂O (12 g) dissolved in dil. HCl (5 mL, 0.1 N) at this temperature with vigorous stirring to form thick green solids. After stirring at 0°C for 4 h, the mixture was centrifuged to remove the aqueous solution. Precipitates were washed twice with dil. HCl (175 mL each, 0.1 N). The green solid was dispersed in distilled water (175 mL) and stirred for 2 h. The pH of the solution was then adjusted to 8.0 by the titration with aq. NH₄OH (0.8 M) and subsequently stirred for 12 h. The suspension was then centrifuged to isolate reddish brown solids. The solid was further stirred in aq. NH₄OH (~150 mL, 0.1 M) for 4 h, centrifuged, and dried in vacuum to afford tetraaniline (A₄) (3.7 g) in 90% yield. Spectroscopic data of A₄: UV-Vis (DMSO, 5.2 × 10⁻⁵ M) λ_{max} (ε) 300 and 586 nm. FT-IR (KBr) ν_{max} 3382 (br), 2911 (w, C-H), 2852 (w, C-H), 1595 (s), 1495 (vs), 1316 (s), 1167 (s), 835, 746, 693, and 502 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃, ppm) δ 6.6–7.3 (m, 17H), 5.8 (s, 1H) and 3.7 (s, 2H).

Synthesis of Hexadecaaniline (A₁₆)

A flask containing tetraaniline (3.7 g) and THF (40 mL) was stirred for a period of 4 h and diluted with ethanol (60 mL) with vigorous stirring. To this solution was added anhydrous hydrazine (8.0 mL) and stirred under sealed conditions for 12 h. The solution was concentrated on a rotavapor to a volume of roughly 50% to give a suspension. It was centrifuged with grey-blue solids isolated. The solid was dissolved in a minimum amount of THF (~50 mL) and added dropwise into dil. HCl solution (800 mL, 0.1 N) with vigorous stirring. It was followed by the addition of a solution of ammonium peroxydisulphate, (NH₄)₂S₂O₈, (4.42 g, 7.5 mmol) in dil. HCl (50 mL, 0.1 N) and stirred vigorously for a period of 3 h. At the end of reaction, the mixture was centrifuged to isolate the solids which were washed twice with dil. HCl (125 mL, 0.1 N). Resulting green solids were stirred overnight in aq. NH₄OH (250 mL, 0.1 M). The solids were then isolated by centrifugation and washed with more aq. NH₄OH (125 mL, 0.1 M) to give purple solids. It was dissolved in a minimum amount of THF (~75 mL) and stirred overnight. Precipitation of the products was effected by the addition of petroleum ether (~175 mL), followed by centrifugation to obtain blue-black solids. The latter redissolution–reprecipitation procedure was repeated twice. Further purification of the products led to isolation of hexadecaaniline (A₁₆) as intense dark blue solids (1.9 g) in 50% yield. Freshly prepared hexadecaaniline was kept in THF in dark prior to the use. Spectroscopic data of A₁₆: UV-Vis (DMSO, 2.4 × 10⁻⁵ M) λ_{max} (ε) 314 and 604 nm. FT-IR (KBr) ν_{max} 3386 (br), 2930 (w, C-H), 2847 (w, C-H), 1597 (s), 1508 (vs), 1291 (s), 1168 (s), 821, 749, 692, and 510 cm⁻¹. ¹H-NMR (400 MHz, DMSO-*d*₆, ppm) δ 6.7–7.9 (m).

Synthesis of Poly(maleic acid-hexadecaanilinamide-*alt*-1-octadecene) (PMAO-A₁₆)

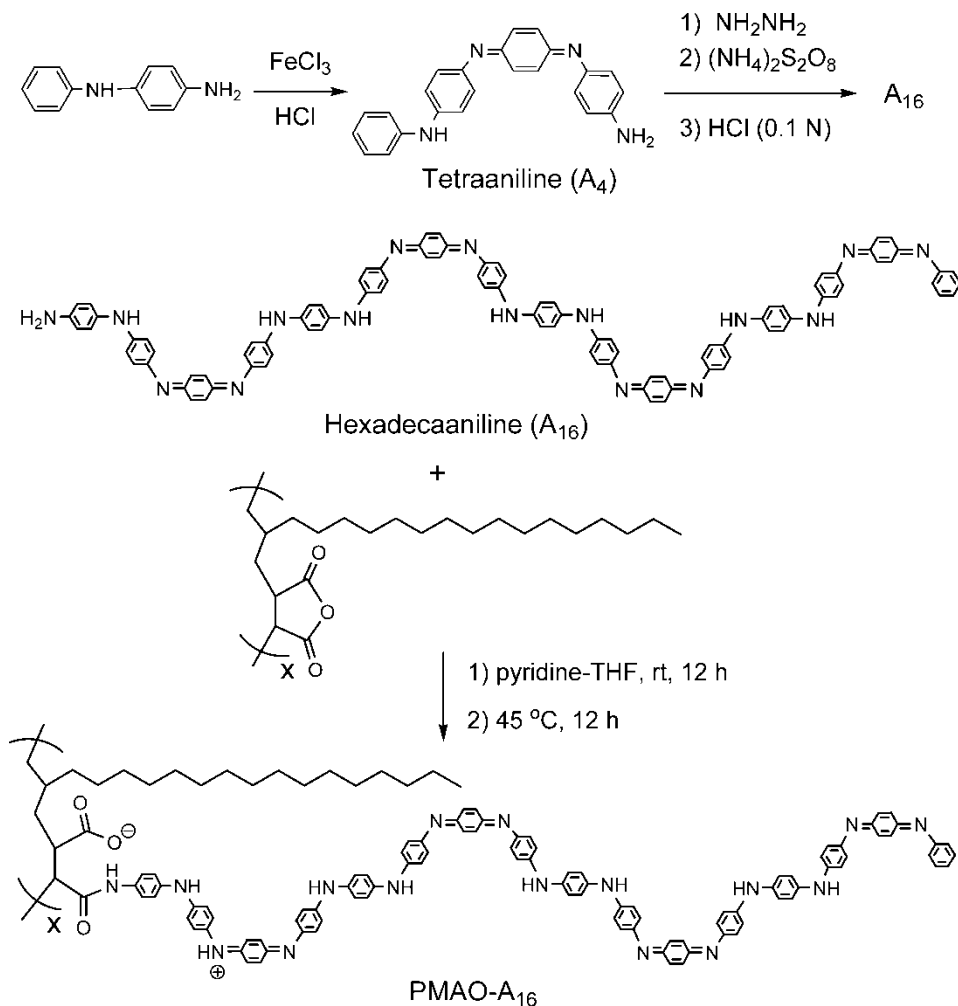
To a solution of hexadecaaniline (1.66 g, 1.14 mmol) in THF (400 mL) was added poly(maleic anhydride-*alt*-1-octadecene) (400 mg, 1.14 mmol based on the monomer

unit weight of 347, M_n 30,000–50,000) in THF (30 mL) and stirred at room temperature to 45°C for 12 h. The reaction mixture was cooled to room temperature and centrifuged to remove insoluble materials. The filtrate liquid was concentrated under reduced pressure to a 25% volume of the solution. Upon addition of petroleum ether (300 mL) to this concentrated solution, solids were precipitated. It was filtered, repeatedly washed with petroleum ether (50 mL each), and dried under vacuum to afford poly(maleic acid-hexadecanilamide-*alt*-1-octadecene) (PMAO- A_{16}) in higher than 85% yield (1.7 g, based on the total amount of reactants used). Spectroscopic data of PMAO- A_{16} : UV-Vis (DMSO, 5.0×10^{-5} M) λ_{\max} (ϵ) 316 and 592 nm. FT-IR (KBr) ν_{\max} 3380 (br), 2922 (C–H), 2844 (C–H), 1661, 1598 (s), 1508 (vs), 1385 (w), 1303 (s), 1173 (s), 825, 750, 695, and 509 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , ppm) δ 0.7–0.9 (m), 1.0–1.2 (m), and 6.7–7.3 (m).

Results and Discussion

Polyanilines are conjugated materials that possess reversible electron reduction-oxidation cycles and protonation-deprotonation ability with high conductivity and excellent environment stability of doped polymers. However, intermolecular hydrogen bonding between benzenoid and quinonoid moieties tends to link linear long PANi chains together into intractable bundles in the solid phase that makes PANi solids difficult to dissolve in common organic solvents for material processing. By utilization of a low molecular weight version of PANi, such as hexadecaniline (A_{16}), for conductive composite application, retention of appropriate conductivity on HCl-doped A_{16} complexes was achieved along with largely enhanced solubility in DMF and improved compatibility with polar polymers. Further grafting hexadecanilines onto a soft polymer backbone should inhibit a long range aggregation of A_{16} into intractable phase-separated domains. Instead, a homogeneous dispersion of A_{16} in the host polymer leading to thin films with consistent electronic properties is to be expected.

Hexadecaniline was synthesized from tetraaniline (A_4) in a fully reduced form by oxidative coupling reactions in the presence of ammonium peroxydisulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and dil. HCl in THF at ambient temperature for 3 h, as depicted in Scheme 1. Reduction of tetraaniline was carried out by the treatment of A_4 with anhydrous hydrazine in a solvent mixture of THF and ethanol (1:2 in a volume ratio) at ambient temperature for 12 h. Preparation of tetraaniline was made by a similar oxidative dimerization reaction using inexpensive, readily available *N*-phenyl-1,4-phenylene diamine as the starting material and ferric chloride hexahydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, as an oxidant in HCl– H_2O at 0°C for 4 h. From this reaction, green solids of protonated A_4 was obtained indicating expected chemical conversion of dianiline. A deprotonation step was made by washings with dilute ammonium hydroxide solution to afford tetraaniline in emeraldine base (EB) form as light blue solids. The oxidative coupling reaction of A_4 may produce a number of oligomers including octaaniline (A_8), dodecaniline (A_{12}), hexadecaniline (A_{16}), and higher oligoanilines ($A_{>16}$) with a progressive decline of the solubility in ether–THF upon an increase of the molecular weight. Therefore, solubility differentiation among starting tetraaniline and resulting products by extensive solvent extractions became the simplest method for purification of the major product A_{16} . Byproducts were mostly oligoanilines in a lower molecular weight than A_{16} . Based on our recent systematic chromatographic evaluation of these products using pure A_4 and A_{16} samples as the references, all A_4 , A_8 , A_{12} , A_{16} , and higher oligoanilines can be assigned each by a peak at a different retention time



Scheme 1. Synthesis of poly(maleic acid-hexadecaanilinamide-*alt*-1-octadecene) (PMAO-A₁₆) by the thermal reaction of A₁₆^S with anhydride moieties of PMAO.

(17, 18). Only one relatively small chromatographic shoulder band above the main peak of A₁₆ was found indicating a limited amount of A_{>16} produced under the oxidative condition applied. Accordingly, high purity of A₁₆ was confirmed by a single chromatographic peak after workup procedures. Other than unreacted A₄, hexadecaaniline was produced in a major quantity in roughly 50% yield under reaction conditions. Infrared spectra (FT-IR, Figure 1b) of hexadecaaniline in its EB form showed the characteristic absorption peaks of oligoaniline segment at 3200–3600 cm⁻¹ for N–H stretching, 3000–2880 (weak) cm⁻¹ for C_{aromatic}-H stretching, and 7 bands centered at 1590, 1510, 1312, 1173, 825, 750, and 695 cm⁻¹ for quinonoid –N=C₆H₄=N– and benzenoid –HN–C₆H₄–NH– vibrational stretching modes.

Covalent grafting reaction of hexadecaaniline with poly(maleic anhydride-*alt*-1-octadecene) (PMAO) was carried out by nucleophilic attack of the primary amine moiety of A₁₆ on a maleic anhydride moiety of PMAO in the presence of pyridine in THF at

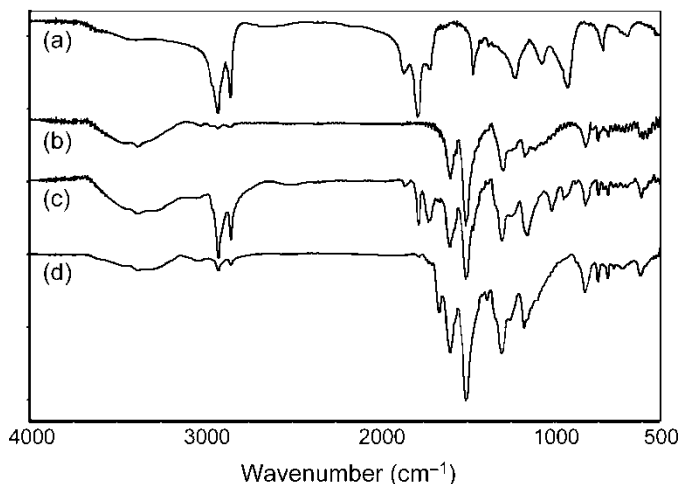


Figure 1. FT-IR spectra of (a) PMAO, (b) hexadecaniline (A_{16}), (c) intermediate PMAO- A_{16} prepared at r.t. for 12 h, and (d) the final PMAO- A_{16} product after treatment at 60°C for another 12 h in addition to (c) and purification.

room temperature for 12 h and then at 60°C for another 12 h, as shown in Scheme 1. A molar equivalent amount of A_{16} to maleic anhydride moiety was applied. Completion of the reaction was monitored periodically by the disappearance of anhydride carbonyl absorption peaks at 1850 and 1774 cm^{-1} in infrared spectrum (Figure 1a) of the reaction mixture at different intermediate stages. During the course of reaction, a small sample quantity was collected, precipitated by petroleum ether, and dried under vacuum prior to the recording of FT-IR spectrum. As shown in Figure 1c, progressive loss of anhydride carbonyl absorption peaks in intensity was obvious after the reaction at ambient temperature for 12 h. This spectrum is in nearly superimpose of Figure 1a of PMAO and Figure 1b of A_{16} with a relative peak intensity ratio corresponding to an estimated 40–50% of the reaction proceeding. The peak at 1774 cm^{-1} vanished in full only after the thermal treatment at 60°C for a period longer than 12 h. At the end of the reaction, resulting mixtures were concentrated with the products precipitated by the addition of petroleum ether to afford poly(maleic acid-hexadecanilamide-*alt*-1-octadecene) (PMAO- A_{16}) as blue solids in higher than 85% yield by weight.

Infrared spectrum of PMAO- A_{16} (Figure 1d) clearly displayed several strong characteristic absorption peaks of A_{16} segments centered at 1598, 1507, 1303, 1173, 825, 750, and 695 cm^{-1} as the main dominate feature of the spectrum with two $\text{C}_{\text{aliphatic}}\text{-H}$ stretching bands at 2922 and 2844 cm^{-1} in a relatively smaller intensity, implying a high degree of A_{16} attachments. Most importantly, a new peak appearing at 1661 cm^{-1} corresponding to optical absorption of amide $-(\text{C}=\text{O})\text{-NH-}$ groups that provided the clear confirmation of covalent grafting of A_{16} s onto the polymer backbone of PMAO. The absence of carbonyl absorption at 1725 cm^{-1} with the detection of 1600 cm^{-1} peak in enhanced intensity also revealed the formation of $-(\text{C}=\text{O})\text{-O}^-$ acid salt instead of $-(\text{C}=\text{O})\text{-OH}$, as shown in Scheme 1.

Attachment of A_{16} on PMAO was also verified by the comparison of steady state UV-Vis absorption spectra between Figure 2b for hexadecaniline and Figure 2c for PMAO- A_{16} in DMSO. Two major peaks centered at 314 and 604 nm for A_{16} and at

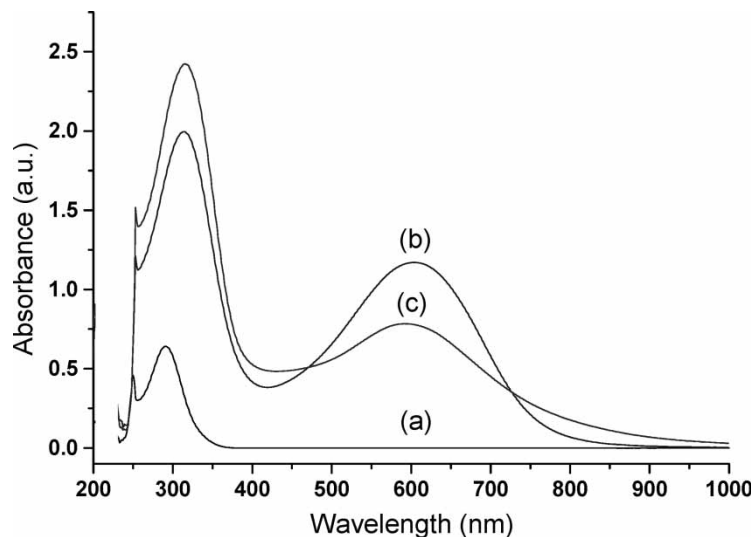


Figure 2. Steady state UV-Vis spectra of (a) *N*-phenyl-1,4-phenylenediamine, (b) hexadecaaniline, and (c) PMAO-A₁₆ in DMSO at 5.0×10^{-5} M.

316 and 592 nm for PMAO-A₁₆ corresponding to the absorption of benzenoid moieties ($-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-$) and quinonoid moieties ($-\text{N}=\text{C}_6\text{H}_4=\text{N}-$), respectively. An obvious change of the relative peak intensity ratio of these two bands with a higher $I_{604/314}$ value for A₁₆ and a lower $I_{592/316}$ value for PMAO-A₁₆ was detected, corresponding to a decrease of quinonoid moieties with an increase of benzenoid moieties in the A₁₆-grafted polymer. One plausible interpretation was made by the partial protonation of quinonoid units (Scheme 1) that leads the red-shift of optical absorption to longer wavelengths beyond 900 nm.

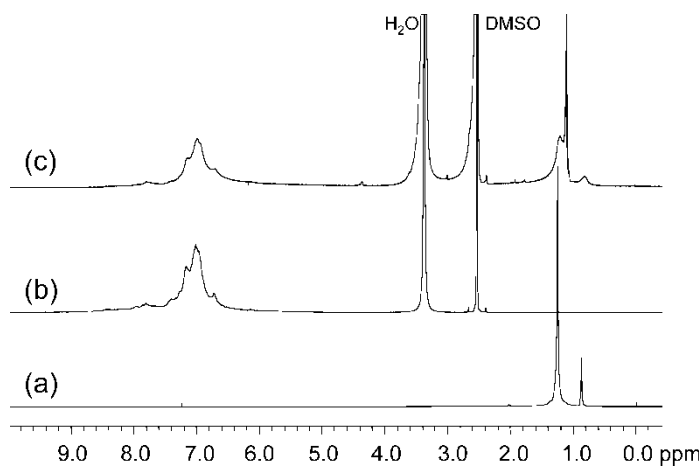


Figure 3. ¹H-NMR spectra of (a) PMAO in CDCl₃, (b) hexadecaaniline, and (c) PMAO-A₁₆ in DMSO-*d*₆.

Incorporation of A₁₆ on PMAO was further substantiated by ¹H-NMR spectrum of grafted polymer PMAO-A₁₆ in DMSO-*d*₆, as shown in Figure 3. Nearly identical chemical shift range and the relative intensity of oligoanilinylic aromatic proton peaks to those of hexadecaniline were observed at δ 6.7–7.3 with the peak maximum centered at δ 7.0, indicating retention of the EB oxidation state of A₁₆. The same spectrum also displayed aliphatic proton peaks as two broadened bands at δ 1.0–1.2 and 0.7–0.9. These two bands are apparently different from sharp peaks of PMAO at δ 1.21 and 0.88, respectively, with a \sim 0.1 ppm shift of the latter peak at the peak maximum. Degree of the peak broadening can be correlated to the degree of phase separation of hexadecane side-chains in DMSO. This observation may reveal molecular self-assembly phenomena of PMAO-A₁₆ where A₁₆ is the dispersed phase in the solvent. Microaggregation of hexadecane side-chains resulted in the loss of proton peak resolution and peak intensity. Therefore, intensity integration of all proton peaks can not be applied for the calculation of the degree of A₁₆ grafting in this spectrum.

Thermal stability of hexadecaniline and PMAO-A₁₆ was evaluated by thermogravimetric analysis (TGA), as shown in Figure 4. As a result, high thermal stability of both materials was evident showing the onset decomposition temperature at 440°C for A₁₆ with only a 7.5% wt loss at this temperature, presumably, due to evaporation of strongly physisorbed solvent molecules. As the temperature reaches 600°C, the total weight loss was found to be 45%, in a considerably low value as compared with conventional organic polymers. In the case of hexadecaniline-grafted polymer PMAO-A₁₆, onset decomposition temperature was measured to be 365°C with a 10% wt loss at this temperature (Figure 4b). This weight loss may involve the elimination of H₂O, residual solvent molecules, and CO₂, with the latter as the result of thermal decarboxylation of acid moieties. An additional 50% wt loss was observed as the temperature continued to rise above 550–600°C giving a difference of 12.5% higher than the calculated weight loss of A₁₆ as 37.5% (Figure 4a) in the same temperature range. The difference can be accounted for facile elimination of hexadecane side-chains at high temperatures above 450°C. The value agrees well with the weight percentage of total hexadecane side-chains as 12.7% in the structure of PMAO-A₁₆ assuming a 100% efficiency of A₁₆ grafting with no remaining anhydride subunits. The data substantiated nearly full completion of nucleophilic reaction in the conversion of PMAO into PMAO-A₁₆.

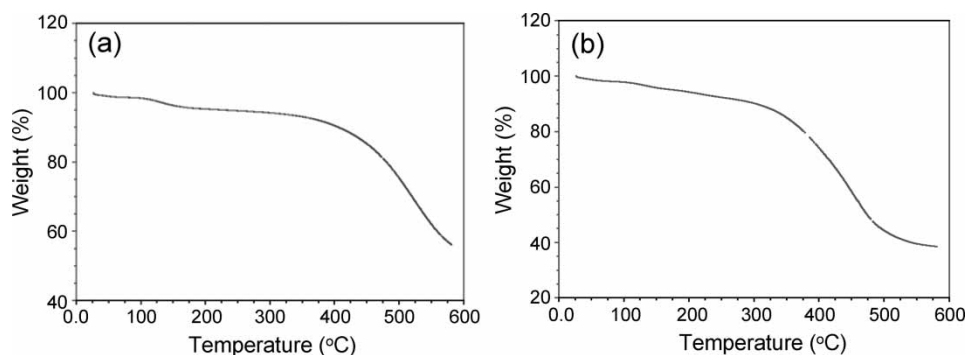


Figure 4. Thermogravimetric analysis (TGA) profiles of (a) hexadecaniline and (b) PMAO-A₁₆ showing high stability of both materials.

Conclusions

Processable hexadecaniline (A₁₆)-grafted polyolefin derivatives poly(maleic acid-hexadecanilinamide-*alt*-1-octadecene) (PMAO-A₁₆) were synthesized and characterized. It is in a prototype comb-like structure with alternate linear hexadecane and A₁₆ side-chains in a well-defined chain length. The synthetic approach led to solubility enhancement of the products and minimization of a long range aggregation tendency of hexadecaniline moieties. The structure of PMAO-A₁₆ was substantiated by infrared and UV-Vis spectra showing high intensity of characteristic absorption peaks corresponding to a high degree of A₁₆ attachments. Covalent grafting of hexadecanilines onto the polymer backbone of PMAO was confirmed by the detection of a new amide [-(C=O)-NH-] absorption band appearing at 1661 cm accompanied with the full disappearance of anhydride carbonyl absorptions. Based on the comparison between TGA profiles of PMAO-A₁₆ and hexadecaniline, a 12.5% wt loss at 365–600°C was accounted for full elimination of aliphatic side-chains that matches approximately with the weight percentage of total hexadecane arms (12.7%). The data revealed a nearly quantitative yield of A₁₆ grafting on anhydride subunits and the complete conversion of PMAO into PMAO-A₁₆. Furthermore, preliminary ¹H-NMR study of PMAO-A₁₆ indicated its capability to undergo molecular self-assembly in DMSO where A₁₆s were dispersed in the solvent phase with hexadecane side-chains located in phase-separated domains.

Hexadecaniline exhibits excellent thermal stability up to 440°C and several reversible reduction-oxidation states. Its electroactive responses to reversible doping and de-doping processes may allow the use of comb-like polymers PMAO-A₁₆ as processable materials in the fabrication of sensors, actuators, and electronic devices.

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