Surface Hydrophobic Modification of Polymers with Fluorodiazomethanes

Pengfei Yang,[a,b] Mark G. Moloney,*[,a] Fei Zhang[a,c] and Wei Ji[d]

[a]Chemistry Research Laboratory, Department of Chemistry, University of Oxford, OX1 3TA, UK

[b]School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, P. R. China

[c]School of Chemistry, Cardiff University, CF10 3AT, UK

[d]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070，China

*Corresponding author. mark.moloney@chem.ox.ac.uk.

ABSTRACT: Two fluorinated diazomethanes were synthesized, and used for the modification of polystyrene XAD4, polyacrylate MAC-3, filter paper, and Hybond^{TM} membrane. The structure of modified polymers was confirmed 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 0° to 128.51° (for filter paper) and 120.02°(for Hybond^{TM} membrane), demonstrated hydrophobicity.

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

Introduction

The hydrophobic behavior of solid surfaces has a wide diversity of applications such as self-cleaning surfaces, high adhesive surfaces, antifogging coatings, and antireflection coatings[1]. Different preparation strategies have been developed to fabricate hydrophobic 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. Modification have been developed[15] using carbenes[16] or nitrenes[17], and we have developed a strategy of modification through carbene

insertion reactions derived from aryldiazomethanes,[18-25] which benefits from a short synthetic route and mild reaction conditions.

Experimental

Full experimental details and results are included in the Electronic Supporting Information.

Polymer Beads (**6a-b**, **7a-b**). To a solution of fluorodiazomethane **5a-b** in dichloromethane (10mL) was added the required polymer, and then the mixture was concentrated under vacuum. The polymer was collected and heated at 120°C in an open flask for 30min. 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 fluorodiazomethane **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°C for 30 min. The resulting sheet was washed with acetone for 3 times and dried to yield the functionalized filter paper **8a-b** and Hybond **9a-b**.

Results and Discussion.

In this paper, we report the use of this approach to introduce perfluoroalkyl groups into diazomethanes, to achieve the modification 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 manganese dioxide to obtain fluorodiazomethanes **5a-b**. Before these materials were applied to the preparation of modified polymers polystyrene XAD4, polyacrylate MAC-3, filter paper, and Hybond^{TM} **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.

*[Insert **Scheme 1** here]*

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

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 (Figure 1,SI and Table 1, SI), but significantly, compounds **5a-b** give a good balance of stability and reactivity, which is required in a surface modifying agent.

Of interest is that this strategy was not suitable for the formation 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^{TM} membrane were used as substrates for surface modification with diazo **5a-b**; their colour changed from white to light yellow after modification, 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 Supplementary Information (Figure 2 and 3, SI and Table 2, SI)), for which the carbon spectra of **6a** by $^{19}F \rightarrow ^{13}C$ CP showed the presence 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 Supplementary 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^{TM}. However, the contact angle increased to as large as 128.51° for treated filter paper **8b** and 120.02° for treated Hybond^{TM} **9b** after fluorine was introduced onto their surface (Table 1, water of unmodified filter paper or Hybond^{TM} is 0°). Figure 1 shows the hydrophobic behavior of modified polymer sheets.

*[Insert **Table 1** here]*

Table 1. Water contact angle of filter paper and Hybond^{TM} before and after modification

*[Insert **Figure 1** here]*

Figure 1. Hydrophobic behavior: (1) unmodified filter paper; (2) **8b**; (3) unmodified Hybond^{TM}; (4) **9b**

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 chemical 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.

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China (No. 21406121).

References

1. Liu, K.; Yao, X.; Jiang, L., Recent developments in bio-inspired special wettability. *Chem. Soc. Rev. 39* (8) (2010) 3240-55.
2. Roach, P.; Shirtcliffe, N. J.; Newton, M. I., Progess in superhydrophobic surface development. *Soft Matter 4* (2) (2008) 224-240.
3. Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z., Superhydrophobic surfaces: from structural control to functional application. *J. Mater. Chem. 18* (6) (2008) 621-633.
4. Tian, Y.; Jiang, L., Wetting: Intrinsically robust hydrophobicity. *Nat Mater 12* (4) (2013) 291-292.
5. Wu, R.; Liang, S.; Pan, A.; Yuan, Z.; Tang, Y.; Tan, X.; Guan, D.; Yu, Y., Fabrication of nano-structured super-hydrophobic film on aluminum by controllable immersing method. *Appl. Surf. Sci. 258* (16) (2012) 5933-5937.
6. Zhu, G.; Su, Y.; Bai, P.; Chen, J.; Jing, Q.; Yang, W.; Wang, Z. L., Harvesting Water Wave Energy by Asymmetric Screening of Electrostatic Charges on a Nanostructured Hydrophobic Thin-Film Surface. *ACS Nano 8* (6) (2014) 6031-6037.
7. Guo, Z.; Zhou, F.; Hao, J.; Liu, W., Stable Biomimetic Super-Hydrophobic Engineering Materials. *J. Am., Chem. Soc., 127* (45) (2005) 15670-15671.
8. Luo, S.-C.; Liour, S. S.; Yu, H.-h., Perfluoro-functionalized PEDOT films with controlled morphology as superhydrophobic coatings and biointerfaces with enhanced cell adhesion. *Chem. Commun. 46* (26) (2010) 4731-4733.
9. Wankhede, R. G.; Morey, S.; Khanna, A. S.; Birbilis, N., Development of water-repellent organic–inorganic hybrid sol–gel coatings on aluminum using short chain perfluoro polymer emulsion. *Appl. Surf. Sci. 283*, (2013) 1051-1059.
10. Darmanin, T.; Guittard, F., pH- and Voltage-Switchable Superhydrophobic Surfaces by Electro-Copolymerization of EDOT Derivatives Containing Carboxylic Acids and Long Alkyl Chains. *ChemPhysChem 14* (11) (2013) 2529-2533.
11. Cifuentes, A.; Borrós, S., Comparison of Two Different Plasma Surface-Modification Techniques for the Covalent Immobilization of Protein Monolayers. *Langmuir 29* (22) (2013) 6645-6651.
12. Sadeghi, I.; Aroujalian, A.; Raisi, A.; Dabir, B.; Fathizadeh, M., Surface modification of polyethersulfone ultrafiltration membranes by corona air plasma for separation of oil/water emulsions. *J. Membr. Sci. 430* (2013) 24-36.
13. Wei, X.; Zhao, B.; Li, X.-M.; Wang, Z.; He, B.-Q.; He, T.; Jiang, B., CF4 plasma surface modification of asymmetric hydrophilic polyethersulfone membranes for direct contact membrane distillation. *J. Membr. Sci. 407–408*, (2012) 164-175.
14. Yang, C.; Li, X.-M.; Gilron, J.; Kong, D.-f.; Yin, Y.; Oren, Y.; Linder, C.; He, T., CF4 plasma-modified superhydrophobic PVDF membranes for direct contact membrane distillation. *J. Membr. Sci. 456* (2014) 155-161.
15. Blencowe, A.; Hayes, W., Development and application of diazirines in biological and synthetic macromolecular systems. *Soft Matter 1* (3) (2005) 178.
16. Ghiassian, S.; Ismaili, H.; Lubbock, B. D.; Dube, J. W.; Ragogna, P. J.; Workentin, M. S., Photoinduced carbene generation from diazirine modified task specific phosphonium salts to prepare robust hydrophobic coatings. *Langmuir 28* (33) (2012) 12326-33.

17. Shi, F.; Niu, J.; Liu, Z.; Wang, Z.; Smet, M.; Dehaen, W.; Qiu, Y.; Zhang, X., To Adjust Wetting Properties of Organic Surface by In Situ Photoreaction of Aromatic Azide. *Langmuir 23* (3) (2007) 1253-1257.

18. Awenat, K. M.; Davis, P. J.; Moloney, M. G.; Ebenezer, W., A chemical method for the convenient surface functionalisation of polymers. *Chem. Commun. 41* (8) (2005) 990-992.

19. Moloney, M. G., Functionalized polymers by chemical surface modification. *J. Phys. D: Appl. Phys.*, *41* (17) (2008) 174006.

20. Choong, C.; Griffiths, J. P.; Moloney, M. G.; Triffitt, J.; Swallow, D., Direct introduction of phosphonate by the surface modification of polymers enhances biocompatibility. *React. Funct. Polym. 69* (2) (2009) 77-85.

21. Griffiths, J. P.; Maliha, B.; Moloney, M. G.; Thompson, A. L.; Hussain, I., Surface functional polymers by post-polymerization modification using diarylcarbenes. *Langmuir 26* (17) (2008) 14142-53.

22. Aphaiwong, A.; Moloney, M. G.; Christlieb, M., Surface functional polymer library by post-polymerisation modification using diarylmethylenes. *J. Mater. Chem. 22*(47) (2008) 24627-24636.

23. Choong, C.; Foord, J. S.; Griffiths, J. P.; Parker, E. M.; Baiwen, L.; Bora, M.; Moloney, M. G., Post-polymerisation modification of surface chemical functionality and its effect on protein binding. *New J. Chem. 36*(5) (2012) 1187-1200.

24. Bagwell, C. L.; Leonard, D. M. L.; Griffiths, J.-P.; Moloney, M. G.; Stratton, N. J.; Travers, D. P., Post-Polymerization Modification of Materials using Diaryldiazomethanes: Changes to Surface Macroscopic Properties. *Macromol. React. Eng. 8* (2) (2014) 170-180.

25. Nelson, G. W.; Parker, E. M.; Singh, K.; Blanford, C. F.; Moloney, M. G.; Foord, J. S., Surface characterization and in situ protein adsorption studies on carbene-modified polymers. *Langmuir 31* (2015) 11086-11096.

26. Yang, P.; Moloney, M. G., Surface modification of polymers with bis(arylcarbene)s from bis(aryldiazomethane)s. *RSC Advances 6* (2008) 111276-111290.

27. Tokuda, K. Ogino, T. Kotera, M., Nishino, T., Simple method for lowering poly(methyl methacrylate) surface energy with fluorination, *Polym J*, 47 (2015) 66-70.

28. du Toit, F.J., Sanderson, R.D., Engelbrecht, W.J., Wagener, J.B., The effect of surface fluorination on the wettability of high density polyethylene, *J. Fluorine Chem*., 74 (1995) 43-48.

29. Hayes, L.J., Surface energy of fluorinated surfaces, *J. Fluorine Chem*., 8 (1976) 69-88.

30. Yu, Y., Wang, X. , Chemical modification of polymer surfaces for advanced triboelectric nanogenerator development, *Extreme Mechanics Letters*, 9 (2016) 514-530.

31. Hubert, J., Mertens, J., Dufour, T., Vandencasteele, N., Reniers, F., Viville, P., Lazzaroni, R., Raes, M., Terryn, H., Synthesis and texturization processes of (super)-hydrophobic fluorinated surfaces by atmospheric plasma, *J. Mater. Res.*, 30 (2015) 3177-3191.

32. Darmanin, T., Guittard, F., Superoleophobic surfaces with short fluorinated chains?, *Soft Matter*, 9 (2013) 5982-5990.

33. Kharitonov, A.P., Kharitonova, L.N., Surface modification of polymers by direct fluorination, *Pure Appl. Chem*., 81 (2009) 451–471.

34. Buron, C., Tippmann, E.M., and Platz, M.S., Generation and Characterization of New Fluoro-Substituted Carbenes, J. Phys. Chem. A *108* (6), (2004) 1033-1041