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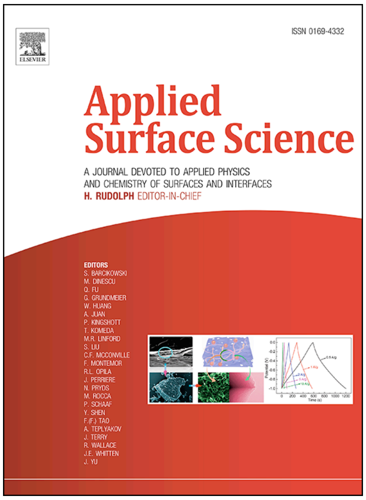

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A Comparative Study of Diaryl Carbene Insertion Reactions at Polymer Surfaces

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Abstract: A detailed investigation of the reactions of diaryldiazo compounds for the surface modification of several polymers has been conducted. This has revealed that the rate of reaction of diaryldiazo compounds is influenced by their substituents, that the reaction is exothermic, and that the polymer itself exerts an influence on the surface modification. The results are consistent with the formation and insertion of a carbene intermediate at the polymer surface. It was further shown that such surface modified polymers, characterized using surface sensitive techniques, display macroscopic behavior consistent with the presence of the newly introduced surface chemical functionality, characterized using a combination of surface sensitive and bulk analytical techniques. This approach is complementary to directed energy deposition approaches, offers an alternative route to functional polymers, and provide a direct link between surface chemistry and observable macroscopic properties.

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1. Introduction

Imparting functionality into otherwise inert materials frequently requires energy intensive techniques such as plasma treatment,[1] γ-radiation in the presence of a reactive monomer group for polymer grafting[2, 3] or harsh wet chemical methods to generate hydroxyl and carboxyl functionality.[4, 5] Chemical treatment of materials permits post-polymerisation adjustment of surface properties, without affecting bulk properties;[6] examples include alkoxysilane formation with hydroxyl containing polymers[7] and carbodiimide coupling for the preparation of amide and ester bonds on carboxyl, hydroxyl and amine containing polymers.[8] Such modified polymers have found application, for example, in light responsive,[9-11] biocompatibilised[12-14] and antibacterial surfaces.[15, 16] As an alternative, we have developed a chemical treatment utilising diaryldiazo compounds.[17]

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These diaryl diazo compounds are stable enough that they can be applied to materials easily in a suitable solution, but upon heating or exposure to UV light after the removal of solvent, a carbene can be generated which reacts with the surface; such highly reactive intermediates and are known to undergo fast insertion and addition reactions[18] and their unusual modes of reactivity in solid matrices have been the focus of a detailed study.[19] A key advantage of this approach is that the diaryldiazo compounds may carry remote functional groups, and that the initially modified surface may be further reacted by a secondary diazonium coupling reaction to impart further new chemical functionality.[20] This breadth of reactivity allows for a flexible and efficient method of modification that can be applied to a wide range of materials, including organic and inorganic polymers[21, 22] and which has been demonstrated to permit the introduction of visible[17] and fluorescent[23] chromophores, biocompatible and biocidal groups,[24] along with protein, cellular and interfacial adhesion,[20, 25] and hydrophobicity[22, 26] effects. Much of this work has focused on the change in macroscopic properties from the surface modification process, but this paper presents a more in-depth investigation into the modification reaction itself, in which we seek to understand the interplay of the chemistry of diaryldiazo compounds and polymers in their reactions at the surface, by detailed analysis of the surface modification and its consequent effect on the macroscopic properties of the polymer.

2. Materials and Methods

Reactions were carried out in oven dried flasks open to the atmosphere using standard solvents. Where necessary, temperatures below room temperature were achieved using a cooling baths of ice/water (0 ˚C) and ice/NaCl/water (-5 ˚C). Reactions were followed using ESI mass spectrometry and TLC analysis. Characterisation of compounds was done using the following equipment and settings: melting points were measured with a Stuart Scientific SMP1 melting point apparatus; Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometers, selected absorption maxima are reported in wavenumbers (cm^{-1}); NMR were recorded on Bruker AVF400 (400 MHz) spectrometer; low resolution mass spectra (*m/z)* were obtained with a Fisons Platform spectrometer with electrospray ionisation (ESI) and a Fisons AutoSpec-oaTpf spectrometer with field ionisation (FI), *m/z* values are reported in Daltons. BET analysis was conducted by the Oxford Surface Analysis Facility, nitrogen adsorption–desorption isotherms were collected on a Micromeritics Tristar-3000 surface area and porosity analyzer at 77 K, on samples previously degassed under vacuum overnight at 120 °C. The BET surface area was calculated from the linear part of the BET plot (P/P_0 = 0.1–0.25). Combustion analysis was provided by MEDAC Ltd. ATR-IR analysis was conducted with a Bio-Rad FTS-6000 with a diamond screw tip accessory. The real time ATR-IR experiments used an ATR accessory featuring gold plated mirrors to direct the IR beam. STA analysis was performed using a Perkin Elmer STA6000.

Amberlite XAD-4 polystyrene was purchased from Sigma Aldrich and has a mesh size of 20-60, washed with acetone and water, then dried before use. The polymers used for the thermal observation of insertion investigations were provided by IRPC: polypropylene is a random polypropylene copolymer with ethylene as co-monomer (3140NN), supplied in granular form; UHMWPE (U320F) in powder form and HDPE was supplied in powder form in hexane and dried *in vacuo* before use.

2.1 General procedure A : Modification of polystyrene XAD-4 beads with diazo compounds [20]

The XAD-4 beads were washed with copious amounts of water then acetone and dried under vacuum on a sinter funnel. The diazo compound (25w/w%, relative to bead weight) was dissolved in Et_2O, then the solution was transferred to a flask containing Amberlite® XAD-4 beads. EtO_2 was added such that the beads were completely submerged then the mixture was concentrated to dryness *in vacuo*. The beads were heated to 120 °C until they had turned from purple to pale yellow in color. The beads were then washed with acetone through a sinter funnel and the beads were left to dry under vacuum to give modified beads.

2.2 General procedure B1: Preparation of Diazonium Salts

A stirred solution of the amine (1 eq) in THF/H_2O was cooled to -5 °C then sodium nitrite (1.1 eq) and 3M hydrochloric acid (2 eq) were added to the mixture was stirred for up to 30 minutes until the color change was complete and the color had reached a constant level of intensity. H-acid confirmed presence of the diazonium salt. The diazonium salts were used immediately.

2.3 General procedure B2: Preparation of Diazonium Salts[20]

A stirred solution of the amine (1 eq) in ethanol was cooled to -5 °C then isopentyl nitrite (1 eq) and tetrafluoroboric acid (2 eq) were added. The mixture was stirred for up to 45 minutes until the color change was complete and the color had reached a constant level of intensity. H-acid confirmed presence of the diazonium salt. The diazonium salts were used immediately.

2.4 H-acid test[20]

Small amount of H-acid (4-amino-5-hydroxy-2,7-napthalene disulfonic acid) (1 mg) was add to a vial and small amount of water was added (~0.25 ml) to produce a beige suspension. A sample of diazonium salt solution (1ml) was added to a new vial and sodium acetate was added to adjust the pH to 4-5. The diazonium salt solution was added to the H-acid mixture, and left to stand at room temperature for 15 minutes. In the presence of diazonium salt, the color changed from beige to dark purple.

2.5 General procedure C: Diazonium Coupling to Modified Beads[20]

The modified polystyrene beads (100 mg, 1 eq) were immersed in a solution of diazonium salt (1.65 mmol, 2 eq). More EtOH was added to beads to ensure they were immersed. The reaction was left to stand at 5 ℃ for 18 hours. The beads were filtered through sinter funnel and washed with copious amount of water and acetone until the washing was colorless then beads were dried under vacuum.

2.6 General procedure D: Hydrogen peroxide loading on the Polystyrene XAD-4 beads.[24]

A sample of polymer (XAD-4) (10-30 mg) was suspended in a concentration of aqueous 30w/v% H_2O_2 (20 ml) for 3 hours and the polymer was collected by filtration and washed with 1-1.5 L of water, collected, and treated with a solution of 20 ml of 10% potassium iodide in 10 ml of 99%-100% acetic acid (total 20 ml). After standing for 5 minutes, a few milliliters of starch was added to the solution, which was left to stand for 1h at room temperature. The resulting dark blue solution was titrated with 0.01 M of sodium thiosulfate until a colorless end point that typically requires 1-5 ml of solution was reached. The solution was left for another hour, and any further blue color of solution was titrated with sodium thiosulfate. The titration of the H_2O_2 stability over time was conducted on blank polystyrene and urea modified polystyrene and the resulting data is given below (average from two experiments).

2.7 General procedure E: Polymer Bioassay.[24]

The samples were tested against *Staphylococcus aureus* and *Escherichia coli*. Using a sterile method, 10-mm-diameter circles were punched in the agar seeded with bacterial. The inner agar was removed to produce empty wells. The test polymer was accurately weighed (10 mg) and added to prepunched wells of the seeded agar plates. The well was then sealed with another 100 µl of molten agar so that a uniform layer of agar was produced. The agar plates were covered and incubated for 18-24 h to encourage bacterial growth. The diameter of the antimicrobial clear zone around each well were measured and recorded per test compound. A blank polymer sample was taken as a reference. The relative potency of the materials calculated from standards prepared using cephalosporin C, where a calibration curve had been prepared of zone size against the log of the molar concentration of cephalosporin C.

2.8 Dopamine Modification Polymer [27, 28]

Dopamine (2 mg/ml) was dissolved in Tris-HCl buffer (PH=8.5), and beads were soaked into the solution. pH-induced oxidation changes the solution color to dark brown. Stirring the solution was necessary to prevent non-specific microparticle deposition on surface. The coated surface were rinsed with water and dried under vacuum.

2.9 Coating of dopamine modified polystyrene with Ag[29]

100 mg beads were dispersed with a magnetic stirrer in 15 ml of ethanol then put in a water bath at 65 ℃. Freshly prepared $[Ag\ (NH_3)_2]^+$ solution (6 ml) was added, stirring gently all the time. 10

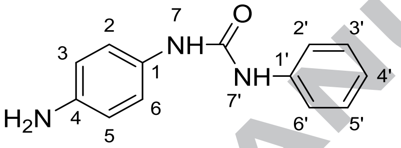
drops of benzaldehyde and 10 drops of 5% glucose solution were added and left for 30 minutes. The beads were filtrated, washed with ethanol, and dried under vacuum.

Preparation of $[Ag\ (NH_3)_2]^+$: ammonium hydroxide was added to $AgNO_3$ (2 g) and brown precipitate was evolved. Ammonium hydroxide was continually added until the solution was colorless. The solution was used immediately.

2.10 Synthesis of diazo compounds

Details regarding the synthesis of diphenyldiazomethane **1a**, bis-4-(methoxyphenyl)diazomethane **1b**, 4,4ˈ-(diazomethylene)bis(*N*,*N*-dimethylaniline) **1d**, bis-4-(chlorophenyl)diazomethane **1c** and 9-diazo-*9H*-fluorene **2**, via their hydrazone precursors have been previously published.[21, 30-32]

1-(4-Aminophenyl)-3-phenylurea[33]



Isocyanatobenzene (275.4 mg, 2.31 mmol) was added in anhydrous chloroform (20 ml) and NEt_3 (0.585 g, 5.78 mmol), then the solution was added to a stirred solution of benzene-1,4-diamine (250 mg, 2.31 mmol) in anhydrous chloroform (10 ml) reacting for 16 hours at room temperature. The precipitate was filtered off after 16 hours then washed with chloroform and dried under vacuum to give the product as an off white solid (0.34 g, 64%). Decomposition temperature: 220 ℃ (lit. 212 ℃) [34]; ν_{max}/cm^{-1} 3295 (N-H and NH_2), 1629 (C=O); δ_H (400 MHz, DMSO-d_6) 4.79 (2H, broad s, NH_2), 6.5-6.53 (2H, m, H-3 and H-5), 6.91-6.95 (1H, tt, *J*=7.4, 1.0, H-4'), 7.07-7.09 (2H, m, H-2 and H-6), 7.23-7.27 (2H, m, H-3'and 5'), 7.41-7.43 (2H, dd, *J*=8.7, 1.2, H-2' and 6'), 8.14 (1H, broad s, NH-7), 8.49 (1H, broad s, NH-7'); δ_C (100.6 MHz, DMSO-d_6) 114.6 (C-3 and 5), 121.8 (C-4'), 121.2 (C-2 and 6), 129.2 (C-3' and C-5'), 118.3 (C-2' and C-6'), 153.4 ($\underline{C}$=O), 140.6, 144.5 (2 × Ar$\underline{C}$); m/z (ESI^+) 228.1 ($[M+H]^+$).

Phenyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methanone 5b

A solution of 4-hydroxybenzophenone (1.0 g, 5.04 mmol) in dichloromethane (20 ml) was added by 3,4-dihydro-*2H*-pyran (1.3 ml, 15.3 mmol) and pyridine *p*-toluenesulfonate (0.235 g, 0.94 mmol) at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C, and for 4 hours at room temperature. Analysis by thin layer chromatography showed complete consumption of 4-hydroxybenzophenone. The mixture was cooled down to 0 °C, added by 10 ml of water and extracted by ethyl acetate (3 × 10 ml). The extract was washed with saturated brine (3 × 10 ml), dried over anhydrous magnesium sulphate and concentrated to give **1** as a pale yellow oil (1.38 g, 97%); m/z (ESI^+) 283.3 ($[M+H]^+$);

ν_{max}/cm^{-1} 1598 (C=O), 1118 (aliphatic C-O-C), 1242 (ArC-O-C), 2943 (C-H); δ_H (400 MHz, $CDCl_3$) 1.56 – 2.06 (3 × 2H, m, H-3″, H-4″ and H-5″), 3.66 (1H, m, H′-6″), 3.90 (1H, m, H″-6″), 5.56 (1H, t, H-2″), 7.14 (2H, m, H-3′ and H-5′), 7.48 (2H, m, H-3 and H-5), 7.58 (1H, m, H-4), 7.78 (2H, m, H-2 and H-6), 7.83 (2H, m, H-2′ and H-6′); δ_C (400 MHz, $CDCl_3$) 18.4 (C-4″), 25.1 (C-5″), 30.6 (C-3″), 62.1 (C-6″), 95.9 (C-2″), 115.8 (C-3′ and C-5′), 128.1 (C-3 and C-5), 129.8 (C-2 and C-6), 130.8 (C-2′ and C-6′), 131.9 (C-4), 132.4 (C-1′), 138.2 (C-1), 160.7 (C-4′), 195.7 (C=O).

Bis(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methanone 5d

A solution of dihydroxybenzophenone (1.0 g, 4.67 mmol) in dichloromethane (20 ml) was added by 3,4-dihydro-2*H*-pyran (1.3 ml, 15.3 mmol) and pyridine *p*-toluenesulfonate (0.235 g, 0.94 mmol) at 0 °C. The reaction mixture was stirred for 10 minutes at 0 °C and for 4 hours at room temperature. Analysis by thin layer chromatography showed complete consumption of dihydroxybenzophenone. The mixture was cooled down to 0 °C, added by 10 ml of water and extracted by ethyl acetate (3 × 10 ml). The extract was washed with saturated brine (3 × 10 ml), dried over anhydrous magnesium sulphate and concentrated to give **2** as a pale yellow oil (1.67 g, 94%); m/z (ESI$^+$) 383.2 ([M+H]$^+$); ν_{max}/cm^{-1} 1599 (C=O), 1115 (aliphatic C-O-C), 1240 (ArC-O-C), 2943 (C-H); δ_H (400 MHz, $CDCl_3$) 1.57 – 1.98 (2 × 6H, m, H-3′, H-4′ and H-5′), 3.58 (2 × 1H, m, H′-6′), 3.82 (2 × 1H, m, H″-6′), 5.46 (2 × 1H, t, H-2′), 7.04 (2 × 2H, d, H-3 and H-5), 7.70 (2 × 2H, d, H-2 and H-6); δ_C (400 MHz, $CDCl_3$) 18.6 (C-4′), 25.1 (C-5′), 30.2 (C-3′), 62.1 (C-6′), 95.9 (C-2′), 115.9 (C-3 and C-5), 132.1 (C-2 and C-6), 132.6 (C-1), 160.6 (C-4), 196.4 (C=O).

Phenyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methylene)hydrazone

To a stirring solution of phenyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methanone (1.35 g, 4.78 mmol), and ethanol (20 ml) was added hydrazine monohydrate (1.16 ml, 23.8 mmol) drop wise. The mixture was heated to reflux for 48 hours. Analysis by mass spectrometry showed complete consumption of bis(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methanone. Water (2 ml) was added and ethanol was then removed *in vacuo*. The residue was dissolved in dichloromethane (10 ml) and washed with water (3 × 10 ml). The mixture was dried over magnesium sulphate, filtered and concentrated to give **3** as a pale yellow oil as a mixture of the cis and trans isomers (1.23 g, 87%); m/z (ESI$^+$) 297.2 ([M+H]$^+$); ν_{max}/cm^{-1} 3407 (N-H), 1507 (C=N), 1110 (aliphatic C-O-C), 1237 (ArC-O-C), 2943 (C-H); δ_H (400 MHz, $CDCl_3$) 1.45 – 1.96 (3 × 2H, m, H-3″, H-4″ and H-5″), 3.50 (1H, m, H′-6″), 3.79 (1H, m, H″-6″), 5.36 (1H, m, H-2″), 5.68 (2H, s, NH_2), 6.87 – 6.92, 7.27 – 7.31 (2 × 2H, m, H-3, H-5, H-3′ and H-5′), 7.17 – 7.23, 7.37 – 7.44 (5H, m, H-2, H-6, H-2′, H-4 and

H-6′); δ_C (400 MHz, $CDCl_3$) 18.7 (C-4′′), 25.2 (C-5′′), 30.4 (C-3′′), 62.3 (C-6′′), 96.4 (C-2′′), 117.1, 128.1, 129.4 (C-3, C-5, C-2′, C-6′, C-3′, C-5′, C-2 and C-6), 130.2, 157.4 (C-4 and C-4′), 133.2, 138.8 (C-1 and C-1′), 149.6 ($\underline{C}$=N).

(Bis(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methylene)hydrazone

To a stirring solution of bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)methanone (1.67 g, 4.22 mmol) and ethanol (20 ml) was added hydrazine monohydrate (1.06 ml, 21.1 mmol) drop wise. The mixture was heated to reflux for 96 hours. Analysis by mass spectrometry showed complete consumption of bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)methanone. Water (2 ml) was added and ethanol was then removed *in vacuo*. The residue was dissolved in dichloromethane (10 ml) and washed with water (3 × 10 ml). The mixture was dried over magnesium sulphate, filtered and concentrated to give **4** as a pale yellow oil as a mixture of the cis and trans isomers (1.45 g, 84%); m/z (ESI^+) 397.2 ($[M+H]^+$); ν_{max}/cm^{-1} 3403 (N-H), 1508 (C=N), 1112 (aliphatic C-O-C), 1239 (ArC-O-C), 2944 (C-H); δ_H (400 MHz, $CDCl_3$) 1.57 – 1.81 (2 × 2H, m, H-4′′ and H-5′′), 1.91 (2H, m, H-3′′), 3.50 (1H, m, H′-6′′), 3.79 (1H, m, H′′-6′′), 5.36 (1H, t, H-2′′), 5.18 (2H, s, $N\underline{H}_2$), 7.11 (2 × 2H, m, H-3 and H-5), 7.28 (2 × 2H, m, H-2 and H-6); δ_C (400 MHz, $CDCl_3$) 18.8 (C-4′′), 25.2 (C-5′′), 30.4 (C-3′′), 62.3 (C-6′′), 96.4 (C-2′′), 116.0 (C-3, C-5, C-3′ and C-5′), 129.4 (C-2, C-6, C-2′ and C-6′), 131.9 (C-1), 133.1 (C-1′), 156.3 ($\underline{C}$=N), 157.2 (C-4 and C-4′).

2-(4-(Diazo(phenyl)methyl)phenoxy)tetrahydro-2*H*-pyran 6a

To a stirring solution of phenyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)methylene)hydrazine (1.23 g, 4.15 mmol) in dichloromethane (10 ml), MnO_2 (0.938 g, 10.8 mmol, 2.6 molar equivalents), KOH (0.245 g, 4.37 mmol) and Na_2SO_4 (0.855 g, 6.02 mmol) were added. The mixture was stirred in the dark for 3 hours, after which analysis by mass spectrometry showed complete consumption of starting material. The mixture was filtered through a celite plug and the filtrate was washed with water (3 × 10 ml). The mixture was dried over magnesium sulphate, filtered and concentrated to give **5** as a purple oil (1.04 g, 85%); m/z (FI^+) 295.1 ($[M+H]^+$); ν_{max}/cm^{-1} 2036 (C=N=N), 1110 (aliphatic C-O-C), 1236 (ArC-O-C), 2942 (C-H); δ_H (400 MHz, $CDCl_3$) 1.80 – 1.91 (6H, m, H-3′′, H-4′′ and H-5′′), 3.52 (1H, m, H′-6′′), 3.83 (1H, m, H′′-6′′), 5.33 (1H, t, H-2′′), 6.94 – 7.27 (9H, m, Ar$\underline{H}$); δ_C (400 MHz, $CDCl_3$) 18.4 (C-4′′), 25.4 (C-5′′), 30.3 (C-3′′) 62.2 (C-6′′), 77.5 ($\underline{C}$=N=N), 96.5 (C-2′′), 117.7 (C-3′ and C-5′), 124.0 (C-1), 127.0 (C-2 and C-6), 128.5 (C-3 and C-5), 128.8 (C-2′ and C-6′), 130.0 (C-4), 130.7 (C-1′), 155.7 (C-4′).

2,2'-(((Diazomethylene)bis(4,1-phenylene))bis(oxy))bis(tetrahydro-2*H*-pyran) 6b

To a stirring solution of (bis(4-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)methylene)hydrazine (0.0795 g, 0.20 mmol) in dichloromethane (10 ml), MnO_2 (0.035 g, 2 molar equivalents, 0.40 mmol), KOH (0.018 g, 0.32 mmol) and Na_2SO_4 (0.064 g, 0.45 mmol) were added. The mixture was stirred in the dark for 3 hours, during which the reaction was followed by mass spectrometry every for consumption of starting material. The mixture was filtered through a celite plug and the filtrate was washed with water (3 × 10 ml). The mixture was dried over magnesium sulphate, filtered and concentrated to give **6** as a dark red oil (0.84 g, 58%); m/z (FI^+) 395.5 ($[M+H]^+$); ν_{max}/cm^{-1} 2033 (C=N=N), 1113 (aliphatic C-O-C), 1240 (ArC-O-C), 2943 (C-H); δ_H (400 MHz, $CDCl_3$) 1.45 – 1.87 (2 × 6H, m, H-3′, H-4′, H-5′), 3.50 (2 × 1H, m, H′-6′), 3.80 (2 × 1H, m, H′′-6′), 5.36 (2 × 1H, t, H-2′), 7.03 (2 × 2 H, m, H-2 and H-6), 6.92 (2 × 2 H, m, H-3 and H-5); δ_C (400 MHz, $CDCl_3$) 18.8 (C-4′), 25.2 (C-5′), 30.4 (C-3′), 62.0 (C-6′), 76.8 ($\underline{C}$=N=N), 96.4 (C-2′), 116.0 (C-3 and C-5), 122.5 (C-1), 130.1 (C-2 and C-6), 157.8 (C-4).

2.11 Real-time ATR-IR analysis of the diazo modification.

Silicon prisms were coated with a 50 % solution of the diazo in diethyl ether, then the solvent allowed to evaporate. The coated prisms were loaded into the ATR accessory and exposed to UV irradiation. IR scans were throughout the curing process took place and examples can be found in the supplementary information.

2.12 Modification of polystyrene to produce 7a,b

2-(4-(Diazo(phenyl)methyl)phenoxy)tetrahydro-2*H*-pyran **6a,b** (20 w/w%, relative to polymer weight) was dissolved in diethyl ether. The polymer was added to the solution and diethyl ether was added such that the beads were completely submerged then the mixture was concentrated to dryness *in vacuo*. The beads were heated to 120 °C until they had turned from purple to pale yellow in colour. The beads were then washed with copious amounts of acetone and water through a sinter funnel and the beads were left to dry under vacuum to give modified beads.

2.13 Removal of protecting group of 7a,b using oxalic acid mixture[35]

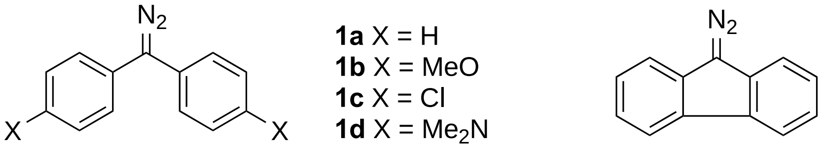
The modified polystyrene beads were immersed in a 5% oxalic acid (by mass) in H_2O/MeOH (1:10). The mixture was left to stand at room temperature for 24 hours. The beads were then washed with acetone and water through a sinter funnel and the beads were left to dry under vacuum to give acid-deprotected modified beads.

2.14 STA Monitoring of Reactions

HDPE, UHMWPE and PP followed the method: heat from 30-250 ˚C for 15 ˚C/min, hold for 5 minutes at 250 ˚C, cool to 30 ˚C at 30 ˚C/min, hold for 1 minute at 30 ˚C. XAD-4 used the same method, but was heated to 350 ˚C.

3. Results and Discussion

A selection of diaryldiazo compounds **1-2** was chosen for investigation of their reactivity (Figure 1). These were synthesised using the literature approach[30] by a two-step method involving firstly, hydrazone formation with hydrazine hydrate, followed by oxidation with manganese dioxide or mercuric oxide.[17] The resulting diazo compounds **1-2** are all intensely coloured (purple or red-orange) solids or viscous oils, and stable for weeks if kept below 0°C. In a preliminary study, the rates of reaction of **1-2** with the polystyrene beads (PS) (commercially available Amberlite® XAD-4, a highly crosslinked and porous polystyrene resin) were examined; these compounds were initially physisorbed onto PS beads from a 25 w/w% diethyl ether solution by careful solvent evaporation under vacuum at 40 ˚C, giving highly coloured materials indicative of the presence of the undecomposed diazo compounds, as compared to colourless pristine XAD-4. Heating at 105 ˚C initiated the insertion reaction; loss of colour of the starting diaryldiazo compounds to a yellow colour consistent with completion of the reaction was easily followed by visual inspection (Table 1 (ESI)). The reaction time for dimethoxy **1b** (7.5 min) was significantly faster than both diphenyl **1a** (20min) and diazofluorene **2** (60min); this reflects the electronic activation of the methoxy groups of the former. The decomposition process could also be followed by attenuated total reflection-infrared spectroscopy (ATR-IR) by observation of the disappearance of the distinctive C=N=N stretch of the starting diazo function.[36] Thus, neat diphenyl **1a** and dimethoxy **1b** exhibit stretches at 2034 and 2029 cm^{-1}, respectively, whilst diazofluorene **2** has two peaks at 2054 and 2084 cm^{-1}, and these clearly decreased during the curing process (Table 1, ESI). Moreover, real time ATR-IR spectroscopic analysis of the reaction with UV photolytic induction allowed the quantitative tracking of the intensity of the diazo signal during surface modification. Thus, diazo compounds **1-2** were coated directly onto silicon prisms from a 50 w/v% solution in diethyl ether, and the solvent was allowed to evaporate. As before, decrease of the diazo peaks over time was observed upon irradiation and allowed the calculation of initial first order reaction rates for systems **1a** and **2** (Table 1, ESI); the dimethoxy system **1b** was too reactive under these conditions to provide meaningful data. This data confirmed that collapse of the diazo function was associated with visible decolourisation, giving a yellow polymer, consistent with surface modification by a carbene intermediate, and that rates of the reaction could be modified by appropriate ring substitution on the diazo precursor.



2

Figure 1

This study provided evidence for thermal or photo-initiated collapse of the diazo function at the polymer surface at rates consistent with the known reactivity of carbenes;[37-40] of interest now was an understanding of the nature of the polymer on the surface modification reaction, and to achieve this, a comparative study of reactions with PS beads, along with the low surface energy materials, medium density polyethylene (MDPE), low density polyethylene (LDPE) and ultra-high molecular weight polyethylene (UHMWPE) using 4,4'-(diazomethylene)bis(*N*,*N*-dimethylaniline) **1d** was made; this diazo compound was chosen for its known high level of reactivity and the ability to determine polymer surface loading levels using nitrogen as the reporter atom.[21, 30, 31] The materials were immersed in THF solutions at 10, 25, 50 and 100 %w/w relative to the mass of polymer. After the solvent was carefully removed, leading to physisorption of the diazo compound onto the surface, heating at 110 ˚C resulted in a colour change from the green diazo **1d** to yellow modified polymer (Table 2, ESI); this colouration is consistent with the introduction of aromatic residues onto the surface, and the intensity of yellow colour broadly correlated with the surface loading (*vide infra*) of the modifying reagent (Table 2, ESI). ATR-IR analysis confirmed the presence of the C-N stretch at 1349-1351 cm^{-1} and the added nitrogen was easily detected by combustion analysis (Table 2, ESI), at a level of about 10^{19} molecules/g. The surface areas of the polymers were measured by BET analysis and found to be 2.0 and 2.5 m^2/g for LDPE and UHMPE, respectively, although the surface area of MDPE was below the detection limit of the equipment; PS has a surface area of 725 m^2/g (manufacturer's data).[31] This data enabled calculation of the surface loading to be ca 10^{13} molecules/cm^2, a value similar to that estimated by previous analysis of related surface modifications.[31] Assuming a molecular limiting value of 1.28×10^{14} molecules/cm^2, the surface area coverage of the chemistry was also calculated and was up to 23% for PS, but significantly higher for LDPE and UHMWPE (Table 2, ESI).

Several outcomes were evident from this analysis. For PS, an increase in concentration of the applied diaryldiazo **1d** solution led to an increase in the observed colour and the degree of modification; this however, was not observed for LDPE and UHMWPE, which showed no significant change in visual appearance or measured loading as the amount of applied diaryldiazo compound was increased. PS coating by the diazo reagent increases steadily with increasing concentration up to 23% of its total area, while LDPE and UHMWPE reached saturation at much lower concentrations and paradoxically become coated at significantly higher surface coverage levels. This appears to be due to the highly porous nature and high surface area of PS, along with the lower surface area of the PE polymers, for which surface saturation of the modifying carbene is more readily achieved. Moreover, although the latter low surface energy polymers are also intrinsically less reactive, multilayer modifications arising because carbene insertion into the underlying modification layer is more likely due to its higher reactivity than with the low surface energy base polymer, become favoured once surface modification commences, and enhancing further modification. Moreover, MDPE, which has the highest nitrogen uptake of the polyolefins, is a branched polymer, with short side chains and higher crystallinity;[41] these expose significantly more primary C-H bonds as well as the branch points capable of reacting with the carbene. By contrast, LDPE polymers typically have longer linear chains[42, 43] while UHMWPE polymers have crystallinity values ranging from 39-75%, depending upon their chain length and synthesis conditions; this imparts lower chemical reactivity at the surface.[44] This approach complements the reported surface modification of low-density polyethylene films by a solution process[45] and for the covalent attachment of lactase.[46]

Simultaneous Thermal Analysis (STA) permitted observation of mass change and thermal events during the surface-modifying carbene reactions for systems **1-2**. Polymers (PS, polypropylene (PP), high-density polyethylene (HDPE) and UHMWPE upon which diazo compounds **1-2** had been physisorbed were heated to 350 ˚C at 15 ˚C/min; during the heating phase up to 130 ˚C, in which the samples changed colour as the diazo function collapsed and the carbene had been generated, an exothermic transition occurs, accompanied by a loss of mass corresponding to the release of nitrogen (Table 1). This outcome is particularly clear for PS, as there is no polymer melting or decomposition until significantly higher temperature (Figure 1, ESI). As the temperature increase continues, another phase of mass loss begins at ~200 ˚C, corresponding to polymer degradation. The onset temperature for decomposition, in the range 107-120^{o}C, corresponds to the observed rate order from the above kinetic experiments (Table 1, ESI). Of interest is that the materials all released amounts of nitrogen between 26-68% of the initially added diazo compound, assuming fully efficient physisorption, and this is consistent with insertion efficiency values reported earlier.[31] For all of the polymers PP, HDPE and UHMWPE, STA traces showed the expected mass change and thermal events during the surface-modifying carbene reactions as had been seen with PS, but the thermal event was a superimposition of the polymer melting transition as well as the collapse of the diazo precursor (Table 1). STA traces obtained during the heating phase of the reaction of dichlorodiazo **1c** with PP, HDPE and UHMWPE are given in Figure 2 by way of example; this is corrected for the polymer melting endotherm. PP consistently showed the lowest enthalpy of reaction and HDPE the highest, for any given diazo compound, and of interest is that the total ΔH values for the reaction of these polyolefins with diaryldiazo compounds are more exothermic than those observed for PS. Moreover, the PE materials also generally exhibited higher loading densities, consistent with the higher levels of coverage calculated independently by nitrogen analysis (Table 1, ESI), but which are best explained by multilayer insertions (*vide infra*). The onset temperature for nitrogen release, calculated from the mass data, is typically between 109-120 ˚C for diphenyl diazo **1**, 97-100 ˚C for dimethoxy diazo **1b** and 114-119 ˚C for dichlorodiazo **1c** (Table 1); clearly dimethoxy diazo **3b** is the most reactive. PP tends to have a higher onset temperature, consistent with its lower reactivity. This data confirms that mass loss and exotherm generation is associated with surface polymer modification, and that the exotherm is polymer dependent, with PE consistently giving the highest ΔH values.

Overall, this work shows that surface chemistry may be manipulated by direct chemical modification and without the need for high energy intervention; such modification is detectable using ATR-IR surface analysis, but also from bulk properties which clearly demonstrate the presence of the expected atomic composition arising from a thermal event during the course of the surface modification.

Table 1: STA Analysis of Reaction of Diazo Compounds with Polymers.[a]

Compound	Polymer	Heat Flow Data		Mass Change Data	
		ΔH (J/g)	T (˚C)	Onset T (˚C)	Efficiency (%)[b]
Diphenyl **1a**	PS	-30	133	111	33
	PP	-48	150	120	64
	HDPE	-58	137	109	77
	UHMWPE	-51	145	115	57
Dimethoxy **1b**	PS	-19	120	107	26
	PP	-12	151	97	10
	HDPE	-84	133	100	22
	UHMWPE	-75	140	101	30
Dichloro **1c**	PS	-30	131	113	55
	PP	-54	145	119	30
	HDPE	-89	136	116	54
	UHMWPE	-49	143	114	50
Fluorenone **2**	PS	-73	157	120	68

[a] STA method: 30 to 200 ˚C at 20 ˚C/min for **1a-c**; 30 to 300 ˚C then at 20 ˚C/min for **2**; [b] Estimated insertion efficiency calculated from the moles N_2 released relative to diaryldiazo added (20% w/w polymer loading).

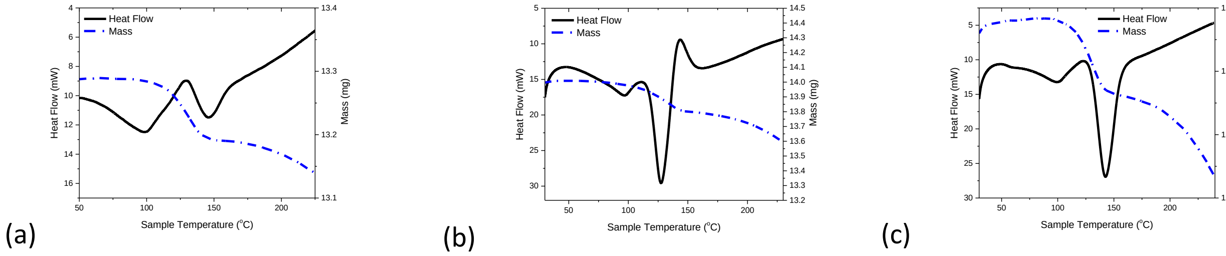
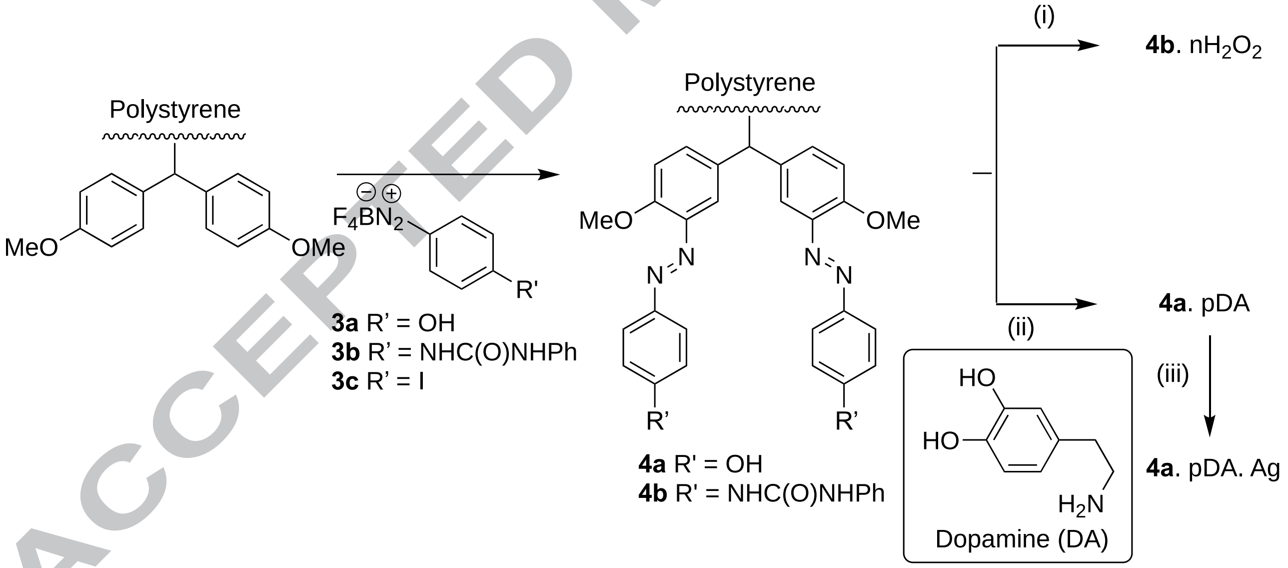


Figure 2: STA profile of the reaction of 4,4'-dichlorodiphenyldiazomethane **1c** with PP (a), HDPE (b) and UHMWPE (c).

Having shown that polymers were capable of modification by carbene insertion, we wished to further demonstrate that polymer surface derivatisation using this method could be used to create observable changes to macroscopic material properties. In the first instance, PS modified with dimethoxy **1b** was further reacted with diazonium salts **3a,b** (Scheme 1)(synthesised from the p-iodoaniline or p-aminophenol, isopentyl nitrite and HBF_4, and whose formation was confirmed by H-acid test[20])[47] to give modified materials **4a,b**, with pendant terminal hydroxyl and urea functional groups respectively. These were characterised using a combination of ATR-IR spectroscopy (Table 3 (ESI)) with modified PS giving significant peaks at 1247 (Aryl-O), 1172 and 1034 cm^{-1} ($O\text{-}CH_3$), and the azo- signal at 1562 and 1563 cm^{-1} respectively (slightly lower than usual value for a diazo (N=N) peak (1630 – 1575 cm^{-1}) due to conjugation with the aromatic system[48]) for urea and hydroxyl-modified beads **4a,b** respectively. Combustion analysis confirmed the presence of nitrogen resulting from the diazonium coupling reaction and permitted estimation of the surface loading (Table 3 (ESI)) to be 8-11 × 10^{12} molecules.cm^{-2}, which corresponds to a surface coverage of about 15-18% (assuming the manufacturer's value for the surface area of polymer to be 725 m^2g^{-1}).[20] This value is consistent with the loading values in related polystyrene systems, previously estimated to be up to 10^{13} molecules.cm^{-2}.[20, 21, 31]

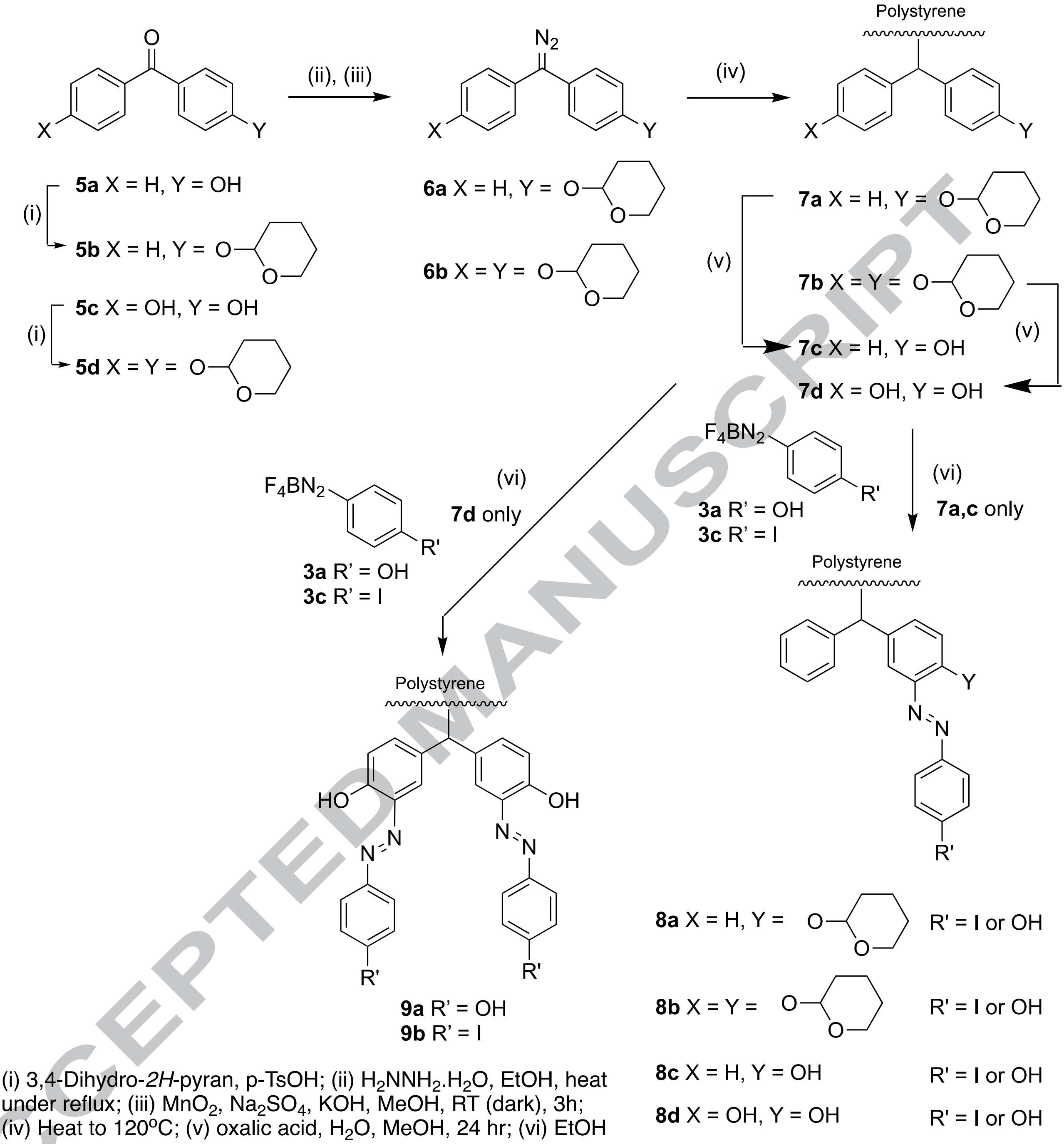


(i) H_2O_2 (30%), 3h; (ii) Dopamine, Tris$^-$HCl buffer pH 8.5, 24 hrs, r.t.; (iii) $[Ag(NH_3)_2]^+$ then PhCHO, glucose

Scheme 1

By way of elaborating this observation further, a key question was whether a more efficient azo-coupling step which would in turn improve the downstream surface modification could be achieved by harnessing the known superior activating properties of aromatic oxy-anion or hydroxy groups towards electrophilic aromatic substitution;[49, 50] of interest was whether this could be achieved with a protected diol system that could be revealed on the surface. To this end, THP-derivatives **5b,d** were prepared from phenols **5a,c** respectively using the standard procedure

(Scheme 2); these ketones were readily converted to diazo derivatives **6a,b**. For surface modification, PS was coated by immersion in a solution of diazo compounds **6a,b** (20 w/w % loading) in diethyl ether, followed by careful solvent removal *in vacuo* at room temperature. These substrates were then heated at 120 °C, to give modified polystyrene beads **7a,b** (Scheme 2 and Table 4(ESI)). After the heating process, the colour of coated beads all changed from mauve/purple to pale yellow, consistent with surface modification. The THP protecting group was removed from the modified polymer using 5% oxalic acid in H_2O/MeOH (1:10)[35] (Scheme 2 and Table 4(ESI)), thereby revealing hydroxyl groups on the surface of polymers **7c,d**. ATR-IR analysis indicated that these samples showed two more significant peaks than blank polystyrene, that is, alkyl-O stretches at 1111 (in **7a**) and 1127 (in **7b**) cm^{-1} respectively belonging to ether groups, and stretches at 1240 and 1239 cm^{-1} respectively, due to aryl C-O-C bonds. Polymer **7a** had significantly smaller peaks than **7b**, indicative of lower surface loading density, probably resulting from the lower relative reactivity of monohydroxy diazo **6a** over dihydroxydiazo **6b**. These materials were further derivatised by diazonium coupling with salts **3a,c**. These couplings were conducted under several conditions: method A used standard diazonium coupling conditions at pH 1 – 2; method B used pH modified conditions using sodium acetate, at pH 4 – 5; method C used 2 molar equivalents of the diazonium salt; and method D used 2 molar equivalents of the diazonium salt. All samples showed significant changes in colour after coupling with the diazonium salts, indicative of formation of the azo linkage with its visible chromophore (Table 4(ESI)).[20] Combustion analysis confirmed the presence of nitrogen in the modified polymers and allowed calculation of the surface coverage (Table 4(ESI)). Notably, iodo-terminated materials demonstrated higher loading and surface coverage than hydroxyl-terminated materials, consistent with the corresponding diazonium agent being more efficient for coupling. Monohydroxy samples **8a** (R’ = I or OH), modified using methods A and B, had similar loading and surface coverage, indicating that diazonium coupling was not strongly pH dependent. Protected dihydroxy **9a,b** modified using method D displayed similar loading and surface coverage to the corresponding protected monohydroxy **8a** (R’ = I or OH) modified using method A, which was consistent with diazonium salts coupling to only one of the two activated aromatic rings. This increased when the amount of the diazonium salt was increased to 4 equivalents (Method D) giving materials **9a,b**, and this outcome is consistent with the better activation of the aryl ring in the linker group towards diazonium coupling with a free hydroxyl function.[51]



(i) 3,4-Dihydro-*2H*-pyran, p-TsOH; (ii) $H_2NNH_2.H_2O$, EtOH, heat under reflux; (iii) MnO_2, Na_2SO_4, KOH, MeOH, RT (dark), 3h; (iv) Heat to 120°C; (v) oxalic acid, H_2O, MeOH, 24 hr; (vi) EtOH

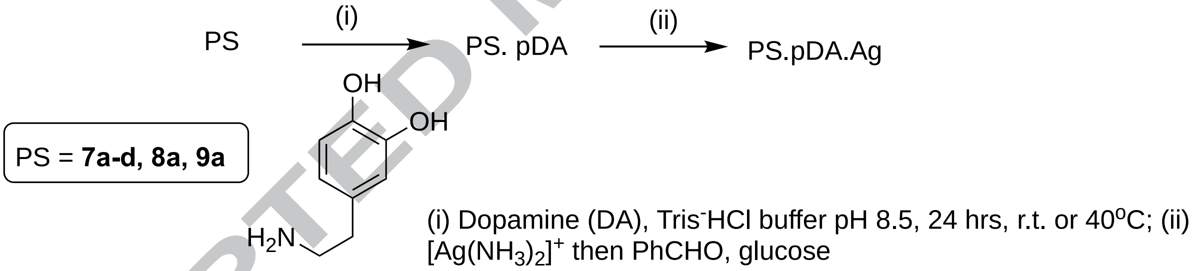
Scheme 2

In order to confirm that these surface modifications led to observable macroscopic outcomes, further derivatisation was examined. Thus, urea modified polymer **4b** was treated with hydrogen peroxide by immersion in 30%w/v of hydrogen peroxide solution for 3 hours to give **4b.**H_2O_2 (Scheme 1); hydrogen peroxide is known to be stabilised by urea as a result of an extensive network of hydrogen bonding and to exhibit potent biocidal properties.[24, 52, 53] The H_2O_2 loading of the modified beads **4b.**H_2O_2 (Table 3 (ESI)), determined by iodometric titration, was 0.85 mmol g^{-1}, significantly higher than methoxy-modified beads alone, which was 0.49 mmolg^{-1};

that this latter value is not zero indicates that the porous polystyrene is capable of stabilising the peroxide by physisorption alone. Moreover, these materials retained 64% of their peroxide loading after 304h, and showed some bactericidal activity; *S. aureus* was found to be sensitive to the peroxide-modified polymer **4b.**H_2O_2, but *E. coli* was not (Table 3 (ESI)), and this activity was greater than the PS blank control.

That this carbene-modification might be suitable as a base layer for further coating was examined using oxidative dopamine self-polymerization; this approach has been reported to give strongly adhesive polydopamine (pDA) layers on a variety of surfaces,[28, 54] and of interest was whether a similar phenomenon might be effective for surface-modified PS (Schemes 1 and 3). Therefore, hydroxyl-modified PS beads **4a** and **7a-d, 8a, 9a** along with representative blanks were immersed in dopamine solution for 24 hours at room temperature, to give **4a.**pDA and **7a-d.**pDA, **8a.**pDA, **9a.**pDA; their colour all changed to dark green and the coating could not be washed off with water (Tables 5 and 6 (ESI)). Combustion analysis confirmed the presence of nitrogen, and ATR-IR spectroscopy showed the presence of significant but broad N-H and O-H peaks at around 3332 and 3259 cm^{-1}, both indicative of successful layer formation. TGA of coated polystyrene beads **7d.**pDA (heated from 30 °C to 600 °C at 10 °C per minute (Figure 2, ESI)) showed a three-stage degradation behaviour; the first stage, between 100 °C and about 110 °C, was associated with loss of absorbed water, with the second stage, between about 110 °C and the decomposition temperature of PS, being attributed to the decomposition of the pDA layer, while a third stage after 397 °C was due to PS decomposition (under these conditions, blank polystyrene XAD-4 beads showed only two stages of weight loss; the first, attributed to the evaporation of absorbed water, and the second stage at 397 °C, assigned to the decomposition of PS). From DSC (Figure 2, ESI), the endothermic enthalpy change of polystyrene decomposition was 236.8 (blank polystyrene) and 198.9 Jg^{-1} (pDA coated **7d.**pDA) respectively, and for dopamine-modified samples, a small increase in PS decomposition temperature was seen relative to blank polystyrene (397 °C vs 405 °C). The combustion analysis values of pDA-modified PS both confirmed the presence of nitrogen at 0.10 – 0.51 %, and allowed the surface loading density to be determined (Table 6 (ESI)); all modified substrates had a higher % loading value than blank PS beads modified with pDA, and the surface loading was broadly similar to that obtained from TGA analysis.

Electroless metallisation of material surfaces has recently become of interest particularly for their electrical[29, 55, 56] and also for their antibacterial[57-60] and biomedical applications,[61, 62] and efficient electroless metallization of surfaces after polydopamine modification has been reported.[28, 29, 58] Modification of dopamine-coated PS **4a**.pDA was done with silver using Tollens' reaction (Scheme 1);[63, 64] thus, the **4a**.pDA beads were dispersed in ethanol at 65°C and then $[Ag(NH_3)_2]^+$ was added, followed by benzaldehyde and glucose as reducing agents, and a grey silver coating was formed on the polymer beads after 30 min. Combustion analysis of the **4a**.pDA.Ag beads again confirmed the presence of nitrogen, suggesting that the dopamine layer was intact underneath the Ag layer (Tables 5 and 6 (ESI)), and low resolution X-ray photoelectron spectroscopy (XPS) spectra showed a significant peak around 372 eV, corresponding to the binding energy of 3d orbital of Ag (Figure 3, ESI); this was not observed on blank PS, as expected. At high resolution (Figure 4, ESI), $3d_{3/2}$ and $3d_{5/2}$ signals further confirmed the presence of silver. The Ag/O ratio was lower for **4a**.pDA.Ag than for the control, PS.Ag, further suggesting that the dopamine layer was intact underneath the surface silver layer. The silver-coated modified samples **7a-d.**pDA.Ag, **8a.**pDA.Ag**,** **9a.**pDA.Ag also exhibited a metallic finish and combustion analysis confirmed the presence of nitrogen, which was not removed during metallization (Scheme 3, and Table 6 (ESI)), corresponding to an intact dopamine coating. The presence of silver on the surface of polymers was further confirmed by XPS analysis (Figures 5 and 6, ESI), which showed a Ag/C ratio that is significantly larger, and an O/C value that is lower, for pDA coated beads than for blank polystyrene beads. Overall, the data is consistent with the hypothesis that polydopamine has been modified onto the polymer, and that the presence of pDA coating aided the subsequent silver deposition process.



(i) Dopamine (DA), Tris-HCl buffer pH 8.5, 24 hrs, r.t. or 40°C; (ii) $[Ag(NH_3)_2]^+$ then PhCHO, glucose

Scheme 3

Antibacterial analysis of blank XAD-4 beads, modified beads **7d**.pDA.Ag and silver coated blank beads against *Escherichia coli* and *Staphylococcus aureus* using hole plate bioassay was made.[24] After incubation for 12 – 16 hours, the diameter of the clear inhibition zone was measured (Table 2). Inhibition zones were observed for both *E. coli* and *S. aureus* for silver coated samples **7d.**pDA.Ag, but these were significantly smaller for *S. aureus* than for *E. coli*. Importantly, blank XAD-4 beads and sample modified with linker and polydopamine only (**7d**.pDA) showed no antibacterial activity, demonstrating that the silver coating was responsible for the antimicrobial behavior. Overall, this analysis gave preliminary indication of antibacterial activity in the silver-coated samples.

Sample	Zone size (mm)	
	S. aureus	E. coli
PS blank	0	0
7d.pDA	0	0
7d.pDA.Ag	10	7

Table 2: Antibacterial assay of modified polymers

4. Conclusions

Application of a range of surface sensitive and bulk analytical techniques has provided evidence for the modification of polymers by diaryldiazomethanes under thermal conditions, with collapse of the diazo function being associated with polymer modification, consistent with the formation of carbenes. It seems likely that these react differently to their normal modes of reactivity in solution,[50] since dispersion on the polymer surface limits diffusion so that singlet/triplet intersystem crossing competes effectively with singlet insertion reactions, leading to a dominance of triplet system reactivity.[19] While the reactivity of diaryldiazo compounds is indeed affected by the substituents on the aryl rings, with electron donating groups destabilising the diazo group, and carbene generation being exothermic, the reactivity of the derived carbenes at the polymer surface has also been found to depend on the polymer; MDPE shows a larger uptake by surface reaction than HDPE and UHMWPE. This outcome demonstrates that surface chemical modification mediated by carbene insertions as espoused in this approach requires tuning of reactivity depending on the nature of the polymer to be modified; in this regard, consideration of the surface energy is no different to directed energy deposition. The level of surface molecular modification is sufficient that metallisation and biocidal properties may be imparted onto the polymer, and the identity of the surface chemical functionality responsible for these properties was readily demonstrated from a combination of ATR-IR and XPS analysis coupled with bulk analysis, such as combustion analysis. Overall, we have demonstrated that a chemical modification based upon carbene insertion for surface functionalization is general, and provides a strategy which complements other carbene surface-modifying approaches which have been reported.

5. Acknowledgements

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- A study of the reactions of diaryl diazo compounds with a range of surfaces has been conducted;
- The reaction outcome is consistent with the intermediacy of carbenes;
- The surface modification which is achieved can be used to enhance the binding of hydrogen peroxide and silver metal;
- Macroscopic surface changes are observable, including the introduction of biocidal activity .

A Comparative Study of Polymer Surface Modifications mediated by Diaryl Carbene Insertion Reactions

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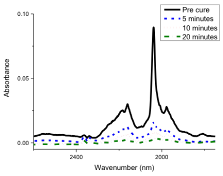

The surface modification of polymers, mediated by carbene insertion, is studied in detail, and used to introduce diverse surface activity.