Chemical modification of materials by reaction with diaryl diazomethanes

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ABSTRACT

A direct chemical method for the surface modification of materials (polystyrene, silica, silicon) by reaction with diaryl diazomethanes, and spectroscopic evidence indicative of modification, is presented.

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The control of surface properties of materials independently of their bulk properties, suitable for diverse applications, presents a significant challenge. Although elegant solutions for the chemical modification of specific substrates exist, for example, by self-assembled monolayer formation on metal surfaces or chlorosilane modification of oxides,[1] or for the introduction of specific properties onto a surface, for example, of bioactive compounds into putative biomaterials,[2] a major limitation is the range of material substrates which are suitable for surface modification. The chemical inertness of a large number of polymeric materials, which is advantageous or even an absolute requirement in many applications, is also a significant impediment when it comes to the chemical modification of surface properties. Thus, a simple but versatile and efficient chemical method for the direct surface modification of a wide range of materials that enables tailored control of their surface properties without compromise of bulk properties would be highly desirable.

We recently reported a highly novel strategy for the modification of the surface of materials, originally for the alteration of their colour,[3,4] but have subsequently shown that this approach can be applied for the introduction of biocidal[5] and fluorescence activity,[6] and biocompatibility.[7] The method relies upon the generation of carbenes by thermolytic or photolytic methods and their irreversible attachment by insertion into available surface chemical groups; a similar approach has recently been reported by Hayes.[8–10] Significantly, this approach permits the possibility of a post-polymerisation step for control of surface properties, but without changing the bulk characteristics of the underlying substrate, and since the applicable substrates may be both organic and inorganic polymers and materials, it is potentially very wide in scope. We have not as yet examined in detail the nature of the surface modification, and report here a study of several substrate types, which have been modified by the introduction of carboxylate, amine and alkyl substituents, using combustion analysis,
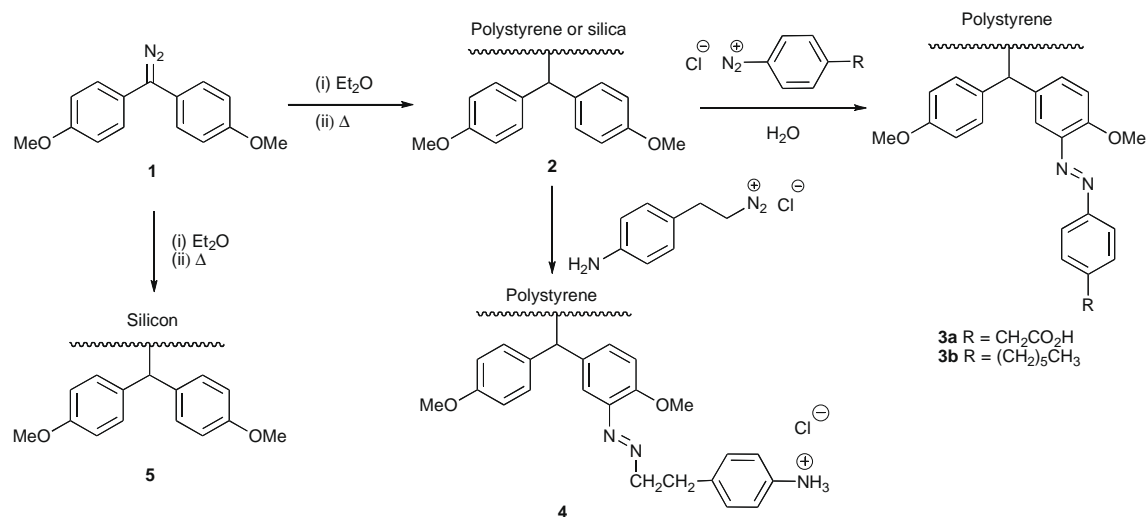
attenuated total reflection (ATR) IR, reflectance UV and X-ray photoelectron spectroscopy (XPS), giving some direct information concerning the chemical and physical nature of the modified substrates.

In order to enable a general approach suitable for the introduction of carboxylate, amine and alkyl substituents onto as wide a range of substrates as possible, we used the known 4,4′-(diazomethylene)bis(methoxybenzene) **1** as the carbene precursor (Scheme 1),[11] since preliminary experiments had indicated that the derived carbene had a high level of reactivity suitable for insertion onto diverse material types. Polystyrene (PS), silica and silicon were found to be particularly useful as substrates, since these materials have a high surface area and are suitable for downstream analysis.[12] The modified material **2** thus obtained was activated to further aromatic substitution, suitable for azo coupling with differently substituted diazonium salts[13] to give the required modified materials **3a,b** and **4**.[14] These materials were examined using a combination of surface analysis techniques, and the results are included in Tables 1 and 2.

Combustion analysis confirmed the presence of nitrogen at a level of 0.1–0.5% (Table 1), consistent with the formation of the expected diazo function, and indicated a loading level of 0.036–0.18 mmol/g, that is, 1.98×10^{12} to 1.5×10^{13} molecules/cm^2, assuming a surface area of 750 m^2/g (manufacturer's data). This compares to a phosphate-modified material which we have previously reported using a related strategy with a loading of 0.37 mmol/g,[7] and commercially available Wang resin which is typically supplied at loadings in the range 0.6–2.0 mmol/g.[15] These data can be further considered in terms of the density of surface coverage of the layer: the limiting area (A_o) for monolayer formation of benzene is 0.24 nm^2/molecule and for substituted anthracenes is 0.45–0.48 nm^2/molecule,[16] and assuming a median value for A_o of about 0.6 nm^2/molecule for materials **3a,b** and **4**, which are modified with the slightly larger benzhydrylmethyl system, this converts to a surface loading density of some 1.8% for **3b**, 1.2% for **4** and up to 9% for **3a**.

Significant in this approach is that the concurrent formation of the azo linkage provides a functional group which is amenable to

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Scheme 1.

Table 1
Combustion analysis and loading data for modified polystyrene products **3a,b** and **4**

Polystyrene	Analysis[a] (%)	Loading (mmol/g)	Loading[b] (molecules/cm^2)	Surface coverage (%)
3a R=CH$_2$COOH	C, 87.74, H, 7.66, N, 0.50 C, 87.76, H, 7.64, N, 0.51	0.18	15×10^{12}	9
3b R=Hexyl	C, 89.49, H, 7.91, N, 0.1 C, 89.45, H, 7.89, N, 0.1	0.036	2.99×10^{12}	1.8
4	C, 57.89, H, 6.70, N, 0.1 C, 57.77, H, 6.71, N, 0.1	0.036	1.98×10^{12}	1.2

[a] Duplicate analyses.
[b] Assumes a surface area of 750 m^2/g.

detection by a variety of surface and bulk analytical techniques. In particular, it provides a visible–UV chromophore, giving a direct indication of the modification of the polymer surface by a change in colour (Table 2); the wavelength is determined by the nature of the substituents on the diazo group, and the intensity would be expected to give a visual indication of the loading. Although the modified polystyrene was not suitable for surface scattering UV analysis, similarly modified silica exhibited maxima at 235 and 275 nm, consistent with the introduction of aromatic residues onto the surface (Table 2).
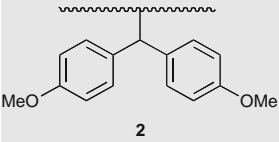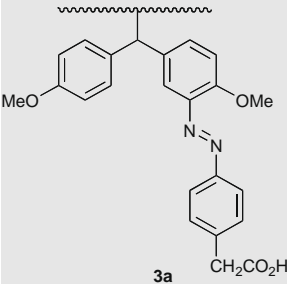
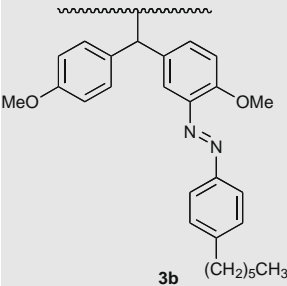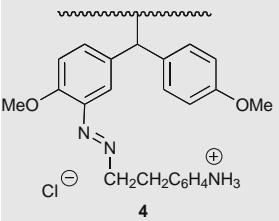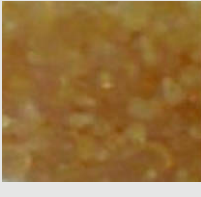ATR-IR analysis of modified polymers provided some additional evidence for the surface modification; unfortunately the diazo absorbance in the 1400–1500 cm^{-1} region tends not to be well defined and is often inactive.[17] However, alternative bands of interest are 1275–1220 cm^{-1} (asymmetric C–O–C stretch), 1075–1020 cm^{-1} (symmetric C–O–C stretch) and 1600–1585 cm^{-1} (aromatic C–C stretch), all of which are associated with the methoxy and aromatic groups which would be expected to be introduced at the polymer surface. Unmodified polystyrene has strong absorbances at 2925, 1601, 1492, 1451, 1028 and 905 cm^{-1},[18] and for the modified materials **3a,b** and **4**, significant absorbances were observed in difference spectra at 1605, 1510, 1245, 1170 and 1035, consistent with modification of the polymer surface (Table 2). Of note for polystyrene **3a** was a broad absorbance at 1710 cm^{-1}, which was attributed to the carboxylate resonance.

XPS analysis provided further evidence for the nature of the surface modification (Table 2). Although both the blank polystyrene beads and modified polystyrene **2** showed the presence of oxidised nitrogen-type species from N1s signals at binding energies (eV) of 400.4 and 402.8, and oxygen O1s signals at 531.8 and 533.3, most likely as a result of surface contamination (no nitrogen was de-

tected in the combustion analysis of blank polystyrene), in the case of the latter, the observed O/C ratio of 0.11 is very close to the expected value of 0.13, assuming the formation of a uniform monolayer of benzhydryl units of molecular formula C$_{15}$H$_{15}$O$_2$. The spectrum of polymer **3a** exhibited a C1s signal at 284.7, indicative of the presence of aromatic rings, and an envelope of N1s signals at binding energies of 399.7, 400.5, 401.7, 403.5 and 404.6 eV, consistent with the introduction of an azo linkage. The O/C and N/C ratios (0.146 and 0.076, respectively) were close to that expected for a uniform monolayer of benzhydryl units in which only one aromatic ring residue was modified by azo coupling; the fact that azo coupling in both rings is not observed is probably a result of steric hindrance after the first aromatic substitution. For polymer **4**, a C1s signal was similarly indicative of the presence of aromatic rings at the surface, but a simple N1s signal at a binding energy of 403.1 eV, suggested a poorer level of azo coupling, and this is consistent with the lower level of colouration in this sample (Table 2). Earlier work had indicated that methoxy-activated ring systems produced lower colour intensity than more reactive amino groups in similar polymer modifications.[4]

In order to gain some information relating to the thickness of the introduced layer, ellipsometry measurements on silicon modified with diaryldiazo compound **5** were made (Scheme 1). The results suggested a layer thickness of 6.3 ± 0.1 nm; assuming that the introduced organic residues are approximately orthogonal to the silicon surface with a height of some 0.75 nm, this gives a layer of about nine molecules high. Thus, the surface modification would more accurately be described as a nanolayer rather than a monolayer. When this material was treated with 4-hexylbenzenediazonium chloride, the layer was effectively cleaved (0.18 ± 0.14 nm) under the acidic reaction conditions, reflecting the lability of the

Table 2
Data for modified polystyrene and silica substrates

Material[a,b]	Appearance[a]	ATR-IR[a] (cm^{-1})	UV[b] (nm)	XPS[a] (atom ratio)
Blank		2925, 1601, 1492, 1451, 1028, 905	No significant absorbance	C_8H_8 Expected O/C = 0, N/C = 0 Found O/C = 0.11, N/C = 0.053
2		1605, 1510, 1245, 1170, 1035	240, 280	$C_{15}H_{15}O_2$ Expected O/C = 0.13, N/C = 0 Found O/C = 0.11, N/C = 0.042
3a		1710, 1605, 1510, 1245, 1170, 1035	235, 275	$C_{23}N_2O_4$ Expected O/C = 0.174, N/C = 0.087 Found O/C = 0.146, N/C = 0.076
3b		1605, 1510, 1245, 1170, 1035	235, 275	Not examined
4		1650, 1530	235, 275	$C_{23}N_3O_2$ Expected O/C = 0.086, N/C = 0.130 Found O/C = 0.084, N/C = 0.013

[a] Polystyrene.
[b] Silica.

newly formed Si–O–C bond in the carbene insertion reaction. We have previously observed that modified silicas of type **2** are highly labile at extremes of pH (<5 and >9), and even exhibit some lability at neutral pH (weight loss approximately 16%).[19]

Application of a range of surface analysis techniques has provided evidence for the modification of polymers by diaryldiazomethanes under thermal conditions. Although we have not been able to obtain direct information relating to the nature of the newly formed covalent bonds at the surface, and initially assumed reaction by the normal modes of reactivity exhibited by carbenes,[20] a substantial review by Tomioka indicates signifi-cantly different modes of behaviour of carbenes in low temperature matrices when compared to solution behaviour,[21] and where diffusion is limited so that singlet/triplet intersystem crossing competes effectively with insertion reactions. Under these conditions, reactions of the triplet system dominate, leading to modes of reactivity not normally observed in solution. Since we conduct these polymer modifications in the absence of solvent, similar diffusion controlled processes cannot occur, and we assume a similar situation operates; noteworthy is a report of similar polymer modifications using triplet carbenes generated photolytically from benzophenones.[22]

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