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Full Length Article

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.

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]. 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

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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 (25 w/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 3 M hydrochloric acid (2 eq) were added to the mixture was stirred for up to 30 min 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 min 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 (1 ml) 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 min. 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 °C for 18 h. 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 30 w/v% H_2O_2 (20 ml) for 3 h 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 min, a few milliliters of starch was added to the solution, which was left to stand for 1 h 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 °C. 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 min. 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.