



# 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.

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## 1. 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].

## 2. Experimental

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

### 2.1. Treatment of PE with diaryldiazo derivatives

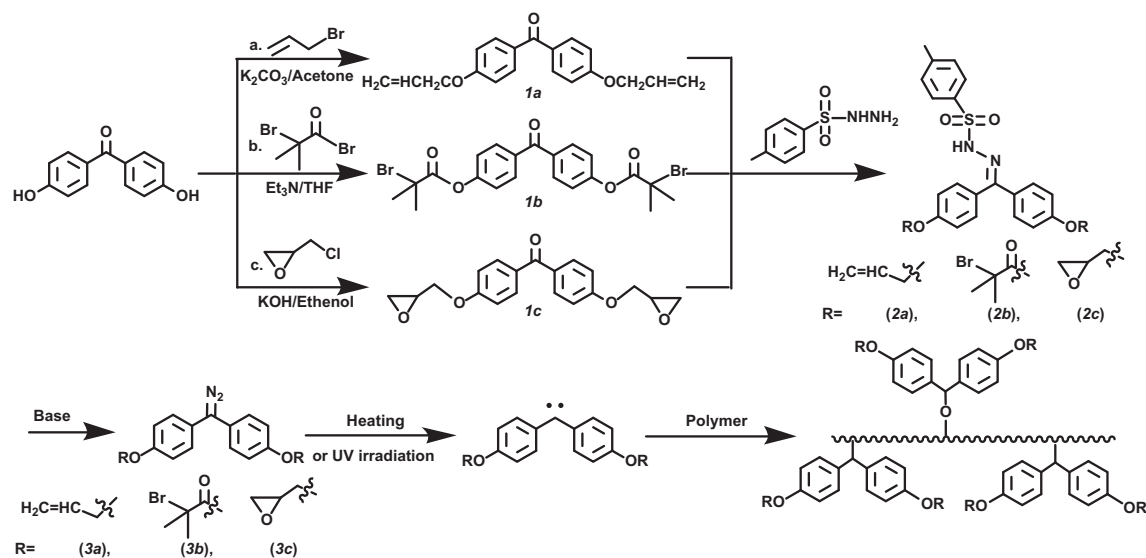
PE was washed with water and acetone and activated by plasma treatment (RF plasma barrel etcher (PT 7100) under O<sub>2</sub>). The diaryldiazo derivatives **3a–c** (0.25 mmol) were dissolved in 5 ml Et<sub>2</sub>O, and the PE particles were added to the solution. The solvent was carefully removed under vacuum, and the particles heated at 100–120 °C. The final product was washed with acetone and water several times.

## 3. Results and discussion

The typical procedure for diarylcarbene synthesis usually proceeds via hydrazone formation from a benzophenone using

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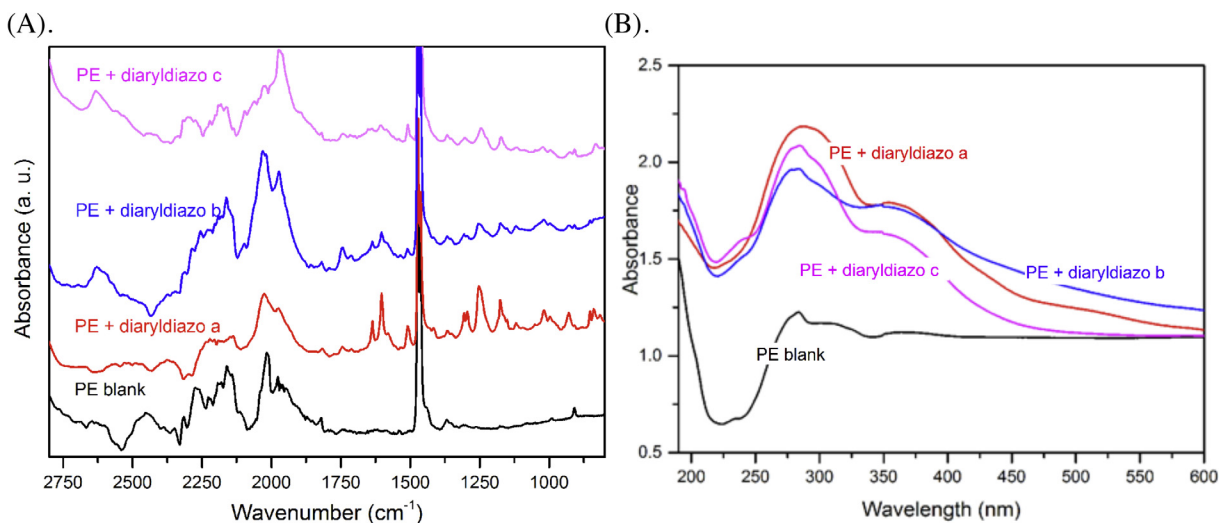
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**Scheme 1.** The surface modification of PE by one-step diarylcarbene insertion, permitting the introduction of (a) allyl, (b) bromodimethylacetyl and (c) glycidyl side chains.

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  $\sim 1510$ ,  $\sim 1577$ ,  $\sim 1600\text{ cm}^{-1}$  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



**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.

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