Advances in cycloaddition polymerizations

Glenn W. Goodall and Wayne Hayes*

Received 10th October 2005
First published as an Advance Article on the web 14th December 2005
DOI: 10.1039/b507209n

Cycloaddition reactions have been employed in polymer synthesis since the mid-nineteen sixties. This *critical review* will highlight recent notable advances in this field. For example, [2 + 2] cycloaddition reactions have been utilized in numerous polymerizations to enable the construction of strained polymer systems such as poly(2-azetidinone)s that can, in turn, afford polyfunctional β-amino acid derived polymers. Polymers have also been synthesized successfully *via* (3 + 2) cycloaddition methods utilizing both thermal and high-pressure conditions. 'Click chemistry' – a process involving the reaction of azides with olefins, has also been adopted to generate linear and hyperbranched polymer architectures in a very efficient manner. [4 + 2] Cycloadditions have also been utilized under thermal and high-pressure conditions to produce rigid polymers such as polyimides and polyphenylenes. These cycloaddition polymerization methods afford polymers with potential for use in high performance polymers applications such as high temperature resistant coatings and polymeric organic light emitting diodes.

1. Introduction

Pericyclic reactions[1] feature the synchronous breakage and formation of bonds in a concerted manner and involve cyclic conjugated transition states. These transition states possess stabilizing aromatic character that involves delocalized π-electrons. In addition, during the course of the reaction intermediates are not isolated which thereby support the concerted reaction mechanism. The rates of pericyclic reactions are only affected in a minimal fashion by the solvent medium used. Furthermore, these pericyclic reactions can be promoted by either thermal or photochemical means. This class of reaction includes cheletropic reactions, electrocyclic reactions, sigmatropic rearrangements and cycloaddition reactions. From these subclasses of pericyclic processes, cycloadditions have proven to be the most useful in polymer synthesis.

Cycloaddition reactions lead to the formation of new σ-bonds *via* a cyclic transition state resulting ultimately in the creation of cyclic products. Cycloaddition processes involves phase matched interactions between the highest occupied molecular orbital (HOMO) of one component of the unsaturated starting material with the lowest unoccupied molecular orbital (LUMO) of the other substrate, resulting in the formation of bonding molecular orbitals in a concerted manner. There are also several subclasses of cycloaddition processes such as [2 + 2] and [4 + 2] cycloadditions, this notation describes the number of π-electrons that are involved in the cycloaddition process, *i.e.* [$\pi 4_s + \pi 2_s$] or [$\pi 2_s + \pi 2_a$]. 1,3-Dipolar cycloadditions involve 6 π-electrons and can be

School of Chemistry, The University of Reading, PO BOX 224, Whiteknights, Reading, Berkshire, UK RG6 6AD
E-mail: w.c.hayes@reading.ac.uk; Fax: +44 (0)118 378-6331;
Tel: +44 (0)118 378-6491

Glenn W. Goodall

Glenn W. Goodall obtained his first degree (MSci Chemistry) from Kings College, University of London in July 2001. He then worked in the polymer industry as a research scientist (ICI Paints Ltd, Slough UK under the guidance of Dr P. Taylor), before returning to academia in 2003 to undertake a PhD degree at The University of Reading under the supervision of Dr Wayne Hayes. He is currently studying in the field of polymer synthesis with the specific objectives of developing the use of 1,3-dipolar cycloadditions in combination with high pressure reaction techniques to afford novel linear and hyperbranched macromolecular architectures.

Wayne Hayes

Wayne Hayes is a Lecturer in the School of Chemistry at Reading. His current research involves the development of polymerization methods to create novel hyperbranched polymers, electroactive polymer architectures, molecular imprinted resins and the use of MALDI-TOF mass spectrometry in polymer analysis. He was awarded recently the 2004 Young Researchers award by the MacroGroup UK for his work on novel dendritic and hyperbranched polymers.

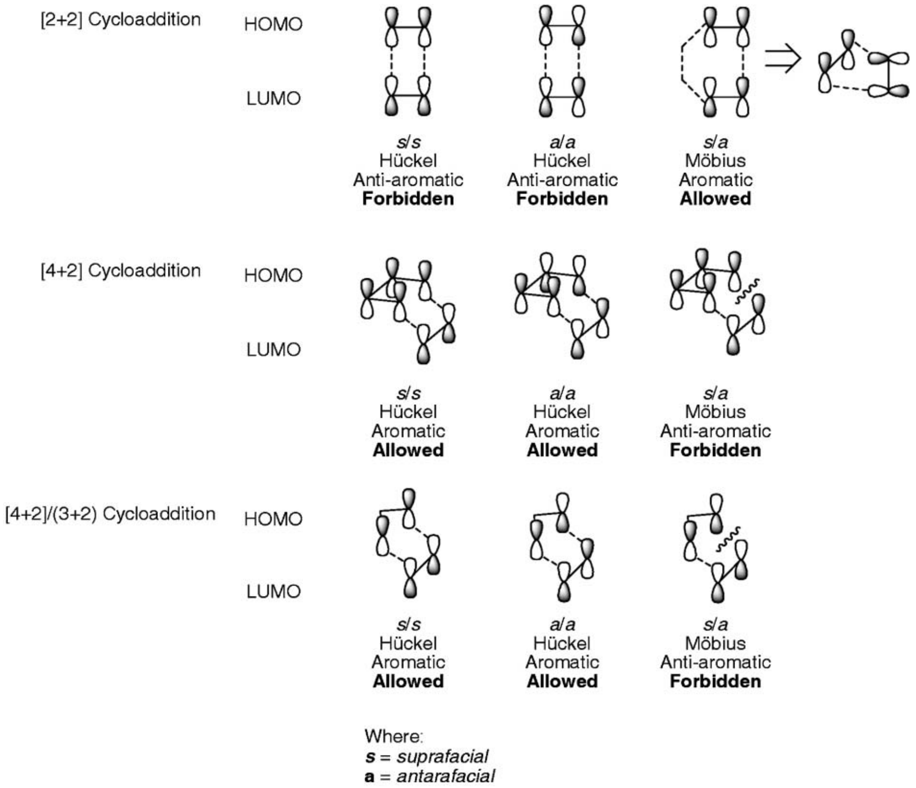


Fig. 1 A summary of the *suprafacial* and *antarafacial* orbital interactions that are permitted or disallowed according to the Woodward and Hoffmann selection rules.[2,3]

formally described as a [4 + 2] type cycloaddition. However, for ease of understanding, 1,3-dipolar cycloaddition are referred to as a (3 + 2) process to discriminate from other [4 + 2] cycloadditions, this alternative descriptor highlights the number of atoms in the two components involved in the cycloaddition reaction. Cycloaddition reactions can occur either across the same face of the π-orbital system in the case of a *suprafacial* addition or across opposite faces of the π-orbital system—in the case of an *antarafacial* addition process (see Fig. 1).

Woodward and Hoffmann[2] proposed a series of selection rules to predict permissible cycloadditions and those that are forbidden when thermal conditions are employed. Furthermore, these selection rules revealed that reactions which feature $4n + 2$ π-electrons (where n = integer value) are allowed when the starting materials are heated whereas those cycloaddition reactions which feature $4n$ π-electrons are forbidden thermally, yet are allowed under photochemical exposure.

These selection rules define concerted cycloadditions based upon the reaction conditions and an orbital symmetry approach, as summarized in Table 1.

However, these selection rules do not account for the reactivity, *endo*/*exo* selectivity and regioselectivity exhibited in cycloaddition reactions. Indeed, any mechanistic detail cannot be inferred directly from the selection rules alone. Indeed, the precise mechanisms of cycloaddition reactions still remain the source of significant debate.

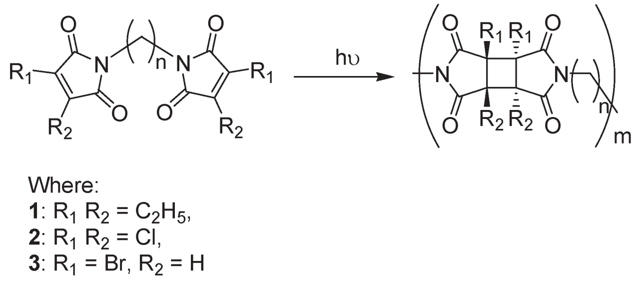
In addition, pericyclic reactions possess favourable attributes required for pressurized conditions to have an effect upon the rate of the reaction. The cyclic transition states involved are condensed and possess a substantially negative activation volume ($\Delta V^{\ddagger}$) when compared to the initial bimolecular state. Therefore, when pressurized reaction conditions are employed, the transition state forms favourably leading to the desired cycloadduct.

Describing these mechanistic concepts in detail is beyond the remit of this *critical review*, however, there have been several excellent books[3,4] and reviews[5] that have been written to which the reader is directed for further reference. Using cycloaddition reactions for polymerization purposes allows rapid access to linear, hyperbranched and cross-linked polymer architectures that feature interesting heterocyclic or strained multicyclic units within the polymer backbone. Indeed, heterocyclic polymers produced *via* cycloaddition chemistries have afforded viable routes to high performance polymers such as poly(perfluorobutane) that are used in electro-optical devices such as sensors. The efficiency and minimal generation of side products in these cycloaddition processes thus lend these reactions readily to the production of polymeric architectures.

Table 1 A summary of the Woodward and Hoffmann selection rules

	Thermal			Photochemical		
Number of electrons	*s*/*s*	*s*/*a*	*a*/*a*	*s*/*s*	*s*/*a*	*a*/*a*
4*n*	✗	✓	✗	✓	✗	✓
4*n* + 2	✓	✗	✓	✗	✓	✗

[a] Where, *a* = antarafacial and *s* = suprafacial; see Fig. 1. ✗ = Forbidden and ✓ = Allowed.



Scheme 1 Photochemical cycloaddition polymerization of bifunctional *N*,*N*′-alkylbismaleimide monomers **1** to **3**.[6]

The following review outlines notable advances in the variety of cycloaddition processes in polymer synthesis.

2. Polymerizations *via* [2 + 2] cycloadditions

[2 + 2] Cycloadditions that involve either a *suprafacial* or *antarafacial* molecular orbital interactions are allowed under thermal treatment according to the Woodward and Hoffmann selection rules (Fig. 1).[3] However, thermal [2 + 2] cycloadditions involve geometrically strained transition states and are thus very rare. Although forbidden thermally, *suprafacial–suprafacial* additions are allowed *via* photochemical means. Incomplete orbital symmetry is overcome by photochemical excitation of the alkene (or alkyne) *via* the promotion of one electron from a π to π*-orbital. The HOMO of the alkene component in a photochemically excited state thus has the correct orbital symmetry with which to interact with the LUMO ground state of the other unsaturated species thus resulting in bond formation. Therefore, polymeric architectures can be produced *via* multiple [2 + 2] cycloaddition dimerization reactions between bifunctional monomers *via* photochemical means.

2.2 Photocycloaddition polymerizations

[2 + 2] Cycloaddition reactions can be utilized in polymerizations in which bifunctional A_2-type monomers are employed. Each reactive moiety can independently become photochemically excited. However, potential side reactions such as radical polymerization and cross-linking pose significant practical problems. Undesirable side reactions lead to an uncontrollable polymerization, variable physical properties, and ultimately low molecular weight materials. However, despite these deficiencies, De Schryver *et al.* have utilized[6] this polymerization approach by employing maleimide monomers as a consequence of their ease of synthesis. Initial polymerization attempts led to insoluble, highly cross-linked polymers as a result of side reactions. *N*,*N*′-Alkylbismaleimide monomers were thus tailored to eliminate the disadvantageous reactions. Furthermore, it was observed that as the number of methylene units in the alkyl linker between the maleimide moieties was increased, the occurrence of homo-cycloaddition decreased. The optimized polymerizations led to polycyclobutanes (see **1–3** in Scheme 1) possessing molecular weights up to 30,000. These polymers exhibited melting points in the range useful (*ca.* 200 °C) for hot-melt adhesives applications.

Solid-state [2 + 2] reactions promoted *via* thermal or photochemical means are referred to as topochemical reactions and allow rapid access to complex macromolecular architectures.[7] Indeed, reactions of this type feature high yields and stereoselectivity as a consequence of the highly ordered, rigid molecular arrangement of reactive unsaturated moieties in the solid-state. Through supramolecular templating in the solid-state, MacGillivray *et al.* have demonstrated[8] the application of topochemistry in [2 + 2] cycloadditions in the synthesis of [*n*]ladderanes – *cis*-fused poly(cyclobutane)s. *Trans*-1,2-*bis*(4-pyridyl)ethylene **4** crystallizes in a layered arrangement with reactive vinyl moieties that lie 6.52 Å apart—in order for [2 + 2] cycloadditions to occur these reactive units must be separated by less than 4.2 Å. However, upon co-crystallization of **4** with resorcinol **5**, a stable four component macrocyclic assembly forms between two molecules each of **4** and **5** *via* four hydrogen bonds (Scheme 2). Within the resultant assembly the vinylic moieties lay 3.65 Å apart in a parallel fashion, and 4.71 Å apart between adjacent assemblies in the solid-state. As a direct consequence [2 + 2] cycloadditions were limited to within discrete assemblies. Irradiation of the powdered crystalline assembly between **4** and **5** for a period of 42 hours afforded the dimer *rctt*-tetrakis(4-pyridyl)cyclobutane† **6** in excellent yield (>99%) and with high stereocontrol. This self assembled system was expanded to form tricyclic systems from co-crystals of **5** and 1,4-bis[2-(4-pyridyl)ethenyl]benzene **7** affording the [2.2]paracyclophane **8** in good yield (60%) and with *exo*-selectivity upon irradiation. The single dimer was produced during these cycloaddition reactions in moderate yield (30%). However, when **7** was co-crystallized with the template 4-benzylbenzene-1,3-diol, the separation between vinyl moieties within the assemblies increased from 3.77 to 3.91 Å. Upon irradiation of the solid-state assemble of 4-benzylbenzene-1,3-diol and **7** only the tricyclic [2.2]paracyclophane **8** was afforded in an improved yield (>99%).

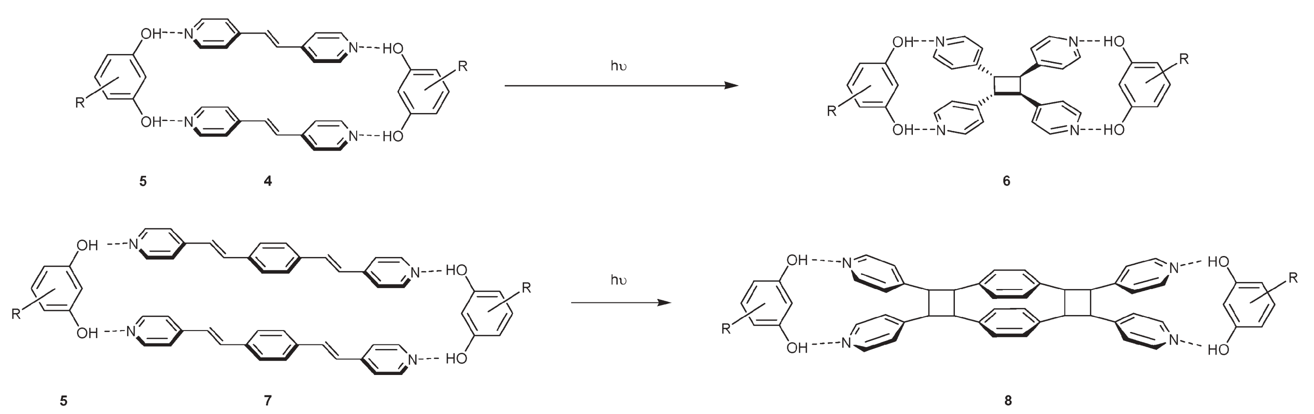
The resultant 'polyene' moieties, such as **4** and **7**, are of interest when employed in photosensitive polymers (*vide infra*), molecular assemblies and in UV filter applications. Indeed, polymers featuring cinnamates functionalities have been utilized[8] as a negative photoresist in the photolithography industry.

To produce [*n*]ladderanes featuring *cis*-fused poly(cyclobutane) frameworks, MacGillivray *et al.* also utilized[9] a solid-state cycloaddition approach. This methodology allowed the preorganization of all-*trans*-*bis*(4-pyridyl)polyene through the formation of assemblies *via* hydrogen bonding. Indeed, within these assemblies the inter-vinylic moiety separation ranges from 3.78 and 3.97 Å in a manner dependent upon the length of the polyene. Upon irradiation of (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene and (1*E*,3*E*,5*E*)-1,6-diphenylhexa-1,3,5-triene for 72 or 120 hours, [3]ladderane **9** and [5]ladderanes **10** were produced, respectively, in excellent yield (>99%) and in a stereoselective fashion (Fig. 2).

Coates and Grubbs *et al.*[10] have shown that the [2 + 2] cycloaddition reaction of stilbenes can be utilized to achieve solid-state polymerization of carefully tailored monomers.

---

† Orientation of substituents around cyclobutane are expressed by the IUPAC notation *rctt*, where *r* = reference, *c* = *cis* and *t* = *trans*



Scheme 2 Molecular recognition directed [2 + 2] cycloaddition approaches to the production of ladderanes.[7]

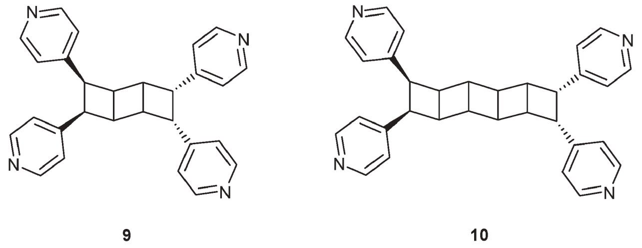
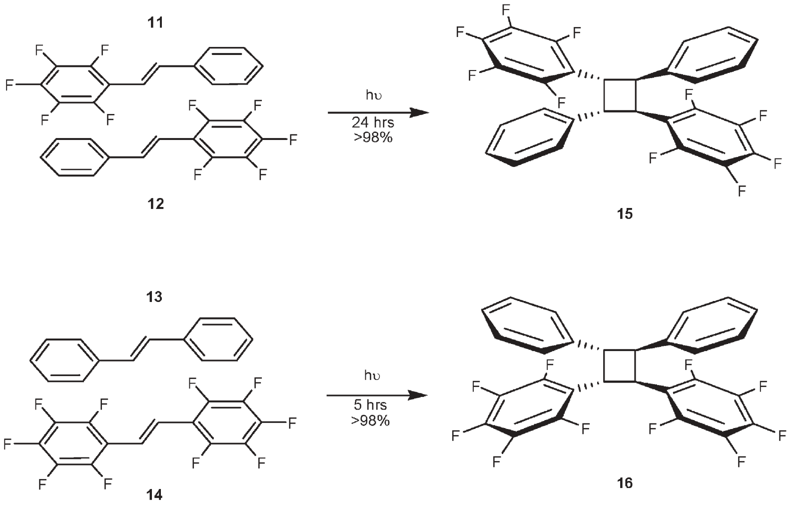


Fig. 2 [3]Ladderane **9** and [5]ladderane **10** produced[8] *via* a solid state templated polycycloaddition strategy.

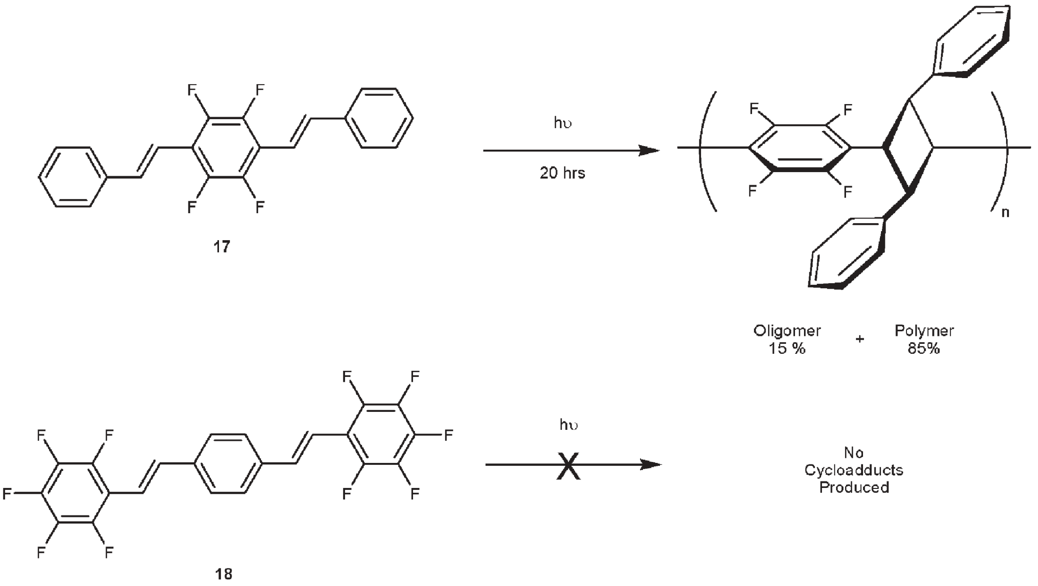
Stilbene type monomers were employed which induce favourable non-covalent forces to thus engineer crystal packing.[11] This packing resulted in optimal parallel arrangement of vinyl moieties of proximal monomers to generate centre–centre separations between 3.5 to 4.2 Å required for the occurrence of solid-state [2 + 2] cycloadditions (*vide supra*). Benzene assumes edge-to-face alignments, whereas, in contrast the 1: 1 complex formed between benzene–perfluorobenzene adopts face-to-face alignments generated in the solid state. This packing arrangement forms as a consequence of both molecules possessing large quadrupoles with opposite signs that thus influence the orientation of the monomers. The cycloaddition concept was proved *via* model reactions (Scheme 3) in which monomers **11** + **12** and **13** + **14** all packed as predicted leading to efficient [2 + 2] cycloadditions to afford the desired cycloadducts **15** and **16**.

This model assembly was expanded to produce polymeric material in the solid-state. The centre–centre separation between parallel vinyl groups of the stilbene monomer **17** in the solid-state was determined to be 3.8 Å. Upon irradiation for 20 hours oligomers (confirmed *via* GPC analysis as dimers and trimers) and insoluble polymers were formed (Scheme 4). However, when the stilbene **18** was irradiated under analogous conditions a cycloaddition did not occur, even after a period of 24 hours. The lack of cycloaddition was attributed to the large centre–centre separation (4.9 Å) in the solid-state between parallel vinyl groups that were too great for the desired reaction to occur. However, when the complementary stilbene monomers **17** and **18** were co-crystallized and then irradiated for a period of 20 hours, polymeric material was produced in excellent yield (>98%). The ease with which phenyl and perfluorophenyl moieties can be coupled to a wide range of polymerisable substituents thus enables rapid access to a range of structurally interesting monomers and polymers *via* this crystal engineering[11] approach.

In addition, [2 + 2] cycloaddition polymerization methodologies has been coupled with well-established conventional



Scheme 3 The use of π–π stacking between benzene and perfluorobenzene stilbene derivatives to direct [2 + 2] cycloaddition chemistries.[10]



Scheme 4 [2 + 2] Cycloaddition polymerization of fluorinated stilbene derivatives.[10]

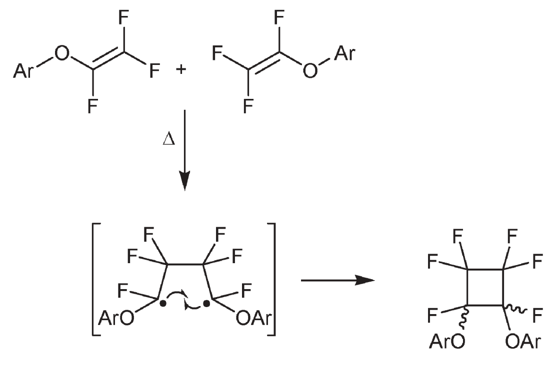
polymerization techniques to access new polymer architectures optimized for specific materials applications. For example, when considering a material capable of photochemical 'fracture healing', Chung *et al.* considered[12] the use of cinnamoyl moieties which dimerize readily *via* [2 + 2] cycloaddition reactions. Cycloaddition cross-linking of cinnamoyl moieties afford cyclobutane linkages that could decompose *via* retrocycloaddition process to afford the starting materials in the solid-state at the point of fracture. Within the polymer structure the cyclobutane linkages are weak as a result of ring-strain and thus present a cleavage point. Upon irradiation these fractures could thus potentially be sealed. To simulate fracturing, samples of viable 'cycloaddition cross-link' cured poly(methacrylate) were ground into fine particles. ^{1}H NMR and FT-IR spectroscopic analysis revealed that cinnamoyl moieties were present as a consequence of retro-cycloaddition process. Upon irradiation (>280 nm) evidence of the vinyl groups of the cinnamoyl moieties disappeared thus indicating that [2 + 2] cycloaddition reactions had occurred. However, this cycloaddition may have occurred merely at the surface of particles between proximal cinnamates and not necessarily between particles thus fusing them together. Strips of the hardened transparent poly(methacrylate) featuring cyclobutane cross-links were thus cracked using a small hammer but not completely broken. These strips were then irradiated (>280 nm) for a period of 10 minutes, the flexible strength was tested before and after fracturing and then post-irradiation. Irradiation alone led to a strength recovery of 3 MPa, whereas heating the strip at 100 °C for 10 minutes led to minimal recovery of strength. However, the combination of irradiation and heating led to an increased strength recovery of 8 MPa for a polymer strip featuring 40% cinnamoyl cross-linker units. The heating was considered to assist diffusion of low molecular weight polymer fragments into the crack voids and to also aid rearrangement of cinnamoyl groups to facilitate the desired [2 + 2] cycloaddition.

Ring-opening metathesis polymerization (ROMP)[13] involves release of ring strain from bicycle[2.2.1]heptane systems to afford, for example, polyalkene architectures. These reactions are catalysed by metal alkylidenes, such as the ruthenium based 'first generation' so-called Grubbs Catalyst.[14] Enholm *et al.* proposed[15] the production of biocompatible materials for temporary filling bone and teeth *via* subsequent photochemical hardening of such flexible polyalkenes *via* [2 + 2] cycloaddition cross-linking reactions. Norbornene monomers were produced featuring electron rich norborane moieties selective for use in ROMP, whilst electron deficient conjugated cinnamoyl and coumarin moieties were also developed that would participate solely in [2 + 2] cycloaddition cross-linking reactions. ROMP was performed with coumarin monomers to afford linear polyalkenes in good yield (77%, 8 : 1 *cis*/*trans*) with number-average molecular weight (M_n) of 6000 and *via* cinnamoyl monomers also in good yield (79%) with M_n of 25000—both polymers were soluble in common organic solvents. Upon irradiation, [2 + 2] cycloaddition cross-linking afforded an off-white polymer that was insoluble in common organic solvents and useful as potential bone scaffolds. However, it should be noted that detailed assessment of residual ruthenium concentrations within these polymeric resins is required prior to *in vivo* applications.

2.3 Radical cycloaddition polymerizations

Thermal [2 + 2] cycloadditions are possible *via* non-concerted thermal and radical mediated mechanisms. Cycloadditions of this type proceed with minimal control of stereochemistry as a consequence of intermediates that can be detected and analysed. These cycloadditions are non-pericyclic in nature since there is a lack of cyclic transition state and intermediate formation.

Smith Jr. and co-workers have produced[16–18] numerous polymers *via* this approach since the mid-nineteen nineties. This research program has focused on the production of



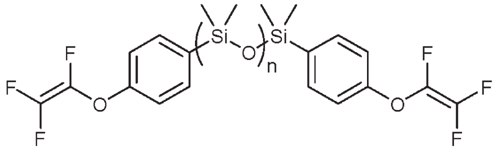
19

Scheme 5 Thermal cyclodimerization of trifluorovinyl aromatic ethers *via* a radical mechanism.[16–18]

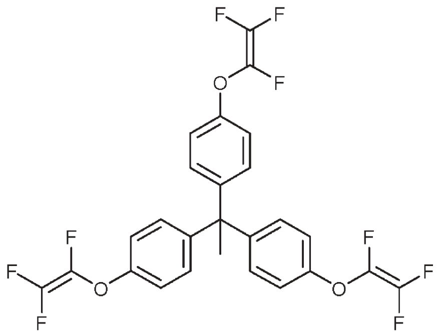
polymers featuring perfluorobutane rings within the repeat units. These polymers were formed utilizing the thermodynamically favourable cyclodimerization of trifluorovinyl ether moieties. When compared to vinyl radical polymerization, the dimerization route exploits the increased strain and lower π-bond energy in the fluorinated alkene unit and the increased strength of the carbon–carbon bond thus formed (when compared to the hydrocarbon equivalent), and thus this cycloaddition predominates. Cycloaddition occurs *via* a stable initial diradical intermediate (Scheme 5) that under goes rapid and irreversible ring closure to yield the desired perfluorobutane ring **19**. This process proceeds *via* a head-to-head manner as a consequence of radical stability.

A range of poly(perfluorocyclobutane aromatic ether)s were prepared[16] from difunctional monomers featuring siloxane spaces (**20** to **22**) and trifunctional B_3-type monomers (see **23**, Fig. 3). Thermal treatment of monomers (*ca.* 150 to 200 °C) was employed to induce the step-growth cyclopolymerization process without the need for initiators or catalysts.

Bulk homopolymerization of the bistrifluorovinyl monomer **20** proceeded by heating the monomers up to 210 °C over a 14 hour period to afford a clear flexible film. Polymerization ceased upon cooling to leave a polymer possessing a M_n value of 10,000, weight-average molecular weight value (M_w) of 34,000 and a polydispersity index (PDI) of 3.4. End group analysis *via* ^{1}H and ^{1}F NMR spectroscopy revealed the presence of trifluorovinyl ether moieties. Further exposure to heat (200 °C for 19 hours) increased the molecular weight up to M_n = 20,000 whilst the PDI value remained constant. This phenomenon allowed the methodology to be used to produce well defined block co-polymers. Homopolymerization of the bistrifluorovinyl monomers **21** and **22** was achieved by similar means to afford polymer films with M_n value of 12,000 and 124,000, respectively. The resultant polymers produced exhibited glass transition temperatures (T_g) of −19 °C and −34 °C, respectively, in contrast to homopolymer of **20** which was a far harder material possessing a higher T_g value of 18 °C. Copolymerization of monomer **20** with **23** was also carried out and afforded an insoluble thermoset material with a T_g value of 120 °C and that decomposed in the temperature (T_d) range 423 to 435 °C. In addition, homopolymerization of tristrifluorovinyl monomer **23** also produced a relatively harder (T_g > 400 °C) and insoluble thermoset material that decomposed at a higher temperature (>461 °C). These polymers featuring perfluorobutane rings display high thermal and oxidative stability, chemical resistance and electrical insulating properties with potential applications in a wide range of technologies such as liquid crystal displays. The trifluorovinyl ether monomers were modified[17] further to include α-methylstilbene linkers (see **24** in Fig. 4). The perfluorobutane rings formed in subsequent polymers could then impact on the bulk properties such as permittivity and

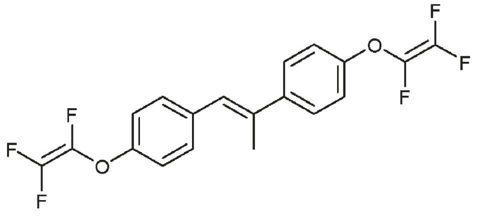


Where:
20: n = 1
21: n = 2
22: n = 3

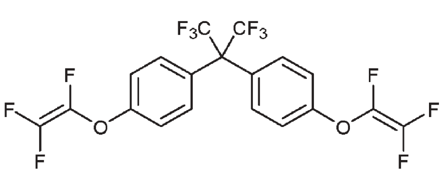


23

Fig. 3 Di- and trifluorovinyl ether monomers structures used[16] in radical [2 + 2] cyclopolymerizations.



24



25

Fig. 4 Stilbene and hexafluoro-2,2-diphenylpropane derived monomers used in the synthesis of liquid crystalline polymers *via* radical mediated [2 + 2] cycloaddition polymerization.[17]

surface organization. Bulk co-polymerization of stilbene monomer **24** with 10 mol% of **22** was carried out at 150 °C for a period of 48 hours to afford a low molecular weight polymer with M_n value of 2300 and M_w value of 4100. This polymer was then cured further at 250 °C to afford the cycloadduct polymer that possessed a M_n value of 4300 and a PDI value of 3.4. Furthermore, by using an alternative linker group (see **25** in Fig. 4) highly crystalline polymers were achieved[18] as a consequence of the crystallization enhancement resulting from the two central trifluoromethane functionalities. Homopolymerization was carried out (*vide supra*) at 220 °C for a period of 32 hours to achieve a monomer conversion in excess of 99% and a resultant polymer with M_n value of 35,000 and M_w value of 67,000. The resultant transparent film was tough and flexible and has potential applications in the field of electro-optical polymers.

2.4 Cycloaddition polymerizations *via* thermal treatment

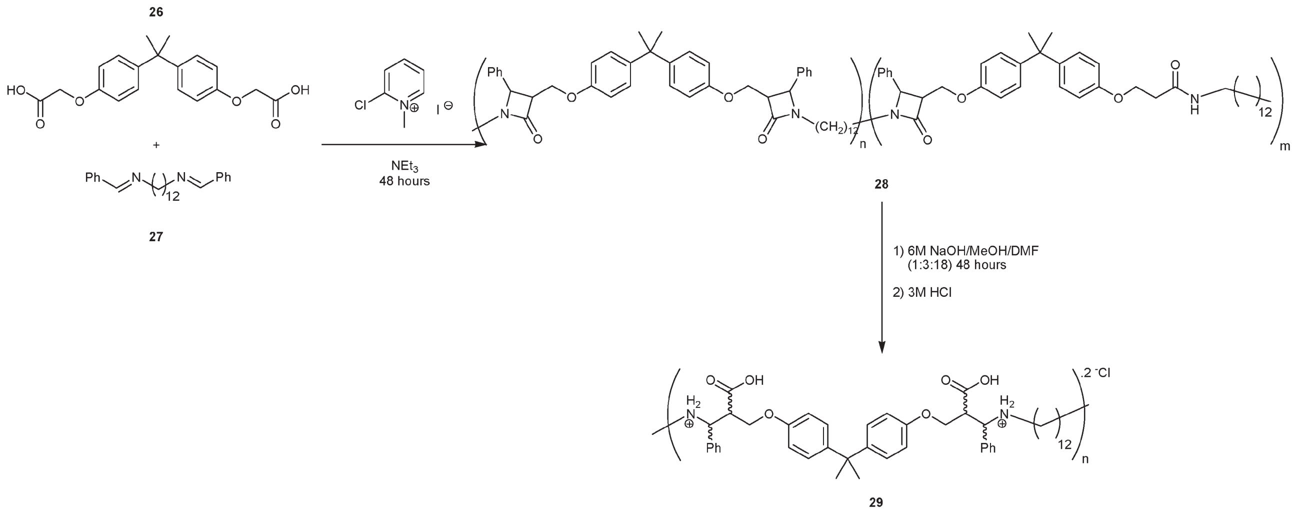
The most abundant concerted thermal [2 + 2] cycloaddition reactions that are allowed according to the Woodward and Hoffmann selection rules are those that involve ketene moieties. The linear nature of ketene moieties limits steric repulsion encountered in the antarafacial transition state. Furthermore, these moieties cyclodimerize readily to afford 1,3-cyclobutanedione heterocycles.

Endo and Sudo have explored[19] the reaction of ketenes with imines *via* [2 + 2] cycloadditions to product 2-azetidinone heterocycles. The *in situ* formation of bisketenes, formed from the corresponding biscarboxylic acids, was employed to limit ketene dimerization within the cycloaddition polymerization process. Model reactions involving monofunctional imines proceeded in the presence of triethylamine. However, the required di(2-azetidinone) was produced in the presence of mono(2-azetidinone) and monoamide units, as a result of the hydrolysis of zwitterionic intermediates. Alteration of the solvent and basic reagents did not promote the desired di(2-azetidinone) formation. However, addition of molecular sieves (3 and 4 Å) limited this hydrolysis process.

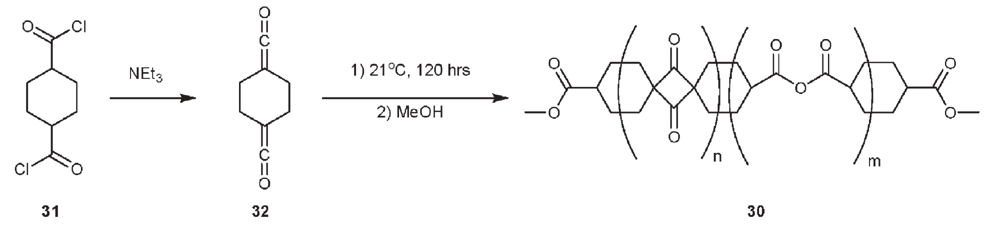
Copolymerization of the diacid **26** and bisimine **27** (Scheme 6) afforded the poly(2-azetidinone) **28** with good monomer conversion (~88%) and M_n values up to 15,400. Unfortunately, hydrolysis of the propagating poly(2-azetidinone) **28** also occurred during the course of the polymerization as supported by ^{1}H NMR spectroscopic analysis.

Poly(2-azetidinone) **28** was then hydrolysed in a controlled fashion by treatment with sodium hydroxide to effect ring opening and afford a multifunctional polymer featuring β-amino acid moieties. However, ^{1}H NMR spectroscopic analysis suggested that the desired polymer **29** was obtained in a yield of only 40%. Upon further hydrolysis the yield of polymer **29** increased to 90% and disadvantageous amide cross-link formation were not observed.

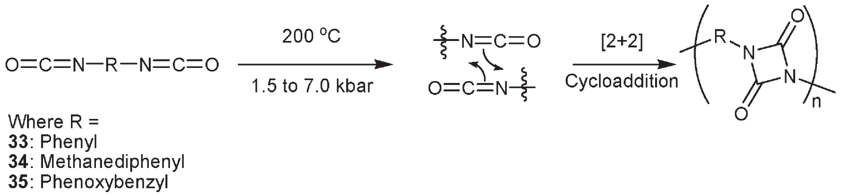
Naka *et al.* have utilized[20] the dimerization of bisketenes as a cycloaddition polymerization route. This approach afforded interesting poly(*spiro*-2,4-dicyclohexylcyclobutane-1,3-dione)s (see **30** in Scheme 7) that have good thermal and chemical stabilities. Bisketenes **31** were produced *in situ* from 1,4-cyclohexanedicarbonyl chloride (**32**) that was heated to afford



Scheme 6 Synthesis of poly(2-azetidinone) *via* [2+2] cycloaddition polymerization and subsequent hydrolysis to afford multi-functional polymer **29**.[19]



Scheme 7 Cycloaddition polymerization of bisketenes to yield poly(*spiro*-2,4-dicyclohexylcyclobutane-1,3-dione)s (**30**).[20]



Scheme 8 The synthesis of poly(diazetidinedione)s from diisocyanate precursors.[21]

the *spiro*-polymer **30** which in turn was end-capped with methanol and precipitated from hexane. After 48 hours, polymer **30** was produced with a M_n value of 10,300, broad PDI (4.5) and with disappointing monomer conversion (only 29%). When repeated for a period of 120 hours the polymerization afforded a higher molecular weight material (M_n value of 34,500) that possessed a broader PDI value (5.4) and a moderate increase in monomer conversion (40%). Thermogravimetric analysis (TGA) analysis under nitrogen revealed significant weight losses at 130 °C, and 210 °C, respectively. In addition to the predicted spiro-linkage, ^{13}C NMR spectroscopic analysis suggested the presence of cleavable anhydride linkages within the polymer chain.

Isocyanates are isoelectronic with ketenes and can also form cyclic dimers (1,3-diazetidine-2,4-diones) and trimers (trisubstituted triazetidinediones) when basic conditions are used. Imai *et al.* have investigated[21] this process in polymer synthesis. Under high pressure conditions (and without solvent or catalysts), cycloaddition processes are favoured when compared to linear homopolymerizations with concomitant loss of carbon dioxide gas. However, thermal homopolymerization of bisisocyanate monomers **33** to **35** (Scheme 8) at 200 °C for 15 hours produced linear poly(carbiimide)s. In contrast, high pressure conditions (1.5 to 7.0 kbar, 120 to 200 °C for 15 to 20 hours) afforded only poly(1,3-diazetidine-2,4-dione) efficiently with monomer conversions up to 99%. The polymer thus obtained was an insoluble, opaque, hard solid as a consequence of the rigid polymer backbone and potential cross-links. These poly(1,3-diazetidine-2,4-dione)s exhibited melting temperature (T_m) values ranging from 166 to 195 °C. When monomers **33** to **35** were subjected to high pressure and temperatures ranging in between 280 and 340 °C interesting hyperbranched[20] poly(triazetidinediones) architectures were produced.[21]

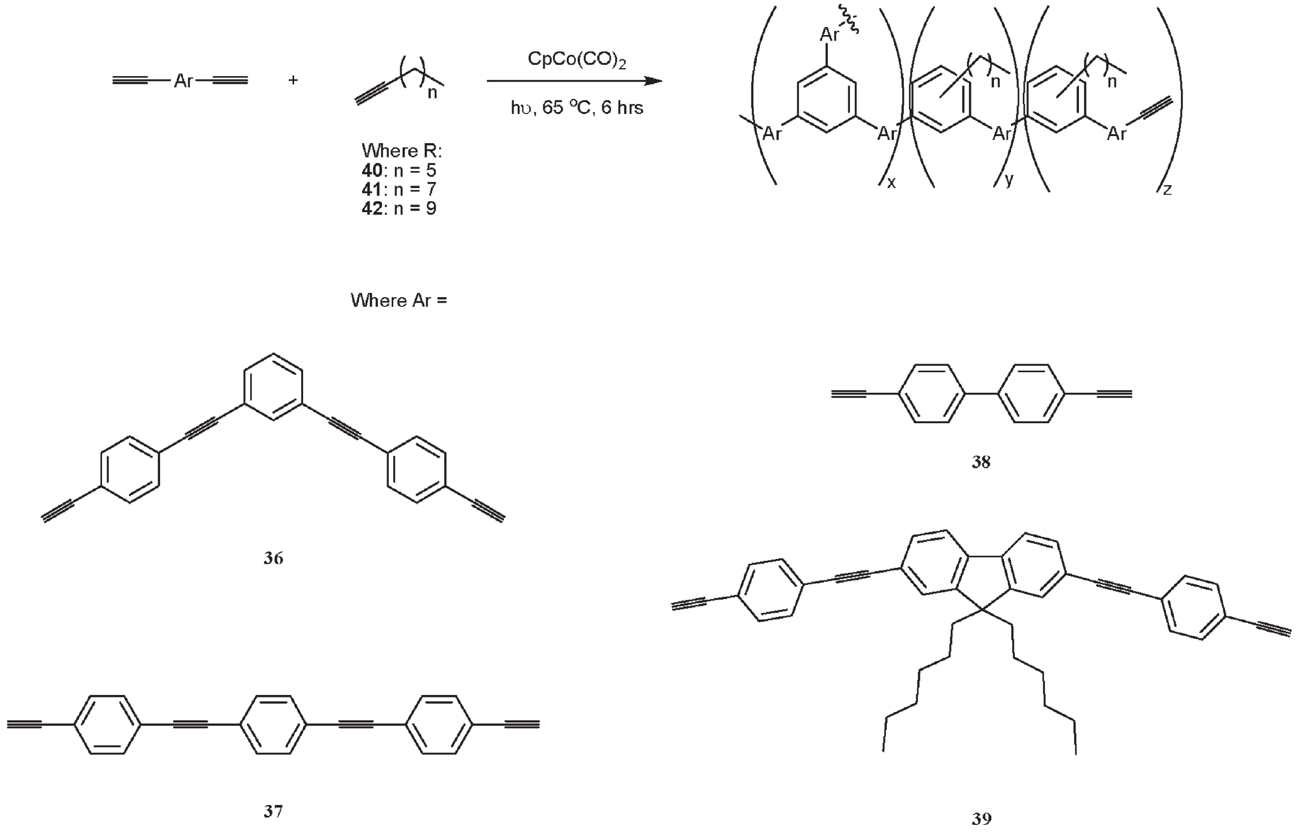
2.5 [2 + 2 + 2] Cycloaddition polymerization routes

Unlike branched polymers, hyperbranched polymers[21] exhibit low melt viscosities as polymer chain entanglement is disfavoured. Hyperbranched polymers can thus feature numerous functionalities and possess enhanced solubility in common organic solvents relative to their linear analogues. Synthesis of hyperbranched polymers usually involves a one-step polymerization process from AB_x-type monomers or a combination of A_2 and B_3-type substrates. Unfortunately, the degree of branching achieved *via* these approaches is frequently less than 100% as a consequence of structural defects and inefficient monomer coupling.

Tang *et al.* have produced[23–25] hyperbranched poly(arylene ethynylene) architectures from three component [2 + 2 + 2] cycloaddition polymerizations between bifunctional alkynes and monofunctional alkyne monomers, utilizing either tantalum, niobium or cobalt catalysts. High molecular weight linear poly(arylene ethynylene) have been produced, but are insoluble in common organic solvents that limited the application of these materials. Homopolymerization of the bis-arylene ethynylene monomers (**36** to **39**) afforded highly rigid yet insoluble polymers (Scheme 9). In contrast, copolymerization of the bis-arylene ethynylene **36** with the acetylene monomer **40** involving tantalum catalysts such as $TaCl_5$–Ph_4Sn proceeded in excellent conversion (97%) to afford a hyperbranched polymer that was soluble in common organic solvents with M_w of 28,000 and PDI of 1.7. Analogous polymerizations using the acetylenic monomers **37** and **40** in conjunction with an irradiated cobalt cyclopentadiene dicarbonyl catalyst ($CpCo(CO)_2$) system proceeded with a monomer conversion of 83% to yield a polymer possessing M_w value of 26,000 and PDI of 3.1 which was insoluble in common organic solvents as a result of the sparingly solubility of monomer **37** in the reaction solvent used (toluene).

In comparison, the bisacetylene monomer **36** was also copolymerized with the alkyl acetylene systems **41** and **42** to afford polymers that exhibited enhanced solubility in common organic solvents, whilst thermogravimetric analysis (TGA) revealed a weight loss of only 5% up to 449 °C.[23] Copolymerization of the acetylenic species **38** and **40** was also carried out utilizing an irradiated cobalt catalyst ($CpCo(CO)_2$) system and afforded polymer that possess a M_w value of 20,000 with similar PDI and this polymer decomposed at extremely high temperatures (T_d of 585 °C).[24] The poly(arylene ethynylene)s thus produced exhibited desired photoluminescence and optical limiting properties and are thus of use in novel light emitting devices. Furthermore, the thermal properties render these systems suitable for high performance polymer applications.

Dendrimers are hyperbranched macromolecules which possess[26] perfect branching and globular architectures. There are two principle synthetic strategies used to generate dendrimers: i) the divergent route and ii) the convergent approach. These synthetic strategies permit the outer surface of the dendrimer to be chemically different in nature to the core environment allowing access to novel catalysts and other structurally interesting materials. Fréchet and Hecht have produced[27] a range of acetylene–polyaromatic ether dendrons *via* a convergent strategy by first reacting two polyaromatic ether bromide dendrons (ranging from benzyl bromide to the third generation bromide) with 2-butyne-1,4-diol *via* Williamson ether coupling methods. [2 + 2 + 2]. Cycloadditions were then achieved between three of the



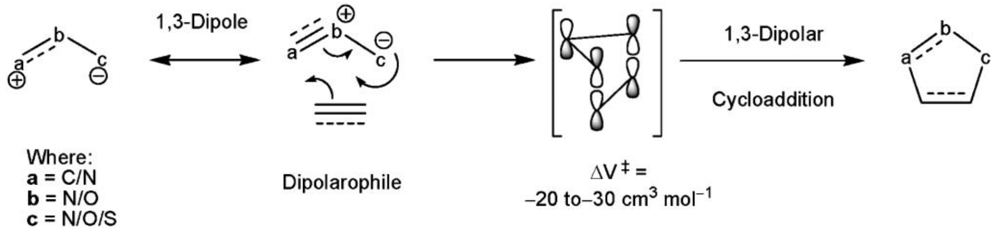
Scheme 9 Use of cobalt mediated [2 + 2 + 2] cycloaddition chemistries to afford hyperbranched poly(arylene ethynylene) architectures.[22–25]

dendrons in toluene (110 °C) in the presence of a dicobalt octacarbonyl catalyst. The resultant dendrimers were afforded in yields ranging from 86 to 36%, the low yields were attributed to steric crowding effects when larger generation dendrons were employed. The cycloaddition reaction was exceedingly clean, affording only the symmetric dendrimers or the starting materials thus facilitating easy purification. The structures of dendritic architectures were confirmed by MALDI-TOF mass spectrometry and GPC analyses.

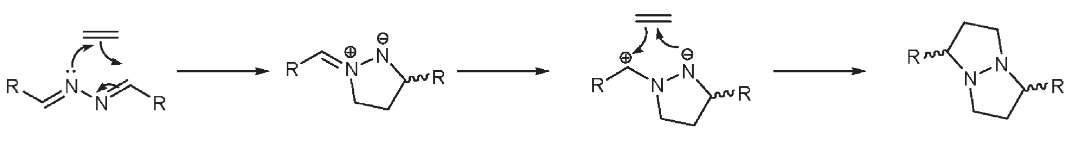
3. (3 + 2) Cycloaddition polymerizations

(3 + 2) Cycloadditions—also known as 1,3-dipolar cycloadditions[28,29] are analogous to Diels–Alder type cycloadditions since both processes feature the involvement of [π4s + π2s] electrons in the FMO interactions (Scheme 10). Although 1,3-dipoles are formally charged species, this charge is stabilized by resonance between the mesomeric forms of the substituent. The highest electron density resides at the terminal atoms and lowest at the central atom, hence these species are referred to as 1,3-dipoles. The cyclic transition state is controlled[3] by frontier molecular orbital (FMO) interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of both the 1,3-dipole and dipolarophile. The majority of these cycloadditions are regioselective as a consequence of contribution of electronic and steric factors—substituted dipolarophiles can be employed to affect the electron rich or deficient character of the reagents and thus alter the orbital symmetry. However, reactions with dipolarophiles featuring alkynes can result in loss of regiocontrol as a consequence of frontier molecular orbital symmetry.

The (3 + 2) cycloaddition is a convenient one-step route for the construction of a variety of complex five-membered heterocycles. These cycloaddition reactions are high yielding in nature (>99%) and involve difunctional monomers which are synthesized easily and thus are suitable for polymerization



Scheme 10 Outline of (3 + 2) cycloadditions used to yield unsaturated dipolarophiles.



43 **44** **45**

Scheme 11 The 'criss-cross' dual (3 + 2) cycloaddition process.[29]

applications. However, this reactivity can lead to adverse side reactions between 1,3-dipoles such as dimerizations and rearrangements (*cf.* sigmatropic shifts).

3.1 Polymerizations *via* 'criss-cross' cycloadditions

Azine moieties **43** can be subjected to dual (3 + 2) cycloaddition reactions (so-called 'criss-cross' cycloadditions) with alkenes to afford interesting 1,5-diazobicycle[3.3.0]octane structures **44** (see Scheme 11). This cycloaddition proceeds in a two-step process *via* an intermediate azomethine imine 1,3-dipole **45**, which undergoes subsequently a second (3 + 2) cycloaddition reaction. The potential [4 + 2] cycloaddition between the azine **43** and the unsaturated species does not occur as a consequence of lone-pair repulsion between the nitrogen atoms and in addition the *syn*-periplanar configuration of the azine required for the [4 + 2] cycloaddition has been shown to be unfavourable.

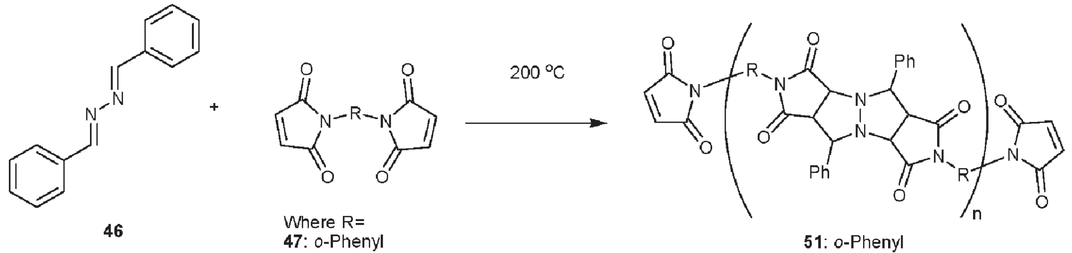
Stille and Anyos first utilized[30] this criss-cross cycloaddition to produce poly(4,8-diphenyl-1,5-diazabicyclo[3.3.0]octane-2,3,6,7-imine) architectures. Initially, benzalazine **46** was reacted with *N*-butylmaleimide in the melt phase at 200 °C for 15 minutes. The dual (3 + 2) cycloaddition occurred rapidly and in good yield (79%), however, when the reaction was carried out in benzene the desired cycloadduct was not obtained. This criss-cross methodology was utilized to produce a range of polyimides (see **51** to **54** in Scheme 12) *via* the reaction of azine **46** with various bismaleimides (**47** to **50**). When the azine **46** was reacted with bismaleimide **47** in ratios of 1 : 1 and 2 : 1, the yields of the polycycloadducts were 50 and 99%, respectively. The molecular weight of the polymer produced from azine monomers **46** and **50** was found to be only M_n = 3400, as determined by the vapour phase osmometry.[31] The resultant polymers exhibited T_d values ranging from 310 to 450 °C that will enable these polymers to be utilized in high performance high temperature applications.

Hexafluoroacetone azine has also been employed successfully in criss-cross type dual-cycloaddition polymerizations. When reacted with cyclic, electron rich unsaturated moieties rapid cycloaddition polymerization occurs, thus circumventing disadvantageous side reactions which hinder the second (3 + 2) cycloaddition process. However, use of the hexafluoroacetone azine monomer has several disadvantages—expense and toxicity. Indeed, within the criss-cross methodology there is potential for the production of hexafluoroisobutene as a consequence of the low thermal stability of the intermediate azomethine imine. Hexafluoroisobutene is highly toxic and renders future melt applications unattractive.

Maier *et al.* discovered[32] that hexafluoroacetone azine reacts with linear bifunctional unsaturated monomers in the bulk and at a temperature of only 21 °C to afford poly(4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyco[3.3.0]octane) architectures in excellent yield. The resultant polymer afforded after 4 days from hexafluoroacetone azine and 1,5-hexadiene was sparingly soluble (5%) in tetrahydrafuran (THF). Gel permeation chromatographic (GPC) analysis of the resultant polymer determined that the M_n value was 5800 and with a PDI value of 4.8, while the structure was confirmed by a combination of IR and NMR spectroscopic analysis. When hexafluoroacetone azine was reacted with 1,9-decadiene and 1,21-docosadiene the solubility increased markedly in THF. However, the molecular weights obtained were considerably lower (M_n value of 3800 and 800, respectively) and the polymers decomposed at temperatures >200 °C.

In general, the criss-cross cycloaddition involving hexafluoroacetone azine occurs in a regioselective manner to yield 2,6-disubstituted poly(4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane)s architectures. The central 1,5-diazabicyco[3.3.0]octane repeat unit can possess *cis–trans* isomers with respect to the fused bicycle (Fig. 5). However, ^{19}F NMR spectroscopic analysis upon these polymers (*vide supra*) suggested the less sterically-hindered *trans*-2,6-isomer predominates (~98%).

When bismaleimide monomers **47** to **50** featuring maleimide moieties were reacted with hexafluoroacetone azine the desired



46

Where R=
47: *o*-Phenyl
48: *m*-Phenyl
49: *p*-Phenyl
50: Hexyl

51: *o*-Phenyl
52: *m*-Phenyl
53: *p*-Phenyl
54: Hexyl

Scheme 12 Polyimides produced *via* 'criss-cross' cycloadditions.[29]

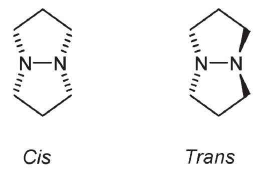


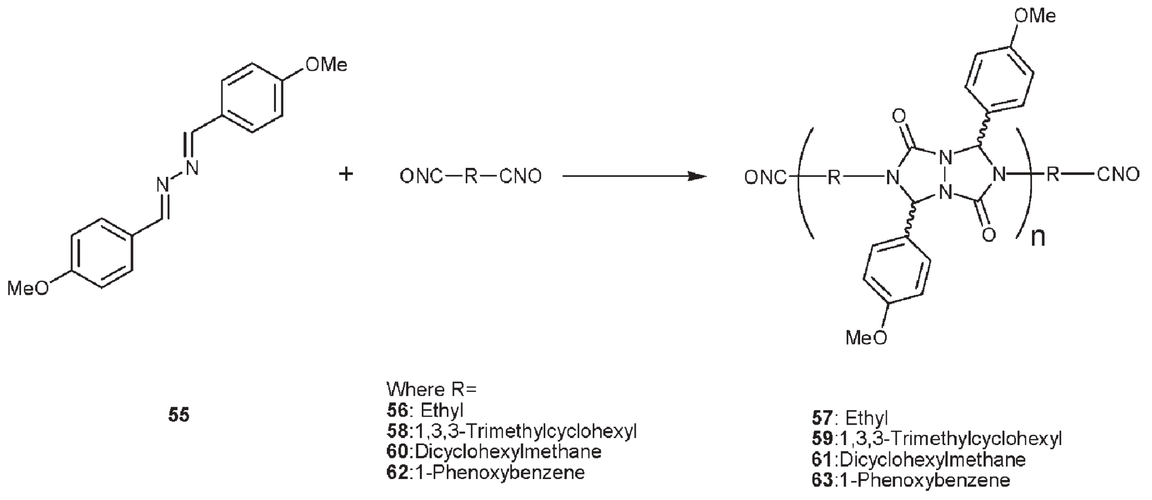
Fig. 5 *Cis-trans* isomeric forms of the 1,5-diazabicyclo[3.3.0]octane repeat unit found in 'criss-cross' polymers.[29]

polymerization did not occur as a consequence of a rapid hydrogen-shift that disabled the secondary (3 + 2) cycloaddition process. Maier *et al.* discovered[32] that this disadvantageous hydrogen-shift could be overcome by separating the imido group from the vinylic moieties with a highly strained cyclic system. Consequently, dinadimide monomers were employed to overcome these side reactions. However, unfortunately this approach led to solubility problems for the resultant poly(8,8,16,16-tetrakis(trifluoromethyl)-1,9-diazahexacycloc[7.7.0.1.1.0.0]octadecane-4,5,12,13-tetracarboxdiimido) architectures.

In the light of the disadvantages of the use of azines, Maier *et al.* focused[33] upon the reaction of diisocyanates with azines to produce alternative criss-cross polymeric architectures. When hexamethylene diisocyanate **56** was reacted with electron deficient azines such as all-*trans*-1,2-bis(4-chlorobenzylidene)hydrazine, long reaction times (*ca.* 40 hours) were required and low yields of the desired product resulted (17%). However, electron rich azines such as all-*trans*-1,2-bis(4-methoxybenzylidene)hydrazine **55** proved to be highly reactive with **56** and afforded the desired polymer in high yield (87%) in a rapid fashion (*ca.* 3 hours). The increased yields and rates of reaction occurred as a consequence of orbital symmetry control whereby π-electron deficient isocyanates react by criss-cross cycloaddition exclusively with π-electron rich azines. In addition, π-electron rich unsaturated moieties will react exclusively with π-electron deficient azines such as hexafluoroacetone azine. Thus, the hexafluoroacetone azine monomer would be incompatible with diisocyanate monomers and the desired criss-cross cycloaddition would not occur. A series of diisocyanates were co-polymerized with **55** either in a solvated state (dibutyl phthalate) or in the bulk at temperatures up to 170 °C (Scheme 13). The polymerizations were influenced by steric hindrance with close proximity to the isocyanate moieties. Monomers featuring primary diisocyanates such as **56** required a period of 72 hours to afford polymer **57** that possessed a M_n value of 16,000. The thermal properties of polymer **57** were comparable to those exhibited by the fluorinated polymeric analogues (*vide supra*), *i.e.* decomposing at *ca.* 250 °C and with T_g values of *ca.* 87 °C. When azine **55** was reacted with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane **58** for 70 hours polymer **59** was afforded with a considerably lower M_n value (5500). Furthermore, when the azine **55** was reacted with bis(4-isocyanatocyclohexyl)methane **60** for 20 hours and 1-(4-isocyanatophenoxy)-4-isocyanatobenzene **62** for a period of 3 hours, polymers **61** and **63** were produced with lower M_n values of 6100 and 7700, respectively, as a consequence of steric hindrance exhibited by secondary isocyanate moieties. The polymers **61** and **63** were also relatively tougher materials exhibiting T_g values of 151 and 142 °C, respectively.

Interestingly, the dual cycloaddition mechanism always leads to telechelic polymer architectures. Indeed, the primary (3 + 2) cycloaddition leads to terminal 1,3-dipole azomethine imine moieties that will either react with another diisocyanate unit or participate in a retro cycloaddition process. Both of these routes afford ultimately isocyanate terminal residues. The telechelic nature of the resultant polymers allows the possibility of chain extension and formation of block co-polymers. For example, polymer **63** was reacted with 4-(4-aminophenoxy)benzene amine and hexane-1,6-diamine over a period of 20 hours. Chain extension increased the M_n value to 21,000 and 29,000, respectively, when compared to the original polymer **63**. In addition, the polymer extended with aromatic ether linkages possessed a T_g value of 150 °C whereas the polymer featuring aliphatic linkages exhibited a lower T_g value of 125 °C.

Utilization of this block co-polymer strategy has allowed access to optimized[34] thermoplastic elastomers that feature alternating hard and soft segments. If thermoplastic elastomers of this type could be designed with higher operational



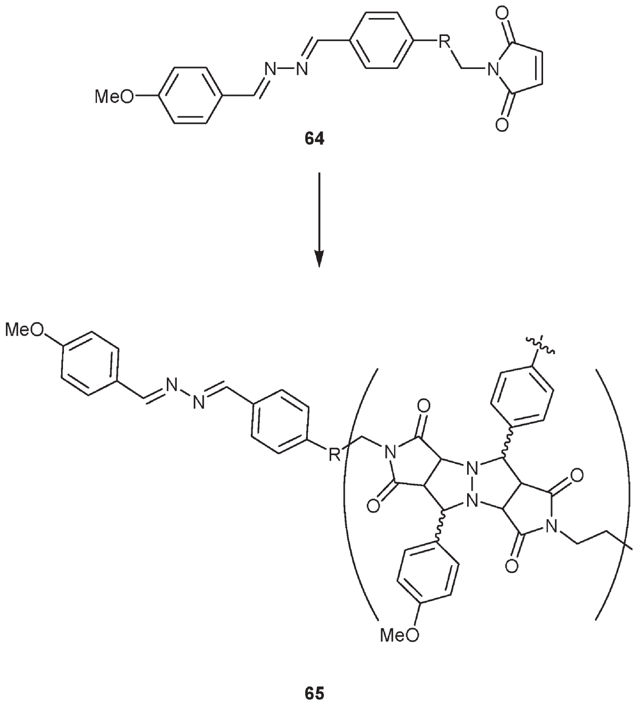
Scheme 13 The dual (3 + 2) cycloaddition of diisocyanates and a π-electron rich azine **55** to afford thermoplastic elastomeric polymers.[32]

temperatures and yet low temperature elasticity these materials would be of great industrial importance, however, this objective has proved extremely challenging to date.

The criss-cross poly(imine) **63** was remade in triplicate to afford oligomers possessing M_n values of 1600, 2000 and 3900, respectively, thus generating a range of 'hard' blocks possessing a T_g value of 159 °C that decomposed at *ca.* 240 °C. In addition, a range of telechelic poly(oxytetramethylene)s and poly(oxymethyleneoxytetramethylene)s were produced as the corresponding 'soft' block with T_g values of -60, -71 and -77 °C with M_n values of 1000, 2900 and 5800, respectively. Block co-polymers prepared from **63** with $M_n > 2000$ and the 'soft' segments afforded block co-polymers that featured only four to eight polymeric blocks. However, when the criss-cross poly(imine) **63** (with M_n value of 1600) were employed the resultant block co-polymers produced comprised up to 22 and 30 'hard' and 'soft' blocks. These block co-polymers could be compression moulded successfully at 160 °C and 48 bar over a 2 hour period but, unfortunately, yellowing of the polymer occurred during this processing step. However, clear films could be produced from chloroform with ease. It became apparent from differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) that the blocks were incompatible and microdomains formed in the bulk polymer as a consequence of microphase separation.

Maier, Voit and co-workers envisaged[35] using low M_n (4100) hydroxyl-terminated liquid natural rubbers as the soft segments ($T_g \sim -50$ °C) within a block co-polymer strategy to afford low temperature crystallization and elasticity. This soft segment was block co-polymerized with a low molecular weight (M_n value of 2800) 'hard' telechelic polymer **59** (*vide supra*) segment to produce a series of potential thermoplastic elastomers. After 8 hours at 80 °C in the presence of dibutyl tin dilaurate catalyst, a block co-polymer with an M_n of 21,000 consisting of three blocks was generated. Unfortunately, the tensile strength observed for this block copolymer was far lower (0.9 MPa) than block co-polymer thermoplastic elastomers that are employed commercially. Use of scanning electron microscopy revealed microdomains in the cycloadduct block copolymer and phase separation could be visualized clearly.

By utilizing a criss-cross cycloaddition polymerization approach, Maier, Voit and co-workers have described[34] a strategy to produce hyperbranched polymers with degrees of branching that approach 100%. Polymers of this type would be structurally analogous to dendrimers but synthesized *via* a cost-effective one step process. Azine and maleimide moieties undergo an initial reversible (3 + 2) cycloaddition assembling azomethine imine *via* an intermediate 1,3-dipole. This intermediate can either decompose back to the starting azide and maleimide or react with a further maleimide moiety *via* a secondary (3 + 2) cycloaddition. Thus the mechanism of criss-cross cycloadditions potentially allows access to hyperbranched polymers with approaching 100% degree of branching, featuring a core maleimide and unreacted azide moieties (Scheme 14).



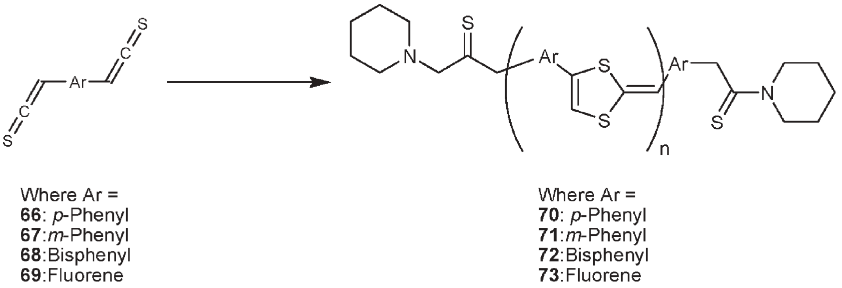
Scheme 14 Synthesis of hyperbranched polyimides *via* use of a 'criss-cross' cycloaddition approach of the AB_2-type monomer **64**.[34]

Melt homopolymerization of the AB_2-type monomer **64** was carried out at 185 °C for 15 minutes under anhydrous conditions to afford the desired hyperbranched cycloaddition polymer **65** with a relatively low M_n value of 5700 (in comparison to the linear equivalent with an M_n value $\sim$ 12,000). However, the hyperbranched polymer **65** produced exhibited increased solubility in common organic solvents and possessed a lower T_g value (136 °C) than the linear analogue ($T_g \sim 152$ °C). ^{13}C NMR spectroscopic analysis was used to assess the occurrence of structural defects caused by 1,4-hydrogen shifts, electrocyclic ring closure and dimerization of the intermediate 1,3-dipole. The detailed spectroscopic analysis carried out implied that there were minimal structural defects, but MALDI-TOF mass spectrometric analysis was required for definitive evidence. Unfortunately, the peripheral azide moieties present within the structure absorbed radiation close to the emission wavelength of the MALDI-TOF MS laser and thus only fragments of the hyperbranched polymer could be detected and the precise structures of the hyperbranched polymer could not be elucidated.

3.2 Thermal cycloaddition polymerizations: utilization of the thioketene pseudo-1,3-dipole

1,3-Dithiafulvene systems are π-electron donors and can form stable charge-transfer or radical ion complexes with numerous electron acceptor functionalities. Consequently, attempts have been made to fashion polymers that incorporate these heterocyclic units. However, examples of π-conjugated polymers that feature dithiafulvene units are rare. Polymers of this type would allow access to improved conducting materials and greater doped conductivity as a consequence of electron mobility across the bulk polymer architecture.

Naka, Uemura and Chujo utilized[36] a range of aromatic bis(thioketene) monomers (**66** to **69**) to afford novel polymer



Scheme 15 (3 + 2) Cycloaddition polymerization of aromatic bis(thioketene)s (**66** to **69**) to afford poly(dithiafulvene)s (**70** to **73**).[36]

architectures (**70** to **73**) *via* a (3 + 2) cycloaddition process. The short-lived and highly reactive thioketene moieties were produced *in situ* during the cycloaddition polymerization process in a manner similar to ketene polymerizations (Scheme 15). The reaction was quenched after a period of 3 hours with pipridine and the product was then precipitated to afford an orange coloured polymer in acceptable yield (up to 76%).

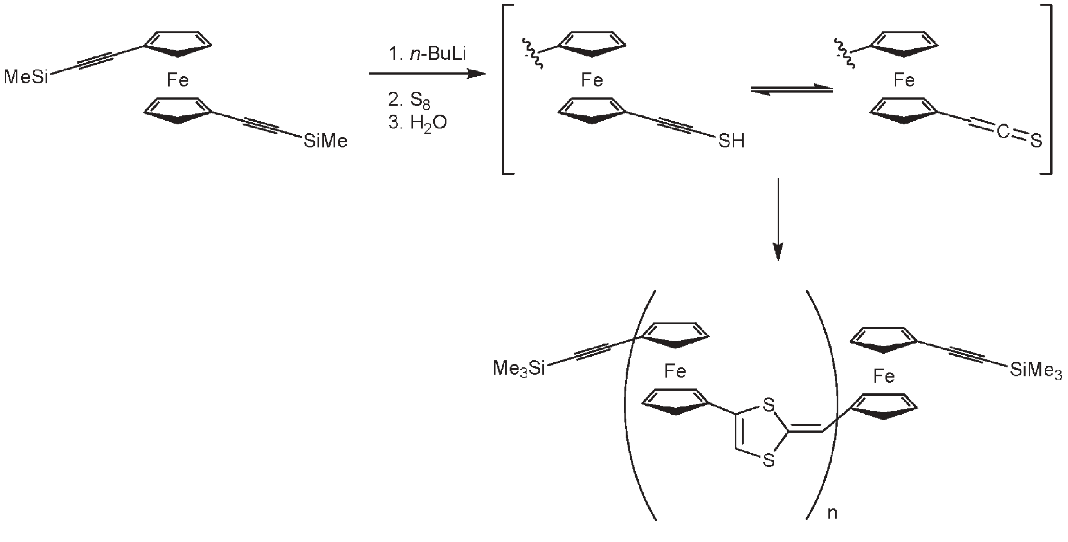
The polymer structure was elucidated using a combination of ^{1}H NMR and FT-IR spectroscopic analysis—the strong absorption band at 1578 cm^{-1} indicated the presence of the unsaturated alkene of the dithiafulvene moiety. Furthermore, UV-visible spectroscopic analysis identified a π–π* transition within the polymers at between 359 to 401 nm—the redshift was dependent on the specific polymer architecture. The high thermal stability of these polymers (T_d of *ca.* 430 °C) renders them useful materials with application in electrical devices. The redox characteristics of the polymers were determined *via* cyclic voltammetry (CV) and compared to relevant model compounds. The dithiafulvene, as a component of the π-conjugated system, affected stabilization of the polymer against oxidation. In addition, irreversible oxidation peaks occurred before the reversible redox peaks, thereby suggesting that the oxidation caused dimerization between proximal dithiafulvene moieties.

The repeating dithiafulvene unit is capable of forming 1 : 1 charge-transfer complexes with π-electron-acceptors such as tetracyanoquinodimethene (TCNQ). When poly(thioketene) **70** was treated with the electron-acceptor TCNQ, a dark green coloured homogeneous charge-transfer complex was formed. ESR spectroscopic analysis confirmed the presence of the stable anion radical of TCNQ. The charge-transfer nature of the polymer was confirmed by CV analysis, however, the π-electron density of the dithiafulvene unit was reduced as a consequence of positive charge delocalization *via* the charge-transfer reaction. Before doping, cast films of poly(thioketene) **70** exhibited electron conduction of 3.0 × 10^{-7} S cm^{-1} but once complexed with TCNQ this value increased by two orders of magnitude. The π-conjugated polymer architectures featuring donor–acceptor pairs exhibit relatively small band-gaps as a result of intramolecular charge-transfer complex formation. This small band-gap leads ultimately to greater intrinsic conductivity that approaches metallic like values.

Naka, Uemura and Chujo also investigated the production[37] of π-conjugated polymers that possessed alternating dithiafulvene and heteroaromatic moieties such as thiophene or pyridine in place of the benzyl units within the poly(thioketene) **70**. When CV analysis was conducted on these derivatives, broadening and an anodic-shift of the oxidation peaks occurred when compared to model compounds, a trend that is common in electrochemically active π-conjugated polymers. Indeed, the oxidation potential of poly(thioketene thiophene) was higher than that observed for polymer **70** as a result of greater electron donation by the thiophene unit. Thus, poly(thioketene thiophene) exhibited lower stabilization against oxidation as a consequence of inferior π-electron delocalization. The reverse effect was observed for poly(thioketene pyridine) that incorporated pyridine units—this system exhibited a large oxidation potential as a consequence of the π-deficient pyridine moiety. A dark green charge-transfer complex was obtained upon treatment of the resultant polymers with the electron acceptor TCNQ. Poly(thioketene pyridine) exhibited increased charge-transfer than poly(thioketene thiophene) as a result of its higher oxidation potential and greater formation of the anion radical over the charge-transfer complex. It was thus postulated that the charge-transfer complex of poly(thioketene thiophene) could accept more charge from the stronger electron donating thiophene moieties. The electronic conduction was relatively high for the poly(thioketene thiophene) and poly(thioketene pyridine), 1.2 × 10^{-6} and 1.6 × 10^{-4} S cm^{-1}, respectively—the latter value was obtained as a consequence of the π-deficient pyridine moiety. The charge-transfer complex of poly(thioketene thiophene) with TCNQ possessed a conductivity that was two orders of magnitude greater, whereas the conductivity of poly(thioketene thiophene) remained relatively unaffected upon complexation with TCNQ. These high conductivity characteristics render the polymers useful within semiconductor applications.

Polymer hybrids that feature organic and inorganic components are of great interest, featuring potentially tuneable properties *via* transition metal incorporation. Materials of this type would feature electronic interaction between polymer units and the incorporated metal centre. Attention has thus focused upon production of polymers that feature two redox centres *via* dithiafulvene and ferrocene moieties.[38] Naka, Uemura and Chujo followed a similar (3 + 2) cycloaddition strategy used to afford polymer **70** (Scheme 16) in order to generate the polyferrocene **74** in moderate yield (50%) and molecular weight (M_n = 1930), as a consequence of the low reactivity of the methylsilane protecting groups of the acceptor moieties with *n*-butyl lithium.

Polymer **74** featured two redox centres. However, CV analysis only revealed a single broad oxidation and reduction



74

Scheme 16 (3 + 2) Cycloaddition polymerization of ferrocene thioketene derivatives to afford a polyferrocene system **74** that features two redox centres located in an alternating fashion along the polymer backbone.[38]

peak that implied an interaction between the electron donors. In addition, the low potentials of the oxidation peaks (between $E^{\text{ox}} = +0.9$ and $+1.4$) were characteristic of a highly delocalized π-system. When complexed with TCNQ, the resultant charge-transfer complex exhibited paramagnetic properties. The conductivity of this complex was found to be 5.0×10^{-6} S cm^{-1} and when doped with iodine this value increased by three orders of magnitude. These properties render polymer **74** useful in devices such as sensors[39] or even in electrocatalysis applications.

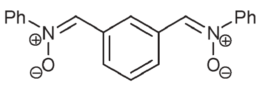
3.3 Thermal cycloaddition polymerizations: utilization of nitrones

Nitrone moieties[40] are extremely stable species and undergo readily (3 + 2) cycloadditions with alkenes and alkynes to afford isoxazolidine and isoxazoline rings, respectively, in a regioselective manner with electron rich or deficient dipolarophiles, as a consequence of orbital symmetry matching. When subjected to photochemical conditions,[41] cyclization of the nitrone moiety occurs to afford oxaziridine structures. Furthermore, nitrone based (3 + 2) cycloadditions have been utilized in solid-supported applications[42] to allow access to interesting 1,3-amino alcohols *via* reductive cleavage of the intermediate cycloadducts. These nitrone moieties are synthesized readily, are stable to ambient conditions and a variety of thermal conditions. Despite the wide range of inter- and intramolecular (3 + 2) cycloadditions involving nitrones that have been reported, very few examples of polymers have been produced *via* this approach.

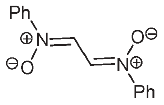
Manecke and Klawitter have employed two strategies to afford poly(isoxazolidine)s *via* (3 + 2) cycloaddition polymerization of monomers featuring nitrone moieties. Initially a strategy involving the polymerization of A_2 and B_2-type monomers was employed.[43] Bis(nitrone)s **75** and **76** were reacted, in turn, with bis(maleimide)s **48** and **49** in dimethylformamide at 110 °C (Fig. 6).

The desired (3 + 2) cycloaddition polymerizations afforded a range of poly(isoxazolidine) architectures in good yield (>99%) but that possessed low molecular weights (M_n values ranging from 2400 to 3600). The structures were confirmed by FT-IR spectroscopic analysis. In addition, Manecke and Klawitter employed AB type monomers utilizing *p*-maleimidophenyl-*N*-phenylnitrone (see **77** in Fig. 7) that was synthesized in 86% yield.[43] Upon homopolymerization of the AB monomer **77** both in solution and under solid-phase conditions poly(isoxazolidine)s possessing M_n values up to 6200 were generated. These poly(isoxazolidine)s proved to be soluble in common organic solvents such as dimethyl sulfoxide and dimethylformamide, but not in ethanol or acetone.

After initially producing polymers[44] featuring pendent nitrone moieties for optical data storage applications, Ritter and Vretik employed a polymerization strategy involving A_2 and B_2 type monomers to produce[45] novel poly(isoxazolidine)

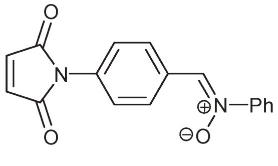


75



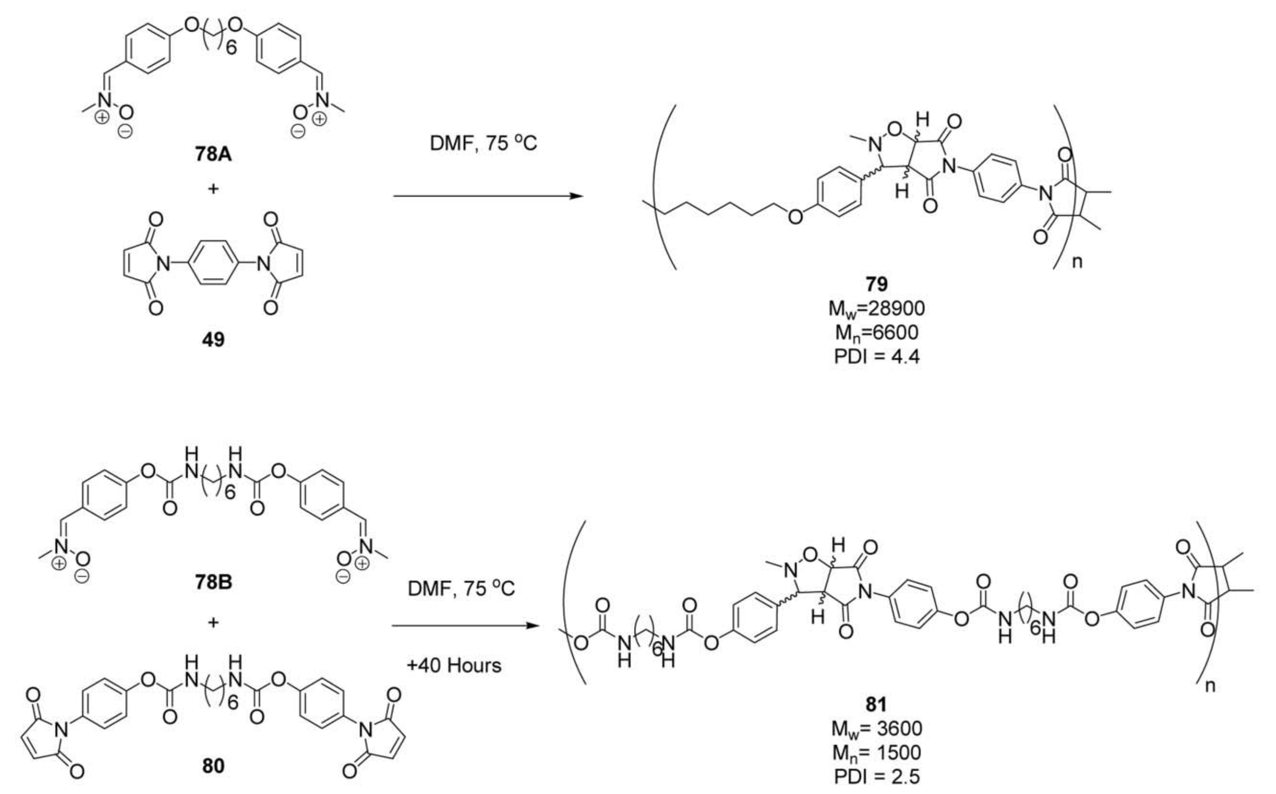
76

Fig. 6 Bisnitrone monomers **75** and **76** employed[43] by Manecke and Klawitter in the production of poly(isoxazolidines).



77

Fig. 7 The AB-type monomer *p*-maleimidophenyl-*N*-phenylnitrone **77**.[43]



Scheme 17 The (3 + 2) cycloaddition strategy employed[45] by Ritter and Vretik to generate polyimides from the bisnitrone **78 A** and **B** and bismaleimides **49** and **79**.

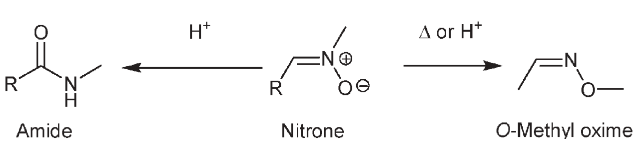
architectures. These polymers were produced to possess both good film forming capabilities for coatings applications and good high temperature performance. A_2- (**78**) and B_2-type monomers (**49** and **79**) were synthesized bearing both nitrone and maleimide moieties—initially a simple phenyl group was used as a spacing unit between the nitrone or maleimide moieties (Scheme 17). This initial polymerization lead to insoluble material **80** that could not be characterized easily and thus the spacer group between was altered. The rigid phenyl spacer of **49** was replaced with a flexible phenyl alkyl ether linker to generate **81**. Initially this monomer **78** was employed to increase the solubility of nitrone monomers, but was also adopted for the maleimide B_2-type monomers in order to tune the bulk polymer properties.

Unfortunately, the desired high molecular weight poly(isoxazolidine)s were not produced. This result was attributed to degradation of the nitrone functionality prior to the occurrence of the desired 1,3-dipolar cycloaddition. The cycloaddition conditions chosen involved exposure of the nitrone group to heat for prolonged periods in dimethylformamide and acidic (or basic) reaction conditions. Both of these experimental factors led to degradation of the nitrone moiety to the corresponding amides and *O*-methyl oximes, respectively (Scheme 18).

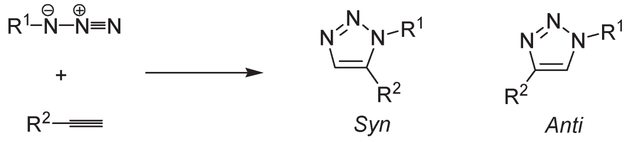
3.4 Thermal cycloaddition polymerizations: utilizing 'click-chemistry'

Through 'click-chemistry' Sharpless *et al.* has attempted to emulate[46] the efficiency of biological chemistries with the specific aim of producing macromolecules by covalently binding together smaller subunits *via* heteroatom linkages. In order to imitate the efficiency of natural chemical processes several chemistries were employed. These chemistries were chosen as a consequence of the efficiency and reliability of these processes in order to generate specific organic molecules with minimal by-product formation. A range of selective reactions were required that had to be high yielding, regioselective, stereoselective, and generate minimal by-products that were removed easily in order to achieve this significant objective. A wide range of reactions were surveyed and the (3 + 2) cycloaddition of azides with alkynes developed by Huigen and co-workers to afford triazoles (Scheme 19) proved to be the most effective 'click' reaction—applications of this reaction now include drug discovery[47] and selective molecular recognition directed coupling reactions.[48] However, azide moieties are not shock or impact sensitive and at temperatures >100 °C explosive decomposition can occur and thus care must be taken when using substances of this type.

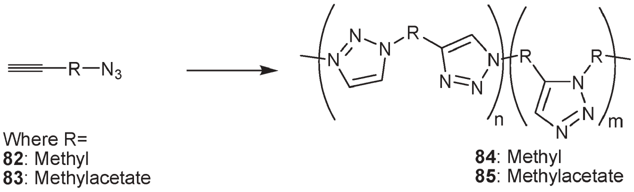
Unfortunately, minimal control of regiochemistry in the (3 + 2) cycloaddition of azides with alkynes arises as a consequence



Scheme 18 Potential degradation pathways for the nitrone group during polymerization under acidic conditions.



Scheme 19 The (3 + 2) cycloaddition of azides with alkynes developed by Huisgen and co-workers.[5]

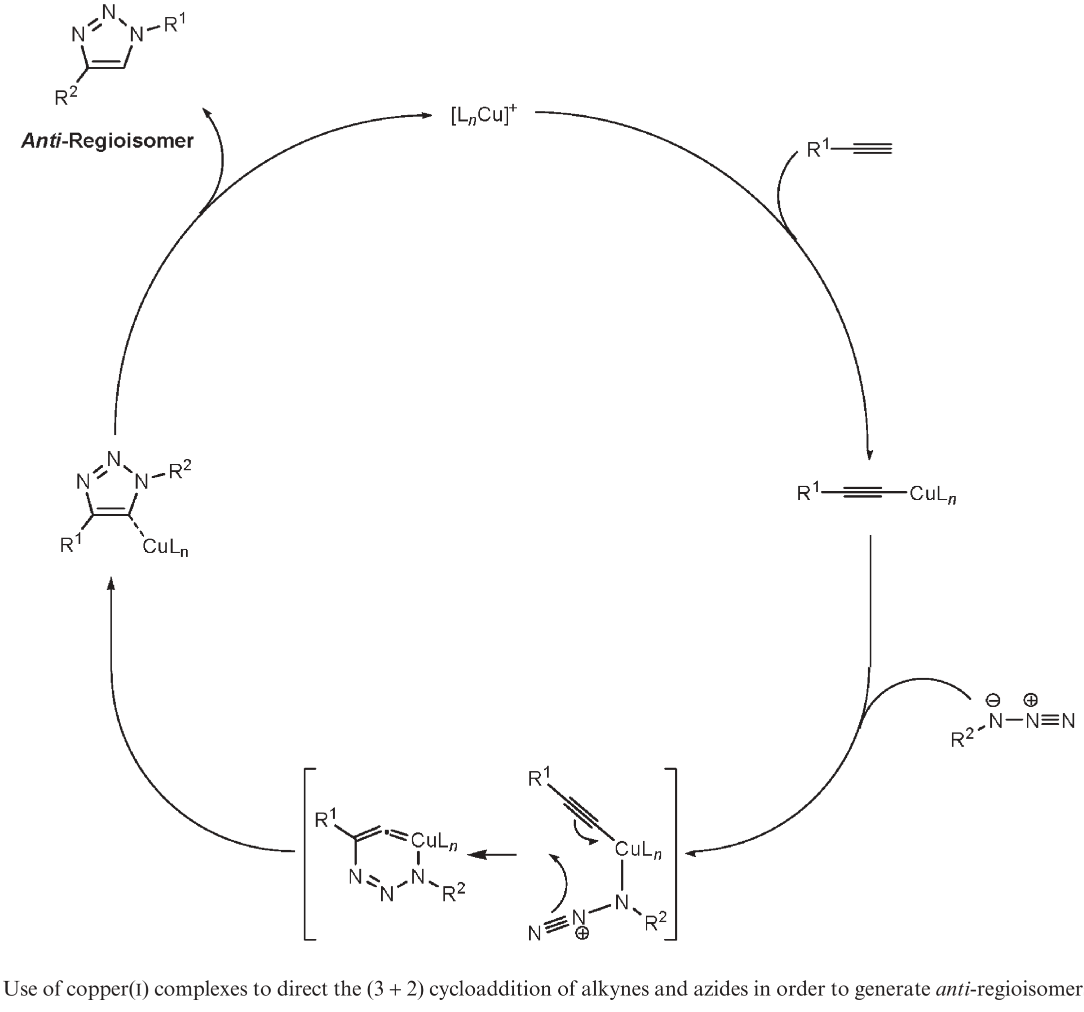


Scheme 21 The production of atactic poly(triazole)s from AB-type monomers **82** and **83** that feature both alkyne and azide moieties.[50]

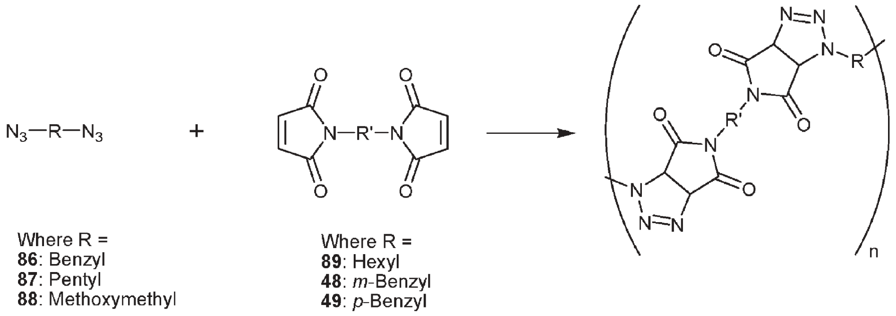
of the orbital symmetry and the cycloaddition reaction leads to the production of two regioisomers *via syn* and *anti* approaches. However, the *anti*-regioisomer can be obtained by employing a copper mediated[49] cycloaddition reaction (Scheme 20).

During the 1960's this (3 + 2) cycloaddition reaction was utilized to produce linear poly(triazole)s. For example, Baldwin *et al.* produced[50] a variety of poly(triazole)s *via* cycloaddition homopolymerization of AB-type monomers (**82** to **83**) that feature both alkyne and azide moieties, in the form of brittle glasses (Scheme 21). In particular, poly(triazole)s **84** and **85** exhibited high decomposition temperatures (170 to 200 °C and >500 °C, respectively). The lack of regioselectivity in the polymerization reaction led to polymer architectures with a random combination of 1,4- and 1,5-substituted triazoles repeat units and the material thus produced featured atactic morphologies.

A range of linear polystyrene[51,52] and poly(methyl methacrylate)[53,54] architectures have been prepared utilizing atom transfer radical polymerization (ATRP)[55] in conjunction with copper mediated 'click' (3 + 2) cycloaddition chemistries. These methodologies are of considerable use when generating novel block co-polymers. van Hest and Opsteen have employed[51] ATRP to afford polystyrene blocks of desired molecular weight featuring protected terminal alkyne moieties. Azide moieties were then installed either by post-polymerization or *via* the introduction of functionalized initiators. These blocks were then tethered together using copper mediated 'click' (3 + 2) cycloadditions to afford the desired block co-polymers. In a



Scheme 20 Use of copper(I) complexes to direct the (3 + 2) cycloaddition of alkynes and azides in order to generate *anti*-regioisomers in a selective fashion.[49]



Scheme 22 The synthesis of poly(triazole)s described by Gilliams and Smets.[58]

similar fashion, Matyjaszewski *et al.* have also prepared[52,56] a variety of novel block co-polymers. Polymers prepared *via* ATRP have also been modified post-polymerization using copper mediated 'click' (3 + 2) cycloadditions reactions. This method allows efficient capping of these polymers with specific terminal molecules such as dyes.[53] Furthermore, specific functionalities can be grafted onto multi-functional poly(methyl methacrylate)s (that was prepared *via* ATRP) utilizing efficient copper mediated 'click' cycloaddition chemistries.[54]

Linear triazole-linked conjugated polyfluorenes have been produced successfully by van Maarseveen, Reek *et al.* utilizing[57] copper mediated 'click' cycloaddition polymerizations. The resultant polyfluorenes exhibited interesting electrochemical and photochemical behaviour which render them useful in light emitting diode and non-linear optical applications.

In a similarly fashion, Gilliams and Smets adopted[58] a strategy involving the polymerization of A_2 and B_2 type azides (**86** to **88**) and alkyne monomers (**48**, **49**, **89**) to produce poly(triazole) architectures. Initially, the (3 + 2) cycloaddition polymerizations were carried out between 1,4-diazobenzene **86** and 1,4-diethynylbenzene at 110 °C in dimethylformamide to afford the desired poly(triazole) (Scheme 22). This polymerization was achieved with good monomer conversion (75 to 80%) although an extended reaction time (8 days) was required. Unfortunately, the poly(triazole) thus produced was only sparingly soluble in common organic solvents, but did exhibit a high melting point (>500 °C). In addition, a range of poly(triazole)s were produced using a similar approach (Scheme 22). The poly(triazole)s thus produced possessed moderate molecular weights (up to 5000) and higher molecular weight fragments that were less soluble in processing solvents. The poly(triazole)s, when analysed *via* FT-IR spectroscopy, exhibited an absorption band at 2100 cm^{-1} associated with terminal azide moieties and thus chain extension is viable for these polymers.

Sachinvala *et al.* utilized[59] Huigen's (3 + 2) cycloaddition process to couple smaller units efficiently to produce desirable block co-polymer macromolecules. Polymers compatible with cotton were required to enhance strength and increase abrasion resistance. Thus, soft poly(ethylene oxide)-1450 **90** was modified with terminal azide moieties and co-polymerized with 2,2′-bis(4-(prop-2-ynoyloxy)phenyl)propane **91** (Fig. 8). Thermoplastic elastomers were thus produced with desirable physical properties.

Independently, the research groups of Voit *et al.*[60] and Smet *et al.*[61] have produced hyperbranched poly(triazole)s *via* comparable approaches utilizing Huigen's (3 + 2) cycloaddition reaction. Voit *et al.* utilized the strategy[60] involving the homopolymerization of AB_2- and A_2B-type monomers (see **92** and **93** in Fig. 9). These monomers featured both alkyne and azide moieties and were homopolymerized *via* a one-pot process.

The monomer 3,5-bis(propargyloxy)benzyl azide **92** was polymerized *via* two different methods the first route involving heating to 21 °C to afford a brittle yellow polymer which was soluble in common organic solvents. This method did not, however, afford a regiospecific polymer and indeed, *via* ^{1}H and ^{13}C NMR spectroscopic analysis, the ratio of 1,4- to 1,5-substituted was determined to be 64 : 36. DSC analysis determined the initial T_g of the resultant cycloadduct to be 61 °C and an exothermic peak at 110 °C; upon a second heating cycle the T_g value rose by 15 °C, indicating that further solid-state polymerizations had occurred during the analysis process.

The second polymerization approach employed the copper mediated (3 + 2) cycloaddition technique to lead to a 1,4-substituted poly(triazole) structure. This reaction occurred rapidly to afford a brown rubbery polymer that possessed poor solubility in organic solvents. The poly(triazole) was characterized *via* ^{1}H and ^{13}C high-resolution magic-angle-spinning (HR-MAS) NMR spectroscopy. This spectroscopic analysis confirmed that a hyperbranched structure had been produced and the degree of branching was determined to be 50%.

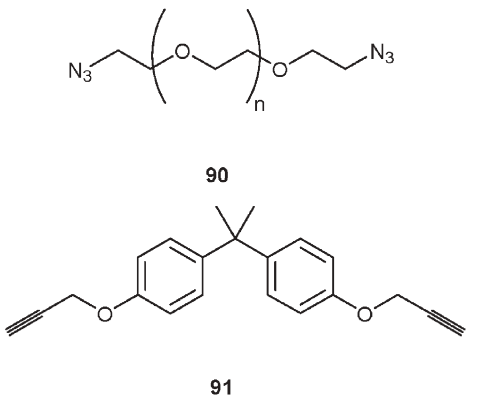
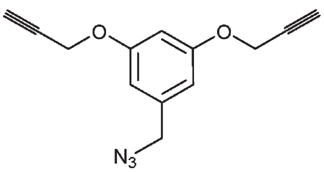
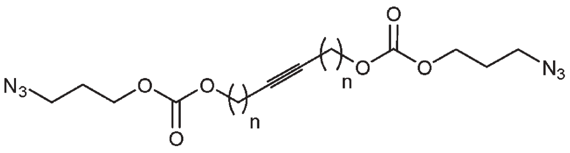


Fig. 8 The polyethylene oxide bisazide **90** and 2,2′-*bis*(prop-2-ynoyloxy)phenyl)propane **91** used[59] to generate thermoplastic elastomers *via* a (3 + 2) cycloaddition approach.



92



93
n = 1,2,3

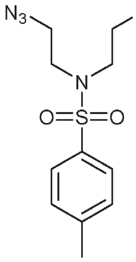
Fig. 9 AB_2 and A_2B-type monomers employed[61] in (3 + 2) cycloaddition homopolymerizations to afford hyperbranched poly(triazole)s.

Following this initial study, a strategy involving A_2B type monomers such as **93** was also employed. Since the copper mediated catalytic cycle requires terminal alkynes only a thermal means could be deployed for the homopolymerization of **93**. Unfortunately, the bulk polymerization of **93** at 45 °C even after extended periods did not yield any polymeric material. However, polymerization did occur when the reaction was carried out at 60 °C a soluble polymer was generated. ^1H and ^{13}C NMR spectroscopic analysis verified the proposed hyperbranched architecture and found that the degree of branching was 50%. Carbonate linkages within the polymer structure that are susceptible to decomposition at *ca.* 200 °C render these polymers useful as porogens.

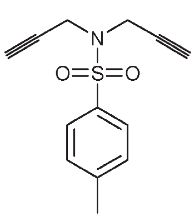
Furthermore, similar systems were explored[61] by Smet *et al.* to produce hyperbranched poly(triazole)s with comparable results. Indeed, after slow thermal polymerization of the AB_2 type monomer **92** in 1,2-dichloroethane precipitated oligomers were re-dissolved in acetonitrile and polymerized further. In storage, cross-linking occurred that was attributed to decomposition of azide to reactive nitrene moieties to afford the insoluble materials. Thus, upon completion of the (3 + 2) cycloaddition polymerizations unreacted azide moieties were treated with triphenylphosphine to afford the corresponding amides, which in turn were acylated subsequently with stearoyl chloride to impede further cross-linking.

Finn and Díaz *et al.* utilized[62] the rapid copper mediated 'click' (3 + 2) cycloaddition in fast cure adhesive applications. Furthermore, the poly(triazole) thus produced could inhibit corrosion of copper surfaces by forming an inert barrier layer over the outermost copper oxide surface. A model polymer afforded from monomers **94** and **95** (Fig. 10) was found to possess M_n values up to *ca.* 12,000 (by mass spectroscopy). However, in order for this system to achieve adhesion the copper surface must act as a copper(I) ion source and the growing polymer must adhere to the metal surface. Fortunately, both of these processes occur and indeed, triazoles have a great affinity for metal ions and the copper surfaces.

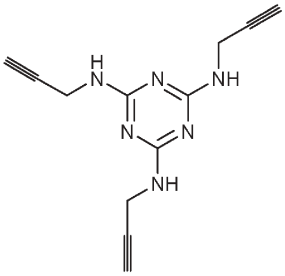
A range of di-,tri- and tetra-alkynes and azides monomers were prepared (**95** to **99**) and subsequent polymer adhesives tested in terms of strength. The resultant adhesive systems performed better than commercially available systems on copper and copper containing substrates. Indeed, those featuring tripropargylamide centres such as **100** significantly out performed commercial adhesives. Furthermore, the co-polymerization of **97** and **99** on the substrate was found to be capable of withstanding a greater load than that for **96** and **98**,



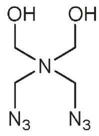
94



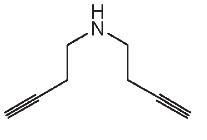
95



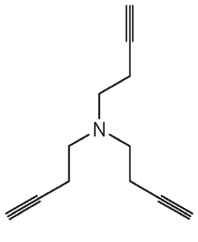
96



97



98



99

Fig. 10 Diazide and dialkyne monomers employed in adhesive systems.[62]

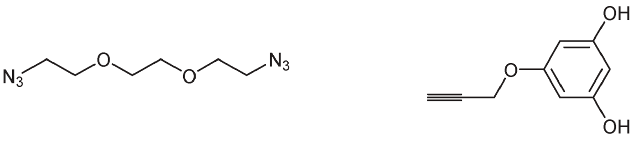
thus tri-alkynes are more efficient adhesives than dialkynes when co-polymerized with diazides. The methodology was expanded to other metal surfaces such as zinc. Although zinc does not catalyse the (3 + 2) cycloaddition, a copper(I) ion source was added to the monomer mixture, once polymerization occurred the triazoles would thus be capable of adhering to the zinc surface. Unfortunately, not all of the monomer mixes performed well on the zinc surface. However, this application of 'click' chemistry clearly has potential in industrial scale processes.

There has been significant interest in the production of dendritic–linear polymers[63] for a variety of applications including devices such as sensors. There are three methodologies that can be employed to achieve dendritic–linear polymers: i) divergent-growth of dendrons from a linear polymer, ii) convergent-graft of dendrons to a linear polymer, or iii) the preparation of dendritic monomers which are then polymerized to afford the dendritic polymer. The latter route is disadvantageous when large dendrons are used as steric hindrance impedes the desired polymerization and leads to the production of low molecular weight oligomers.

Fréchet *et al.* utilized[64] the concept of convergent-graft of dendrons onto a linear polymer *via* copper mediated (3 + 2) cycloadditions. Polyaromatic ether dendrons were furnished with azide moieties and reacted with a poly(vinylacetylene) that featured pendent alkyne moieties. The desired reaction was carried out in a mixture of water/THF (1 : 1) in the presence of the copper(I) catalyst. The production of poly(vinylacetylene) with first generation dendrons required a reaction time of a couple of hours whereas larger dendrons required the addition of fresh catalyst, and the reaction involving the fourth generation dendron proved unsuccessful. This reactivity profile was kinetically controlled, the dendritic alkyne moieties react with copper(I) ions to afford the corresponding copper(II)-acetylides. However, upon reaction with the dendritic-azide steric hindrance was encountered for larger dendron generations. As the size of the dendron increased the steric hindrance about the azide was amplified by the globular nature of the dendron. The polymer structures were confirmed by ^{1}H NMR and FT-IR spectroscopic analysis which confirmed the reaction of excess azide and an absence of residual acetylene moieties. Increases in molecular weight with increasing generation of dendron were also observed by GPC analysis. Furthermore, atomic force microscopy (AFM) was employed to inspect the morphology of the polymer which was observed to be a rigid rod as opposed to a random coil. This method of generating dendronized polymers allows access to poly(vinylacetylene)s that are decorated with functionalized dendrons to suit specific applications such as catalysts, drug delivery or rheology modifiers.

There is a need to discover a cost-effective methodology towards dendrimer synthesis to allow large scale access to these structurally interesting polymer architectures. To date 'click' chemistry and, in particular, copper mediated 'click' (3 + 2) cycloadditions, offer an opportunity to realise this goal to a degree by affording hyperbranched macromolecules in an efficient and regiospecific manner.

Hawker and Wooley *et al.* utilized[65] Huigen's (3 + 2) cycloaddition approach to afford dendritic architectures *via* a divergent-growth methodology. 1,3-Bis(2-azidoethoxy)ethane **100** was reacted with 5-(prop-2-ynyloxy)benzene-1,3-diol **101** to afford a cycloadduct featuring phenolic moieties (Fig. 11). These phenolic units can be used to furnish a dendrimer with further azide or alkyne moieties. These azide or alkyne moieties could facilitate further dendron growth or afford multifunctional dendrimers useful for cross-linking applications such as surface coatings.



100 **101**

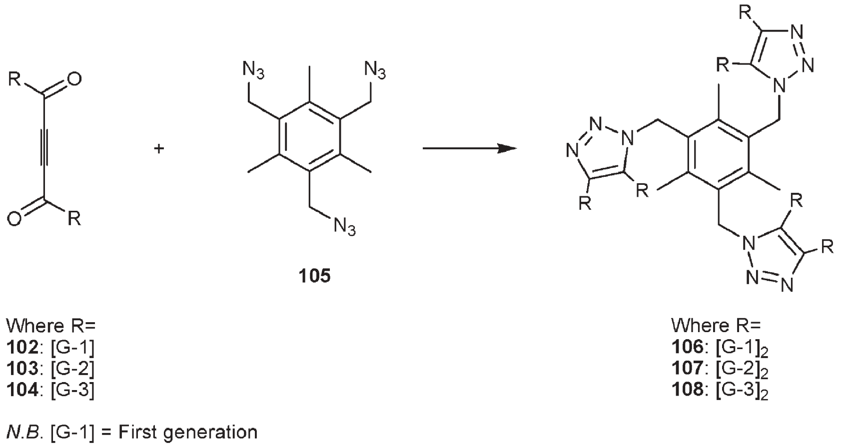
Fig. 11 Diazide **100** and alkyne **101** monomers used **58** in 'click' chemistry approaches to dendritic macromolecules.

Dehaen *et al.* have utilized[66] a convergent-growth methodology to afford polyaromatic ether triazole dendrimers. Initially, a range of polyaromatic ether dendrons were coupled to an acetylenedicarboxylate core to afford polyaromatic ether dendrimers (**102** to **104**). These dendrimers were then reacted with the triazide **105** at 70 °C in toluene for several days to afford polyaromatic ether dendrimers (see **106** to **108** in Scheme 23). The dendrimer structures were confirmed by ^{1}H and ^{13}C NMR spectroscopic and MALDI-TOF mass spectrometric analyses. Unfortunately, the third generation acetylene dendron **104** did not produce the corresponding dendrimer **108** upon reaction with the triazide **105** even after extending the period reaction time as a consequence of significant steric hindrance encountered when large dendrons are used.

Dehaen *et al.* have also produced polyaromatic triazole dendrimer architectures utilizing a homopolymerization strategy involving A_2B-type monomers. The A_2B-type monomer **109** was synthesized featuring diethylene glycol spacers between the peripheral azide and protected core alkyne moieties to thus limit detrimental steric effects. This monomer was reacted with acetylenecarboxylate ester **110** and then with zinc and iodine to deprotect the acetylene core to afford the dendrimer precursor **111**. This pre-dendrimer was, in turn, reacted with the multi-azide core **112** to afford the desired dendrimer **113** (Scheme 24).

A_2B-type monomer **109** was also be reacted with the dendritic precursor **111** and following deprotection afforded the second generation dendritic-acetylene, which was then reacted with another equivalent of **111** and again deprotected to afford the third generation dendritic-acetylene. Higher generation dendrimers can thus be produced upon reaction with the multi-azide core **112**. Unfortunately, only the second generation dendritic-acetylene was accessible *via* this methodology as a result of steric limitations when deprotecting the acetylene moieties at high generation numbers. However, the efficiency of Huigen's (3 + 2) cycloaddition was not the limiting factor. Fortunately, the density of triazole motifs within the dendrimer architecture offers potential for use in homogeneous catalysis applications as a consequence of the numerous heterocyclic metal binding sites present.

In a similar approach, Lee and Kim produced dendrimers *via* convergent-growth utilizing[67] a 'click' (3 + 2) cycloaddition



Scheme 23 The synthesis[66] reported by Dehaen *et al.* of polyaromatic ether dendrimers *via* a 'click' (3 + 2) cycloaddition approach.

mediated by a copper(I) catalyst. The triacetylene monomer **99** (*vide supra*) and polyaromatic ether dendrons furnished with focal azide moieties were reacted in the presence of copper(I) ions to afford poly(triazole) dendrimers. The reaction was monitored by FT-IR spectroscopy by observing the disappearance of the absorption band associated with azide moieties (2100 cm^{-1}). Once again first, second and third generation dendrimers were produced in decreasing yields of 93, 81 and 42%, respectively as a consequence of increasing steric hindrance.

Hawker, Voit, Fréchet, and Sharpless *et al.* utilized[68] the efficiency of copper mediated 'click' (3 + 2) cycloaddition reactions to produce polyaromatic triazole dendrimers in high yield with minimal purification required. Stoichiometric quantities of AB_2-type monomers (see **114**, **115** and **116** in Fig. 12) were utilized in these efficient cycloadditions, thus eradicating the need for numerous column chromatography purifications after each coupling stage.

These AB_2 monomers were reacted with azide **117** featuring desired surface functionalities and was then treated subsequently with sodium azide to afford the first generation azide dendron efficiently (95% yield). By repetition of these steps higher generation dendrons were accessed. The dendrons were then reacted with various di- and tri-alkyne cores to afford target dendrimers with desired surface functional decoration and size (Scheme 25), the regioselectivity of the cycloaddition process was ensured *via* use of copper catalysis (*vide supra*).

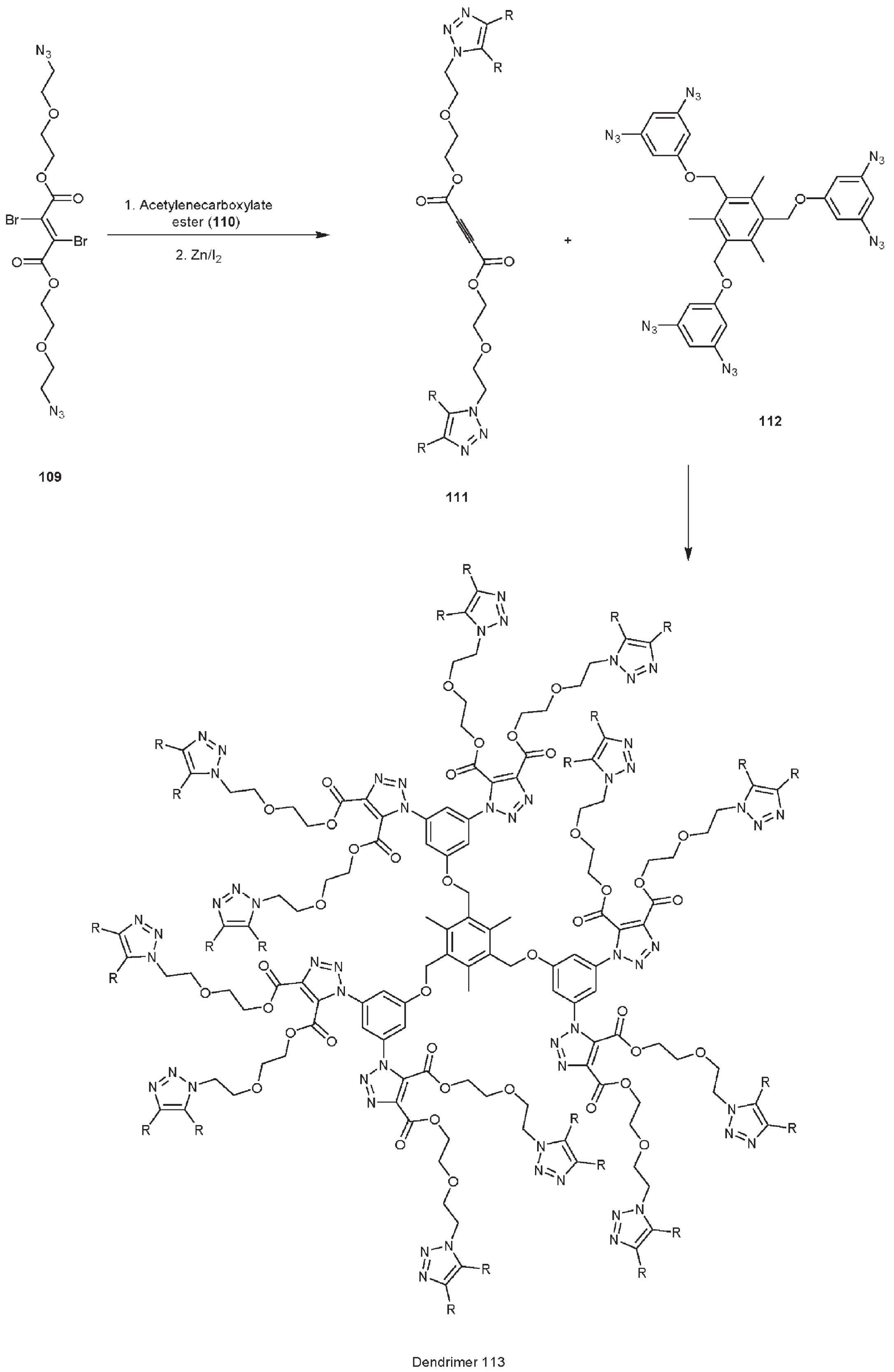
The dendrimer and dendron architectures were confirmed by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometric analyses, which indicated there were minimal defects within the dendrimer structure. All of the dendrimers produced up to the third generation were isolated without the need for column chromatography thus rendering this methodology useful for future large scale industrial production of poly(triazole) dendrimers of this type.

3.5 Thermal cycloaddition polymerizations: utilizing nitrile *N*-oxide 1,3-dipoles

Nitrile *N*-oxide moieties efficiently undergo (3 + 2) cycloadditions to afford isoxazole or isoxazoline heterocyclic structures. These structures serve as intermediates to α-cyanoketone or β-diketone moieties from isoxazoles and stereospecific β-hydroxyketones from isoxazoline precursors. The highly reactive nature of the nitrile *N*-oxide moiety leads to instability and rapid dimerization[69] can occur to yield furoxan structures. However, stable nitrile *N*-oxides can be produced *via* introduction of sterically bulky groups or aromatic units such as phenyl-1,4-nitrile-*N*-oxides. Protected hydroximinoyl chlorides[70] or *O*-tributylstannylaldoximes[71] can also be deployed, which, upon deprotection by treatment with base, afford the corresponding nitrile *N*-oxide moieties *in situ*. This route presents a controlled methodology to achieve polymer architectures.

It is a common observation that cycloaddition polymerizations only afford oligomeric materials and that these mixtures can feature a mixture of macrocycles and this approach thus presents a route to macrocycle synthesis. Macrocyclic isoxazolines are useful in host–guest chemistry. Kim *et al.* utilized a strategy[72] involving A_2 and B_2 type monomers to afford an array of crown ether type macrocycles (Scheme 26) featuring isoxazoline rings. Hydroxaminoyl chloride moieties were utilized in this process which can be converted easily to the corresponding nitrile *N*-oxides *in situ*. This strategy allowed tailoring of the macrocyclic ring size and composition by altering the spacer groups between the reactive moieties and deploying either *para*- or *meta*-substituted dinitrile *N*-oxides monomers (**118** and **119**). The structures were confirmed *via* X-ray crystallographic analysis and the host–guest capabilities probed with L-ascorbic acid. Utilizing this methodology Kim *et al.* prepared[72] a range of crown ethers, silomacrocycles and calixarenes. The isoxazoline heterocycle features could be cleaved to afford readily β-hydroxyketones and thus generating further macrocyclic structures which can be exploited.

Akiyama and Shiraishi *et al.* have utilized[73] a related strategy to generate poly(isoxazoline) architectures. Initially, model reactions were carried out between dihydroxaminoyl chloride monomer **118** or **119** and an array of monofunctional monomers. A series of polymers were prepared from the dihydroxaminoyl chlorides **118** or **119** with dimaleimide monomers **48** and **49** in dioxane at 25 °C for a period of 24 hours to afford poly(isoxazoline)s in good yield (77%) that possessed high decomposition temperatures (*ca.* 400 °C). In a



Scheme 24 The convergent synthesis of triazole dendrimers *via* a (3 + 2) cycloaddition strategy.[66]

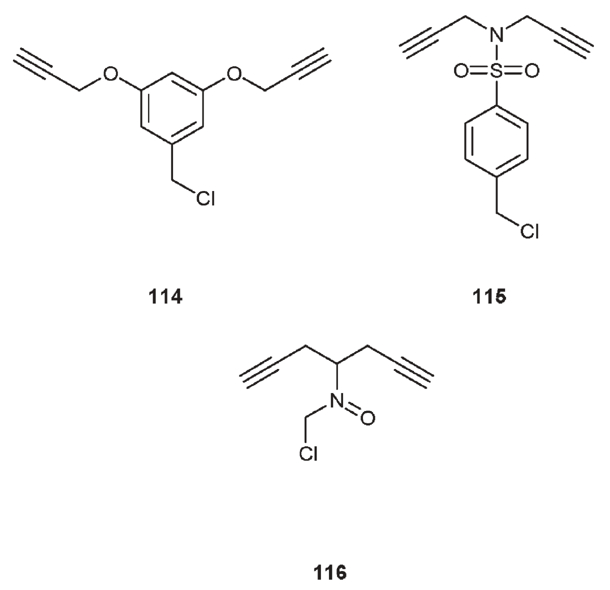
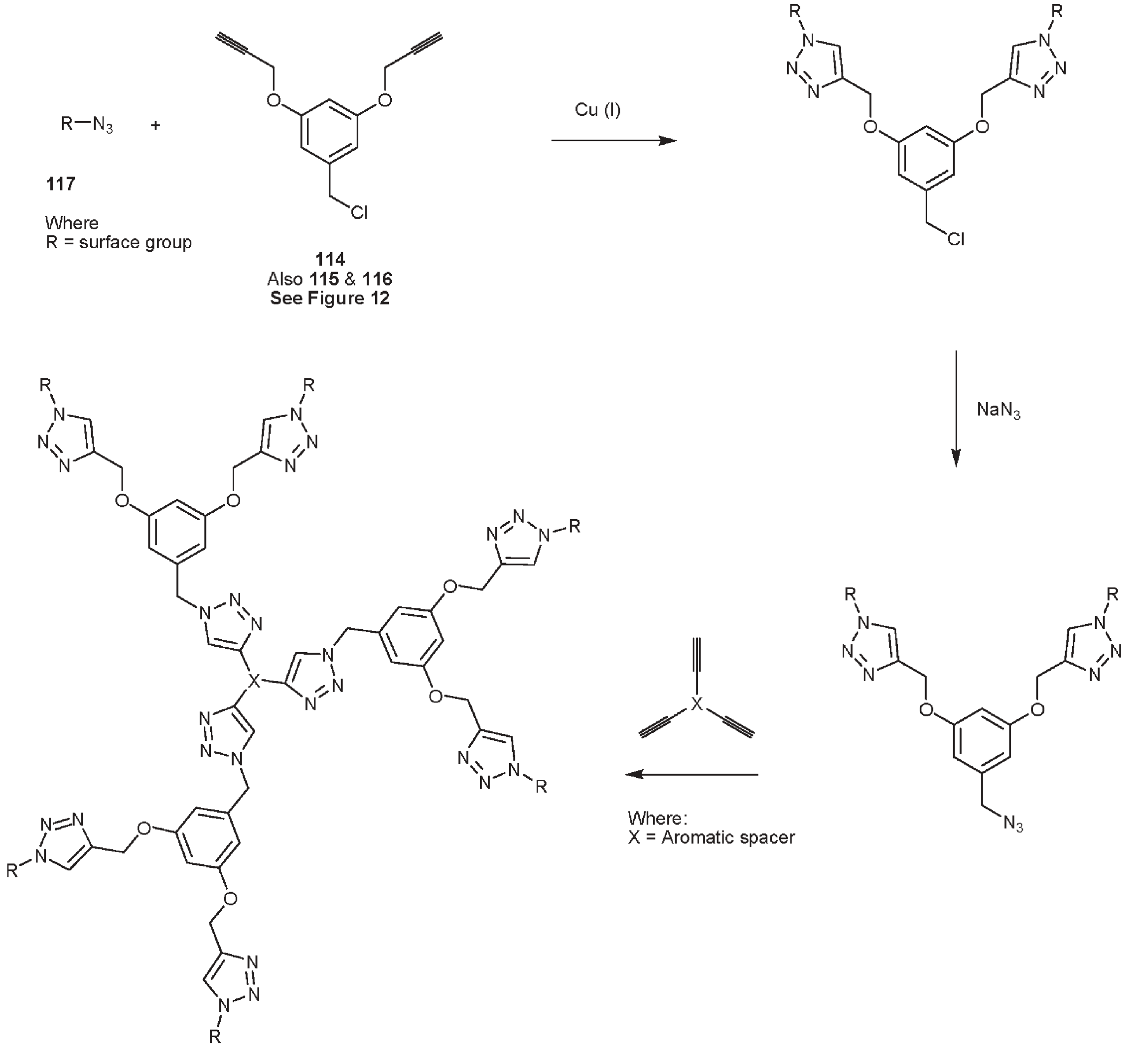


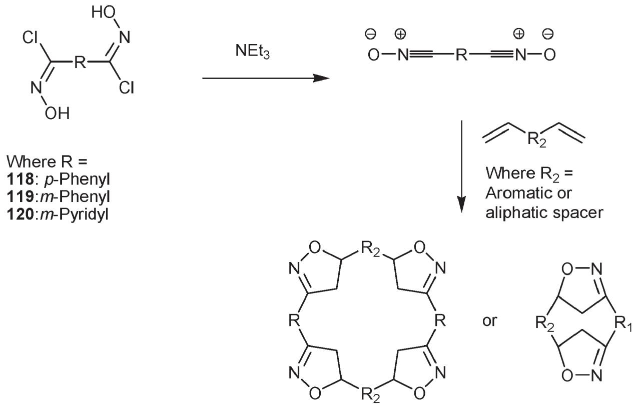
Fig. 12 AB$_2$-type monomers used[68] in copper(I) mediated 'click' (3 + 2) cycloadditions to generate polyaromatic triazole dendrimers.

similar fashion, the dinitrile *N*-oxides were reacted with 1,4-ethylenedimethacrylate under similar conditions to afford poly(isoxazole)s in moderate yields (*ca.* 55%). However, these polymers decomposed at lower temperatures (*ca.* 170 °C).

Overberger and Fujimoto produced[74] poly(isoxazole)s and poly(isoxazoline)s from the dihydroxaminoyl chloride monomer **118** and bifunctional co-monomers including quinone, cyclopentadiene and 1,4-diethynylbenzene **67**. When the dihydroxaminoyl chloride **118** was reacted with each of the co-monomers separately, polymers were afforded in excellent yield (>99%) that exhibited strikingly different decomposition temperatures (240 °C with quinone and 400 °C for dialkyne **67**). These thermal properties render the polymers useful in high temperature applications. Overberger and Fujimoto also investigated topochemical homopolymerization of the dihydroxaminoyl chloride **118** in the solid-state, since in solution nitrile *N*-oxides rapidly dimerise. X-ray crystallographic analysis of single crystal of **118** revealed a monoclinic structure with $C_{2/m}$ point group, and the proximal nitrile *N*-oxide moieties were 3.6 Å apart. Solid-state homopolymerization proceeded at 100 °C for a period of 24 hours to afford a light brown polymer and X-ray diffraction analysis revealed an



Scheme 25 The 'click' (3 + 2) cycloaddition synthesis of triazole dendrimers mediated by copper(I) complexes.[68]



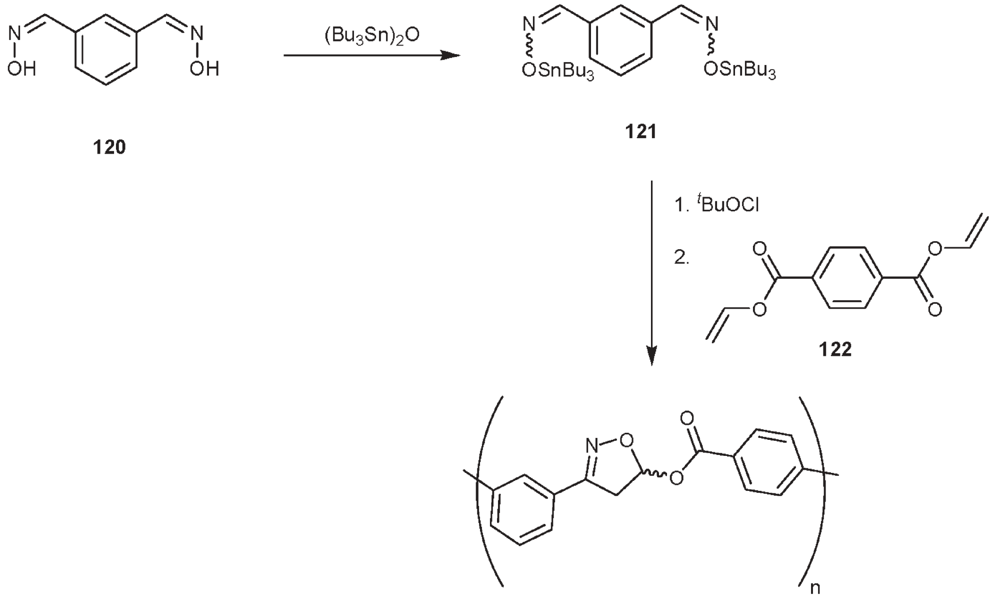
Scheme 26 Synthesis of novel macrocyclic isoxazolines[72] *via* a (3 + 2) cycloaddition approach.

amorphous structure. In contrast, homopolymerization of **118** in solution was carried out in dimethylformamide at 21 °C for 20 hours to afford a yellow polymer with excellent monomer conversion (89%). However, FT-IR spectroscopic analysis revealed that a poly(phenylene furoxan) structure had been produced.

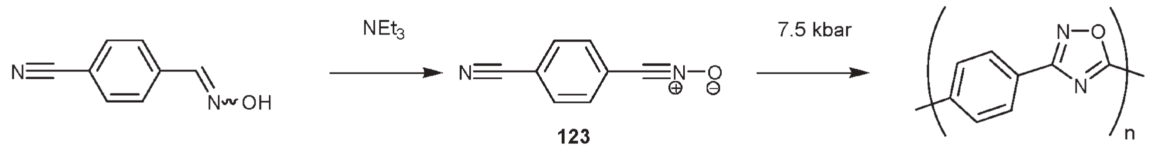
When utilizing bisnitrile *N*-oxides in a strategy involving A_2 and B_2 type monomers, the potential for dimerization reduces the degree of polymerization of the desired polymer. Iwakura *et al.* thus employed[75] hydroxaminoyl chlorides such as monomer **118** as masked bisnitrile *N*-oxides. This monomer was then reacted in turn with various dipolarophilic monomers including **48**, **49**, and **67** at 110 °C in toluene for *ca.* 30 hours to afford poly(isoxazole)s and poly(isoxazoline)s in excellent yield (90 to 98%) which decomposed at 262, 326, and 318 °C, respectively. This synthetic approach was found to increase the crystallinity of the polymers when compared to analogues as a result of limitation of the dimerization process. In addition, electron spin resonance spectroscopic analysis revealed[76] that two stable radical centres were present within the poly(isoxazole) architecture. Furthermore, phenylene units could potentially act as electron donors and the isoxazole units as electron acceptors thus forming an intramolecular charge-transfer system. Indeed, when investigating the electrical resistivities,[77] these polymers appeared to exhibit semiconducting properties. In particular, the poly(isoxazole) exhibited greater resistance with increasing temperature and a negative energy gap. This renders the poly(isoxazole) useful as a positive thermister—the corresponding poly(isoxazoline) exhibited contrasting results.

Moriya and Endo utilized[71,78] an alternative protection strategy by employing *O*-tributylstannylaldoximes which upon treatment with *tert*-butylhypochlorite afforded the nitrile *N*-oxide moieties *in situ* (Scheme 27). This strategy was deployed to produce polymers from monomer **121** and a range of bisalkenes. When **121** was reacted divinyl terephthalate **122**, poly(isoxazoline)s were produced with M_n values *ca.* 11,000 and these polymers exhibited excellent solubility in common organic solvents. The poly(isoxazoline)s structure was confirmed by a combination of FT-IR, ^1H and ^{13}C NMR spectroscopic analyses.

Since the dipolarophiles used were olefinic in nature, susceptibility[80] to auto radical polymerization is also possible. Optimal conditions are thus required which restrict the occurrence of undesirable side reactions such as uncontrolled polymerizations. One approach to achieve selective cycloaddition polymerization was to employ high pressured reaction conditions. It has been shown that both nitrones and nitrile *N*-oxides can undergo 1,3-dipolar cycloadditions at high pressures. Furthermore, experimental evidence suggests that stereoselectivities of the cycloaddition process can be controlled[45] under pressurized conditions. The *exo* or *endo* transition states involved in such cycloadditions have differing



Scheme 27 Synthesis of poly(isoxazoline) *via* *O*-tributylstannylaldoxime protected nitrile *N*-oxides.[71]



Scheme 28 Synthesis of poly(4-phenylene-1,2,4-oxadiazole) from (3 + 2) cycloaddition of 4-cyanobenzonitrile *N*-oxide **123**.[72,74]

activation volumes ($\Delta V^{\ddagger}$) and thus one of the transition states could be favoured under pressurized conditions. The promotion of one transition state under high pressure reaction conditions has been observed to be minimal. This limited selectivity occurs as a consequence of the minimal energy difference between the two transition states.

Polymers have also been produced *via* high pressure conditions utilizing nitrile *N*-oxides. For example, Fukunaga *et al.* have generated[79] poly(4-phenylene-1,2,4-oxadiazole) architectures using this approach that are capable of withstanding temperatures in excess of 400 °C. Furthermore, poly(oxadiazole) polymers have been shown[74] to possess conducting properties thus rendering them suitable for use in polymer light emitting diode applications. The AB type monomer 4-cyanobenzonitrile *N*-oxide **123** was deployed as a result of its stability, and polymerized (Scheme 28) under high pressure conditions to afford poly(4-phenylene-1,2,4-oxadiazole). Initially, a model polymer was prepared at atmospheric temperature (21 °C) and pressure (1 bar) and the reaction was monitored by polymer viscosity and FT-IR spectroscopic analysis as a consequence of poor solubility in common organic solvents. After a period of six days, the viscosity was 0.19 dl g^{-1} and after further twenty days it had risen to 0.24 dl g^{-1}, FT-IR spectroscopic analysis of the polymer revealed that residual monomer was still present in the polymerization mixture. The polymer mixture was thus heated for a period of 40 hours at 200 °C in order to cure the excess monomer remaining. In contrast, the high pressure homopolymerization was carried out at 20 °C for 40 hours. The optimum pressure was found to be 7.5 kbar by comparing model reaction data for viscosity *versus* pressure. The polymers were produced using both routes at varying temperatures up to 150 °C, beyond this temperature explosive decomposition occurred. The high pressure reaction proceeded at an accelerated rate taking advantage of the condensed volume of activation of the transition state compared to the reaction carried out at atmospheric temperature and pressure.

4. [4 + 2] Cycloaddition polymerizations

[4 + 2] Cycloaddition reactions (also known as Diels–Alder cycloadditions) involve the reaction of a conjugated diene with a dieneophile to afford a 6-membered ring (Scheme 29). The dieneophile employed in [4 + 2] cycloaddition reactions can be compared to the dipolarophile used in (3 + 2) cycloadditions.

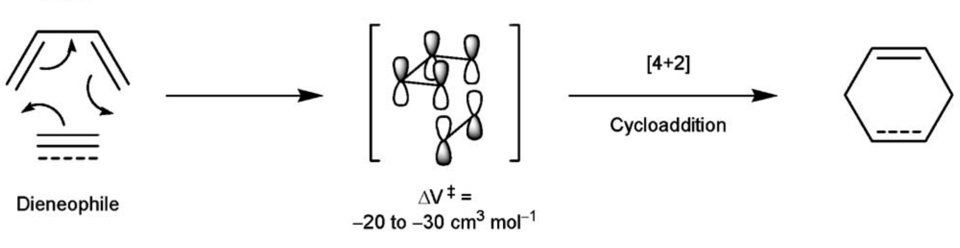
Extensive theoretical and mechanistic studies of this class of cycloaddition have led to the [4 + 2] cycloaddition being considered as a concerted process with frontier molecular orbitals combining in a suprafacial manner. In general, [4 + 2] cycloadditions are highly stereospecific in nature thus supporting the concerted mechanism and access to up to 4 controllable stereocentres is feasible. In general, the *endo* transition state predominates in [4 + 2] cycloadditions and this phenomenon has been attributed to secondary orbital overlap. In terms of volume of activation, [4 + 2] cycloadditions feature a more condensed transition state ($\Delta V^{\ddagger}$ −25 to −50 cm^3 mol^{-1}) when compared[82] to equivalent (3 + 2) cycloadditions ($\Delta V^{\ddagger}$ −20 to −30 cm^3 mol^{-1}).

This methodology can, therefore, be applied to the production of polymeric materials and where applicable high pressure reaction conditions can be utilized.

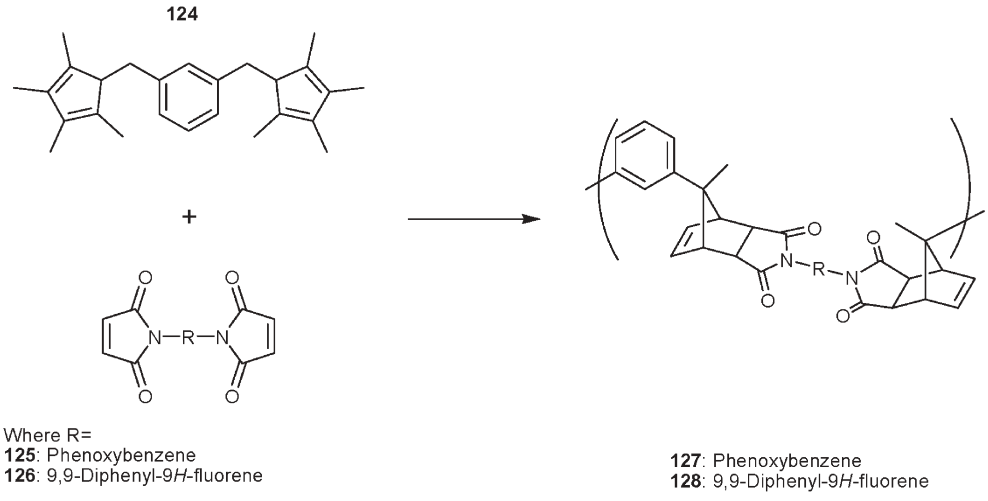
4.1 The production of polyimides *via* Diels–Alder cycloaddition polymerizations

Polyimides are a class of polymers that possess good thermal and chemical stability as well as usable mechanical properties which render these polymers useful in high performance applications. For example, composite polyimide materials[83] have been utilized in applications such as gas separation[84] and moisture adsorption.[85] Furthermore, polyimides have been used in applications such as electrolyte membranes[86] within fuel cells and within dielectric layered electronic devices.[87]

Polyimide architectures can be produced *via* polycondensation of amines with carboxylic acids. However, these architectures can also be accessed *via* [4 + 2] cycloaddition



Scheme 29 The general [4 + 2] cycloaddition reaction scheme of a diene system interacting with an unsaturated dieneophile to afford a cycloadduct product.



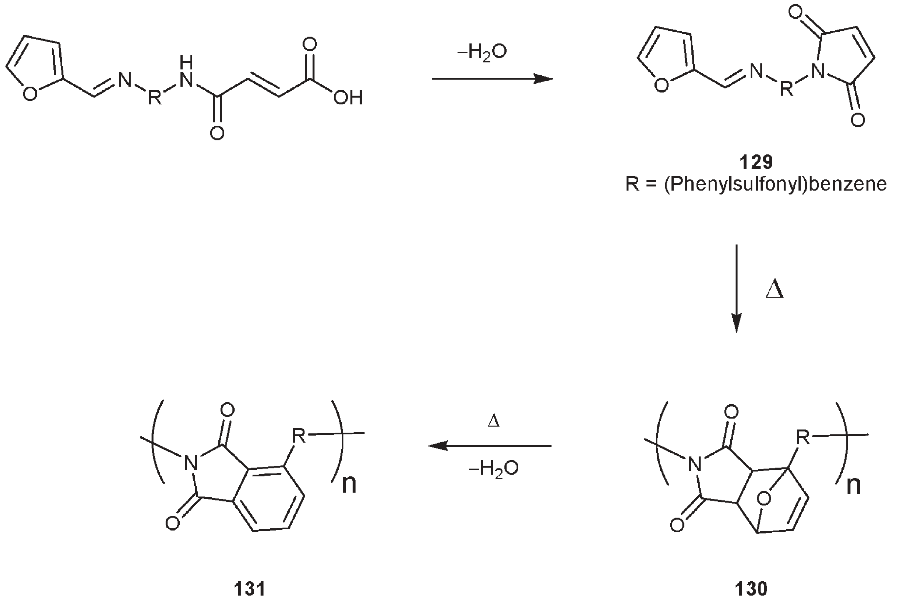
Scheme 30 The synthesis of polyimides *via* AB-type monomers generated *in situ*.[88]

polymerizations. Unfortunately, disadvantageous retro [4 + 2] cycloadditions can limit control of the molecular weight characteristics. Retro [4 + 2] cycloadditions can be overcome by utilizing substances such as α-pyrones which can form AB type monomers from A_2 type monomers *in situ*, and once polymerization has been achieved irreversible aromatization occurs *via* concomitant loss of carbon dioxide.

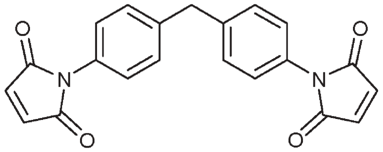
Sillion *et al.* produced[88] poly(pentamethylnadimide) utilizing A_2 and B_2 monomers featuring biscyclopentadiene **124** and bismaleimide units **125** and **126**. A range of bismaleimides were produced featuring different spacer groups such as diphenylmethane **125** and 9,9-diphenyl-9*H*-fluorene **126**, and polymerization with the diene **124** was carried out in dimethylformamide at 140 to 150 °C (Scheme 30). ^{1}H NMR spectroscopic analysis of model compounds implied that the *endo* isomer predominates as a result of steric hindrance. Polymer **127** was produced in 24 hours in excellent yield (95%) and polymer **128** was produced in 17 hours in good yield (67%). In air the decomposition temperature (T_d) was lower than under nitrogen as a result of oxidation interfering with retro [4 + 2] cycloaddition pathway. All of the polymers exhibited high T_d values of *ca.* 300 °C thus rendering the polymers suitable for high temperature applications.

Mikroyannidis employed[89] AB type monomers featuring furyl and maleimide moieties to produce polyimide architectures. A range of monomers were prepared including **129** that featured a (phenylsulfonyl)benzene spacer and this monomer was homopolymerized at 180 °C for 6 hours. This polymerization proceeded *via* an epoxide intermediate **130** which afforded polyimide **131** after dehydration (Scheme 31).

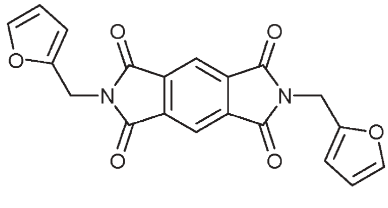
The majority of polyimides produced were insoluble in common organic solvents except the derivative **131** which was soluble in dimethylformamide. This polymer exhibited a high decomposition temperature of 377 °C in air and 537 °C under



Scheme 31 Polyimides synthesized by Mikroyannidis and Diakoumakos utilizing[89] a Diels–Alder cycloaddition polymerization approach.



132

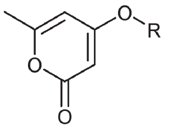


133

Fig. 13 The A_2 and B_2-type monomers utilized in polyimide production.[89]

nitrogen. Mikroyannidis and Diakoumakos also employed A_2 and B_2 type monomers to afford similar polyimides. Bifunctional monomers **132** and **133** (Fig. 13) were prepared and melt copolymerized at 265 °C for a period of 20 hours with subsequent dehydration to afford dark brown polyimides.

Union Carbide patented a synthetic methodology[90] to polyimides *via* thermal means (>150 °C) utilizing an AB-type monomer produced *in situ* from the reaction of α-pyrone and bismaleimides following concomitant loss of carbon dioxide, which inhibits potential retro [4 + 2] cycloaddition. This AB-type monomer then underwent homopolymerization to afford polyimide architectures (Scheme 32) with T_g value of *ca.* 150 °C and T_d ranging from 300 to 500 °C. The polyimides' physical properties rendered it suitable for tough thermoplastics applications, although the stereochemical outcome of the cycloaddition process was not reported.



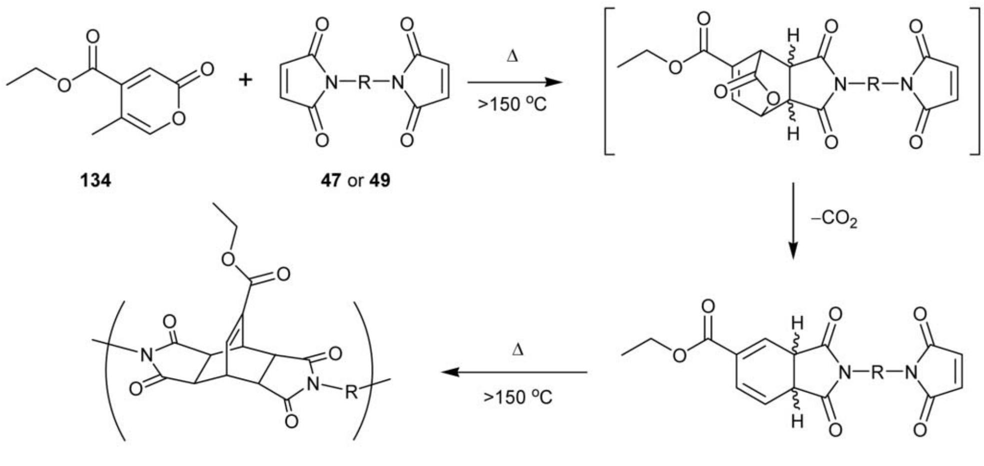
135
Where R = aliphatic chain

Fig. 14 The modified α-pyrone **135** used by Klemm *et al.* in conjunction with bismaleimides to generate polyimides.[91]

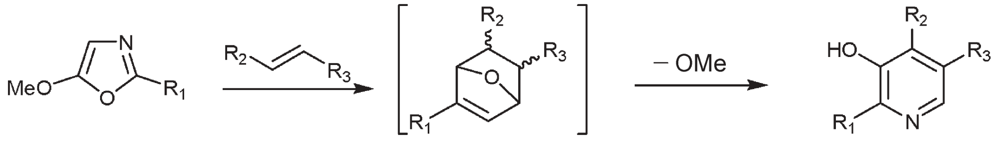
Klemm *et al.* have used a similar system[91] utilizing a modified α-pyrone (see **135** in Fig. 14). A variety of diolefinic monomers were prepared and polymerized at 210 °C in trichlorobenzene to afford polyimides in good yield (60 to 83%) and molecular weights (M_n values up to 34000) that were affected by sterically bulky R-groups of the α-pyrone derivative **134**. All of these polyimides were soluble in common organic solvents—X-ray crystallographic and ^{1}H NMR spectroscopic analyse confirmed that *endo*-selectivity was also dominant as observed in model reactions.

Ritter and Reinecke utilized an analogous methodology[92] featuring an 5-alkoxyoxazole in order to generate an AB-type monomer *in situ* upon reaction with *trans*-alkenes (Scheme 33). Bis-5-alkoxyoxazole (**136**) and bismaleimide monomers (**48** and **49**) were thus prepared and copolymerized at 100 °C in dimethyl sulfoxide for a period of 5 hours to afford polypyridylimides with M_n values *ca.* 9000 and a high T_d values ∼250 °C.

Ritter and Reinecke also investigated[93] sorboyl systems produce from renewable feedstocks. Bifunctional monomers **137** and **138** (Fig. 15) were prepared and copolymerized at 90 °C in dimethylformamide for four days to afford polyimide architectures. The structure was confirmed *via* ^{1}H NMR and FT-IR spectroscopic analysis which, unfortunately, also indicated the occurrence of side reactions and that selective stereocontrol had not occurred. DSC analysis of the polyimide revealed a high T_g value of *ca.* 160 °C for these materials.



Scheme 32 Synthesis of thermoplastic polyimides *via* an irreversible Diels–Alder cycloaddition polymerization of α-pyrone **134** and bismaleimide **47** or **49**.[90]



136

Scheme 33 Formation of hydroxylpyridine from the [4 + 2] cycloaddition of 5-alkoxyoxazole with a range of *trans*-alkenes.[85]

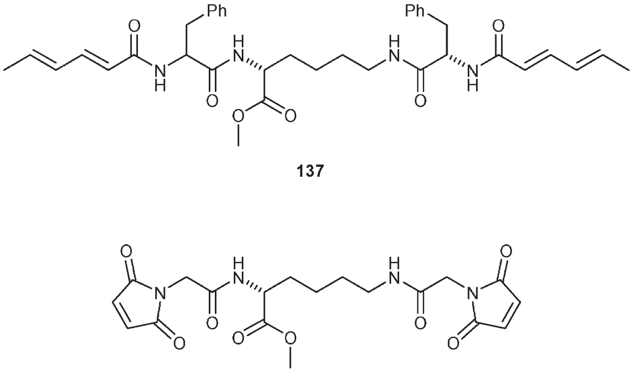


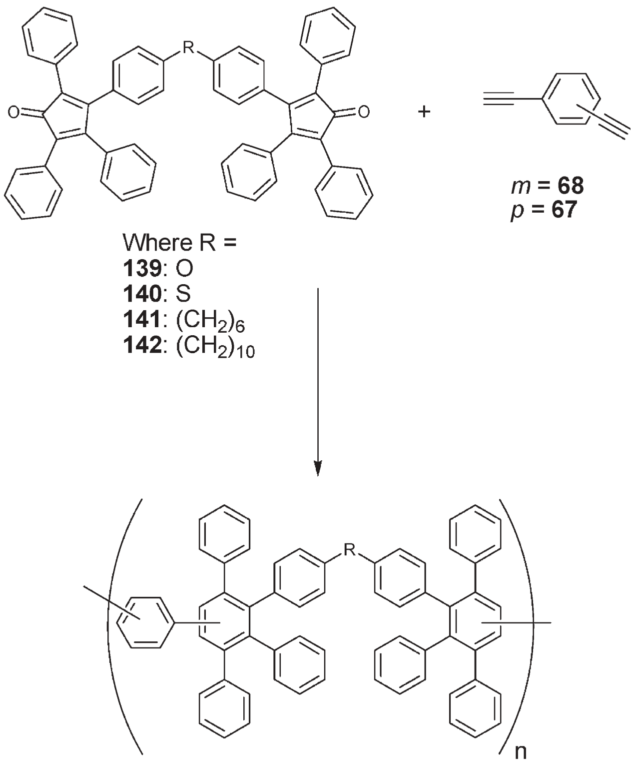
Fig. 15 Diene and dieneophile monomers prepared[93] from renewable feedstocks by Ritter and Reinecke.

4.2 Polyphenylenes *via* Diels–Alder cycloaddition polymerizations

Polymer architectures that feature aromatic linked structures are extremely thermally and chemically stable. Furthermore, the aromatic nature of these systems renders these polymers suitable for numerous high performance and technological applications. Linear polyphenylenes have exhibited interesting radiation-induced conductivity[94] although conduction was lower when compared to other phenylated polymers. In addition, polyphenylene oxide composites have been utilized[95] in direct methanol fuel cells. Hyperbranched and dendritic polyphenylenes exhibit controllable conductivity[96] and organic light emitting diode applications[97] *via* modification of peripheral moieties.

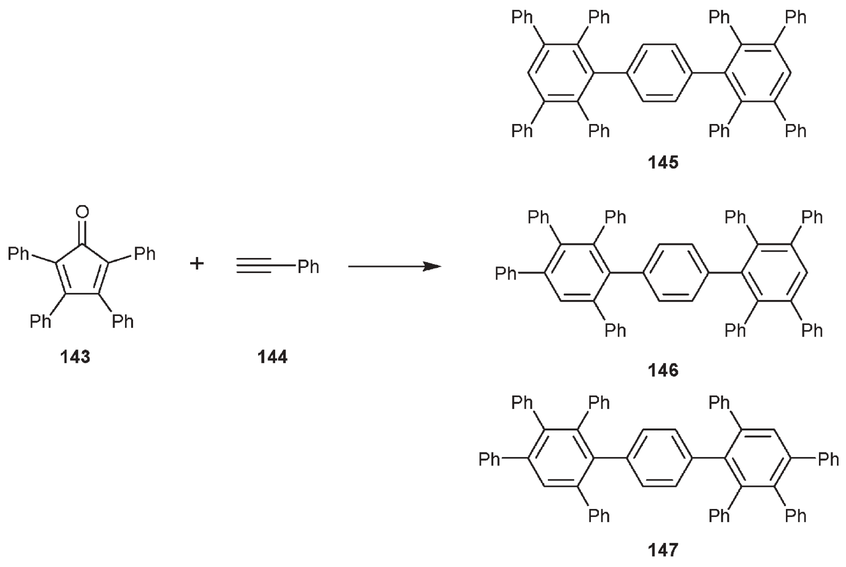
High molecular weight polymers *via* [4 + 2] cycloaddition polymerizations are difficult to achieve as a consequence of side reactions and the occurrence of retro [4 + 2] cycloadditions. However, by following a [4 + 2] cycloaddition strategy involving a synchronous aromatization and irreversible loss of a small molecule (such as carbon monoxide (*vide supra*)) the detrimental retro [4 + 2] cycloaddition pathway can be eliminated.

Stille *et al.* produced[98] linear phenylated polyphenylene architectures *via* [4 + 2] cycloaddition polymerization of monomers featuring bistetracyclones or diethynyl moieties (Scheme 34). A range of monomers were prepared and polymerizations were then carried out (typically in toluene) using a sealed reaction vessel at 200 °C for a period of up to 24 hours to afford colourless polyphenylenes.



Scheme 34 The synthesis of polyphenylenes reported[91] by Stille and co-workers involving an initial [4 + 2] cycloaddition reaction followed by irreversible aromatization.

This [4 + 2] cycloaddition polymerization was achieved in excellent yield (77 to 98%) and the polymers were all soluble in common organic solvents in contrast to unfunctionalized linear polyphenylenes. Investigation into the reaction mechanism implied the polymerizations occurred *via* secondary-order rate kinetics. In particular, polymers produced from reacting monomers **141** with bismaleimide **67** and **142** with bismaleimide **68** featured high M_n values of 45,000 and 51,000, respectively, and decomposition temperatures up to *ca.* 480 °C which render these polymers suitable for high temperature applications. Unfortunately, the polymerization reaction exhibits limited regioselectivity and thus both *meta*- and *para*-cycloadducts were formed. Consequently, Stille *et al.* carried out model reactions at various temperatures (100 to 255 °C) in an attempt to predict the proportions of each regioisomer present.[99] The activation energy difference between the two regioisomers was small (6.7 kJ mol^{-1}) and at low temperatures the *meta*-regioisomer predominated whereas the *para*-regioisomer was produced at elevated temperature. Clear, colourless, amorphous films were drawn which exhibited good insulating electrical properties at 21 °C. The polymerization was also carried out between



Scheme 35 The model reaction carried out between the tetraphenylcyclopentadienone **143** and phenylacetylene **144** by Müllen *et al.* to determine[100] the regiochemical preference of this Diels–Alder cycloaddition process.

bistetracyclone **139** and bismaleimides (**67** and **68**) to afford comparatively less thermally stable polymers that dehydrogenated readily at high temperatures.

Müllen *et al.* carried out model reactions between phenylacetylene **144** and 1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene **143** in order to ascertain the proportion of the three possible regioisomers (*meta*, *meta*-**145**, *meta*, *para*-**146** and *para*, *para*-**147** cycloadducts) produced (Scheme 35).[100]

The cycloadducts were synthesized in excellent yield (92%), and one regioisomer was isolated as 83% of the total cycloadduct mixture. This cycloadduct was found to be the *meta*, *meta*-cycloadduct *via* ^{1}H–^{13}C COSY NMR, NOE, FT-IR spectroscopic and X-ray crystallographic analysis, in contrast to the observations of Stille *et al.*[98] (*vide supra*).

Tetraphenylcyclopentadienone **143** was then utilized to produce polyphenylenes by the reaction of bisalkynes **67** or **68** in a sealed vessel at 200 °C for 48 hours. The cycloadduct polymer was produced in excellent yield (93%) with M_n values *ca.* 27,000. This polymer was then treated with copper(II) trifluoromethanesulfonate and aluminium chloride to effect oxidative cyclohydrogenation and to afford polycyclic aromatic hydrocarbon architectures. Unfortunately, these structures (which are currently of great interest in the field of molecular electronics) proved to be insoluble in common organic solvents and thus could only be characterized *via* FT-IR and Raman spectroscopic analysis.

Morgenroth and Müllen expanded[101] this cycloaddition methodology by employing AB$_2$-type tetraphenylcyclopentadienone derivatives to afford hyperbranched polyphenylene architectures. A range of AB$_2$ monomers were prepared including **149** that upon treatment with tetrabutylammonium fluoride at 180 °C produced **148** *in situ* (Fig. 16). After a period of 12 hours the desired branched cycloadduct was generated with M_w values of 17,000 and a high PDI value of 6.9. In contrast, the polymerization of monomer **150** produced branched polyphenylenes with M_w values of 107,000 and a significantly lower PDI (4.3) after a period of 45 hours. Both of these polyphenylenes were soluble in common organic solvents but unfortunately, end-group analysis proved difficult.

In a similar fashion, Harrison and Feast have reported[102] the synthesis of hyperbranched polymers *via* AB$_2$ type monomers featuring maleimide and cyclopenadienone moieties. These polyimides were also soluble in common organic solvents. This methodology led to hyperbranched polyphenylenes with dense benzene ring packing within the structure that allowed access to macroscopic polycyclic aromatic hydrocarbons that are suitable for advanced coating applications.

Müllen and Wiesler have also produced[103] dendrimer architectures *via* this [4 + 2] cycloaddition methodology in a convergent manner. 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone (**143**) was reacted with the AB$_2$ monomer **151** to afford the first generation dendritic precursor **152** which, in turn, was reacted with 1,3-diphenylacetone *via* condensation reaction to afford the first generation dendron **153** in 85% yield. Reaction of the dendron **153** with another equivalent of the bisacetylene **151** afforded the corresponding second generation dendron **154** in 89% yield. Unfortunately further reaction with 1,3-diphenylacetone yielded a mixture of products as a consequence of steric hindrance (Scheme 36).

The dendron **153** was reacted with multifunctional core molecules to afford polyphenylene dendrimers, that exhibited

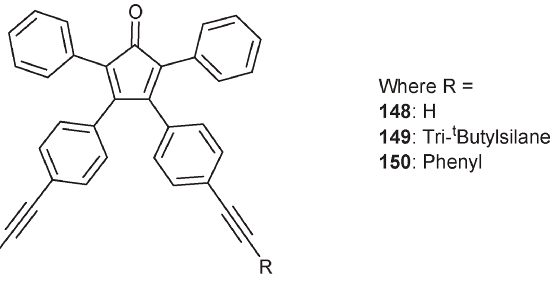
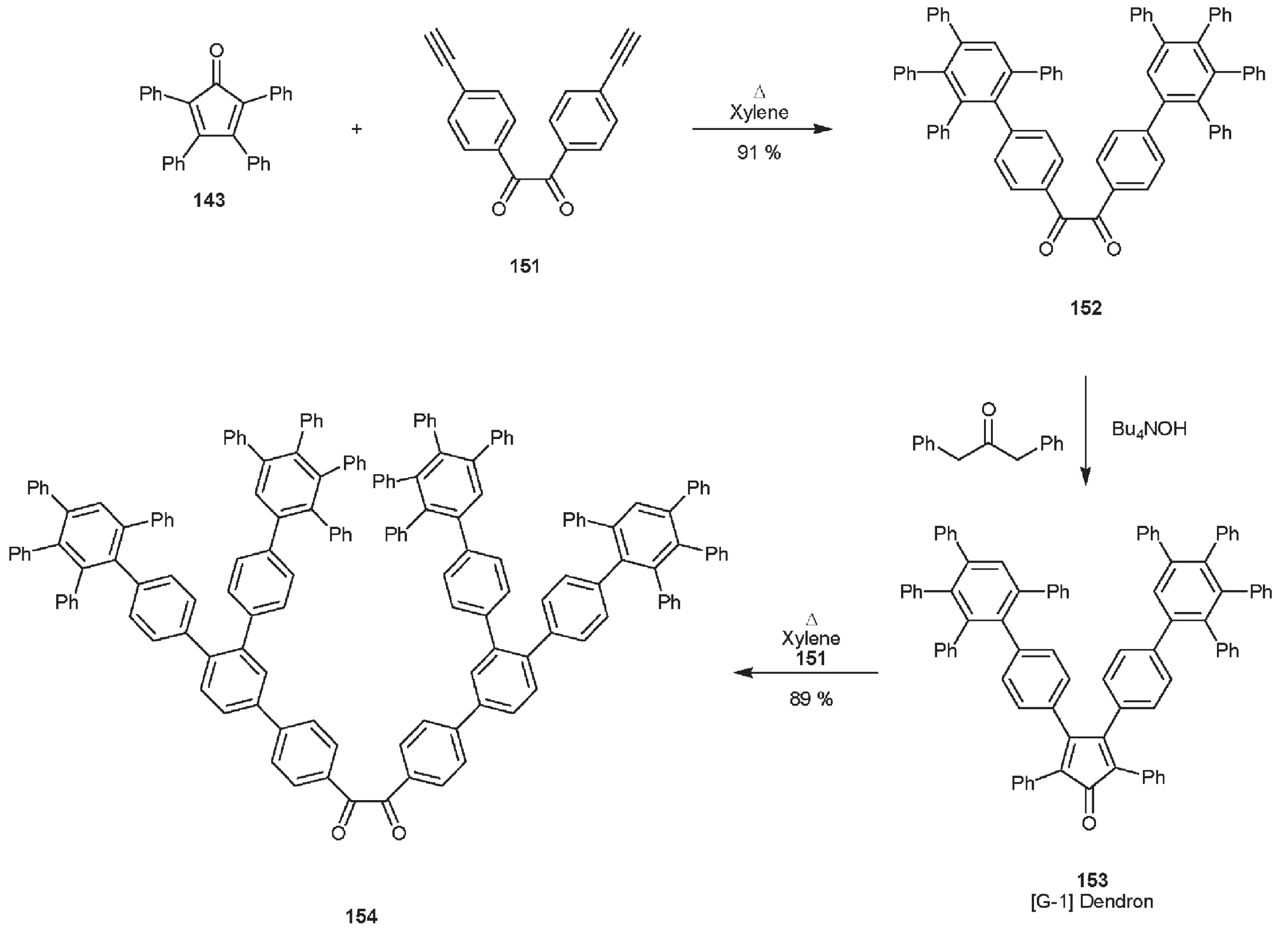


Fig. 16 Tetraphenylcyclopentadienone derived AB$_2$-type monomers employed by Morgenroth and Müllen to generate polyphenylenes.[101]



Scheme 36 Polyphenylene dendrimer synthesis utilizing an irreversible Diels–Alder cycloaddition approach.[96]

decomposition temperatures (*ca.* 550 °C). Higher generation dendritic species were also achieved *via* the use of a divergent-growth strategy. However, these could only be furnished with one peripheral moiety. In contrast, the convergent strategy allowed access to dendrimers that featured several surface moieties thus rendering them suitable for high performance applications.

4.3 Ladder polymers *via* thermal and high pressure [4 + 2] cycloaddition methods

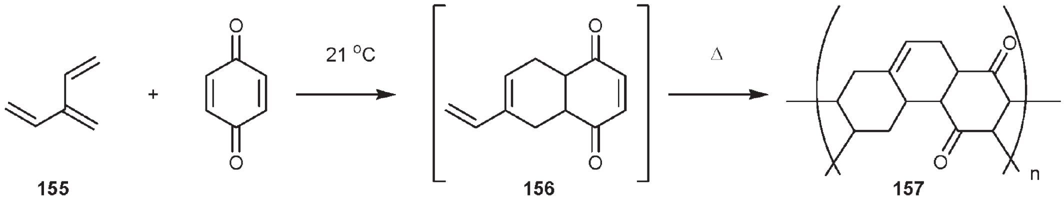
Ladder polymers are defined[104,105] as polymers which are composed entirely of spiro or fused cyclic repeat structures and are thus highly rigid. This fused cyclic structure infers great thermal, mechanical and even chemical stability as a consequence of the improbability of two bonds within one cycle breaking within the polymer bulk architecture. Unfortunately, these structures can render the ladder polymers extremely insoluble in common organic solvents. Ladder polymers also exhibit interesting properties such as electronic conductance and indeed, these types of polymers can exhibit semiconducting[106] and electroluminescence[107] phenomena and have been utilized in thin-film transistors.[108] Ladder polymers can be synthesized *via* numerous route offering access to a range of structures featuring interesting properties which have been reviewed thoroughly.[105,109]

[4 + 2] Cycloaddition reactions offer an efficient route for synthesis of fused cyclic structures and thus ladder polymer production with regio- and stereoselectively. The concerted mechanism allows access to defect free ladder polymers as the transition state leads directly to products without intermediates and thus with minimal side reactions.

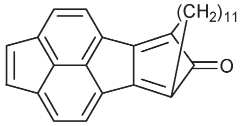
Initial attempts to access ladder architectures involved homopolymerization of cyclopentadiene[110] *via* repetitive [4 + 2] cycloadditions of cyclopentadiene to the newly formed cycloadduct dieneophile. Unfortunately, the new dieneophile proved unreactive, requiring extreme conditions to facilitate the desired [4 + 2] cycloaddition and only low molecular weight oligomeric material was produced.

Bailey *et al.* proposed[111] a simple strategy to overcome this detrimental unreactivity by first reacting a diene with a bifunctional dieneophile to product an activated AB type monomer that featured both diene and dieneophile moieties (Scheme 37).

Consequently, 2-vinylbutadiene **155** was first reacted with benzoquinone at 21 °C to afford an activated AB-type monomers **156** *in situ*. This intermediate was then heated to encourage the desired [4 + 2] cycloaddition polymerization. The soluble fraction of the resultant polymer **157** melted between 170–200 °C and had a molecular weight (M_n) value of *ca.* 2000, whereas the bulk polymer melted at greater



Scheme 37 The [4 + 2] cycloaddition strategy[111] used by Bailey and co-workers to produce ladder polymers.



158

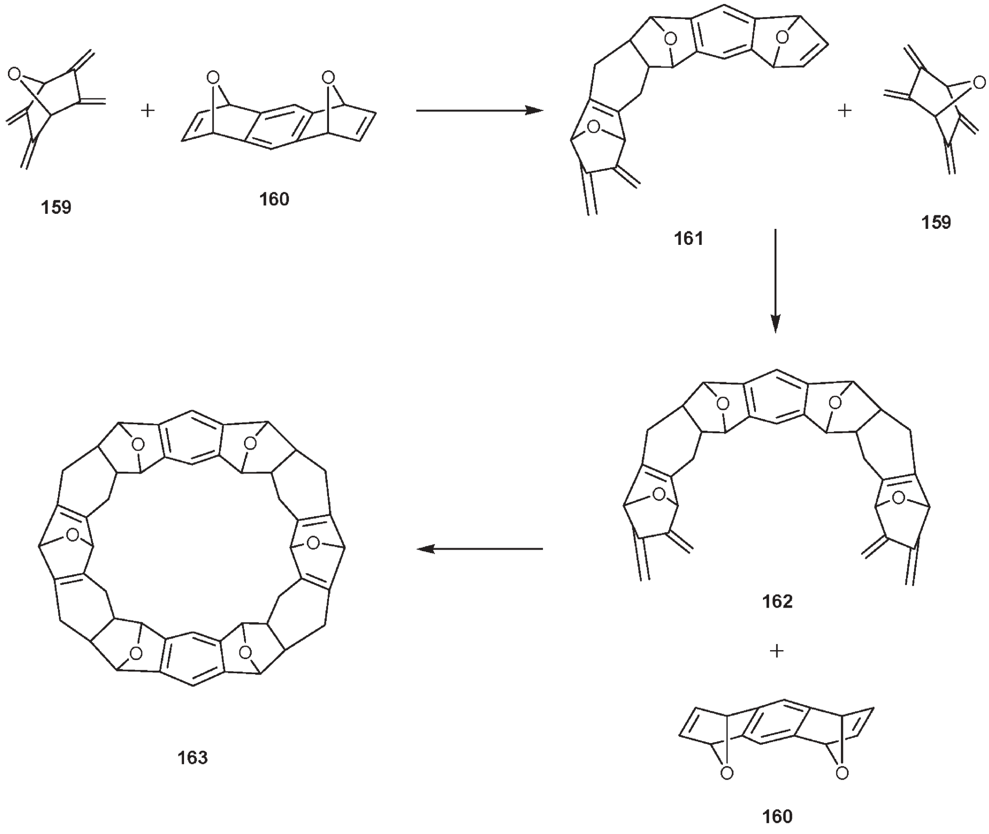
Fig. 17 The AB-type cyclopentadienone monomer **158** developed by Löffler and Schlüter to generate ladder type polymers.[102]

temperatures (340–400 °C). Monomer **155** was also reacted with bismaleimides **48** and **49** to afford white polymers which melted at >500 °C, but these products were insoluble in common organic solvents and thus difficult to process.

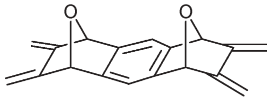
In an effort to afford high molecular weight ladder polymers, Löffler and Schlüter employed[112] monomer **158** (Fig. 17) in a cycloaddition polymerization route and the large alkyl bridging unit present in **158** was designed to increase the solubility of the ladder polymer.

Monomer **158** was prepared in good yield (70%) and was then homopolymerized using toluene in a sealed vessel at 120 °C for 2 to 3 days to afford the desired cycloadduct polymer. Unfortunately, this product was not as soluble as predicted and the soluble fraction also had a molecular weight value of only 2200.

The highly negative volume of activation ($\Delta V^{\ddagger}$ −25 to −50 cm^3 mol^{-1})[82] exhibited by the transition states in [4 + 2] cycloadditions allows greater rates of reaction under high pressure conditions. Stoddart *et al.* utilized[113] the π-facial diastereoselectivity of two monomer (see **159** and **160** in Scheme 38) to afford macrocyclic cage architectures *via* repeated [4 + 2] cycloadditions. Predominantly the cycloaddition proceeds between the *exo*-face of **159** and the *endo*-face of **160** (*syn*/*endo*) yielding a bow shaped 2-dimensional ladder cycloadduct. Reactions utilizing a 1 : 1 stoichiometric ration of monomers **159** and **160** afforded the 1 : 1 cycloadduct **161** in low yield (24%) and the 2 : 1 cycloadduct **162** in an improved yield (64%). Altering the ratio of **159** and **160** to 2 : 1 afforded



Scheme 38 The synthetic approach utilized[113] by Stoddart *et al.* to produce macrocyclic cage architectures.



164

Fig. 18 The bisdiene monomer **164** deployed by Stoddart and co-workers in ladder polymer production.[113]

162 in significantly higher yield (80%). X-ray crystallographic analysis confirmed that each cycloadduct was produced solely *via* the *syn*/*endo* approach. Further thermal treatment of the 1:1 cycloadduct **159** (xylene under reflux) afforded a macrocyclic cage architecture that degraded to yield **159**. Indeed, the thermal reaction proceeded poorly to afford the macrocyclic cage **163** in a yield of 3.5%. However, by employing high pressure conditions (18 kbar, 50 °C) led to improvement in the reaction efficiency and after 72 hours the macrocyclic cage **163** was produced in increased yield (47%). The two benzene rings within the macrocycle were located 7.9 Å apart across the central cavity, thus rendering this macromolecule suitable for use as a host receptor for aromatic guests.

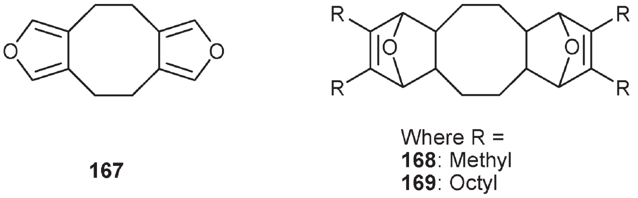
When monomer **160** was reacted with monomer **164** (Fig. 18) in a ratio of 1 : 2 at 10 kbar, three cycloadducts were produced. A 2 : 1 cycloadduct *via syn*/*endo* addition predominated (25%), but there was also evidence of the presence of *anti*/*endo*-*syn*/*endo* cycloadduct (1.5%) and a larger 3 : 2 cycloadduct (2%).

Wegener and Müllen expanded[114] this methodology to produce polymeric ladder structures utilizing high pressure conditions. When monomers **165** and **166** (Fig. 19) were heated together (110 °C) in toluene for a period of 24 hours only 1:1 and 2:1 type cycloadducts were observed. When the same reaction was carried out at 7.5 kbar and 65 °C in either toluene or dichloromethane, a ladder polymer was afforded with M_n of 8800, and epoxy dieneophile terminal groups were observed by ^{1}H and ^{13}C NMR spectroscopic analysis. Increasing the temperature had minimal effect upon the molecular weight up to a value of 100 °C after which polymer was not produced as a consequence of monomer degradation *via* epoxide ring opening. The ladder polymer was found to decompose at temperatures >200 °C and the T_g was found to be 119 °C after quenching the polymer in liquid nitrogen.

At high pressure the *endo* transition state has a more negative volume of activation when compared to the *exo*-transition state, and thus this approach vector in the cycloaddition reaction dominates. From model reactions between the diene **165** and the dienophile **166** the *syn*/*endo*-isomer was found to dominate (8.5 : 1.5) over the *anti*/*endo*-isomer—an outcome in agreement with the results reported by Stoddart and co-workers.[113]

165 **166**

Fig. 19 The bisdiene **165** and dieneophile **166** employed[114] by Wegener and Müllen for model cycloaddition reactions.



167

Fig. 20 The bisfuran **167** and bisoxanorbornene **168–169** monomers employed by Pollmann and Müllen.[115]

Pollmann and Müllen then employed[115] A_2- and B_2-type monomers (**167** to **169** in Fig. 20) to produce flexible ladder polymers. Unfortunately, when reacted under thermal conditions (80 °C) only 1 : 1 cycloadducts were produced. However, when the monomers were reacted at 8 kbar for 1 to 2 days ladder polymers were produced from the reaction of the bisdiene **164** with **169** and the bisdiene **165** with **169** in 40 and 80% yield, respectively. FT-IR and ^{1}H NMR spectroscopic analysis revealed that side reactions had not occurred and defect-free polymers were afforded.

5. Summary

The aim of this review was to highlight key developments in this rapidly growing area of polymer synthesis and describe these advances in a critical manner for the benefit of the chemistry community. It is clear from this *critical review* that cycloaddition reactions have been utilized successfully to yield a wide range of functionalized polymers and materials. Polymers produced *via* cycloaddition chemistries have found use in several advanced applications such as liquid crystal displays, semi-conductors, electrolyte membranes and high temperature performance polymers. In addition, cycloaddition polymerization have found applications in more conventional fields in polymer science such as adhesives. It is clear from this survey that the application of these cycloaddition technologies will continue to impact upon polymer synthesis in the future.

Acknowledgements

The authors would like to thank the DuPont Fellows Forum and the University of Reading Research Endowment Trust Fund for a postgraduate studentship for GWG.

References

1 I. Fleming, *Pericyclic Reactions (Oxford Chemistry Primer)*, Oxford University Press, Oxford, 1999; G. B. Gill and M. R. Willis, *Pericyclic Reactions*, Chapman & Hall, London, 1974; N. S. Isaacs, *Physical Organic Chemistry*, Longman, Harlow, 2nd edn., 1995, vol. 1, pp 701; C. P. Dell, *Contemp. Org. Synth.*, 1997, **4**, 87; C. P. Dell, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3873 and references therein.
2 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie GmbH, Weinheim/Bergstr, 1970; K. N. Houk, *Acc. Chem. Res.*, 1975, **8**, 361; T. L. Gilchrist and R. C. Storr, *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, 1979, and references therein.
3 I. Fleming, *Frontier Orbitals in Organic Chemical Reactions*, Wiley-Interscience, Chichester, 1976.
4 A. Padwa, *1,3-Dipolar Cycloaddition Chemistry*, Wiley-Interscience, New York, 1984; W. Carruthers, *Cycloaddition*

Reactions in Organic Systems, Pergamon Press, Oxford, 1991 and references therein.

5 R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 321; W. C. Herndon, *Chem. Rev.*, 1972, **72**, 157; K. N. Houk, J. González and Y. Li, *Acc. Chem. Rev.*, 1995, **28**, 81.

6 F. C. De Schryver, W. J. Feast and G. Smets, *J. Polym. Sci., Chem. Ed.*, 1970, **8**, 1939; F. C. De Schryver, N. Boens and G. Smets, *Macromolecules*, 1976, **7**, 399.

7 H. Stobbe and A. Lehfelt, *Chem. Ber.*, 1925, **58**, 2415; C. C. Unruh and C. F. H. Allen, *US. Pat.*, 2716102, 1955.

8 L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *WO Pat.*, 00 63140, 2000; L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2000, **122**, 7818; D. B. Varshney, G. S. Papaefstathiou and L. R. MacGillivray, *Chem. Commun.*, 2002, 1964; G. S. Papaefstathiou and L. R. MacGillivray, *Angew. Chem., Int. Ed.*, 2002, **41**, 2070.

9 X. Gao, T. Friščič and L. R. MacGillivray, *Angew. Chem., Int. Ed.*, 2004, **43**, 232.

10 G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky and R. H. Grubbs, *J. Am. Chem. Soc.*, 1998, **120**, 3641.

11 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989.

12 C. Chung, Y. Roh, S. Cho and J. Kim, *Chem. Mater.*, 2004, **16**, 3982.

13 B. R. Maughon and R. H. Grubbs, *Macromolecules*, 1997, **30**, 3459; R. H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, Weinheim, 2003.

14 M. S. Sanford, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **23**, 5384; T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.

15 E. Enholm, A. Joshi and D. Wright, *Tetrahedron Lett.*, 2004, **45**, 8635.

16 D. W. Smith, Jr. and D. A. Babb, *Macromolecules*, 1996, **29**, 852.

17 D. W. Smith, Jr., H. W. Boone, R. Traiphol, H. V. Shah and D. Perahia, *Macromolecules*, 2000, **33**, 1126.

18 D. W. Smith, Jr., J. Jin, H. V. Shah, Y. Xie and D. D. DesMarteau, *Polymer*, 2004, **45**, 5755.

19 A. Sudo and T. Endo, *Macromolecules*, 1998, **31**, 7996.

20 K. Naka, T. Uemura and Y. Chujo, *Polym. Bull.*, 1999, **42**, 367.

21 K. Itoya, M. Kakimoto and Y. Imai, *Macromolecules*, 1994, **27**, 7231.

22 M. Jikei and M. Kakimoto, *Prog. Polym. Sci.*, 2001, **26**, 1233; C. Gao and D. Yan, *Prog. Polym. Sci.*, 2004, **29**, 183; B. Voit, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 2679.

23 H. Peng, J. W. Y. Lam, D. Jia and B. Z. Tang, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2004, **45**, 819.

24 H. Peng, L. Cheng, J. Luo, K. Xu, Q. Sun, Y. Dong, F. Salhi, P. P. S. Lee, J. Chen and B. Z. Tang, *Macromolecules*, 2002, **35**, 5349.

25 H. Peng, J. W. Y. Lam and B. Z. Tang, *Macromol. Rapid Commun.*, 2005, **26**, 673.

26 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; D. A. Tomalia and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2719; S. Hecht, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 1047; J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3713.

27 S. Hecht and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1999, **121**, 4084.

28 A. Padwa, *General Heterocyclic Chemistry: 1,3-Dipolar Cycloaddition Chemistry*, John Wiley and Sons, Chichester, 1985, vol. 2; K. V. Gothelf and K. A. Jørgensen, *Chem. Rev.*, 1998, **98**, 863.

29 R. Huisgen, *J. Org. Chem.*, 1968, **33**, 2291; R. A. Firestone, *J. Org. Chem.*, 1968, **33**, 2285; R. A. Firestone, *J. Chem. Soc. A*, 1970, 1570; R. A. Firestone, *J. Org. Chem.*, 1972, **37**, 2181; R. Huisgen, *J. Org. Chem.*, 1976, **41**, 403; R. A. Firestone, *Tetrahedron*, 1977, **33**, 3009.

30 J. K. Stille and T. Anyos, *J. Polym. Sci., Part A: Polym. Chem.*, 1964, **2**, 1487.

31 J. W. Nicholson, *The Chemistry of Polymers*, RSC Paperbacks, Cambridge, 2nd edn., 1994, pp 97.

32 O. Nuyken, G. Maier and K. Burger, *Makromol. Chem.*, 1988, **189**, 2245; O. Nuyken, G. Maier, K. Burger and A. S. Albet, *Makromol. Chem.*, 1989, **190**, 1953; O. Nuyken, G. Maier and K. Burger, *Makromol. Chem.*, 1990, **191**, 2455.

33 O. Nuyken, G. Maier and K. Losert, *Makromol. Chem., Macromol. Symp.*, 1993, **75**, 199; G. Maier, K. Losert and O. Nuyken, *Makromol. Chem.*, 1993, **194**, 2413; G. Maier, *Macromol. Chem. Phys.*, 1996, **197**, 3067; G. Maier, A. Fenchl and G. Sigl, *Macromol. Chem. Phys.*, 1997, **198**, 137.

34 G. Maier, V. Knopfova, B. Voit, P. H. Ly, B. T. Dung and D. B. Thanh, *Macromol. Mater. Eng.*, 2004, **289**, 927.

35 G. Maier and A. Fenchi, *Macromol. Symp.*, 1997, **122**, 297; G. Maier, C. Zech, B. Voit and H. Komber, *Macromol. Chem. Phys.*, 1998, **199**, 2655; G. Maier, C. Zech, B. Voit and H. Komber, *Macromol. Symp.*, 2001, **163**, 75.

36 K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 1998, **31**, 7570; K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 1999, **32**, 4641; K. Naka, T. Uemura and Y. Chujo, *Polym. J.*, 2000, **32**, 435.

37 K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 2000, **33**, 4733.

38 K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 2000, **33**, 6965.

39 T. Horiuchi and O. Niwa, *Bio Industry*, 2001, **18**, 56; M. B. Nielsen, J. C. Petersen, N. Thorup, M. Jessing, A. S. Andersson, A. S. Jepsen, J.-P. Gisselbrecht, C. Boudon and M. Gross, *J. Mater. Chem.*, 2005, **15**, 2599.

40 J. Hamer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473; G. R. Delpierre and M. Lamchen, *J. Chem. Soc.*, 1965, 329.

41 G. J. Smets and S. Matsumoto, *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**, 2983.

42 K. Rück-Braun, T. H. E. Freysoldt and F. Wierchem, *Chem. Soc. Rev.*, 2005, **34**, 507.

43 V. G. Manecke and J. Klawitter, *Makromol. Chem.*, 1967, **108**, 292; V. G. Manecke and J. Klawitter, *Makromol. Chem.*, 1971, **142**, 253.

44 M. Heinenberg, B. Menges, S. Mitter and H. Ritter, *Macromolecules*, 2002, **35**, 3448.

45 L. Vretik and H. Ritter, *Macromolecules*, 2003, **36**, 6340.

46 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004.

47 H. C. Kolb and K. B. Sharpless, *Drug Discovery Today*, 2003, **8**, 1128.

48 S. J. Howell, N. Spencer and D. Philp, *Org. Lett.*, 2002, **4**, 273.

49 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.

50 K. E. Johnson, J. A. Lovinger, C. O. Parker and M. G. Baldwin, *J. Polym. Sci., Polym. Lett. Ed.*, 1966, **4**, 977; M. G. Baldwin, K. E. Johnson, J. A. Lovinger and C. O. Parker, *J. Polym. Sci., Polym. Lett. Ed.*, 1967, **5**, 803.

51 J. A. Opsteen and J. C. M. van Hest, *Chem. Commun.*, 2005, **57**, 57.

52 N. V. Tsarevsky, B. S. Sumerlin and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 3558.

53 G. Mantovani, V. Ladmiral, L. Tao and D. M. Haddleton, *Chem. Commun.*, 2005, 2089.

54 B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 7540.

55 J. Xia and K. Matyjaszewski, *Chem. Rev.*, 2001, **101**, 2921; C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, **101**, 3661; M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689.

56 N. V. Tsarevsky, K. V. Bernaerts, B. Dufour, F. E. Du Prez and K. Matyjaszewski, *Macromolecules*, 2004, **37**, 9308.

57 D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen and J. N. H. Reek, *Chem. Commun.*, 2005, 4333.

58 Y. Gilliams and G. Smets, *Makromol. Chem.*, 1968, **117**, 1; Y. Gilliams and G. Smets, *Makromol. Chem.*, 1969, **128**, 263.

59 S. Chang, N. T. Prevost, N. D. Sachinvala, D. V. Parikh, A. A. Lambert, III, P. A. Sawhney and W. A. Jarrett, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2005, **46**, 737.

60 B. Voit, A. Scheel, H. Komber, G. Maier, C. Zech and C. Hawker, *Polym. Mater. Sci. Eng.*, 2004, **91**, 258; A. Scheel, H. Komber and B. Voit, *Macromol. Rapid Commun.*, 2004, **25**, 1175.

61 M. Smet, K. Metten and W. Dehaen, *Collect. Czech. Chem. Commun.*, 2004, **64**, 1097.

62 N. Le Baut, H. R. Brown, M. G. Finn, D. D. Díaz and S. Punna, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2005, **46**,

456; D. D. Díaz, S. Punna, P. Holzer, A. K. McPherson, K. B. Sharpless, V. V. Fokin and M. G. Finn, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4392.

63 A. D. Schlüter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 864.

64 B. Helms, J. L. Mynar, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 15020.

65 M. J. Joralemon, A. K. Nugent, J. B. Matson, R. K. O'Reilly, C. J. Hawker and K. L. Wooley, *Polym. Mater. Sci. Eng.*, 2004, **91**, 195.

66 G. Van Wuytswinkel, B. Verheyde, F. Compernolle, S. Toppet and W. Dehaen, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1337.

67 J. W. Lee and B. K. Kim, *Bull. Korean Chem. Soc.*, 2005, **26**, 658.

68 C. J. Hawker, J. Pyun, J. M. J. Fréchet, A. Scheel and B. Voit, *Proceedings of the 3rd International Dendrimer Symposium*, Berlin, 2003, 36; J. Pyun and C. J. Hawker, *Proceedings of the 3rd International Dendrimer Symposium*, Berlin, 2003, 128; P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.*, 2004, **43**, 2.

69 R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, 1960, **25**, 546; C. Grundmann and J. M. Dean, *J. Org. Chem.*, 1965, **30**, 2809.

70 K. C. Liu, B. R. Shelton and R. K. Howe, *J. Org. Chem.*, 1980, **45**, 3917; K. E. Larsen and K. B. G. Torssell, *Tetrahedron*, 1984, **40**, 2985; S. Kanemasa, H. Matsuda, A. Kamimura and T. Kakinami, *Tetrahedron*, 2000, **56**, 1057; J. E. Moore, K. M. Goodenough, D. Spinks and J. P. A. Harrity, *Synlett*, 2002, **12**, 2071; M. W. Davies, R. A. J. Wybrow, C. N. Johnson and J. P. A. Harrity, *Chem. Commun.*, 2001, 1558.

71 O. Moriya, H. Takenaka, M. Iyoda, Y. Urata and T. Endo, *J. Chem. Soc., Perkin Trans. 1*, 1994, 413.

72 B. H. Kim, E. Jeong and W. H. Jung, *J. Am. Chem. Soc.*, 1995, **117**, 6390; B. H. Kim, E. Jeong, G. T. Hwang and N. Venkatesan, *Synthesis*, 2001, **14**, 2180.

73 Y. Iwakura, S. Shiraishi and M. Akiyama, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 335; Y. Iwakura, S. Shiraishi, M. Akiyama and M. Yuyama, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1648.

74 C. G. Overberger, *J. Polym. Sci., Polym. Lett. Ed.*, 1965, **3**, 735; S. Fujimoto, *J. Polym. Sci., Polym. Lett. Ed.*., 1967, **5**, 301; C. G. Overberger and S. Fujimoto, *J. Polym. Sci., Polym. Symp. Ed.*, 1968, **16**, 4161; C. G. Overberger and R. A. Nelson, *Macromolecular Synthesis*, 1974, **5**, 21.

75 Y. Iwakura, K. Uno, S. J. Hong and T. Hongu, *Polym. J. (Tokyo)*, 1971, **2**, 36; S. J. Hong, *J. Korean Chem. Soc.*, 1971, **15**, 121.

76 S. J. Hong, Y. Iwakura and K. Uno, *Polymer*, 1971, **12**, 521.

77 S. J. Hong, *Polymer*, 1973, **14**, 286.

78 O. Moriya and T. Endo, *Polym. J. (Tokyo)*, 1997, **29**, 467.

79 K. Itoyta, M. Kakimoto, Y. Imai and O. Fukunaga, *Polym. J. (Tokyo)*, 1992, **24**, 979.

80 G. B. Guarise, *J. Am. Chem. Soc.*, 1966, 497.

81 J. H. Kim and H. Lee, *Synth. Met.*, 2004, **143**, 13.

82 N. S. Isaacs, *Liquid Phase High Pressure Chemistry*, John Wiley & Sons, Chichester, 1st Edn., 1981.

83 A. Yamamoto, H. Sano and G. B. Zheng, *Mater. Sci. Forum*, 2005, **486-487**, 493.

84 J. J. Oin and T. S. Chung, *Abstr. Pap.–Am. Chem. Soc.*, 2005, **229**, 919.

85 A. Jain, V. Gupta and S. N. Basu, *Acta Mater.*, 2005, **53**, 3147.

86 J. M. Song, N. Asano, K. Miyatake, H. Uchida and M. Watanabe, *Chem. Lett.*, 2005, **34**, 996.

87 T. Sekitani, Y. Kato, S. Iba and T. Someya, *Jpn. J. Appl. Phys., Part 1*, 2005, **44**, 2841.

88 H. B. Romdhane, M. Baklouti, M. R. Chaâbouni, M. F. Grenier-Loustalot, F. Delome and B. Sillion, *Polymer*, 2002, **43**, 255.

89 J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 125; C. D. Diakoumakos and J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2559.

90 E. A. Kraiman, *US Pat.*, 2890207, 1959.

91 G. Alhakimi, H. Görls and E. Klemm, *Macromol. Chem. Phys.*, 1994, **195**, 1569.

92 M. Reinecke and H. Ritter, *Pure Appl. Chem.*, 1997, **A34**, 2321.

93 H. Ritter, D. Edelmann, M. Reinecke, R. Sperber, C. Lepilleur and M. Born, *Macromol. Rep.*, 1994, **31**, 977; M. Reinecke and H. Ritter, *Macromol. Chem. Phys.*, 1994, **195**, 2445.

94 A. P. Tyutnev, M. L. Keshtov, V. S. Saenko, E. D. Pozhidaev, A. L. Rusanov and Yu. I. Sezonov, *Polym. Sci., Ser. B*, 2001, **43**, 137.

95 J. Sauk, J. Byun and H. Kim, *J. Power Sources*, 2005, **143**, 136.

96 G. Cheng, L. Zhao and Y. C. Wang, *Acta Polym. Sin.*, 2005, 285.

97 R. W. Gymer, R. H. Friend, H. Ahmed and A. B. Holmes, *Synth. Met.*, 1994, **67**, 299; N. Gobert, P. L. Burn, S. Gilmour, J. P. J. Markham and I. D. W. Samuel, *Appl. Phys. Lett.*, 2003, **83**, 5347; H. John, R. Bauer, P. Espindola, P. Sonar, J. Heinze and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 2447.

98 J. K. Stille, F. W. Harris, R. O. Rakutis and H. Mukamal, *J. Polym. Sci., Polym. Lett. Ed.*., 1966, **4**, 791; H. Mukamal, F. W. Harris and J. K. Stille, *J. Polym. Sci., Part A1*, 1967, **5**, 2721; J. K. Stille, R. O. Rakutis, H. Mukamal and F. W. Harris, *Macromolecules*, 1968, **1**, 431; C. L. Schilling, J. A. Reed and J. K. Stille, *Macromolecules*, 1969, **2**, 85; J. K. Stille and G. K. Noren, *Macromolecules*, 1972, **5**, 49.

99 J. K. Stille, *Makromol. Chem.*, 1972, **154**, 49.

100 Z. B. Shifrina, M. S. Averina, A. L. Rusanov, M. Wagner and K. Müllen, *Macromolecules*, 2000, **33**, 3525.

101 F. Morgenroth and K. Müllen, *Tetrahedron*, 1997, **53**, 15349.

102 R. M. Harrison and W. J. Feast, *Polym. Mater. Sci. Eng.*, 1997, **77**, 162.

103 U.-M. Wiesler and K. Müllen, *Chem. Commun.*, 1999, 2293.

104 F. H. Winslow, *J. Polym. Sci.*, 1955, **16**, 101.

105 C. G. Overberger and J. A. Moore, *Adv. Polym. Sci.*, 1970, **7**, 113.

106 U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, **14**, 477.

107 S. Qiu, P. Lu, X. Liu, F. Shen, L. Liu, Y. Ma and J. Shen, *Macromolecules*, 2003, **36**, 9823.

108 S. A. Jenekhe and A. Babel, *Abstr. Pap.–Am. Chem. Soc.*, 2003, **226**, 399.

109 A.-D. Schlüter, *Adv. Mater.*, 1991, **3**, 282.

110 K. Alder and G. Stein, *Chem. Ber.*, 1934, **67**, 613.

111 W. J. Bailey, J. Economy and M. E. Hermes, *J. Org. Chem.*, 1962, **27**, 3295.

112 M. Löffer and A.-D. Schlüter, *Macromol. Symp.*, 1994, **77**, 359.

113 F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 892; F. H. Kohnke, J. P. Mathias and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1103; F. H. Kohnke and J. F. Stoddart, *Pure Appl. Chem.*, 1989, **61**, 1581; P. R. Ashton, G. R. Brown, N. S. Isaacs, D. Giuffrida, F. H. Kohnke, J. P. Mathias, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 6330.

114 S. Wegener and K. Müllen, *Macromolecules*, 1993, **26**, 3037.

115 M. Pollmann and K. Müllen, *J. Am. Chem. Soc.*, 1994, **116**, 2318.