Surface hydrophobic modification of polymers with fluorodiazomethanes

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abstract

Two fluorinated diazomethanes were synthesized, and used for the modification of polystyrene XAD4, polyacrylate MAC-3, filter paper, and Hybond™ membrane. The structure of modified polymers was con-firmed by XPS and solid-state NMR spectra, with a surface loading of 8.28 10^{12}–1.68 10^{13} molecules per cm^2. Water contact angle values, which increased from 0L to 128.51L (for filter paper) and 120.02L (for Hybond™ membrane), demonstrated hydrophobicity.

1. Introduction

The hydrophobic behavior of solid surfaces has a wide diversity of applications such as self-cleaning surfaces, high adhesive sur-faces, antifogging coatings, and antireflection coatings [1]. Different preparation strategies have been developed to fabricate hydropho-bic surfaces [2,3], which include nanoparticles doping [4–6], the introduction of fluoric or silicic or long alkyl chain chemistry [7–10], and plasma treatment [11,12]. He et al. [13,14] used CF_4 plasma modification for the conversion of a hydrophilic membrane into a hydrophobic membrane but a simple, universal and efficient chemical method for the direct hydrophobic modification of a wide range of polymers would be highly desirable. Modifications have been developed [15] using carbenes [16] or nitrenes [17], and we have developed a strategy of modification through carbene inser-tion reactions derived from aryldiazomethanes [18–25], which benefits from a short synthetic route and mild reaction conditions.

2. Experimental

Full experimental details and results are included in the Elec-tronic Supporting Information.

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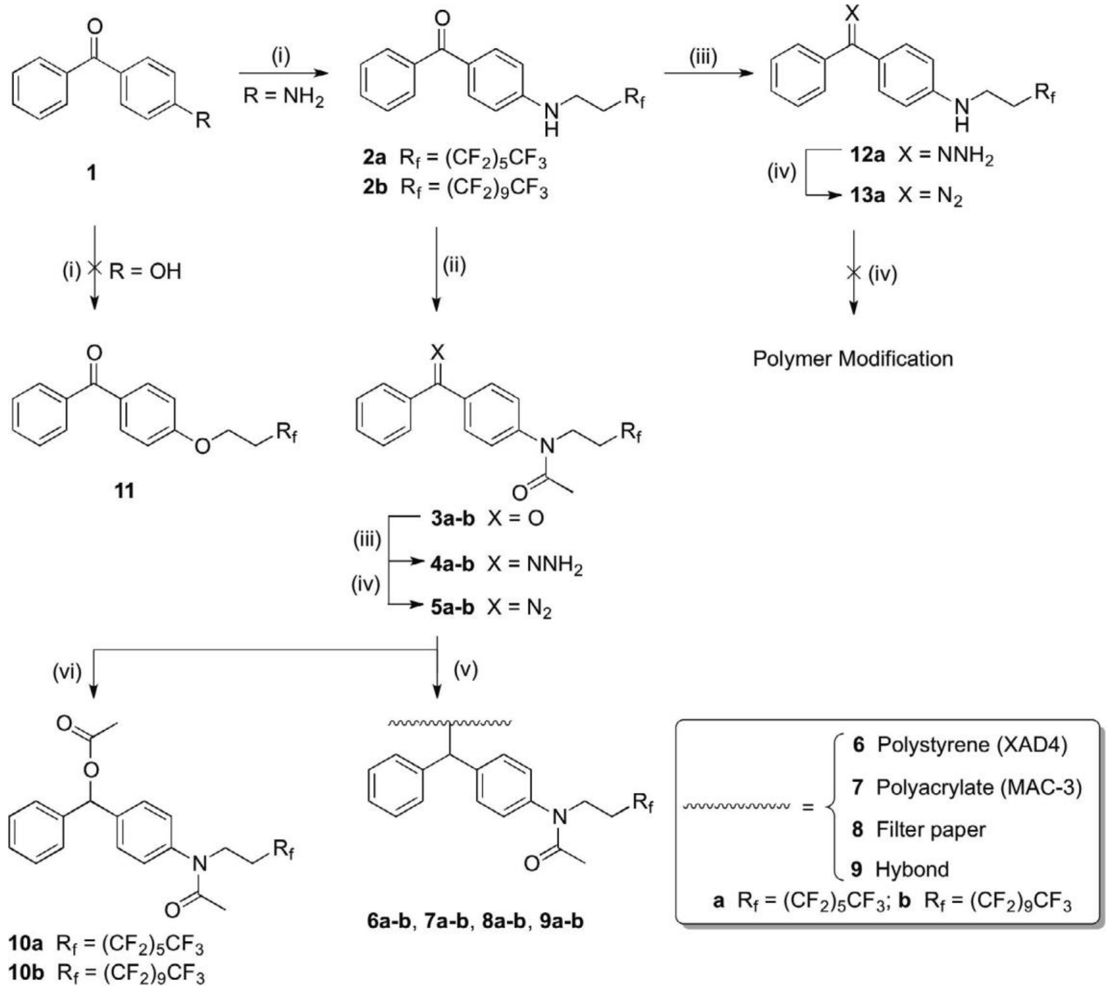
Polymer Beads (6a–b, 7a–b). To a solution of fluorodia-zomethane 5a–b in dichloromethane (10 mL) was added the required polymer, and then the mixture was concentrated under vacuum. The polymer was collected and heated at 120 LC in an open flask for 30 min. The resulting solid was washed with acetone for 3 times and dried to yield the functionalized polystyrene 6a–b and polyacrylate 7a–b.

Polymer Sheets (8a–b, 9a–b). To a solution of fluorodia-zomethane 5a–b in dichloromethane (2 mL) was added the required sheet. After it absorbed the solution completely, polymer sheet was taken out and dried under N_2 flow. Then, it was heated in an open beaker to 120 LC for 30 min. The resulting sheet was washed with acetone for 3 times and dried to yield the functional-ized filter paper 8a–b and Hybond 9a–b.

3. Results and discussion

In this paper, we report the use of this approach to introduce perfluoroalkyl groups into diazomethanes, to achieve the modifica-tion of different polymer beads and sheets, giving surfaces with hydrophobic properties. 4-Aminobenzophenone was used to react with a perfluoroalkyl iodide to obtain fluorobenzophenones 2a–b, followed by acetylation to generate fluorobenzophenones 3a–b (Scheme 1). These were treated with hydrazine monohydrate to generate fluorohydrazones 4a–b, which were in turn oxidized with



Scheme 1. Synthesis of precursor, and modification of polymers. Conditions: (i) $I(CH_2)_2C_nF_{2n+1}$, 140 LC, 18 h, (26–52%); (ii) K_2CO_3, DMAP, DCM, r.t. 3 h, (88–96%); (iii) NH_2NH_2 H_2O, HOAc, EtOH, reflux, 40 h, (83–90%); (iv) MnO_2, Na_2SO_4, KOH, DCM, r.t., 2 h (98–99%); (v) 120 LC; (vi) HOAc, Et_2O, r.t., 30 min (50–55%).

manganese dioxide to obtain fluorodiazomethanes 5a–b. Before these materials were applied to the preparation of modified poly-mers polystyrene XAD4, polyacrylate MAC-3, filter paper, and Hybond™ 6–9 respectively (vide infra), their chemical reactivity was assessed by reaction with acetic acid to give the esters 10a– b, and compared to that of several other diazomethanes.

For fluorodiazomethane 5a in dichloromethane, clear changes of the UV spectra at 519 nm were observed after acetic acid was added, and these could be used for kinetic studies; details of the analysis are included in the Supplementary Information (Fig. 1, SI and Table 1, SI), but significantly, compounds 5a–b give a good bal-ance of stability and reactivity, which is required in a surface mod-ifying agent.

Of interest is that this strategy was not suitable for the forma-tion of fluorobenzophenone 11 from 4-hydroxybenzophenone regardless of the base used to deprotonate the phenolic hydroxyl. Furthermore, although fluorobenzophenone 2a could be converted to fluorodiazomethane 13a in the usual way, it proved to be too reactive to be used for subsequent modification, and this outcome emphasized the importance of the presence of the acetyl group for the successful isolation of diazo 5a–b.

Polystyrene XAD4, MAC-3, filter paper, and Hybond™ mem-brane were used as substrates for surface modification with diazo 5a–b; their colour changed from white to light yellow after modi-fication, consistent with the introduction of aromatic functionality. Clear changes of surface elements were found by XPS analysis and by solid state NMR spectroscopy (full details are given in the Sup-plementary Information (Figs. 2 and 3, SI and Table 2, SI)), for which the carbon spectra of 6a by ^{19}F ? ^{13}C CP showed the pres-ence of the perfluoroalkyl groups. This confirmed the successful modification with fluorodiazomethanes 5a–b. The surface loadings of 6a–b could be determined by a combination of surface area measurement by BET analysis and quantitation of nitrogen content by elemental combustion analysis (full details are given in the Sup-plementary Information (Table 3, SI)), and are very similar to the values that have been reported [26].

The surface-loaded fluoroalkyl chains generated hydrophobic behavior, which could be clearly demonstrated from the water contact angle of the modified filter paper and Hybond™. However, the contact angle increased to as large as 128.51L for treated filter paper 8b and 120.02L for treated Hybond™ 9b after fluorine was introduced onto their surface (Table 1, water of unmodified filter

Table 1
Water contact angle of filter paper and Hybond™ membrane before and after modification.

Polymer sheets	Unmodified	a (C_6F_{13}-Modified)	b ($C_{10}F_{21}$-Modified)
8 (Filter paper)	0L	120.0 ± 4.4L	128.5 ± 0.4L
9 (Hybond membrane)	0L	112.6 ± 7.6L	120.0 ± 2.2L

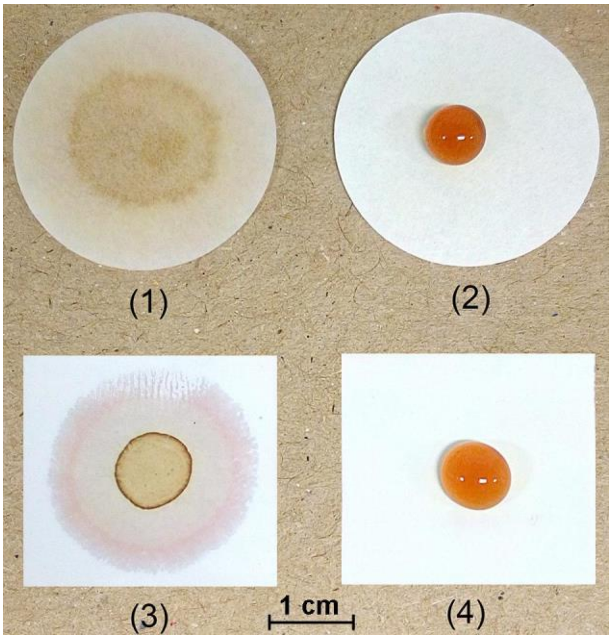


Fig. 1. Hydrophobic behavior: (1) unmodified filter paper; (2) 8b; (3) unmodified Hybond™; (4) 9b.

paper or Hybond™ is 0L). Fig. 1 shows the hydrophobic behavior of modified polymer sheets.

4. Conclusion

The effect of fluorination on surface wettability is well known [27–29], and often achieved with plasma mediated fluorination and while although other approaches have been developed [30–33], the work reported here offers a direct and effective chem-ical reagent which makes use of comparatively rare fluoro-substituted carbenes [34] suitable for the introduction of fluorine to diverse surfaces under mild reaction conditions to give a hydrophobic polymer surface on polystyrene, polyacrylate, filter paper, and Hybond™ substrates.

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