One-step chemical functionalization of polyethylene surfaces via diarylcarbene insertion

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Abstract: Three diarylcarbene derivatives with reactive groups were synthesized and used to graft functional groups onto a plasma-modified polyethylene surface via one-step carbene insertion. The modification is observable spectroscopically, and this one-step strategy provides facile and efficient tool to modify the surface macroscopic properties of low surface energy materials.

KEYWORDS: diaryldiazomethane; functionality; surface modification; hydrophobic; post-polymerisation

Introduction

The surface modification of polymer materials can introduce new chemical functional groups, giving rise to materials with different properties. However, since many polymer surfaces are chemically inert, such surface modification is not always straightforward, and it would be of substantial value if a method giving specific, controlled introduction of functional groups, independent of the bulk properties of the polymer, was possible. Carbenes are highly reactive intermediates, and *N*-heterocyclic carbenes [1-4], diazirines [5, 6], and diarylcarbene derivatives [7-9], which may be readily prepared [10] have been used to modify the macroscopic properties of material surfaces [11]. Using this approach, it has been possible to introduce a range of macroscopic properties [8,9,12-17]. However, despite these appealing features, diarylcarbenes have not been used to directly introduce reactive groups by a one-step reaction, since their synthesis generally precluded incorporation of such functionality. We report a novel and mild one-step approach to prepare three diarylcarbenes each with remote but reactive functional groups, suitable for decoration of a polymer surface; polyethylene (PE) macroparticles, a typical low surface energy polymer, was chosen as a model system. To the best of our knowledge, this is the first report of such

functionalized diaryldiazomethanes, and their application for modification of low surface energy materials, although a variety of other methods for the manipulation of such materials has been reported [18-22].

Scheme 1. The surface modification of PE by one-step diarylcarbene insertion, permitting the introduction of (a) allyl, (b) bromodimethylacetyl and (c) glycidyl side chains.

Experimental

The preparation details and characterization of the diaryldiazomethanes are shown in the Supporting Information (relevant spectra are included in Figures S1-S5).

Treatment of PE with diaryldiazo derivatives

PE was washed with water and acetone and activated by plasma treatment (RF plasma barrel etcher (PT 7100) under O_2 .) The diaryldiazo derivatives **3a-c** (0.25 mmol) were dissolved in 5 ml Et_2O , and the PE particles were added to the solution. The solvent was carefully removed under vacuum, and the particles heated at 100-120 °C. The final product was washed with acetone and water several times.

Results and Discussion.

The typical procedure for diarylcarbene synthesis usually proceeds via hydrazone formation from a benzophenone using hydrazine followed by oxidation [23]; however, these conditions require that the benzophenone does not contain reactive substituents, and as a result, previous studies mainly focused on diarylcarbenes with non-reactive substituents. In this study, the starting material, **4**,

4,4'-dihydroxybenzophenone was used to prepare side-chain derivatives **1a-c** which were in turn used in a sequence proceeding via formation of the tosylhydrazones **2a-c** and then alkaline conditions to form the diazomethanes **3a-c** (Scheme 1). Thermolysis gave rise to the expected carbene intermediates which were then reacted directly with polymers. We found this milder synthetic route gave a successful outcome and the appearance of PE subjected to this process, which is pale yellow or orange in color as a result of the introduction of the aromatic residues, gives a direct visual indication of a successful surface modification (Fig. S6, Supplementary Information). In order to further enhance the modification efficiency, PE was also first activated by oxygen plasma to introduce O-H functional groups and increase the reactivity of the polymer [18-22].

The modified PE surfaces were characterized by ATR-IR spectroscopy, which provided direct evidence for surface modification. In order to better compare the intensity of peaks, the data were normalized to the peak intensity at $\sim 2870\text{ cm}^{-1}$ (C-H stretching vibration, the strongest peak of PE polymer; blank PE refers to as-sourced PE). All the PE samples show a noticeable absorption at $\sim 1471\text{ cm}^{-1}$ corresponding to the C-H bending vibration (Fig. 1A). After diarylcarbene functionalization, additional peaks at ~ 1510 , ~ 1577 , $\sim 1600\text{ cm}^{-1}$ were observed for all modified PE materials, which most likely resulted from C=C vibration of the introduced benzene rings. In addition, characteristic bands for aromatic ether bending at $\sim 1017\text{ cm}^{-1}$ (R-O) and $\sim 1250\text{ cm}^{-1}$ (Ar-O) are also present for the modified samples. Besides the above changes, the IR spectra also provide evidence for the introduction of specific functional groups. The sample (PE + diaryldiazo **a**) shows an obvious peak at $\sim 1637\text{ cm}^{-1}$ attributed to C=C vibration of the olefin; the (PE + diaryldiazo **b**) presents the characteristic bands for ester C=O bending at $\sim 1744\text{ cm}^{-1}$; while the (PE + diaryldiazo **c**) shows absorption at ~ 830 , $\sim 910\text{ cm}^{-1}$ corresponding to the epoxy group.

Fig. 1. Spectra of modified PE via one-step diarylcarbene insertion using **3a-c**, for the (a) allyl, (b) bromodimethylacetyl and (c) glycidyl side chains, (A) ATR-IR, and (B) UV-Vis.

The covalent link between PE and diarylcarbene was further confirmed by surface reflectance UV-Vis spectroscopy (Fig. 1B). As the PE does not contain unsaturated bonds, the pristine sample does not show any obvious UV absorption. Strong characteristic absorption in UV-Vis spectrum of the aromatic residues gave a broad peak at ~285 nm for all the modified PE samples. The appearance of these peaks is fully consistent with successful grafting of diarylcarbene on the PE via one-step diazo chemistry.

The successful functionalization of the PE was further confirmed by solid-state ^{13}C NMR spectra (Fig. 2). For sample PE + diaryldiazo **a**, the introduced C=C bonds in the allyl group gave signals at ~120 ppm, which unfortunately overlapped with the aromatic carbon signals. However, the sample PE + diaryldiazo **a** also showed a peak at ~68 ppm, which corresponds to the allylic carbons of the C=C groups. The ^{13}C NMR spectrum of PE + diaryldiazo **b** exhibited additional peaks at ~45 and ~175 ppm, which may be attributed to C-Br and ester C=O carbons. Similarly, for PE + diaryldiazo **c**, the resonance located at ~39 ppm may be attributed to the grafted epoxy carbons.

Fig. 2. The solid state ^{13}C NMR spectra of modified PE via one-step diarylcarbene insertion. (a) PE

+ diaryldiazo **3a**, (b) PE + diaryldiazo **3b**, (c) PE + diaryldiazo **3c** (side chains = (a) allyl, (b) bromodimethylacetyl and (c) glycidyl).

The surface chemical composition of modified PE was further examined by XPS (Supporting Information, Fig. S7). The oxygen plasma treatment of untreated PE increases the atomic ratio of oxygen from 3.2 to 17.6% (data not shown). Quantitative analysis shows that the element mass ratios of oxygen in the PE + diaryldiazo **a**, **b** and **c** increased further to 32.7, 35.6 and 22.1%, respectively, which can be attributed to the introduction of diarylcarbene groups. Besides the additional oxygen, PE + diaryldiazo **b** shows small peaks at ~182 and ~70 eV which may be attributed to the bromine 3p_{3/2} and 3d_{3/2} signals respectively, and which indicate the successful introduction of the ATRP initiator residues. Furthermore, according to the element mass ratio of Br, the mole ratio of the diaryldiazo **b** segment on PE surface may be calculated to be 2.78×10^{-4} mol/g PE.

Taken together, this data is consistent with surface modification of polyethylene with the expected chemical functional groups.

Conclusion

Three diarylcarbene derivatives with reactive groups were designed, synthesized and grafted to PE, pre-activated by oxygen plasma exposure, by one-step carbene insertion. This novel and efficient method is suitable for the modification of low surface energy materials, and should be suitable for modification not only of PE, but also of other polymers and nanomaterials.

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