

Functionalised Polymers By Covalent Surface Modification

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Abstract

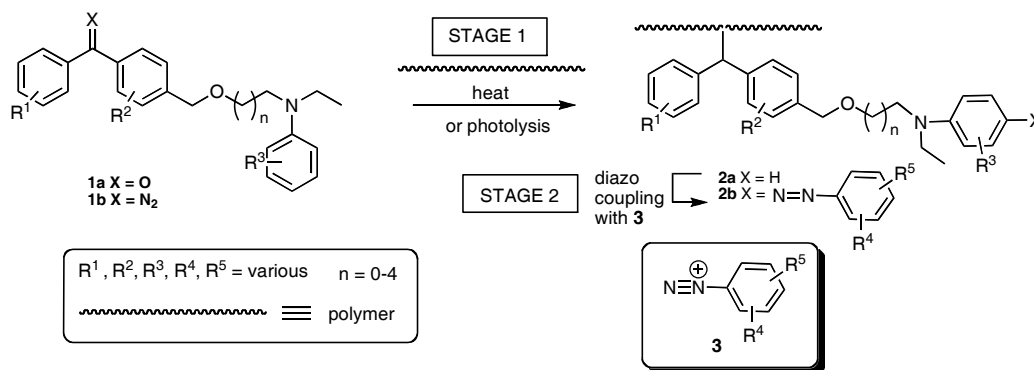
We report here a chemical treatment which permits the direct modification of the surface properties of a polymer, but without changing its bulk properties. The method relies upon the insertion of diarylcarbenes into a variety of material types, leading to irreversible carbon-carbon bond formation; depending on the substituents on the carbene, it is possible to incorporate an array of chemical function, including hydrocarbon and alkoxyether chains, and carboxylic acid, sulfonic acid, diazo, urea and phosphonate residues. It is versatile and simple to execute, and capable of immediate adaptation to dip or spray processes. We have demonstrated that it can be used for the manipulation of the surface chromophoric, biocidal, biocompatibility, hydrophobicity/philicity, oleophobicity/philicity and adhesive characteristics of polymers, for a very broad range of substrate types, in particular low surface energy organic polymers such as polypropylene, polyimide and polyester, as well as other materials such as silica, glass and diamond. This method offers the opportunity for tailoring the surface properties of diverse polymers for a wide variety of applications, including electronics, medical devices, healthcare and security.

The use of advanced materials with properties carefully tailored to the desired specific application is critical in many modern products. These properties can rarely be achieved with one homogeneous material, but are readily available by coating or laminating one material onto another, giving a composite whose properties combine the desired properties of each component. Of particular importance is the achievement of nanolayer surface modifications, since this changes the surface characteristics of the polymer, but without changing the bulk (e.g. mechanical strength) properties of the substrate. Although composite materials possessing hybrid properties find wide application, frequently as components which are critical for successful function of a device or product, they can be expensive to produce and suffer from limited functional lifetimes. Polymers are well known for their wide availability and low cost, and have

been used for a myriad of product applications, but their surface properties are often less than optimal for the desired application; adhesion between dissimilar materials is an important example. It would be of substantial value if a method for the reliable modification of a polymer surface were available so that novel surface characteristics could be introduced. In particular, it would be highly advantageous to be able to manipulate macroscopic properties and surface characteristics independently, so as to maintain favoured bulk properties of the polymer, but to adjust surface properties to suit a given application, and this approach has received some attention;¹⁻³ common methods include abrasion and sand blasting, chemical treatment, and surface activation. Amongst the latter, a diversity of techniques has been developed²: atom bombardment,^{4, 5} plasma treatment,⁶⁻¹⁵ ion implantation,¹⁶ laser treatment,¹⁷⁻¹⁹ electron beam,²⁰ and welding²¹ are all well known. Although effective and widely used in industrial applications, the disadvantage with many of these techniques can be their high operating cost or large infrastructure requirements. Polymer surface modification has been reported using chemical surface treatments; for example, cured epoxy polymers containing reactive hydroxyl groups was chemically modified with trichlorotriazine followed by either iminodiacetic acid or imidazole, in order to enhance the electrochemical deposition of copper.²²⁻²⁴

We have shown that highly reactive diarylmethylcarbene intermediates could be easily generated under thermolytic conditions, and used for the modification of a variety of organic and inorganic polymers, to introduce a range of surface activity, exemplified by the introduction of colour.²⁵⁻²⁸ The protocol uses a two step process (Scheme 1), involving firstly, pre-activation of the polymer by carbene insertion (Stage 1, Scheme 1) using the reagent **1b**. The structure of this reagent has been carefully optimised, and consists of a diaryldiazo unit, a spacer unit and an electron rich aminoaryl unit, each of which play an essential function in the process, as demonstrated by the careful use of controls.²⁸ The diazo compound **1b** is easily available from ketone **1a** in a simple two-step sequence (hydrazone formation followed by oxidation). Adsorption of diazo compound **1b** onto a polymer substrate is followed by heating (ca. 150°C), which generates a carbene *in situ*, whereupon insertion to the polymer occurs, and the product **2a** can be isolated free from any by-products by a simple washing procedure. The attachment of the carbene to the polymer is *via* insertion into a covalent bond, probably a C-H bond in most cases, in which case a new carbon-carbon bond is formed. When this occurs, the surface bound residue will therefore be hydrolysis insensitive, providing irreversible polymer surface modification. Treatment of the modified polymer **2a** (Stage 2, Scheme 1) with any of a wide range of commercially available diazonium salts **3** in aqueous solution gives the highly coloured products

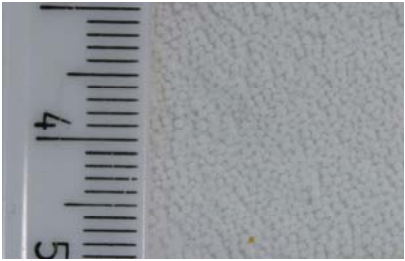
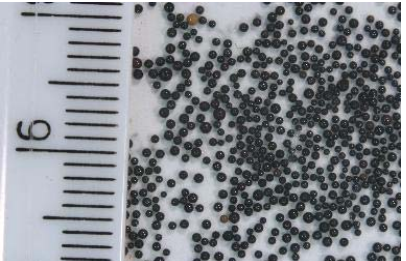
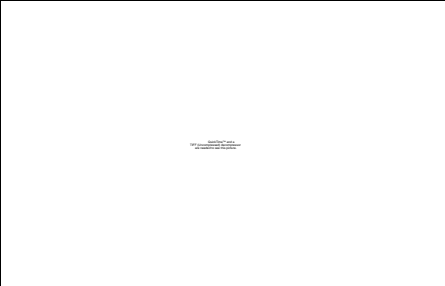
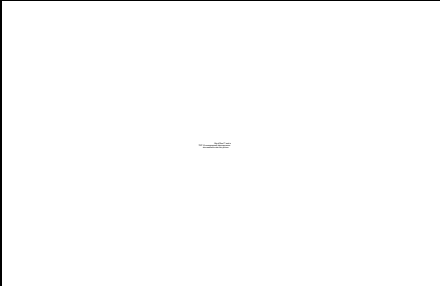
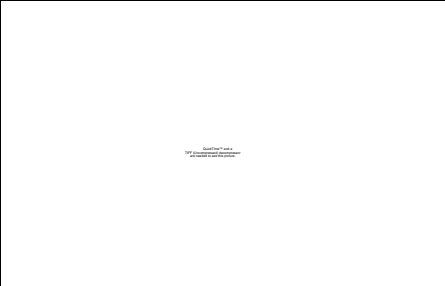
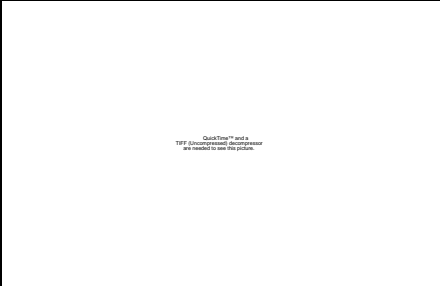


2b, which are isolated by a simple washing procedure. This second step depends crucially on the presence of the electron-rich aminophenyl side-chain in **2a**, which after coupling with the diazonium salts **3**, generates highly-coloured surface-modified polymers whose absorption characteristics depend on the choice of diazonium salt **3** used in Stage 2. In order to demonstrate the substrate flexibility of this process, we have been able to dye chemically diverse natural and synthetic polymers, and in the most successful cases to produce intense red, yellow, brown, orange and blue colours; for example, appropriate selection of diazonium salt **3** gives a spectrum of colour (Table 1). The methodology is therefore intrinsically flexible, by suitable modification of the reagents used in the Stage 2, permitting the introduction of useful functionality on to what would otherwise be considered to be inert materials, by a chemically irreversible modification the polymer, as opposed to a physical dispersion. A modification of this approach, in which the activating amino group is incorporated directly into the diarylmethyl residue, has been found to permit the colouring by diazo coupling of a wider variety of materials, significantly including low surface energy polymers.²⁹

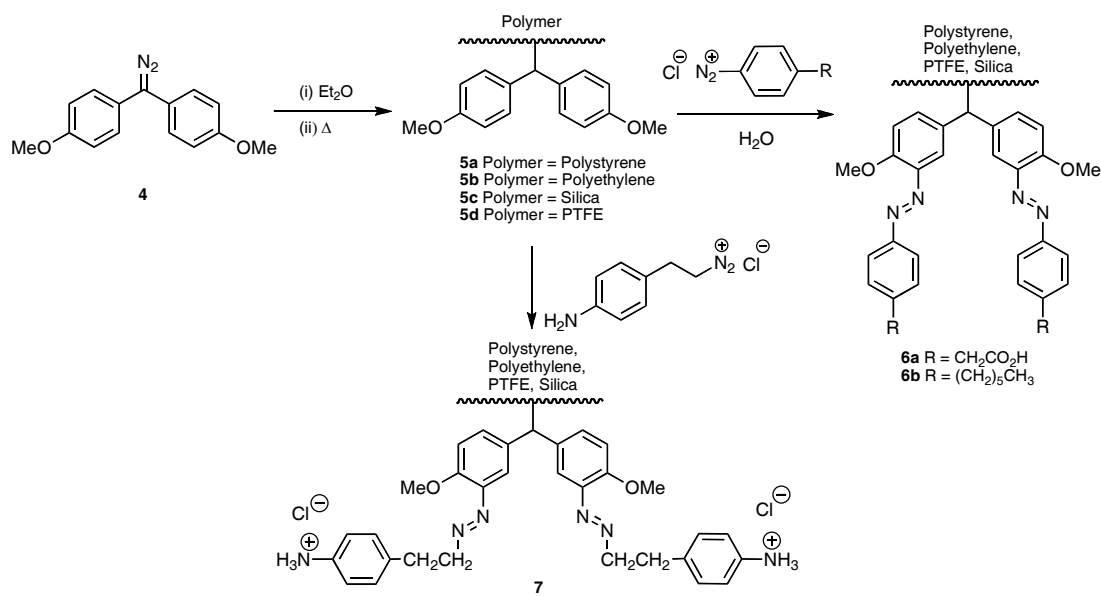


Furthermore, we have shown that the required activation step on polystyrene, polythene and polytetrafluoroethylene can not only be conducted under thermal conditions, but also under photolytic conditions (low or medium pressure mercury lamp), a method which is more suited to thermally sensitive materials such as PS50 and PES100. This offers the potential for direct application in online processes.

Examination of polystyrene modified as shown in Scheme 2 has been used to determine in more detail the nature of the surface modification; ATR IR showed resonances consistent with presence of the expected functionality and combustion analysis both demonstrated the presence of nitrogen, indicative of the formation of the azo link, and quantification showed a loading level of 0.18 mmol g^{-1} or $15 \times 10^{12} \text{ molecules cm}^{-2}$ for the most favourable case when $\text{R} = \text{COOH}$. This gives a surface loading of about 9%.

Table 1: Colouration of Organic, Inorganic and Natural materials after application of Stages 1 and 2 of the protocol shown in Scheme 1

	Blank polymer	Modified polymer
Polystyrene		
Hybond Nylon		
Controlled Pore Glass		
Woven Cotton		

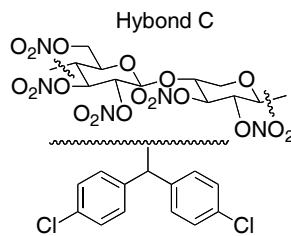


Scheme 2

Table 3: Surface characterisation data for Polystyrene modified as shown in Scheme 1

Material	IR (cm ⁻¹)	Combustion Analysis (% N)
Blank	1605, 1510, 1245, 1170, 1035	Nil
R = COOH	1605, 1510, 1245, 1170, 1035	0.18 mmolg ⁻¹ 15 x 10 ¹² moleculescm ⁻²
R = Hexyl	1605, 1510, 1245, 1170, 1035	0.036 mmolg ⁻¹ 3 x 10 ¹² moleculescm ⁻²
R = Amine	1650, 1530	0.036 mmolg ⁻¹ 3 x 10 ¹² moleculescm ⁻²

Examination of the surface of Hybond C, a nitrocellulose material, after it has been modified as shown in Figure 1, using XPS demonstrated the presence of C-O and C-C bonds, and Cl itself, as expected from the modification.



Blank Hybond C (C1s at 280 eV)

Modified Hybond C (C1s at 280 eV)

Modified Hybond C (Cl2p at 198 eV)

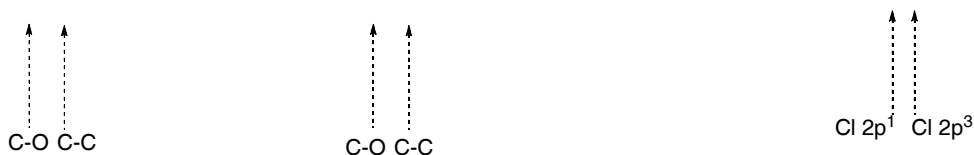


Figure 1

Having demonstrated the application of this concept for the introduction of colour to a series of organic and inorganic polymeric materials, and that this arose by surface modification in the expected way, we extended the approach to incorporate valuable function, including biocidal, biocompatible and fluorescence activity onto otherwise inert materials.

The introduction of biocidal function, that is, the capacity of a polymeric material to kill bacteria on contact, is of particular interest for a wide range of application. Since reactive oxygen species are capable of exerting antibacterial activity^{30, 31} and antibodies produce hydrogen peroxide when irradiated in the presence of oxygen, exerting an immediate and effective bactericidal activity,^{32, 33} a biocidal polymer which released hydrogen peroxide would mimic some natural antibacterial processes, and might represent an alternative solution to the problem of antifouling of material surfaces. We found that the modification of polystyrene as shown in Scheme 3 readily enabled the introduction of urea groups, and that this polymer was capable of adsorbing hydrogen peroxide. The modified polystyrene bound hydrogen peroxide at a level of about 8.42×10^{-5} mol/g polymer (Table 5). This modified polystyrene material was found to exhibit strong antibacterial activity against *S. aureus* after overnight incubation.

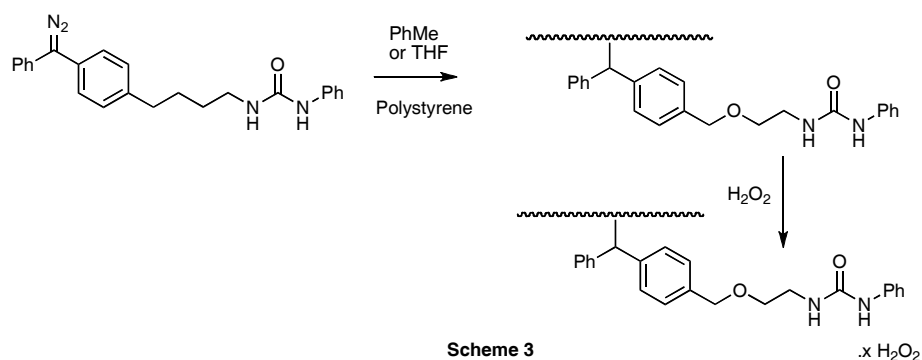


Table 5: Peroxide loading on Polystyrene after application of Stages 1 and 2 of the protocol shown in Scheme 3

Time Interval / h	H ₂ O ₂ Loading (mol/g polymer)
0	8.42 x 10 ⁻⁵
24	8.01 x 10 ⁻⁵
48	9.61 x 10 ⁻⁵
72	6.44 x 10 ⁻⁵
96	4.13 x 10 ⁻⁵

In addition to the biocidal activity indicated above, we have also shown that enhanced biocompatibility is also possible, again by appropriate surface modification. We used a phosphonate-substituted diaryldiazo compound to modify polystyrene (Scheme 4). This polymer was tested for biocompatibility and cytotoxicity against the MG63 human osteosarcoma cell line, and in the case of Hybond-modified membrane, the 5 and 8 day growth relative to the control was lower (40 and 55% respectively) but after 13 days this had recovered to a level similar to the control (108%). The calcium phosphonate-modified Hybond membrane gave similar 5 day growth (45% relative to the control), but this was followed by equivalent (99%) and then significantly higher (128%) level of cell proliferation at 8 and 13 days respectively (Table 6).

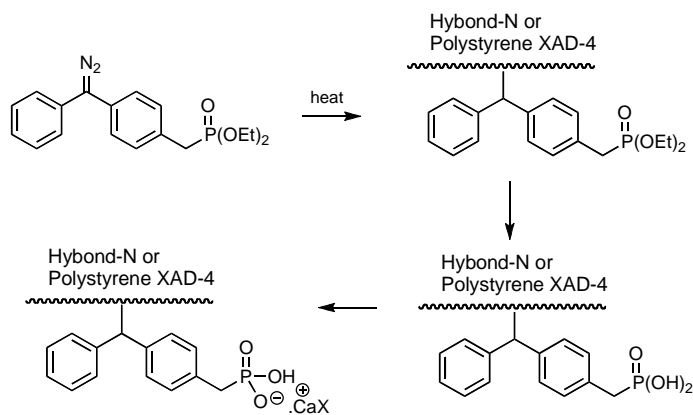
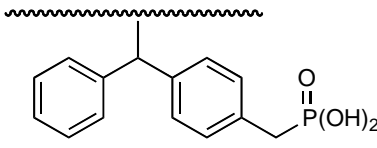
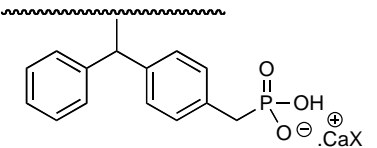


Table 6: Growth of Human MG63 osteosarcoma cell line after application of the protocol shown in Scheme 4 to Hybond-N membrane and Polystyrene bead polymers

Growth relative to control		
Hybond-N	Day 5: 40% Day 8: 55% Day 13: 108%	Day 5: 45% Day 8: 99% Day 13: 128%
Polystyrene	Day 13: 287%	Day 13: 328%

In recent years, it has been demonstrated that diamond is an excellent platform for chemical sensors, since it has exceptional electrical conducting, hardness, thermal and electrical conductivity, optical transparency, and chemical inertness.³⁴ Diverse applications of surface modified CVD diamond (chemical vapour deposition) and ND (nanocrystalline diamond) are beginning to emerge, and these include modified diamond surfaces suitable for (bio)chemical sensing³⁵⁻³⁸ and electronic applications.³⁹⁻⁴¹ Despite this potential, reliable and versatile modification of diamond and carbon nanotubes is still being developed,⁴² and typically relies upon electrochemical oxidation to provide reactive functionality on the diamond surface, although radical, electrochemical, photochemically-mediated processes are emerging. Application of our surface modification approach was therefore of interest. To this end, we treated CVD diamond according to Scheme 5, and in the final stage introduced fluorescein as the

fluorophore.⁸⁶ The choice of diamond as a substrate enabled tracking of the surface structure by XPS; after heating of the sample to generate the reactive carbene and reduction with sodium sulphide, XPS analysis clearly indicated the presence of signals derived from the reduced amine function. Coupling with fluorescein isocyanate gave diamond in which fluorescent sections were clearly visible on the surface.

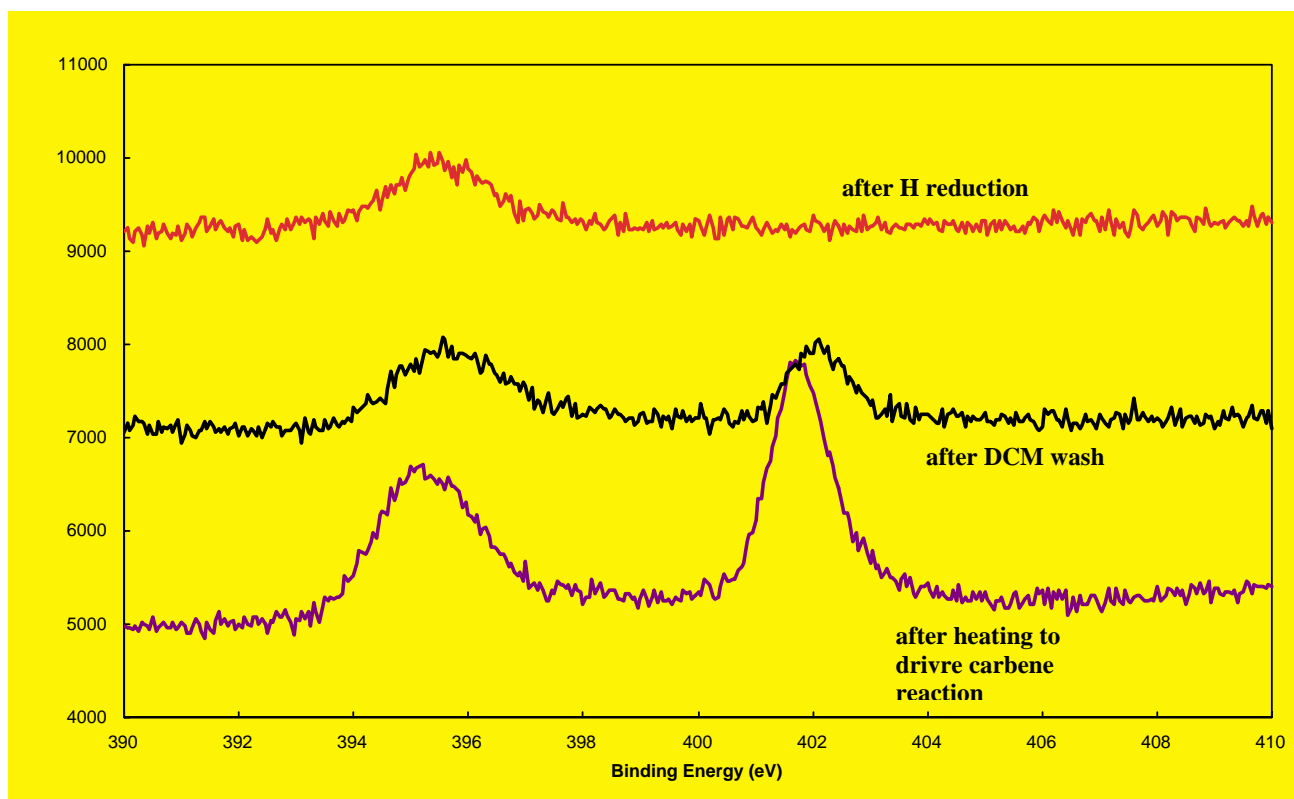
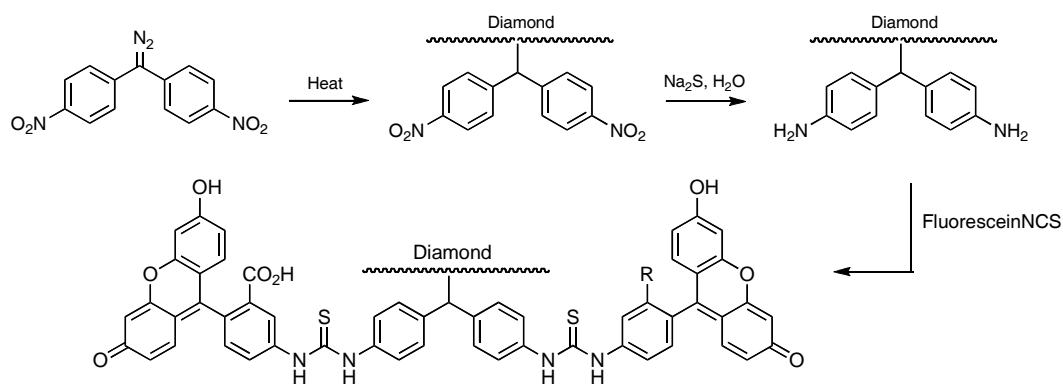


Figure 3: XPS examination of the modified CVD diamond.

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