Functional Polymers By Covalent Surface Modification

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QuickTime™ and a
GIF decompressor
are needed to see this picture.

Performance Materials

- Technology is urgently needed to provide direct access to performance polymers with tailored properties.

- Desirable properties in one area often compromised by undesirable properties in another.

- Increasing demand for surfaces with carefully controlled properties.

- Most directly achieved by bulk modification or lamination of polymer, but this can lead to unwanted and unpredictable side effects.

- Surface modification provides the possibility of control of surface characteristics independently of properties of the bulk material.

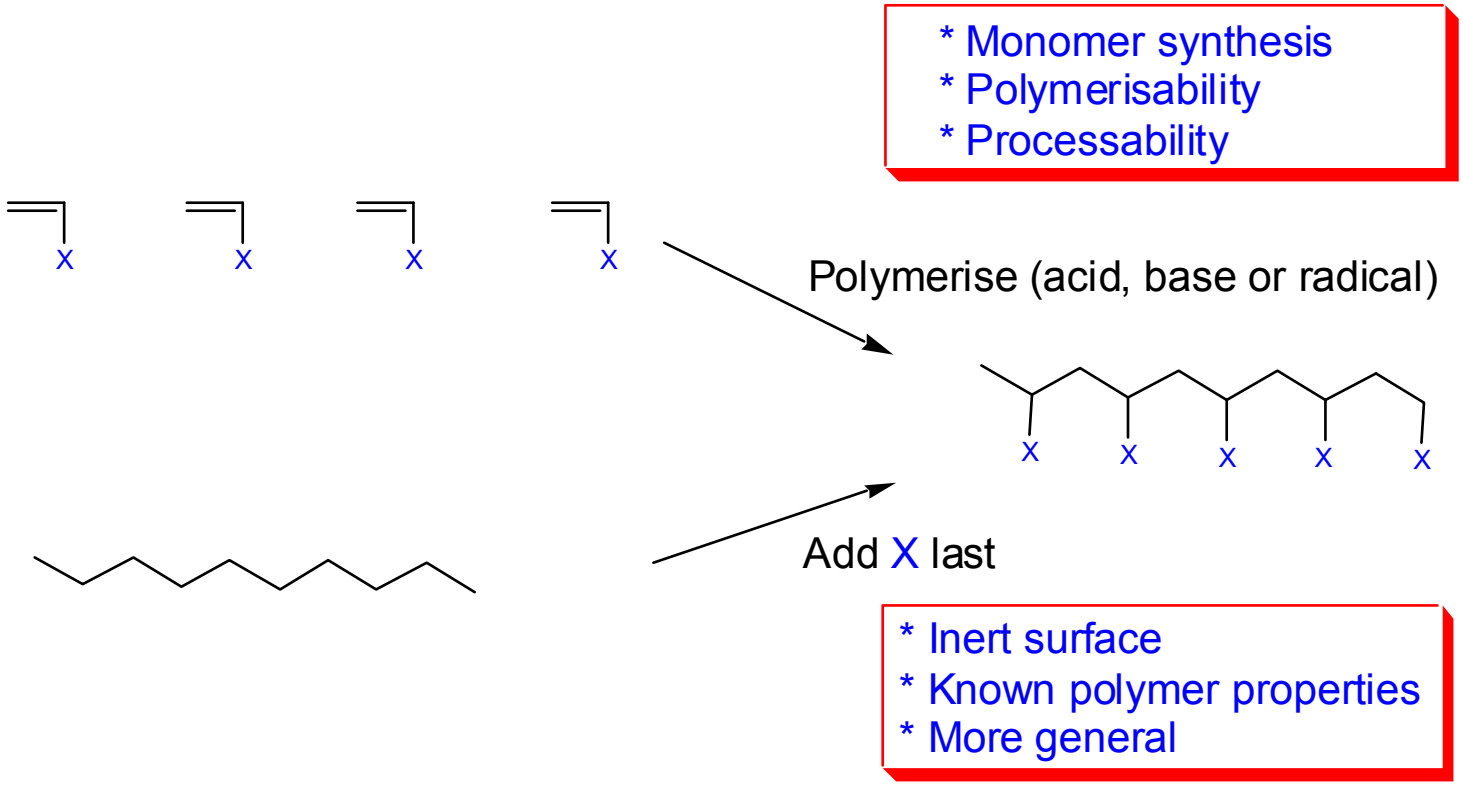
- Polymers often inert and difficult to modify (synthetic organic and inorganic polymers).

Existing surface coating treatments

- Abrasion and surface roughening
- Flame treatment
- Corona discharge
- Plasma treatment
- Chemical Priming

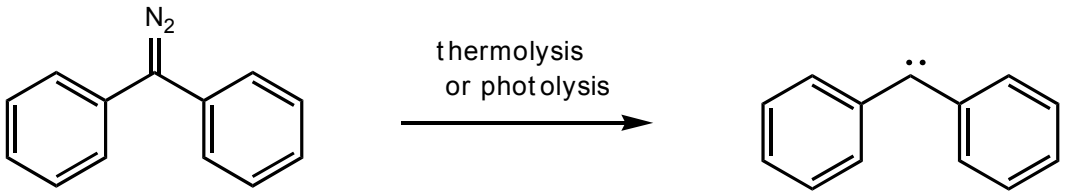
Could a simple chemical modification procedure be developed which would be directly adaptable to existing unit processes?

Natural fibres can be modified using reactive dyes, but this method is unsuitable for chemically inert polymers



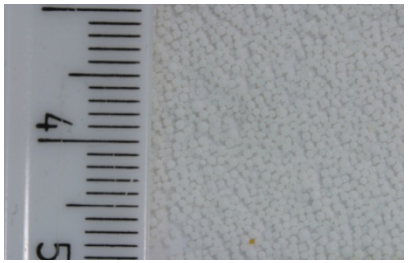
PROBLEM: How can the surface of a polymer be modified by irreversible bond formation?

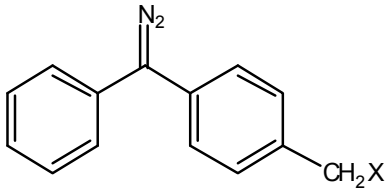
Might simple diaryl carbenes generated from diazo decomposition be useful?



- Diazo compounds easily prepared from available starting materials;
- Diaryldiazo compounds are stable at 0°C for extended periods;
- Readily thermolysed or photolysed;
- Carbene will react with diverse chemical functionality present in many polymers;
- Two aromatic rings offer the potential for controlling carbene chemistry and acting as carriers for useful functionality.

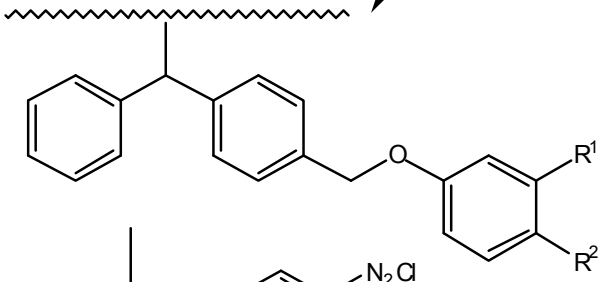
Coloured Polymers: Polystyrene

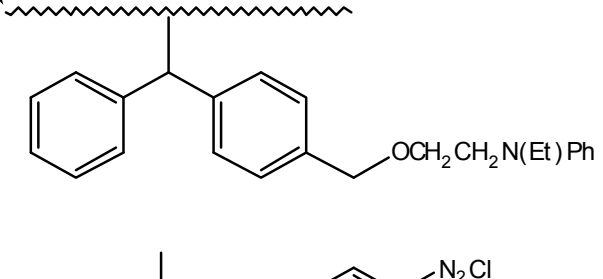


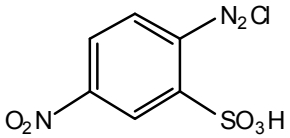


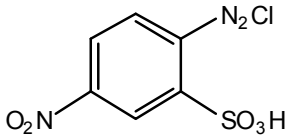
X = $CH_2O(3,4\text{-}(MeO)_2C_6H_3)$
X = $CH_2O(3\text{-}Et_2NC_6H_4)$
X = $CH_2OCH_2CH_2N(Et)Ph$

Polystyrene XAD



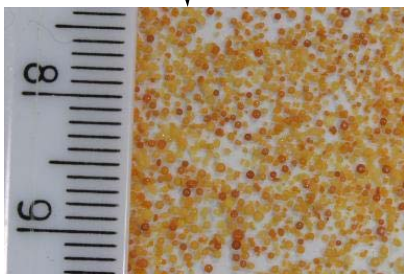


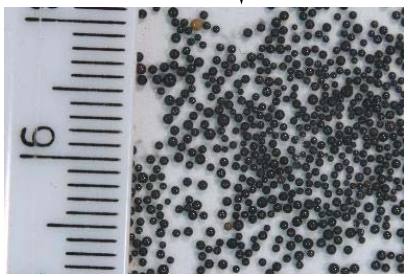


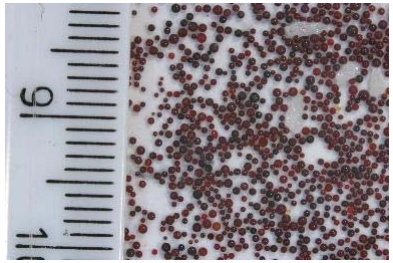


$R^1 = R^2 = MeO$

$R^1 = NEt_2$, $R^2 = H$



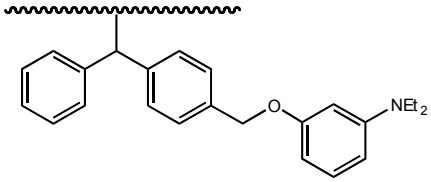




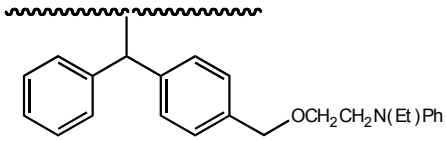
Chem. Commun, 2005, 990 - 992
GB9824023 D0 (1998-12-30);

Coloured materials

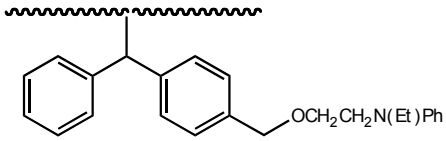
Hybond N



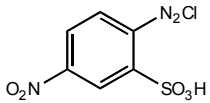
Controlled Pore Glass



Cotton

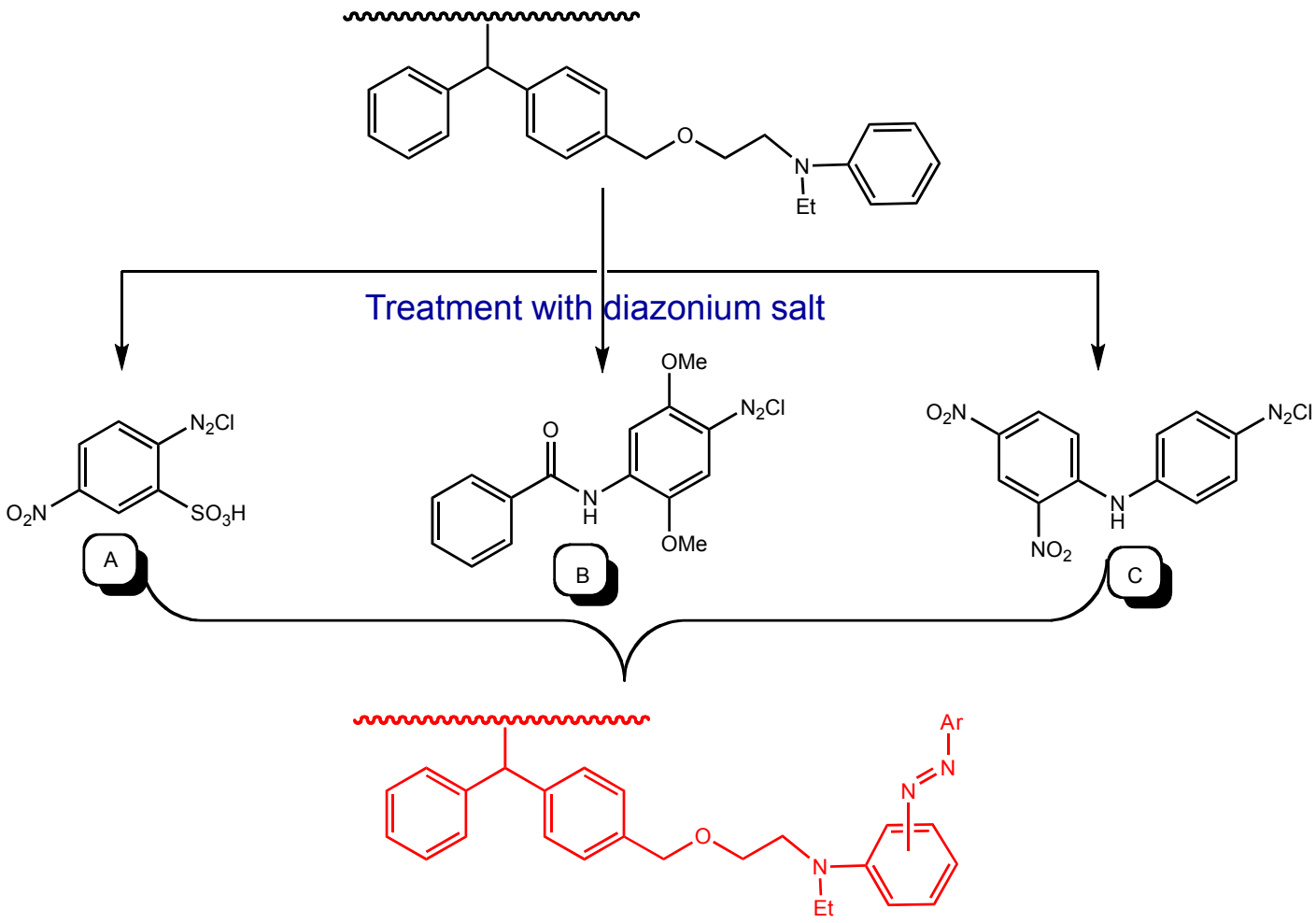


Untreated

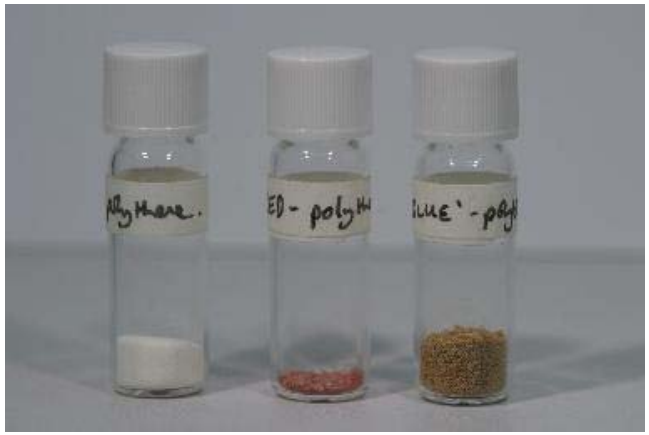


Chem. Commun, 2005, 990 - 992
GB9824023 D0 (1998-12-30);

Materials: range of colours



Polythene (L to R): unmodified; modified with carbene precursor followed by diazonium salt **A**; modified with precursor followed by diazonium salt **B**.



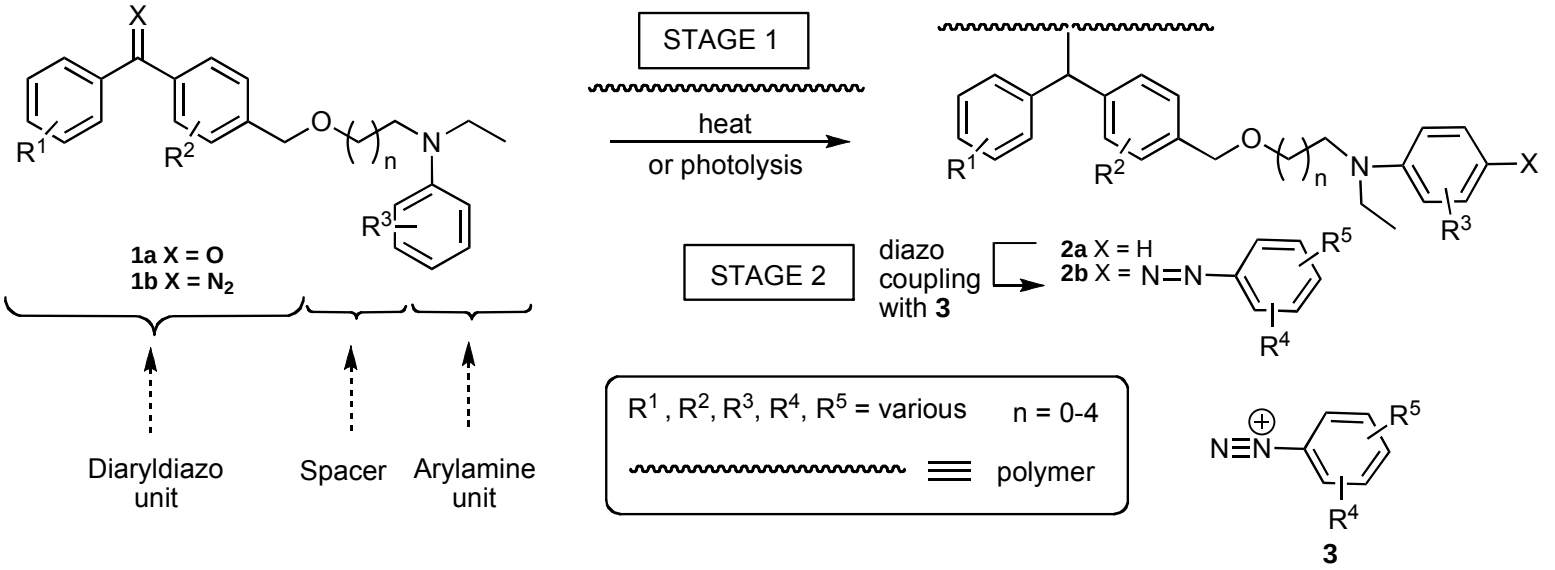
Silica (L to R): unmodified; modified with carbene precursor followed by coupling with diazonium salt **A**; coupling with diazonium salt **B**; coupling with diazonium salt **C**; coupling with diazonium salt **A** followed by treatment at pH 2.2; coupling with diazonium salt **A** followed by treatment at pH 9.0; coupling with diazonium salt **B** followed by treatment at pH 9.0.

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

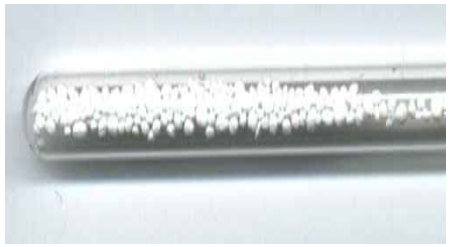
Blank Polymer	Polymer + Carbene + Diazonium A	Polymer + Carbene + DiazoniumB
		
		

Heat shrinkable polymers (top: 2H-SCE and TMS-SCE (white); bottom: TMS-SCE (yellow)): modified with carbene precursor under thermal conditions followed by diazonium salt **A** or **B**.

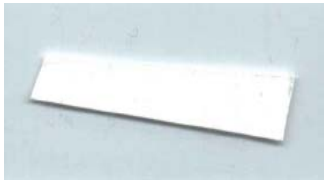
Photolytic activation



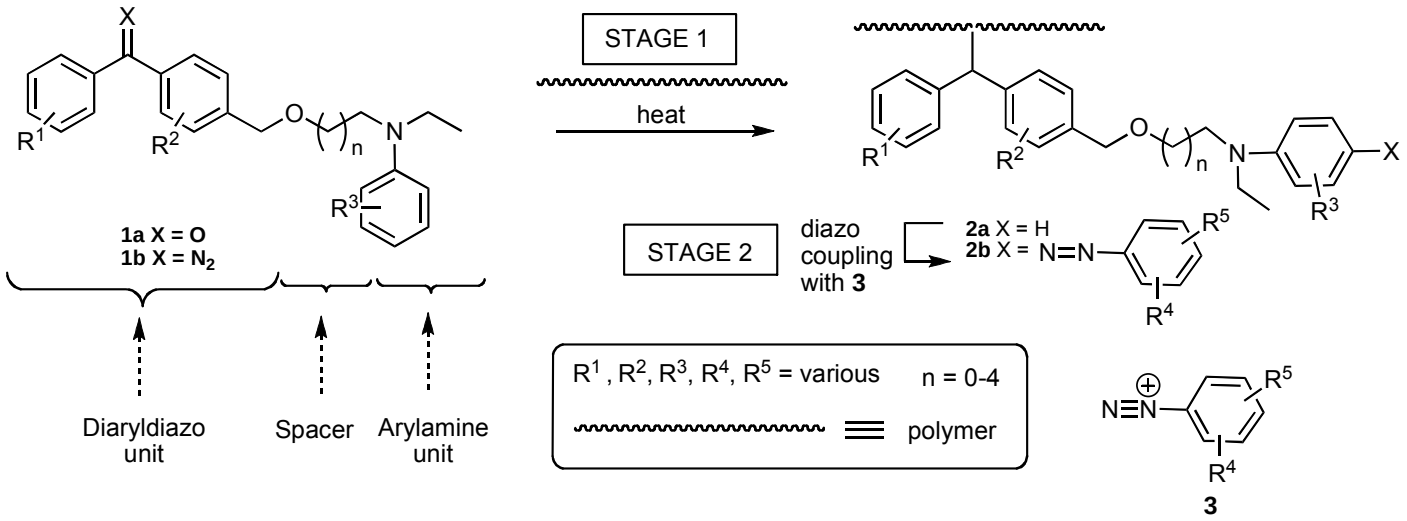
Photolytic activation: Polythene and PTFE

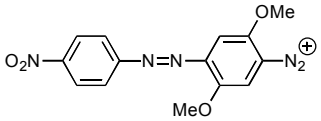
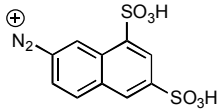
	Unmodified	Modified with carbene then Diazonium salt **A**
Polythene		
PTFE		
Polystyrene		

Photolytic activation: PS50 and PES100

	Untreated	After adsorption of diazo compound	After photolysis	After coupling with diazonium salt **B**
PS50				
PES100				

Polycaprolactone

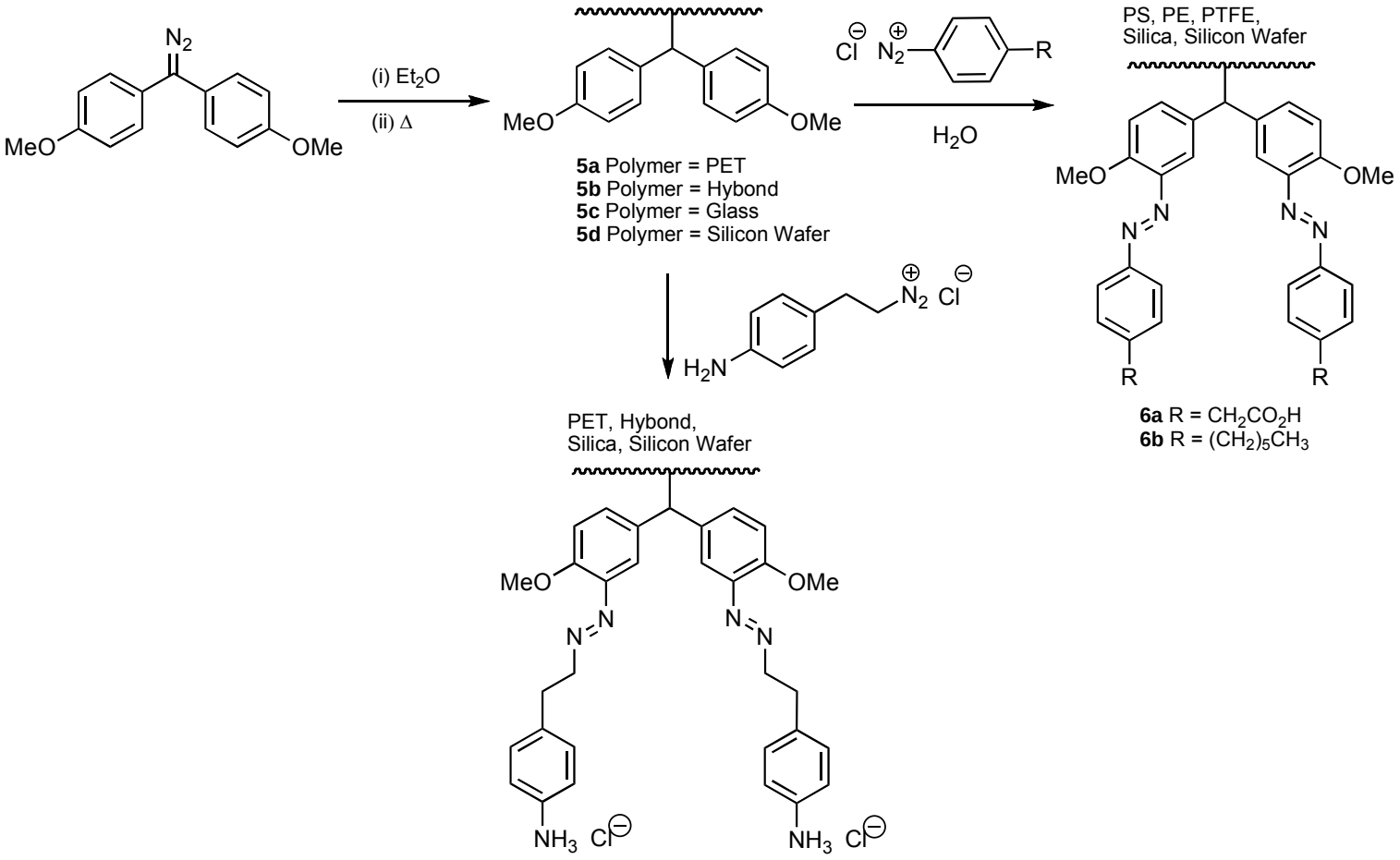


Diazo 3		Diazo 3	
			
Test	**Control**	**Test**	**Control**
			

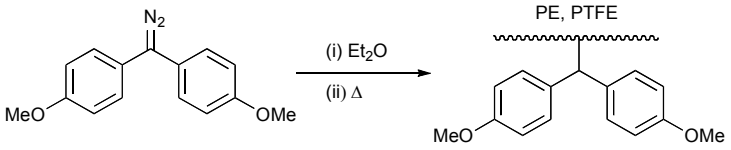
[redacted]

Applicable to various forms of material

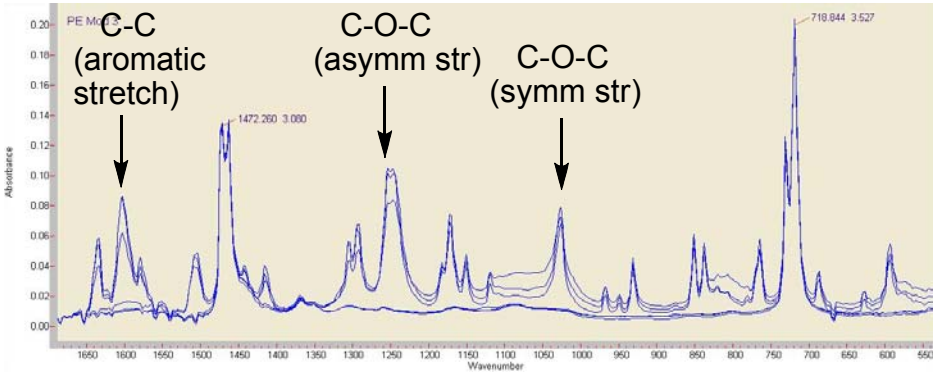
Systematic control of surface properties



ATR-IR

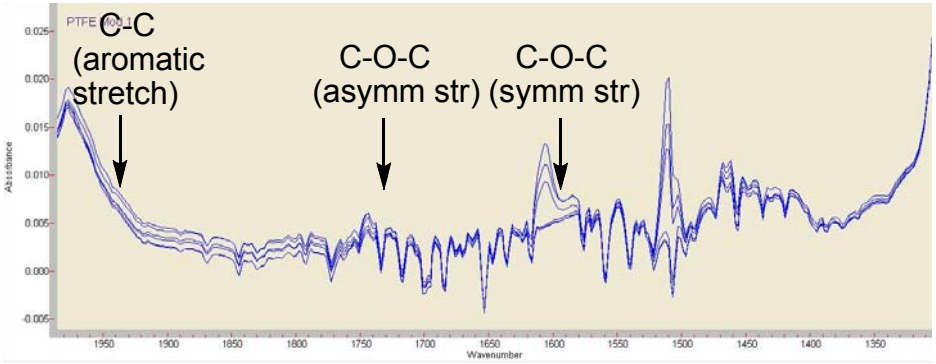


PE



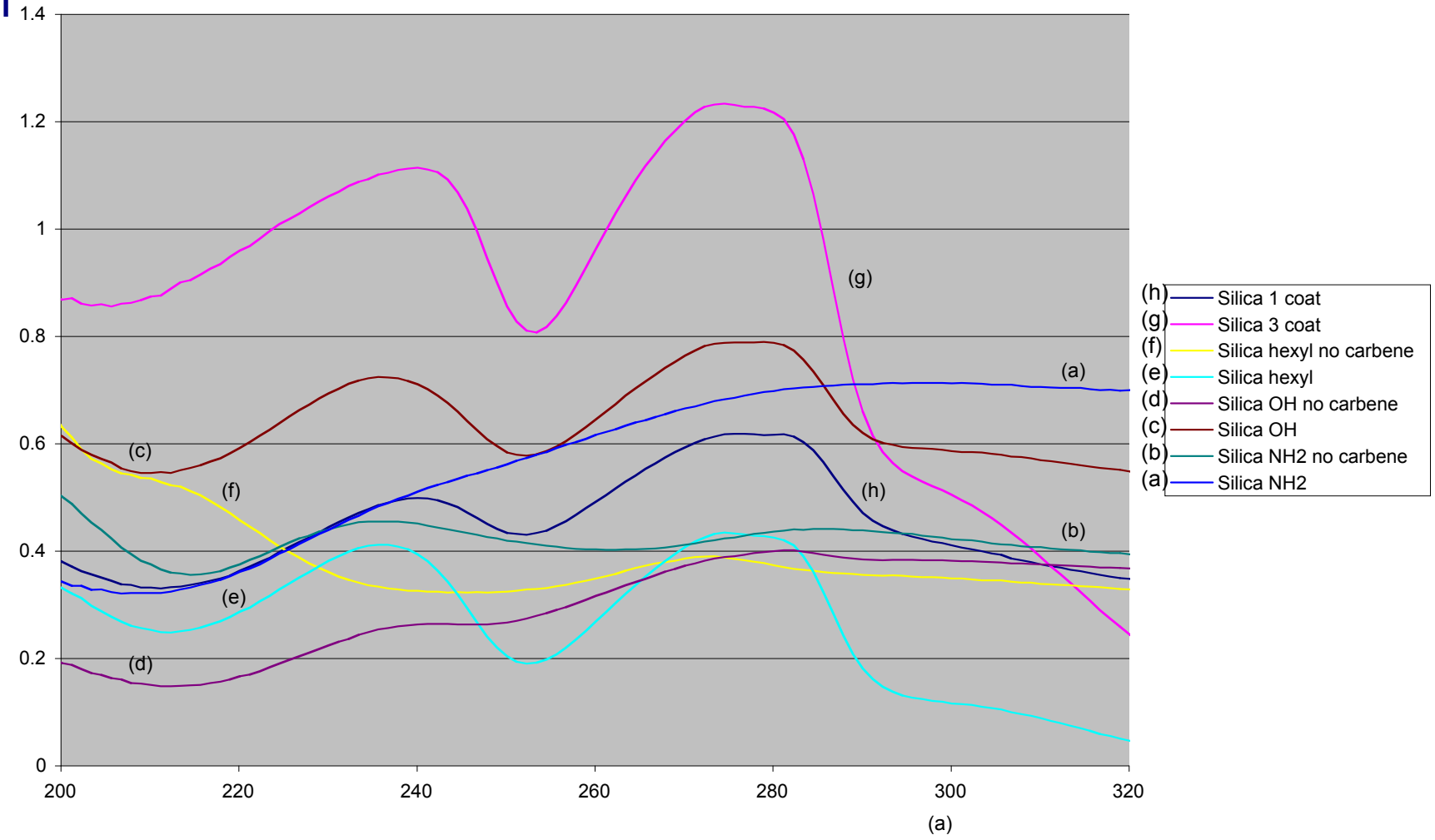
Modified (upper)
Blank (lower)

PTFE



Modified (upper)
Blank (lower)

Surface Reflectance UV

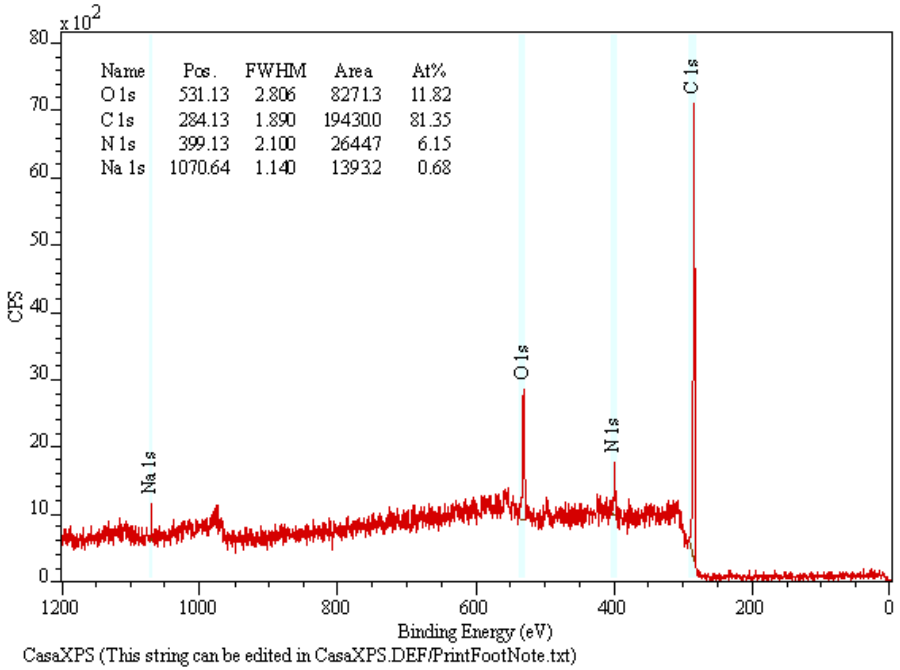


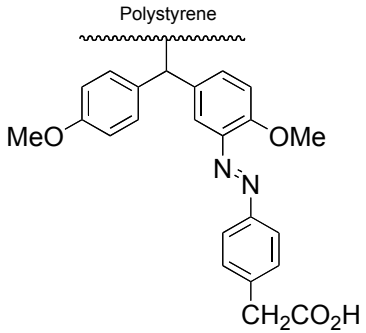
Characterisation: Polystyrene beads

	Colour	IR (cm^{-1})	Combustion Analysis (% N)
Raw	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.	1605, 1510, 1245, 1170, 1035	Nil
R = COOH	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.	1605, 1510, 1245, 1170, 1035	0.18 $mmolg^{-1}$ 15 x 10^{12} $moleculescm^{-2}$
R = Hexyl	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.	1605, 1510, 1245, 1170, 1035	0.036 $mmolg^{-1}$ 3 x 10^{12} $moleculescm^{-2}$
R = Amine	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.	1650, 1530	0.036 $mmolg^{-1}$ 3 x 10^{12} $moleculescm^{-2}$

From this loading data, assuming a loading of 3-10 x 10^{12} $moleculescm^{-2}$ and a cross-sectional area of the benzhydryl unit of about 8 x 10^{-15} $cm^2molecule^{-1}$, estimate a surface coverage of 2.5 - 8%

XPS Analysis of Polystyrene beads





$C_{23}N_2O_4$

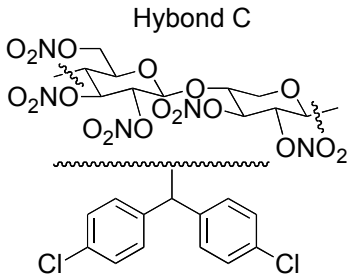
Expected O/C = 0.174
N/C = 0.087

Found O/C = 0.146
N/C = 0.076

Confirms the presence of diazo functional group, with only one diazo coupling per benzhydryl group

Surface analysis matches that of the inserted residue, but no evidence of deeper layers; suggests layer that is ≈ 5 - 10 molecules thick and up to 20 - 40 Å): nanolayer coating

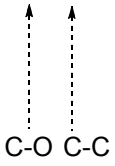
Evidence for Surface Modification: XPS analysis

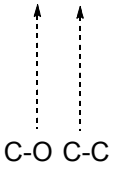


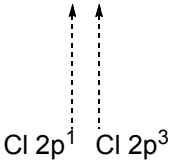
Blank Hybond C (C1s at 280 eV)

Modified Hybond C (C1s at 280 eV)

Modified Hybond C (Cl2p at 198 eV)

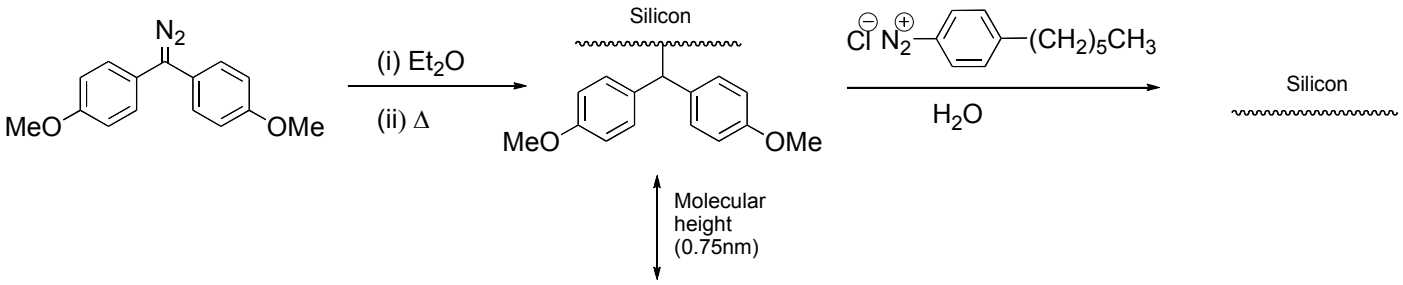






- change in ratio of electronegatively substituted carbons after modification
- presence of Cl indicated by a signal at 198 eV

Evidence for Surface Modification: Ellipsometry



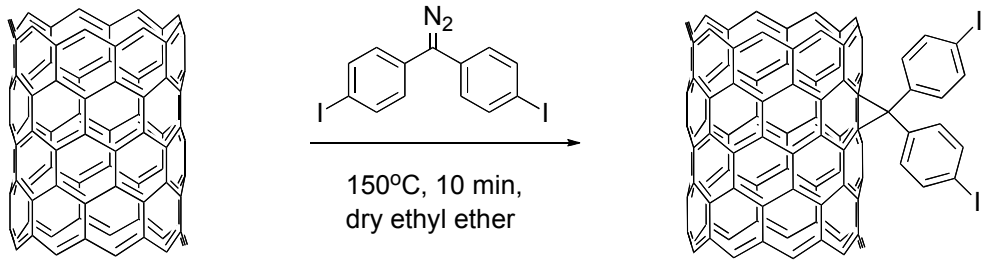
Nanolayer: 6.28 ± 0.14 nm

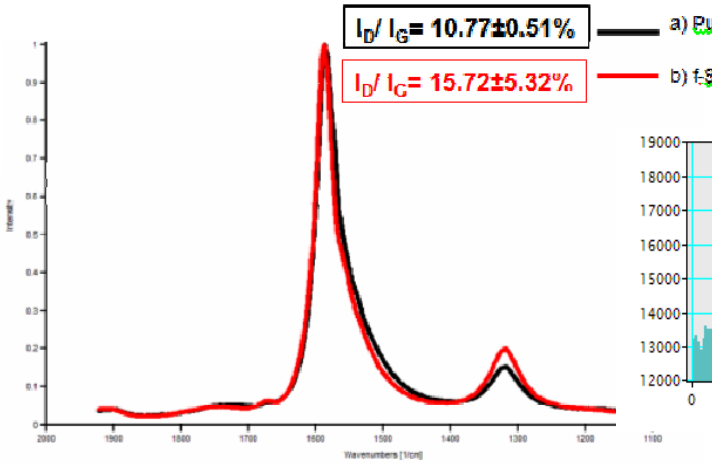
(about 9 molecular layers deep)

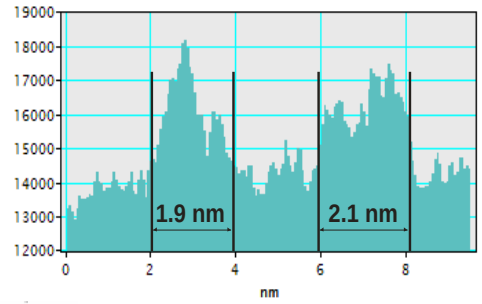
0.18 ± 0.14 nm

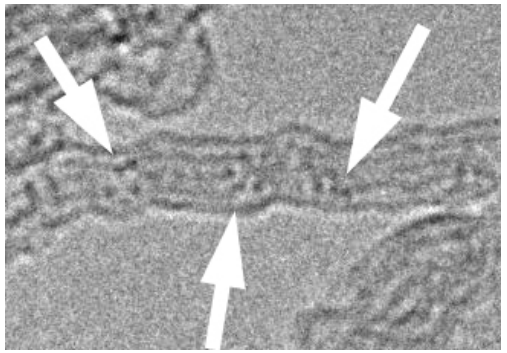
Acidic diazonium cleaves, with effectively no layer

Surface modification of carbon nanotubes

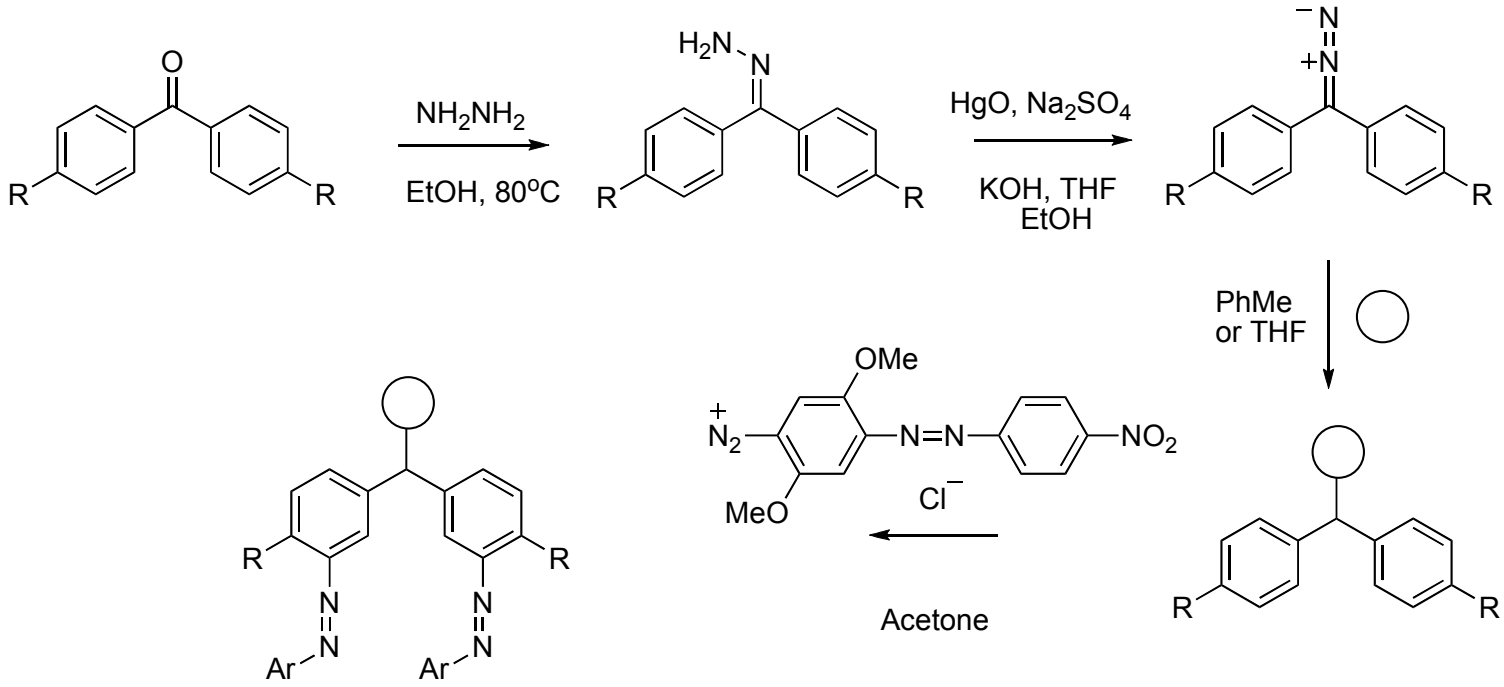








Second Generation



○ =	XAD-4	Tencel
	PSXL-S	Viscose
	UHMWPE	NK-Cotton
	PES	MW-Cotton
	PP	Cotton Wool
	PPS	PET
	N-610	Silica Gel
	Hybond-N	Alumina
	Kevlar	Nomex

Beads and Powders

	Modified with Fast Black only	Modified with carbene precursor only	Modified with carbene then Fast Black
Polystyrene			
Polythene	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.		
UHMWPolythene			
Polypropylene	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.		

Sheets and fibres

	Modified with Fast Black only	Modified with carbene precursor only	Modified with carbene then Fast Black
Extruded polypropylene sheet	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.		
Extruded polyethylene-terephthalate sheet	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.		
Woven kevlar fibres	QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.		

Comparison of First and Second Generation - UHMWPE

First generation

Second generation

Comparison of First and Second Generation - Kevlar

First generation

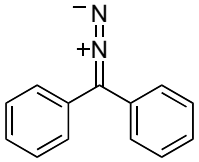
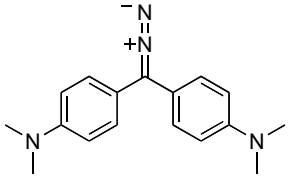
Second generation

Comparison of First and Second Generation - PPP

First generation

Second generation

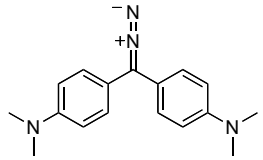
Metallisation of polypropylene with silver

	Unmodified	Silver treated
Blank	QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.	
Treated with 	QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.	
Treated with 	QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.	

Metallisation of inorganics with silver

Treated with

Blank



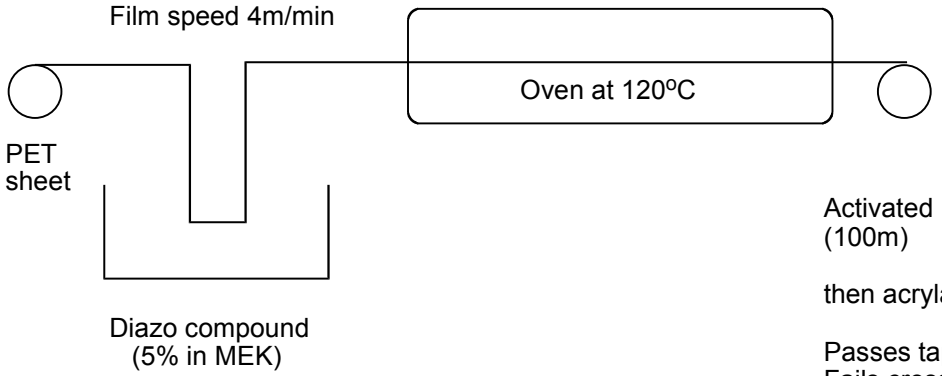
Alumina

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Silica

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Pilot Plant: PET coating



Activated PET sheet (100m)

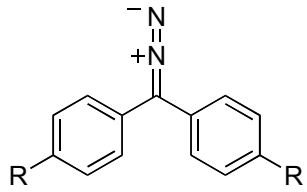
then acrylate coat (UV cure)

Passes tape test
Fails cross-hatch test, but performance better than any existing treatment

Hydrophilicity/hydrophobicity

Untreated Glass

Modified Glass

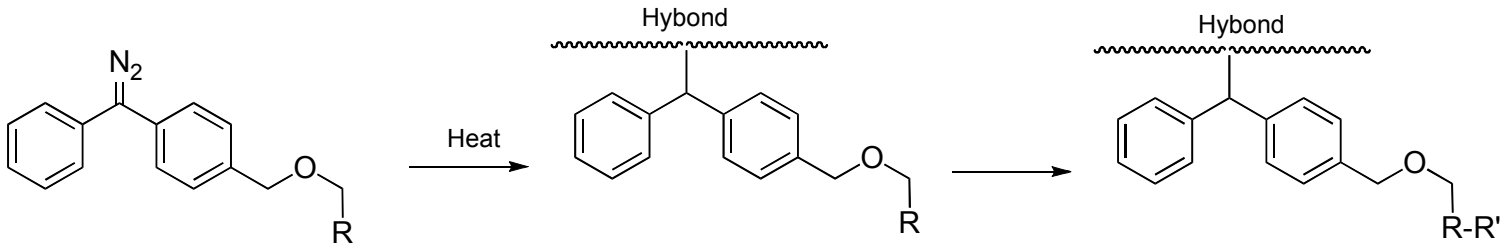


R = hydrophilic ⟶ R = hydrophobic

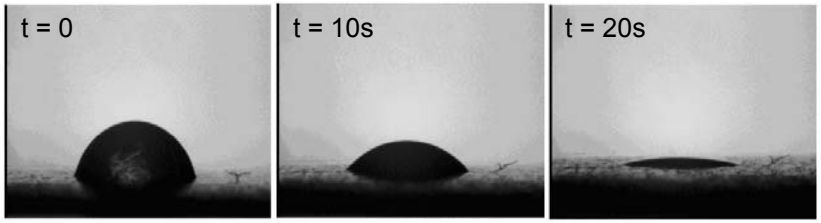
Contact angle

	Untreated	R = R^1	R = R^2	R = H
Glass	40.2±0.9	20.9±1.4	49.2±2.5	73.6±1.2
PET	82.0±3.1	73.8±1.8	78.0±1.2	85.6±1.1
Silicon wafer	49.9±2.3	48.1±4.8	48.9±1.0	80.8±0.7

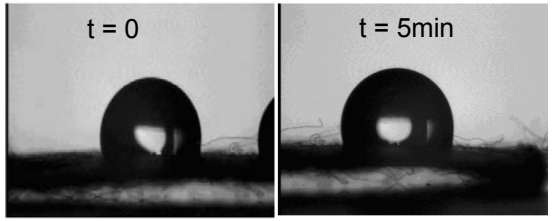
Hydrophilicity/hydrophobicity



Untreated Hybond

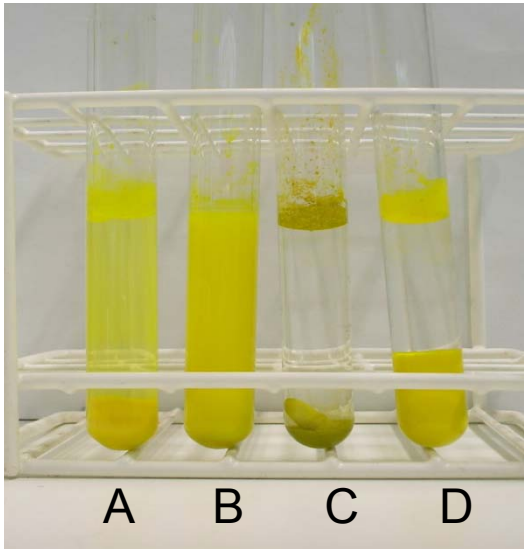


Modified Hybond



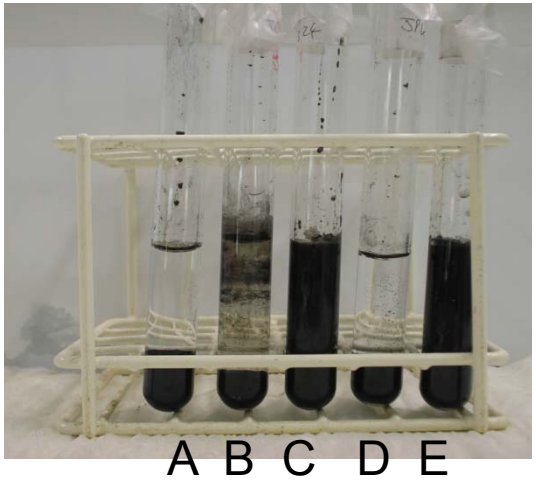
Dispersion in aqueous systems

Hansa Brilliant Yellow after 3 days



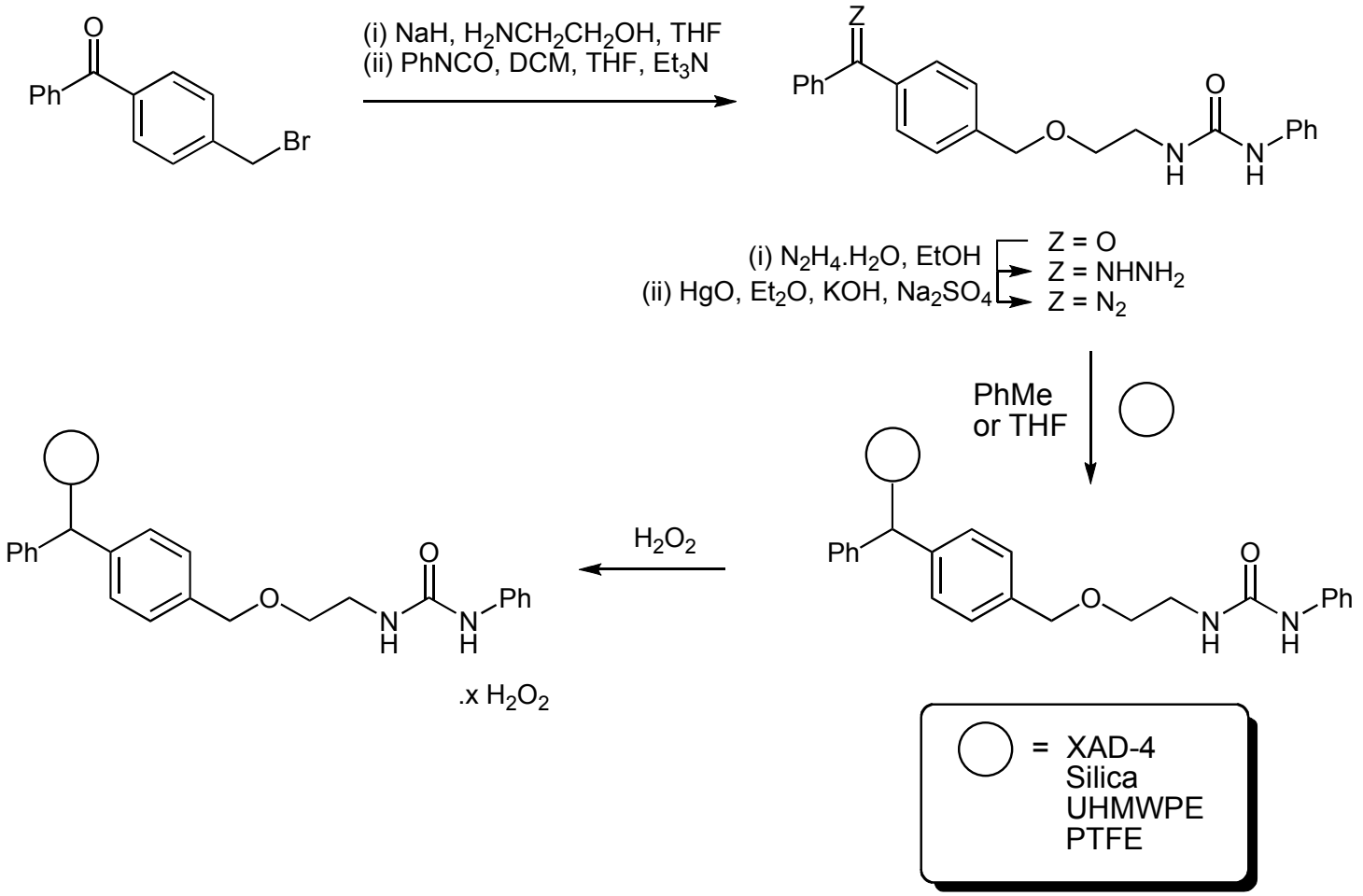
A = unmodified
B, C, D = modified

Carbon black after 35 days



A = unmodified
B, C, D, E = modified

Biocidal activity



Stability of PS Treated with H_2O_2

Time Interval / h	H_2O_2 Loading (mmol/g polymer)
0	8.42×10^{-2}
24	8.01×10^{-2}
48	9.61×10^{-2}
72	6.44×10^{-2}
96	4.13×10^{-2}

This corresponds to a loading of about 3.7×10^{-4} $\mu g/cm^2$

Biocidal activity: improved loading level

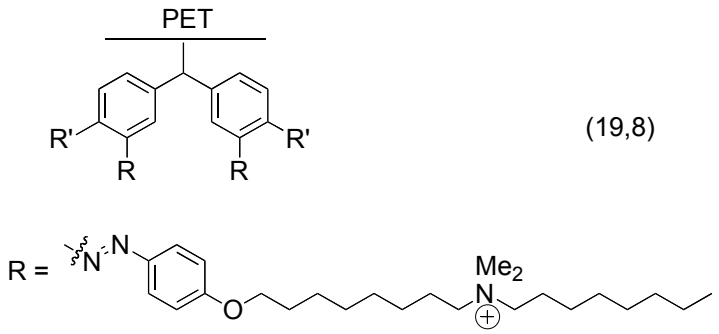
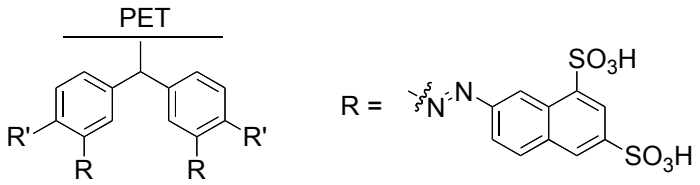
Polymer	H_2O_2 Loading (mol/g polymer)	*S. aureus* Zone size / mm
PS XAD-4	7.9×10^{-4}	38
UHMWPE	2.6×10^{-4}	37
PPP	1.1×10^{-5}	22

A B

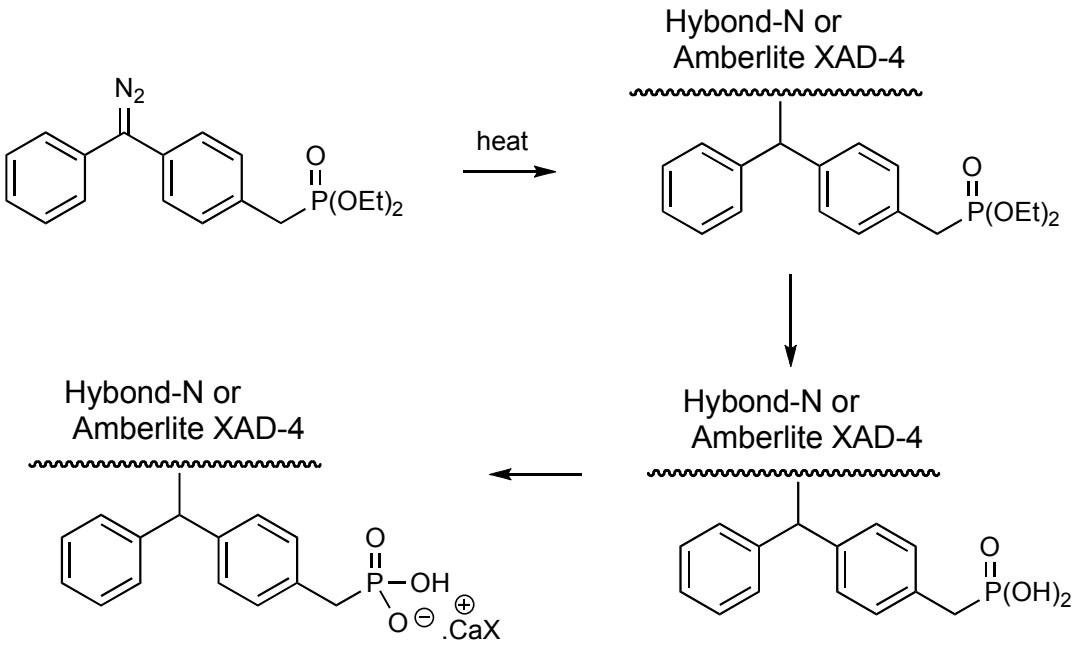
A = Polystyrene XAD
B = UHMWPE

[redacted]

Biocompatibility

Polymer	Log Reduction	
	S. aureus	*E. coli*
	0.51	0.46
	0.19	-1.6

Biocompatibility

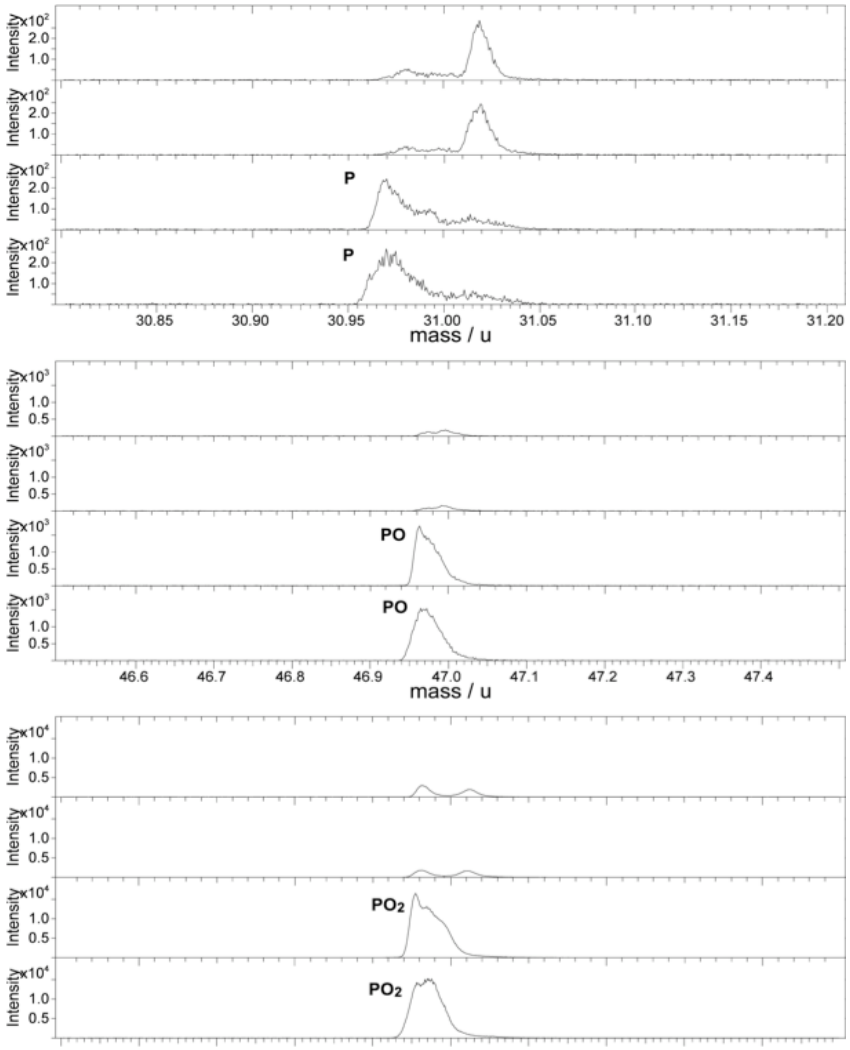


Characterisation of Phosphonate modified PS

Elemental analysis confirms P at 1.1%, giving 0.37mmol/g (3 x 10^{13} molecules/cm^2 or 2.3 x 10^{-2} $\mu g/cm^2$)

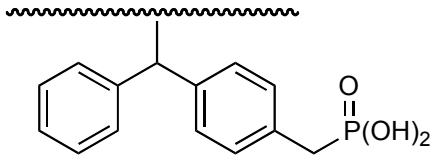
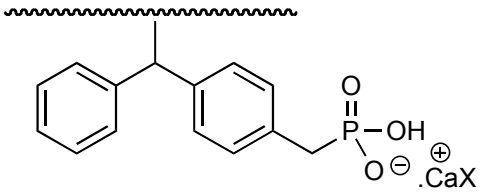
IR gives P=O at 1217cm^{-1}

TOF-SIMS confirms presence of phosphate modification



Biocompatibility

Polymer tested for biocompatibility and cytoxicity against the MG63 human osteosarcoma cell line

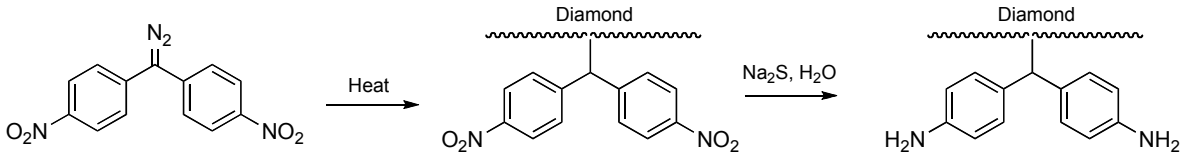
Growth relative to control		
Hybond-N	Day 5: 40% Day 8: 55% Day 13: 108%	Day 5: 45% Day 8: 99% Day 13: 128%
Polystyrene	Day 13: 287%	Day 13: 328%

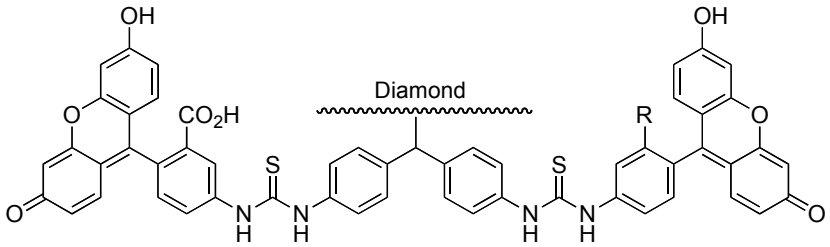
[redacted]

Diamond Surface Modification

- Diamond is a robust platform for chemical sensors for a specific analyte in a chemical mixture.
- High performance signal conversion and electrochemical readout.
- Require surface functionalisation with sensitising functional groups.
- Diamond is relatively inert, and require simple derivatisation technique.
- Some strategies have evolved for chemical functionalisation of diamond, including thermal oxidation, radical, electrochemical, photochemical alkene coupling etc
- Might carbenes be useful?

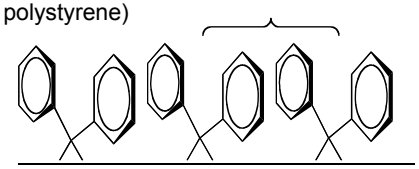
Addition of fluorescent marker



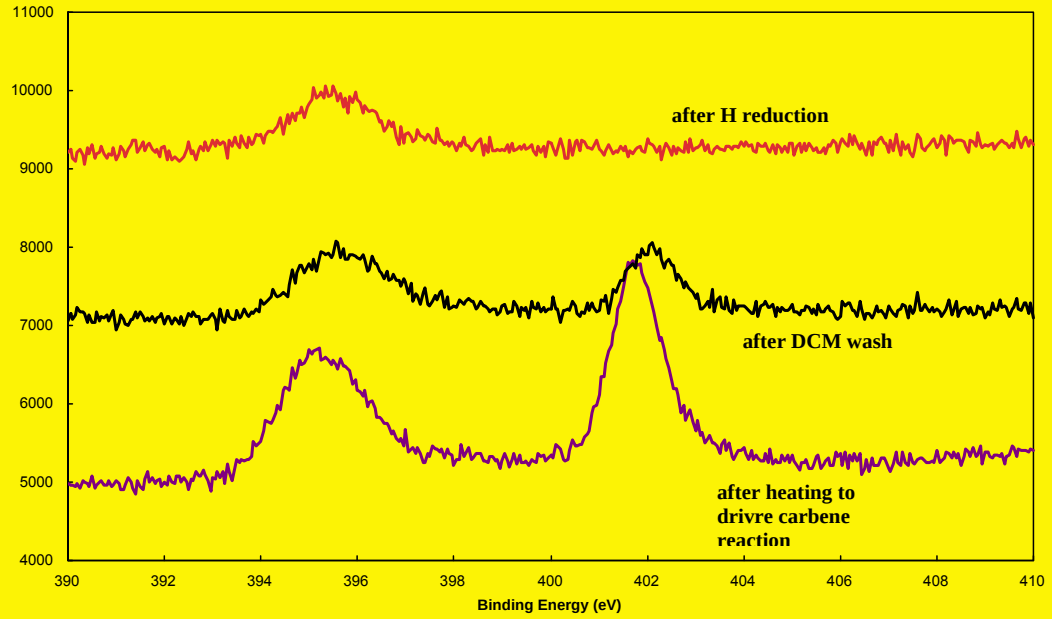


FluoresceinNCS

not less than 3.5 -4.2 A (π–π stacking distance in crystalline benzene and interplanar distance in polystyrene)



Loading on diamond = 10^{14} molecules/cm^2 from XPS data giving overall surface area coverage of not more than 7-10% and a loading of about 60mg/m^2



Summary

- Converts readily available bulk polymers into high value-added products.

- Combines properties of bulk polymer and surface monolayer.

- Avoids need for *de novo* polymer synthesis.

- Integrates into existing unit manufacturing processes.

- Proven application to polyethylene (PE), polystyrene, polysulfones, Kevlar, Nomex, inorganics, glass, diamond.

- Useful for low surface energy materials, including polypropylene (PPP), polyethylene terephthalate (PET).

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