

Synthesis of hyperbranched poly(aryl amine)s *via* a carbene insertion approach

Anton Blencowe,^{†a} William Fagour,^a Chris Blencowe,^a Kevin Cosstick^b and Wayne Hayes^{*a}

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A novel diazirine functionalised aniline derivative, 3-(3-aminophenyl)-3-methyldiazirine **1**, was prepared and employed as an AB₂-type monomer in the synthesis of hyperbranched polymers; thus providing the first instance in which polyamines have been prepared *via* carbene insertion polymerisation. Photolysis of the monomer **1** in bulk and in solution resulted in the formation of hyperbranched poly(aryl amine)s with degrees of polymerisation (DP) varying from 9 to 26 as determined by gel permeation chromatography (GPC). In solution, an increase in the initial monomer concentration was generally found to result in a decrease in the molecular weight characteristics of the resulting poly(aryl amine)s. Subsequent thermal treatment of the poly(aryl amine)s caused a further increase in the DP values up to a maximum of 31. Nuclear magnetic resonance (NMR) spectroscopic analysis revealed that the increase in molecular weight upon thermal treatment resulted from hydroamination of styrenic species formed in the initial photopolymerisation or activation of diazirine moieties.

Introduction

Hyperbranched polyamine macromolecules (including dendrimers) have received significant attention over the past 20 years as a result of their wide range of potential biomedical and materials applications, including adhesives, printing inks, dyes, fixative agents, cationic dispersants, chelating agents and scavenger resins.¹ The most widely developed dendritic polyamines are the poly(propylene imine) (PPI) series developed by Meijer and co-workers.² However, PPI dendrimers are prepared *via* a labour intensive multi-step divergent strategy involving repetitive Michael additions and reductions. More recently, Haag and co-workers have produced hyperbranched analogues³ of PPI dendrimers by utilising poly(ethylene imine)s (PEI) as branching scaffolds. Modified PEI/PPI hyperbranched polymers and PPI dendrimers are currently being investigated for a number of biochemical applications, including non-viral gene transfer vector design,^{3,4} drug delivery^{5,6} and as antimicrobial agents.⁷ Hyperbranched allylamines have been prepared *via* palladium catalysed decarboxylative multi-branching ring-opening polymerisation of cyclic carbamates, such as 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one, using primary or secondary amines as initiators.⁸ Although the monomers do not contain branch points, branching units are generated through propagation reactions leading to the formation of hyperbranched polyamines with a degree of polymerisation (DP) between 16 and 47, and a degree of branching (DB) between 44 and 81%. Hyperbranched polyanilines⁹ and poly(amino arylene)s^{10,11} have also been investigated thoroughly for their potential application to conducting and magnetic polymeric materials—hyperbranched *m*-polyanilines prepared *via* a palladium catalysed

process possessed enhanced solubility and processability whilst retaining highly desirable magnetic properties similar to their linear analogues. Highly conjugated hyperbranched poly(amino arylene)s prepared from functionalised triphenylamines exhibit a variety of enhanced functional properties, such as polyradical cations with high-spin states,¹² high light-emitting efficiencies and photoconductivity,^{10,11} and, therefore, have potential in an array of technological applications in organic electronics, photonics and spintronics.

After successfully developing a carbene insertion polymerisation approach to hyperbranched polyethers,¹³ we decided to investigate the preparation of hyperbranched polyamines *via* a similar strategy. Herein, we present the foremost preparation of hyperbranched polyamines using a diazirine functionalised aniline derivative, 3-(3-aminophenyl)-3-methyldiazirine **1**, as an AB₂-type monomer. The polymerisation proceeds by way of photochemical activation of the diazirine moieties yielding highly reactive carbenes that are capable of inserting into N–H bonds to afford secondary (linear units) and tertiary (branched units) amines. The polymerisation process was examined at various monomer concentrations and in a variety of inert fluorinated solvents and the resulting hyperbranched polyamines were analysed *via* GPC, and NMR, UV-vis and IR spectroscopies.

Results and discussion

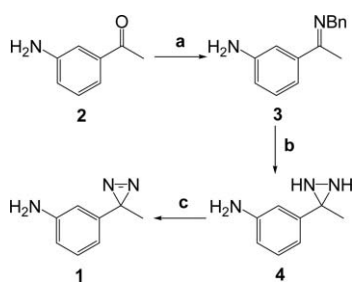
The aminodiazirine **1** was prepared in 4 steps from 3-aminoacetophenone **2** (Scheme 1) using a similar procedure to that reported by Liu *et al.*¹⁴ The acetophenone derivative **2** was firstly converted to its corresponding benzylimine **3** through reaction with benzylamine in the presence of zinc(II) chloride. The crude imine **3** was subsequently reacted with hydroxylamine-*O*-sulfonic acid (HOSA) in liquid ammonia to afford the diaziridine **4**, which was then oxidised to the aminodiazirine **1** using chromic acid.¹⁵

Polymerisation of the aminodiazirine monomer **1** (Scheme 2) was conducted in bulk, as suspensions in perfluorinated solvents and in solution. Initially, the monomer **1** and solvent were added

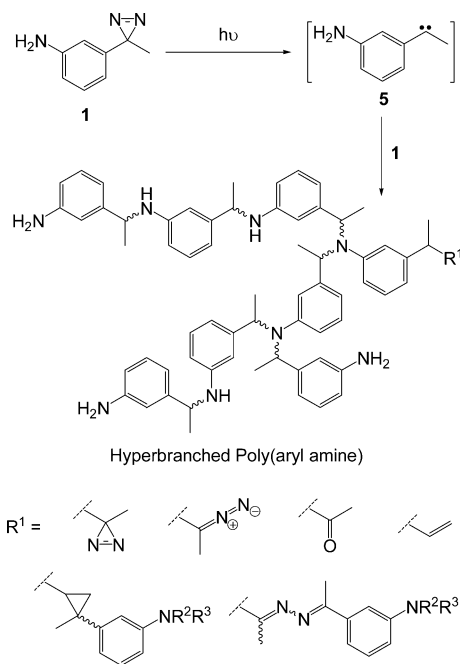
^aDepartment of Chemistry, The University of Reading, Whiteknights, Reading, UK RG6 6AD. E-mail: w.c.hayes@reading.ac.uk.; Tel: +44 (0)118 378 6491

^bInvista (UK), P.O. Box 401, Wilton Site, Middlesbrough, Cleveland, UK TS6 8JJ

[†]Current address: Polymer Science Group, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Melbourne, Victoria 3010, Australia.



Scheme 1 Synthesis of 3-(3-aminophenyl)-3-methyldiazirine **1**: (a) BnNH_2 , ZnCl_2 , Δ ; (b) NH_3 , HOSA, -78°C ; (c) NaCr_2O_7 , H_2SO_4 .



Scheme 2 Synthesis of hyperbranched polyamines from the aminodiazirine **1**.

to a glass vial fitted with a stirrer bar, which was argon flushed and sealed. The vial was placed 2 cm away from a 125 watt high-power mercury vapour lamp and irradiated for 24 h. Suspension phase reactions were vortexed at 1200 rpm prior to irradiation to produce a fine suspension of the monomer in the solvent, which was maintained during the reaction with rapid stirring. Perfluorinated solvents were employed to eliminate any unwanted reaction of the photogenerated carbenes with the reaction medium, as the inherent strength of C–F bonds ($\Delta H_{\text{bond}} \approx 488 \text{ kJ mol}^{-1}$) deters carbene insertion. The solvent was removed *in vacuo* and the residue dried to afford polyamines **P1a–e** (94–99%) as yellow to brown solids. To ensure complete decomposition of the diazirine moieties and any diazoalkanes (formed *via* isomerisation of the diazirines¹⁶) the polymers were heated at 150°C *in vacuo* for 12 h to afford polyamines **P2a–e**, respectively, as glassy brown solids with a reduction in weight of 0–4%. All of the polymers with the exception of **P2e** were soluble in methanol, *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The insolubility of **P2e** was attributed to extensive intermolecular cross-linking upon thermal treatment.

The polymers were analysed by GPC coupled with RI detection (Fig. 1) using linear polystyrene calibrants. Although it has

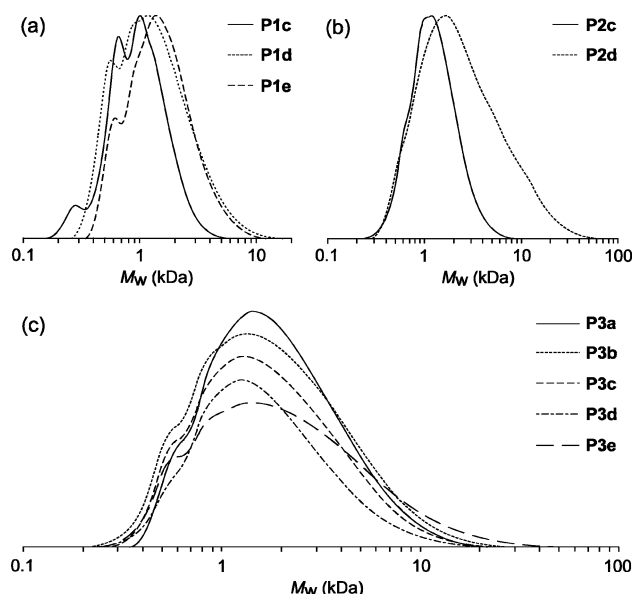


Fig. 1 GPC RI traces of poly(aryl amines) prepared: (a) from photolysis of monomer **1** in bulk (**P1c**), hexafluorobenzene (**P1d**) and perfluoropyridine (**P1e**); (b) from photolysis and thermolysis of monomer **1** in bulk (**P2c**) and hexafluorobenzene (**P2d**); (c) at monomer concentrations of 0.08, 0.17, 0.34, 0.68 and 1.35 M (**P3a–e**, respectively).

been well established¹⁷ that conventional calibration with linear polymers underestimates the molecular weight characteristics of hyperbranched macromolecules, it enabled comparison of the polyamines prepared *via* different conditions without providing absolute molecular weights.

The polyamines **P1a–c** prepared *via* photolysis in bulk or as suspensions had comparable molecular weights corresponding to a DP of 9 (Table 1). Solution phase polymerisations conducted in hexafluorobenzene (C_6F_6) and perfluoropyridine ($\text{C}_5\text{F}_5\text{N}$) afforded polyamines **P1d–e**, which possessed DPs of 13 and 14, respectively. The difference in molecular weight of polyamines prepared in solution and those in bulk is believed to arise from the close proximity of the monomers in bulk and suspension photopolymerisations, which results in the formation of azines¹⁸ that compete with the desired carbene insertion mechanism. Upon thermal treatment all the polymers increased in molecular weight to afford polyamines **P2a–d** with DPs of 12–31. This increase was most prominent for polymer **P2d**, for which the DP more than doubled. This increase in M_w can clearly be observed in the GPC RI trace of polymer **P2d** (Fig. 1, (b)), which shows the disappearance of a low molecular weight shoulder present at *ca.* 0.6 kDa in the trace of polymer **P1d** (Fig. 1, (a)) and a significant increase in the upper molecular weight range from *ca.* 10 to 50 kDa. The observed increase in molecular weight was postulated to occur as result of: (i) the formation of reactive carbenes from the activation of diazirine or diazoalkane moieties present after the initial photopolymerisation, and/or (ii) hydroamination of styrenic species formed from 1,2-hydrogen migration of photogenerated carbenes.^{19,20}

In order to investigate the effect of monomer concentration on the photopolymerisation a series of reactions were conducted. As the monomer concentration was increased from 0.08 to 0.68 M the molecular weight and polydispersity of the resulting polyamines

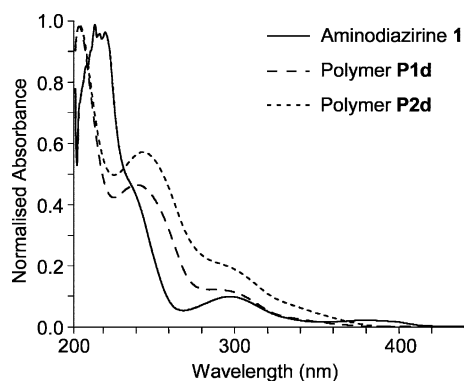
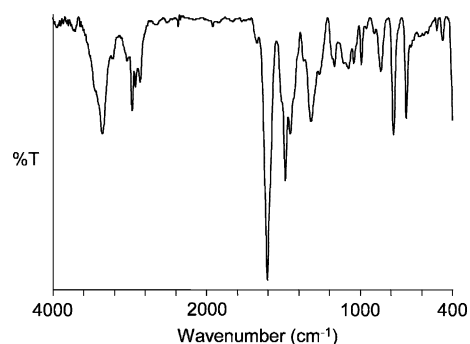
Table 1 Reaction conditions employed for the synthesis of polyamines **P1a–P3e** and their molecular weight characteristics

Polyamine	Conditions	Solvent ^a	Conc. ^a /M	M_w^b /kDa	M_n^b /kDa	PDI ^b	DP
P1a	$h\nu$	FC-72 ^{®c}	N/A ^e	1.1	0.9	1.2	9
P1b	$h\nu$	C ₆ F ₁₅ N ^d	N/A	1.1	0.9	1.2	9
P1c	$h\nu$	Neat	N/A	1.1	0.8	1.4	9
P1d	$h\nu$	C ₆ F ₆	0.67	1.6	1.0	1.6	13
P1e	$h\nu$	C ₅ F ₅ N	0.67	1.7	1.2	1.4	14
P2a	$h\nu/\Delta$	FC-72 [®]	N/A	1.8	1.2	1.5	15
P2b	$h\nu/\Delta$	C ₆ F ₁₅ N	N/A	1.6	1.2	1.4	13
P2c	$h\nu/\Delta$	Neat	N/A	1.4	1.1	1.3	12
P2d	$h\nu/\Delta$	C ₆ F ₆	0.67	3.7	1.6	2.3	31
P2e	$h\nu/\Delta$	C ₅ F ₅ N	0.67	Insoluble ^f			
P3a	$h\nu$	C ₆ F ₆	0.08	3.1	1.4	2.2	26
P3b	$h\nu$	C ₆ F ₆	0.17	2.5	1.3	1.9	21
P3c	$h\nu$	C ₆ F ₆	0.34	2.3	1.3	1.8	19
P3d	$h\nu$	C ₆ F ₆	0.68	2.1	1.3	1.6	17
P3e	$h\nu$	C ₆ F ₆	1.35	2.4	1.4	1.7	20

^a Solvent and concentration used in photochemical polymerisation stage. ^b GPC analysis was conducted in DMF containing 0.05 M LiBr at 60 °C and using polystyrene calibrants. ^c Perfluoro-*n*-hexane. ^d Perfluorotriethylamine. ^e N/A = not applicable. ^f Polymer is insoluble in solvent used for GPC analysis.

(**P3a–d**) decreased, however, when the monomer concentration was further increased to 1.35 M (**P3e**) a slight increase in molecular weight was observed. The decrease in molecular weight with increasing monomer concentration can be accounted for by consideration of carbene N–H insertion *versus* azine formation. At high monomer concentration interaction between carbenes and diazirines or diazoalkanes is more probable, thus azine formation is favoured.^{20,21} At low monomer concentrations the relative proportion of carbenes is higher resulting in a higher yield of insertion products and as result, higher molecular weight polyamines.

UV-visible spectroscopic analysis of the aminodiazirine **1** (Fig. 2) revealed an absorption centred at $\lambda = 378$ nm corresponding to a $\pi\text{--}\pi^*$ transition of the diazirine moiety. In comparison, the absence of this absorption band in the spectra of polyamines **P1d** and **P2d** indicated that the majority of the diazirine moieties had decomposed under the conditions employed. IR spectroscopic analysis of the polyamine **P1d** (representative of all the polyamines—see Fig. 3) revealed several strong absorptions at *ca.* 3355, 1604 and 1320 cm^{-1} corresponding to N–H, aromatic C–C and C–N bonds, respectively. The absence of an absorption band at *ca.* 1700 cm^{-1} implied that the polymer end groups were not terminated by acetophenone type moieties (Scheme 2), which

**Fig. 2** UV-visible spectra of aminodiazirine **1** and poly(aryl amine)s **P1d** and **P2d**.**Fig. 3** IR spectrum of poly(aryl amine) **P1d**.

would have been expected if the intermediate carbenes had reacted with oxygen.²² Furthermore, the absence of absorption bands at *ca.* 2050 cm^{-1} implied²⁰ that diazoalkane moieties were not present after the initial photochemical polymerisation.

¹H and ¹³C NMR spectroscopic analysis of the polyamine **P1d** was dominated by resonances consistent with the desired amine linkages formed through the insertion of carbenes into N–H bonds. For example, the ¹H NMR spectrum of **P1d** (Fig. 4, (a)) consisted of resonances at *ca.* δ_H 1.3 and 4.2 ppm, corresponding to methyl and methine protons, β and α to amine groups, respectively.²³ Minor resonances at *ca.* δ_H 2.15 and 5.2/5.6 ppm, corresponding to methyl protons adjacent to azine linkages and geminal vinylic protons present in styrenic end groups (Scheme 2), respectively, could also be observed. Furthermore, ¹³C NMR spectroscopic analysis revealed resonances between δ_C 54.9–55.4 ppm, corresponding to methine carbons adjacent to aromatic and amine functionalities.²³ Upon thermal treatment the ¹H NMR spectrum of the resulting polyamine **P2d** (Fig. 4, (b)) remained similar to that of **P1d**, with the exception that the resonances resulting from the styrenic protons were now absent. Therefore, it can be deduced that the observed increase in molecular weight upon thermal treatment originates from thermally driven hydroamination of styrenic moieties with amine functionalities or activation of trace amounts of diazirine moieties. ¹H NMR spectroscopic analysis of the polyamine **P1c** prepared

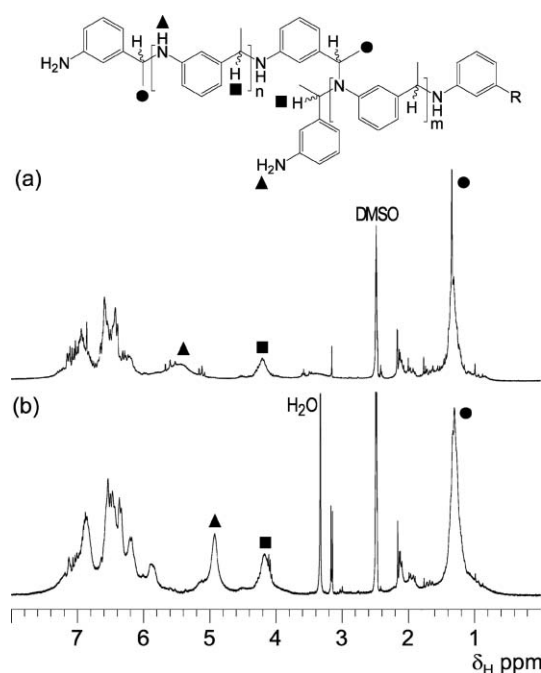
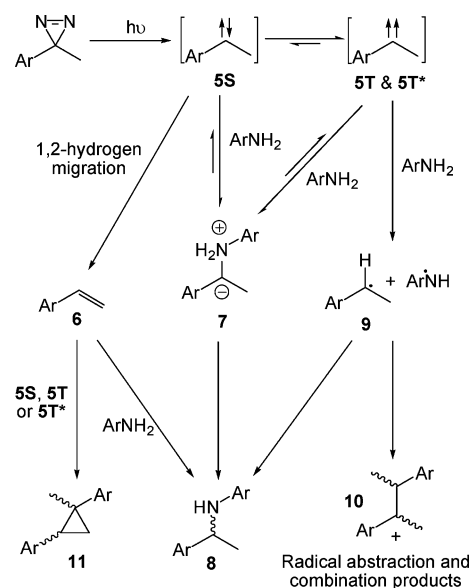


Fig. 4 ^1H NMR spectra of poly(aryl amine) **P1d** (a) and its thermally cured derivative **P2d** (b).

from photolysis of neat aminodiazirine **1** revealed a significant increase in resonances at δ_{H} 2.15 ppm (relative to other methyl proton resonances) corresponding to methyl protons adjacent to azine linkages. This observation accounts for the difference in molecular weight between the polyamines prepared in solution (**P1d–e**) and those prepared in neat (**P1c**) or suspension phase reactions (**P1a–b**), as the formation of azine leads to retardation of the growing polymer chain.

From the ^1H NMR spectroscopic evidence presented it was possible to estimate the relative percentages of each functional group present in the polyamines, presuming that all resonances between δ_{H} 0.7 and 2.2 ppm originated from methyl protons and the resonances corresponding to styrenic geminal protons originated from 1,2-hydrogen migration of carbenes adjacent to methyl groups. Polyamine **P1d** was found to possess amine, azine and styrenic groups in relative percentages of 69, 9 and 8%, with the remainder originating from unidentified functionalities, hypothesised to be stilbene and cyclopropane derivatives, which are common in arylalkylcarbene reactions. The thermally cured derivative **P2d** was found to possess amine and azine groups in relative percentages of 76 and 10%, further confirming that the styrenic species present after photopolymerisation had undergone reaction to afford secondary or tertiary amines. Similar yields of N–H insertion products have also been observed in studies with diphenylcarbene^{21,24} and fluorenylidene.²⁵

Given the high reactivity of carbenes it is not surprising that a diverse range of functional groups and polymeric linkages are formed in the photopolymerisation of the aminodiazirine **1**. The mechanism of formation of these functional groups is complex, but can be accounted for by interpretation of previous chemical and kinetic studies. Photolysis of substituted 3-aryl-3-methyldiazirines leads to nitrogen extrusion and the generation of carbenes in singlet electronic states (**5S**) (Scheme 3) as a result of spin



Scheme 3 Proposed reaction pathways operating during photopolymerisation of the aminodiazirine **1**.

conversion.²⁶ In general, these singlet-state carbenes undergo rapid relaxation and inter-system crossing (ISC) to the ground triplet state (**5T**)²⁷ or intramolecular 1,2-hydrogen migration to form styrenic species (**6**) (Scheme 3).²⁸ Although there is a significant energy barrier to 1,2-hydrogen migration in the singlet state, polar solvents such as acetonitrile dramatically accelerate the intramolecular rearrangement.²⁹ Alternatively, as is observed for diarylcarbenes, the excited singlet-state carbenes could undergo ISC to afford excited triplet-state carbenes (**5T***), which then relax to the ground triplet state (**5T**).³⁰ In addition, the triplet carbenes can interact with other species present in the reaction mixture leading to ISC back to the low-lying singlet state.²⁶

As observed in previous studies involving reaction of arylcarbenes with pyridine^{29,31} and alkylamines^{21,24,32} it is reasonable to assume that ylide **7** (Scheme 3) or tight ion pair formation, with rate constants that approach a diffusion-limited rate,³³ are dominant in the initial stage of the photopolymerisation. The resulting ylide **7** ultimately undergoes N–H insertion to afford secondary **8** or tertiary amines,^{21,24} which accounts for the majority of polymeric linkages in the polyamines. Whereas the singlet-state carbene **5S** is predominately responsible for the formation of ylide **7**, it is not exclusively the only reaction pathway by which secondary or tertiary amines can be formed in the polymerisation. Theoretically, an excited triplet-state carbene **5T*** (which, like its singlet-state counterpart, possesses an empty low-lying orbital) might also be involved in the formation of the secondary amine **8**, as it has been proposed that reaction of excited triplet-state carbenes with amines initially forms a triplet charge transfer intermediate that can decay by ISC into the singlet manifold producing either a singlet charged transfer complex or an ion pair/ylide.³² These species are then capable of dissociation to afford a singlet-state carbene and amine, or undergoing N–H insertion to afford the amine **8**. In comparison, the formation of the amine **8** via a ground-state triplet carbene **5T** would be expected to follow a radical abstraction–recombination type mechanistic pathway,²¹ although potentially carbene **5T** and an amine could

form a complex which undergoes ISC to give the N–H insertion product.³⁴ Predominantly, reaction of carbene **5T** with a primary or secondary amine would lead to hydrogen abstraction and the formation of free radical **9** and an aminyl radical (Scheme 3), which can potentially combine to afford the amine **8**, participate in further abstraction events or undergo radical combination to yield derivatives such as 2,3-diarybutane **10**.

A distinguishing feature of singlet-state aryl, diaryl and arylalkylcarbenes is the ability of these species to form azines *via* reaction with their diazirine or diazoalkane precursors, which in the absence of other reactants is generally the dominant reaction.¹⁸ Therefore, the formation of azine linkages in the photopolymerisation of aminodiazirine **1** was unsurprising. Whereas the azine moieties formed in the polymerisation are unlikely to participate in secondary reactions, the styrenic species formed can potentially react with carbenes to afford cyclopropane derivatives **11** (Scheme 3).³⁵ Thus, the relative percentage of styrenic end groups calculated from integration of the ¹H NMR spectrum of the polyamine **P1d** may underestimate the extent to which 1,2-hydrogen migration occurs in the polymerisation. Given that there is a significant energy barrier to 1,2-hydrogen migration and that ylide formation is a near diffusion-limited rate process one would expect that photopolymerisations conducted in electron donating solvents such as perfluoropyridine and perfluorotriethylamine (C₆F₁₅N) would yield polymers with different molecular weight characteristics. However, the application of perfluoropyridine and perfluorotriethylamine as reaction solvents appears to play no distinguishable part in ylide formation as the polyamines synthesised in these solvents are analogous to those prepared in non-electron donating solvents. The apparent lack of ylide formation in these solvents can be accounted for by consideration of their electron deficient nature, which results from the electron withdrawing properties of the fluorine groups. In common with studies of other hyperbranched polymers reported in the literature,³⁶ the degree of branching of these polymers proved difficult to ascertain given the structural diversity of the linear and branching units within the polyamine architecture.

Conclusion

Hyperbranched polyamines with DP ranging from 9–31 were prepared successfully *via* carbene insertion polymerisation of carbenes generated from an AB₂-type aminodiazirine monomer—carbene insertion reactions can occur twice at the amine group. Although the architecture of the polyamines consisted predominantly of amine linkages, structural analysis also indicated the presence of other moieties, such as azines, which are observed commonly in the reactions of arylalkylcarbenes. The initial photopolymerisation of the monomer clearly results in the formation of polyamines with styrenic end groups that are accessible for further reaction upon thermal treatment, as evidenced by the observed increase in molecular weight of the polymers. Although the exact mechanism of formation of the amine linkages is undetermined, it is evident that such groups could originate from reaction of both singlet- and triplet-state carbenes with amines. Photopolymerisations conducted in bulk and as suspensions were found to yield polyamines consisting of large proportions of azine moieties relative to polymerisations conducted in solution. Therefore, polymerisations conducted in solution yielded

polyamines with higher molecular weights. In addition, an increase in the concentration of the monomer led to a decrease in the molecular weight of the resulting polyamine. As a result of the structural diversity of the polyamines determination of the degree of branching proved to be unattainable. It is quite clear that this carbene insertion polymerisation approach can produce highly functional polyamines in a manner similar to that used to afford less reactive polyethers. Indeed, this approach may prove amenable to the production of functional polyamines suitable for use in molecular electronics or in solid supported scavengers.

Experimental

General

Reagents were purchased from either Fluorochem, Apollo, Acros Chimica or the Aldrich Chemical Company and were used without further purification, unless stated otherwise. FC-72[®], perfluorotriethylamine, hexafluorobenzene and perfluoropyridine were distilled from CaH₂ and stored over 4 Å molecular sieves. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with Merck silica gel 60 F₂₅₄. Developed TLC plates were stained with potassium permanganate solution or scrutinized under 254 nm UV light. Column chromatography was performed using SI60 Sorbent silica (40–63 µm) supplied from VWR International. ¹H Nuclear magnetic resonance (NMR) spectroscopy was performed on either a Bruker DPX250 (250 MHz) or a Bruker AMX400 (400 MHz) spectrometer (using TMS and the deuterated solvent as lock and residual solvent). ¹³C NMR spectroscopy was performed on Bruker AC250 (62.5 MHz) or Bruker AMX400 (100 MHz) spectrometers. Infrared spectroscopy was performed using a Perkin Elmer 1720-X spectrometer with the samples analysed as thin films. UV-visible analysis was performed on a Perkin Elmer Lambda 25 UV/VIS spectrometer using methanol as the solvent. Mass spectra (MS) were obtained using either a Fisons VG Autospec instrument or a Finnigan MAT 95 instrument operating in chemical ionization mode, using ammonia as the impact gas. Gel permeation chromatography (GPC) was performed on a Polymer Laboratories PL-GPC 220 high temperature chromatograph using PL Mixed Gel columns at 60 °C, GPC grade DMF containing 0.05 M LiBr as eluent and PL Easy-Cal polystyrene calibrants. Samples were dissolved in GPC grade DMF containing 0.05 M LiBr (2–4 mg mL⁻¹).

Synthetic details

Synthesis of 3-(3-aminophenyl)-3-methyldiazirine 1. 3-Aminoacetophenone **2** (10.0 g, 74.2 mmol), benzylamine (16.2 mL, 148 mmol) and ZnCl₂ (2 mol%, 0.21 g, 1.50 mmol) were added to toluene (250 mL) and heated under reflux using azeotropic distillation to remove the water produced. After 16 h the mixture was cooled, filtered through a pad of Celite[®] and the filtrate was concentrated *in vacuo* to afford crude 3-(1-(benzylimino)ethyl)benzenimine **3** as a yellow oil. The crude imine **3** was dissolved in dichloromethane (20 mL) and added to condensed ammonia (220 mL) at –78 °C under an argon atmosphere over a period of 30 min. The mixture was stirred vigorously at –78 °C for 6 h and then HOSA (16.7 g, 148 mmol) dissolved in methanol (80 mL) was added over a period of

40 min. After a further 20 h the mixture was warmed to room temperature and water (200 mL) was added. The organic phase was removed and the aqueous phase extracted with dichloromethane (4 × 75 mL). The combined organic extracts were concentrated *in vacuo* to afford the crude diaziridine **4** as a yellow/orange oil, which was dissolved in 1 : 1 water–acetone (300 mL) and sodium dichromate (39.7 g, 148 mmol) and concentrated H₂SO₄ (2 mL, 40.8 mmol) were added. The mixture was stirred in the dark for 20 h and then added to saturated sodium metabisulfite (1 L) and stirred rapidly for a further 20 hours in the dark. The resulting mixture was filtered through a pad of Celite® and the insoluble residues were washed with dichloromethane (600 mL). The organic phase was removed from the filtrate and the aqueous phase was extracted with dichloromethane (2 × 200 mL). The combined organic extracts were dried (MgSO₄), filtered and concentrated *in vacuo* to afford a brown oil. The oil was purified *via* repeated column chromatography on silica (4 : 1 hexane–diethyl ether) in the dark to afford 3-(3-aminophenyl)-3-methyldiazirine **1** as a yellow oil, 0.98 g (9% from 3-aminoacetophenone **2**). $\nu_{\max}/\text{cm}^{-1}$ (thin film) 1238, 1328, 1457, 1503, 1588, 1620 (N=N), 3215, 3367, 3453. $\lambda_{\max}(\text{MeOH})/\text{nm}$ 377.6 (364 $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (N=N). δ_{H} (250 MHz, CDCl₃, Me₄Si) 1.48 (3H, s, CH₃), 3.68 (2H, br s, NH₂), 6.14–6.16 (1H, m, ArH), 6.32–6.36 (1H, m, ArH), 6.58–6.62 (1H, m, ArH), 7.11 (1H, m, ArH) ppm. δ_{C} (62.5 MHz, CDCl₃) 18.0 (CH₃), 26.2 (CN₂), 112.3 (ArCH), 114.6 (ArCH), 116.4 (ArCH), 129.6 (ArCH), 141.6 (ArCC), 146.7 (ArCN) ppm. HRMS (CI) *m/z* calculated for M⁺: 147.0796; found: 147.0797.

General procedure for the synthesis of poly(aryl amine)s.

Photochemical polymerisation. Aminodiazirine **1** was weighed into a dry screw-top vial (3 mL) and for suspension and solution phase polymerisations the required amount of anhydrous solvent and a stirrer bar were added. The vials were flushed with argon, sealed and then placed 2 cm away from a 125 W high pressure mercury lamp equipped with a water cooling jacket and irradiated for 24 h. For suspension polymerisations the mixture was vortexed at 1200 rpm prior to irradiation. After photolysis the solvent was removed from suspension and solution phase polymerisation mixtures and the residue was dried *in vacuo* (0.1 mbar) at 50 °C for 12 h to yield the desired polymers. The polymers were analysed using IR, UV-visible and NMR spectroscopic analyses and the molecular weight characteristics were determined using GPC coupled with RI detection.

Thermal treatment. The polymer was weighted into a dry vial (3 cm³) that was placed in a drying tube surrounded by a heating jacket. The vials were then heated at 150 °C *in vacuo* (0.1 mbar) for 12 h to afford glassy solids. The resulting polymeric materials were analysed using IR, UV-visible and NMR spectroscopic analyses and the molecular weight characteristics were determined using GPC coupled to an RI detector.

Poly(aryl amine) P2d. The analytical data presented are for the poly(aryl amine) **P2d** and are representative of the all the poly(aryl amine) synthesised from the AB₂-type aminodiazirine monomer **1**. Starting from **1** (40.0 mg, 0.27 mmol) and hexafluorobenzene (0.4 mL) the polyamine **P2d** was obtained as a glassy brown/yellow solid, 30.9 mg (95% based on total decomposition of diazirine *via* nitrogen extrusion). $\nu_{\max}/\text{cm}^{-1}$ (thin film) 1096, 1172, 1259, 1317, 1480, 1541, 1604, 1645, 2974, 3366. $\lambda_{\max}(\text{MeOH})/\text{nm}$ 204, 242. δ_{H} (250 MHz; *d*₆-DMSO; Me₄Si) 1.32

(br s), 1.64–1.79 (m), 1.90–2.03 (m), 2.08–2.22 (m), 3.17 (d), 4.00–4.36 (m), 4.93 (br s), 5.89–7.38 (m) ppm. δ_{C} (62.5 MHz; *d*₆-DMSO) 25.2–25.6 (m), 27.1–27.2 (m), 31.3 (s), 35.8 (s), 37.1 (s), 54.9–55.4 (m), 112.8–113.9 (m), 114.4–114.9 (m), 115.5–115.7 (m), 116.6–116.8 (m), 117.8–118.2 (m), 118.5 (m), 119.4–120.0 (m), 120.7–120.9 (m), 121.5 (s), 123.5–123.7 (m), 126.6 (s), 129.8–130.9 (m), 139.1 (s), 140.1–141.0 (m), 147.3–150.2 (m) ppm. GPC (0.05 M LiBr in DMF) $M_w = 3.7$ kDa, $M_n = 1.6$ kDa, PDI = 2.3.

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