

Post-Polymerization Modification of Materials using Diaryldiazomethanes: Changes to Surface Macroscopic Properties¹

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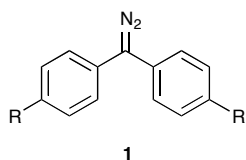
Abstract: Diarylcarbenes have been shown to be suitable for the surface modification of a diverse range of polymers, including low surface energy materials, and this allows the modification of surface macroscopic effects, exemplified by changes in wetting behaviour, pH sensing and bactericidal activity.

Introduction

The independent manipulation of both macroscopic properties and surface characteristics of polymeric materials is highly advantageous, so as to both maintain desirable bulk properties of the polymer but also to adjust surface properties to suit a given application; this approach has received some attention^[1-3] and common methods include abrasion, chemical treatment, and surface activation. Amongst the latter, a diversity of techniques has been developed^[2]: atom bombardment,^[4, 5] plasma treatment,^[6-14] ion implantation,^[15] laser treatment,^[16-18] electron beam,^[19] ion beam irradiation,^[20] and

¹ **Supporting Information** is available at Wiley Online Library or from the author.

welding^[21] are all well known. A recent report of a milder approach using hyperthermal hydrogen induced cross-linking represents an important advance.^[22] Polymer surface modification has also been reported using chemical surface treatments, including silanisation, oxidation, chlorination, acylation and quaternisation^[23-25] as well as lithiation.^[26] However, the frequent requirement for significant infrastructure, harsh reaction conditions, and limitation to specific polymer types which must possess suitable chemical functionality capable of direct modification (e.g. polystyrene,^[27] polybutadiene^[28] or SBS-rubber^[29]) led us to consider alternative chemical methods which would be amenable to a large range of polymers, permitting direct chemical modification under mild conditions and ideally using inexpensive reagents. Although reports of polymer modifications leading to changes in surface tension, permeability or photophysical characteristics mediated by carbene insertion have been made,^[30-35] limitations to that methodology include the need for volatile and highly reactive carbenes, high temperature, and metal catalysts. Perhaps as a result of this, carbene insertion appears to have been largely overlooked as a method applicable to polymer modification.^[36] We considered, however, that this approach was worthy of further investigation, particularly if the issues of generation of the carbene could be addressed,^[37] since the well known reactivity of carbenes with C-H and X-H (X=O, N, S) by bond insertion, and with C-C double bonds by addition reactions, would be expected to afford a very general process of potential application to a wide range of materials;^[38-40] notably, these reactions are irreversible. In the event, we established an approach based upon substituted diaryldiazomethanes **1**, in which a transient carbene is generated thermally or photochemically.^[37] Alternative approaches using tosyl hydrazones^[41] or diazirines,^[42-45] both well-known carbene precursors, have also been identified;^[46] the latter have found wide application in biological applications.^[47] Our approach has been used to introduce colour,^[48] fluorescence,^[49] biocompatibility,^[50] protein adhesion,^[51] biocidal,^[52] hydrophobicity,^[53] and payload delivery^[54] effects onto substrates,^[55] with a loading of the diarylmethyl unit onto the material surface of the order of $2\text{--}15 \times 10^{12}$ molecules per cm^2 .^[56] This approach compares favourably to alternative approaches^[57] and avoids multi-step processes which have been recently reported.^[58] We report here the results of some investigations to expand the scope of types of material amenable to this surface modification approach, including low surface energy materials.



Results and Discussion

The activation of low surface energy materials presents a particular chemical challenge, and requires a suitably reactive system. Literature precedent for the use of azides as labelling agents^[59] as precursors for the insertion of nitrenes specifically into amines^[60] and sulfur^[61] functional groups, but also non-specifically,^[62] suggested that they may also be suitable for surface modification more generally. Our own work (Figure 1), however, indicated that, although successful modification of cross-linked polystyrene could be achieved with the activated amino sulfonyl azides **2** (R = H), prepared using the literature method,^[63] low surface energy polymers, exemplified by ultra high molecular weight polyethylene (UHMWPE), could not, since the high thermolysis temperatures (170 °C) for conversion to the required nitrene generally led to concomitant polymer degradation. If these processes were run at lower temperature (120 °C), in which polymer degradation did not occur, only the more reactive polymer (polystyrene) was modified, and UHMWPE was recovered unchanged. These results were confirmed from a literature report which indicated the successful modification of UHMWPE with sulfonyl azides could only be achieved at the elevated temperature and pressure conditions achieved by melt processing.^[63] We therefore considered sulfonyl azides to be unsuitable candidates for further development.

Figure 1 near here

Carbenes, on the other hand, are reported to insert with high efficiency into O-H and C-H bonds^[64] but we found in preliminary investigations that diaryldiazomethanes do not necessarily exhibit high reactivity in solution^[41, 65] despite their reported reactivity with carboxylic acids,^[66, 67] alcohols,^[37] amines^[68] and alkenes,^[65] amongst other functional groups.^[65, 69-75] We wondered if the incorporation of electronically modifying groups might give an acceptable balance of stability and reactivity, favouring insertion into low surface energy polymers, and preliminary work with methoxy-activated systems **1** (R = OMe) indicated that although polymer modification was possible,^[37, 56] even more reactive systems would be desirable. We therefore examined the bis(dimethylamino)diaryl system **1** (R = NMe₂), which has been used for the modification of buckminsterfullerene and carbon nanotube systems;^[76-80] no complete synthesis has been reported for this unstable compound, and we found careful modification of the generic synthesis was required to achieve a successful synthetic outcome, as indicated in Scheme 1. Thus, conversion of commercially available Michler's ketone (bis(4-(dimethylamino)phenyl)methanone) **3a** to the hydrazone **3b** and thence to the burgundy-coloured diazo derivative **3c** proceeded efficiently by oxidation with mercuric oxide under alkaline conditions. This

diazo compound is considerably less stable than other diaryl systems^[37] and needs to be kept at sub-ambient temperatures and to be used as rapidly after synthesis as practicable. In order to achieve material modification, diazo compound **3c** was dissolved in toluene or THF and applied to the polymer of interest; evaporation of the solvent gave physisorbed material, which was thermolysed (110°C) and washed with acetone, to give the chemically modified (since the unwanted side products from the insertion reaction such as the benzophenone and azine are both highly acetone soluble, modification of the surface properties must be due to chemisorption) materials **4a-t**, in a process which proceeded with loss of the diazo colouration, generally giving polymers which were yellow or pale yellow in colour (Table 1 and Scheme 1 (Stage 1)). Polymers applicable for this sequence included polystyrene, polypropylene, polyethylene, polyethyleneterephthalate, polyaramide (Kevlar), polyester, nylon, all of which may be in powder, bead, pellet, film and sheet form, as well as woven and non-woven fabrics. These activated materials were then further treated with commercially available Fast Black K Salt, leading to diazo coupling, giving coloured materials **5a-t** (Table 1 and Scheme 1 (Stage 2)); this gave direct visual indication of a successful surface modification sequence.^[56] This colour change was shown to be reversible with change of pH; thus, modified XAD **5a** after treatment with 5% NaHCO₃ gave material with a reduction in colour intensity (Figure 2) which could be restored to the original colour by washing with 5% HCl.

Table 1 and Scheme 1 near here

Figure 2 near here

Given the expected low level of loading, detailed physical characterisation of the surface-modified materials **4a-t** and **5a-t** was expected to be difficult, and a combination of techniques (FTIR, combustion analysis, XPS, and water contact angle) were applied to the most suitable substrates. Thus, the presence of aromatic nitro groups in samples **5f,o,q,s,t** was indicated in the FTIR analysis (at 1300-1390 and ca 1510-1520), and of ether links in **5d,s,t** (at 1060-1160cm⁻¹) (Table 2). Combustion analysis, which had previously permitted good (upper) estimates of surface loading,^[56] was less successful for all the materials in this work, presumably as a result of their low surface loading density when compared to the bulk of the substrate, and nitrogen levels for **4c,f,q** and **5c,f,q** were all found to be <0.1% (Table 1). However, for modified polystyrenes **4a** and **5a**, both of which possess a very high surface area, combustion analysis confirmed the presence of nitrogen at a level of 0.86 and 0.44%

respectively, consistent with the formation of the expected diazo function, and indicated a loading level of 0.045-0.31 mmol/g, that is 3.6×10^{12} to 3.3×10^{13} molecules/cm², assuming a surface area of 750 m²/g (manufacturer's data). This is about 10 times better than the corresponding system **1** (R = OMe),^[56] and reflects the higher reactivity of the bis(dimethylamino) system **1** (R = NMe₂). More successful was XPS analysis (Table 2), which confirmed the presence of low levels of N for polystyrenes **4a** and **5a**, polyethylenes **4d** and **5d** and PETs **4p** and **5p**; the N/C loading levels are lower than that expected for a complete monolayer of surface coverage, as might be expected. In the case of polytetrafluoroethylene **5t**, although chemical functionality could be detected by IR spectroscopy, the loading level was too low to be confirmed by XPS analysis. Following this modification of the polymer surface, which led to a functionally rich substrate from one which had been chemically inert, further modification to enhance the properties of the material becomes possible.

Table 2 near here

In view of the low loading of these materials, we sought both to obtain an estimate of the chemical group loading density by binding hydrogen peroxide and to examine these materials for antibacterial activity; hydrogen peroxide is both a common oxidising agent as well as a general purpose environmentally benign biocide. Although the formation of a urea-hydrogen peroxide complex is well known,^[81] the formation of strong hydrogen bonds with tertiary amines also occurs;^[82] these adducts readily decompose exothermically at only just above ambient temperature to give the corresponding tertiary amine oxides. Furthermore, tertiary amine oxides are capable of co-crystallisation with hydrogen peroxide to give 1:1 adducts, and these are sufficiently stable that heating is required for decomposition to occur.^[83] Although native tertiary amine oxide modified surfaces have been reported to inhibit protein adhesion,^[84] we were interested in exploiting this surface functionality which had been introduced onto the various polymer surfaces as described above to reversibly bind hydrogen peroxide. In an initial assessment, we treated modified materials **4a-s** with hydrogen peroxide to give materials **6a-s** (immersion of the MK modified materials in a 50% aqueous hydrogen peroxide solution was followed by filtration, washing with copious amounts of deionised water (around 1-1.5L per 100mg of modified material) in order to remove any physisorbed hydrogen peroxide). The oxidant load was determined by iodometric titration; highest loadings were observed for modified adsorbent polystyrene **6a** (almost 10⁻³ mol/g), reflecting its very high surface area, but for all the other materials, values were typically 10-20 fold lower (Table 3), as a result of their much lower surface area. Of interest is that, on

application of the starch and potassium iodide during the iodometric titration, the characteristic blue colouration was observed to be generated at the surface of the modified material, rather than in the bulk water media, confirming that the hydrogen peroxide present is bound to the surface of the modified material and does not leach into the surrounding aqueous media. Although an attempt to increase the peroxide loading density by coupling UHMWPE **4c** with diazonium salt **7b** gave material **8**, but which when converted to adduct **9** did not exhibit any higher loading than the base material. That these loading levels had potential application was suggested by incubation of modified XAD **6a**, UHMWPE **6c**, and PP **6f** with *S. aureus* overnight,^[85, 86] and these demonstrated substantial levels of antibacterial activity, with kill zones of 38, 37 and 22mm (a zone of 11mm is considered to be inactive) (Figure 3). That this bioactivity resulted from the combination of surface modification and the presence of hydrogen peroxide was established from appropriate controls; thus, modified polymers **4a**, **c** and **f** which were not treated with hydrogen peroxide, and unmodified polystyrene XAD-4, UHMWPE, and PP which were all treated with hydrogen peroxide followed by washing, displayed no biocidal activity in identical assays.

Table 3 and 4 near here, Figure 3 near here

With this library of diversely functionalised materials in hand, an assessment of the changes of macroscopic behaviour was made. Thus, water contact angle measurements of materials **4e,g,p** and **5e,g,p** gave the data shown in Table 4. PE showed only small changes in contact angle upon modification to **4e** and **5e**, PP showed no statistically significant change in contact angle on modification to **4g**, but an increase on further modification with Fast Black (**5g**), consistent with an increase in hydrophobicity. PET showed more complex behaviour, with initial modification to **4p** leading to lower contact angle, and but further modification to **5p** returning the contact angle much closer to the starting value of unmodified material. Generally only small changes of contact angle were observed, probably because of the low surface loading.

We also examined water permeability for suitable substrates; the time for complete entry of a 50 ul drop of coloured water into the modified material was measured (Table 5). Amongst the entry times for the blank materials, Tencel® cotton woven fabrics, and cotton wool were all easily penetrated by water (entry times < 10 sec) but the other materials (Hybond™, Kevlar™, viscose fabric) were much slower, being more hydrophobic. Of interest is that Stage 1 modification of materials with diazo **3c** made little difference to entry time for the polar substrates **4k, m, n**, but for the less polar materials

4i, **j**, and **l**, significant reduction in water entry times was observed, consistent with an increase in hydrophilicity. Further modification with Fast Black generally led to more complex effects, and either slowed (**5k**, **5j**, **5l**, **5n**), accelerated (**5i**, **5o**) or made no change (**5m**), to water entry times, relative to the blank control. Although this behaviour is complex, it is nonetheless clear that the newly introduced chemical functionality can have significant effects on the permeability of the modified material. It is known that for chemically modified cotton fibres, the penetration rate and wicking distance are both reduced; this is attributed to changes in capillary action as a result of filling of channels during the chemical modification leading to water repellancy.^[87]

Table 5 near here

The wetting behaviour of modified polyethylene film with a range of non-ionisable and ionisable organic functional groups at the polymer-water interface has been investigated in detail, and the relationship between functional group polarity and ionization with water contact angle established.^[88] Moreover, it has been suggested that simultaneous manipulation and exploitation of surface material properties at various length scales, from atomic level chemical properties to the nano- and micro scales, will permit the use of chemical polarity and surface topography effects to design and construct surfaces with controlled hydrophobicity/hydrophilicity.^[89] The work reported here-in indicates that polarity modification by introducing a diversity of chemical functional groups onto a wider range of materials using a simple chemical approach is feasible, and has the potential for a role in the development of novel surfaces with controlled wetting properties.

Conclusion

We have shown that a diverse range of materials may be readily modified using direct reaction with diarylcarbenes, giving material which displays modified wetting, colouration and permeability behaviour, at chemically significant levels which permit binding with hydrogen peroxide. The levels of chemical modification are such that bactericidal properties can be observed. Significantly, the list of applicable substrates includes low surface energy materials, and ones which are generally only considered to be functionalisable under high energy conditions. This approach offers the potential for the modification and control of surface properties of a wide range of materials using a simple chemical process, in which surface and bulk properties are manipulated independently. In particular, this provides a novel approach to azo-modified polymers, materials with useful properties.^[90]

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Experimental Section

4,4-Bis-*N,N*-dimethylaminobenzophenone hydrazone **3b**

A suspension of Michler's ketone **3a** (5.0 g, 19 mmol) in ethanol (10 ml) was treated with hydrazine hydrate (5.0 ml, 100 mmol). The resulting mixture was heated to a gentle reflux for 72h., cooled and concentrated *in vacuo*. The residue was diluted with 2-propanol (50 ml) and the resulting solid collected by filtration and dried *in vacuo* to yield **2** (4.8 g, 91 %) as a beige solid; m.p. 151-152°C; δ_{H} (d_6 -DMSO, 200 MHz) 2.89 (s, 2H, 2xNCH₃), 2.97 (s, 2H, 2xNCH₃), 5.81 (br s, 2H, NNH₂), 6.64 (d, 2H, $J = 8.9$ Hz, 3-, 5-*H*), 6.86 (d, 2H, $J = 8.8$ Hz, 3'-, 5'-*H*), 7.05 (d, 2H, $J = 8.8$ Hz, 2'-, 6'-*H*), 7.22 (d, 2H, $J = 8.9$ Hz, 2-, 6-*H*); δ_{C} (d_6 -DMSO, 200 MHz) 40.9 (4x NCH₃), 112.6 (3-, 5-C), 113.2 (3'-, 5'-C), 121.1 (1-C), 127.8 (2-, 6-C), 128.7 (1'-C), 130.3 (2'-, 6'-C), 150.6 (Ar₂C=NNH₂); ν_{max} 1626, 1545, 1350, 1180 cm⁻¹; ms 283 ([M+H]⁺, 100%), 305 ([M+Na]⁺, 10%).

Bis-4,4'-*N,N*-Dimethylaniline diazomethane **3c**

To a vigorously stirred mixture of yellow mercury oxide (0.46 g, 2.1 mmol), sodium sulfate (0.35 g, 2.5 mmol) and sat. potassium hydroxide in ethanol (3 ml) was added a solution of **3b** (0.5 g, 1.8 mmol) in tetrahydrofuran (10 ml). The mixture was stirred for 18h. in the dark, then filtered through a pad of celite. The filtrate was collected and concentrated *in vacuo* to yield **3c** (0.5 g, 100 %) as a dark green solid which required storage at sub-ambient temperature to avoid decomposition; m.p. 94 °C (dec.); δ_{H} (CDCl₃, 200 MHz) 2.96 (s, 12H, 4xNCH₃), 6.81 (d, 4H, $J = 6.8$ Hz, 3-, 3'-, 5-, 5'-*H*), 7.17 (d, 4H, $J =$

6.8 Hz, 2-, 2'-, 6-, 6'-H); δ_C (CDCl₃, 200 MHz) 149.1 (4-, 4'-C), 132.7 (1-, 1'-C), 126.8 (3-, 3'-, 5-, 5'-C), 114.0 (2-, 2'-, 6-, 6'-C), 41.1 (4xNCH₃); ν_{\max} 2020 (Ar₂C=N⁺=N⁻), 1606, 1519, 1356 cm⁻¹.

Functionalisation of polymer beads / powder / fabric (4a-t) with Diazomethane 3c

To a solution of diazomethane **3c** in either toluene or tetrahydrofuran (10 ml) (Table 1) was added the required polymer and the mixture concentrated *in vacuo*. The polymer was collected and heated *in vacuo* to 110°C for 15 minutes. The resulting solid was Soxhlet extracted with acetone for 6h and the solid collected and dried to yield the functionalised polymer **4a-t** (Scheme 1 and Table 1).

Fast Black dyed polymers 5a-t

Polymers **4a-t** were dyed by immersing the functionalised polymer in a 0.1M solution of Fast Black K salt in acetone for 18h. The polymer was then collected by filtration and washed with acetone to furnish the corresponding azopolymers **5a-t** (Scheme 1 and Tables 1 and 2).

4-N,N-Dimethylaminobenzene diazonium chloride 7b

To an ice cold solution of *N,N*-dimethyl-*p*-phenylene diamine **7a** (1.0 g, 7.3 mmol) in ethanol (10 ml) was added concentrated hydrochloric acid (0.72 ml, 7.3 mmol) and isoamyl nitrite (1.6 ml, 12 mmol). The mixture was stirred for 10 minutes, then diluted with diethyl ether (50 ml). The resulting solid was filtered and washed with diethyl ether. Drying *in vacuo* yielded **7b** (1.1g, 77%) as a dark green solid. δ_H (d₆-DMSO, 200 MHz) 3.29 (s, 6H, 2xNCH₃), 7.10 (d, 2H, *J* = 7.8 Hz, 3-, 5-H), 8.30 (d, 2H, *J* = 7.8 Hz, 2-, 6-H); δ_C (d₆-DMSO, 200 MHz) 157.0 (4-C), 134.9 (2-, 6-C), 114.8 (3-, 5-C), 89.91 (1-C), 41.4 (2xNCH₃).

4-N,N-Dimethylamino benzene diazonium dyed UHMWPE 8

UHMWPE **4c** was immersed in a 1M solution of **7b** in methanol for 18h (Scheme 2). The polymer was collected by filtration and washed with acetone, water and methanol to furnish the corresponding diazo polymer **8**.

Binding of hydrogen peroxide to functionalised polymers (6a-s, 9)

To a flask containing hydrogen peroxide (50 % aqueous solution, 10 ml) was added the functionalised polymer (**4a-p**, **r-t** or **8**) and the mixture allowed to stand at room temperature in the dark for 16h. The modified polymers were isolated by filtration and the solid washed with water (1-1.5l) to yield the polymer hydrogen peroxide adducts **6a-s** or **9** (Scheme 1 and Tables 1 and 2).

Method for determination of oxidant loading.

A sample of the required polymer was suspended in 50% aqueous hydrogen peroxide for 18h. The polymer was filtered and washed with water, collected and treated with solution of 10% aqueous potassium iodide (0.1 M) in acetic acid. After standing for 5 minutes a 1% aqueous starch solution was added and the suspension left to stand for 1h. The resulting dark blue coloured solution was titrated with sodium thiosulfate until the colourless endpoint. The mixture was left for an hour and any further blue coloration of the solution was further titrated with sodium thiosulfate until no further colour persisted (Table 3).

Method for Biotesting.^[85, 86] Microbiological assays were performed by the hole- plate method with the test organism *Staphylococcus aureus* N.C.T.C. 6571. An agar plate inoculated with *S. aureus* was punched with 10mm wells. To these wells was added 20µl of molten agar. When set, the polymer sample was added to the well so that an even thin layer of polymer was produced. The well was then sealed with a further 50µl of molten agar, the plate incubated overnight at 37°C and the zones measured (Figure 3).

Supporting Information

Videos of wetting behaviour for various substrates are available from the author.

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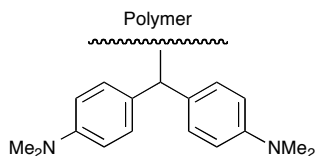
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Post-Polymerization Modification of Materials using Diaryldiazomethanes: Changes to Surface Macroscopic Properties

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Polymer surface modification can be used for the modification of low surface energy materials. This can be used for the control of macroscopic behaviour, depending on the identity of the chemical functional group introduced at the surface. The method has been exemplified for the modification of wetting behaviour and the introduction of bactericidal properties.



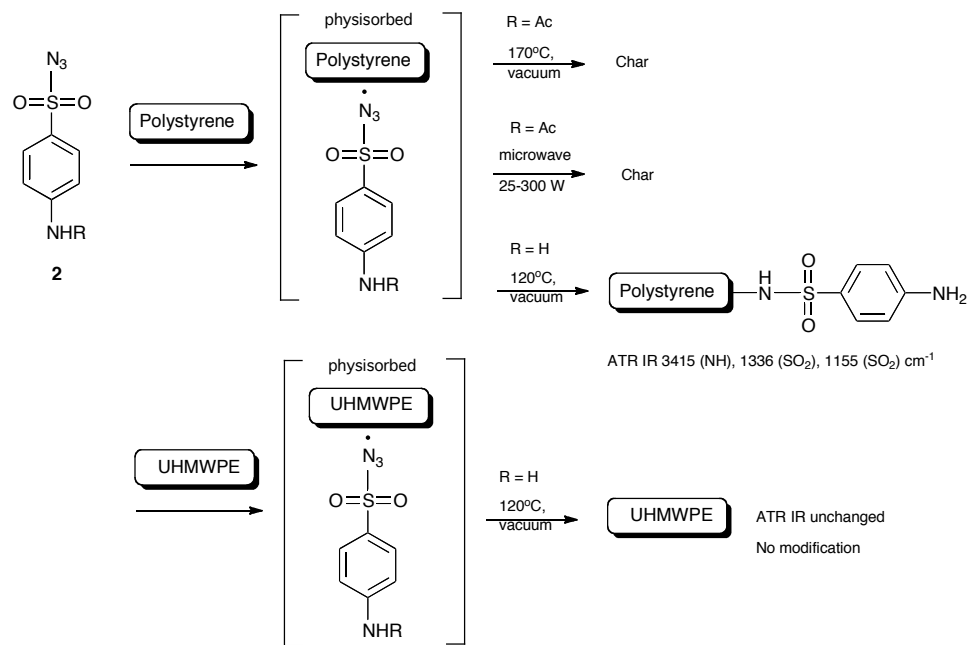
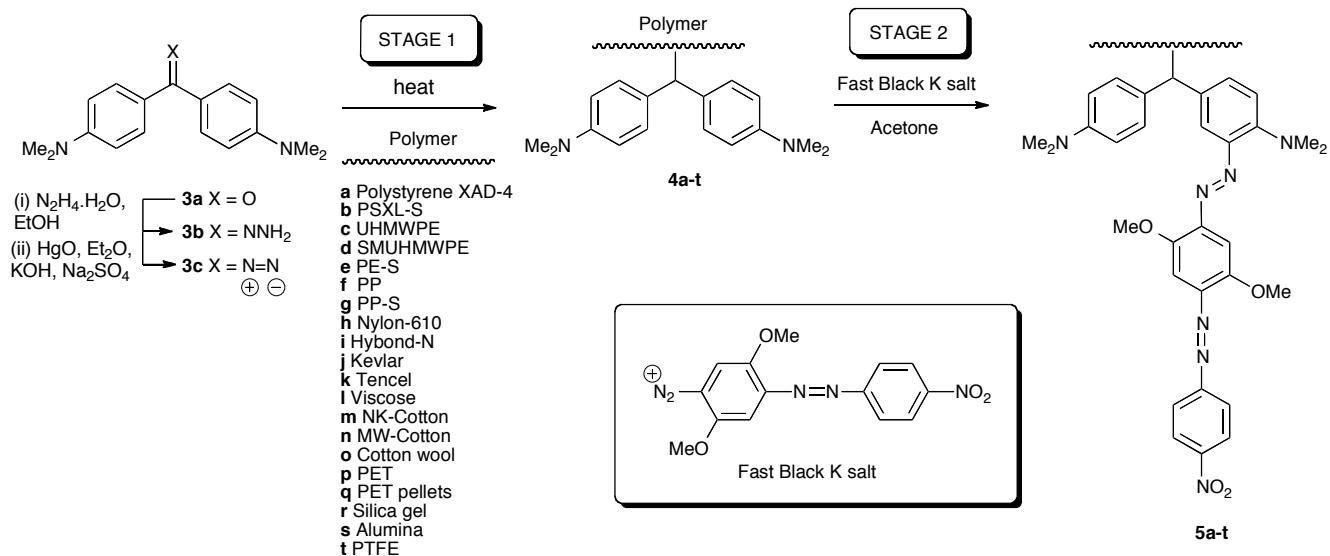
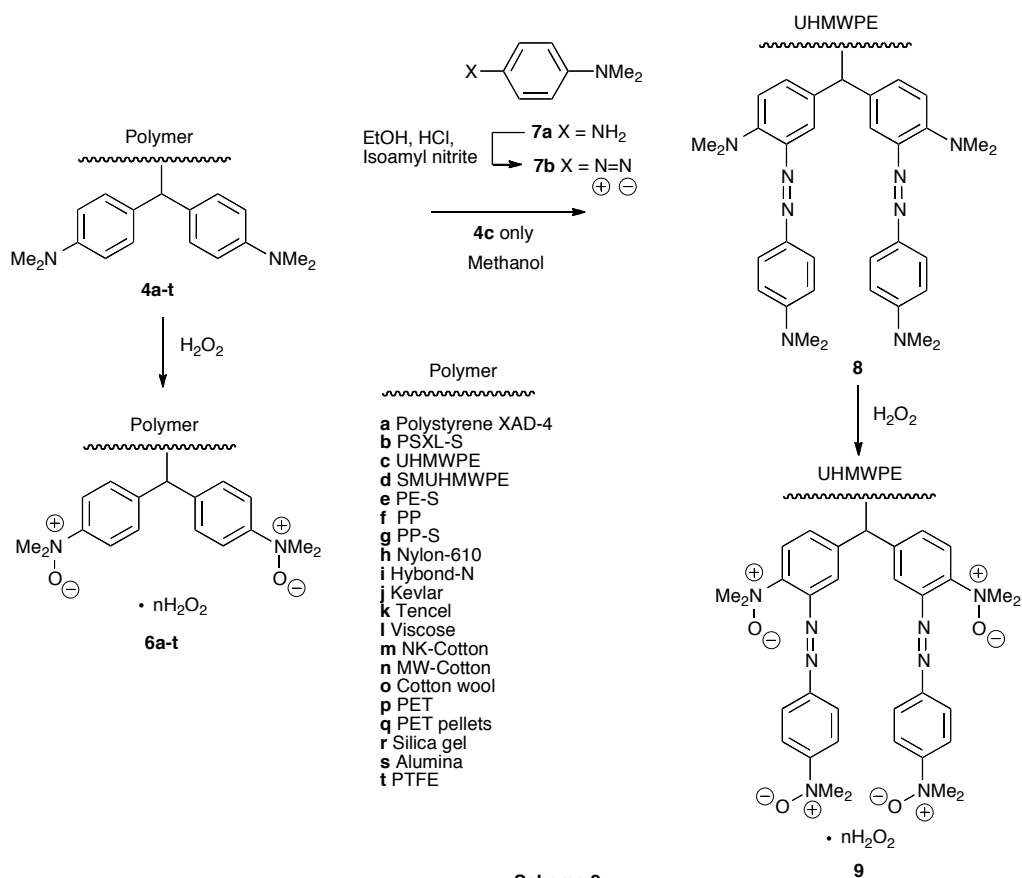


Figure 1


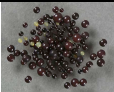






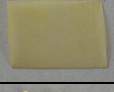


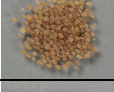
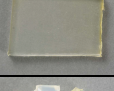
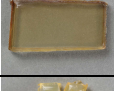



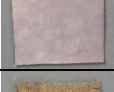


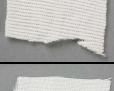

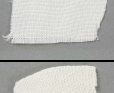





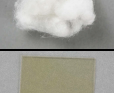













Scheme 1



Scheme 2

Table 1: Functionalised polymers prepared according to the protocol of Scheme 1.

Polymer	Form	Ratio ^a	Solvent ^b	Stage 1		Stage 2	
				Sample	Colour	Sample	Colour
XAD-4 ^b	Beads	1:1	THF	4a		5a	
PSXL-S	Sheet	1:1	THF	4b		5b	
UHMWPE	Powder	1:1	THF	4c		5c	
SMUHMWPE	Powder	1:1	THF	4d		5d	
PE-S	Film	1:2	Toluene	4e		5e	
PP	Beads	1:1	Toluene	4f		5f	
PP-S	Sheet	1:2	THF	4g		5g	
Nylon-610	Granules	1:4	THF	4h		5h	
Hybond-N	Sheet	1:1	THF	4i		5i	
Kevlar	Fabric	1:1	THF	4j		5j	
Tencel	Fabric	1:2	THF	4k		5k	
Viscose	Fabric	1:2	THF	4l		5l	
NK-Cotton	Fabric	1:2	THF	4m		5m	
MW-Cotton	Fabric	1:2	THF	4n		5n	
Cotton wool	Fibre	1:1	THF	4o		5o	
PET	Sheet	1:4	THF	4p		5p	

PET	Pellets	1:4	THF	4q		5q	
Silica Gel	Powder	1:1	THF	4r		5r	
Alumina	Powder	1:1	THF	4s		5s	
PTFE	Beads	1:1	Toluene	4t		5t	

^a Weight ratio of diazomethane to polymer used during functionalisation step. ^b Solvent used for diazo absorption onto the polymer; THF = tetrahydrofuran.

Table 2: Characterisation data for selected modified polymers **4** and **5**.

Polymer	ATR-IR (cm ⁻¹) ^a	Combustion Analysis/wt % (mmolg ⁻¹)	XPS Analysis ^b
4a	-	N 0.86 (0.31)	C ₁₈ H ₂₁ N ₂ Expected: N/C = 11.1% Found: N/C = 4.10%
4c	-	N < 0.1 (<0.036)	C ₁₈ H ₂₁ N ₂ No N detected
4d	-	-	C ₁₈ H ₂₁ N ₂ Expected: N/C = 11.1% Found: N/C = 3.40%
4f	-	N < 0.1 (<0.036)	C ₁₈ H ₂₁ N ₂ No N detected
4p	-	-	C ₁₈ H ₂₁ N ₂ Expected: N/C = 11.1% Found: N/C = 1.12%
4q	-	N < 0.1 (<0.036)	-
4t	-	-	C ₁₈ H ₂₁ N ₂ No N detected
5a	-	N 0.44 (0.045)	C ₃₂ H ₃₂ N ₇ O ₄ Expected: N/C = 21.9% Found: N/C = 4.10%
5c	-	N < 0.1(<0.010)	C ₃₂ H ₃₂ N ₇ O ₄ No N detected
5d	1160	-	C ₃₂ H ₃₂ N ₇ O ₄ Expected: N/C = 21.9% Found: N/C = 2.78%
5f	1290,1327	N < 0.1 (<0.010)	C ₃₂ H ₃₂ N ₇ O ₄ No N detected
5h	1192,1260	-	-
5k	1261	-	-
5o	1510	-	-
5p	-	-	C ₃₂ H ₃₂ N ₇ O ₄ Expected: N/C = 21.9% Found: N/C = 4.37%
5q	1386	N < 0.1 (<0.010)	-
5s	1103, 1342	-	-
5t	1065, 1355, 1519, 2800	-	C ₃₂ H ₃₂ N ₇ O ₄ No N detected

^a Blank polystyrene exhibited characteristic absorbances in the region of 2929, 1602, 1465, 1443, 989, 902 cm⁻¹, in keeping with literature data (See Ref. 25); ^b Expected values calculated from molecular formulae assuming a surface monolayer of carbene insertion product.

Table 3: Hydrogen peroxide loading on functionalised polymers **6a-s** and **9** prepared according to the protocol of Scheme 2.

Polymer	Form	Sample	Hydrogen Peroxide Loading/ mol g ⁻¹
XAD-4 ^b	Beads	6a	7.9x10 ⁻⁴
PSXL-S	Sheet	6b	1.2x10 ⁻⁴
UHMWPE	Powder	6c	2.6x10 ⁻⁴
SMUHMWPE	Powder	6d	8.9x10 ⁻⁵
PE-S	Film	6e	2.6x10 ⁻⁵
PP	Pellets	6f	1.1x10 ⁻⁵
PP-S	Sheet	6g	1.2x10 ⁻⁶
Nylon-610	Granules	6h	1.5x10 ⁻⁴
Hybond TM	Sheet	6i	6.6x10 ⁻⁵
Kevlar TM	Fabric	6j	5.3x10 ⁻⁵
Tencel®	Fabric	6k	2.7x10 ⁻⁵
Viscose	Fabric	6l	1.7x10 ⁻⁵
Cotton-NK	Fabric	6m	2.5x10 ⁻⁵
Cotton-MW	Fabric	6n	4.3x10 ⁻⁶
Cotton wool	Fibre	6o	3.2x10 ⁻⁶
PET	Granules	6q	4.3x10 ⁻⁴
Silica Gel	Powder	6r	2.4x10 ⁻⁶
Alumina	Powder	6s	5.9x10 ⁻⁶
UHMWPE	Powder	9	2.3x10 ⁻⁴

Table 4: Water contact angle (WCA/°) for modified polymer films **4e,g,p** and **5e,g,p**.

Material	Blank Material WCA	Blank + Diazo 3c		Blank + Diazo 3c + Fast Black	
		Sample	WCA	Sample	WCA
PE	94.4±2.4	4e	99.2±2.9	5e	93.6±1.9
PPP	97.1±2.3	4g	97.6±0.9	5g	101.5±1.1
PET	84.1±1.7	4p	77.9±9.7	5p	83.1±2.5

Table 5: Water entry times for selected modified polymers.

Material		Material (Stage 1)		Material (Stage 2)	
Blank	Entry Time/sec	Sample	Entry Time/sec	Sample	Entry Time/sec
Tencel®	<1	4k	<1	5k	22 ± 0.5
Cotton-NK	<1	4m	<1	5m	<1
Cotton-MW	1 ± 0.5	4n	1 ± 0.5	5n	5 ± 0.5
Cotton wool	14 ± 0.5	4o	6 ± 0.5	5o	<1
Hybond TM	>24	4i	14 ± 0.5	5i	8 ± 0.5

Kevlar™	>27	4j	4 ± 0.5	5j	>36
Viscose	76	4l	5 ± 0.5	5l	12 ± 0.5



Figure 2. Material **5a** after (a) washing with 5% HCl; (b) washing with 5% NaHCO₃; (c) washing with 5% HCl.

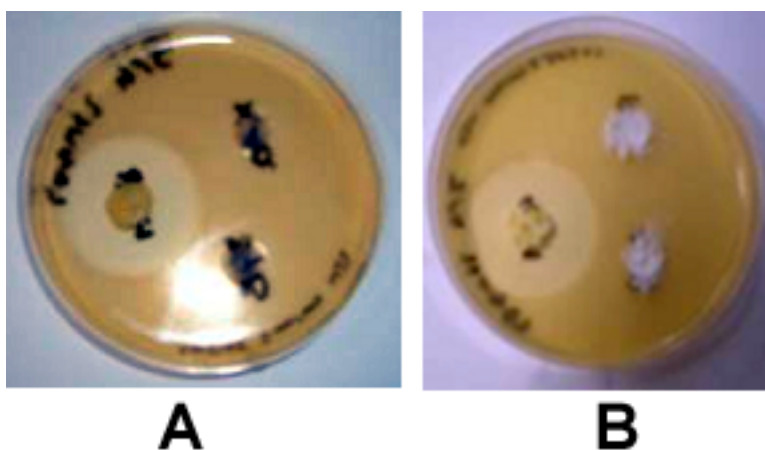


Figure 3. Clockwise from top:(A) blank XAD-4+H₂O₂, **4a**, **6a**; (B) Clockwise from top blank UHMWPE+H₂O₂, **4c**, **6c**.