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Surface Modification of Polymers with Bis(arylcabene)s from Bis(aryldiazomethane)s: Preparation, Dyeing and Characterization

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ABSTRACT: Modification of polymer beads by bis(arylcabene) insertion provides access to materials with similar bulk properties, but different surface chemical characteristics, compared to the unmodified polymer. A subsequent dyeing process using different diazonium salts generates colored polymers with a variety of surface functional groups. XPS and solid state NMR spectra were used to characterize modified and dyed polymers, which showed this protocol was both successful and general. BET data showed that the surface area changed significantly after modification, while BJH data showed pore size distribution was unchanged. TG/DSC analysis and Elemental Analysis were also used to characterize modified polymers. This permitted calculation and comparison of the loadings of surface area and the modification effects with different chemical structure of bis(arylcabene)s. This work shows that the bis(arylcabene) system is as effective as mono(arylcabene)s, but of significance since the starting bis(aryldiazomethane)s are more easily accessible and easier to handle than the mono(aryldiazomethane)s. All this data indicates that the surface property of polymers is modified.

KEYWORDS: Surface modification, Bis(arylcabene), Azo coupling, Polymer beads

1. INTRODUCTION

Carbenes, which could be generated from diazomethanes by UV light or by heating¹, are widely used for organic synthesis and polymerization²⁻⁵, as well as other important applications in photoresponsive behavior^{6, 7}, ESR measurement⁸, and organomagnetic metals^{9, 10}. By comparison, the application of carbenes for the modification of synthetic polymers has been much rarer¹¹⁻¹³. Thus, since methodology for the modification often required volatile and highly reactive carbenes, high temperature and metal catalysts, carbene insertion has been largely overlooked as a method for polymer modification¹⁴. Recently, Hayes¹⁵⁻¹⁷ and Ragogna¹⁸ reported a protocol using carbenes that are generated from diazirines for the surface modification of polymers. In contrast to their approach, we have developed a new strategy of carbene insertion derived from aryldiazomethanes¹⁹⁻²⁶, which is attractive for polymer modification because of the short synthetic route and mild reaction conditions. Highly reactive arylcabene intermediates could be easily generated under heating conditions (Scheme 1), and could be used to introduce color, fluorescence, biocompatibility, biocidal and payload delivery properties to a wide range of synthetic polymers.

[Insert **Scheme 1** here]

In order to further explore our protocol and increase the surface loadings which can be achieved by introducing an element of crosslinking, a series of bis(aryldiazomethane)s with different functional groups were synthesized, which was never reported before. These bis(aryldiazomethane)s were used to, firstly, modify polymers, and secondly, allow azo coupling reactions with different diazonium salts, which introduced easily detected elements and permit access to polymers with modified surface but unchanged bulk properties. Surface loadings were determined according to the BET data and the Elemental Analysis data, which showed that the method of synthesis, modification and dyeing was reliable and significant.

2. EXPERIMENTAL SECTION

2.1 Materials

1,3-Phenylenebis((4-phenoxyphenyl)methanone) (1,3-EKKE), 1,4-phenylenebis((4-phenoxyphenyl)methanone) (1,4-EKKE), and naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE) were obtained from KetoneX Ltd. 1H, 1H, 2H, 2H-Perfluorooctyl iodide and 1H, 1H, 2H, 2H-perfluorododecyl iodide were purchased from Fluorochem Ltd. Other commercial reagents were purchased from Sigma-Aldrich Co. Two polymer beads, XAD4 and MAC-3, was purchased from Sigma-Aldrich Co and used as received. XAD4 is composed of polystyrene that is crosslinked with divinylbenzene, and is hereinafter referred to as polystyrene beads. Polystyrene beads are mesoporous with large surface area and their size is 20-60 mesh. MAC-3 is composed of polyacrylate with some carboxyl groups on the surface, and is hereinafter referred to as polyacrylate beads. Polyacrylate beads are macroporous without large surface area and their size is 12-50 mesh.

2.2 Synthesis of Hydrazones

1,3-Phenylenebis((4-phenoxyphenyl)methanone) hydrazone (2a). A suspension of 1,3-EKKE **1a** (0.25g, 0.53mmol) in ethanol (7mL) was treated with hydrazine monohydrate (0.52mL, 10.6mmol). A few drops of acetic acid (about 0.2ml) were added as catalyst. The resulting mixture was heated to a gentle reflux for 40 h. After the mixture was cooled, water (50ml) was added, giving a suspension. The mixture was filtered and the precipitate was dried in an oven. The crude product **2a** (77%) of a light yellow solid as a mixture of diastereoisomers was used without further purification. m.p.: 60-62°C; δ H (500.3MHz, DMSO-d₆): 6.16-6.54(m, 4H), 6.90-7.56(m, 22H); δ C (125.8MHz, DMSO-d₆): 118.7, 118.8, 119.1(d), 119.5(d), 119.6, 119.7, 123.3, 123.9, 124.3, 124.4, 125.0, 125.9, 126.2, 127.5, 127.6, 127.8, 127.9, 128.3(d), 129.6, 129.8, 130.5, 130.6, 130.8, 131.1, 131.2, 133.3, 134.7, 134.8, 135.0, 139.3, 140.6, 143.3, 143.4, 144.2, 144.4, 156.5(d), 156.7, 157.0, 157.2, 157.4; IR ν_{\max} (cm⁻¹): 3403, 3039, 2922, 1586, 1502, 1486, 1232, 1164, 1070; HRMS: m/z calcd for C₃₂H₂₇O₂N₄: 499.21285; found: 499.21291 [M+H]⁺.

1,4-Phenylenebis((4-phenoxyphenyl)methanone) hydrazone (2b). A suspension of 1,4-EKKE **1b** (0.25g, 0.53mmol) in ethanol (7mL) was treated with hydrazine monohydrate (0.52mL, 10.6mmol). A few drops of acetic acid (about 0.2ml) were added as catalyst. The resulting mixture was heated to a gentle reflux for 40 h. After cooling, the mixture was filtered and the precipitate was dried in an oven. The crude product **2b** (82%) of a white solid as a mixture of diastereoisomers was used without further purification. m.p.: 181-184°C; δ H (500.3MHz, DMSO-d₆): 6.33(s, 4H), 7.09-7.25(m, 14H), 7.28(s, 4H), 7.44(t, 4H); δ C (125.8MHz, DMSO-d₆): 119.6(d), 124.3, 125.7, 128.3, 130.6, 131.1, 138.3, 144.1, 156.7, 157.3; IR ν_{\max} (cm⁻¹): 3378, 3276, 3038, 1588, 1503, 1488, 1250, 1164, 1070, 872, 840, 755, 691; HRMS: m/z calcd for C₃₂H₂₇O₂N₄: 499.21285; found: 499.21259 [M+H]⁺.

Naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) hydrazone (2c). A suspension of EKNKE **1c** (0.28g, 0.53mmol) in ethanol (7mL) was treated with hydrazine monohydrate (0.52mL, 10.6mmol). A few drops of acetic acid (about 0.2ml) were added as catalyst. The resulting mixture was heated to a gentle reflux for 40 h. After cooling, the mixture was filtered and the precipitate was dried in an oven. The crude product **2c** (84%) of a white solid as a mixture of diastereoisomers was used without further purification. m.p.: 225-227°C; δ H (500.3MHz, DMSO-d₆): 6.34(s, 2H), 6.44(s, 2H), 6.93-7.04(m, 4H), 7.09-7.25(m, 6H), 7.30(m, 2H), 7.35-7.49(m, 8H), 7.70(d, 1H), 7.83(d, 1H), 7.94(s, 1H), 8.18(d, 1H); δ C (125.8MHz, DMSO-d₆): 118.9, 119.0, 119.3, 119.6, 119.7, 124.0(d), 124.2, 124.4, 124.8, 127.3, 127.7, 128.2, 128.3, 128.6, 129.2, 129.9, 130.5, 130.6, 131.3, 132.0, 132.6, 133.5, 134.9, 137.1, 144.1, 144.2, 156.5, 156.7, 157.1, 157.4; IR ν_{\max} (cm⁻¹): 3394, 3357, 3273, 3062, 1587, 1501, 1486, 1235, 1168, 1067; HRMS: m/z calcd for C₃₆H₂₉O₂N₄: 549.22850; found: 549.22812 [M+H]⁺.

4,4'-((((1E,1'E)-1,3-Phenylenebis(hydrazonomethylene))bis(4,1-phenylene))bis(oxy))dianiline (2d). A suspension of **1d** (0.36g, 0.51mmol) in ethanol (7mL) was treated with hydrazine hydrate (0.51mL, 10.2mmol). A few drops of acetic acid (about 0.2ml) were added as catalyst. The resulting mixture was heated to a gentle reflux for 40 h. After cooling, the solution was evaporated under vacuum. The residue was dissolved in DCM (50ml), washed with water (50ml×4), dried with MgSO₄, and evaporated under vacuum. The crude product **2d** (87%) of a white solid as a mixture of diastereoisomers was used without further purification. m.p.: 92-96°C; δ H (500.3MHz, CDCl₃): 3.52(s, 4H), 5.43(s, 4H), 6.52-6.64(m, 4H), 6.70-6.85(m, 6H), 6.89-6.96(m, 2H), 7.05-7.13(m, 3H), 7.25-7.60(m, 5H); δ C (125.8MHz, CDCl₃): 116.2, 116.3, 116.8, 117.5, 117.6, 121.2, 121.3, 121.6, 121.7, 124.7, 125.5, 126.0, 126.4, 126.5, 127.1, 127.8, 127.9, 128.3, 129.3, 129.4, 130.3, 132.3, 132.5, 133.0, 134.4, 138.7,

140.0, 142.9, 143.0, 143.3, 143.4, 147.4, 147.6, 147.8, 148.1, 148.3, 148.8, 149.1, 159.1, 159.3, 159.5, 159.7; IR ν_{\max} (cm⁻¹): 3353, 3210, 3038, 1603, 1495, 1228, 1198, 1165; HRMS: m/z calcd for C₃₂H₂₉O₂N₆: 529.23465; found: 529.23431 [M+H]⁺.

4,4'-((((1Z,1'Z)-1,4-Phenylenebis(hydrazonomethylene))bis(4,1-phenylene))bis(oxy))dianiline (2e). A suspension of **1e** (0.36g, 0.51mmol) in ethanol (7mL) was treated with hydrazine hydrate (0.51mL, 10.2mmol). A few drops of acetic acid (about 0.2ml) were added as catalyst. The resulting mixture was heated to a gentle reflux for 40 h. After cooling, the mixture was filtered and the precipitate was dried in an oven. The crude product **2e** (86%) of a white solid as a mixture of diastereoisomers was used without further purification. m.p.: 106-110°C; δ H (400.3MHz, DMSO-d₆): 5.01(d, 4H), 6.05-6.45(m, 4H), 6.55-6.67(m, 4H), 6.72-6.89(m, 6H), 6.97-7.06(m, 2H), 7.10-7.30(m, 6H), 7.32-7.56(m, 2H); δ C (100.6MHz, DMSO-d₆): 115.3, 115.4, 116.6, 117.4, 117.5, 121.3, 121.4, 121.7(d), 125.7, 126.3, 126.5, 126.7, 127.4, 127.5, 129.0, 130.2, 130.8, 130.9, 132.3, 133.3, 138.4, 139.6, 143.8, 144.4, 144.8, 145.4(d), 145.9, 146.0, 146.3(d), 158.9, 159.5, 159.6; IR ν_{\max} (cm⁻¹): 3423, 3348, 3037, 1603, 1496, 1237, 1199, 1158; HRMS: m/z calcd for C₃₂H₂₉O₂N₆: 529.23465; found: 529.23418 [M+H]⁺.

2.3 Synthesis of Bis(aryldiazomethane)s

1,3-Bis(diazo(4-phenoxyphenyl)methyl)benzene (3a). A mixture of manganese dioxide (0.22g, 2.48mmol), sodium sulfate (0.19g, 1.34mmol), and potassium hydroxide (0.06g, 1.35mmol) was added to a solution of **2a** (0.23g, 0.46mmol) in dichloromethane (15mL). The mixture was vigorously stirred for 2 hours in the dark, and then filtered through a pad of Celite™. The filtrate was concentrated under vacuum to yield **3a** (90%) as a purple solid and then stored at sub-ambient temperature to avoid decomposition. m.p.: 70-74°C; δ H (400.3MHz, CDCl₃): 6.55-7.58(m, 22H); δ C (100.7MHz, CDCl₃): 62.0, 119.0, 119.7, 120.2, 121.5, 123.5, 123.5, 127.3, 129.9, 131.2, 155.7, 157.0; IR ν_{\max} (cm⁻¹): 3039, 2031, 1588, 1503, 1486, 1234, 1165.

1,4-Bis(diazo(4-phenoxyphenyl)methyl)benzene (3b). A mixture of manganese dioxide (0.22g, 2.48mmol), sodium sulfate (0.19g, 1.34mmol), and potassium hydroxide (0.06g, 1.35mmol) was added to a solution of **2b** (0.23g, 0.46mmol) in dichloromethane (120mL). The mixture was vigorously stirred for 2 hours in the dark, and then filtered through a pad of Celite™. The filtrate was concentrated under vacuum to yield **3b** (86%) as a purple solid and then stored at sub-ambient temperature to avoid decomposition. m.p.: 110°C(decompose); δ H (400.3MHz, CDCl₃): 6.92-7.46(m, 22H); δ C (100.7MHz, CDCl₃): 62.0, 118.9, 119.7, 123.5, 123.7, 125.3, 126.5, 127.2, 129.8, 155.6, 157.1; IR ν_{\max} (cm⁻¹): 3035, 2022, 1588, 1503, 1485, 1239, 1164.

2,6-Bis(diazo(4-phenoxyphenyl)methyl)naphthalene (3c). A mixture of manganese dioxide (0.22g, 2.48mmol), sodium sulfate (0.19g, 1.34mmol), and potassium hydroxide (0.06g, 1.35mmol) was added to a solution of **2c** (0.25g, 0.46mmol) in dichloromethane (120mL). The mixture was vigorously stirred for 2 hours in the dark, and then filtered through a pad of Celite™. The filtrate was concentrated under vacuum to yield **3c** (85%) as a purple solid and then stored at sub-ambient temperature to avoid decomposition. m.p.: 118°C(decompose); δ H (500.3MHz, CDCl₃): 6.97-7.04(m, 8H), 7.04-7.09(m, 2H), 7.25-7.33(m, 10H), 7.54(d, 2H), 7.66(d, 2H); δ C (125.8MHz, CDCl₃): 62.5, 119.0, 119.7, 122.1, 123.6, 123.8, 123.8, 126.7, 127.5, 128.2, 129.9, 132.0, 155.9, 157.0; IR ν_{\max} (cm⁻¹): 3057, 3037, 2020, 1643, 1589, 1484, 1249, 1161.

4,4'-((((1,3-Phenylenebis(diazomethylene))bis(4,1-phenylene))bis(oxy))dianiline (3d). A mixture of manganese dioxide (0.22g, 2.48mmol), sodium sulfate (0.19g, 1.34mmol), and potassium hydroxide (0.06g, 1.35mmol) was added to a solution of **2d** (0.24g, 0.46mmol) in dichloromethane (15mL). The mixture was vigorously stirred for 5 hours in the dark, and then filtered through a pad of Celite™. The filtrate was concentrated under vacuum to yield **3d** (89%) as a purple solid and then stored at sub-ambient temperature to avoid decomposition. m.p.: 115°C(Decomposed); δ H (500.3MHz, CDCl₃): 3.52(s, 4H), 6.50-7.34(m, 20H); δ C (125.8MHz, CDCl₃): 61.8, 116.3, 118.1, 119.9, 121.1, 121.1, 127.4, 129.8, 131.3, 142.9, 148.4, 157.5; IR ν_{\max} (cm⁻¹): 3446, 3366, 3038, 2031, 1590, 1495, 1228.

4,4'-((((1,4-Phenylenebis(diazomethylene))bis(4,1-phenylene))bis(oxy))dianiline (3e). A mixture of manganese dioxide (0.22g, 2.48mmol), sodium sulfate (0.19g, 1.34mmol), and potassium hydroxide (0.06g, 1.35mmol) was added to a solution of **2e** (0.24g, 0.46mmol) in dichloromethane (150mL). The mixture was vigorously stirred for 5 hours in the dark, and then filtered through a pad of Celite™. The filtrate was concentrated under vacuum to yield **3e** (92%) as a purple solid and then stored at sub-ambient temperature to avoid decomposition. m.p.:

110°C(Decomposed); δ H (500.3MHz, CDCl_3): 3.53(s, 4H), 6.62(m, 4H), 6.83(m, 4H), 6.91(m, 4H), 7.11-7.18(m, 8H); δ C (125.8MHz, CDCl_3): 61.8, 116.3, 118.1, 121.1, 122.3, 125.1, 126.5, 127.3, 142.9, 148.4, 157.5; IR ν_{max} (cm^{-1}): 3426, 3376, 3295, 3196, 3036, 2023, 1496, 1239.

2.4 Synthesis of Bis(arylester)s

1,3-Phenylenebis((4-phenoxyphenyl)methylene) diacetate (4a). Acetic acid (2.86ml, 50.0mmol) was added to a solution of **3a** (0.25g, 0.5mmol) in DCM (10ml). The mixture was stirred in the dark at room temperature until the color changed from purple to light yellow (about 20 min). The mixture was washed with 2M Na_2CO_3 aq. solution (60ml), water (20ml \times 3), dried with MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (3/1) to give the product **4a** as a light yellow sticky liquid (71%). δ H (400.3MHz, CDCl_3): 2.03(d, 6H), 6.78(s, 2H), 6.87(m, 4H), 6.92(m, 4H), 7.03(t, 2H), 7.15-7.28(m, 12H); δ C (100.7MHz, CDCl_3): 21.3, 76.2, 118.5, 119.2, 123.6, 125.5, 125.6, 126.5, 128.8(d), 128.9(d), 129.8, 134.7, 140.5, 156.8, 157.2, 170.0; IR ν_{max} (cm^{-1}): 3063, 3039, 1740, 1590, 1506, 1488, 1370, 1226, 1168, 1023; HRMS: m/z calcd for $\text{C}_{36}\text{H}_{30}\text{O}_6\text{Na}$: 581.19346; found: 581.19326 $[\text{M}+\text{Na}]^+$.

1,4-Phenylenebis((4-phenoxyphenyl)methylene) diacetate (4b). Acetic acid (2.86ml, 50.0mmol) was added to a solution of **3a** (0.25g, 0.5mmol) in DCM (10ml). The mixture was stirred in the dark at room temperature until the color changed from purple to light yellow (about 20 min). The mixture was washed with 2M Na_2CO_3 aq. solution (60ml), water (20ml \times 3), dried with MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (3/1) to give the product **4b** as a light yellow sticky liquid (67%). δ H (400.3MHz, CDCl_3): 2.07(d, 6H), 6.77(s, 2H), 6.87(m, 4H), 6.93(m, 4H), 7.03(t, 2H), 7.17-7.29(m, 12H); δ C (100.7MHz, CDCl_3): 21.3, 76.2, 118.5, 119.2, 123.6, 127.1, 127.2, 128.7, 129.8, 134.6, 139.9, 156.8, 157.2, 170.0; IR ν_{max} (cm^{-1}): 3061, 3039, 1739, 1590, 1506, 1488, 1370, 1227, 1167, 1019; HRMS: m/z calcd for $\text{C}_{36}\text{H}_{30}\text{O}_6\text{Na}$: 581.19346; found: 581.19376 $[\text{M}+\text{Na}]^+$.

Naphthalene-2,6-diylbis((4-phenoxyphenyl)methylene) diacetate (4c). Acetic acid (2.86ml, 50.0mmol) was added to a solution of **3a** (0.27g, 0.5mmol) in DCM (10ml). The mixture was stirred in the dark at room temperature until the color changed from purple to light yellow (about 20 min). The mixture was washed with 2M Na_2CO_3 aq. solution (60ml), water (20ml \times 3), dried with MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (3/1) to give the product **4c** as a light yellow sticky liquid (70%). δ H (400.3MHz, CDCl_3): 2.08(d, 6H), 6.76-6.93(m, 10H), , 6.98(t, 2H), 7.21(t, 8H), 7.71(d, 4H); δ C (100.7MHz, CDCl_3): 21.4, 76.5, 118.6, 119.2, 123.6, 125.4, 125.6, 128.7, 128.9, 129.9, 132.7, 134.8, 138.1, 156.8, 157.2, 170.1; IR ν_{max} (cm^{-1}): 3039, 1738, 1589, 1505, 1487, 1369, 1223, 1166, 1021; HRMS: m/z calcd for $\text{C}_{40}\text{H}_{32}\text{O}_6\text{Na}$: 631.20911; found: 631.20890 $[\text{M}+\text{Na}]^+$.

1,3-Phenylenebis((4-(4-aminophenoxy)phenyl)methylene) diacetate (4d). Acetic acid (2.86ml, 50.0mmol) was added to a solution of **3d** (0.27g, 0.5mmol) in DCM (10ml). The mixture was stirred in the dark at room temperature until the color changed from purple to light yellow (about 20 min). The mixture was washed with 2M Na_2CO_3 aq. solution (60ml), water (20ml \times 3), dried with MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with DCM / acetone (10/1) to give the product **4d** as a light yellow solid (68%). m.p.: 76-80°C; δ H (500.3MHz, CDCl_3): 2.03(d, 6H), 3.51(s, 4H), 6.51-6.58(m, 4H), 6.70-6.82(m, 10H), 7.08-7.18(m, 6H), 7.18-7.25(m, 2H); δ C (125.9MHz, CDCl_3): 21.3, 76.3, 116.3, 117.0, 121.3, 125.4(d), 126.4(d), 128.8, 133.5, 140.6, 143.1, 148.1, 158.9, 170.1; IR ν_{max} (cm^{-1}): 3453, 3368, 3040, 2980, 1733, 1611, 1498, 1370, 1223, 1167, 1022; HRMS: m/z calcd for $\text{C}_{36}\text{H}_{32}\text{O}_6\text{N}_2\text{Na}$: 611.21526; found: 611.21453 $[\text{M}+\text{Na}]^+$.

1,4-Phenylenebis((4-(4-aminophenoxy)phenyl)methylene) diacetate (4e). Acetic acid (2.86ml, 50.0mmol) was added to a solution of **3e** (0.27g, 0.5mmol) in DCM (10ml). The mixture was stirred in the dark at room temperature until the color changed from purple to light yellow (about 20 min). The mixture was washed with 2M Na_2CO_3 aq. solution (60ml), water (20ml \times 3), dried with MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with DCM / acetone (10/1) to give the product **4e** as a light yellow solid (73%). m.p.: 100-104°C; δ H (500.3MHz, CDCl_3): 2.06(d, 6H), 3.53(s, 4H), 6.55-6.62(m, 4H), 6.70-6.82(m, 10H), 7.10-7.27(m, 8H); δ C (125.9MHz, CDCl_3): 21.3, 76.2, 116.2, 116.9, 121.3, 127.1(d), 128.6(d), 133.5, 139.9, 143.0, 148.1, 158.8, 170.0; IR ν_{max} (cm^{-1}): 3449, 3372, 3038, 2927, 1733, 1612,

1498, 1371, 1227, 1168, 1017; HRMS: m/z calcd for $C_{36}H_{32}O_6N_2Na$: 611.21526; found: 611.21518 $[M+Na]^+$.

2.5 Modification of Polymers

To a solution of diazomethane **3a~c** (0.1g) in dichloromethane (10mL) was added the required polymer (0.4g), and then the mixture was concentrated under vacuum. The polymer was collected and heated in an open flask to 120°C for 30min. The resulting solid was washed with dichloromethane for three times and the solid was dried to yield the functionalized polystyrenes **5a~c** and polyacrylates **6a~c**.

2.6 Preparation of Dyed Polymers

Fast Black Dyed Polymers (7a~c, 8a~c). Polymers **5a~c** and **6a~c** were dyed by immersing the functionalized polymers in a 0.01M solution of Fast Black K salt in acetone/water (1:1) for 18h at room temperature. The polymers were then collected by filtration and washed with acetone to furnish the corresponding polymers **7a~c** and **8a~c**.

Fast Dark Blue Dyed Polymers (9a~c, 10a~c). Polymers **5a~c** and **6a~c** were dyed by immersing the functionalized polymers in a 0.01M solution of Fast Dark Blue R salt in acetone/water (1:1) for 18h at room temperature. The polymers were then collected by filtration and washed with acetone to furnish the corresponding polymers **9a~c** and **10a~c**.

Fast Red Dyed Polymers (11a~c, 12a~c). Polymers **5a~c** and **6a~c** were dyed by immersing the functionalized polymers in a 0.03M solution of Fast Red RC salt in acetone/water (1:4) for 18h at room temperature. The polymers were then collected by filtration and washed with acetone to furnish the corresponding polymers **11a~c** and **12a~c**.

Fluorodiazonium salt Dyed Polymers (13a(f~g), 14a(f~g)). To a solution of fluorodiazonium salt **15f~g** in EtOH (5mL) was added the polymer **5a** or **6a**, and then the mixture was stored in the fridge (0-5°C) for 18h. After that, the polymer was washed with acetone and dried to yield the C_6F_{13} -functionalized polystyrene **13af**, C_6F_{13} -functionalized polyacrylate **13ag**, $C_{10}F_{21}$ -functionalized polystyrene **14af**, $C_{10}F_{21}$ -functionalized polyacrylate **14ag**.

2.7 Synthesis of Bis(arylketone)s

2,2,2-Trifluoro-N-(4-phenoxyphenyl)acetamide (16). 4-Phenoxyaniline (3.0g, 16.2mmol) and pyridine (3.93ml, 48.6mmol) were dissolved in DCM (50ml) with magnetic stirring. After cooling the solution to 5°C in an ice/water bath, a solution of trifluoroacetic anhydride (3.38ml, 24.3mmol) in DCM (15ml) was added dropwise. After the addition, the solution continued stirring overnight at room temperature. After that, the solution was evaporated under vacuum. Acetone (10ml) was added to dissolve the residue and the solution was poured into cold water (300ml) and stirred for 10 minutes. The mixture was filtered under vacuum and the solid was collected and dried in an oven at 80°C (96%). m.p.: 118-120°C; δH (400.3MHz, $CDCl_3$): 6.83-6.95(m, 4H), 7.02(t, 1H), 7.24(t, 2H), 7.40(d, 2H), 8.27(s, 1H); δC (100.7MHz, $CDCl_3$): 115.9(q), 119.1, 119.3, 122.6, 123.8, 129.9, 130.1, 155.2(q), 155.6, 156.8; δF (376.6MHz, $CDCl_3$): 75.6; IR ν_{max} (cm^{-1}): 3293, 1704, 1593, 1540, 1488, 1229, 1151; HRMS: m/z calcd for $C_{14}H_{11}O_2NF_3$: 282.07364; found: 282.07376 $[M+H]^+$.

N,N'-(((Isophthaloylbis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroacetamide (1d). Aluminum chloride (0.49g, 3.70mmol) was added to DCM (20ml) and the solution was cooled to 5°C with an ice/water bath. To that mixture was added **16** (0.42g, 1.48mmol) and isophthaloyl chloride (0.15g, 0.74mmol) in order. The mixture was stirred at room temperature for 2 hours. The reaction mixture was evaporated under vacuum before acetone (10ml) was added. The mixture in acetone was poured into cold water to yield a light pink precipitate, which was filtered and dried in an oven (80°C). After that, the solid was dispersed in DCM (10ml) and filtered again to get rid of unreacted starting material **16**. The mixture was filtered and the precipitate was dried under room temperature to obtain a light pink solid (89%). m.p.: 236-238°C; δH (500.3MHz, Acetone- d_6): 7.14(d, 4H), 7.23(d, 4H), 7.77(t, 1H), 7.85(d, 4H), 7.91(d, 4H), 8.05(d, 2H), 8.11(t, 1H), 10.4(s, 2H); δC (125.8MHz, Acetone- d_6): 116.1(q), 117.2, 120.7, 122.8, 128.8, 130.4, 131.8, 132.4, 132.8, 133.2, 138.1, 152.9, 154.7(q), 161.7, 193.7; δF (376.6MHz, Acetone- d_6): 76.1; IR ν_{max} (cm^{-1}): 3285, 1706, 1650, 1598, 1542, 1504, 1238, 1179, 1152; HRMS: m/z calcd for $C_{36}H_{21}O_6N_2F_6$: 691.13093; found: 691.12988 $[M-H]^-$.

N,N'-(((Terephthaloylbis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroacetamide (1e). Aluminum chloride (0.49g, 3.70mmol) was added to DCM (20ml) and the solution was cooled to 5°C with an ice/water bath.

To that mixture was added **16** (0.42g, 1.48mmol) and terephthaloyl chloride (0.15g, 0.74mmol) in order. The mixture was stirred at room temperature for 2 hours. The reaction mixture was evaporated under vacuum before acetone (10ml) was added. The mixture in acetone was poured into cold water to yield a light pink precipitate, which was filtered and dried in an oven (80°C). After that, the solid was dispersed in acetone (10ml) and filtered again to get rid of unreacted starting material **16**. The mixture was filtered and the precipitate was dried under room temperature to obtain a light pink solid (86%). m.p.: 324-327°C; δ H (400.3MHz, CDCl₃/TFA(1:1)): 7.18(d, 4H), 7.26(d, 4H), 7.67(d, 4H), 7.96(m, 2H), 7.98(m, 6H), 8.70(s, 2H); δ C (100.6MHz, CDCl₃/TFA(1:1)): 114.2(q), 117.5, 121.3, 123.7, 130.0, 130.1, 130.6, 133.9, 140.6, 153.9, 162.2(q), 163.4, 199.9; δ F (376.6MHz, CDCl₃/TFA(1:1)): 76.3; IR ν_{\max} (cm⁻¹): 3280, 2980, 1706, 1647, 1598, 1544, 1507, 1240, 1179, 1151; HRMS: m/z calcd for C₃₆H₂₁O₆N₂F₆: 691.13093; found: 691.13074 [M-H]⁻.

2.8 Synthesis of Fluoro-diazonium Salts

4-Nitrophenyl trifluoroacetamide (17). To a solution of 4-nitroaniline (3.00g, 21.6mmol) and pyridine (5.24ml, 64.8mmol) in dichloromethane (100ml) was added a trifluoroacetic anhydride (4.51ml, 32.4mmol) solution in dichloromethane (15ml) drop by drop. After that, the mixture was stirred for 18h before the solvent was evaporated out. Acetone (50ml) was added to dissolve the residue and the solution was poured to an ice/water mixture (400ml) to crystallize and filter. The solid was collected and dried in an oven (80°C, 4h) to acquire a yellow solid (95%). m.p.: 151-153°C; δ H (400.3MHz, DMSO-d₆): 7.93(d, 2H), 8.26(d, 2H), 11.8(s, 1H); δ C (125.8MHz, DMSO-d₆): 115.9(q), 121.3, 125.2, 142.9, 144.4, 155.4(q); δ F (376.6MHz, DMSO-d₆): -74.1; IR ν_{\max} (cm⁻¹): 3325, 3116, 1742, 1503, 1339, 1159, 1139, 1111; HRMS: m/z calcd for C₈H₄O₃N₂F₃: 233.07195; found: 233.01758 [M-H]⁻.

4-Aminophenyl trifluoroacetamide (18). **17** (1.52g, 6.5mmol) and iron powder (3.63g, 65.0mmol) were added to a mixed solvent of EtOH/H₂O (25ml/5ml). To that was added 2 drops of concentrated HCl aq. solution. The mixture was heated to reflux for 3h, and then filtered with a pad of CeliteTM. The filtrate was evaporated out to obtain a grey solid product **18** (92%). m.p.: 120-124°C; δ H (400.3MHz, DMSO-d₆): 5.16(s, 2H), 6.59(s, 2H), 7.31(s, 2H), 10.9(s, 1H); δ C (125.8MHz, DMSO-d₆): 114.1, 116.6(q), 123.1, 125.3, 147.2, 154.2(q); δ F (376.6MHz, DMSO-d₆): -73.8; IR ν_{\max} (cm⁻¹): 2406, 3335, 3030, 1712, 1515, 1200, 1181, 1150, 1130; HRMS: m/z calcd for C₈H₈ON₂F₃: 205.05832; found: 205.05833 [M+H]⁺.

4-1H, 1H, 2H, 2H-Perfluorooctylaminophenyl trifluoroacetamide (19f). **18** (0.30g, 1.47mmol) and 1H, 1H, 2H, 2H-perfluorooctyl iodide (0.12ml, 0.49mmol) were mixed together and heated to 140°C for 1h. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (8:1) to give the product **19f** as a light yellow solid (70%). m.p.: 68-70°C; δ H (500.3MHz, Acetone-d₆): 2.43(m, 2H), 3.43(q, 2H), 5.10(t, 1H), 6.57(d, 2H), 7.36(d, 2H), 9.82(s, 1H); δ C (125.8MHz, Acetone-d₆): 30.1(t), 35.4(t), 112.4, 116.3(q), 122.5, 126.3, 146.1, 154.2(q); δ F (470.4MHz, Acetone-d₆): -70.9, -76.6, -109.2, -117.3, -118.3, -118.9, -121.6; IR ν_{\max} (cm⁻¹): 3426, 3377, 1700, 1617, 1524, 1244, 1231, 1144; HRMS: m/z calcd for C₁₆H₁₁ON₂F₁₆: 551.06079; found: 551.06077 [M+H]⁺.

4-1H, 1H, 2H, 2H-Perfluorododecylaminophenyl trifluoroacetamide (19g). **18** (0.20g, 0.98mmol) and 1H, 1H, 2H, 2H-perfluorododecyl iodide (0.22g, 0.33mmol) were mixed together and heated to 140°C for 18h. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (8:1) to give the product **11b** as a light yellow solid (49%). m.p.: 120-122°C; δ H (400.3MHz, Acetone-d₆): 2.44(m, 2H), 3.43(q, 2H), 5.13(t, 1H), 6.58(d, 2H), 7.37(d, 2H), 9.85(s, 1H); δ C (125.8MHz, Acetone-d₆): 30.1(t), 35.4(t), 112.4, 116.4(q), 122.5, 126.3, 146.1, 154.2(q); δ F (376.6MHz, Acetone-d₆): -76.1, -81.7, -114.5, -122.3, -122.4, -123.3, -124.1, -126.8; IR ν_{\max} (cm⁻¹): 3311, 1696, 1551, 1523, 1839, 1148; HRMS: m/z calcd for C₂₀H₁₁ON₂F₂₄: 751.04827; found: 751.00783 [M+H]⁺.

4-1H, 1H, 2H, 2H-Perfluorooctylamino aniline (20f). **19f** (1.87g, 3.41mmol) and K₂CO₃ (4.71g, 34.1mmol) were added to a 100ml flask with MeOH (50ml). The mixture was heated to reflux for 18h, and then MeOH was evaporated off. Water (50ml) was added to the residue and ethyl acetate was used to extract (50ml×2). The organic layer was washed with water (50ml×3), dried with MgSO₄, and concentrated to obtain a brown solid. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (2:1) to give the product **20f** as a brown solid (86%). m.p.: 72-74 °C; δ H (400.3MHz, CDCl₃): 2.25(m, 2H), 3.27(s, 3H),

3.35(t, 2H), 6.48(m, 4H); δ C (100.7MHz, CDCl_3): 30.7(t), 37.0, 114.9, 116.9, 138.6, 139.8; δ F (376.6MHz, CDCl_3): -81.0, -114.0, -122.0, -123.0, -123.7, -126.3; IR ν_{max} (cm^{-1}): 3415, 3337, 1608, 1517, 1364, 1324, 1258, 1239, 1140, 1111; HRMS: m/z calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{F}_{13}$: 455.07874; found: 455.07790 $[\text{M}+\text{H}]^+$.

4-1H, 1H, 2H, 2H-Perfluorododecylamino aniline (20g). **19g** (0.66g, 0.87mmol) and K_2CO_3 (1.21g, 8.70mmol) were added to a 100ml flask with MeOH (50ml). The mixture was heated to reflux for 18h, and then MeOH was evaporated off. Water (30ml) was added to the residue and ethyl acetate was used to extract (30ml \times 2). The organic layer was washed with water (30ml \times 3), dried with MgSO_4 , and concentrated to obtain a brown solid. The crude product was purified by chromatography on a silica gel column eluting with petrol ether / ethyl acetate (2:1) to give the product **20g** as a yellow solid (67%). m.p.: 131-133 $^\circ\text{C}$; δ H (400.3MHz, Acetone- d_6): 2.36(m, 2H), 3.30(t, 2H), 3.86(s, 2H), 4.18(t, 1H), 6.40(m, 4H); δ C (100.6MHz, Acetone- d_6): 30.3(t), 36.6, 114.5, 115.9, 139.6, 140.0; δ F (376.6MHz, Acetone- d_6): -81.7, -114.4, -122.3, -122.4, -123.3, -124.1, -126.8; IR ν_{max} (cm^{-1}): 3413, 3336, 1610, 1518, 1201, 1147, 1106; HRMS: m/z calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{F}_{21}$: 655.06597; found: 655.06453 $[\text{M}+\text{H}]^+$.

4-1H, 1H, 2H, 2H-Perfluorooctylamino diazonium salt (15f). **20f** (0.2g, 0.44mmol), isoamyl nitrite (0.059ml, 0.44mmol), tetrafluoroboric acid (0.16ml, 0.88mmol), and EtOH (10ml) were mixed together at 0 $^\circ\text{C}$ for 1h. The mixture was filtered and DCM (50ml) was added to the filtrate to precipitate. The solid was filtered and dried under r.t. for a few minutes to obtain a green solid (82%). m.p.: 138-140 $^\circ\text{C}$ (decomposed); δ H (500.3MHz, Acetone- d_6): 2.68(m, 2H), 4.61(t, 2H), 8.43(d, 2H), 8.98(d, 2H); δ C (125.8MHz, Acetone- d_6): 27.1(t), 34.1(t), 110.6, 119.3, 135.3, 150.9; δ F (376.6MHz, Acetone- d_6): -81.7, -114.9, -122.5, -123.5, -124.0, -126.8, -151.0; IR ν_{max} (cm^{-1}): 3118, 2276, 1589, 1524, 1198, 1146, 1064, 1032.

4-1H, 1H, 2H, 2H-Perfluorododecylamino diazonium salt (15g). **20g** (0.2g, 0.31mmol), isoamyl nitrite (0.041ml, 0.31mmol), tetrafluoroboric acid (0.11ml, 0.62mmol), and EtOH (10ml) were mixed together at 0 $^\circ\text{C}$ for 1h. The presence of the desired diazonium salt was confirmed using the H-acid test.²⁴ A sample of the diazonium salt solution **15g** (1 ml) was adjusted to pH 4 using sodium acetate and then H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid) was added (10 mg). The mixture was mixed well and left to stand at room temperature for 15 minutes. The formation of a dark purple color indicated the generation of diazonium salt.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of Bis(aryldiazomethane)s

As shown in Scheme 2, bis(arylketone)s **1a~e** were treated with hydrazine monohydrate to generate bis(hydrazone)s **2a~e**, which were then oxidized by manganese dioxide to obtain bis(aryldiazomethane)s **3a~e**. The starting materials **1a~c** were commercial reagents, while compounds **1d~e** were synthesized. Overall, five new bis(aryldiazomethane)s were designed both to test the synthetic approach as well as to study the difference of polymer modifications. As for the synthesis of **1d~e** (Scheme 3), 4-phenoxyaniline was treated with trifluoroacetic anhydride to give **16**, followed by the Friedel–Crafts reaction to generate bis(arylketone)s **1d~e** with relatively high yield²⁷. It is worth noting that bis(aryldiazomethane)s **3d~e** contain unprotected amino groups, but they are very stable in the oxidation step with manganese dioxide as oxidant. These oxidation conditions are very mild, allowing selective oxidation of the hydrazone to the diazo compound²⁸⁻³⁰, which leaves free amine undamaged. The greater stability of these systems compared to the diazo compound derived from Michler's ketone is noteworthy²².

[Insert Scheme 2 here]

[Insert Scheme 3 here]

In our former work¹⁹⁻²⁶, the two-step synthesis via hydrazones was reported to be a highly effective approach to obtain aryldiazomethanes. However, it was of interest to examine the reaction of bis(aryldiazomethane)s as compared to mono(aryldiazomethane)s, and for that purpose, acetic acid was used to react with bis(aryldiazomethane), a known very fast reaction used to generate esters^{31, 32}. From the IR spectra, NMR spectra, and MS data, the structures of bis(arylester)s products **4a~e** were confirmed, and no mono(arylester)s

were formed.

3.2 Preparation of Modified or Dyed Polymers

In order to allow rapid access to functionalized polymers, we adapted our previously published approach for surface modification using bis(arylcabene)s and their subsequent dyeing by diazonium salt coupling³³. This is a convenient and efficient method for the introduction of diverse chemical functionality onto a substrate (Scheme 4). Furthermore, polystyrene beads and polyacrylate beads were used as templates, since we have already shown that this approach is equally applicable to other substrates¹⁹. Firstly, polystyrene beads or polyacrylate beads were mixed with bis(aryldiazomethane)s and heated at 120°C, to form modified polystyrenes **5a~e** and modified polyacrylates **6a~e**. In this step, carbenes are generated from diaryldiazomethanes by heating, followed by their insertion reaction with C–H bond (on the surface of XAD4 and MAC-3) or O–H bond (on the surface of MAC-3), which leads to the modified polymer beads. For modified polymer beads **5a~c** or **6a~c**, which only contain phenoxy groups with the elements of carbon, hydrogen, and oxygen, the chemical structure is very similar to starting polymer beads (XAD4 or MAC-3), and hence very difficult to characterize. Therefore, commercially available Fast Black K salt, Fast Dark Blue R salt, and Fast Red RC salt were used to dye those polymers, giving the corresponding derivatives: Fast Black dyed polystyrenes **7a~c**, Fast Black dyed polyacrylates **8a~c**, Fast Dark Blue dyed polystyrenes **9a~c**, Fast Dark Blue dyed polyacrylates **10a~c**, Fast Red dyed polystyrenes **11a~c**, Fast Red dyed polyacrylates **12a~c**. The structure of Fast Black K salt, Fast Dark Blue R salt, and Fast Red RC salt are depicted in Scheme 4. All of those dyes are aromatic diazonium salts, which can easily react with phenoxyl groups by azo coupling reaction. In this way, the elements of nitrogen or chlorine were introduced to the polymer beads **5a~c** or **6a~c**, and which are easily detected by XPS or Elemental Analysis. On the other hand, for modified polystyrene beads **5d~e** and polyacrylate beads **6d~e** that already contain amino groups, there is no need for this dyeing step. In addition, two fluoro-diazonium salts **15(f~g)** were synthesized, and then used to dye polymer beads **5a** and **6a**, to generate fluoro-polystyrenes **13a(f~g)** and fluoro-polyacrylates **14a(f~g)** (Scheme 4). Thus, chemical functionality can be readily introduced to polymers.

[Insert Scheme 4 here]

The synthetic route for the preparation of the fluoro-diazonium salt is shown in Scheme 5. Firstly, 4-nitroaniline was converted into 4-trifluoroacetyl amino aniline **18** by a two-step reaction. This step is required because the strongly electron-withdrawing nitro group makes the amino group very inert, which does not react with perfluoroalkyl iodide. Two kinds of perfluoroalkyl iodide with different numbers of CF₂ unit were then reacted with **18** to generate **19(f~g)**^{34, 35}, and subsequent cleavage of trifluoroacetyl group gave **20(f~g)**. Finally, fluoroamines **20(f~g)** were treated with isoamyl nitrite to give fluoro-diazonium salts **15(f~g)**. The fluorodiazonium salts could be isolated and their chemical structures could be easily verified by IR and NMR analysis, but were best stored below zero degrees Celsius. Application of the H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid) test also confirmed success of the diazo reaction (formation of intense colouration)³⁶.

[Insert Scheme 5 here]

3.3 Surface Properties

3.3.1 Colour

It is interesting that modified polymer beads **5** and **6** show light yellow colour, indicative of the introduction of the weak aromatic chromophore of the carbene unit. After the reaction with commercial dyes by azo coupling in the second step, even more intensely colored polymer beads were obtained, which enabled access to a library of coloured polymers (Table 1).

Table 1 Library of modified and dyed polymer beads

[Insert Table 1 here]

3.3.2 XPS Analysis

As mentioned above, there is no distinct variation of element in polymers **5a~c** and **6a~c** before and after modification with bis(arylcarbene)s so that it is very difficult to test whether the modification protocol is successful or not. Therefore, three commercial diazonium salts, which contain nitrogen and chlorine, and two fluorine containing diazonium salts, were used to dye the modified polymers in a second step. The presence of nitrogen (Figure 1(1), Figure 1(2), and Figure 1(3)), chlorine (Figure 1(5)), fluorine (Figure 1(6)), and their loading density on the surface were confirmed by XPS analysis (Table 2). Similarly, the presence of nitrogen in modified polymers **5d~e** and **6d~e** was directly detected by XPS (Figure 1(4)). The binding energy was calibrated by the HOPG carbon before analysis. All of the detailed data were calculated using the CasaXPS software and the reference library of ALSCOF, and the results were shown in Table 2.

Table 2 XPS data of modified and dyed polymers

[Insert Table 2 here]

[Insert Figure 1 here]

Figure 1 Typical XPS peaks from modified or dyed polymers: (1) **8a** for N; (2) **10a** for N; (3) **12a** for N; (4) **6d** for N; (5) **8a** for Cl; (6) **14ag** for F

From Table 2, the observed N/C ratio confirms the insertion reaction of bis(arylcarbene)s into the polymer, although the detected value is generally smaller than the expected value. Reasons for this have been previously discussed²², but the N/Cl and N/F ratios were in much better accordance with the expected values. It was observed that the modification effect seems better when the substituent in R₂ structure is at the meta-position (**5a**, **5d**, **6a**, **6d**). Moreover, different states of nitrogen in the dyed polymers were detected (Figure 1) with N 1s signals at binding energies of 400 eV (N=N) and 406 eV (NO₂), respectively³⁷. The following is the comparison of dyed polymers (**8a**, **10a**, **12a**) by different diazonium salts, which were obtained from polymer **6a**. There is a nitro group in Fast Black or Fast Blue, so polymer **8a** or **10a** shows a peak at 406 eV in Figure 1(1) or Figure 1(2). The area of that peak is about one quarter to the area of the peak at 400 eV, which belongs to the N=N group. That is greatly in accordance with the quantitative ratio of two different types of nitrogen although the signal to noise ratio of those peaks is very low. However, for the Fast Red system, there is no nitro group so that only one peak at 400 eV is found in polymer **12a** (Figure 1(3)). The same situation occurs in polymer **6d**, which only has amino groups modified on its surface so that one peak at 400 eV is found by XPS.

3.3.3 Surface Area and Pore Size Distribution

The results of BET surface area are shown in Table 3. It can be found that the modification effect of **5a** and **5d** is much better than others because their surface areas were almost half compared to starting polystyrene beads (XAD4). However, for the samples **5b**, **5c**, and **5e**, their surface areas were nearly unchanged and their modification loading was not so good, and this was in accordance with the XPS data in Table 2. After repeating this experiment several times, it was concluded that the poor solubility of **3b**, **3c**, and **3e** in any solvent was responsible, since it did not allow intimate mixing with the polymers in DCM solution in the first step.

Table 3 BET surface area data of modified polystyrene beads

[Insert Table 3 here]

Furthermore, BJH pore size distribution of samples **5a~e** are shown in Figure 2. All the samples have very similar pore size distribution with peaks at about 200 Å, because the pore size in polystyrene samples is much larger than the reacting bis(aryldiazomethane) molecules. That clear feature shows that the modification by bis(arylcarbene) insertion reaction greatly changes the surface property of materials without blocking the mesopores, which has potential application in the research area of catalysts.

[Insert Figure 2 here]

Figure 2 BJH pore size distribution of modified polystyrene beads

Of interest is that because there are two diazo groups in each of **3a~e**, and both can react with the polymer surface by carbene insertion reaction after being heated, there is the possibility of crosslinking; in fact, for modified polyacrylate, connections between polymer beads can be sometimes found, especially for the sample **6d** (Table 1).

3.4 Bulk Properties

Bulk properties are critical in the performance of polymers, since they give the main physical and chemical properties that remain during the lifetime of application³⁸⁻⁴⁰. Hence, it is necessary to show that the change in surface properties is achieved without compromising the bulk properties, and in particular that depolymerisation of the substrate does not result from carbene reaction.

3.4.1 Solid State NMR Spectra

The polymers used in this work cannot be dissolved in any deuterated solvent before or after modification, which is strongly suggestive that depolymerisation during surface modification does not occur. For that reason, solid state ¹³C NMR with CP/MAS is used to confirm their structure. Polymers **4a** and **4d** were chosen for the NMR analysis because their modification loadings were better than the others, and the spectra were shown in Figure 3.

[Insert Figure 3 here]

Figure 3 Solid state NMR spectra of before and after modified polystyrenes

From Figure 3, seven peaks (1~7) in starting polystyrene beads (XAD4) were easily assigned. A new peak (i) in the region of 156.4ppm in polymer **5a** appeared when XAD4 was modified with compound **3a**, belonging to the carbon of phenolic ether, which verified the success of the modification. The chemical shifts of phenolic ether in compound **4a** are 156.8ppm and 157.2ppm, which are very similar to the peak (i) in polymer **5a**.

In contrast, two new peaks (ii and iii) in the region of 158.5ppm and 115.0ppm in **5d** generated after XAD4 was modified with compound **3d**. As shown in Figure 3, the peak (ii) at 158.5ppm belongs to one of the carbons directly attached to oxygen in the phenolic ether, which is very similar to the chemical shift of the same carbon in compound **4d** (158.9ppm). In addition, the peak at 115.0ppm (iii) belongs to the methine group that is nearest to the phenolic ether and on the same side of the amino group (the chemical shift of the same carbon in compound **4d** is 116.3ppm). Moreover, there is a little difference between the NMR spectra of **5a** and **5d**, especially the chemical shift of the carbon in phenolic ether, which lies in the influence of amino groups. All the evidence above proves the reliability of the modification protocol through bis(arylcarbene) insertion, and without depolymerisation.

3.4.2 TG/DSC analysis

Samples **5a** and **5d** were used to run TG/DSC analysis, as well as starting polystyrene beads (XAD4) (Figure 4). There is only one step in the TG curve and the temperature is about 450°C, which belongs to the decomposition of polystyrene⁴¹. Corresponding to that, there is a negative peak at 450°C in the DSC curve, which shows that the decomposition reaction is endothermic. It is very clear that there is nearly no difference between those three samples in the TG/DSC curve, which means that the bulk property of polystyrene is not changed after modification. However, in contrast to the decomposition peak, the glass transition peak (*T_g*) of these highly crosslinked polymers is too weak to be seen, and this is similar to the blank polystyrene material. This indicates that depolymerisation has not occurred, and that structural integrity of the polymer has been maintained during the surface modification process.

[Insert Figure 4 here]

Figure 4 TGA/DSC curve of polystyrene beads before and after modification

3.4.3 Elemental Analysis

Dyed polymers have the element of nitrogen, which can be easily detected by Elemental Analysis. As shown in Table 4, the starting polystyrene beads (XAD4) have no nitrogen, but the dyed polystyrene beads by azo coupling

show clear nitrogen content. That is, nitrogen is introduced onto the surface of XAD4, indicating success of both the carbene modification and the azo coupling reaction. Similarly, the modification by diazomethanes **3a** and **3d** with meta-substitution in the middle aryl ring shows the best modification effect, for the same reason as that stated above. On the basis of these results, polymer **5a** was dyed with fluoro-diazonium salts to give **13a(f~g)** and they were also found to have a relatively high content of nitrogen. When this data was used to calculate an average value for the ratio of unmodified to modified styrene units (*N*) (Table 5), it was found that the most highly modified systems showed modification on one in every 100-200 styrenes (e.g. samples **5d**, **7a**, **9a**) but this dropped markedly for the less efficiently modified systems.

Table 4 Elemental analysis data of modified and dyed polystyrene beads

[Insert Table 4 here]

However, by contrast, nitrogen cannot be found at all in modified polyacrylate beads. This appears to be because MAC-3 is a solid sphere rather than a porous one, and the loading density of nitrogen then falls below the CHN detection limit.

3.5 Loadings of surface-modified polymers

It is assumed that the dyeing process by diazonium salt does not change the crosslinking of polymers but only changes the constituent elements on the surface, and therefore the surface area is invariable before and after dyeing. According to eq. (1) and eq. (2), the loadings of surface-modified polystyrene beads can be calculated.

$$\text{Loadings} \left(\frac{\text{mmol}}{\text{g}} \right) = \left(\frac{\% \text{ of } N}{100} \right) \left(\frac{\text{g of } N}{\text{g of PSXAD}} \right) \times \left(\frac{1 \text{ mol of } N}{14 \text{ g of } N} \right) \times \left(\frac{1 \text{ mol of precursor compound}}{n \text{ mol of } N \text{ atoms}} \right) \times \left(\frac{10^3 \text{ mmol}}{1 \text{ mol}} \right) \quad (1)$$

$$\text{Loadings} \left(\frac{\text{molecules}}{\text{cm}^2} \right) = \text{loading} \left(\frac{\text{mmol}}{\text{g}} \right) \times \left(\frac{10^{-3} \text{ mol}}{1 \text{ mmol}} \right) \times \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) \times \left(\frac{1 \text{ g}}{\text{A cm}^2} \right) \times \left(\frac{1 \text{ m}^2}{10^4 \text{ cm}^2} \right) \quad (2)$$

Using the data contained in Tables 2-4, the surface loadings could be calculated, and are given in Table 5.

Table 5 Surface loadings data of modified and dyed polystyrene beads

[Insert Table 5 here]

It is found that the loading levels are in the range of 9.29×10^{-3} to $4.07 \times 10^{-1} \text{ mmol} \cdot \text{g}^{-1}$ or 6.41×10^{11} to 5.73×10^{13} molecules per cm^2 . These values are similar to other values obtained by surface modification using arylcarbenes²³. It seems that compound **3d** with a functional group of $-\text{NH}_2$ is the best one for bis(arylcarbene) insertion modification, followed by the compound **3a**. Compounds **3b**, **3c** and **3e** are not good structures.

4. CONCLUSION

Polystyrene beads and polyacrylate beads, two typical organic materials, have been examined for modification by a bis(arylcarbene) insertion reaction, followed by the azo coupling reactions to produce differing but controlled surface functionality. The signals of nitrogen, chlorine, and fluorine in XPS spectra show that the protocol is successful. Furthermore, the ratios of N/Cl and N/F can be calculated, which are in accordance with the formula of molecules attached to the surface of polymers. According to the results of solid state NMR spectra, new peaks at 156.4ppm (**5a**), 158.5ppm and 115.0ppm (**5d**) further confirm the significant change of chemical structure on the surface of modified polymers. BET data indicates that the surface area of modified polystyrenes **5a** and **5d** are almost cut to half compared to the unmodified polystyrene. BJH data states that pore size distribution is almost unchanged before and after modification, which means that the modification by bis(arylcarbene) insertion occurs but does not block mesopores on the surface of polystyrene. Furthermore, the bulk property is unchanged, since the result of TG/DSC analysis is very similar before and after modification. The data of BET and Elemental Analysis permits the calculation of the loadings of surface-modified polymers, which are in the range of 9.29×10^{-3} to $4.07 \times 10^{-1} \text{ mmol} \cdot \text{g}^{-1}$ or 6.41×10^{11} to 5.73×10^{13} molecules per cm^2 . This biscarbene-based modification is a useful protocol for organic materials with the promise of imparting new chemical functional groups and macroscopic properties to material surfaces. Moreover, this work shows that the bis(arylcarbene) system is as effective as mono(arylcarbene)s, but of significance since the starting bis(aryldiazomethane)s are more easily

accessible and easier to handle than the mono(aryldiazomethane)s.

ACKNOWLEDGMENTS

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Figures and Tables Contents

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Scheme 2

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Scheme 4

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Figure 1 Typical XPS peaks from modified or dyed polymers: (1) **8a** for N; (2) **10a** for N; (3) **12a** for N; (4) **6d** for N; (5) **8a** for Cl; (6) **14ag** for F

Figure 2 BJH pore size distribution of modified polystyrene beads

Figure 3 Solid state NMR spectra of before and after modified polystyrenes

Figure 4 TGA/DSC curve of polystyrene beads before and after modification

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Table 3 BET surface area data of modified polystyrene beads

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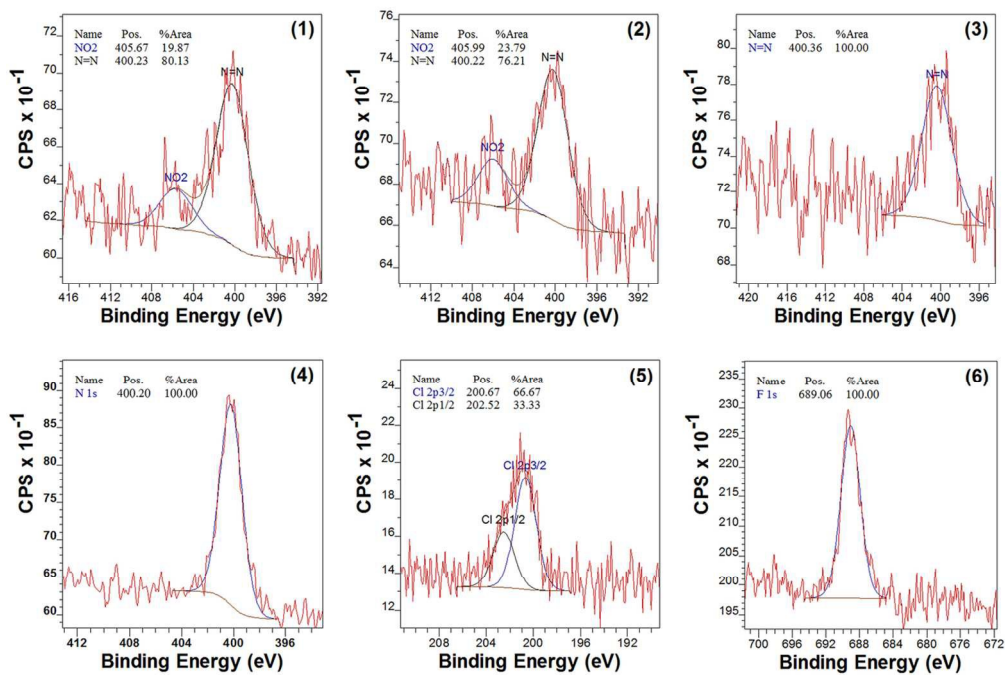


Figure 1 Typical XPS peaks from modified or dyed polymers: (1) **8a** for N; (2) **10a** for N; (3) **12a** for N; (4) **6d** for N; (5) **8a** for Cl; (6) **14ag** for F

Figure 1
116x79mm (300 x 300 DPI)

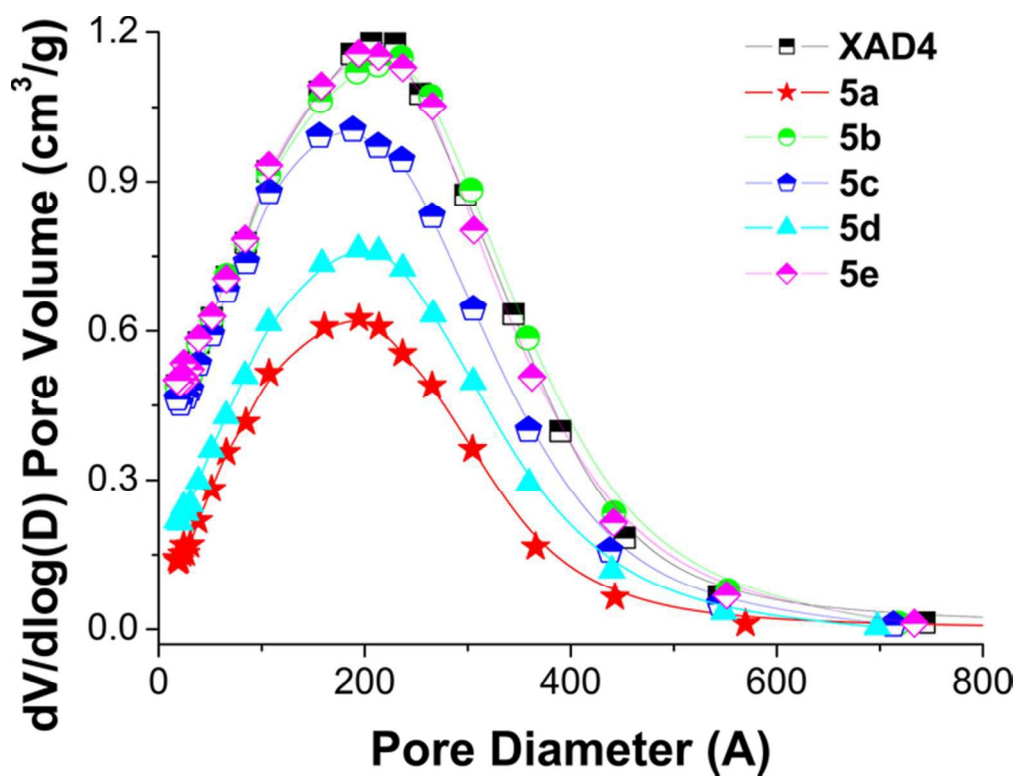


Figure 2 BJH pore size distribution of modified polystyrene beads

Figure 2

62x47mm (300 x 300 DPI)

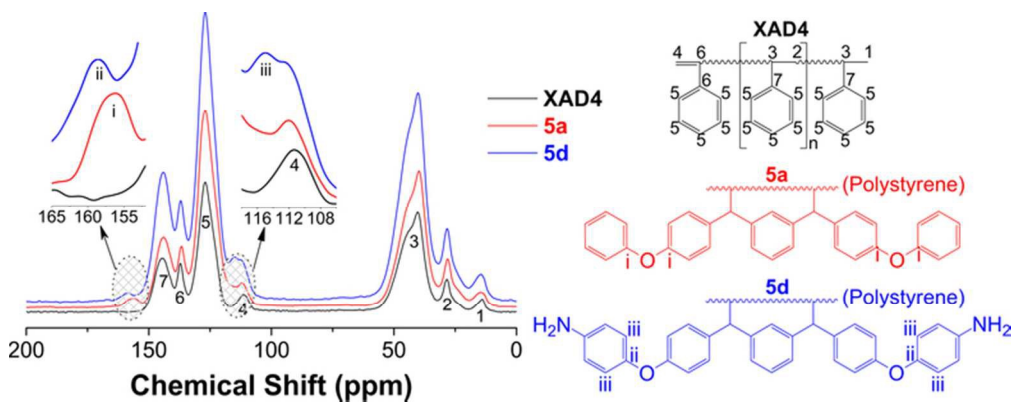


Figure 3 Solid state NMR spectra of before and after modified polystyrenes
Figure 3
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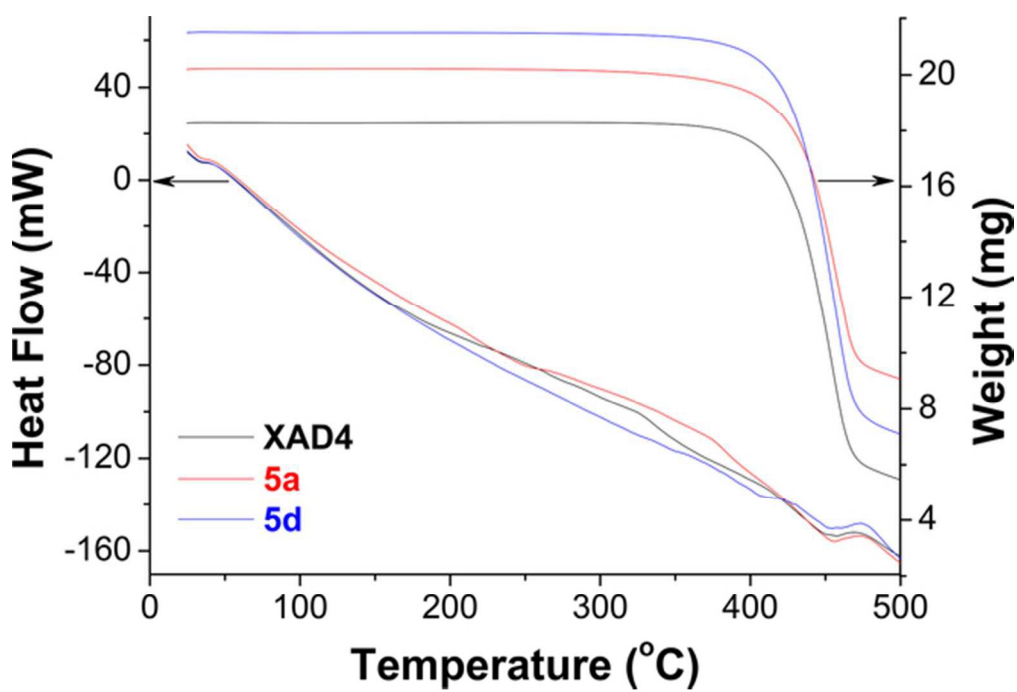

























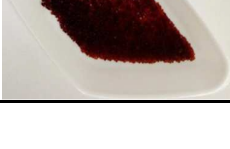


Figure 4 TGA/DSC curve of polystyrene beads before and after modification

Figure 4

55x37mm (300 x 300 DPI)

Table 1 Library of modified and dyed polymer beads

XAD4	Structure	Color	MAC-3	Structure	Color
5a	$R_1 = H$ $R_2 = 1,3-C_6H_4$		6a	$R_1 = H$ $R_2 = 1,3-C_6H_4$	
5b	$R_1 = H$ $R_2 = 1,4-C_6H_4$		6b	$R_1 = H$ $R_2 = 1,4-C_6H_4$	
5c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$		6c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$	
5d	$R_1 = CF_3C(=O)NH$ $R_2 = 1,3-C_6H_4$		6d	$R_1 = CF_3C(=O)NH$ $R_2 = 1,3-C_6H_4$	
5e	$R_1 = CF_3C(=O)NH$ $R_2 = 1,4-C_6H_4$		6e	$R_1 = CF_3C(=O)NH$ $R_2 = 1,4-C_6H_4$	
7a	$R_1 = H$ $R_2 = 1,3-C_6H_4$		8a	$R_1 = H$ $R_2 = 1,3-C_6H_4$	
7b	$R_1 = H$ $R_2 = 1,4-C_6H_4$		8b	$R_1 = H$ $R_2 = 1,4-C_6H_4$	
7c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$		8c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$	
9a	$R_1 = H$ $R_2 = 1,3-C_6H_4$		10a	$R_1 = H$ $R_2 = 1,3-C_6H_4$	
9b	$R_1 = H$ $R_2 = 1,4-C_6H_4$		10b	$R_1 = H$ $R_2 = 1,4-C_6H_4$	
9c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$		10c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$	
11a	$R_1 = H$ $R_2 = 1,3-C_6H_4$		12a	$R_1 = H$ $R_2 = 1,3-C_6H_4$	
11b	$R_1 = H$ $R_2 = 1,4-C_6H_4$		12b	$R_1 = H$ $R_2 = 1,4-C_6H_4$	







11c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$		12c	$R_1 = H$ $R_2 = 1,5-C_{10}H_6$	
13af	$R_1 = H$ $R_2 = 1,3-C_6H_4$ $R_f = C_6F_{13}$		14af	$R_1 = H$ $R_2 = 1,3-C_6H_4$ $R_f = C_6F_{13}$	
13ag	$R_1 = H$ $R_2 = 1,3-C_6H_4$ $R_f = C_{10}F_{21}$		14ag	$R_1 = H$ $R_2 = 1,3-C_6H_4$ $R_f = C_{10}F_{21}$	

Table 2 XPS data of modified and dyed polymers

Sample	Substrate	Formula	N/C expected ^a	XPS N/C found ^b	N/Cl expected ^a	XPS N/Cl found ^b	N/F expected ^a	XPS N/F found ^b
7a	XAD-4	C ₆₀ H ₄₈ N ₁₀ O ₁₀	0.167	0.019	- ^c	- ^c	- ^d	- ^d
8a	MAC-3	C ₆₀ H ₄₈ N ₁₀ O ₁₀	0.167	0.038	- ^c	- ^c	- ^d	- ^d
9a	XAD-4	C ₆₀ H ₄₄ Cl ₄ N ₁₀ O ₁₀	0.167	0.015	2.500	2.652	- ^d	- ^d
10a	MAC-3	C ₆₀ H ₄₄ Cl ₄ N ₁₀ O ₁₀	0.167	0.035	2.500	3.051	- ^d	- ^d
11a	XAD-4	C ₄₆ H ₃₆ Cl ₂ N ₄ O ₂	0.087	0.013	2.000	1.015	- ^d	- ^d
12a	MAC-3	C ₄₆ H ₃₆ Cl ₂ N ₄ O ₂	0.087	0.025	2.000	1.760	- ^d	- ^d
11b	XAD-4	C ₄₆ H ₃₆ Cl ₂ N ₄ O ₂	0.087	0.010	2.000	1.382	- ^d	- ^d
12b	MAC-3	C ₄₆ H ₃₆ Cl ₂ N ₄ O ₂	0.087	0.021	2.000	2.190	- ^d	- ^d
11c	XAD-4	C ₅₀ H ₃₈ Cl ₂ N ₄ O ₂	0.080	0.008	2.000	1.125	- ^d	- ^d
12c	MAC-3	C ₅₀ H ₃₈ Cl ₂ N ₄ O ₂	0.080	0.019	2.000	2.150	- ^d	- ^d
13af	XAD-4	C ₅₆ H ₃₄ F ₂₆ N ₆ O ₂	0.107	0.010	- ^c	- ^c	0.231	0.231
14af	MAC-3	C ₅₆ H ₃₄ F ₂₆ N ₆ O ₂	0.107	0.030	- ^c	- ^c	0.231	0.203
13ag	XAD-4	C ₆₄ H ₃₄ F ₄₂ N ₆ O ₂	0.093	0.019	- ^c	- ^c	0.142	0.155
14ag	MAC-3	C ₆₄ H ₃₄ F ₄₂ N ₆ O ₂	0.093	0.035	- ^c	- ^c	0.142	0.142
5d	XAD-4	C ₃₂ H ₂₈ N ₂ O ₂	0.063	0.019	- ^c	- ^c	- ^d	- ^d
6d	MAC-3	C ₃₂ H ₂₈ N ₂ O ₂	0.063	0.060	- ^c	- ^c	- ^d	- ^d
5e	XAD-4	C ₃₂ H ₂₈ N ₂ O ₂	0.063	0.016	- ^c	- ^c	- ^d	- ^d
6e	MAC-3	C ₃₂ H ₂₈ N ₂ O ₂	0.063	0.056	- ^c	- ^c	- ^d	- ^d

^a Expected values calculated from molecular formula assuming a surface monolayer of carbene insertion product. ^b Ratio taken from nitrogen and carbon counts in a survey spectrum. ^c Samples don't contain nitrogen. ^d Samples don't contain fluorine.

Table 3 BET surface area data of modified polystyrene beads

Samples	BET Surface Area
XAD4	$874.4 \pm 2.4 \text{ m}^2 \cdot \text{g}^{-1}$
5a	$321.5 \pm 0.9 \text{ m}^2 \cdot \text{g}^{-1}$
5b	$871.8 \pm 2.5 \text{ m}^2 \cdot \text{g}^{-1}$
5c	$819.4 \pm 2.3 \text{ m}^2 \cdot \text{g}^{-1}$
5d	$427.7 \pm 1.1 \text{ m}^2 \cdot \text{g}^{-1}$
5e	$886.4 \pm 3.0 \text{ m}^2 \cdot \text{g}^{-1}$

Table 4 Elemental analysis data of modified and dyed polystyrene beads

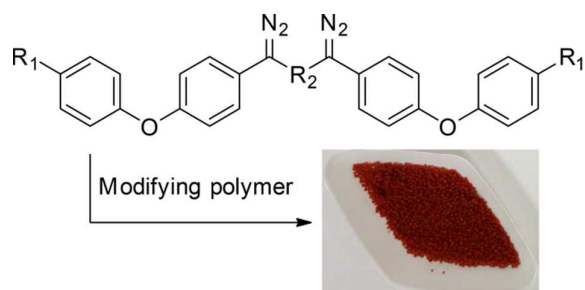
Sample	C%	H%	N%	<i>N</i>
XAD4	89.38	7.92	<0.10	-
7a	84.46	6.76	0.51	260
7b	85.88	7.50	0.13	1030
7c	85.22	7.47	0.15	890
9a	90.04	7.83	0.64	200
9b	90.96	7.87	0.29	460
9c	91.03	8.06	<0.10	>12100
11a	88.73	7.57	0.22	610
11b	89.74	7.60	<0.10	>1300
11c	89.89	7.89	<0.10	>1300
5d	90.39	7.83	1.14	110
5e	91.46	8.40	<0.10	1340
13af	89.49	7.82	0.68	190
13ag	89.92	8.23	0.50	260

Table 5 Surface loadings data of modified and dyed polystyrene beads

Sample	Value of n	Loadings ($\text{mmol} \cdot \text{g}^{-1}$)	Loadings ($\text{molecule} \cdot \text{cm}^{-2}$)
7a	10	3.64×10^{-2}	6.82×10^{12}
7b	10	9.29×10^{-3}	6.41×10^{11}
7c	10	1.07×10^{-2}	7.87×10^{11}
9a	10	4.57×10^{-2}	8.56×10^{12}
11a	4	3.93×10^{-2}	7.36×10^{12}
13af	6	8.09×10^{-2}	7.33×10^{12}
13ag	6	5.95×10^{-2}	5.39×10^{12}
5d	2	4.07×10^{-1}	5.73×10^{13}

Surface Modification of Polymers with Bis(arylcarbene)s from Bis(aryldiazomethane)s: Preparation, Dyeing and Characterization

Pengfei Yang and Mark G. Moloney



Modification of polymer beads by a series of bis(arylcarbene) provides access to materials with different surface chemical characteristics, and a subsequent dyeing process using different diazonium salts generates colored polymers with a variety of surface functional groups.