Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

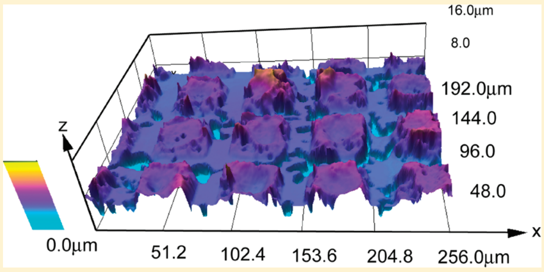
Conjugated Polymers with Pendant Iniferter Units: Versatile Materials for Grafting

Petya K. Ivanova-Mitseva,[†] Vasiliki Fragkou,[†] Dhana Lakshmi,[*,†] Michael J. Whitcombe,[†] Frank Davis,[†] Antonio Guerreiro,[†] Joseph A. Crayston,[‡] Diana K. Ivanova,[†] Petar A. Mitsev,[§] Elena V. Piletska,[†] and Sergey A. Piletsky[†]

[†]Cranfield Health, Vincent Building, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, U.K.
[‡]School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, Scotland, U.K.
[§]School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, U.K.

S *Supporting Information*

ABSTRACT: A novel compound *N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA) was synthesized and fully characterized. Conjugated poly(NDDEAEA), consisting of N-substituted polyaniline (PANI) backbones with dithiocarbamate ester pendant groups (which can act as iniferters), was synthesized by both chemical and electrochemical polymerization. UV-initiated living polymerization was utilized to graft styrene, methacrylic acid (MAA), lauryl methacrylate, and acrylamido-2-methylpropanesulfonic acid (AMPSA) onto the conjugated macroiniferter which had previously been deposited on various surfaces (glass, polypropylene, polystyrene, and gold electrodes). The resultant polymeric surfaces were characterized by static contact angle measurements, XPS, SEM, and AFM. This versatile new material can be used for creating materials with integrated functionalities (e.g., conductivity, molecular recognition, catalysis and controlled transport properties, etc.) for application in sensors and microfluidic devices and for the construction of patterned surfaces.



INTRODUCTION

Surface grafting of polymers is an important process for introducing interfacial and functional properties to both microscopic and macroscopic objects. Examples include modifying the hydrophilicity/hydrophobicity, adhesive, electronic, or electrical properties of the surface and the introduction of features, such as molecular recognition or fluorescence. In this context, the so-called "living" polymerization processes[1−3] (atom-transfer radical polymerization (ATRP),[4,5] reversible addition−fragmentation chain transfer (RAFT),[6−9] nitroxide-mediated[10,11] and iniferter-initiated polymerization[12−16]) offer a number of advantages. These include control of the grafting process due to the stepwise addition of monomers, resulting in a more homogeneous growth of polymer, and the possibility to prepare block copolymer architectures by reinitiation in the presence of new monomers.[17] Of these, the use of photochemically activated iniferters, based on dithiocarbamate esters, is especially convenient for selective grafting to surfaces, since the process can readily be controlled and confined by the selective application of long wavelength UV light.

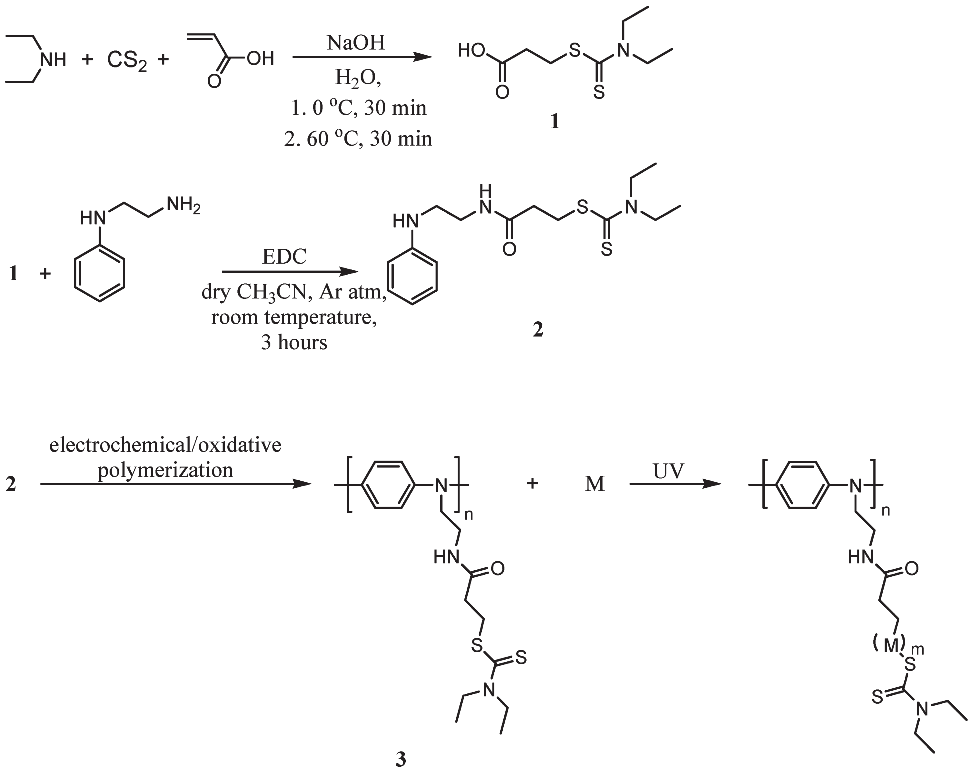
Grafting by any of these methods however requires the immobilization of a suitable initiator species on the surface to be grafted. In the case of iniferters, this requires the *in situ* formation or attachment of a suitable dithiocarbamate ester. This has been achieved in the past by polymer analogous reaction of side-chain residues, such as chloromethylstyrene groups, with a dithiocarbamate salt,[13,15] by use of a polymer bearing dithiocarbamate ester groups,[18−21] by attachment of a surface-reactive dithiocarbamate ester, such as a silane derivative,[16,22] or by photochemical activation of surface-confined double bonds with a soluble dithiocarbamate ester.[23,24] In this article we report the application of a novel conjugated polymer with pendant iniferter groups synthesized from a polyaniline precursor bearing a dithiocarbamate ester.

Conducting polymers (CPs), especially polyanilines (PANIs), have received much attention as a result of their promise in optical and electronic applications such as solar cells, sensors, and light-emitting diodes.[25−27] The design of new monomers as a means of introducing functional groups into conjugated polymers has led to improvements in surface hydrophilicity, biocompatibility, and adhesion properties. Improvements of this type allow the polymer films to be used in many potential applications such as transparent electrodes, chemical and biological sensors, organic electrical conductors, optically active materials, and others by combining the appropriate functional groups with a conjugated polymer backbone. Recently, we reported one example in which a conjugated polymer backbone was combined with the double-bond functionality of a

Received: November 25, 2010
Revised: February 17, 2011
Published: March 14, 2011

dx.doi.org/10.1021/ma102692h | *Macromolecules* 2011, 44, 1856–1865

Scheme 1. Schematic Representation of the Synthesis of *N*-(*N′*,*N′*-Diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA) (2) from *S*-(Carboxypropyl)-*N*,*N*-diethyldithiocarbamic Acid (1) and Its Polymers[a]



[a] Poly(NDDEAEA) (3) formed via electrochemical polymerization or chemical oxidative polymerization giving rise to polyaniline chains with pendant dithiocarbamate moieties. Addition of monomer, M, by UV grafting giving rise to poly(M)/poly(NDDEAEA) graft copolymers.

methacrylamide group in the form of the novel monomer *N*-phenylethylenediamine methacrylamide (NPEDMA).[28] NPEDMA undergoes chemical (oxidative) or electrochemical polymerization to form PANI-based materials derivatized with double bonds. Furthermore, the same material can be utilized as the basis for the construction of an electrochemical sensor (for catechol) by grafting a layer of a catalytically active molecularly imprinted polymer (MIP) over an electropolymerized layer of poly(NPEDMA), deposited on a gold electrode[24] or prepared as nanotubes.[29] The sensors proved to be superior to electrodes prepared by immobilization of MIP particles of essentially the same composition at the surface of a screen-printed electrode. This phenomenon was explained by the conjugated polymer acting as a "molecular wire" resulting in more intimate contact between the catalytically active imprint sites and the conjugated polymer layer than was achievable by immobilization of an electrically insulating polymer onto an unmodified electrode. Grafting of the MIP layer was achieved by irradiating the double-bond-bearing poly(NPEDMA) layer in the presence of *N*,*N*-diethyldithiocarbamic acid benzyl ester. This resulted in the partial conversion of the pendant double bonds into groups capable of initiating further polymerization. It would be desirable however to avoid the use of an additional activation step. This could be achieved if the conjugated polymer precursor was already derivatized with dithiocarbamate ester groups, rather than double bonds. Such a material would allow for the formation of conjugated PANIs, derivatized with dithiocarbamate ester groups and capable of direct UV-activated grafting of addition polymers.

In this work therefore we describe the synthesis, characterization, and polymerization behavior of a new bifunctional monomer, *N*-(*N′*,*N′*-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA) (Scheme 1). NDDEAEA can undergo electropolymerization and chemical oxidative polymerization in a similar manner to NPEDMA to give a conducting form of polyaniline, bearing a high density of dithiocarbamate ester pendant groups. Poly(NDDEAEA) can be formed as thick or thin films, powder, particles, microparticles, or nanoparticles, all of which can act as a macroiniferter in UV-activated graft polymerization. In addition, we report the use of polymers of NDDEAEA as a means of activating a range of surfaces toward grafting of polymer and block copolymers and their characterization.

■ EXPERIMENTAL SECTION

Materials. Carbon disulfide (99%) and sodium hydroxide (97%) were purchased from Acros Organics. 1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (98%) was purchased from Alfa Aeser. Acrylic acid (99%) and *N*-phenylethylenediamine (98%) were purchased from Sigma-Aldrich, and diethylamine (98%) was obtained from Fisher Scientific. All other chemicals and solvents used within this work were purchased from Sigma-Aldrich and were of analytical grade and used as received. Milli-Q distilled water was used in all experiments.

Apparatus. NMR measurements were made using a JEOL ECX 400 MHz NMR, and FT-IR spectra were recorded using KBr disks on a ThermoNicolet Avatar-370 spectrometer (Nicolet, US). For UV irradiation, CERMAX xenon arc lamp (Perkin-Elmer Optoelectronics, Inc.) fiber-optic light source (300 W) or a Philips type HB 171/A self-tanning

UV lamp, fitted with four CLEO 15 W UVA fluorescent tubes (Philips) with continuous output in the region 300−400 nm, delivering 0.09 W $\mathrm{cm^{-2}}$ at a distance of 8 cm, were used. Sessile water contact angle (CA) measurements were made using a Cam 100 optical angle meter (KSV Instruments Ltd., Finland) along with the software provided. Elemental analyses were provided by Medac Ltd., Egham, UK. Optical densities were recorded using a microplate reader (for microtiter plates) or a UV spectrophotometer (UV-1800 Schimadzu, Japan). An Autolab PSTAT-10 instrument (Eco-Chemie BV, Utrecht, Netherlands) was utilized for all electrochemical experiments. AFM experiments were performed using a DI3000 AFM (Digital Instruments, Tonawanda, NY) in tapping mode in air. SEM images were recorded with an FEI XL30 SFEG (scanning field emission gun) microscope. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG ESCAlab (East Grinstead, UK) Mark-2 X-ray photoelectron spectrometer. The X-ray gun was operated at 14 kV and 20 mA. Spectra were collected at 20 eV pass energy with Mg Kα 1253.6 eV radiation at an analysis chamber pressure of 10^{-9} mbar. Elemental composition was calculated using peak areas and tabulated atomic sensitivity factors. A confocal laser scanning 3D color microscope Olympus LEXT (model OLS3000) was used for the imaged layers of chemically polymerized NDDEAEA, and a Dektek 3 surface profiler (Veeco, New York) was used for thickness measurements of grafted films.

Synthesis of *N*-(*N′*,*N′*-Diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA). *S*-(Carboxypropyl)-*N*,*N*-diethyldithiocarbamic acid (CNDDA) (**1**) was synthesized using a method adapted from the patent disclosed by Hook et al.[30] Acrylic acid (0.5 mol, 36.0 g, 1 equiv), diethylamine (0.5 mol, 36.5 g, 1 equiv), and carbon disulfide (0.6 mol, 41.5 g, 1.1 equiv) were added dropwise in that order to a cooled (0 °C) solution of sodium hydroxide (0.5 mol, 20.0 g, 1 equiv) in 200 mL water. The mixture was stirred for 30 min at ambient temperature and then for 30 min at 60 °C (bath temperature). After cooling in ice, the solution was acidified with hydrochloric acid to pH 5.5. The oil formed in the reaction solidified on vigorous stirring. This solid was filtered off and washed well with distilled water. The pale yellow crystals (30% yield) were dried. UV (acetonitrile): $\lambda_{\max}$ = 275 nm, (ε = 4280 $\mathrm{M^{-1}\ L^{-1}}$); 334 nm, (ε = 73 $\mathrm{M^{-1}\ L^{-1}}$). Further analytical characterization of this material is presented in the Supporting Information.

A solution of **1** (0.004 mol, 0.922 g, 1 equiv) in 20 mL of anhydrous acetonitrile was prepared in a dried 50 mL round-bottomed flask, under argon atmosphere with exclusion of light. To this mixture, *N*-phenylethylenediamine (0.004 mol, 0.545 g, 1 equiv) and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (0.008 mol, 1.6 g, 2 equiv) were added in that order. After 3 h of stirring, the solvent was removed *in vacuo*. The crude mixture was dissolved in 40 mL of ethyl acetate and extracted five times with 40 mL of distilled water, the organic layer was dried with anhydrous sodium sulfate and filtered, and the solvent was evaporated *in vacuo* to obtain an oily product that solidified to a white waxy material in 50% overall yield (98% purity by NMR). The product *N*-(*N′*,*N′*-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA) (**2**) (see Scheme 1 and Supporting Information Schemes S1 and S2) was used without further purification.

Spectroscopic Data (NDDEAEA) (2). IR (KBr): 1647.26 (C═O), 1603.77 ((S)C−N), 1508.10 (N−C(O)), 1351.55 (C═S), 1268.93 ($\mathrm{C{-}NC_6H_5}$), 981.92 (C−N), 755.80 ((S)C−S), 694.92 $\mathrm{cm^{-1}}$ ($\mathrm{S{-}CH_3}$).

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.96 (1H, t, $\mathrm{NHC_6}\mathit{H}_5$), 7.01 (2H, t, J = 7.68 Hz, $\mathrm{C_6}\mathit{H}_5$), 6.51 (2H, d, J = 7.68 Hz, $\mathrm{C_6}\mathit{H}_5$), 6.30 (1H, t, J = 7.34 Hz, $\mathrm{C_6}\mathit{H}_5$), 5.49 (1H, t, J = 5.27, $\mathrm{N}\mathit{H}\mathrm{CO}$), 3.90−3.87 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 3.65−3.61 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 3.35 (2H, t, J = 6.99, $\mathrm{C}\mathit{H}_2\mathrm{S}$), 3.20−3.12 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{NHC(O)}$), 3.09−2.90 (2H, m, $\mathrm{C_6H_5NHC}\mathit{H}_2$), 2.44 (2H, t, $\mathrm{NHC(O)C}\mathit{H}_2$), 1.18−1.1 ppm (6H, m, $\mathrm{N(CH_2C}\mathit{H}_3)_2$). ^{1}H NMR (400 MHz, DMSO-d_6, 130 °C): δ 7.51 (1H, s, $\mathrm{N}\mathit{H}\mathrm{C_6H_5}$), 7.00 (2H, t, J = 7.68 Hz, $\mathrm{C_6}\mathit{H}_5$), 6.52 (2H, d, J = 7.68 Hz, $\mathrm{C_6}\mathit{H}_5$), 6.48 (1H, t, J = 7.34 Hz, $\mathrm{C_6}\mathit{H}_5$), 5.04 (1H, s, $\mathrm{N}\mathit{H}\mathrm{CO}$), 3.88−3.74 (4H, m, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 3.40 (2H, t, J = 6.99, $\mathrm{C}\mathit{H}_2\mathrm{S}$), 3.24−3.20 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{NHCO}$), 3.20−3.00 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{NHC(O)}$), 2.47 (2H, t, J = 6.99 Hz, $\mathrm{NHC(O)C}\mathit{H}_2$), 1.18 ppm (6H, t, $\mathrm{N(CH_2C}\mathit{H}_3)_2$).

^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 193.86 ($\mathit{C}\mathrm{(S)S}$), 170.40 ($\mathit{C}\mathrm{(O)}$), 148.57, 128.89, 115.69, 111.91 ($\mathit{C}_6\mathrm{H_5}$), 49.60 ($\mathrm{\mathit{C}H_2CH_3}$), 46.80 ($\mathrm{\mathit{C}H_2CH_3}$), 42.10 ($\mathrm{C_5H_6NH\mathit{C}H_2}$), 39.00 ($\mathrm{\mathit{C}H_2NHC(O)}$), 34.30 ($\mathrm{NHC(O)\mathit{C}H_2}$), 32.40 ($\mathrm{\mathit{C}H_2SC(S)}$), 12.23 ($\mathrm{CH_2\mathit{C}H_3}$), 11.36 ppm - ($\mathrm{CH_2\mathit{C}H_3}$). ^{13}C NMR (100 MHz, DMSO-d_6, 130 °C): δ 194.33 ($\mathit{C}\mathrm{(S)S}$), 169.75 ($\mathit{C}\mathrm{(O)}$), 148.18, 128.11, 115.40, 111.77 ($\mathit{C}_6\mathrm{H_5}$), 48.50 ($\mathrm{\mathit{C}H_2CH_3}$), 42.10 ($\mathrm{C_5H_6NH\mathit{C}H_2}$), 38.00 ($\mathrm{\mathit{C}H_2NHC(O)}$), 34.00 ($\mathrm{NHC(O)\mathit{C}H_2}$), 32.00 ($\mathrm{\mathit{C}H_2SC(S)}$), 11.21 ppm ($\mathrm{N(CH_2\mathit{C}H_3)_2}$). (The assignments were based on COSY, DEPT, and HMQC experiments made in DMSO-d_6.)

HRMS (ES): Calculated mass for $\mathrm{C_{16}H_{25}N_3NaOS_2}$ $[\mathrm{M+Na}]^+$: m/z: 362.13. Found: 362.14. Elemental analysis ($\mathrm{C_{16}H_{25}N_3OS_2}$): C, 56.60; H 7.42; N 12.38, O 4.71, S 18.89. Found 1: C 57.85, H 7.65, N 13.01, S 18.25; R_f = 0.24 (50% ethyl acetate/hexane). All spectra are provided in the Supporting Information, Figures S1−S5.

Electropolymerization of the Aniline Group of NDDEAEA. Screen printed gold electrodes (SPE) (4.0 mm diameter, from Dropsens) were used, with gold working and counter electrodes and Ag/AgCl reference electrode. Before polymerization each new electrode was cleaned and pretreated by cycling the potential between 0 and +0.7 V, 50 mV $\mathrm{s^{-1}}$ scan rate in 1.5 M HCl, five cycles. For the deposition step, electrodes were cycled (20 times) between −0.2 and +0.9 V at a scan rate of 100 mV $\mathrm{s^{-1}}$ (step potential 7 mV) in a 0.2 M solution of NDDEAEA in 0.56 M HCl in a 3:1 water−acetonitrile mixture. Stock solution was prepared by adding 1.25 mL of acetonitrile solution of 0.8 M NDDEAEA into a 5 mL beaker containing 1.87 mL of 1.5 M HCl and 1.9 mL of water. Solutions were mixed well and degassed for 10 min by purging with argon or nitrogen, and the solution was kept covered with aluminum foil to protect from light before deposition. CV measurements were performed by placing 50 μL of the test solution of NDDEAEA onto the surface of the SPE for electropolymerization. Electropolymerization was carried out under argon and in the dark. Electropolymerized films were rinsed with deionized water (once), dried in a stream of nitrogen, and stored dry and in the dark. A blue-green layer of poly(NDDEAEA) was observed to have formed on the working electrode.

Surface-Confined Photografting of Various Addition Polymers onto Electropolymerized Films of NDDEAEA. An electropolymerized poly(NDDEAEA)-modified SPE was placed horizontally in a glass vial and the working electrode covered with 50 μL of a 0.1 M solution of unsaturated monomer in acetonitrile under dark conditions. The monomer solutions had been purged with nitrogen for 10 min to remove oxygen prior to irradiation. The vial was sealed with Parafilm and continuously purged with nitrogen to maintain an inert atmosphere over the solution during irradiation. The electrode surface was then UV-irradiated for 20 min with a fiber-optic light source (CERMAX xenon arc lamp). The photografted electrodes were then rinsed in a mixture of 50:50 v/v methanol:deionized water and dried in a stream of nitrogen. Contact angle measurements were used to characterize changes that had occurred in the functionality and hydrophobic/hydrophilic nature of the polymeric film after grafting.

Several polymers were grafted onto poly(NDDEAEA) following the protocol described above. Solutions (0.1 M) of methacrylic acid, AMPSA, or styrene were utilized to produce grafted films of the respective polymers via UV irradiation. As well as grafting single polymers onto poly(NDDEAEA), layered (block copolymer grafted) structures, MAA followed by styrene, could also be constructed. For the layer-by-layer grafting experiment, a poly(MAA) grafted SPE electrode, prepared as described in above, was treated with a solution of styrene (50 μL of 0.1 M in acetonitrile) and irradiated under the same conditions as described above for the grafting of polymer layers. The contact angles of the grafted films were measured and their thickness determined by Dektek analysis. All surfaces were characterized using SEM and AFM (Supporting Information Figures S6−S8).

Polymerization of NDDEAEA by chemical oxidation could also be used for the formation of thick or thin (transparent) coatings on a range of supports (polystyrene microtiter plates, cuvettes, and polypropylene filtration membranes). Experimental parameters were optimized in order to obtain films of the desired thickness, which could then be used as substrates in a number of grafting procedures (see Supporting Information, method A (Figure S9) and method B (Figures S10−S12) for the effect of varying the experimental parameter on film growth). Polymerization resulted in the formation of green coatings of poly(NDDEAEA) on the surfaces of the microplate wells. The washed wells were filled with dilute acid (0.01 M HCl, pH = 1), and the absorbance was measured at 405 nm. Thin transparent layers (absorbance = 0.17, Figure S9) were formed under the conditions: NDDEAEA (25 mM), HCl (225 mM) and ammonium persulfate (18.3 mM), polymerized for 2 h in 25% acetonitrile:water. Similarly thicker films were obtained (absorbance (measured in water at 550 nm) = 3.5, Figures S10 and S11) under the conditions: NDDEAEA (80 mM), HCl (0.6 M), and ammonium persulfate (50 mM), polymerized for 1 h in 25% acetonitrile:water.

Chemical Oxidative Polymerization of NDDEAEA on Polypropylene (PP) Ultrafiltration Membranes (Thinner Films). PP membranes (with a nominal cutoff pore diameter of 0.2 μm and thickness of 150 μm, PP 2E-HF, Membrana, Germany) were cut into small disks of 25 mm diameter. Membranes were pretreated with methanol for 1 h in a Petri dish. Oxidative polymerization was performed using ammonium persulfate (APS) under the following conditions: 0.018 M APS, 0.025 M NDDEAEA, 0.225 M HCl, 25% acetonitrile in water, 1.45 h polymerization in the dark at room temperature. The reaction mixture was prepared by combining 0.75 mL of NDDEAEA (0.1 M in acetonitrile) with 0.6 mL of an aqueous solution of APS (0.0915 M), 675 μL of HCl (0.1 M), and 0.98 mL of water. Polymerization resulted in the deposition of a thin, green layer of functionalized PANI coating over the membrane surfaces. Poly(NDDEAEA)-coated PP membranes were washed in three cycles of water, followed by 0.1 M HCl. The degree of grafting was determined gravimetrically and expressed as a percentage change in mass. The following equation was used:

$$\mathrm{DG}\ (\%) = (W_1 - W_0)/W_0 \times 100\%$$

Here W_0 and W_1 represent the weights of the membrane before and after grafting, respectively. Contact angles were also measured.

Photografting by UV Polymerization of Monomers onto Chemically Oxidized Poly(NDDEAEA)-Modified PP Membranes and Glass Slides. The preweighed poly(NDDEAEA)-coated membranes were immersed in a Petri dish containing 3 mL of 0.1 M monomer solution (methacrylic acid or AMPSA was dissolved in water and styrene in acetonitrile) which had been degassed by bubbling with nitrogen for 10 min. The Petri dish was then placed inside a homemade box supplied with an inlet for continuous flow of nitrogen throughout the period of polymerization and irradiated (Philips UV lamp) for 45 min. After drying at 45 °C overnight, the degree of grafting was calculated. Contact angles were measured before and after grafting. Similarly, chemical oxidative polymerization of NDDEAEA was performed onto glass microscope slides to obtain thicker films The slide was placed in a 500 mL glass beaker, and 30 mL of a solution containing 0.08 M NDDEAEA, 0.6 M HCl, and 0.05 M APS in 25% acetonitrile/water was added. The polymerization was allowed to proceed at ambient temperature for 1 h. The glass slide was then rinsed with water and dried at ambient temperature for 12 h. Half of the poly(NDDEAEA)-modified glass slide was then masked with aluminum foil, and UV photografting of a hydrophobic monomer (styrene) was performed on the unmasked half. The sample was then rinsed, the styrene-modified area was masked, and the other half was grafted with a hydrophilic monomer (AMPSA) as described above. Again contact angles were measured for the coatings.

Surface-Confined Photografting of Various Monomers on Poly(NDDEAEA)-Modified Microtiter Plates. Poly(NDDEAEA)-coated polystyrene microtiter plates were placed horizontally in a Petri dish. A solution of monomer (200 μL, 0.1 M, degassed with nitrogen for 10 min) was placed in each of the wells in which grafting was to be carried out, in the dark. The Petri dish and microplate were placed inside a sealed homemade box purged with nitrogen. Monomer solutions were made up in water (methacrylic acid or AMPSA) or acetonitrile (lauryl methacrylate). The contents of the box were irradiated for 45 min using a Philips UV lamp, mounted at a distance of 8 cm from the well bottoms. The photografted surfaces were rinsed with deionized water and dried in a stream of nitrogen. Contact angle measurements were performed on the grafted films. Control experiments were performed in the same manner using unsubstituted polyaniline in place of the poly(NDDEAEA) films.

Spatially Confined Grafting of Poly(*N*-(3-aminopropyl)-methacrylamide) over Chemically Polymerized Poly(NDDEEA) Using a TEM Grid as a Photomask. A solution comprising NDDEAEA (0.08 M), HCl (0.6 M), and APS (0.05 M) in 8 mL of 25% acetonitrile/water was allowed to react for 1 h in the dark. The resultant polymer formed as a precipitate at the bottom of the vial was washed several times by the addition and decantation of water. The washed residue was dissolved in 1 mL of methanol. One drop of this solution was placed on a precleaned gold-coated glass slide (2 × 2 cm), and the solvent was allowed to evaporate to deposit a cast film of poly(NDDEAEA). A TEM grid (G213, Bal-Tec, 200 mesh copper with 100 μm × 100 μm square holes) was placed on the surface of the polymeric film, and then a drop of a previously degassed solution of *N*-(3-aminopropyl)methacrylamide (0.43 M in 20% acetonitrile−water mixture) was placed onto the grid. The grid was covered with a standard microscope cover glass slide, and the assembly was then placed in a plastic bag with a nitrogen atmosphere. After 5 min purging with nitrogen, the assembly was UV irradiated for 20 min with the Philips UV lamp. The slide was rinsed with water and left to dry for 12 h at room temperature. Confocal microscopy (10× magnification) was used to record 3D images of grafted poly-*N*-(3-aminopropyl)methacrylamide structures, before and after removal of the TEM grid.

RESULTS AND DISCUSSION

A new monomer, *N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA), was prepared by coupling *S*-(carboxypropyl)-*N*,*N*-diethyldithiocarbamic acid, prepared by reaction of acrylic acid, CS_2, and diethylamine in the presence of base,[30] with *N*-phenylethylenediamine (Scheme 1). NDDEAEA was fully characterized (see Supporting Information). The ^{1}H NMR spectrum of NDDEAEA, recorded at room temperature (Figure S1, Supporting Information), showed that some signals were split due to the existence of two conformers as a result of hindered rotation about the N−C(=S) single bond.[21] NMR spectra recorded at 100 and 130 °C (Figures S2 and S3) showed coalescence of these signals to single peaks. This can be explained by overcoming the torsional barrier at higher thermal energy, resulting in rapid interconversion of the two forms on the NMR time scale.[21]

Polymerization of the aniline functionality of NDDEAEA should result in the formation of a conjugated polymer bearing a high density of dithiocarbamate ester (iniferter) as pendant side chains. The ability of polyaniline to form stable coatings on both hydrophilic and hydrophobic surfaces[31−33] suggests that this

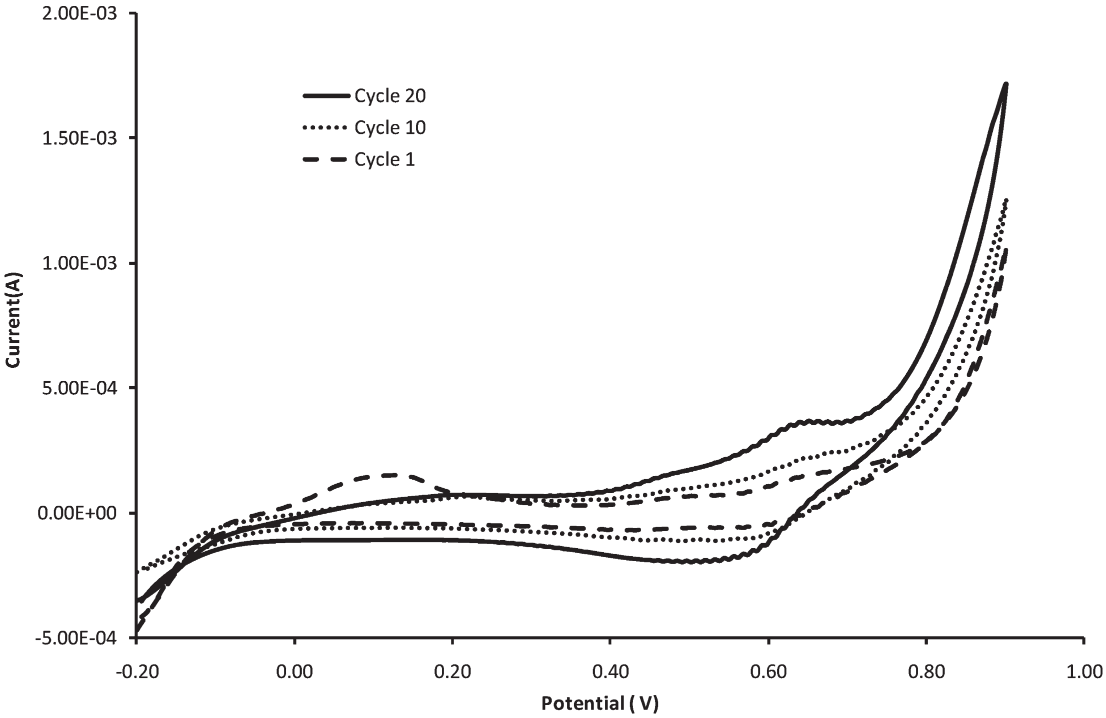


Figure 1. Cyclic voltammogram obtained during deposition of electropolymerized *N*-(*N′*,*N′*-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA) films on gold screen-printed electrodes. Electropolymerization of NDDEAEA (0.1 M in 0.75 M HCl/25% acetonitrile/water) on a screen printed gold electrode by cyclic voltammetry (potential range: −0.2 to 0.9 V vs Ag/AgCl, at 100 mV s^{-1} scan rate, 20 sweeps), under a nitrogen atmosphere and in the dark, giving rise to poly(NDDEAEA).

approach would allow a range of articles with different surface characteristics to be coated with "living" initiator species. The conjugated nature of the polymer may also have a number of advantages in the construction of electrochemical sensors[24] and other electronic devices. While there are examples of styrene- and methacrylate-based polymers bearing dithiocarbamate side chains, there are practically no examples of conjugated polymer backbones derivatized with iniferter groups. The polymeric macroinifeters of Lutsen and Vanderzande,[34] consisting of poly(vinylene phenylene) with pendant dithiocarbamate ester side groups, formed by the partial elimination of dithiocarbamate ester groups from a precursor polymer are a marked exception. However, these polymers neither carry a high density of dithiocarbamate ester groups nor do they have a continuously conjugated structure since each remaining iniferter group is a result of incomplete elimination from the precursor.

The aniline functionality of NDDEAEA has the potential to be polymerized both electrochemically and using chemical oxidants such as ammonium persulfate. It was important to ascertain whether either route could be employed with this monomer and to show whether the integrity of the dithiocarbamate groups was compromised by either method of polymerization.

Electropolymerization of NDDEAEA. Electropolymerization of NDDEAEA was carried out in cyclic voltammetry (CV) mode. Figure 1 shows the CV obtained during the electropolymerization (20 cycles) of a solution of NDDEAEA in a 3:1 v:v mixture of HCl (0.75 M) and acetonitrile. The CV clearly shows oxidation and reduction peaks at +0.65 and +0.52 V (vs Ag/AgCl), respectively. The observed electrochemical behavior is quite similar to that obtained during the polymerization of aniline and ring-substituted anilines dissolved in acidic solutions.[24,35−39] The large currents observed at the maximum positive potential are due to the superposition of two distinct processes: one is electron transfer from poly(NDDEAEA), corresponding to the oxidation of the PANI film, and the other is electron transfer from the monomer, NDDEAEA, to the electrode, corresponding to the oxidation of NDDEAEA to produce a precursor of polyaniline formation. In order to investigate the stability of poly(NDDEAEA) films, the electropolymerized electrodes were dipped into a solution of HCl (0.75 M), and the CV was measured. The CV showed quasi-reversible peaks: one at +0.12 V, which corresponds to oxidation of the leucoemeraldine to protonated emeraldine form,[40] and also a peak at +0.65 V, resulting from the oxidation of emeraldine and deprotonation of the polymer.[40] Both these peaks are quite stable. It has been reported that during the electropolymerization of substituted anilines in acidic aqueous solutions an intermediate with high stability is formed.[41,42] It is therefore possible to perform both kinetic and mechanistic studies of the polymerization reaction of poly(*N*-alkylaniline) derivatives.

The electrochemistry of poly(*N*-alkylanilines) is less complicated by comparison with PANI due to the absence of the pH-sensitive emeraldine base-emeraldine salt transition. Polymerization of NDDEAEA, which contains both aniline and dithiocarbamate ester groups, may offer more advantages, provided the latter are stable under the conditions of polymerization. Dithiocarbamate anions are unstable under aqueous acidic conditions,[43] undergoing protonation and subsequent decomposition into carbon disulfide and amine, so there was some initial concern about the stability of the esters under the conditions necessary to polymerize NDDEAEA. It was also not clear whether the iniferter groups would be affected by the electrical

Table 1. Static Water Contact Angles in Air for Various Substrates, Substrates Modified with Poly(NDDEAEA) and after Surface-Grafting of Polymers

nature of the surface	water contact angle (deg)
pretreated screen-printed gold electrode (SPE)	66.0
electropolymerized poly(NDDEAEA)	29.4
poly(MAA) surface-grafted to electropolymerized poly(NDDEAEA) film	45.1
poly(AMPSA) surface-grafted to electropolymerized poly(NDDEAEA) film	33.0
polystyrene surface-grafted to electropolymerized poly(NDDEAEA) film	64.3
polystyrene over poly(MAA) surface-grafted to electropolymerized poly(NDDEAEA) film (layer-by-layer grafting)	64.4
bare polypropylene membranes	132.3
poly(NDDEAEA) grafted layer over PP membrane by chemical oxidative polymerization	85.2
poly(MAA) surface-grafted to chemically polymerized poly(NDDEAEA) film onto PP membrane	57.6
poly(AMPSA) surface-grafted to chemically polymerized poly(NDDEAEA) film onto PP membrane	37.2
polystyrene surface-grafted to chemically polymerized poly(NDDEAEA) film onto PP membrane	72.8
glass microscope slides	27.9
poly(NDDEAEA) chemically polymerized over glass surface	55.6
polystyrene surface-grafted to chemically polymerized poly(NDDEAEA) film onto glass slide	88.3
poly(AMPSA) surface-grafted to chemically polymerized poly(NDDEAEA) film	35.3

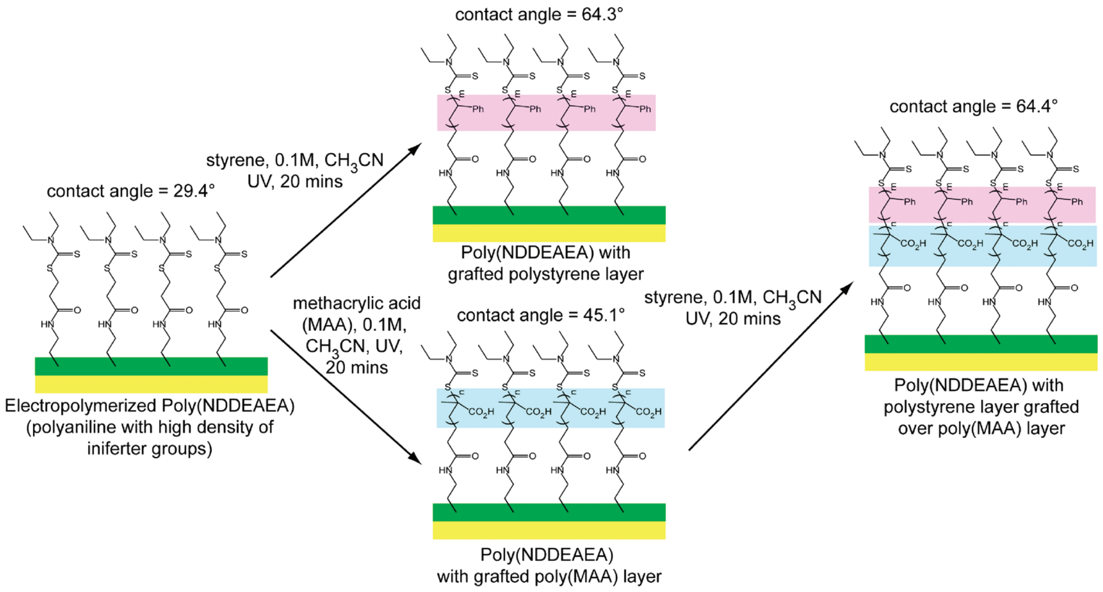


Figure 2. Electropolymerized poly(*N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline) (poly(NDDEAEA)) films UV irradiated for 20 min in the presence of styrene or methacrylic acid (0.1 M, acetonitrile), leading to surface-confined grafted polymer layers. Also the layer-by-layer (block copolymer) grafting of poly(styrene) over a grafted poly(methacrylic acid) layer is displayed. The static water contact angle shows changes consistent with the uppermost surface layer of the grafted polymer, such that polystyrene grafted over poly(MAA) shows the same contact angle as a single polystyrene grafted layer.

potential needed for electropolymerization of the monomer. It appears however that these fears were unfounded and suitable conditions were discovered for electropolymerization of NDDEAEA, in which the integrity of the pendant groups were preserved (Figure 1). The existence of a high density of iniferter groups was confirmed by XPS analysis and through grafting experiments. NMR measurements on NDDEAEA and its polymer also show no significant spectral changes with time under acidic conditions.

Surface-confined grafting of polymers was readily initiated upon UV irradiation of electropolymerized poly(NDDEAEA) layers in the presence of deoxygenated solutions of monomers such as AMPSA (Table 1), methacrylic acid (MAA), or styrene (Figure 2). This allowed precise control of the macromolecular architectures of the grafted surfaces (Figure 2). Grafting was readily achieved despite the highly colored nature of the polyaniline backbone, presumably due to the high density of dithiocarbamate ester groups available at the surface. XPS analysis and water contact angle measurements (Table 1) performed before and after grafting provided evidence that polymerization proceeded at the surface only during photoirradiation. The results of XPS measurements (Figure 3 and Table 2) revealed an appreciable amount of sulfur in the electropolymerized poly(NDDEAEA) surfaces even after 20 min of UV irradiation and that irradiation in the presence of monomers can be used to graft any other layer onto the poly(NDDEAEA). SEM and AFM

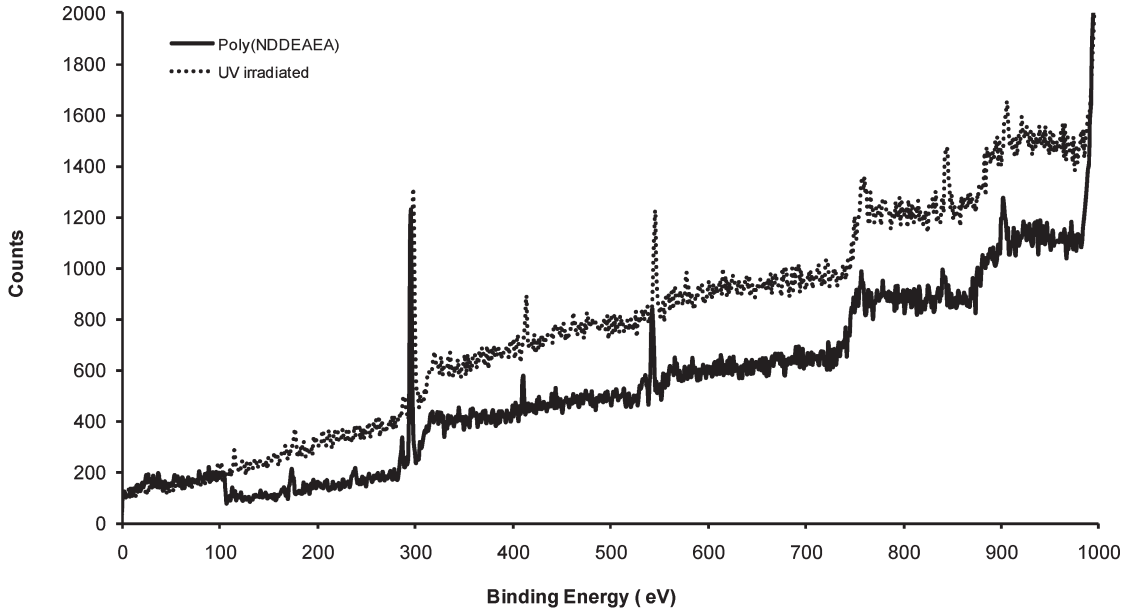


Figure 3. XPS spectra of electropolymerized film of poly(NDDEAEA) on a gold screen-printed electrode before UV irradiation (solid line) and after UV irradiation (dotted line).

Table 2. XPS Element Composition (wt %) of the NDDEAEA Monomer and Its Polymers

compound	S	N	O	C	Au	Bi	total	S 2p intensity	N 1s intensity	ratio S/N
NDDEAEA monomer	5	8	11	76			100	3.83	4.74	0.80
electropolymerized NDDEAEA	4	7	10	79			100	3.26	4.5	0.73
UV irradiated electropolymerized NDDEAEA	3	7	13	77			100	2.332	4.79	0.49
bare electrode			28	60	7	5	100			

observations showed the surface morphology of grafted surfaces (Supporting Information Figures S6−S8).

Grafted polymeric surfaces were characterized by contact angle measurements. Table 1 shows the static water contact angles for various grafted polymeric surfaces. Control of the surface contact angle through changes in the surface functionality, while retaining the bulk material properties, is useful for many applications, including sensors, flow control, and cell patterning. Layer-by-layer grafting of polymers, as shown in Figure 2, provides evidence for "living" iniferter-initiated polymerization at the poly(NDDEAEA) surface. According to the literature, initiation with this type of iniferter can result in undesirable side reactions during photolysis of end groups on poly(methyl methacrylate) and low reactivity with acrylate ester monomers, potentially resulting in a less efficient grafting of a second layer.[44,45] However, in our experiments, we have a confined two-dimensional photopolymerization processes due to the presence of high density of DTC groups; therefore, the surface-growing polymer end explores only a two-dimensional space and grows in a uniform way for the first and second polymeric layer. As expected, the contact angle (CA) measurements demonstrate that the electropolymerized poly(NDDEAEA) was quite hydrophilic, with CA of 29.4° (probably because it was deposited from an acidic solution and so exists in a protonated form). Considering these results together with those from XPS analysis, photoactivation of the dithiocarbamate ester unit was confirmed.[46] The poly(methacrylic acid) grafted layer was relatively more hydrophobic with a contact angle of 45.1°, while poly(AMPSA) was more hydrophilic (CA of 33.0°) due to the sulfonic acid moiety. On the other hand, polystyrene grafting led to increased hydrophobicity with a CA of 64.3°. A contact angle consistent with grafting of the second monomer (styrene, CA = 64.4°), on top of an initial methacrylic acid grafted layer (CA = 45.1°), was found, as expected (Table 1). The thickness of the poly(NDDEAEA) layer on the modified SPEs was measured as ∼150−200 nm, and the grafted poly(methacrylic acid) and poly(AMPSA) layers were ∼50 nm as revealed by Dektek analysis.

From SEM and AFM images it is possible to observe grafting of monomers onto electropolymerized poly(NDDEAEA) (Supporting Information Figures S6−S8). In general, the uniformity of the grafted polymer on the modified electrode surface is usually crucial to control the grafting efficiency. SEM reveals a globular structure of the pretreated SPE surface which displays an obvious change (some holes appear) associated with the electropolymerization of NDDEAEA. After grafting of hydrophilic monomers, MAA and AMPSA, onto electropolymerized poly(NDDEAEA), the films show rather smooth surfaces and compact film structures compared to the surface with grafted styrene which displayed some uneven hollow structures. These results imply that the phase separation and structural heterogeneity are dependent on the monomer used. Surface characterizations of the grafted electrodes were also performed using XPS. Figure 3 shows the XPS spectra of electropolymerized poly(NDDEAEA) films before and after UV irradiation.

The XPS spectra of NDDEAEA powder and electropolymerized poly(NDDEAEA) films before and after UV irradiation exhibit N 1s and S 2p peaks due to the presence of the polyaniline and dithiocarbamyl groups which are of comparable intensities. In addition, the S 2p (~174 eV) and N 1s (~411 eV) peaks are still observable after electropolymerization and UV-irradiation. This indicates that a substantial amount of dithiocarbamate ester groups remained in the surface layer of poly(NDDEAEA) There is also no significant change in the elemental composition (wt %) which also provides evidence that the dithiocarbamate ester groups are still located at the surface.

XPS measurements allow the determination of elemental ratios within the films (Table 2). It was observed that the peak intensities of NDDEAEA corresponding to sulfur and carbon (296 eV) did not vary greatly before and after electropolymerization. Upon 20 min UV irradiation of the poly(NDDEAEA)-coated electrode in 0.75 M HCl solution and subsequent washing with water, the S 2p peak was still observed, although the intensity is reduced by about 30% of the initial value. No appreciable spectral change is observed after extensive washing with water.

Deposition of Poly(NDDEAEA) Films Using Chemical Oxidation. Polymerization of NDDEAEA can also be achieved using chemical oxidizing agents, such as persulfate, to deposit a layer of the conductive polymer onto a range of substrates, such as microtiter plates, cuvettes, membranes, glass, etc. This layer of dithiocarbamate ester-functionalized PANI can function as a vehicle to further coat the material with a layer of grafted addition polymer in a controlled manner.[24] PANIs have previously been employed in the development of sensor devices by deposition as thin films over various surfaces followed by immobilization of various species capable of sensing applications. It is a popular material due to its good optical properties, its pH and redox sensitivity, conducting nature, and stability. To obtain poly(NDDEAEA) films by chemical oxidative polymerization over hydrophobic polypropylene membranes and on glass surfaces (or any suitable substrate), the first step was to optimize the various deposition parameters within polystyrene cuvettes and microtiter plates by measuring the optical densities after chemical oxidative polymerization of NDDEAEA with varying concentrations of monomer, oxidant, pH, time of polymerization, etc. Two protocols were identified and optimized by variation in the concentrations of the reagents, according to whether thin transparent films for optical measurement were to be prepared or thicker coatings required. The details are presented in the Supporting Information (see Figures S9−S11). For thin films, a monomer concentration of 0.025 M in the presence of HCl (0.225 M) and ammonium persulfate (0.0183 M) for 2 h in 25% acetonitrile/water was judged to be optimum (Figures S9 and S13). Similarly, thicker films for grafting experiments were obtained at a monomer concentration of 0.08 M in the presence of HCl (0.6 M) and ammonium persulfate (0.05 M) in 25% acetonitrile/water polymerized for 1 h (Figures S10 and S11).

To determine the effect of pH on contact angles, microtiter plates coated with thin poly(NDDEAEA) films were treated with solutions of varying pH for 1 h and their contact angles measured after drying. Contact angles decreased with decreasing pH; thus, at pH 12.0 the films were relatively hydrophobic with a contact angle of 82.2° whereas at pH 1.0 the contact angle was 39.5°, behavior consistent with that reported in the literature for polyaniline.[47]

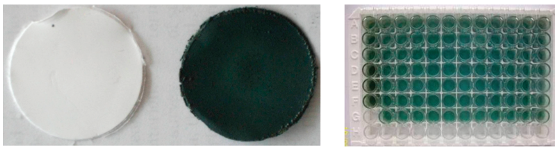

a. b.

Figure 4. (a) Polypropylene membrane (left) and poly(*N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline) (poly(NDDEAEA))-coated membrane (right) and (b) microtiter plate showing deposition of poly(NDDEAEA) in the wells.

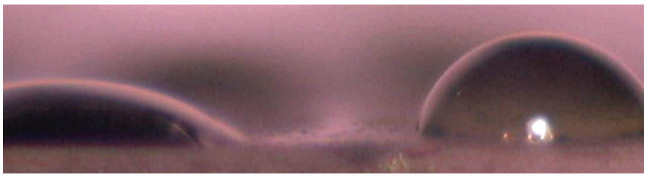


Figure 5. Water contact angle image of chemically polymerized poly(*N*-(*N*′,*N*′-diethyldithiocarbamoylethylamido ethyl)aniline) over glass slide after UV grafting of poly(acrylamido-2-methylpropanesulfonic acid) (left) and polystyrene (right).

It was shown that deposition of poly(NDDEAEA) onto solid surfaces is quite reproducible. IR spectra of the chemically oxidized poly(NDDEAEA) polymers which had been deposited onto microtiter plates, scraped off, and redispersed in KBr disks were obtained (Figure S14) and showed two intense absorption bands at 1208 and 1491 cm^{-1}, respectively, which are assigned to stretching vibrations (N−C(S)). Other bands characteristic of *N*,*N*-diethyldithiocarbamate were also confirmed by the presence of absorption bands at 2921, 1375, and 1175 cm^{-1} (CH_3 stretching and bending vibrations and the C=S stretching vibration, respectively). Also, a peak at 1350 cm^{-1} was observed due to bending vibrations of CH_2. Other peaks at 1021, 910, and 1452 cm^{-1} which are also characteristic of dithiocarbamates were seen. There were peaks at 3430 cm^{-1} due to N−H stretching vibrations, 700 cm^{-1} due to aromatic C−H bending, 1140 cm^{-1} due to C−N bending, and 1600 and 1480 cm^{-1} due to the presence of quinoid and benzenoid rings in the polyaniline backbone, respectively.[21,22,48]

The UV spectrum of a solution of poly(NDDEAEA) (1 mg mL^{-1} in methanol) showed absorption peaks at λ_{max} = 247 and 275 nm. These were attributed to the diethyldithiocarbamate ester group (Figure S15). The spectrum also showed three characteristic absorption bands due to PANI at around 320, 400, and 735 nm. The characteristic peaks of PANI appear at about 320 nm due to the $\pi-\pi^*$ transition of the benzenoid ring and at about 400−430 and 730−825 nm due to polaron−π^* and π−polaron band transitions, respectively, showing that PANI is present in the doped state.[49]

A second substrate of choice was hydrophobic polypropylene microfiltration membranes, onto which oxidative polymerization of poly(NDDEAEA) was performed which resulted in the deposition of a thin, bluish-greenish layer of functionalized PANI coating across the membrane surfaces (see Experimental Section, Supporting Information and Figures 4 and S13). Contact angles were measured (Table 1) and the degree of grafting determined gravimetrically. PP membranes showed a 13.3% mass increase for thin films and up to 54.2% for thick film deposition (Figure 4a).

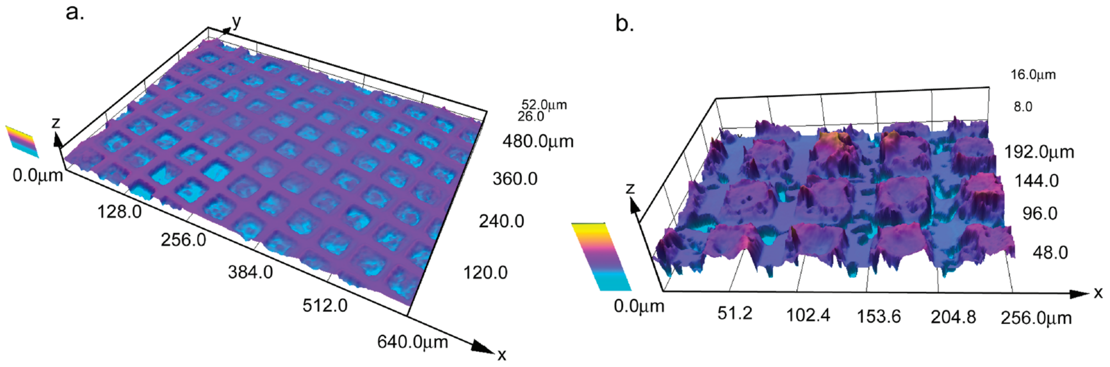


Figure 6. Poly(aminopropylmethacrylamide) grafted over poly(*N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline) cast film over gold sputtered glass slide through chemical polymerization: (a) before removal of TEM grid; (b) after removal of TEM grid. Features are of the dimensions 200 μm × 200 μm.

Further grafting experiments with poly(NDDEAEA) chemically deposited onto microtiter plates (Figure 4b) showed that MAA, AMPSA, and lauryl methacrylate could be successfully grafted (giving rise to contact angles of 52.2°, 30.6°, and 102.5°, respectively). Control experiments were performed using unfunctionalized polyaniline-coated microtiter plates which did not show any change in contact angle after irradiation in the presence of monomers, confirming the necessity of the dithiocarbamate ester functionality for photografting experiments. Similarly, photochemical polymerization over poly(NDDEAEA)-modified PP membranes allowed the growth of various hydrophobic and hydrophilic polymers (AMPSA, MAA, and styrene) as shown by changes in the contact angles (Table 1).

Glass slides were also coated with poly(NDDEAEA) using similar conditions, and the contact angle was measured to confirm successful polymerization (Table 1). By successively masking two sides of a coated glass slide (aluminum foil), it was possible to graft poly(AMPSA) and polystyrene on adjacent areas of the glass, producing areas with very different contact angles on the same slide (Figure 5). The measured contact angles are reported in Table 1.

Grafting of Poly(*N*-(3-aminopropyl)methacrylamide) over Chemically Polymerized Poly(NDDEAEA) through a TEM Grid. Poly(NDDEAEA), cast from solution in methanol onto a gold-sputtered glass slides, was then grafted with poly(3-aminopropylmethacrylamide) from a solution of the monomer in 20% acetonitrile/water via UV-initiation through a TEM grid. Confocal microscopy clearly confirms the growth of polymer in a pattern determined by the shape of the TEM grid.

■ CONCLUSIONS

A new bifunctional monomer, *N*-(*N*′,*N*′-diethyldithiocarbamoylethylamidoethyl)aniline (NDDEAEA), incorporating both aniline and dithiocarbamate ester groups, was synthesized and fully characterized. Conjugated poly(NDDEAEA), consisting of N-substituted PANI backbones bearing a high density of dithiocarbamate ester groups (iniferter), was produced, by either electrochemical polymerization or chemical oxidation using ammonium persulfate. Polymerization of the aniline functionality of NDDEAEA was performed on a number of substrates, namely, polystyrene (cuvettes and microtiter plates), polypropylene filtration membranes, screen-printed gold electrodes, and glass. UV-activation of the dithiocarbamate ester-based iniferter groups of these polymeric materials deposited on solid surfaces allowed grafting of further addition polymers or block copolymers. Monomers utilized for grafting were methacrylic acid, styrene, acrylamido-2-methylpropanesulfonic acid, lauryl methacrylate, and 3-aminopropylmethacrylamide. That these polymers were also capable of reinitiating polymerization upon reapplication of UV light was confirmed by the grafting of polystyrene over a poly(MMA) grafted film. UV-initiated surface graft polymerization was also shown to be capable of producing fine surface designs via a masking process.

Photochemical grating of various monomers and XPS studies (before and after polymerization) clearly indicated that the dithiocarbamate ester groups survived oxidative polymerization and retain their “living” behavior. This versatile new material has the potential for the creation of materials with integrated functionalities (e.g., conductivity and molecular recognition, catalysis, controlled transport properties, etc.) for application in sensors, microfluidic devices, and surface patterning. Our results suggest that NDDEAEA is a versatile monomer for use within the fabrication of sensors and optoelectronic devices and in polymer and material chemistry applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel +44 1234 758328; e-mail d.lakshmi.s06@cranfield.ac.uk.

■ ACKNOWLEDGMENT

We thank the European Commission for funding this work (FP7, WaterMIM, CP-FP 226524). Dr. Matthew Kershaw is gratefully acknowledged for his assistance with XPS and SEM analysis.

■ REFERENCES

(1) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, 32, 93–146.

(2) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H. A. *Chem. Rev.* **2009**, *109*, 5437–5527.

(3) Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.

(4) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337–377.

(5) Gam-Derouich, S.; Nguyen, M. N.; Madani, A.; Maouche, N.; Lang, P.; Perruchot, C.; Chehimi, M. M. *Surf. Interface Sci.* **2010**, *42*, 1050–1056.

(6) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.

(7) Smith, A. E.; Xu, X. W.; McCormick, C. L. *Prog. Polym. Sci.* **2010**, *35*, 45–93.

(8) Li, Y.; Zhou, W. H.; Yang, H. H.; Wang, X. R. *Talanta* **2009**, *79*, 141–145.

(9) Southard, G. E.; Van Houten, K. A.; Ott, E. W.; Murray, G. M. *Anal. Chim. Acta* **2007**, *581*, 202–207.

(10) Brinks, M. K.; Studer, A. *Macromol. Rapid Commun.* **2009**, *30*, 1043–1057.

(11) Boonpangrak, S.; Whitcombe, M. J.; Prachayasittikul, V.; Mosbach, K.; Ye, L. *Biosens. Bioelectron.* **2006**, *22*, 349–354.

(12) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121–2136.

(13) Sellergren, B.; Rückert, B.; Hall, A. J. *Adv. Mater.* **2002**, *14*, 1204–1208.

(14) Barahona, F.; Turiel, E.; Cormack, P. A. G.; Martín-Esteban, A. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1058–1066.

(15) Pérez-Moral, N.; Mayes, A. G. *Macromol. Rapid Commun.* **2007**, *28*, 2170–2175.

(16) Bossi, A.; Whitcombe, M. J.; Uludag, Y.; Fowler, S.; Chianella, I.; Subrahmanyam, S.; Sanchez, I.; Piletsky, S. A. *Biosens. Bioelectron.* **2010**, *25*, 2149–2155.

(17) Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **2001**, *34*, 4375–4383.

(18) Otsu, T.; Yamashita, K.; Tsuda, K. *Macromolecules* **1986**, *19*, 287–290.

(19) Qin, S. H.; Qiu, K. Y. *Eur. Polym. J.* **2001**, *37*, 711–717.

(20) Luo, N.; Hutchison, J. B.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1885–1891.

(21) García-Con, L. M.; Whitcombe, M. J.; Piletska, E. V.; Piletsky, S. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 4075–4078.

(22) Kobayashi, T.; Takahashi, S.; Nosaka, Y.; Fujii, N. *Chem. Lett.* **1992**, 1321–1324.

(23) Mijangos, I.; Guerreiro, A.; Piletska, E.; Whitcombe, M. J.; Karim, K.; Chianella, I.; Piletsky, S. *J. Sep. Sci.* **2009**, *32*, 3340–3346.

(24) Lakshmi, D.; Bossi, A.; Whitcombe, M. J.; Chianella, I.; Fowler, S. A.; Subrahmanyam, S.; Piletska, E. V.; Piletsky, S. A. *Anal. Chem.* **2009**, *81*, 3576–3584.

(25) Malkaj, P.; Dalas, E.; Vitoratos, E.; Sakkopoulos, S. *J. Appl. Polym. Sci.* **2006**, *101*, 1853–1856.

(26) Mu, S. L.; Chen, C. X.; Wang, J. M. *Synth. Met.* **1997**, *88*, 249–254.

(27) Novak, P.; Muller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207–282.

(28) Lakshmi, D.; Whitcombe, M. J.; Davis, F.; Chianella, I.; Piletska, E. V.; Guerreiro, A.; Subrahmanyam, S.; Brito, P. S.; Fowler, S. A.; Piletsky, S. A. *Chem. Commun.* **2009**, 2759–2761.

(29) Berti, F.; Todros, S.; Lakshmi, D.; Whitcombe, M. J.; Chianella, I.; Ferroni, M.; Piletsky, S. A.; Turner, A. P. F.; Marrazza, G. *Biosens. Bioelectron.* **2010**, *26*, 497–503.

(30) Hook, E. O.; Beegle, L. C.; Wystrach, V. P. US Patent 2786866, 1957.

(31) Bossi, A.; Piletsky, S. A.; Piletska, E. V.; Righetti, P. G.; Turner, A. P. F. *Anal. Chem.* **2000**, *72*, 4296–4300.

(32) Piletsky, S.; Piletska, E.; Bossi, A.; Turner, N.; Turner, A. *Biotechnol. Bioeng.* **2003**, *82*, 86–92.

(33) Piletsky, S. A.; Panasyuk, T. L.; Piletskaya, E. V.; Sergeeva, T. A.; El'skaya, A. V.; Pringsheim, E.; Wolfbeis, O. S. *Fresenius J. Anal. Chem.* **2000**, *366*, 807–810.

(34) Lutsen, L.; Vanderzande, D. US Patent 7649048, 2006.

(35) Bidan, G.; Genies, E. M.; Penneau, J. F. *J. Electroanal. Chem.* **1989**, *271*, 59–68.

(36) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *111*, 111–114.

(37) Schomburg, K. C.; McCarley, R. L. *Langmuir* **2001**, *17*, 1993–1998.

(38) Hayes, W. A.; Shannon, C. *Langmuir* **1996**, *12*, 3688–3694.

(39) Ulgut, B.; Zhao, Y.; Grose, J. E.; Ralph, D. C.; Abruña, H. D. *Langmuir* **2006**, *22*, 4433–4437.

(40) Inzelt, G.; Horányi, G. *Electrochim. Acta* **1990**, *35*, 27–34.

(41) Malinauskas, A.; Holze, R. *Ber. Bunsen. Phys. Chem.* **1997**, *101*, 1859–1864.

(42) Malinauskas, A.; Holze, R. *Electrochim. Acta* **1998**, *43*, 2413–2422.

(43) Ewing, S. P.; Lockshon, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 3072–3084.

(44) Manga, J. D.; Polton, A.; Tardi, M.; Sigwalt, P. *Polym. Int.* **1998**, *45*, 14–21.

(45) Turner, S. R.; Blevins, R. W. *Macromolecules* **1990**, *23*, 1856–1859.

(46) Nakayama, Y.; Matsuda, T. *Macromolecules* **1996**, *29*, 8622–8630.

(47) Blinova, N. V.; Stejskal, J.; Trchová, M.; Prokes, J. *Polym. Int.* **2008**, *57*, 66–69.

(48) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 5th ed.; McGraw-Hill: Maidenhead, U.K., 1995.

(49) Abdiryim, T.; Zhang, X. G.; Jamal, R. *Mater. Chem. Phys.* **2005**, *90*, 367–372.