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Full Paper

Synthesis of a Novel Polyaniline Glycopolymer and its Lectin Binding Studies

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We report the multistep synthesis and polymerisation of a novel aniline derivative with a pendant α-D-mannose substituent. The α-D-mannose functionality was successfully introduced before polymerisation via copper-catalysed azide alkyne click chemistry and the resulting monomer was polymerised using general oxidative polymerisation conditions, producing a water soluble mannosylated polyaniline. The polymer was characterised by several techniques and compared with standard polyaniline. The selective binding of the polymer to Concanavalin A (ConA) was successfully demonstrated by the precipitation of polymer–ConA aggregates. Potential applications of these novel polyaniline glycopolymers could include the development of electroactive biomaterials with the ability to bind mannose receptors, or as sensors for proteins or microbes.

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Introduction

Carbohydrate mimics are increasingly becoming a large and interesting area of research for polymer scientists because of the importance of carbohydrates in a wide variety of biological communication events such as cellular recognition, inflammation, signal transmission, and the infection of pathogens.[1] For instance, attachment of uropathogenic *Escherichia coli* occurs via binding of the FimH protein to mannose or mannose-like ligands on mucosal cells.[2–5] Further examples include the binding of the influenza virus to *N*-acetylneuraminic acid residues on the target cells through haemagglutinin lectins, and also the ability of anionic polysaccharides in inhibiting binding of the human immunodeficiency virus to the host cell by blocking its CD-4 receptors.[6]

Glycopolymers are synthetic polymers that comprise a carbohydrate moiety, which enables recognition by surface lectins on a cell.[7–12] The interactions between carbohydrates and lectins can be greatly enhanced by the multivalent display of the carbohydrate ligands along the polymer backbone, referred to as the 'cluster glycoside effect', which is used in nature to enhance the typically weak binding between a single lectin and the carbohydrate.[13] The attachment of different carbohydrate ligands can also impart selectivity to the glycopolymer because of the specific affinity of lectin receptors for target carbohydrates.[14]

Though many types of glycopolymers have been reported,[7–12,15] there are relatively few examples of conducting polymers, such as polyaniline, being used as polymer backbones.[16–18] The advantages of polyanilines (PANI) include intrinsic electrical conductivity, facile and inexpensive synthesis, free radical scavenging action, and thermal stability up to 300°C.[19] By incorporating carbohydrate moieties into a polyaniline backbone, a synergistic interaction between the carbohydrate and the corresponding lectin is expected. This interaction could potentially induce a physicochemical change in the properties of the polyaniline, e.g. its electrical conductivity, and therefore provide a useful tool that could be used for sensing.[18]

Wang et al. have synthesised a mannose-functionalised aniline monomer via successive electrochemical polymerisation processes on an indium-doped tin oxide electrode.[18] The sensing ability of this material was demonstrated by measuring the interaction between ConA and the mannose-functionalised polyaniline electrode that was characterised by electrochemical impedance spectroscopy, UV–Vis spectroscopy, and cyclic voltammetry. Li et al. reported the successful attachment of quinone, cholic acid, iminodiacetic acid, and a carbohydrate moiety to pyrrole through click chemistry.[17] These functionalised pyrrole monomers were electropolymerised to produce conducting glycopolymers. Gondran et al. attached a lactose group to the polypyrrole backbone[16] and demonstrated the application of these polypyrrole glycopolymers as sensors and in surface plasmon resonance studies to evaluate the

attachment of *Maackia amurensis* and *Arachis hypogaea* plant lectins onto the lactosyl groups. These examples demonstrate the great potential and possible applications of glycopolymers, in particular conducting glycopolymers, as sensors; hence our interest in this area of materials science.

In this work, we report the synthesis and polymerisation of a novel mannose-functionalised aniline monomer, and its ability to bind to mannose receptors. The carbohydrate moiety was delivered to aniline through a copper-catalysed azide alkyne click (CuAAC) reaction. To the best of our knowledge, this is the first example of a carbohydrate covalently bound to polyaniline through click chemistry.

Results and Discussion

Recently, click chemistry has been widely adopted by polymer chemists as a simple and efficient way of combining two different functionalities.[20] The versatility of such a reaction in multiple solvent systems, its applicability to various functional groups, and its ability to give quantitative yields have generated increasing research interest.[21] This concept was used in the present study to develop a synthetic route to combine an azide-functionalised mannose **1** to an alkyne-substituted aniline.

The azide-containing mannose intermediate **1** was synthesized via a three-step procedure, as reported by Geng et al. (Scheme 1), resulting in good-to-excellent yields at each step.[22] The CuAAC process was then investigated. The substituted aniline monomer **2** was successfully prepared, with excellent yield, under general CuAAC conditions. The copper(II) sulphate pentahydrate-catalysed reaction of azide intermediate **1** with commercially available 2-ethynylaniline in the presence of a reducing agent, sodium ascorbate, produced the desired monomer **2,** containing a 1,2,3-triazole spacer group, as a white powder with a yield of 97 % (Scheme 2). Detailed ^{1}H NMR, ^{13}C NMR, and fourier transform infrared (FTIR) data are available in the Supplementary Material section.

The cyclic voltammograms (CV) for the electropolymerisation of pure aniline and monomer **2** are shown in Fig. 1. The voltammograms were obtained at a scan rate of 100 mV s^{-1}. Both aniline and monomer **2** exhibited a similar rise in the

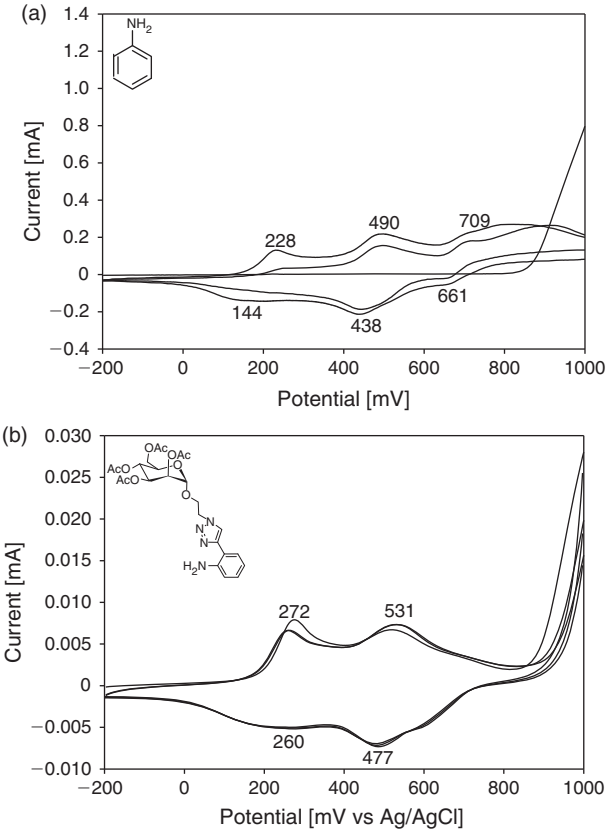
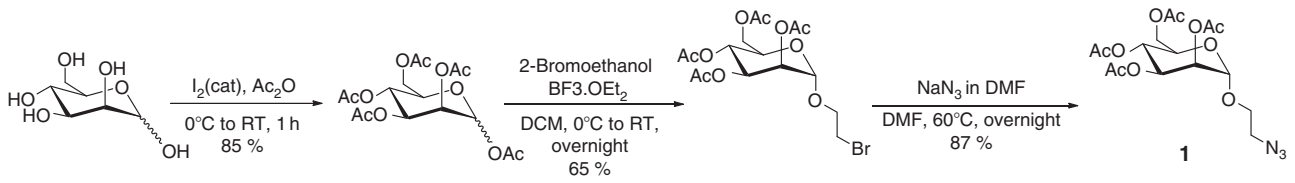
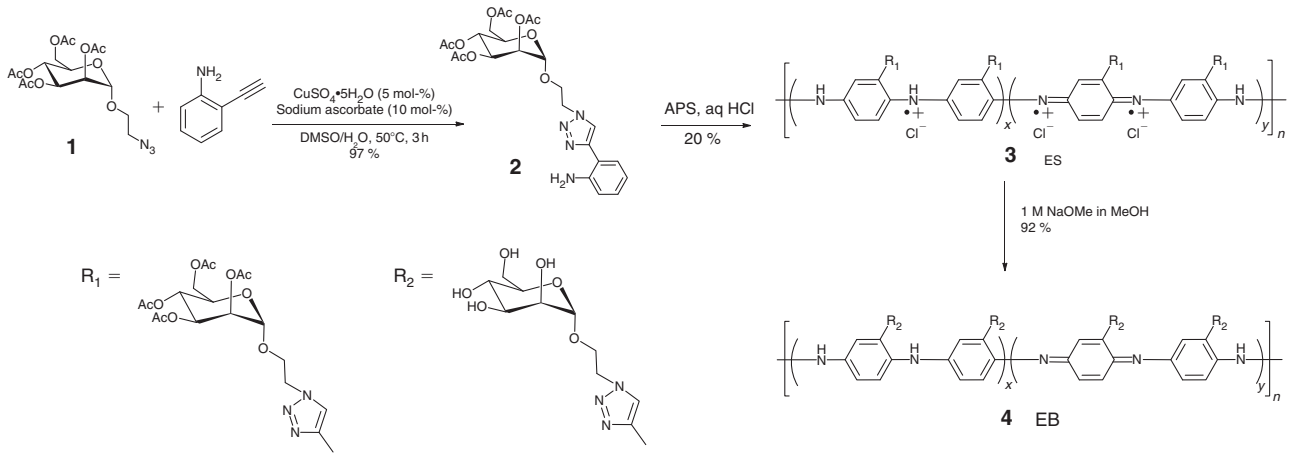


Fig. 1. Cyclic voltammograms of (a) aniline and (b) monomer **2**, obtained with a glassy carbon working electrode and Ag/AgCl reference electrode.



Scheme 1.



Scheme 2.

anodic current at potentials greater than 900 mV, corresponding to oxidation of the respective monomers.[23] The first oxidation peak for the polymer formed from monomer **2** occurred at 272 mV; an associated broad cathodic peak for this process was observed at 260 mV. These potential values were slightly larger than those observed for pure polyaniline (i.e. 228 mV and 144 mV, respectively). This first set of redox peaks corresponds to electron transfer between the fully reduced leucoemeraldine and partially oxidized emeraldine forms of the electrodeposited PANI film.[23] A second oxidation peak was observed at 531 mV for the polymer formed from monomer **2**, and relates to further oxidation of the emeraldine to the fully oxidized pernigraniline form of the polymer. This process occurred at a higher electrode potential with regular polyaniline (peak at 709 mV). In the polyaniline case, an additional set of intermediate peaks (oxidation peak at 490 mV) was observed, which can be associated with the occurrence of polymer over-oxidation processes at the relatively high electropolymerisation potential, leading to the formation of quinone derivatives or cross-linked phenazine rings, which are electroactive in this potential range.[24,25] The two main sets of redox peaks of monomer **2** are at closer proximity when compared with those of pure aniline. This trend is typical of substituted anilines.[26] PANI, a high-conducting polymer, showed successive film layer formation in its CV, as indicated by the higher current values for polymer redox processes after each cycle. In contrast, this was not observed for monomer **2**, whereby polymer growth was limited. This indicates that the resulting electrochemically deposited polymer **3** is intrinsically poorly conductive and forms an insulating layer that prevents further film formation. This difference in conductivity is likely caused by a reduced degree of planarity in the structure of the polyaniline because of the large D-mannose substituent[27] and the electronic inductive effect exerted by the triazole group.

Following cyclic voltammetry study of the monomer to determine the oxidative polymerisation reactivity, solution polymerisation of monomer **2** was carried out under conventional oxidative polymerisation conditions similar to those used for the preparation of pure polyaniline. Ammonium persulphate (APS) aqueous solution was used as the oxidant and was added to a solution of monomer **2** in dilute aqueous HCl with a monomer : oxidant molar ratio of 1 : 1.5. A dilute solution of HCl was used to prevent the destruction of the pendant mannose moieties during the polymerisation process. A cloudy solution was obtained after 30 min. Formation of solid particles on the glass wall of the reaction vessel was still not apparent following a reaction time of 1 h. A dark coloured solution with obvious solid formation was only obtained after the reaction was left standing overnight. Polymer **3** was retrieved as a dark green–black powder and showed film forming ability. However, the yield of this polymerisation reaction was relatively low; an average yield of ~20 % was obtained over five runs. The low yield is likely because of the steric hindrance exerted by the large pendant group.[27] Following isolation of polymer **3**, the acetyl protecting groups were removed from the mannose functional group by adding a solution of polymer **3** in dimethylformamide (DMF) to a solution of 1 M sodium methoxide (NaOMe) in methanol to produce polymer **4.** Polymer **4** was then purified by dialysis against distilled water for two days using a dialysis tubing with a molecular weight cut off (MWCO) of 1000 Da. Polymer **4** was collected as a light brown powder (92 % yield). The solubility properties of polymers **3** and **4** were investigated; both polymers were completely soluble in methanol, water, and *N*-methylpyrrolidone (NMP).

FTIR spectra of PANI EB (emeraldine base), and polymers **3** and **4** are shown in Fig. 2. The data were collected via conventional KBr disks rather by the attenuated total reflectance method as the refractive index of polyaniline-type materials is similar to that of the diamond crystal. Polymer **3** displayed two very broad peaks at 1755 and 1237 cm^{-1}, which were absent in the FTIR spectra of polymer **4** and PANI. These peaks respectively correspond to C=O and C–O stretching vibration modes from the acetyl protecting groups. These stretches were mostly absent in the spectrum of polymer **4**, thereby indicating that deprotection of most of the pendant mannose groups on the polymer was achieved. For polymer **4**, the peaks at 1600 and 1450 cm^{-1} correspond to the typical benzoid and quinoid ring stretches of the polyaniline backbone, and are very similar to those observed for pure polyaniline.[28,29] Notably, the peak at 1377 cm^{-1} is considerably broader in the spectra of polymers **3** and **4** when compared with that observed in the spectrum of PANI. This peak can be attributed to phenazine ring formation and could indicate that a larger amount of phenazine formed for the target polymers relative to pure PANI.[29] Characteristic carbohydrate signals in the spectra of both polymer **3** and **4** were evidenced by the C–O, C–C, and C–OH stretching vibrations in the region of 1040–1150 cm^{-1}.[30,31] 1,2,3-Triazole rings are expected to display characteristic absorbance peak at ~3130 cm^{-1}, however this is masked by the broad OH and NH hydrogen bonding bands.[32,33]

UV–Vis spectroscopy is another useful characterisation technique for PANI-type conducting polymers because of their extended conjugation. The emeraldine base (EB) form of PANI is significantly more soluble than the electrically conducting emeraldine salt (ES) form. Figure 3 shows the UV–Vis spectra of PANI, monomer **2**, and polymers **3** and polymer **4** between 250 and 800 nm. Monomer **2** shows two absorption peaks at 260 and 325 nm, which correspond to the 1,2,3-triazole π–π* transition and the benzene π–π* transition, respectively.[34] The emeraldine base form of PANI shows two absorption peaks at 325 nm and 630 nm. As noted earlier, the absorption at 325 nm is due to the benzene π electrons. The other significant peak at 630 nm corresponds to the single polaron formation.[35,36] In comparison with monomer **2**, polymers **3** and **4** showed broader absorption bands, which are a good indication of the presence of longer chain polymeric structures. The peak at

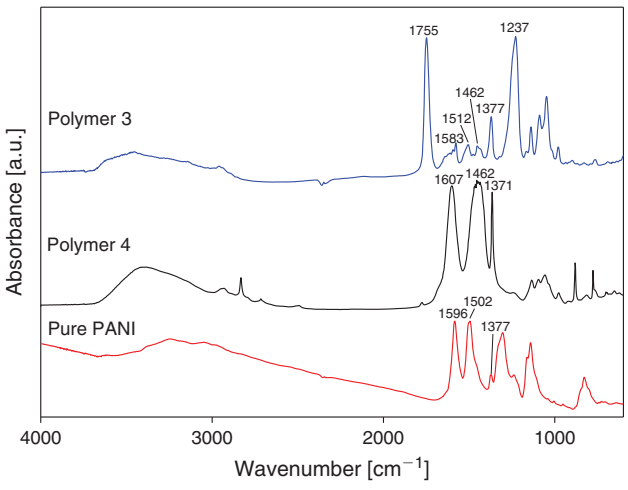


Fig. 2. FTIR spectra of polymer **3**, polymer **4**, and PANI emeraldine base (EB form).

around 300 nm, as observed in the spectrum of polymer **3**, but which is absent in polymer **4**, could correspond to the acetyl protecting groups. Polymers **3** and **4** both showed a peak at ~400 nm that was absent in the spectra of the monomer and PANI; the observed peak could be due to phenazine structures formed as a by-product. A very weak broad band around 580 nm, which was observed in the spectrum of pure PANI, was also noted herein. However, it was blue shifted. The blue shift of the band may be an indication of the presence of shorter polymer chains, and generally occurs with decreased conjugation length.

Gel permeation chromatography (GPC) was conducted on the acetyl-protected polymer **3** to measure its molecular weight. The sample was examined in NMP because of the high solubility of the polymer and PANI in this solvent. Multi-angle laser light scattering data could not be collected because conducting polymers, e.g. polyaniline, strongly absorb light at the operating wavelengths of the detectors.[37] The GPC trace (Supplementary Material, Fig. S4) showed a bimodal distribution at ~22500 and ~1000, corresponding to the larger and lower M_ws; the data were collected over two runs and averaged. The data agree with both the FTIR and UV–Vis results, indicating the possible existence of phenazine oligomers, which formed by head-to-head polymerisation rather than the favoured head-to-tail fashion. Compared with the reduced sterically hindered aniline polymerisation, the large mannose pendant substituent group in the *ortho*-position of the aniline blocks the polymerisation pathway and hinders the preferred head-to-tail positioning.

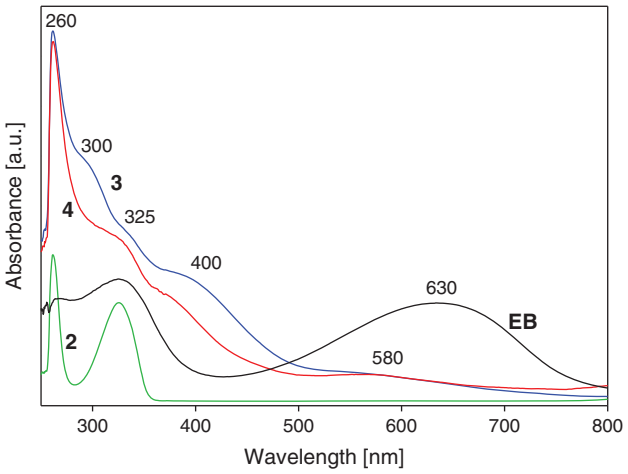


Fig. 3. UV–Vis spectra of monomer **2**, polyaniline EB, polymer **3**, and polymer **4** in NMP.

ConA was chosen as the model α-mannose binding lectin because it shows well-documented binding to various mannose structures and is also similar to many animal and bacterial lectins in cell communications.[38,39] In a recent paper by Wang et al.,[18] the authors successfully demonstrated the extreme sensitivity and selective binding of a novel mannosylated polyaniline to the target lectin. To confirm the biological activity of polymer **4** as synthesised herein, a solution-based ConA assay[40] was selected to investigate binding (see detailed procedure in the Experimental section). This assay was conducted by incubating polymer **4** solutions of different concentrations with a solution of ConA at room temperature for 12 h. Figure 4a, b shows macroscopic confirmation of the binding, as indicated by precipitate formation, presumably polymer–ConA aggregates, following introduction of polymer **4** to the solution of ConA. Subsequently, the dissolution of the precipitate upon addition of methyl α-D-mannopyranoside ligand, which competes for binding sites on ConA, is demonstrated (Fig. 4).

The precipitate (pellet) resulting from the interaction of the polymer with ConA could be separated from the supernatant by centrifugation and redissolved in a methyl α-D-mannopyranoside solution for UV–Vis measurements at 280 nm. Figure 5 shows the results of the assay whereby an increase in the ConA content in the pellet was observed when the concentration of polymer **4** increased. Ideally, we would expect a decrease of the

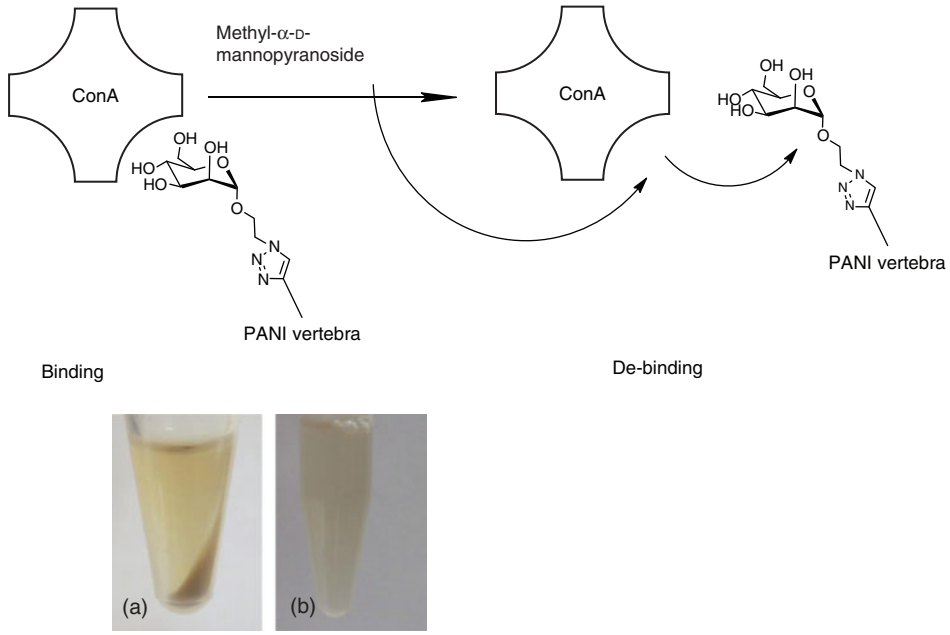


Fig. 4. Schematic representation of ConA–polymer binding and de-binding. Optical images show (a) the precipitate formed by interaction of polymer **4** with ConA and (b) the clear solution obtained after addition of α-D-mannopyranoside. Both solutions were allowed to stand for 1 h following addition and centrifugation.

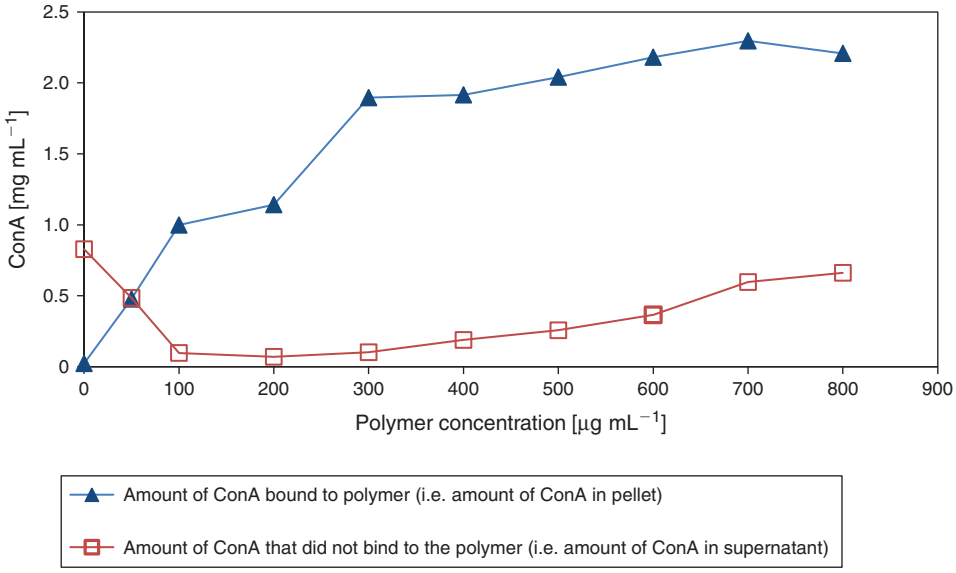


Fig. 5. ConA assay results that describe the presence of ConA in the pellet and the supernatant solution as a function of polymer concentration.

ConA absorbance in the supernatant layer upon precipitation by polymer **4**. An initial drop in the ConA absorbance was observed. However, after adding 200–300 μg mL^{-1} of polymer **4**, the supernatant absorbance signal increased again, likely because of the strong absorption of excess polymer **4** at 280 nm.

Conclusion

We have reported the synthesis of a pendant α-D-mannose moiety attached to aniline through a copper-catalysed azide alkyne click (CuAAC) reaction, and subsequent polymerisation of the monomer via chemical oxidative processes. Cyclic voltammetry and UV–Vis spectroscopy were used to characterise the electronic and spectroscopic properties of the resulting monomer and polymers, and their similarities to pure PANI were investigated. FTIR studies confirm polymerisation of monomer **2**, as indicated by the prominent benzoid and quinoid peaks, and also retention of the mannose moiety signals. A phenazine-type by-product was also observed, which is consistent with the bimodal GPC data. ConA assay demonstrates the ability of polymer **4** to interact with ConA lectins and provides foundation for future work, which will include investigating the ability of this polymer to bind and probe bacteria, in particular *Escherichia coli*. Preparation of the polymer with a higher molecular weight and yield will also be examined.

Experimental

Materials

Unless stated otherwise, all solvents and reagents were used as supplied from commercial sources. All moisture sensitive reactions were performed in oven-dried glassware under an inert, dry nitrogen atmosphere. Analytical thin layer chromatography was performed using Kieselgel F254 0.2 mm silica plates (Merck), and the plates were visualised under ultraviolet irradiation (254 nm) and/or by staining with vanillin. Flash chromatography was performed using Kieselgel S 63–100 μm silica gel (Riedel-de-Hahn). The solvent compositions used for all chromatographic separations are reported on a (v/v) basis. Spectra/Por Dialysis Membrane MWCO 1000 was used as the dialysis tubing. Polyaniline in both emeraldine base and emeraldine salt forms were prepared in-house according to standard synthesis procedures.[41]

1,2,3,4,6-Penta-O-acetyl-α-D-mannopyranoside

D-mannose (7 g, 38.9 mmol) was gradually added (in five portions) to a stirred solution of iodine (0.4 g, 1.55 mmol) in acetic anhydride (40 mL, 432 mmol) at 0°C. The reaction mixture was allowed to stir at this temperature for 30 min and then allowed to warm up to room temperature. After 1 h at room temperature, methanol (20 mL) was added and the mixture was stirred for a further 30 min, followed by evaporation of the solvent under vacuum. The residue was dissolved in dichloromethane (DCM; 50 mL) and washed with $Na_2S_2O_5$ solution (2 × 50 mL). The layers were separated and the resulting colourless organic phase was washed with $NaHCO_3$ solution (4 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford a pale yellow oil (12.9 g, 85 %) as an anomeric mixture (α : β, 4 : 1), as determined by ^{1}H NMR. The product was used in the next step without any further purification. δ_H (400 MHz, $CDCl_3$) 1.97 (s, 3H, OC(O)CH_3), 2.02 (s, 3H, OC(O)CH_3), 2.06 (s, 3H, OC(O)CH_3), 2.14 (s, 3H, OC(O)CH_3), 2.15 (s, 3H, OC(O)CH_3), 4.01–4.13 (m, 2H, CH_2OAc), 4.23–4.29 (m, 1H, C*H*), 5.22–5.32 (m, 3H, 3 × C*H*), 6.05 (d, *J* 1.9, 1H, C*H*). Resonances for minor β anomer: δ_H (400 MHz, $CDCl_3$) 2.00 (s, 3H, OC(O)CH_3), 2.07 (s, 3H, OC(O)CH_3), 2.18 (s, 3H, OC(O)CH_3), 3.77–3.81 (m, 1H, C*H*), 5.10 (dd, *J* 6.6, 3.4, 1H, C*H*), 5.43–5.46 (m, 1H, C*H*), 5.83 (d, *J* 1.2, 1H, C*H*). Data were consistent with that reported in the literature.[42]

2-Bromoethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside

Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$; 7.9 mL, 64.05 mmol) was added dropwise to a solution of 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranoside (5 g, 12.81 mmol) and 2-bromoethanol (1.82 mL, 25.62 mmol) in dry DCM (80 mL) at 0°C. After 1 h, the ice bath was removed and the reaction was continued at room temperature overnight. The reaction mixture was then slowly added to cold water (80 mL) and the organic layer was separated. The aqueous layer was extracted with DCM (50 mL) and the organic layers combined and washed

successively with water (100 mL), saturated $NaHCO_3$ (2 × 100 mL), and water (100 mL). The solution was dried over $MgSO_4$ and concentrated under reduced pressure to afford a yellow oil. The product was precipitated from diethyl ether to produce a white powder that was filtered, washed with diethyl ether, and dried under high vacuum (4.03 g, 65 %). δ_H (400 MHz, $CDCl_3$) 1.99 (s, 3H, OC(O)CH_3), 2.05 (s, 3H, OC(O)CH_3), 2.11 (s, 3H, OC(O)CH_3), 2.16 (s, 3H, OC(O)CH_3), 3.50–3.53 (m, 2H, CH_2Br), 3.79–3.91 (m, 2H, OCH_2), 4.10–4.15 (m, 2H, CH_2OAc), 4.24–4.29 (m, 1H, C*H*), 4.87 (d, *J* 1.7, 1H, C*H*), 5.26–5.33 (m, 3H, 3 × C*H*). δ_c (100 MHz, $CDCl_3$) 20.6, 20.7, 20.8, 20.9 (*C*H_3), 29.6 (*C*H_2Br), 62.4 (*C*H_2OAc), 66.0, 68.5, 68.9 (*C*H), 69.0 (O*C*H_2CH$_2$Br), 69.4 (*C*H), 97.8 (*C*H), 169.7, 169.8, 170.0, 170.6 (O*C*(O)CH$_3$). Data are consistent with that reported in the literature.[22]

2′Azidoethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside (*1*)

2-Bromoethyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (2 g, 4.4 mmol) and sodium azide (2.28 g, 35.12 mmol) were dissolved in dry DMF (60 mL) and the reaction was stirred under N_2 at 60°C for 6 h before cooling to room temperature and stirring overnight. The reaction mixture was then poured into ethyl acetate (150 mL) and washed with water (3 × 100 mL) and brine (2 × 100 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (ethyl acetate : hexane, 2 : 1) to afford product **1** as white crystals (1.59 g, 87 %). δ_H (400 MHz, $CDCl_3$) 1.99 (s, 3H, OC(O)CH_3), 2.05 (s, 3H, OC(O)CH_3), 2.12 (s, 3H, OC(O)CH_3), 2.16 (s, 3H, OC(O)CH_3), 3.46–3.49 (m, 2H, OCH$_2$CH_2N$_3$), 3.65–3.70 (m, 1H, OCH_2CH$_2$N$_3$), 3.85–3.89 (m, 1H, OCH_2CH$_2$N$_3$), 4.02–4.15 (m, 2H, CH_2OAc), 4.27–4.31 (dd, *J* 5.4, 12.1, 1H, C*H*), 4.87 (d, *J* 1.5, 1H, C*H*), 5.27–5.35 (m, 3H, 3 × C*H*). δ_c (100 MHz, $CDCl_3$) 20.6, 20.7, 20.7, 20.9 (*C*H_3), 50.5 (OCH$_2$*C*H$_2$N$_3$), 62.5 (O*C*H$_2$CH$_2$N$_3$), 66.0 (*C*H), 67.0 (*C*H_2OAc), 68.9 (*C*H), 69.4 (*C*H), 97.8 (*C*H), 169.8, 169.9, 170.2, 170.8 (O*C*(O)CH$_3$). Data are consistent with that reported in the literature.[43]

Synthesis of Monomer *2*

Copper(II) sulphate pentahydrate (23 mg, 0.0935 mmol), sodium ascorbate (37 mg, 0.187 mmol), and 2-ethynylaniline (0.26 mL, 2.25 mmol) were dissolved in water (20 mL) and heated at 50°C under a N_2 atmosphere for 10 min. 2′Azidoethyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (1.00 g, 1.87 mmol) in DMSO (40 mL) was added to the solution and the mixture was left to stir at 50°C for 3 h. The reaction mixture was then diluted with DCM (50 mL) and washed with brine (4 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (ethyl acetate : hexane, 6 : 1) to afford *product **2*** as a white solid that was dried under high vacuum (973 mg, 97 %), mp 54–57°C. $[\alpha]_D^{20}$ 40.7 (*c* 0.26 g/100 mL in MeOH). ν_{max} (KBr)/cm^{-1} 755, 977, 1042s, 1087, 1136, 1221s, 1368, 1442, 1618, 1741s, 3456w. δ_H (400 MHz, $CDCl_3$) 1.77 (s, 3H, OC(O)CH_3), 1.99 (s, 3H, OC(O)CH_3), 2.07 (s, 3H, OC(O)CH_3), 2.13 (s, 3H, OC(O)CH_3), 3.14–3.17 (m, 1H, C*H*), 3.88–3.98 (m, 2H, CH$_2$CH_2N), 4.07–4.17 (m, 2H, CH_2CH$_2$N), 4.58–4.72 (m, 2H, CH_2OAc), 4.82 (d, *J* 0.8, 1H, C*H*), 5.15–5.19 (m, 3H, 3 × C*H*), 6.68–6.75 (m, 2H, 2 × Ar*H*), 7.07–7.11 (m, 1H, Ar*H*), 7.42 (dd, *J* 1.4, 7.8, 1H, Ar*H*), 7.93 (s, 1H, triazole-*H*). δ_c (100 MHz, $CDCl_3$) 20.2, 20.6, 20.7, 20.8 (*C*H$_3$), 49.8 (CH$_2$*C*H$_2$N), 62.1 (*C*H$_2$CH$_2$N), 65.4 (*C*H), 65.8 (*C*H$_2$OAc), 68.9 (2 × *C*H), 69.2 (*C*H), 96.9 (*C*H), 113.4 (Ar*C*), 116.7 (Ar*C*), 117.4 (Ar*C*), 121.2 (triazole-*C*H), 128.0 (Ar*C*), 129.0 (Ar*C*) 145.1 (Ar*C*NH$_2$), 148.7 (triazole-*C*), 169.7, 169.9, 170.0, 170.5 (O*C*(O)CH$_3$). *m/z* (ESI) 535.2 [M+H]$^+$. HRMS (ESI) $C_{24}H_{30}N_4O_{10}$ requires 557.1854 [M+Na]. Found: 557.1849 [M+Na].

Synthesis of Polymer *3*

Polymerisation was conducted using the general oxidative polymerisation procedure as employed for the synthesis of aniline. Monomer **2** (100 mg, 0.187 mmol) was weighed into a beaker and HCl (0.05 M, 5 mL) was added. The resulting mixture was sonicated for five minutes to ensure complete dissolution. Ammonium persulphate (APS) (64.07 mg, 0.281 mmol) was weighed into a separate beaker and completely dissolved in HCl (0.05 M, 0.5 mL). The APS solution was then added to the solution containing monomer **2**. The resulting solution was briefly stirred and then allowed to stand at room temperature. A dark green–black precipitate was obtained after 24 h. The precipitate and remaining solution were poured into a 50-mL centrifuge tube and distilled water was used to ensure quantitative transfer. The sample was then centrifuged at 2500 *g* for 15 min at room temperature. The supernatant was decanted and distilled water (20 mL) was added. Re-suspension of the precipitate was conducted by vortex. The washing process was repeated thrice. The precipitate was then dried in a vacuum oven at 40°C overnight to afford a dark powder (20 % average yield).

Synthesis of Polymer *4*

The resulting polymer **3** was deprotected using sodium methoxide. A solution containing sodium methoxide (0.1 M) in methanol was prepared. Polymer **3** (10 mg) that was dissolved in DMF (1 mL) was then added to this solution (0.2 mL). The reaction proceeded for 24 h after which cold diethyl ether (30 mL) was added dropwise, producing a brown precipitate. This mixture was centrifuged (2500 *g*, 5 min, room temperature) and the ether was decanted. The washing process with ether was repeated thrice. The final product was dialysed against distilled water for two days using a dialysis tubing with a MWCO of 1000. Finally, the product was freeze-dried to afford a brown powder (92 % yield).

Characterisation

^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer and the data are reported in parts per million (ppm) on the δ scale relative to $CDCl_3$ (δ 7.26); ^{13}C NMR spectra were recorded on a 100 MHz Bruker spectrometer and the data are reported in parts per million (ppm) on the δ scale relative to $CDCl_3$ (δ 77.16). The multiplicities of the ^{1}H signals are designated by the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad; dd doublet of doublets; dt = doublet of triplets; and dm = doublet of multiplets. All coupling constants, *J*, are reported in hertz.

Cyclic voltammetry was conducted on a BAS100B electrochemical analyser using a three-electrode setup comprising a glassy carbon working electrode, platinum counter electrode, and Ag/AgCl reference. The experiments started at a potential of −200 mV that increased to 1000 mV at a scan rate of 100 mV s^{-1} and a sensitivity of 10 μA V^{-1}. The solutions for the electrochemical polymerisation were 0.1 M of monomer in 0.5 M H_2SO_4 supporting electrolyte. All electropolymerisation

solutions were degassed under oxygen-free nitrogen for at least 15 min before use.

FTIR was conducted as KBr disks on a Thermo Nicolet 8700 FTIR spectrophotometer. KBr was dried in an oven at 100°C before use. The disks were prepared with 150–200 mg of KBr and 1 mg of polymer. The powders were combined and ground in a mortar and pressed under 5 tons of pressure for 5 min in a pellet press.

UV–Vis spectra were collected on a Shimadzu UV-2101PC UV–Vis scanning spectrophotometer. NMP was used as the solvent.

Gel permeation chromatography (GPC) was used for polymer molecular weight measurements. The system consisted of a Waters 515 HPLC pump, a Degassex DG-4400 on-line degasser connected to a TSK Gel Super AWM-H column (9 µm, 6 × 150 mm) with guard, 0.5-µm in-line filters, a Rheodyne manual injector, and a Waters column oven. The eluent was NMP and the flow rate was 0.12 mL/min. Samples concentrations were 10 mg mL^{-1} and the injection volume was 200 µL. The solution was filtered through 0.45-µm syringe PTFE filters before injection. Agilent Easical GPC/Scalibration was used as the polystyrene standards. Data acquisition and processing were performed using the *ASTRA 4* software (Wyatt Technologies Corporation). The detector was a Shimadzu RID-10A Differential Refractive Index detector. The columns and refractive index detector were maintained at 35°C.

Concanavalin A (ConA) is a binding lectin from the jack bean *Canavalia ensiformis*. The procedure used for the ConA assay is as follows[40]: a buffer solution (0.1 M tris-HCl pH 7.2, 0.9 M NaCl, 1 mM $CaCl_2$, 1 mM $MnCl_2$) was prepared and used to dissolve all solids including ConA and polymer **4**. All mixtures were placed on a vortex for 5 min to achieve complete dissolution, and centrifuged (2500 *g*, 2 min, room temperature) to remove residual solids. The polymer stock solution was prepared by dissolving polymer **4** (4 mg) in the buffer solution (400 µL). This stock solution was diluted to achieve the following polymer solutions at concentrations of 800, 700, 600, 500, 400, 300, 200, 100, 50, and 0 µg mL^{-1}. A separate ConA stock solution was prepared by dissolving ConA (30.42 mg, 90 µM, assuming ConA tetramer with a molecular weight of 104000 Da) in the buffer solution (1.63 mL). Each polymer sample (125 µL) was mixed with ConA solution (125 µL) and left overnight. The solution was then centrifuged (2500 *g*, 2 min, room temperature) and the supernatant was removed using a pipette. The precipitate (pellet) was then redissolved in methyl α-D-mannopyranoside (1 M, 1 mL). UV–Vis measurements of the supernatant solution containing the pellet were conducted at 280 nm in a quartz cuvette; an average of two scans were taken.

Supplementary Material

Spectra and schemes are available as on the Journal's website.

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