## Chimeric polymers formed from a monomer capable of free radical, oxidative and electrochemical polymerisation<sup>†</sup>

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A new monomer, which incorporates both aniline and methacrylamide functional groups, was shown to possess orthogonal polymerisation behaviour to produce conjugated polyaniline suitable for a wide range of applications.

Polyaniline has been widely studied as a conductive organic polymer. Its advantages include good stability in air and in the presence of moisture, ease of polymerisation by simple chemical or electrochemical procedures and good electrical conductivity.<sup>1</sup> Modern methods of synthesis have also been used to produce polyaniline in a number of forms including nanowires, nanotubes, films and micropheres.<sup>2</sup> A wide range of potential uses for this material have been proposed and developed, including electrochromic devices,<sup>3</sup> and sensors for a wide variety of targets.<sup>4</sup> One major problem with polyaniline, however, lies in its relative intractability; solutions of polyaniline can only be obtained using aggressive and toxic solvents such as *N*-methyl pyrrolidinone or by incorporation of bulky counterions such as camphor sulfonic acid as dopants.<sup>5</sup>

There have been many attempts to improve the processability of polyaniline, including the introduction of sulfonic acid groups, to give self-doped water-soluble polymers<sup>6</sup> or by blending with polyvinyl alcohol<sup>7</sup> or anionic polymers such as polyacrylic acid or polystyrene sulfonate.<sup>8</sup> Incorporation of polyaniline into composites with polyacrylamide has also been used to enhance polymer stability<sup>9</sup> or to modify the mechanical properties of the material.<sup>10</sup> A major problem with blending of polymers, however, is the possibility of phase separation.

Here we present a new difunctional monomer, *N*-phenylethylenediamine methacrylamide (NPEDMA), which contains both an aniline and a methacrylamide group, capable of polymerisation by free radical methods.‡ This allows the synthesis of homo or co-polymers containing the aniline moiety which can be subsequently polymerised to yield polyaniline. Cross-linking agents can also be incorporated, yielding final materials comprising interpenetrating polymethacrylamide–polyaniline networks, where the high degree of cross-linking prevents phase separation. The monomer can also be polymerised electrochemically onto a suitable electrode, giving a conductive polymer surface with a high density of double bonds, capable of cross-linking the polymer or being utilised as reactive sites to enable the grafting of further polymeric or biological materials. Potential applications may exist in microelectronics, sensors, electrochromic devices, biofuel cells, protective and antistatic coatings, catalysts, photolithographic materials, molecularly imprinted polymers and in biosensors.

Some of the various chemical and electrochemical polymerisation sequences involving the difunctional monomer are represented diagrammatically (Fig. 1). The following examples demonstrate these procedures in detail. At the heart of each of these possibilities are the unusual properties of NPEDMA which can be polymerised using free radical, chemical oxidative and electrochemical polymerisation methods.

Initial studies were made on polymers synthesised by free radical methods. NPEDMA was polymerised (to PNPEDMA) using a free radical initiator in toluene or DMF. Cross-linked polymers were also prepared by the incorporation of ethylene glycol dimethacrylate in the polymerisation mixture. The solid



Fig. 1 Structure of the monomer NPEDMA and its polymers, the structure and functional properties of which depend on the order of polymerisation. NPEDMA = N-phenylethylenediamine methacrylamide.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Additional experimental details, including polymerisation protocols, polymer compositions, NMR, FTIR and XPS spectra, figure showing effect of irradiation on electrochemical behaviour of the polymer, AFM, UV-vis spectrum of polymer. See DOI: 10.1039/b821409c

**Table 1** Conductivity of the vinyl addition polymers, following polyaniline formation using ammonium persulfate in HCl at 0  $^{\circ}$ C, compared with aniline polymers prepared in the same way at either 0  $^{\circ}$ C or at room temperature

Polymer <sup>a</sup>	Conductivity/S cm <sup>-1</sup>
PNPEDMA	6.18
PNPEDMA-5	12.66
PNPEDMA-10	7.94
PNPEDMA-25	4.7
PNPEDMA-50	0.83
PNPEDMA-OX	8.06
Polyaniline (0 °C)	6.86
Polyaniline (RT)	3.54
Poly( <i>N</i> -phenylethylenediamine) (0 °C)	0.02
Poly(NPEDAc) (0 °C)	>0.02
" See Table S1, ESI <sup>†</sup> .	

polymers, both the homopolymer (PNPEDMA) and those cross-linked with ethylene glycol dimethacrylate, were oxidised using ammonium persulfate to form conductive materials (labelled as PNPEDMA-x where x is the percentage of cross-linker), see Table S1 (ESI<sup>†</sup>). Direct oxidation of the monomer also led to formation of a conductive material (PNPEDMA-OX). The conductivities of the synthesised materials are given in Table 1. Oxidative polymerisation of NPEDMA gave a polymer with a higher conductivity than polyaniline itself synthesised under similar conditions; this was not true for either poly(N-phenyl ethylene diamine) or for the equivalent acetvlated material PNPEDAc (Table 1). Initially it was expected that PNPEDMA would have a lower conductivity due to the presence of the N-substituted sidechain, as was found for polymers of N-methyl aniline<sup>11,12</sup> and for the polymer of N-phenylethylenediamine; however, this does not appear to be the case. Material prepared by oxidation of the linear polymer was slightly less conductive than polyaniline, but the incorporation of 5% of ethylene glycol dimethacrylate (EGDMA) led to a two-fold increase in conductivity. Again a simplistic model would predict a drop in overall conductivity due to the presence of a non-conjugated co-monomer. At 10% EGDMA the conductivity was slightly higher than polyaniline, although further increases in cross-linking led to a reduction of the conductivity. Possibly in the former case cross-linking of the polymer led to a closer association between polymer chains within the network, facilitating charge transport through the polymer. Previous work has already shown that the physical morphology of polyaniline has a great effect on its conductivity.<sup>12,13</sup> Cross-linking could possibly affect the crystallinity and orientation of the polyaniline chains, leading to the observed increases in conductivity; however, since higher levels of cross-linking lead to a decrease in conductivity, this hypothesis may not be the most likely explanation for this phenomenon.

Porosities were determined using nitrogen BET measurements. The polymer PNPEDMA-25 showed the highest porosity, with a surface area of 22.8 m<sup>2</sup> g<sup>-1</sup>, average pore radius of 225.3 Å and total pore volume of 0.1434 mL g<sup>-1</sup> for pores smaller than 705.1 Å, which after oxidation with persulfate gave a surface area of 48.7 m<sup>2</sup> g<sup>-1</sup>, average pore radius of 529.4 Å and total pore volume of 0.129 mL g<sup>-1</sup> for pores smaller than 700.25 Å (at  $P/P_0 = 0.98608$ ). The corresponding

measurements for PNPEDMA-50 gave a surface area of 14.6 m<sup>2</sup> g<sup>-1</sup>, average pore radius of 143 Å and total pore volume of 0.1026 mL g<sup>-1</sup> for pores smaller than 731.0 Å before chemical oxidation and a surface area of 38.0 m<sup>2</sup> g<sup>-1</sup>, average pore radius of 805.6 Å and total pore volume of 0.171 mL g<sup>-1</sup> for pores smaller than 886.78 Å after chemical oxidation. PNPEDMA-10 was essentially non-porous but following chemical oxidation had a surface area of 4.3 m<sup>2</sup> g<sup>-1</sup>. Both PNPEDMA and PNPEDMA-5 were non-porous before and after oxidation. Oxidative cross-linking appears to increase the porosity, perhaps by reducing the movement of the polymer chains and thereby increasing the free volume.

Ammonium persulfate is known not only to polymerise anilines, but also to initiate polymerisation of acrylamide groups,<sup>14</sup> so it is possible that cross-linking occurs within this system. The FTIR spectra of the monomer and polymer obtained via polymerisation with ammonium persulfate were recorded (Fig. S1, ESI<sup>†</sup>). Bands observed in the spectrum of the monomer include those for aromatic N-H stretch at 3350 cm<sup>-1</sup>, aromatic C-H stretch at 2930 cm<sup>-1</sup>, amide C=O at 1650  $\text{cm}^{-1}$  and =CH out-of-plane deformation at  $930 \text{ cm}^{-1}$ . The polymer spectrum contains bands corresponding to most of the vibrational modes associated with conductive polyaniline between 2800 and 2200 cm<sup>-1</sup> and at 1150 cm<sup>-1</sup>. A band associated with CH out-of-plane bending of 1,4-disubstituted aromatic rings is present at  $830 \text{ cm}^{-1}$ ; however, there was only a minimal change in the amide C=O band, indicating no loss of conjugation due to polymerisation of the C=C bond. This indicates that during the polymerisation with persulfate the reaction progressed preferentially via aniline oxidation.

As an alternative to chemical polymerisation methods, the ability of NPEDMA to electropolymerise and to perform subsequent reactions using free radical addition or polymerisation was investigated. After voltammetric sweeping of the gold or indium tin oxide (ITO) electrode in a solution of NPEDMA, a greenish film was clearly visible, indicating deposition of a conjugated polymer. Fig. 2 shows the CV obtained during the electropolymerisation (sweep number 15) of NPEDMA in 50 mM HClO<sub>4</sub> solution, clearly displaying oxidation and reduction peaks at +0.7 and +0.45 V (on Au



**Fig. 2** Cyclic voltammograms obtained during the deposition of electropolymerised *N*-phenylethylenediamine methacrylamide films on gold (solid line) and indium tin oxide (dashed line) electrodes.

substrate), respectively (*versus* Ag/AgCl). Ellipsometry measurements indicated a film thickness of 40 nm. The polymer film exhibited a sessile water contact angle of  $69^{\circ}$  (unmodified gold electrodes gave contact angles of  $77^{\circ}$ ) showing that the polymer is relatively hydrophilic.

To demonstrate the possibility of further modification, the double bonds of electrosynthesised PNPEDMA were cross-linked using N,N-diethyldithiocarbamic acid benzyl ester (iniferter) as initiator, as described in the ESI<sup>+</sup>. The contact angle of the cross-linked material increased to 71°, indicating that grafting of hydrophobic moieties had occurred. X-Ray photoelectron spectroscopy (XPS) measurements of washed polymer films demonstrated the presence of sulfur following iniferter grafting (see ESI<sup>†</sup>, Fig. S2 and S3). Grafting of poly(methacrylic acid) brushes to the iniferteractivated film (see ESI<sup>†</sup>) gave a contact angle of 62°; in addition the grafting of molecularly imprinted polymers to the PNPEDMA layer has been carried out and will be reported elsewhere. An electrode coated with an inifertertreated electropolymerised film was immersed in a control solution (50 mM HClO<sub>4</sub> solution, purged with nitrogen for 10 minutes, then irradiated for 20 minutes) to investigate the effect of UV exposure on the electrochemical behaviour of the film. Electrochemical characterisation was carried out using differential pulse voltammetry and showed a noticeable increase in the current-voltage characteristics with increased irradiation (Fig. S4, ESI<sup>+</sup>). The reason for this behaviour is not known: however, it is highly likely that the iniferter grafted to the electropolymerised film via the vinyl moieties produces macroradicals upon irradiation, which can combine to form additional cross-links between neighbouring polymer chains. As was seen in the previous case, increased cross-linking facilitates charge transport through the film, resulting in a higher measured conductivity.

AFM measurements were also made on the films prepared during the grafting of poly(methacrylic acid) to an electropolymerised layer of NPEDMA (Fig. S5, ESI†). As can be seen, the bare gold electrode (Fig. S5a)† displays a typically grainy morphology. Electropolymerisation of the monomer leads to deposition of polymer on the surface, smoothing out many of these features, but with a much greater average roughness ( $21 \pm 5$  nm, Fig. S5b) due to the formation of "bumps" in the polymer film. A UV-vis spectrum of a similarly deposited film on indium tin oxide-coated glass was recorded (Fig. S6, ESI†) and clearly shows the formation of a conjugated polymer, with a spectrum very similar to the emeraldine salt form of polyaniline.<sup>15</sup> Following grafting of a poly(methacrylic acid) coating, the roughness was again reduced ( $4 \pm 2$  nm, Fig. S5c).†

This monomer adds to the range of orthogonally polymerisable bifunctional monomers, for example the "Jekyll and Hyde" monomer glycidyl methacrylate,<sup>16</sup> and others.<sup>17</sup> These can be exploited *via* the differential reactivity of the two monomer species. Another interesting application of unsymmetrical monomers is their ability to form OMNiMIPs.<sup>18</sup> The authors would like to thank Yildiz Uludag for the ellipsometry results. This project was supported by the award of a Royal Society International Incoming Fellowship (to D.L.), Grant Reference: FI071114.

## Notes and references

‡ Synthesis of NPEDMA: *N*-phenylethylenediamine (1.0 g, 0.96 mL, 7.3 mmol) was dissolved in methanol (20 mL) which was cooled in ice before the addition of methacrylic anhydride (1.1 g, 1.06 mL, 7.1 mmol). The stirred mixture was held at 0 °C for 3 h before warming to room temperature. The solvent was removed using a rotary evaporator and the residue dispersed in diethyl ether (25 mL). The ether phase was washed with 0.1 M NaOH (4 × 25 mL), followed by water (1 × 25 mL), dried over anhydrous magnesium sulfate and evaporated to give a brown oil which formed colourless crystals on standing in a refrigerator. The yield was 99%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\vartheta$ ): 1.9 (s, 3H,  $-CH_3$ ), 3.3 (d, 2H,  $-CH_2$ ), 5.7 (c, 1H,  $=CH_2$ ), 5.6 (d, 2H,  $\vartheta$ -H), 6.7 (t, 1H, p-H), 7.2 (m, 2H, m-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\vartheta$ ): 18.6, 39.3, 43.9, 112.7, 117.7, 119.9, 129.3, 139.7 147.9, 169.0; IR (KBr disc): 3345, 3000, 2920, 1655, 1603, 1514, 1322, 750, 694 cm<sup>-1</sup>.

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