

Mackay, University of Delaware and Professor Stuart Rowan, Case Western Reserve University) we have successfully designed and created a very dramatic supramolecular polymer blend system (**Figure 2**) that is capable being healed when exposed to moderate temperatures. Indeed, this supramolecular polymer blend recovers its physical and mechanical properties after thermal repair of a damaged site. The supramolecular interactions that enable the low molecular weight polymeric components to assemble (and disassemble during thermal healing) are weak π - π stacking interactions between aromatic π -electron rich chain ends of polyamides and chain-folding sequences of π -electron deficient polyaromatic imides. The resultant supramolecular polymer blend is deep red in colour which indicates strong interactions between these key recognition units. Environmental scanning electron microscopy (carried out at the University's Centre for Advanced Microscopy) revealed how a damaged site could be repaired rapidly when the temperature was increased above 50 °C (**Figure 2**).

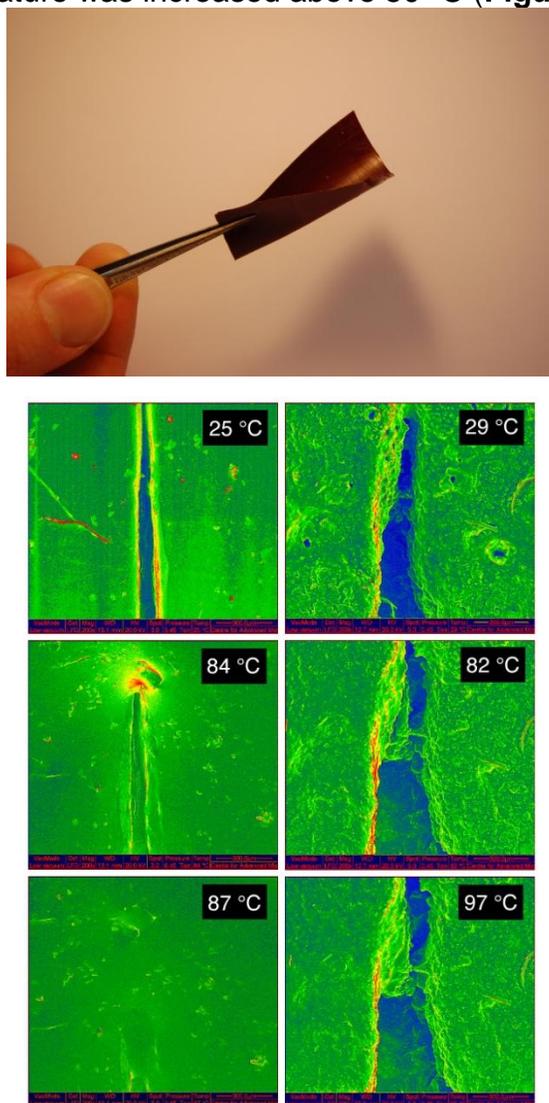


Figure 2 Top: Self-supporting and flexible healable film of the healable supramolecular polymer blend; Bottom: False-colour ESEM images ($\times 200$) demonstrating the homogeneity and healing characteristics of the supramolecular polymer system (left

hand column), and the absence of such characteristics for the phase-separated control material (right hand column) The heating rate was 5 °C min⁻¹.

References:

Thermally Responsive Elastomeric Supramolecular Polymers Featuring Flexible Aliphatic Hydrogen Bonding End-Groups, P Woodward, D Hermida Merino, I W Hamley, A T Slark and **W Hayes**, *Aus. J. Chem.*, **2009**, 62, 790–793.

Facile bisurethane supramolecular polymers containing flexible alicyclic receptor units, P Woodward, A Clarke, B W Greenland, D Hermida Merino, L Yates, A T Slark, J F Miravet and **W Hayes**, *Soft Matter*, **2009**, 5, 2000–2010.

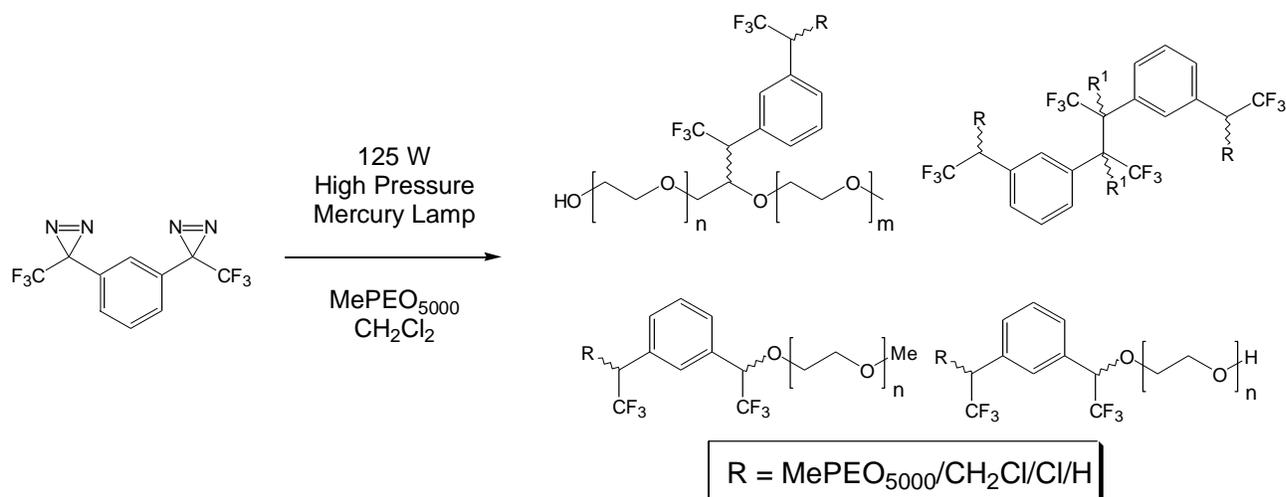
'Novel material forming supramolecular structures, process and uses', W. Hayes, P.J. Woodward, A. Clarke, A.T. Slark, EU Patent, **2007**, EP1792925.

A novel self-healing supramolecular polymer system, S Burattini, H M Colquhoun, B W Greenland and **W Hayes**, *Faraday Transactions*, **2009**, In the press, DOI: [10.1039/b900859d](https://doi.org/10.1039/b900859d).

A Self-Repairing, Supramolecular Polymer System: Healability as a Consequence of Donor-Acceptor π - π -Stacking Interactions, S Burattini, H M Colquhoun, J D. Fox, D Friedmann, B W. Greenland, P J F Harris, **W Hayes**, M E Mackay and S J Rowan, *Chem. Commun.*, **2009**, in the press.

2. Polymer Synthesis using Photochemistry

At Reading we have developed very efficient photochemically driven carbene insertion chemistries to generate hyperbranched polymers, new surface coating technologies and cross-linked polymer gel networks (see **Scheme 1** and **Figure 3**). The chemistries involved are based upon diazirines – very stable, yet highly strained unsaturated three-membered heterocycles. Upon appropriate photochemical activation, these species liberated highly reactive carbenes that can insert into virtually any chemical bond.



Scheme 1

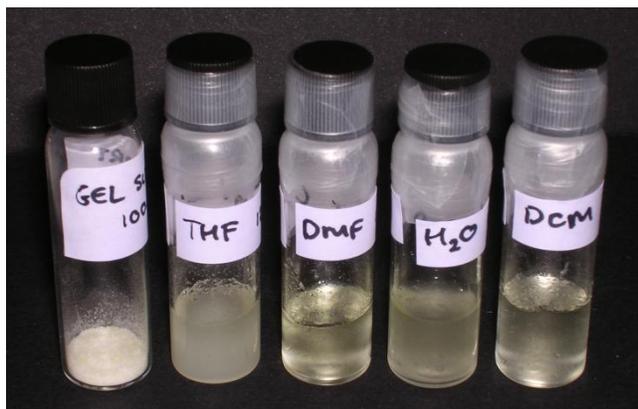


Figure 3 Solid gel (100 mg) obtained at a Diazirine:MePEO₅₀₀₀ mole ratio of 2:1 and gel swollen in THF (125 mg mL⁻¹), dimethylformamide (125 mg mL⁻¹), water (110 mg mL⁻¹) and dichloromethane (90 mg mL⁻¹)

References:

A Carbene Insertion Approach to Hyperbranched Poly(aryl amine)s, A Blencowe, K Cosstick, W Fagour and **W Hayes**, *Organic and Biomolecular Chemistry*, **2008**, 6, 2327-2333.

A carbene insertion approach to functionalised poly(ethylene oxide)-based gels, A Blencowe, C Blencowe, K Cosstick and **W Hayes**, *Reactive and Functional Polymers*, **2008**, 68, 868-875.

Synthesis of Hyperbranched Poly(aryl ether)s via Carbene Insertion Processes, A Blencowe, N Caiulo, K Cosstick, W Fagour, P Heath and **W Hayes**, *Macromolecules*, **2007**, 40, 939-949.

Surface modification of Nylon 6,6 using a carbene insertion approach, A Blencowe, K Cosstick and **W Hayes**, *New J. Chem.*, **2006**, 1, 53-58.

Development and Application of Diazirines in Biological and Synthetic Macromolecular Systems, A Blencowe and **W Hayes**, *Soft Matter*, **2005**, 1, 178-205.

3. Dendrimers and Hyperbranched Polymeric Materials

A synthetic programme investigating novel hyperbranched polymer architectures (including dendrimers) has been established at Reading and is targeting the development of novel materials in several areas, notably in the fields of novel coatings and drug delivery systems. Support for these activities has been received from EPSRC, DuPont, Unilever and more recently from ICI. In addition, research in this field has led to the generation of new hyperbranched oxidation catalysts, synthesis of polyamide fragrance release systems (see **Figure 4**), the development of responsive fluorescent polyamide dendrimers and the creation of hyperbranched polyesters featuring rigid acetylene units.

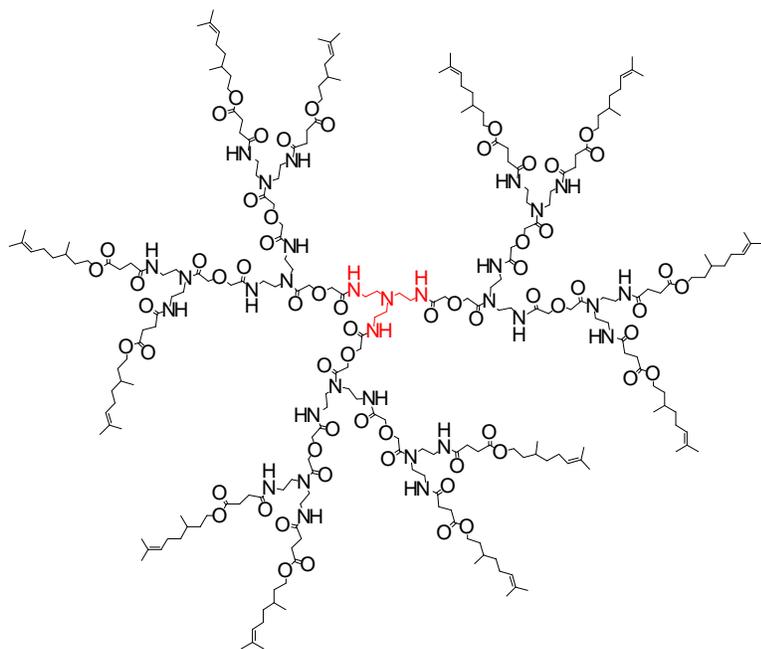


Figure 4

References:

Fragrance release from the surface of branched poly(amide)s, F Aulenta, M G B Drew, A Foster, **W Hayes**, S Rannard, D W Thornthwaite, and T G A Youngs, *Molecules*, **2005**, *10*, 81-97.

Synthesis and characterisation of fluorescent poly(aromatic amide) dendrimers, F Aulenta, M G B Drew, A Foster, **W Hayes**, S Rannard, D W Thornthwaite, D R Worrall and T G A Youngs, *J. Org. Chem.*, **2005**, *70*, 63-78.

Utilisation of Dendritic Architectures in Molecular Recognition and Self-assembly Processes, C R Yates and **W Hayes**, *Mini Reviews in Organic Synthesis*, **2005**, *2*, 1-22.

Poly(ethylene glycol)-supported nitroxyls: branched catalysts for the selective oxidation of alcohols, P Ferreira, E Phillips, D Rippon, S C Tsang and **W Hayes**, *J. Org. Chem.*, **2004**, *69*, 6851-6859.

Synthesis and Properties of Chiral Polyaromatic Dendrimers, B Romagnoli, I van Baal, L M Harwood, D W Price and **W Hayes**, *Eur. J. Org. Chem.*, **2004**, 4148-4157.

Synthesis and Applications of Hyperbranched Polymers, C R Yates and **W Hayes**, *Eur. Polym. J.*, **2004**, *40*, 1257-1281.

Synthesis and Characterisation of Hyperbranched Polyesters incorporating the AB₂ monomer 3,5-bis(3-hydroxyprop-1-ynyl)benzoic acid, A Blencowe, L Davidson and **W Hayes**, *Eur. Polym. J.*, *Eur. Polym. J.*, **2003**, *39*, 1955-1963.

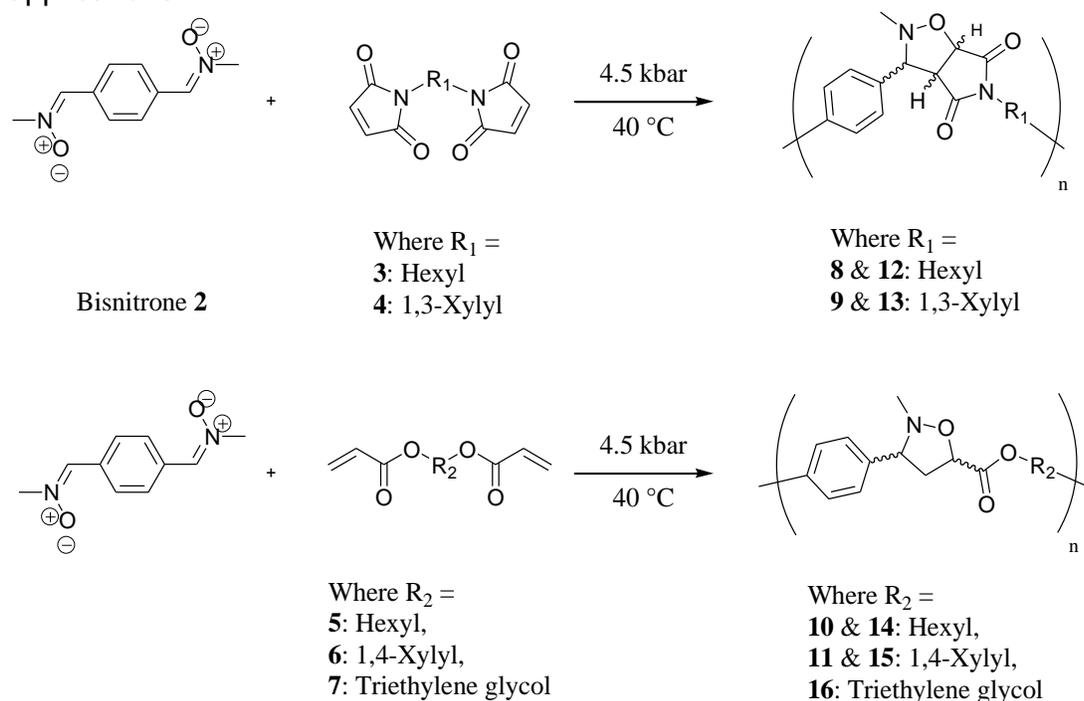
One-pot synthesis of multivalent arrays of mannose mono- and disaccharides, **W Hayes**, H M I Osborn, S D Osborne, R A Rastall and B Romagnoli, *Tetrahedron*, **2003**, *59*, 7983-7996.

Synthesis of Polyaromatic Dendrimers Possessing a Repetitive Amide-Ester Coupling Sequence, B Romagnoli, P R Ashton, L M Harwood D Philp, D W Price, M H Smith and **W Hayes**, *Tetrahedron*, **2003**, *59*, 3975-3988.

Dendrimers: A new class of nanoscopic containers and delivery devices, F Aulenta, S. Rannard and **W Hayes**, *Eur. Polym. J.*, **2003**, *39*, 1741-1771.

4. Polymer Synthesis using Cycloaddition Chemistries

A high pressure mediated (3+2) cycloaddition polymerization strategy has been employed to afford linear poly(isoxazolidine) architectures. Our interest in these polymers stems from the fact that isoxazolidine substituted heterocycles exhibit anti-bacterial, anti-fungal and biological activities. It is not unreasonable to thus propose that poly(isoxazolidine)s could potentially exhibit similar biological activities and render these polymers useful in biomedical coatings. We have utilised high pressure conditions in conjunction with this cycloaddition process to generate polymers that feature predominantly *endo*-heterocycles to thus affect the tacticity and resultant properties of the polymer (**Scheme 2**). This stereoselectivity occurred as a result of the *endo*-transition state possessing a lower volume of activation and the cycloaddition proceeding via a 'type-I' regime ($\text{HOMO}_{\text{Dipole}}\text{-LUMO}_{\text{Dipolarophile}}$) that features secondary orbital interactions within the extended molecular orbitals. A variety of linker segments were employed in an attempt to affect the physical properties of the polymeric cycloadducts such as T_g and solubility in order to tailor these materials for use in coating applications.



Scheme 2

References:

Endo-Selective (3+2) Cycloaddition Polymerizations of Nitron Monomers with Olefins utilising High Pressure Conditions, G W Goodall, K Cosstick, S C Richards and **W Hayes**, *Eur. Polym. J.*, **2008**, 44, 1881-1890.

Application of Cycloaddition Reactions in Polymer Synthesis, G Goodall and **W Hayes**, *Chem. Soc. Rev.*, **2006**, 35, 280-312.