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## 6 Synthesis of man-made polymers

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Steve Rimmer

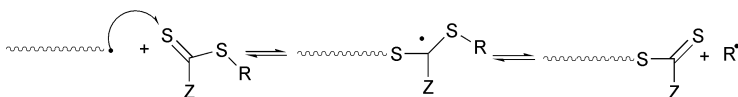
*The Polymer Centre, The Department of Chemistry, University of Sheffield, Sheffield, South Yorkshire, UK S3 7HF*

### 1 Introduction

The following review covers the literature reported during 1998 and 1999 concerned with the synthesis of man-made polymers. No attempt to cover the literature relating to polymer-immobilized synthesis of low molecular weight compounds has been made.

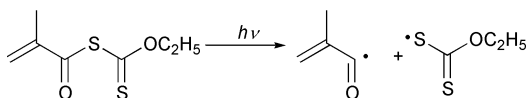
### 2 Radical polymerizations

Perhaps the most significant advance in the field has been the introduction of the RAFT (Radical Addition Fragmentation Termination) process: a variant of the well-known transfer routes to end-functional polymers.<sup>1-3</sup> The process, shown in Scheme 1, involves reversible addition of the propagating radical to an *S*-thiocarbonyl group of a dithionate ester and yields polymers of narrow polydispersity and dithionate chain-end functionality.



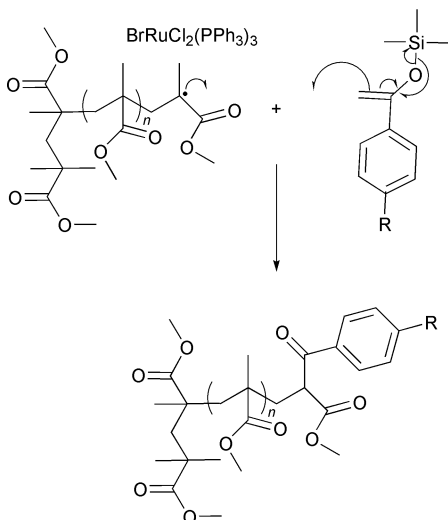
**Scheme 1** The proposed controlling reversible transfer equilibria in the RAFT process.

A photolytic process based on reversible end-capping by dithio radicals has been reported by Ajayaghosh and Francis.<sup>4</sup> The method relies on the photolytic scission of an initiator such as **1** as shown in Scheme 2. However, the process produces oligomers with vinyl ketone end groups, which are probably copolymerized along with the added monomer.



**1**  
**Scheme 2** Photolytic fragmentation of *O*-ethyl xanthate **1**.

ATRP (Atom Transfer Radical Polymerization) also continues to attract interest and several new initiators have been reported.<sup>5-9</sup> The methodology has been modified to produce well-defined stars by use of star shaped alkyl halides.<sup>10</sup> The use of ruthenium hydrides, in place of the usual halide catalysts, has been reported to allow polymerization at temperatures as low as 30 °C<sup>11</sup> and a new rhenium based catalyst has also been shown to be effective in the low temperature ATRP of styrene.<sup>12</sup> Similar low temperature polymerizations of methyl methacrylate, mediated by copper(II) *N*-alkyl-2-pyridylmethanimine, have been reported by Haddleton *et al.*<sup>13</sup> On the other hand the reverse ATRP system avoids the use of the alkyl halide initiator by utilizing conventional radical initiators and higher oxidation state metals. Chen *et al.* have used this concept to prepare  $\alpha$ -hydrogen  $\omega$ -chloro PMMA, with narrow polydispersity, by utilizing 1,1,2,2-tetraphenylethane-1,2-diol as the thermal source of radicals and FeCl<sub>3</sub>/PPh<sub>3</sub> as the controlling species.<sup>14</sup> An important advance in the field was reported by Moineau *et al.*, who have shown that controlled radical polymerization of MMA is possible by incorporating FeCl<sub>3</sub> in the polymerization mixture and that the use of the activated alkyl halide was not necessary in this system.<sup>15</sup> ATRP in aqueous media has been reported for oligoethylene oxide macromonomers and methacrylic acid salts.<sup>16-18</sup> The polymerizations were controlled by addition of CuCl and the polymers have low polydispersities. The end capping of controlled radical polymerizations has only recently been studied and capping with silyl enol ethers is an efficient route to polymers with ketone end groups and narrow polydispersity.<sup>19</sup> The reaction is shown in Scheme 3.



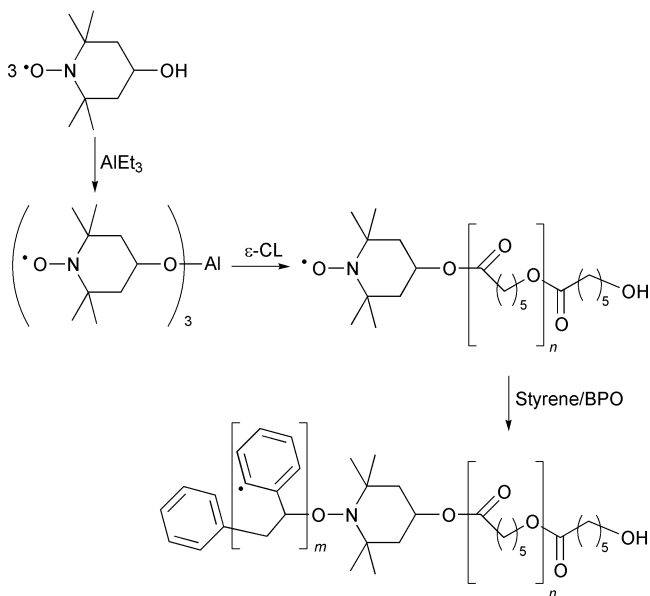
**Scheme 3** Chain end capping of living PMMA macroradical with a silyl enol ether.

A new variant on the controlled polymerization of styrene has been reported that uses diphenyl telluride as the trapping agent.<sup>20</sup>

Destarac and Boutevin have now introduced a new method of block copolymerization that uses both conventional and controlled radical polymerizations.<sup>21</sup> The method involves the use of a trichloromethyl-terminated azo initiator, which is used to

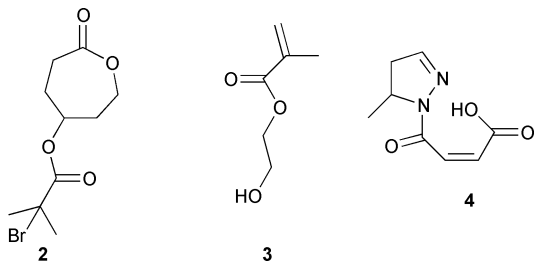
prepare the first block with trichloromethyl chain-end-functionality. This material is then used as an initiator in ATRP.

Nitroxide-mediated polymerization is now accepted as a generally useful technique for the controlled polymerization of styryl derivatives and several variants have been recently reported. For example, Yoshida and Osagawa have reported the use of poly( $\epsilon$ -caprolactone) end-functionalized with TEMPO to control the polymerization of styrene, which then leads to the synthesis of poly( $\epsilon$ -caprolactone-*block*-styrene)s.<sup>22</sup> The synthesis is outlined below in Scheme 4. An important aspect of this work was the report that the synthesis of the TEMPO functionalized poly( $\epsilon$ -caprolactone) did succeed in the presence of mono TEMPO alkoxide diethylaluminium. Styrene has also been prepared in emulsion *via* TEMPO mediated radical polymerization but only low conversions were achieved.<sup>23</sup>



**Scheme 4** Synthesis of poly( $\epsilon$ -caprolactone-*block*-styrene).

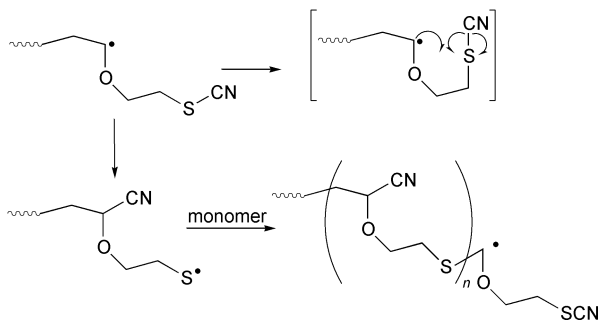
One of the most significant advances in the use of controlled radical polymerization as a tool in the synthesis of designed polymers is the concept of concurrent polymerizations. In one example of this approach hyperbranched block copolymers composed of poly(caprolactone) and methacrylate blocks have been prepared by ring-opening polymerization of monomer **2**, with transfer to **3** and initiation of the ATRP of monomer **3** by the tertiary alkyl bromide group of **2**.<sup>24</sup> This type of polymer of course also presents a considerable analytical challenge if the necessary full characterization data are to be assembled. Compound **1** has also been used to prepare graft copolymers.<sup>25</sup> Graft copolymers were prepared either by synthesis of a copolymer of **2** with  $\epsilon$ -caprolactone followed by ATRP of MMA initiated by the pendant bromide (synthesis of PMMA with a lactone end group followed by ring-



opening copolymerization of this macromonomer with  $\epsilon$ -caprolactone) or concurrent polymerization of both MMA and  $\epsilon$ -caprolactone.

The concept of concurrent polymerization has also been used to prepare poly(oxazoline-*b*-styrene)s, by simultaneous cationic ring opening and nitroxide mediated radical polymerization, and poly(lactide-*b*-styrene)s, by simultaneous anionic ring-opening and nitroxide mediated radical polymerization.<sup>26</sup>

Vinyl ethers are usually very prone to chain transfer to monomer in radical polymerization. However, if transfer to the propagating monomer can be promoted the transfer reaction can be used to prepare polymers containing main-chain ether groups. Thus, Sato *et al.* have achieved this by use of 2-thiocyanatovinyl ether as shown in Scheme 5.<sup>27</sup> A radical polymerization of the unusual monomer **4**, which is formed by simple mixing of acetaldehydrazine and maleic anhydride, has been reported.<sup>28</sup> Solid state polymerization is also unusual and has been used to produce ultra-high molecular weight and stereoregular poly((*Z,Z*)-hexa-2,4-dienedioate).<sup>29</sup>



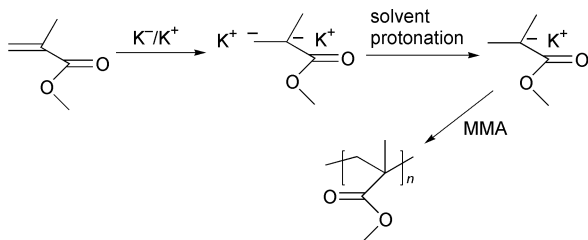
**Scheme 5** Transfer to the propagating monomer during the radical polymerization of 2-thiocyanatovinyl ether.

### 3 Ionic polymerizations

#### Anionic

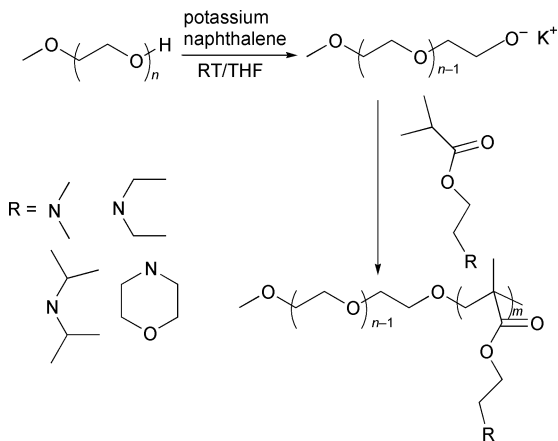
Rate activation by complexation of alkali counter-ions in anionic polymerizations has been known for many years. However, Janeczka *et al.*<sup>30</sup> have reported a useful variant

in which elemental sodium/potassium or potassium disproportionates in the presence of 18C6. They propose that electron transfer to monomer generates a dianion, which is immediately monoprotonated by the solvent (however, the fate of the solvent anion is not discussed) leaving a monomer (MMA) anion that initiates polymerization. The process gives high molecular weights and narrow polydispersities at room temperature and is shown in Scheme 6.



**Scheme 6** Initiation of anionic polymerization of MMA by 18C6-K complex.

Lee and Ryu have also used crown ether complexation of the sodium gegen ion in a new living anionic polymerization of isocyanates.<sup>31</sup> Alkoxy anions are not normally regarded as good initiators of anionic polymerization. However, Vamvakaki *et al.* have now shown that the potassium alkoxide can be used as a macroinitiator for the polymerization of the water soluble methacrylates shown in Scheme 7.<sup>32</sup>

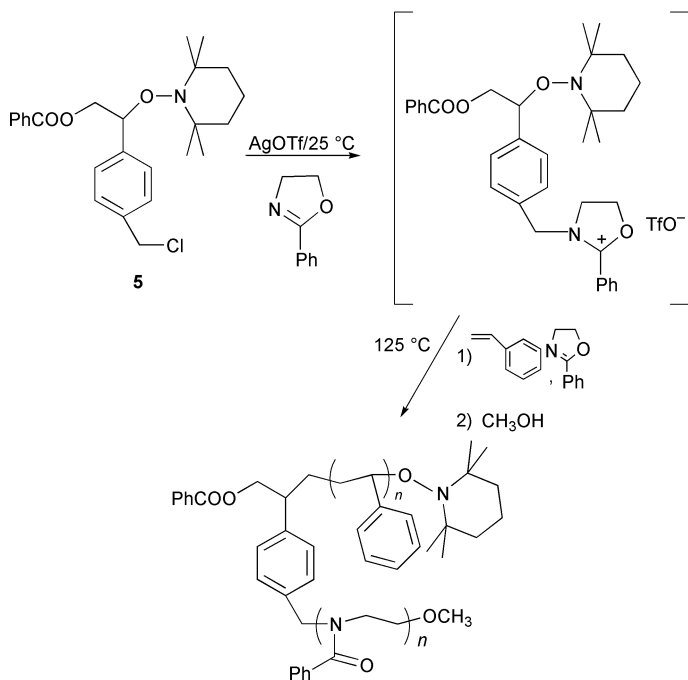


**Scheme 7** Synthesis of polyethylene oxide-*block*-tertiary amine methacrylates.

Anionic polymerization also continues to be a major tool for the synthesis of designed macromolecular structures. Novel examples include the synthesis of comb-like polystyrene by nucleophilic substitution of styryllithium onto poly(chlorovinyl ether);<sup>33</sup> the synthesis of P(EG-*block*-LA) functionalized at the terminus of the PEG chain with aldehyde;<sup>34</sup> grafting of polyisoprene anions, which were first modified by reaction with 1,1-diphenylethylene, to chloromethylated polystyrene;<sup>35</sup> and the synthesis of polyisoprene-polymethyl methacrylate heteroarm stars.<sup>36</sup> Perhaps the

most intriguing of these designed syntheses involves the addition of six living polystyryl macroanions to  $C_{60}$ . Subsequent reinitiation by only one of the resultant  $C_{60}$  anions then yields a polymer with a 'palm tree-like' architecture.<sup>37</sup>

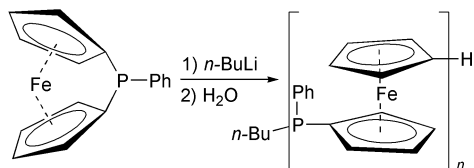
Carrying out polymerizations simultaneously with two or more mechanisms has several advantages for block copolymer synthesis but, often, finding compatible polymerizations is difficult. The method requires that the different monomers polymerize under similar reaction conditions and that the polymerizations do not cross over or interfere. A recently reported application of the concept involves the use of compound **5** as a multifunctional initiator for controlled radical polymerization of styrene and either anionic or cationic polymerization.<sup>38</sup> An example of the cationic version is shown in Scheme 8.



**Scheme 8** Simultaneous polymerization of styrene and 2-phenyloxazolidine.

Biodegradable polymers with similar properties to polymers derived from polymerization of vinyl monomers could be of use in applications such as drug delivery, *etc.* One method that could deliver these materials is the copolymerization of lactones with methacrylates. With this in mind Wu *et al.* have reported that MMA and  $\epsilon$ -caprolactone can be copolymerized by isobutylaluminum.<sup>39</sup>

Metal-containing polymers have potential as catalysts as well as offering new physical properties. One such material has been prepared by the ring-opening polymerization of phosphorus bridged ferrocenes and is shown in Scheme 9.<sup>40</sup>



**Scheme 9** Polymerization to give poly(ferrocenylphosphine).

## Cationic

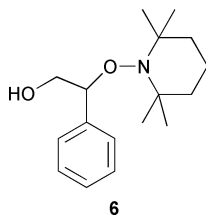
By far the most significant advance in the field of Lewis acid mediated reactions has been the introduction of the water resistant, recyclable, strong Lewis acids derived from scandium and lanthanide triflates. The most successful of the systems reported for cationic polymerization involves the use of ytterbium triflate, which has been used to initiate the polymerizations of *p*-methoxystyrene.<sup>41</sup> Lanthanide Lewis acids have been used to initiate ring-opening polymerization.<sup>42</sup> Other interesting Lewis acids include titanium-based species that can be used to give isotactic poly(isobutyl vinyl ether). Metallocenes are now well established catalysts for insertion polymerization. However, metallocenes are also strong Lewis acids and this aspect of their chemistry has been used to initiate the cationic polymerization of isobutylene.<sup>43</sup> Ouchi *et al.* have begun to tackle the control of stereochemistry in cationic polymerization by design of the Lewis acid.<sup>44</sup> They report that highly stereospecific polymerization of isobutyl vinyl ether can be achieved with the Lewis acid bis(2,6-diisopropylphenoxy)-titanium dichloride.

Functional block copolymers can have use in biotechnology and some of these materials have been prepared by living cationic polymerization. Thus, a polymer that recognises plant lecithins has been developed by Yamada *et al.*<sup>45</sup> The second functional block of the polymer was produced from an acetyl glucosamine functional vinyl ether, protected at positions 2, 4 and 6 by *O*-acetylation. The authors found that in order to produce a block copolymer with isobutyl vinyl ether it was necessary to polymerize the latter monomer first. They present some evidence for block copolymer formation in the form of SEC data.

## 4 New block and graft copolymers

Several new methods of block copolymer synthesis have been reported that are not covered in other sections of this review. An important advance in this area was achieved by Kricheldorf and Eggerstedt<sup>46</sup> who demonstrated ring opening of tin-containing macrocyclic  $\epsilon$ -caprolactone by isophthaloyl chloride followed by condensation with silylated bisphenol A. Simultaneous polymerizations, which involve using two independent polymerizations, can be used to produce block copolymers. With this in mind Hawker *et al.* have carried out nitroxide-mediated polymerizations of styrene and ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of the double headed initiator **6**.<sup>47</sup>

Polymer colloids (nano-particles) are rarely used as catalyst supports because of the difficulty in separating the colloid from the reaction products. However, they do have



advantages over conventional beads in that they possess much higher surface area and are more mechanically robust. One method of separating the colloid from the reaction medium is to flocculate it, ideally in a reversible manner. This has now been achieved with thermally responsive colloids that are surface functionalized with platinum.<sup>48</sup>

The ring-opening polymerization of macrocycles can yield block copolymers if they are copolymerized with other monomers. Such a route was used by Kricheldorf and Eggerstedt to prepare block copolyesters containing polycaprolactone blocks derived from tin-containing macrocycles.<sup>49</sup> Another less used methodology is to react preformed telechelic oligomers. The problems with this route are related to the difficulty in attaining the precise control over stoichiometry required for high molecular weight polymers to be produced in a step growth polymerization whilst maintaining reaction rates that are high enough for polymerization. However, the condensation of PEG diacid functional oligomers with oligo( $\epsilon$ -caprolactone) diols has been reported.<sup>50</sup>

## 5 Networks

Many applications require materials that are resistant to solvent and/or display elastomeric properties, and so new methods for producing cross-linked networks are of commercial importance.

The Diels–Alder reaction is a useful cross-linking method since it does not produce small molecule by-products. However, the reaction is reversible so that the networks may be prone to thermal degradation. Recent examples include the bismaleimide cross-linking of anthracene-2,6-dicarboxylate-containing polyesters.<sup>51</sup> Another furan functional polymer has been reported to be produced by the condensation of hydrogen sulfide with furfuryl aldehyde.<sup>52</sup> Polyesters derived from bacterial sources were cross-linked *via* reaction of epoxide groups, which were incorporated into the main chain by oxidation of pendant alkenes (from hydroxyundec-10-enoate repeat units).<sup>53</sup>

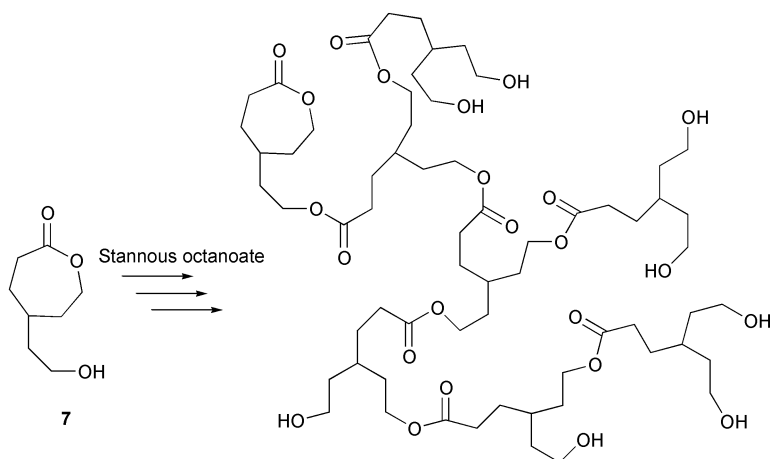
Cross-linkable high-performance polymers, such as glycidyl functional poly(ether sulfonamide)s, can find uses in solvent resistant materials.<sup>54</sup>

Conetworks are cross-linked polymers in which the chains are segmented, usually into sequences of differing solvent solubility. The inclusion of the cross-links usually alters the phase structure of these materials compared to the linear block copolymers or similar binary blends. Currently only a few methods are available for their synthesis: either di- or polyfunctional macromonomers, composed of one of the blocks, are copolymerized with low molecular weight monomers or telechelic oligomers, with differing repeat units, are coupled together. Du Prez *et al.* have

reported an example of the latter process which produces networks with shape memory capability.<sup>55</sup> The networks were prepared by radical polymerization of a poly-(octadecyl vinyl ether) with  $\alpha,\omega$ -bismethacrylate chain ends. Also, Rimmer *et al.* used macromonomers derived from the cleavage of high molecular weight polymers in the synthesis of amphiphilic networks.<sup>56</sup>

## 6 Highly branched polymers

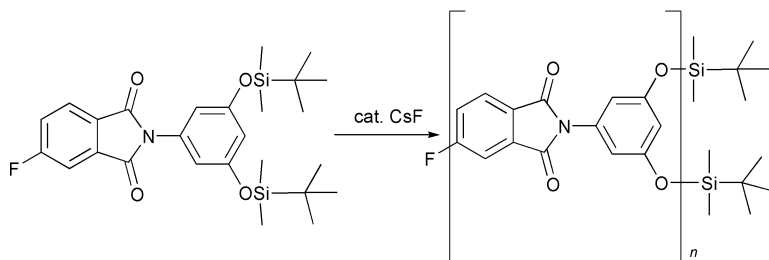
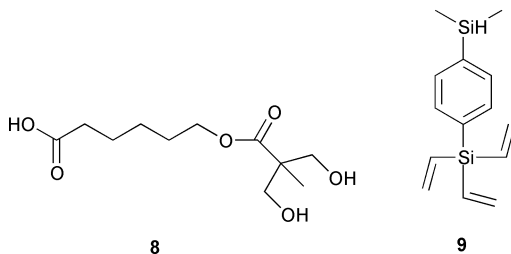
Highly branched polymers, arborescent polymers, hyperbranched polymers and dendrimers, have useful properties associated with their high end group content and several new methods for their synthesis have been reported. Liu *et al.* have extended the concept of self-condensing vinyl polymerization to insertion ring opening polymerization by use of a hydroxy functional  $\epsilon$ -caprolactone, **7** (see Scheme 10). The ring-opening polymerization proceeds with transfer to the hydroxy group.<sup>57</sup> This methodology has been extended by the incorporation of a bromo-functional  $\epsilon$ -caprolactone monomer.<sup>58,59</sup> The latter self-condensing polymerizations and simultaneous polymerizations involve carrying out more than one polymerization in the same pot and at the same time. Another approach to hyperbranched poly( $\epsilon$ -caprolactone) involves polyesterification of the macromonomer, **8**.<sup>60,61</sup>



**Scheme 10** Synthesis of hyperbranched poly( $\epsilon$ -caprolactone).

Hyperbranched poly(ether imides) have been prepared by the catalytic condensation of  $AB_2$  monomers containing aryl fluoride and  $2 \times$  *tert*-butyldimethylsilyloxy groups (see Scheme 11).<sup>62</sup> An important aspect of this synthesis was the use of the *tert*-butyldimethylsilyloxy protection groups, which were found to have enhanced stability when compared to the trimethylsilyloxy variant.

The unique properties of hyperbranched polymers have also been used to increase the solubility of polycarbosilanes. The polymerization is based on the polyhydrosilation of monomer, **9**.<sup>63</sup>



**Scheme 11** Synthesis of hyperbranched poly(ether imides).

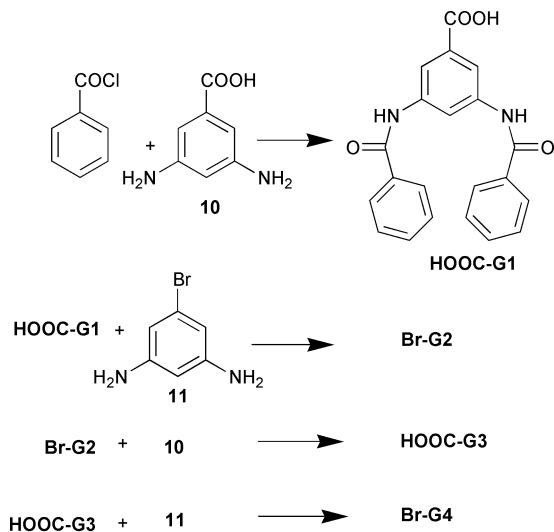
Emrick *et al.* have demonstrated that it is possible to produce hyperbranched polymers from A2 + B3 type polymerizations by control of conversion and stoichiometry. These authors used 1,2,7,8-diepoxyoctane and 1,1,1-tris(hydroxymethyl)ethane as the A2 and B3 monomers respectively.<sup>64</sup> Other new hyperbranched polymers include poly(aryl ether ketone)s with carboxylic acid end groups derived from condensation of 5-phenoxyisophthalic acid.<sup>65</sup> Further functionalization of the chain ends of dendrimers was achieved by palladium-catalysed cross coupling,<sup>66</sup> hydroboration/oxidation<sup>67</sup> or reaction with sugar-substituted  $\alpha$ -amino acid *N*-carboxyanhydrides (glycoNCAs).<sup>68</sup> The orthogonal synthesis route was used to prepare aromatic polyamide dendrimers using the route shown in Scheme 12.<sup>69</sup>

## 7 Topological systems

Topological polymers present synthetic challenges and should possess rheological properties that differ from the usual covalently linked polymers.

Although many reports of rotaxanes have been published only a few polycatenanes are known. Poly(catenanes) have been prepared by Muscat *et al.*<sup>70</sup>

Cyclodextrins are useful readily available cyclic components of topological systems and have found uses in enhancing monomer solubility in water<sup>71-74</sup> and as components of rotaxanes.<sup>75</sup> Ritter *et al.* have shown that cyclodextrins dethread when attempts to produce rotaxanes by radical polymerization of vinyl monomers in the presence of cyclodextrins in water are carried out.<sup>76</sup> However, Gibson *et al.* have now shown that threading of crown ethers can be achieved in the polymerization of styrene if bulky initiators, which produce bulky stopper end groups, are used.<sup>77</sup> Other syntheses of



**Scheme 12** Synthesis of aromatic polyamide dendrimers.

macrocyclic compounds include the oxidative synthesis of cyclic arylene sulfides.<sup>78</sup> Other cyclic oligomers that may find uses in the synthesis of rotaxanes and catenanes include cyclic polyesters produced by depolymerization of polyundecanoate.<sup>79</sup>

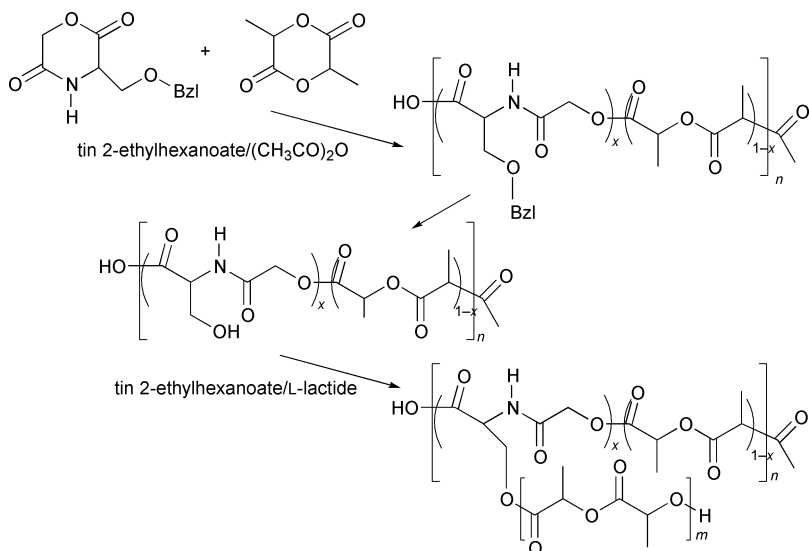
Polyrotaxanes have been proposed for several applications, including drug delivery and with this latter aspect in mind Ooya and Yui have prepared a rotaxane with peptidic biodegradable termini.<sup>80</sup> Another rotaxane has been produced by a reaction involving simultaneous threading of the macrocycle cucurbituril during polymerization.<sup>81</sup> Branched polymers can be prepared by a method that has been named 'macromolecular knitting' by Gibson. The method involves the threading of polymers into main rings resident on another polymer chain.<sup>82</sup>

## 8 Polymers for biological applications

Polymers form an essential aspect of many biotechnologies and many polymer groups are now turning their attention to the synthesis of polymers for specific biotechnological tasks. Many of the pseudodesign approaches involve the synthesis of polymers containing biodegradable units or biochemical signalling groups. However, true engineering design is not yet possible since structure/bioproperty relationships in many cases remain elusive.

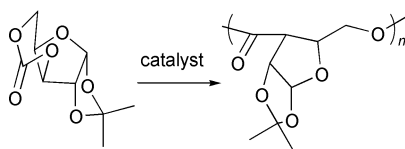
The well-established metal-insertion mechanism that operates in the ring-opening polymerization of lactones and related monomers can also be used to copolymerize cyclic amide-ester monomers and yields depsipeptides. In an attempt to control *in vivo* degradation Tasaka *et al.* have extended this work to the synthesis of comb-like polymers by transfer to hydroxy groups on serine units of a linear depsipeptide.<sup>83</sup> The

methodology is shown in Scheme 13. The same metal-insertion route has also been used to produce sugar functional polyglycolates.<sup>82</sup>



**Scheme 13** Synthesis of branched depsipeptides.

Enzymatic ring-opening polymerization of lactides has several advantages over the transition metal mediated insertion process. However, esterases that can efficiently polymerize lactide monomers have not been reported. This is well illustrated by the work of Deng and Gross.<sup>84</sup> These authors polymerized  $\epsilon$ -caprolactone from the 6-O position of ethyl glucopyranoside with catalysis by porcine pancreatic lipase. However, further elaboration of the ethyl glucopyranoside core with poly lactide chains required catalysis with stannous octanoate. Many other polymers containing sugar groups are available but very few involve placing the sugar moiety within the polymer backbone. One way of doing this involves the ring-opening copolymerization of 1,2-*O*-isopropylidene-*D*-xylofuranose-3,5-cyclic carbonate.<sup>85,86</sup> The method shown in Scheme 14 involves the ring-opening polymerization of cyclic carbonate *via* either coordinative or anionic catalysis. An aluminium–salen complex has also been shown to be a room temperature initiator for the controlled ring-opening polymerization of lactides.<sup>87</sup>



**Scheme 14** Ring-opening polymerization of 1,2-*O*-isopropylidene-*D*-xylofuranose-3,5-cyclic carbonate.

Photocross-linking is a useful method for producing networks in film form and the method has now been extended to the synthesis of biodegradable polyamino acid hydrogels. The method involves the  $2\pi + 2\pi$  photocycloaddition of lysines containing coumaryl units.<sup>88</sup> Functionalization of polylactides can be achieved by copolymerization with monomers such as 2,2-[pent-2-ene-1,5-diyl]trimethylene carbonate.<sup>89</sup>

$\alpha$ -Amino,  $\omega$ -carboxylic oligomers are useful as comonomers in the synthesis of polyamino acid block copolymers and the living cationic polymerization of tetrahydrofuran initiated by ethyl 6-hydroxyhexanoate and terminated with hexamethylenetetramine is a recently reported example.<sup>90</sup> Many biological structures are amphiphilic, in that proteins and glycosylated structures often contain both hydrophilic and hydrophobic sequences (blocks). Therefore, there is considerable interest in the biological properties of synthetic analogues of these materials. For example, tissue compatible multi-block copolymers have been reported by Lendlein *et al.*<sup>91</sup>

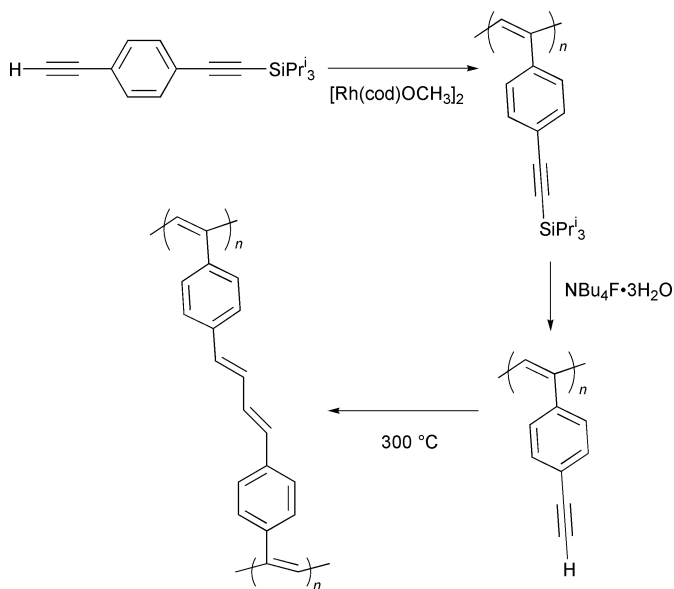
## 9 Conducting and electroluminescent polymers

Many new conjugated polymers have been reported. The main objectives of these works are: tuning of the wavelengths of emission; enhanced processability; and increasing the emission life times. Examples include: a green-light emitting material [poly(bicarbazolyene-*alt*-phenylene(cyanovinylene))], which was prepared by a nitrile Knoevenagel condensation,<sup>92</sup> soluble polythiophenes prepared by oxidative polymerization of alkylsulfanyl substituted thiophenes;<sup>93</sup> nematic alkyl substituted polythiophenes that were prepared by condensation of diformyl thiophenes with hydrazine;<sup>94</sup> a synthesis of a polyacetylene with phenyleneethynylene side groups;<sup>95</sup> and a blue emitting rigid rod polyamide.<sup>96</sup> Low yields of a new polymer that may possess donor/acceptor and aryl passivating functionalities have been reported by Devasagayaraj and Tour.<sup>97</sup> The synthesis involves poly-Stille coupling. However, in common with many of these polyaryl syntheses, full analysis of the product was not reported.

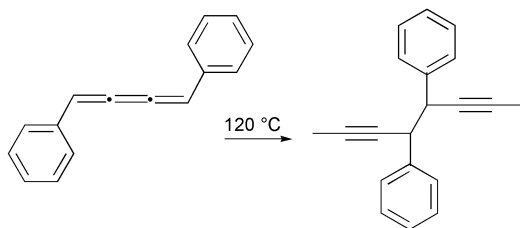
Block copolymers have been proposed as a means of controlling the conjugation length and thus the colour of light emitted from electroluminescent polymers. An example is the synthesis of poly(*p*-phenyleneethynylene)-*b*-poly(ethylene oxide) rod-coil block copolymer.<sup>98</sup>

Conjugated networks can offer some unique properties. A successful approach to such materials is shown in Scheme 15 and was reported by Lavastre *et al.*<sup>99</sup> The novel step in this procedure is the use of the silyl-protected monomer.

A new method for the preparation of polyacetylenes involves the base-catalysed rearrangement of butatrienes (Scheme 16).<sup>100</sup> One of the oldest routes to useful polymeric materials involves the condensation of formaldehyde with phenol and derivatives of phenol. However, the reaction has recently been used to produce polymers with potential for conduction *via* hole transport.<sup>101</sup> The synthesis involves condensation of either formaldehyde or benzaldehyde with an aryl amine, **12**, as shown in Scheme 17.



**Scheme 15** Synthesis of conjugated network derived from cross-linking of poly[(4-ethynylphenyl)acetylene].

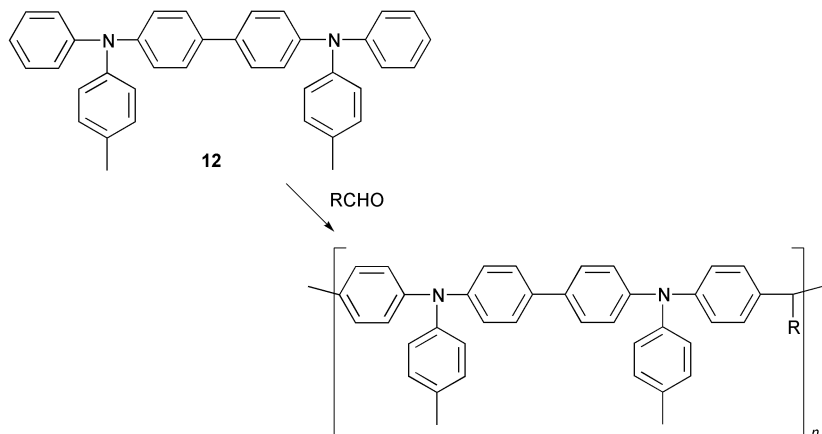


**Scheme 16** Polymerization of butatrienes.

Highly branched electroactive materials may offer some new properties. With this in mind Malenfant *et al.*<sup>102</sup> have polymerized 2,2'-bithien-5-yltrimethylstannane in the presence of a bromothiophene functional dendrimer. Also, Morgenroth *et al.* have used Diels–Alder condensations to prepare dendritic polyphenylenes.<sup>103</sup> With the aim of modifying the solubility of oligothiophenes, oligothiophenes that emanate from the core of polyether dendrimers have been prepared. The procedure involved esterification of the free hydroxy group on the core of a G3 dendron.<sup>104</sup>

## 10 Organometallic mediated polymerizations

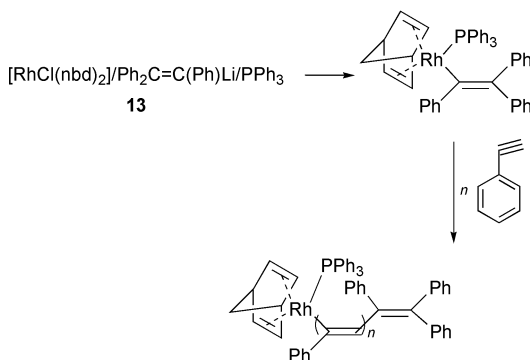
Organometallic compounds often offer useful catalytic routes to both polymers and related small molecules. In this section we review some of the newer uses of these



**Scheme 17** Polycondensation of *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)biphenyl-4,4'-diamine with aldehydes.

materials and in particular highlight systems that provide either more control over existing polymerizations or new routes to polymers that could otherwise not be synthesized. However, radical polymerizations that are mediated by organometallics are dealt with in the section on radical polymerizations.

Control of the coordination polymerization of phenyl acetylenes has been achieved using  $\text{RhCl}(\text{nbd})_2/\text{Ar}_2\text{C}=\text{C}(\text{Ph})\text{Li}/\text{PPh}_3$  catalysts, **13**. The proposed propagating species is shown in Scheme 18.<sup>105</sup>



**Scheme 18** The initiation and propagation of phenylacetylene achieved with **13**.

Polycarbosilanes can be prepared by thermal ring opening of 1,3-disilacyclobutanes but Wu *et al.* have now shown  $\text{Pt}(\text{acac})_2$  can catalyse an extremely efficient low temperature ring-opening photopolymerization.<sup>106</sup> The synthesis of narrow polydispersity polydienes with a high content of 1,4-*cis* repeat units has until now been

difficult. However, Kaito *et al.* have now reported that lanthanide metallocene complexes such as  $(Cp_5Me_5)_2LnR$  or  $(Cp_5Me_5)_2Sm(THF)_2$  when modified with methylaluminumoxane/isobutylaluminumoxane produced polymerization of butadiene.<sup>107</sup> The polydispersities were relatively narrow ( $<2$ ) and the polymers had very high 1,4-*cis* contents.

Supercritical solvents such as  $CO_2$  are often claimed as environmentally friendly reaction media that can support cationic and transition metal mediated reactions. An interesting advance in the field has been the use of supercritical  $CO_2$  as the reaction medium for the rhodium catalysed polymerization of phenylacetylene.<sup>108</sup> The use of a fluorinated triphenylphosphine as the catalyst ligand produced an increase in selectivity for the *cis-trans* polymer.

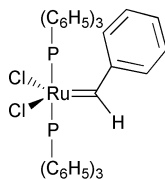
Functionalized polyolefins are interesting materials since they can provide chemical functionality whilst maintaining the mechanical properties of polyolefins. One method of preparing these materials is to use the new generation of metallocene catalysts such as metallocene/borates.<sup>109</sup> Other ethylene polymerization catalysts include: Schiff base complexes of aluminium;<sup>110</sup> bis(imino)pyridyl iron and cobalt complexes;<sup>111</sup> chromium(III)  $\beta$ -diketonate or pyrrolide-imine complexes;<sup>112</sup> zirconium-based<sup>113</sup> and palladium iminophosphine<sup>114</sup> catalysts. Hydrogen has been added to ethylene polymerizations and can be used to control the molecular weight distribution.<sup>115</sup> Telechelic olefins are very useful building blocks for block, graft and network synthesis but few methods are available for their synthesis. Polypropylene telechelics have now been prepared and the synthesis involves a  $V(acac)_3/AlEt_2Cl$  catalyst.<sup>116</sup> Polymerization of cyclopentene has been achieved with  $\alpha$ -diimine complexes of nickel and palladium. The resultant polymer had a new crystalline form and is reported to have different physical properties to any other previously reported poly(cyclopentene).<sup>117</sup>

Metalloproteins are of enormous importance in biological catalysis and some efforts are underway to mimic these structures with synthetic polymers. One method of preparing these polymers is to use the metallo-initiator approach in which the metal is present as part of the initiator residue on the final polymer. The method has been pioneered by Fraser and includes, for example, star shaped poly(2-ethyl-2-oxazoline) prepared by initiation with multi-functional initiators of general formula  $[(bipy)_n\{bipy(CH_2Cl_2)\}_{3-n}](PF_6)_2$ .<sup>118</sup>

## 11 Metathesis

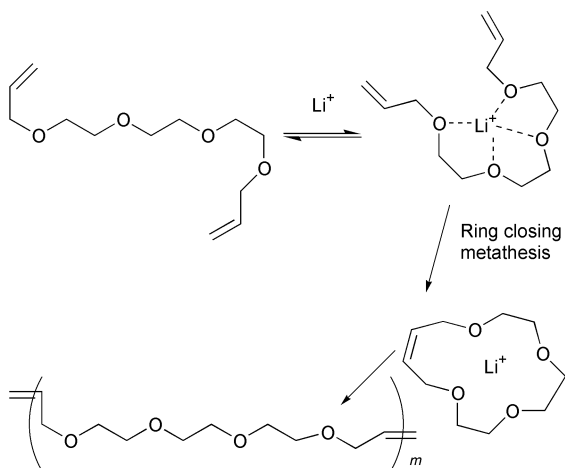
Phosphorus-containing polymers with potential as fire retardants were prepared by Allcock *et al.*<sup>119</sup> Classical ROMP (Ring Opening Metathesis Polymerization) initiators such as  $WCl_6Bu_4Sn$  were subject to side reactions and yielded only oligomers. However, complexes such as **14** are known to coordinate soft alkenes in preference to polar groups such as alcohol, aldehyde, *etc.* and polymerized the phosphazine-functionalized norbornenes to moderate degrees of polymerization.

A new route, shown in Scheme 19, to polyether polyols, of potential use in synthesis of segmented elastomers, has been reported. The route involves first ring-closing



14

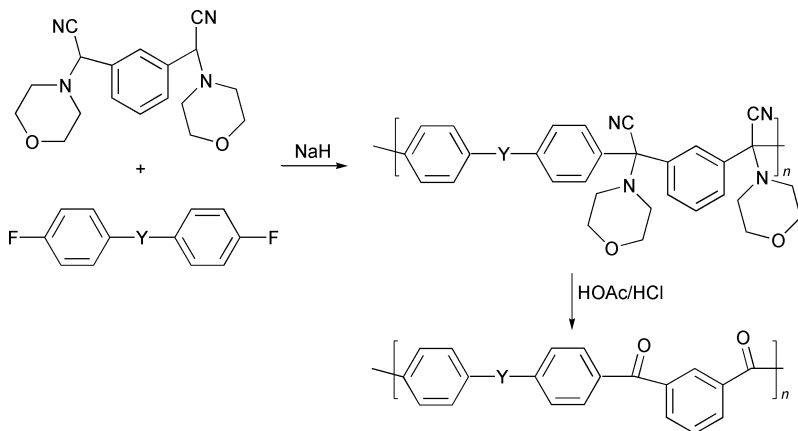
metathesis, in the presence of an alkali metal ion template, followed by ROMP.<sup>120</sup> The ROMP of [2]carbothiaferrocenophane has been reported and is claimed to be the first cationic ring-opening polymerization of a metal-containing ring.<sup>121</sup> ROMP of 2,3-diazanorborn-5-ene derivatives has been studied using molybdenum-based initiators and can lead to narrow molecular weight distributions.<sup>121</sup>



Scheme 19 Synthesis of polyethylene oxides *via* ROMP.

## 12 Polyaryls

Polyarylates are technologically important materials due to their excellent resistance to thermal, chemical, radioactive degradation. However, processing is often problematic and several approaches to soluble materials have been proposed. A recent development is the use of nucleophilic substitution reactions by carbanions derived from bis( $\alpha$ -aminonitrile)s on aryl fluorides.<sup>122,123</sup> As shown in Scheme 20, the method produces initially, polymers that are soluble due to the presence of morpholino nitrile groups. However, following processing, they can be converted into aryl ketone groups. The polymerization of cyclic oligomers is a relatively new development in the



**Scheme 20** Synthesis of polyaryl ketones *via* soluble morpholino nitrile precursors.

synthesis of high-performance polymers. An example is the polymerization of cyclic oligomers of poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene).<sup>124</sup>

### 13 Miscellaneous polymerizations

Ladder polymers have been prepared in an A-R-B condensation of 2-furfuryl-maleimide.<sup>125</sup> Furfuryl polymers can also be prepared by bubbling hydrogen sulfide through furfuraldehyde solutions.<sup>126</sup> The use of common gases, such as carbon dioxide, as monomers has environmental advantages and this gas has been copolymerized with cyclohexene oxide to yield polycarbonates.<sup>127</sup>

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