

# A chemical method for the convenient surface functionalisation of polymers†

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A method for the application of carbenes as reactive intermediates for surface modification of polymeric substrates has been developed; the efficacy of the process has been demonstrated by irreversible dyeing of polystyrene, polythene, nylon, silica, and controlled pore glass, and to a limited extent, polytetrafluoroethylene.

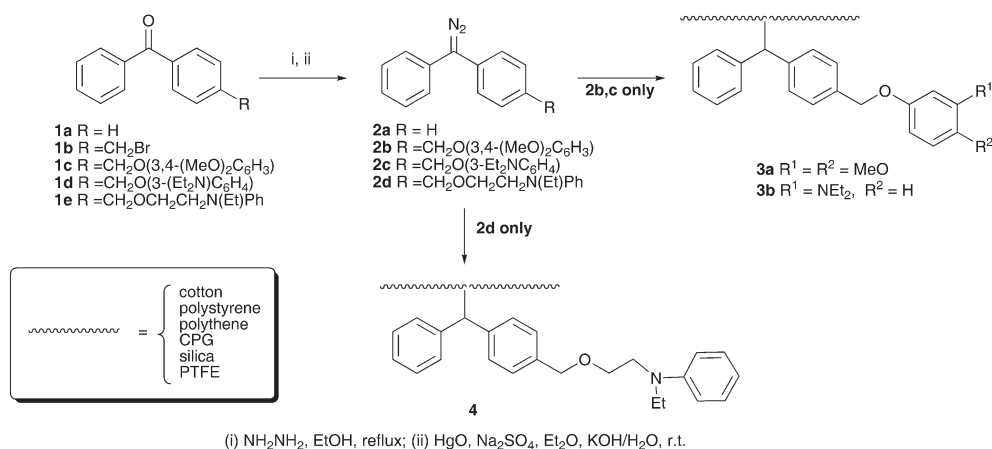
The chemical modification of the surfaces of polymers is of increasing importance in many diverse aspects of modern technology, with applications which include solid phase chemical synthesis related to drug discovery, chemical catalysis, biocompatible medical implants and prostheses, diagnostic devices, and surface-modified fabrics, amongst many others. Whilst there are a number of existing physical (*e.g.* corona or plasma discharge, ion beam irradiation<sup>1</sup>) and chemical (*e.g.* silanisation, oxidation, chlorination, acylation and quaternisation<sup>2–4</sup>) methods for the surface modification of polymers, the frequent requirement for significant infrastructure, harsh reaction conditions, and limitation to specific polymer types (*e.g.* polybutadiene<sup>5</sup>), which must possess suitable chemical functionality capable of direct modification, led us to consider alternative chemical methods. Of interest to us was an alternative that would be amenable to a large range of polymers, permitting direct chemical modification under mild conditions and using inexpensive reagents. Although reports of polymer modifications mediated by carbene insertion have been made,<sup>6–14</sup> 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.<sup>15</sup> Nonetheless, changes in polymer surface tension, permeability or photophysical characteristics were shown to be possible. We considered that modification of a polymer surface by carbene insertion was an excellent candidate worthy of further investigation, particularly if the issues of generation of the carbene could be addressed, 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; notably, these reactions are irreversible. We report here the results of some investigations for the development of diarylcarbenes as reactive intermediates suitable for polymer surface modification.

Diarylcarbenes have been widely studied<sup>16–18</sup> and are easily obtained by thermolysis or photolysis of the corresponding diazo compound **2a**, which in turn are readily prepared from the benzophenone **1a** in a two step sequence *via* an intermediate benzophenone hydrazone (Scheme 1). We found that the required diazo compounds were most readily prepared by treating the benzophenone **1a** with hydrazine hydrate in refluxing ethanol overnight, followed by removal of the solvent and extraction into dichloromethane;† the hydrazone product needed to be used immediately, since facile interconversion to the azine was observed in all cases on storage even overnight. Oxidation of this intermediate to the diazo compound **2a** was most conveniently performed with mercuric oxide in ether, and provided the hydrazone starting material had been obtained in sufficiently pure form, the diazo product needed no further purification.

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b4/b414856h/>

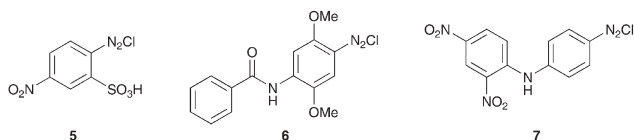
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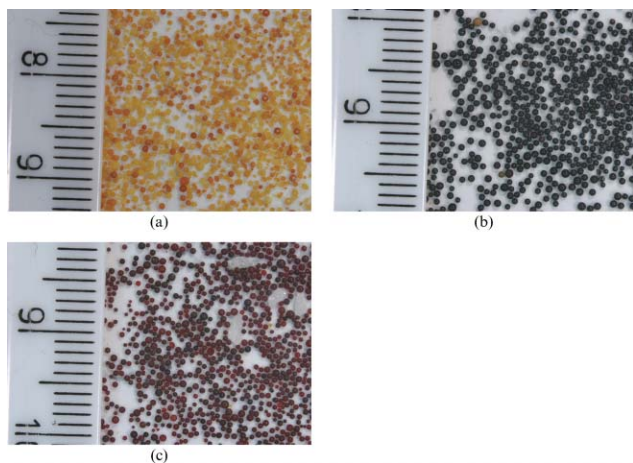
Scheme 1

Application of this sequence to ketones **1c–e**, readily prepared from 4-bromomethylbenzophenone **1b**<sup>19</sup> and the alkoxides derived from either 3,4-dimethoxyphenol, 3-*N,N*-diethylaminophenol, or 2-*N*-ethylaminoethanol, gave diazo compounds **2b–d** in excellent yield and as intensely coloured oils; these materials could be safely and conveniently stored at 0 °C, and without significant decomposition over extended periods.

The suitability of compounds **2b–d** for the modification of several substrates (mercerised woven cotton, Nylon membrane (Hybond M, ex Amersham International, Cat. No. RPN203N), polystyrene (Amberlite XAD-4 non-ionic polymeric adsorbent beads), Controlled Pore Glass (CPG) and silica (Sorbisil<sup>®</sup> C<sub>60</sub>H (40–60 μm) silica gel)) was then investigated. Thus, each substrate was treated with the diazo compounds **2b–d** in ether solution and the solvent allowed to evaporate slowly. The coloured substrate was then heated, both to decompose the diazo compound and to cause reaction of the generated carbene with the polymer surface; this process led to rapid decolourisation of the substrate, consistent with the decomposition of the diazo compound. Polymeric substrates **3a,b** and **4**, activated with an electron-rich aromatic residue (Scheme 1) were thereby obtained.‡



Reaction of modified polystyrenes **3a,b** and **4** with diazonium salt **5** gave intense colouration, arising from the expected diazo coupling (Fig. 1a, b and c); the dimethoxy substituted system of substrate **3a** gave less intense colouration than the more strongly activated systems present in **3b** and **4**. The intense colouration which was achieved was consistent with initial modification of the base polymer with the carbene derived from diazo compounds **2b–d** followed by diazo coupling with diazonium salt **5**. In further experiments, nine controls were run simultaneously to verify that the resulting colouration of the polymer was not due merely to physical adsorption of dye for the substrates mercerized woven cotton, polystyrene (Amberlite XAD-4), silica and nylon



**Fig. 1** Polystyrene XAD: (a) modified with precursor **2b** followed by diazonium salt **5**; (b) modified with precursor **2c** followed by diazonium salt **5**; (c) modified with precursor **2d** followed by diazonium salt **5**.

(Hybond<sup>™</sup>); thus, each polymer was subjected to the successful three-step colouration process (initial adsorption, heating, and treatment with diazonium salt **5**) either without any carbene precursor, with benzophenone **1e**, or with diazo compound **2d**. The results from these experiments indicated that maximum colouration required the combination of carbene insertion derived from **2d** and diazonium reagent **5**, consistent with initial carbene surface insertion onto the polymer followed by diazonium coupling to generate a diazo chromophore.† The intensity of colouration which was achieved was both a function of the nature of the substrate, the efficiency of carbene insertion, and the UV chromophore which is generated in the diazo coupling step (Figs. 1, 2 and 3). The method is particularly effective for the highly adsorbant polystyrene XAD substrate due to its high surface area (725 m<sup>2</sup>/g), but silica and nylon also gave intense colouration; cotton however proved to be less receptive to this approach than the synthetic polymers. These results suggest that the method is likely to be broadly applicable across a range of polymeric substrates. The colouration process routinely used an extensive washing process (involving sequential washes with hot water, acetone, alkali and acid), but in order to ensure that the dye was fixed irreversibly, samples of cotton, nylon and polystyrene were extracted using a Soxhlet apparatus with acetone and aqueous solutions of pH 1 and 15; high level retention of colour was observed in all cases.

Application of this approach to other polymeric substrates and other diazonium salts indicates that the method is likely to be general. Thus, treatment of polythene, silica, and controlled pore glass with diazo compound **2d** and diazonium salts **5**, **6** and/or **7** gave the coloured products shown in Figs. 2 and 3; the



**Fig. 2** Silica (L to R): unmodified; modified with precursor **2d** followed by diazonium salt **5**; modified with precursor **2d** followed by coupling with diazonium salt **6** under alkaline conditions; modified with precursor **2d** followed by diazonium salt **6** with acid wash; modified with precursor **2d** followed by diazonium salt **7**.



**Fig. 3** Polythene (L to R): unmodified; modified with precursor **2d** followed by diazonium salt **5**; modified with precursor **2d** followed by diazonium salt **6**.



**Fig. 4** PTFE (L to R): unmodified; modified with precursor **2d** followed by diazonium salt **6**; modified with precursor **2d** followed by diazonium salt **5**.

chromophore of products derived from the coupling with Disperse Yellow **7** depended on whether the diazo coupling made use of alkaline or acidic conditions.<sup>4</sup> Surprisingly, polytetrafluoroethylene gave some colouration, although it was of very low intensity (Fig. 4).

By using the colouration of polymers as a diagnostic step, we have established the proof of the principle of the modification of polymers using carbenes. However, this method is not restricted to colouration of polymers, and is potentially applicable to the introduction of diverse functionality with desirable chemical and/or physical properties in a chemical coupling step which makes use of the electron-rich aromatic ring introduced in the carbene coupling step. Additionally, the method allows functionalisation of diverse polymer types, and offers the potential for the convenient incorporation of chemical functionality *after* the polymer fabrication process;<sup>20,21</sup> investigations in that regard are currently in progress and will be reported in due course.

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## Notes and references

‡ Preliminary experiments using XPS on polystyrene and polythene modified with the carbene derived from 4,4'-dichloro(diazo)diarylmethane revealed a well-defined Cl 2p peak associated with aryl chlorine atoms. For the polythene substrate, the Cl2p/Cl1s intensity ratio had a value of about 1/100 (R. H. Bowdler, R. G. Egdell, and M. G. Moloney, unpublished results).

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