

# **Synthesis and Characterization of Poly(arylene ether sulfone)s with Novel Structures and Architectures**

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy  
In  
Chemistry

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April 9, 2009  
Blacksburg, Virginia

Keywords: poly(arylene ether sulfone)s, poly(arylene ether ketone)s, dendritic polymers, linear-dendritic copolymers, structure-property relationship

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# **Synthesis and Characterization of Poly(arylene ether sulfone)s with Novel Structures and Architectures**

**Keiichi Osano**

## **ABSTRACT**

Poly(arylene ether sulfone)s with dendritic terminal groups were synthesized by step-growth polymerization of two difunctional monomers in the presence of preformed dendritic end-cappers. These polymers were characterized by NMR, SEC, DSC, TGA, melt rheology and tensile tests. The melt viscosities of these polymers in the high frequency region were lower than the control while the stress-strain properties were comparable to those of the control, suggesting that it is possible to reduce the high shear melt viscosities of this type of polymers without affecting the stress-strain properties by introducing bulky dendritic terminal groups.

Poly(arylene ether sulfone)s with hyperbranched terminal groups were also synthesized. These polymers were synthesized by reacting fluoro-terminated poly(arylene ether sulfone) chains with an arylene ether ketone AB<sub>2</sub> monomer. The terminal groups of these polymers were capped by tert-butylphenol. The results from NMR and SEC showed that multiple tert-butyl units were successfully introduced onto the polymer chains, suggesting that this synthetic method could be useful for introducing multiple functional groups onto the polymer chain ends in fewer synthetic steps than an analogous method using preformed dendritic end-cappers. It was also demonstrated that multiple sulfonated phenols were attached to the terminal groups of polysulfones by this method.

A novel cyclohexyl-containing difunctional monomer was prepared and successfully incorporated into poly(arylene ether sulfone) backbones. These polymers

were characterized by NMR, SEC, DSC, TGA, DMA and tensile tests and compared to terephthaloyl analogs. Tensile tests and DMA showed the cyclohexyl units impart a higher magnitude of secondary relaxation than the terephthaloyl units while maintaining high modulus, suggesting that these polymers may have higher impact strength than the ones with no cyclohexyl units.

## Acknowledgements

I would like to thank my research advisor, Dr. S. Richard Turner, for his diligent and inspiring guidance throughout my graduate work at Virginia Tech. He not only gives me many useful ideas on my research but also encourages and allows me to try my own ideas. He has also been spending a lot of time to read and check this dissertation for me. I would also like to acknowledge my advisory committee members, Dr. James McGrath, Dr. Judy Riffle, Dr. Herve Marand and Dr. Harry Gibson for their useful advice, suggestions and help on my research.

I would like to thank Dr. Thomas Ward, Dr. Herve Marand and Dr. Garth Wilkes for taking their precious time to discuss some of our research results with us.

I would like to express my gratitude to Dr. Timothy Long for allowing me to use many of his instruments. Many of the research results that I report in this dissertation were measured by his instruments. He was also one of my advisory committee members in the early years of my graduate school and took a lot of his time to give me valuable suggestions on my research.

I have been greatly encouraged and helped by my colleagues in the lab, Min Mao, Shauntrece Hardrict, LaShonda Cureton, Yanchun Liu, Yi Li, Bin Zhang, Zheyun Lu and Xu Zhou. Special thanks go to Min Mao, who worked as a mentor for me in the early years of my graduate school. He also gave me a lot of valuable help outside the lab.

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## Chapter 1: Dissertation Overview

The focus of this dissertation is on the synthesis of poly(arylene ether sulfone)s with novel structures/architectures and characterization of such polymers. This thesis starts with a literature review on synthesis of branched polymers and linear-branched copolymers, and the mechanical and rheological properties of these structures. The focus of the next three chapters (Chapter 3, 4 and 5) is on the synthesis and characterization of poly(arylene ether sulfone)s with branched terminal groups, followed by two chapters (Chapter 6 and 7) describing the synthesis and characterization of novel poly(arylene ether ketone sulfone)s containing 1,4-cyclohexyl units in the polymer backbones.

Chapter 3 describes the synthesis and characterization of linear poly(arylene ether sulfone)s with arylene ether ketone dendrons on the polymer chain ends and the investigation of structure-property relationship of this architecture. These polymers with ABA architecture were prepared by step-growth polymerization of two difunctional monomers and monofunctional end-cappers. Chapter 4 discusses the synthesis of linear poly(arylene ether sulfone)s with hyperbranched arylene ether ketone terminal groups. These polymers differ from those in Chapter 3 in that the hyperbranched terminal groups were constructed from the chain ends of poly(arylene ether sulfone)s instead of reacting preformed monofunctional end-cappers with polymer chain ends. Chapter 5 discusses efforts on various synthetic routes to functional and non-functional dendritic end-cappers for poly(arylene ether sulfone)s. Chapter 6 describes the synthesis and characterization of bisphenol A (BPA) based poly(arylene ether ketone sulfone)s containing cyclohexyl-groups in the polymer backbone. In this work, novel 1,4-cyclohexyl-containing monomer



units were incorporated into the polymer backbones and their effects on the thermal and mechanical properties were investigated. Chapter 7 discusses the synthesis of cyclohexyl-containing poly(arylene ether ketone sulfone)s containing different bisphenols. Chapter 8 shows the preliminary results of our ongoing experiments and possible future work based on these results. Preliminary results of sulfonated linear-dendritic ABA architecture for Proton Exchange Membrane (PEM) applications are discussed. Also, some ideas to introduce pendant functional groups onto poly(arylene ether) backbones as well as new strategies to build linear-dendritic ABA architectures using other types of polymer backbones are discussed.

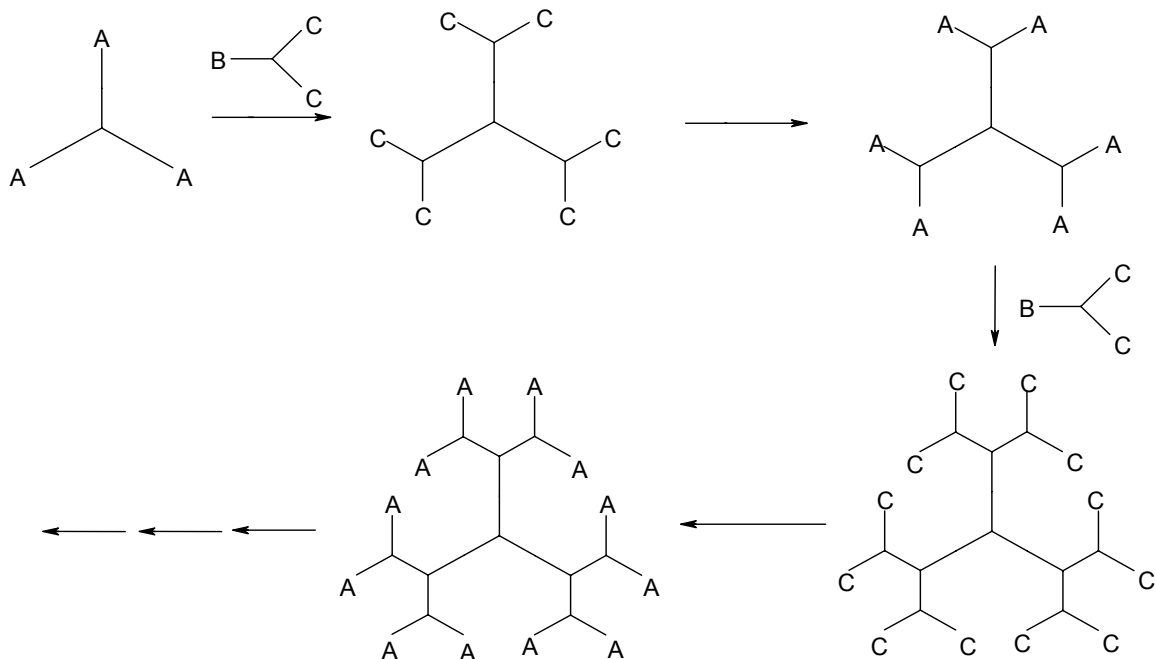
## **Chapter 2: Literature Review on Synthesis and Properties of Dendritic and Linear-Dendritic Copolymers**

### **2.1 Introduction**

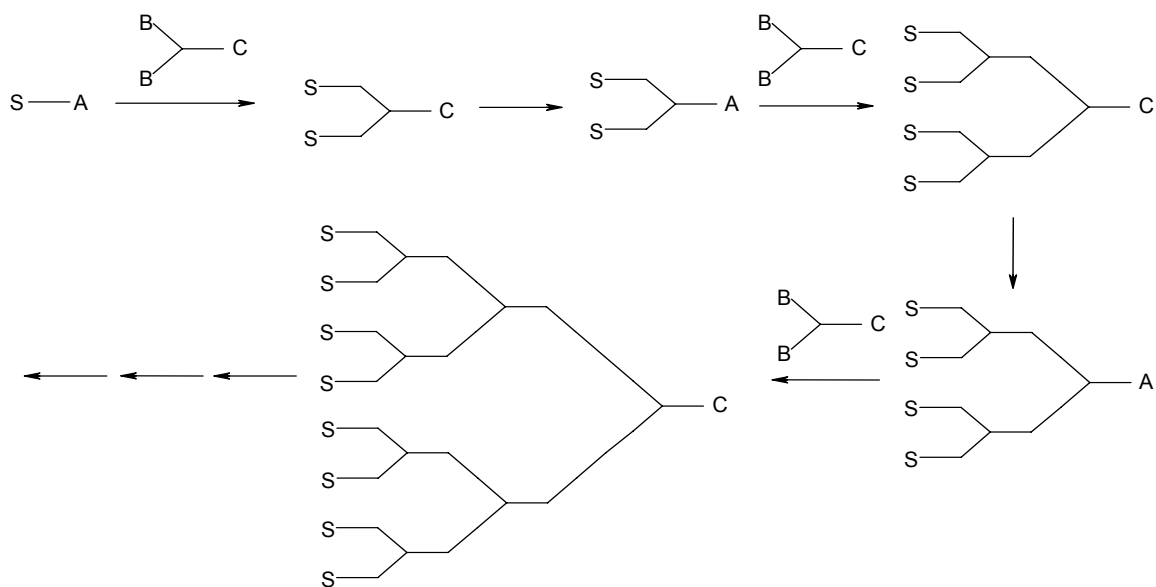
This chapter describes the history, synthetic methods and properties of dendritic and linear-dendritic copolymers.

### **2.2 Dendritic Polymers**

The first theoretical prediction of the synthesis of highly branched polymers based on  $AB_n$  type monomers (where  $n \geq 2$  and A can only react with B and vice versa) without forming an infinite network was reported by Flory in 1952.<sup>1</sup> It was, however, not until the early 1980s that the first successful synthesis of a dendrimer was reported although Vögtle et al. synthesized low molecular weight branched amines using what they call an “interactive cascade method” in 1978.<sup>2, 3</sup> This pioneering work was done by Tomalia et al., who synthesized what he called starburst dendrimers starting with ammonia as a core and divergently attached methyl acrylate and ethylenediamine repeatedly using Michael addition and amidation.<sup>2, 4</sup> At almost the same time, Newkome et al. also reported the synthesis of polyamide dendrimers by the divergent method.<sup>4, 5</sup> In 1990, Fréchet et al. reported the successful synthesis of a dendrimer by the convergent growth approach, in which dendrimer construction starts at the periphery of the final macromolecule and proceeds inward by adding branched monomers repeatedly, followed by the attachment of each dendron to a polyfunctional core.<sup>6</sup> 3,5-dihydroxybenzyl alcohol was used as the monomer and 1,1,1-tris(4'-hydroxyphenyl)ethane as the core.<sup>6</sup>



**Figure 2.1** Divergent growth method.<sup>2</sup>



**Figure 2.2** Convergent growth method.<sup>6</sup>

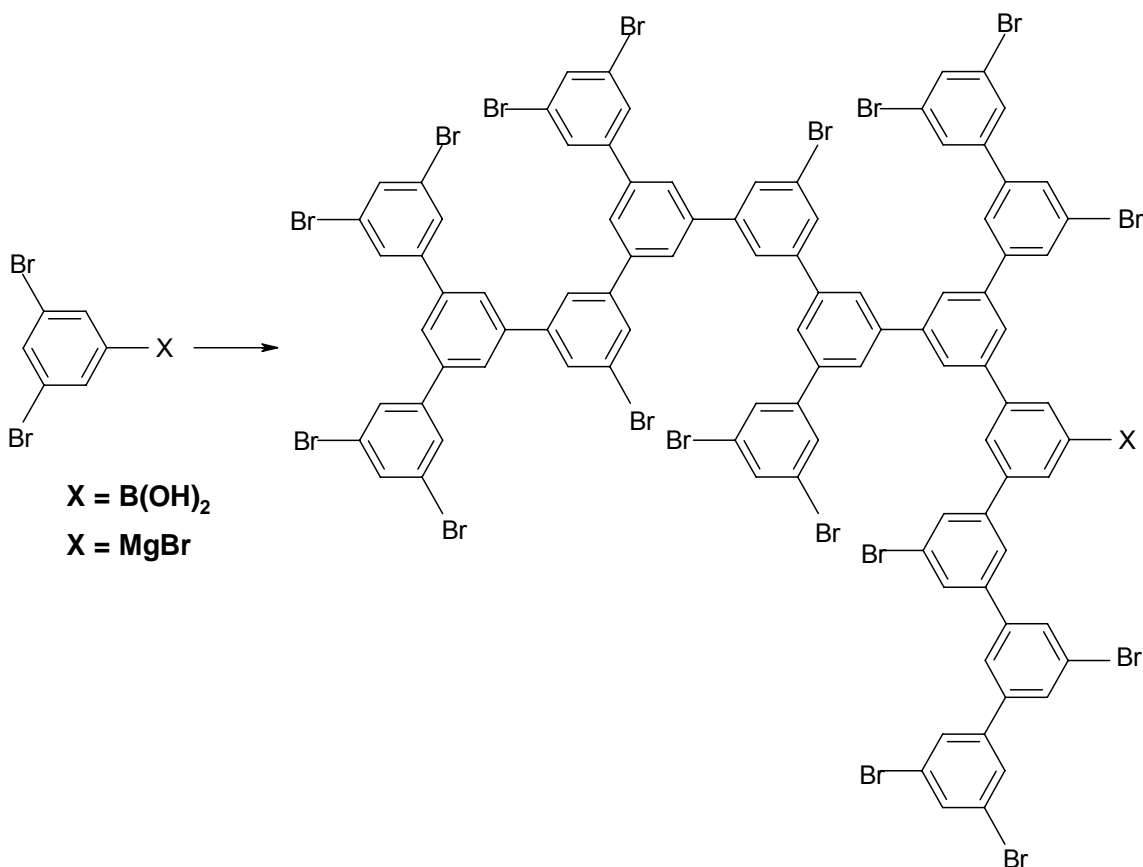
Figure 2.1 and Figure 2.2 show the divergent and convergent growth methods. In these figures, A and B are reactive functional groups, C is a protecting group, and S is an

inert moiety in the synthesis. The convergent growth method offers several advantages over the divergent-growth approach because fewer reactions are involved per molecule during coupling and activation steps, which result in fewer defect structures.<sup>7</sup> Also, the fact that the structures of defect species produced in the convergent-growth method are often sufficiently different from the ideal dendron or dendrimer, whereas they are extremely similar to each other in the divergent-growth method makes the isolation of intermediates or final target macromolecules in the convergent-growth approach easier.<sup>7</sup> Furthermore, since fewer reactions are involved per molecule during coupling and activation steps in the convergent growth approach, only a small excess of reagent is needed to drive the reactions to completion whereas the divergent-growth approach requires a large excess of reagent.<sup>7</sup>

Since the discoveries of Tomalia et al., Newkome et al. and Fréchet et al., the interest in the fields of dendrimers has been rapidly growing and a wide variety of dendrons and dendrimers have been synthesized including structures based on polyacetylene<sup>8</sup>, polyamides<sup>9-14</sup>, poly(carbosilane)s<sup>15</sup>, poly(amino acid)s<sup>11, 12</sup>, poly(ether ketone)s<sup>16-19</sup>, poly(thio ether)s<sup>20</sup>, polyesters<sup>21-27</sup>, poly(ester amine)s<sup>28, 29</sup>, poly(ether urethane)s<sup>30</sup>, polyurethanes<sup>31-33</sup>, polyazobenzene<sup>34</sup>, polyethers<sup>35, 36</sup> and polycarbonates<sup>37</sup>. In addition, organometallic dendrimers<sup>38-46</sup>, chiral dendrimers<sup>24, 47-52</sup> and dendrimers containing ions such as ammonium<sup>29, 53</sup> and carboxylate<sup>54</sup> have been reported.

There is another class of highly branched polymers called hyperbranched polymers, which can be prepared by the polymerization of AB<sub>n</sub> type monomers. Although the theoretical study of highly branched polymers was done by Flory early in the 1950s, this field did not attract people's attention until 1990 when Kim and Webster

reported their randomly branched polyphenylenes based on 3,5-dibromophenylboronic acid and 3,5-dibromomagnesium bromide.<sup>55</sup> Figure 2.3 shows the structures of these polymers.



**Figure 2.3** Hyperbranched polymers based on 3,5-dibromophenylboronic acid and 3,5-dibromomagnesium bromide.<sup>55</sup>

In addition to the  $\text{AB}_n$  approach, hyperbranched polymers can be alternatively prepared from the polymerization of  $\text{A}_2$  and  $\text{B}_3$  monomers. Preparations of hyperbranched polymers using this method usually require reaction conditions, such as stoichiometry, monomer concentrations and reaction time, be carefully controlled in order to avoid gelation because gel formation is much more common in  $\text{A}_2+\text{B}_3$  approach

than in  $AB_n$  approach.<sup>56</sup> Furthermore, hyperbranched polymers prepared by these two methods are structurally different from each other in that each hyperbranched polymer prepared by  $AB_n$  approach has always one focal unit assuming that there are no side reactions such as cyclics and gel formations, whereas  $A_2+B_3$  approach results in a mixture of hyperbranched polymers with and without focal points.<sup>56</sup> Nevertheless,  $A_2+B_3$  approach is a useful alternative to prepare hyperbranched polymers especially when  $AB_n$  type monomer of interest is neither commercially available nor easy to synthesize.

Since the discovery of Kim and Webster, a wide variety of hyperbranched polymers have been synthesized based on structures such as polyethylene<sup>57</sup>, polystyrene<sup>58</sup>,<sup>59</sup>, poly(sulfone amine)s<sup>60-62</sup>, polyureas<sup>63</sup>, polyacrylates<sup>64</sup>, polyamides,<sup>65-72</sup> polyurethanes<sup>73-75</sup>, poly(ether urethane)s<sup>76</sup>, polyethers<sup>77</sup>, poly(arylene acetylene)s<sup>78</sup>, poly(ether amide)s<sup>79</sup>, polyesters<sup>74, 75, 80-108</sup>, poly(ether ester)s<sup>109, 110</sup>, poly(ester amide)s<sup>111</sup>,<sup>112</sup>, polycarbonates<sup>113-115</sup>, poly(ether ketone)s<sup>19, 116-121</sup>, poly(amido amine)s<sup>122</sup>, poly(ether sulfone)s<sup>120, 121, 123, 124</sup>, liquid crystalline polymers<sup>87, 91, 94</sup>, and organometallic polymers<sup>125</sup>. In addition to these successful syntheses of numerous hyperbranched polymers, gelation presumably caused by trace amounts of impurities was also observed during the thermal self-condensation of 3,5-bis(trimethylsiloxy)benzyl chloride.<sup>80</sup>

Hyperbranched polymers are usually synthesized in one or two steps, as opposed to laborious stepwise synthesis of dendrimers, making it easier to synthesize larger quantities for studies or applications although there is a significant amount of unreacted or defect-containing units in these polymers. In other words, a hyperbranched polymer is an intermediate between a traditional linear polymer and a dendrimer in terms of degree

of branching. Degree of branching is defined as the sum of terminal groups and branched groups divided by the sum of all the repeat units.<sup>80</sup>

$$DB = (\Sigma \text{ Branched} + \Sigma \text{ Terminal}) / (\Sigma \text{ Branched} + \Sigma \text{ Terminal} + \Sigma \text{ Linear})$$

A hyperbranched polymer has a wide range of degree of branching depending on the nature of repeat units whereas a dendrimer, by definition, has a degree of branching equal to 100%. Statistically, the degree of branching of a hyperbranched polymer synthesized from an AB<sub>2</sub> monomer, where both B groups are equal in reactivity before and after one B group has been reacted, is 50%. In other words, if the reaction of one B group activates or deactivates the other B group, a deviation from this statistical value results. Most hyperbranched polymers have degree of branching of 40-60%.<sup>80, 99-102</sup> In spite of their lower degrees of branching and broader molecular weight distributions than ideal dendrimers, hyperbranched polymers have some physical properties similar to dendrimers.<sup>65, 80, 99-101, 103, 104, 118, 126-133</sup> Thus, hyperbranched polymers may expect to find applications in industry such as rheology modifiers, coatings, thermosets and adhesives where perfect monodisperse polymers are not necessary.<sup>134-138</sup> On the other hand, dendrimers have been studied for high precision applications such as drug delivery, gene vectoring, MRI diagnosis, and catalysis.<sup>139-143</sup> Although hyperbranched polymers have broad molecular weight distributions, fractionation of polydisperse hyperbranched polymers into fractions of narrow molecular weight distributions have been reported and this technique is expected to greatly broaden the potential applications of hyperbranched polymers.<sup>144, 145</sup>

## 2.3 Rheological Properties

Dendrimers are widely known to have unique physical properties that their linear analogs do not exhibit.<sup>139</sup> They show significantly lower melt and solution viscosities and higher solubility in common organic solvents than their linear analogs of the equivalent molecular weights because of the absence of intermolecular entanglements due to their dense periphery and globular shapes.<sup>139</sup> It has been shown that when dendrimers reach a certain generation (often 4<sup>th</sup>), they start to assume a globular shape and terminal groups experience significant congestions which lead to reduced crystallinity, higher solubility, lower solution viscosity and deviation from the Mark-Houwink relationship.<sup>146-148</sup>

$[\eta] = KM^a$  where K is a constant, M is molecular weight and a varies depending on the shape and size of the molecule

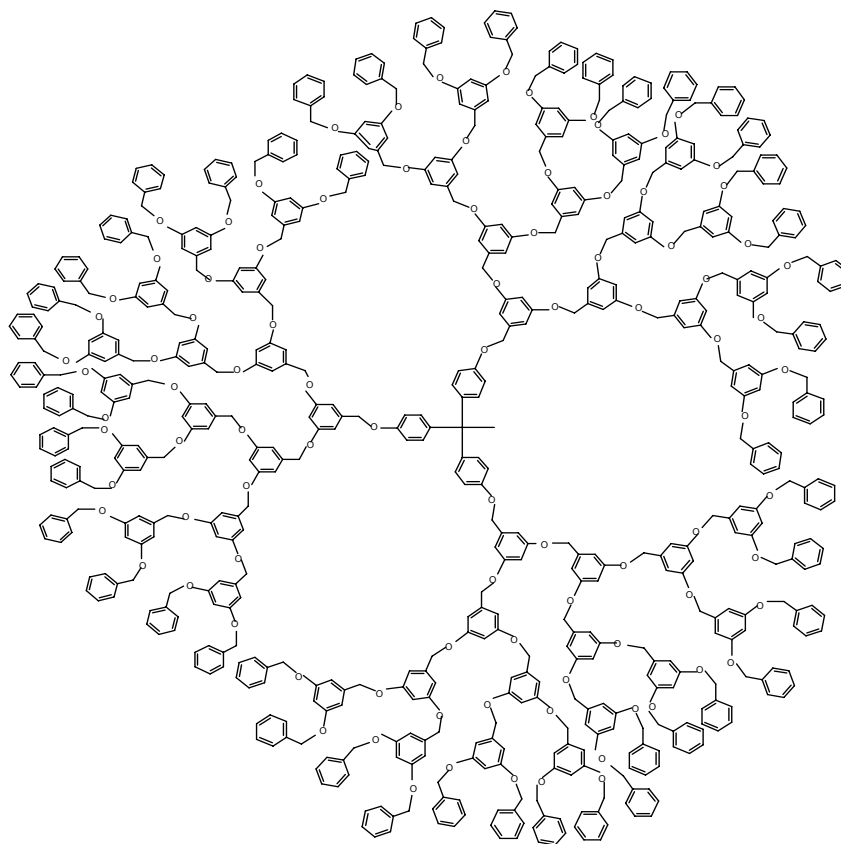
In addition, the zero-shear viscosity of a dendrimer is quite different from that of a traditional linear polymer whose dependence of zero-shear viscosity on molecular weight, as widely known, can be predicted by the following power law.<sup>80</sup>

$\eta_0 = KM^\alpha$  where  $\alpha$  is  $\sim 1.0$  for short chain polymers ( $M < M_c$ ) and  $\sim 3.4$  for long chain polymers ( $M > M_c$ )

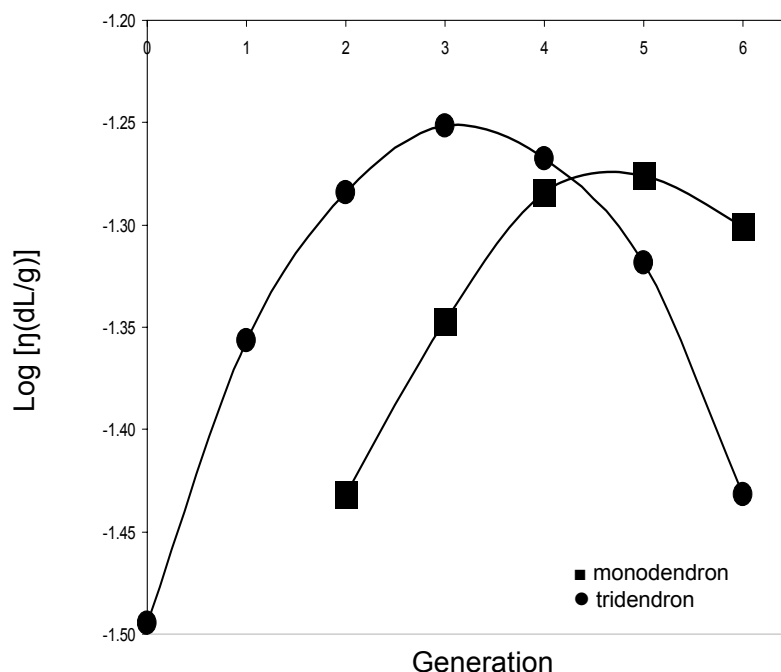
Many traditional linear polymers exhibit a sharp increase of the slope from 1.0 to 3.4 upon reaching their critical molecular weights for entanglement. As discussed shortly, a dendrimer does not show the sharp increase of  $\alpha$  from 1.0 to 3.4.<sup>149-152</sup>



Mourey et al. showed that a plot of intrinsic viscosity versus molecular weight for arylene ether dendrons and dendrimers, synthesized by the convergent-growth method, exhibited bell-shaped curves indicating that Mark-Houwink relationship is not valid for these dendritic polymers.<sup>146</sup> Figure 2.4 and Figure 2.5 show the structure of the G4 dendrimer and the viscosity-molecular weight plot, respectively.

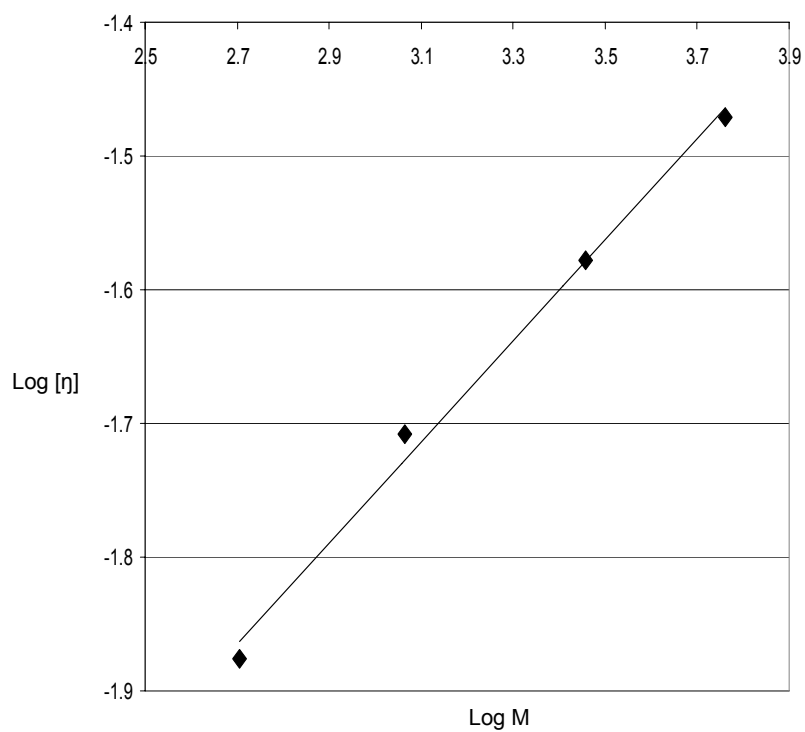


**Figure 2.4** Polyarylether dendrimer.<sup>146</sup>

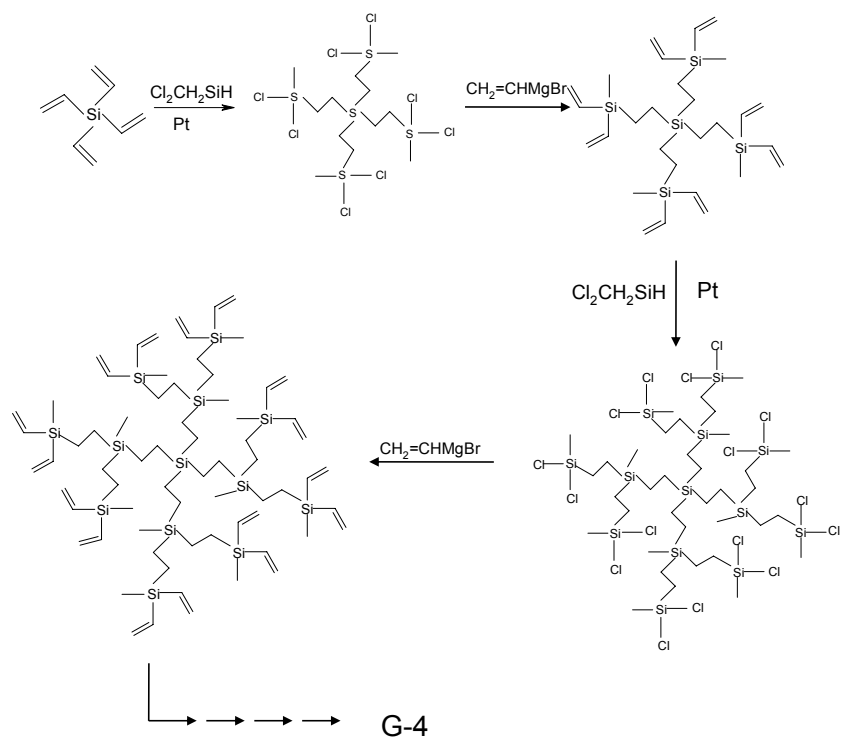


**Figure 2.5** Plot of  $\log [\eta]$  versus  $\log M_w$ .<sup>146</sup>

The low molecular weight carbosilane dendrimers synthesized by Zhou et al. using the divergent-growth method were also soluble in many organic solvents and exhibited lower viscosities than linear polymers.<sup>15</sup> Figure 2.6 and Figure 2.7 show the plot of intrinsic viscosity versus molecular weight for carbosilane dendrimers and the synthetic scheme for the carbosilane dendrimers, respectively. As we can see, the viscosity-molecular weight curve in Figure 2.6 is not bell-shaped like that observed in Figure 2.5 for dendritic poly(arylether)s because these dendrimers are fourth generation and below. This curve is expected to become bell-shaped if the data for the fifth generation and above are added to this plot.<sup>15</sup>



**Figure 2.6** Plot of  $\log [\eta]$  versus  $\log M_w$  for dendritic poly(carbosilane)s.<sup>15</sup>



**Figure 2.7** Synthetic scheme for dendritic poly(carbosilane)s.<sup>15</sup>

Hawker et al. and Farrington et al. studied the melt viscosities of mono- and tri-dendrons based on 3,5-dihydroxybenzyl alcohol and showed that the viscosity data for mono- and tri-dendrons fall onto a single curve on melt viscosity versus molecular weight plot, indicating that their viscosities are dependent on the molecular weights, not on focal point architectures.<sup>150, 151</sup> Another significant discovery was that the melt viscosities at molecular weights above  $10^4$  Da fell on a straight line with a slope of  $\sim 1.1$ , which is close to the Rouse prediction, but a sharp increase of slope to 3.4 was not observed, indicating that the viscosity behavior is not dominated by intermolecular entanglements.<sup>150</sup> The absence of an abrupt increase in  $\alpha$  value was also observed for polyamidoamine dendrimers by Uppuluri et al.<sup>152</sup> and for poly(propylenimine) dendrimers by Sendjarevic et al.<sup>149</sup>

Hyperbranched polymers exhibit significantly low solution and melt viscosities, high solubilities and low crystallinities, compared to the linear analogs of the equivalent molecular weights.<sup>153, 154</sup> This is not too surprising because it is known that an incorporation of branch structures into a linear polymer leads to lower viscosity and crystallinity than the branch-free linear polymer analog with the equivalent molecular weight.<sup>153, 154</sup> Turner et al. showed that the solution viscosity-molecular weight behavior of hyperbranched polyesters with acetate terminal groups, synthesized by melt condensation of 3,5-diacetoxybenzoic acid, followed the Mark-Houwink relationship like linear polymers, but differed from linear polymers in that these hyperbranched polyesters exhibited much lower viscosities than linear polymers of the same molecular weights.<sup>99</sup> In spite of the high molecular weights (up to  $\sim 1 \times 10^6$  Da), these hyperbranched polymers were soluble in common organic solvents such as THF and DMF.<sup>99</sup> The “a” value of the

Mark-Houwink plot was below 0.5, indicating that the hyperbranched polymers have highly branched, compact and globular structures.<sup>99</sup> Subsequently, Turner et al. synthesized the same hyperbranched polymers but with carboxylic acid end groups instead of acetate, using melt condensation of 5-acetoxyisophthalic acid.<sup>100</sup> These hyperbranched polymers gave a very similar relationship between solution viscosity and molecular weight and the value of “a” in the Mark-Houwink equation was below 0.5, which is consistent with the result just mentioned above.<sup>99, 100</sup> Plummer et al. also reported that their hyperbranched polyesters followed the Mark-Houwink law.<sup>155</sup> Nunez et al. reported that their hyperbranched polyester based on 2,2-dimethylol propionic acid and pentaerythritol core exhibited Newtonian behaviors in solution over a wide range of shear rate, which is good evidence of the absence of intermolecular entanglements.<sup>156</sup> Ahn et al. showed that hyperbranched poly(ether ketone)s exhibited more and more Newtonian-like behavior with increasing degree of branching, suggesting that the amount of entanglements decreased with increasing degree of branching.<sup>157</sup> Magnusson et al. also reported a similar relationship between degree of branching and Newtonian behavior using hyperbranched aliphatic polyethers.<sup>158</sup> Pettersson reported that a plot of viscosity of neat aliphatic hyperbranched polyester with a B<sub>4</sub> type core versus molecular weight showed the absence of intermolecular entanglements.<sup>159</sup> Luciani et al. reported that a plot of the melt viscosity versus molecular weight of hydroxy terminated aliphatic hyperbranched polymers showed no entanglement regimes.<sup>133</sup>

Theoretically, the number of end groups on an AB<sub>2</sub>-type hyperbranched polymer with n repeat units is equal to n+1. Therefore it is expected that end groups on a hyperbranched polymer have a significant effect on its physical properties, whereas the

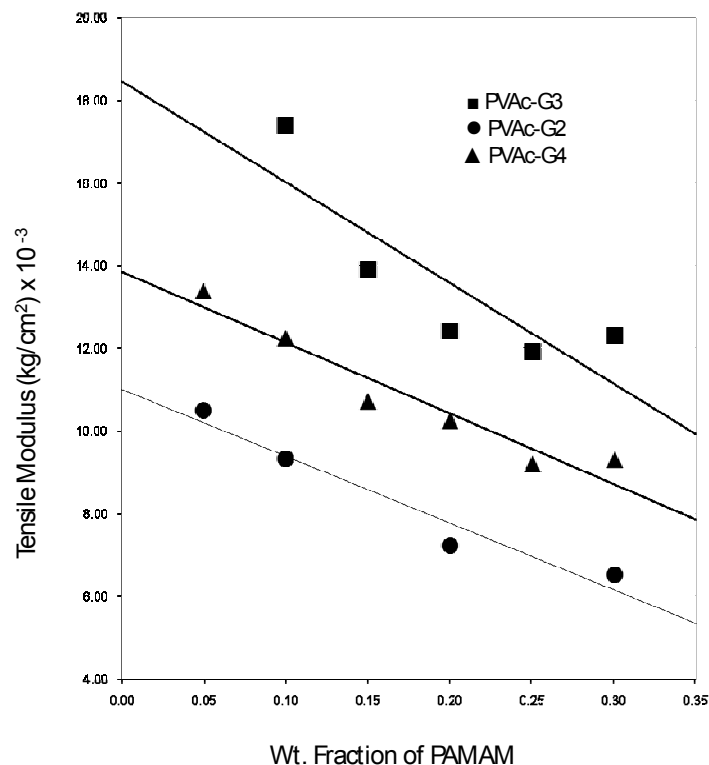
effects of end groups of a linear polymer should get smaller with increasing length of the polymer chain. The effects of end groups on the  $T_g$ s and other properties of hyperbranched polyesters have been reported to be strongly dependent on the nature of the end groups due to the large number of functional groups and it has been shown that  $T_g$  generally increases with increasing polarity of terminal groups.<sup>116, 160-162</sup>

Hyperbranched polymers can also be used as additives to reduce viscosity and/or crystallinity of materials.<sup>163-168</sup> Kim et al. reported that the melt viscosity of polystyrene could be reduced when blended with hyperbranched polyphenylene.<sup>164</sup> Jang et al. studied the crystallization behavior of a poly(ethylene terephthalate)s (PET) blended with hyperbranched aliphatic polyesters with  $B_3$  type cores and various terminal groups and showed that the hyperbranched aliphatic polyesters with hydroxyl terminal groups could effectively reduce both crystallinity and complex viscosity of the PET.<sup>163</sup> Similar results were observed in PET blended with a linear polyester, but the decrease in crystallinity and complex viscosity in this case was not as large as that exhibited by the PET-HBP blend.<sup>163</sup> Huber et al. demonstrated that the melt viscosity of polyamide-6 could be reduced without sacrificing the mechanical properties by blending hyperbranched poly(ether amide).<sup>167</sup> Böhme et al. mixed hyperbranched poly(ether amide)s with linear polyamide-6 and a significant reduction of melt viscosity was achieved without deteriorating the mechanical properties of the matrix polymers.<sup>169</sup>

## **2.4 Mechanical Properties**

Since dendrimers and hyperbranched polymers with high molecular weights usually have low degrees of entanglements, they exhibit poor mechanical properties (i.e.,

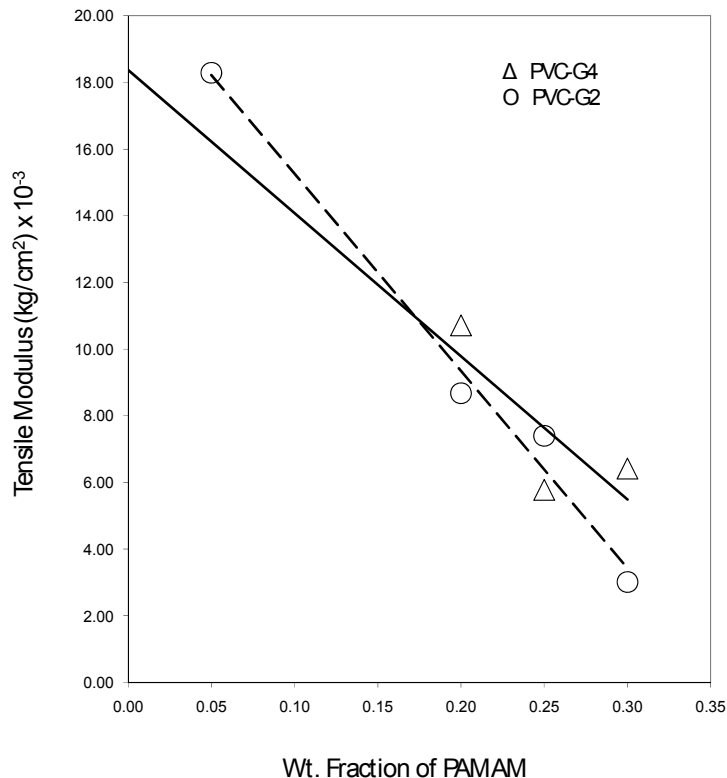
poor film forming abilities) unless used in combination with other types of polymers such as linear polymers that can have high degrees of entanglements.<sup>170</sup> Hyperbranched polyesters prepared by Turner et al., for example, showed no rubbery plateau in dynamic mechanical measurements.<sup>171</sup> Thus dendrimers and hyperbranched polymers have been investigated for their potential to modify the mechanical properties of existing linear polymers as additives, rather than as neat polymers. Ahn et al. studied the dynamic mechanical properties of hyperbranched poly(ether ketone)s having various degrees of branching and discovered that these hyperbranched poly(ether ketone)s exhibited higher brittleness with increasing degree of branching, indicating that the amount of entanglements decreased with increasing degree of branching.<sup>157</sup> Massa et al. showed that adding aromatic hyperbranched polyesters with hydroxyl and acetoxy terminal groups to linear polycarbonate resulted in higher tensile and compressive moduli and lower toughness.<sup>172</sup> Nunez et al. reported the tensile moduli of poly(amidoamine) dendrimer blends with poly(vinyl chloride) and poly(vinyl acetate) decreased with increasing dendrimer content.<sup>173</sup> Figure 2.8 and Figure 2.9 show the effects of dendrimer contents on the tensile moduli of PVAc and PVC films, respectively.



**Figure 2.8** Tensile modulus of PVAc-dendrimer blend film as a function of dendrimer content.<sup>173</sup>

Feast et al. studied the effects of blending linear PET with two aryl ester dendrimers of different sizes and reported that the mechanical properties of the blends were influenced by the size and/or shape of added dendrimer by showing that the smaller dendrimer acted as a plasticizer whereas the larger dendrimer acted as an antiplasticizer.<sup>174</sup> Pettersson reported that hydroxyl-terminated hyperbranched aliphatic polyesters, when used as additives in epoxy resins, led to an enhancement of toughness of the resins without the changing tensile modulus whereas commercial tougheners of various types did not give an enhanced toughness without lowering the tensile modulus.<sup>159</sup>



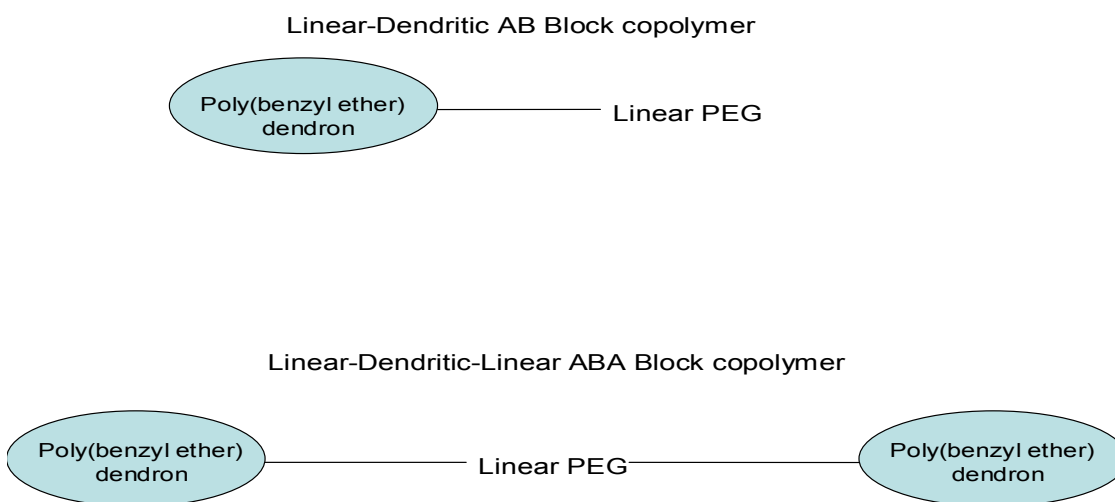


**Figure 2.9** Tensile modulus of PVC-dendrimer blend film as a function of dendrimer content.<sup>173</sup>

## 2.5 Linear-Dendritic Copolymers

A few years after the first examples of dendrimers and hyperbranched polymers were reported, hybrid linear-dendritic di- and triblock copolymers started to appear in the literature.<sup>175-177</sup> Figure 2.10 shows the simplified cartoon representations of the architectures of these hybrid polymers. Dendritic macromolecules have been attached to one or both ends of linear polymers by the coupling reaction of poly(ethylene oxide)s (PEOs) or poly(ethylene glycol)s (PEGs) and aryether dendrons to make linear-dendritic AB and dendritic-linear-dendritic ABA block copolymers.<sup>175-177</sup> Polystyrene and dendritic poly(benzyl ether) were also used to make a dendritic-linear-dendritic ABA block copolymer by the attachment of two dendritic units to a linear polystyrene

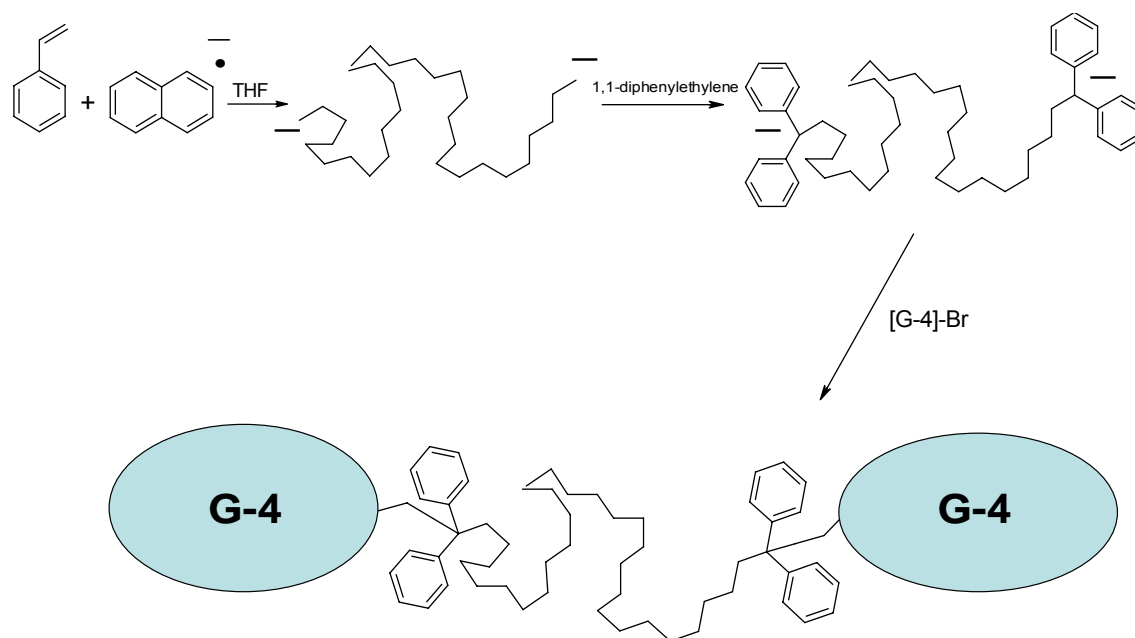
dianion.<sup>178</sup> This synthetic route is shown below. The linear polystyrene is represented in an abbreviated form in Figure 2.11. Malenfant et al. synthesized linear-dendritic triblock copolymer with poly(benzyl ether) dendrons as the terminal groups and oligothiophene as the linear segment by the coupling reactions of the preformed polymers.<sup>179</sup>



**Figure 2.10** Linear-dendritic hybrid polymers.

Successful syntheses of linear-dendritic AB block copolymers and dendritic-linear-dendritic ABA block copolymers by TEMPO were also reported.<sup>180, 181</sup> Dendritic-linear AB block copolymers were also synthesized by ring opening polymerization of lactones and lactides.<sup>182</sup> Froimowicz et al. synthesized hybrid dendritic-linear-dendritic triblock copolymers by divergently growing dendritic segments at the ends of a commercially available amine-terminated polyether using Michael addition, amidation, hydrogenation and hydrolysis reactions.<sup>183</sup> Namazi made triazine-PEG-triazine triblock copolymers by divergently growing the dendritic triazine.<sup>184, 185</sup> These AB and ABA hybrid architectures were reported to give rise to interesting properties such as microphase-separated structures<sup>186</sup>, alternating crystalline and amorphous layers<sup>187</sup>, and

unique rheological properties<sup>176, 188-197</sup>. Some of the AB and ABA copolymers reported by Gitsov et al. which was mentioned briefly above, exhibited lower solution viscosities than the pure linear polymers with no terminal dendrons.<sup>176</sup> Table 2.1 shows the solution behaviors of the preformed polymers and linear-dendritic hybrids. As we can see, the solution viscosity of the dendritic aryl ether-PEO46000 copolymer is significantly lower than that of the pure PEO46000 although the opposite effect is observed for some of the other hybrid polymers.<sup>176</sup> Table 2.2 shows the solution behaviors of the preformed PEGs and their ABA block copolymers with benzyl ether dendrons of various generations.<sup>176</sup> As we can see, the interesting point is that the hybrid polymers, [G-1]-PEG11000-[G-1], [G-2]-PEG11000-[G-2] and [G-3]-PEG11000-[G-3] exhibited lower solution viscosities than the pure PEG11000 whereas most of the other hybrids have higher solution viscosities than the pure PEGs.<sup>176</sup> Subsequent studies showed that these linear-dendritic AB block copolymers and dendritic-linear-dendritic ABA copolymers change their conformations depending on the surrounding medium by forming various macromolecular micelle structures.<sup>190-192</sup>



**Figure 2.11** Synthetic route to linear-dendritic-linear ABA block copolymers using polystyrene and dendritic poly(benzyl ether).<sup>178</sup>

**Table 2.1** Solution behavior of PEOs, benzylether dendrons and AB block copolymers in THF at 40 °C.<sup>176</sup>

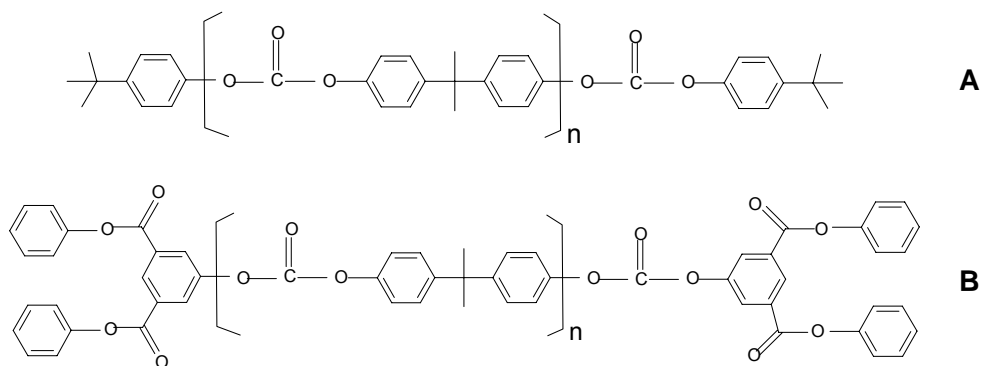
Initial block	$[\eta]$ , dL/g	$R_g$ , nm	AB/ABA copolymer	$[\eta]$ , dL/g	$R_g$ , nm
[G-1]-OH	0.023	0.56	-	-	-
[G-2]-OH	0.028	0.84	-	-	-
[G-3]-OH	0.035	1.10	-	-	-
[G-4]-OH	0.039	1.41	-	-	-
PEO4000	0.082	2.08	PEO4000-[G-4]	0.096	2.12
PEO7500	0.145	2.75	PEO7500-[G-4]	0.161	2.62
PEO26000	0.273	3.73	PEO26000-[G-4]	0.236	3.91
PEO46000	0.487	3.82	PEO46000-[G-4]	0.210	4.19
PEO7500	0.145	2.75	PEO7500-[G-1]	0.116	2.26
PEO7500	0.145	2.75	PEO7500-[G-2]	0.168	2.51
PEO7500	0.145	2.75	PEO7500-[G-3]	0.165	2.54
PEO7500	0.145	2.75	PEO7500-[G-4]	0.161	2.62

**Table 2.2** Solution behavior of PEGs and their ABA copolymers with benzyl etherdendrons in THF at 40 °C.<sup>176</sup>

A block	$[\eta]$ , dL/g	$R_g$ , nm	Copolymer	$[\eta]$ , dL/g	$R_g$ , nm
PEG1000	0.035	1.04	[G-1]-PEG1000-[G-1]	0.048	0.91
PEG1000	0.035	1.04	[G-2]-PEG1000-[G-2]	0.053	0.88
PEG1000	0.035	1.04	[G-3]-PEG1000-[G-3]	0.056	1.51
PEG1000	0.035	1.04	[G-4]-PEG1000-[G-4]	0.059	1.45
PEG2000	0.055	1.27	[G-1]-PEG2000-[G-1]	0.063	1.08
PEG2000	0.055	1.27	[G-2]-PEG2000-[G-2]	0.059	1.07
PEG2000	0.055	1.27	[G-3]-PEG2000-[G-3]	0.062	1.28
PEG2000	0.055	1.27	[G-4]-PEG2000-[G-4]	0.062	2.01
PEG5000	0.093	1.62	[G-1]-PEG5000-[G-1]	0.092	1.61
PEG5000	0.093	1.62	[G-2]-PEG5000-[G-2]	0.094	1.62
PEG5000	0.093	1.62	[G-3]-PEG5000-[G-3]	0.092	1.72
PEG5000	0.093	1.62	[G-4]-PEG5000-[G-4]	0.098	1.90
PEG11000	0.125	2.83	[G-1]-PEG11000-[G-1]	0.057	2.33
PEG11000	0.125	2.83	[G-2]-PEG11000-[G-2]	0.077	2.25
PEG11000	0.125	2.83	[G-3]-PEG11000-[G-3]	0.110	2.53
PEG11000	0.125	2.83	[G-4]-PEG11000-[G-4]	0.143	2.67

Jeong et al. investigated the intrinsic viscosities of linear-dendritic diblock copolymers with benzyl ether dendrons and polystyrene and reported that the intrinsic viscosities of diblock copolymers of certain molecular weights in a good solvent for both segments were lower than linear polystyrene.<sup>189</sup> Kwak et al. synthesized ABA copolymers using arylether ketone building blocks and reported that these polymers were entangled, which points out the possibility of improving poor mechanical properties of dendritic polymers by utilizing this ABA triblock architecture.<sup>193</sup> The effects of small branched terminal groups on the physical properties of linear polymers have also been studied by other groups and it has been shown that branched terminal groups lead to

lower viscosity of a linear polycarbonate.<sup>188</sup> Figure 2.12 shows the structures of polycarbonates with and without branched terminal groups and Table 2.3 shows the molecular weights, viscosities, and  $T_g$ s of the two polymers. As we can see, **B**, the one with a branched terminal groups, has a lower viscosity than **A** although the  $T_g$ s and molecular weights of the two polymers are essentially the same.<sup>188</sup>



**Figure 2.12** Structures of polycarbonates with (B) and without (A) branched terminal groups.<sup>188</sup>

**Table 2.3** Viscosities and  $T_g$ s of polycarbonates A and B.<sup>188</sup>

Polymer	M (g/mol)	$\eta_0$ @ 270 °C (Pa.s)	$T_g$ (°C)
<b>A</b>	$M_w=1.66 \times 10^4$ $M_n=7.92 \times 10^3$	216	145
<b>B</b>	$M_w=1.62 \times 10^4$ $M_n=7.83 \times 10^3$	182	142

The intrinsic viscosity of linear-dendritic block copolymers consisting of poly(acrylic acid) (PAA) as the linear segment and poly(benzyl ether) as the dendritic segment in aqueous media was measured by Zhu et al. and the Mark-Houwink constant was determined to be 1.23 for [G-2]-PAA and 1.42 for [G-3]-PAA.<sup>195</sup> Sill et al. prepared

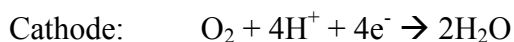
dendritic-linear-dendritic triblock copolymers with polycyclooctene as the linear segment and poly(benzyl ether)s as the dendritic segments via ring opening metathesis polymerization (ROMP) and the subsequent hydrogenation of the polycyclooctene segment converted the linear segment into polyethylene.<sup>198</sup> Zhu et al. synthesized a linear-dendritic diblock copolymer using benzyl ether as the dendritic segment and poly(N-isopropylacrylamide) (PNIPAM) as the linear segment via atom transfer radical polymerization.<sup>199</sup> This amphiphilic copolymer changed its shape at a certain temperature.<sup>199</sup> Chapman et al. prepared surfactants with linear-dendritic diblock architecture using PEO linear segment and poly( $\alpha,\epsilon$ -L-lysine) dendritic segment.<sup>200</sup> Linear-hyperbranched diblock copolymers were synthesized by grafting branched AB<sub>2</sub> type carbosilane blocks from a polybutadiene-polystyrene linear block by slow monomer addition.<sup>201</sup> The monomer was added slowly to the concentrated solution of the linear block to prevent the monomer from adding to itself. These linear-hyperbranched copolymers were studied by TEM, AFM, SAXS and DSC and showed microphase separation with increasing size of the hyperbranched block as well as two T<sub>g</sub>s, one for the linear block and one for the hyperbranched block.<sup>201</sup> The conformation of linear-dendritic diblock copolymers consisting of benzylether G-4 dendron and PEO was analyzed with Small Angle Neutron Scattering (SANS) and Dynamic Light Scattering (DLS) and it was found that with increasing molecular weight of the linear segment, the linear block changed its conformation from a knitted coil, where the linear chain weaves in and out of the dendron, to a random coil and also caused the dendron to change its conformation from a sphere to an extended cone.<sup>202</sup> Linear-dendritic hybrids have also been attracting a lot of attention for drug delivery applications. Gillies et al. synthesized pH-responsive

linear-dendritic copolymers with PEO and either polylysine or polyester dendron having acid-sensitive cyclic acetals at its periphery.<sup>203</sup> These copolymers formed micelles which can encapsulate a fluorescent probe at neutral pH and disintegrate at mildly acidic pH, suggesting that these systems might be useful for controlled release.<sup>203</sup> It has been known that a drug-PEG conjugate, in some cases, outperforms the free drug and that PEGylation of new and existing drugs have been extensively investigated although the potential problem of this method is that the attachment of a low molecular weight drug to a PEG results in a low concentration of the active drug.<sup>204</sup> Linear-dendritic hybrid systems, on the other hand, may be useful to increase the active drug concentration because a larger number of drug molecules could be attached to these systems.

## **2.6 Branched Polymers in Proton Exchange Membrane Fuel Cells (PEMFCs)**

Branched polymers have been extensively explored as a tool to introduce a large number of functional groups on polymer chains.<sup>205</sup> A field of PEMFCs is a good examples of the areas where branched polymers have been actively investigated because in PEMs, polymers need to possess a large number of sulfonic acid groups at specific sites.<sup>205</sup>

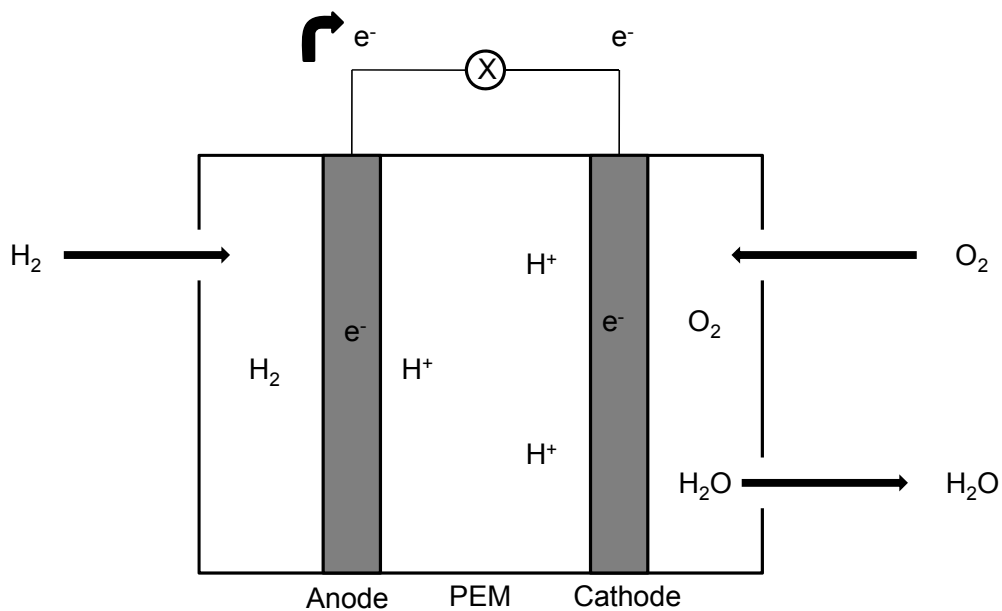
PEMFCs, one of the most promising clean future power sources, are electrochemical devices that convert chemical energy into electricity. The electricity in PEMFCs is generated by the redox reaction between oxygen and hydrogen.<sup>206</sup>



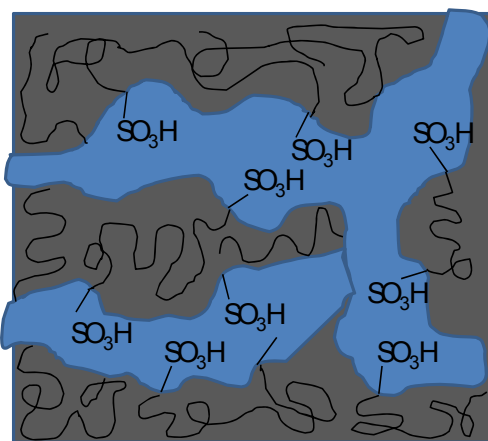


In this type of devices, PEM is an essential part of the system which separates the anode and cathode. But at the same time, the PEM needs to allow the passage of protons in order for the redox reaction to take place. Figure 2.13 shows a simple schematic diagram of PEMFC and Figure 2.14 illustrates PEM with ionic channels through which protons travel.

Nafion®, commercially available perfluorinated polymers, are the most widely used materials for PEMs today because of their excellent chemical and electrochemical stabilities.<sup>205</sup> Nafion® is a random copolymer based on tetrafluoroethylene and perfluoro(alkyl vinyl ether) carrying sulfonic acid groups.<sup>206</sup> The high proton conductivity of Nafion is ascribed to the microphase separation between hydrophilic and hydrophobic segments, forming continuous ionic channels through which protons can travel.<sup>207-210</sup> Nafion®, however, has some drawbacks such as high cost and low dimensional stability at elevated temperatures due to its relatively low  $T_g$ , limiting the use temperature below 80 °C.<sup>205, 208, 211</sup> In order to avoid these drawbacks, an extensive amount of research has been focused on other types of polymer backbones. Poly(arylene ether)s such as poly(arylene ether sulfone)s, poly(arylene ether ketone)s and poly(arylene ether sulfide)s have been attracting much attention as alternatives for PEMs due to their excellent chemical, thermal and dimensional stabilities.<sup>205, 208, 211</sup> In addition, the chemical structures of these polymers allow for further chemical modifications to tune their physical properties.



**Figure 2.13** Diagram showing how PEMFCs generate electricity.<sup>206</sup>



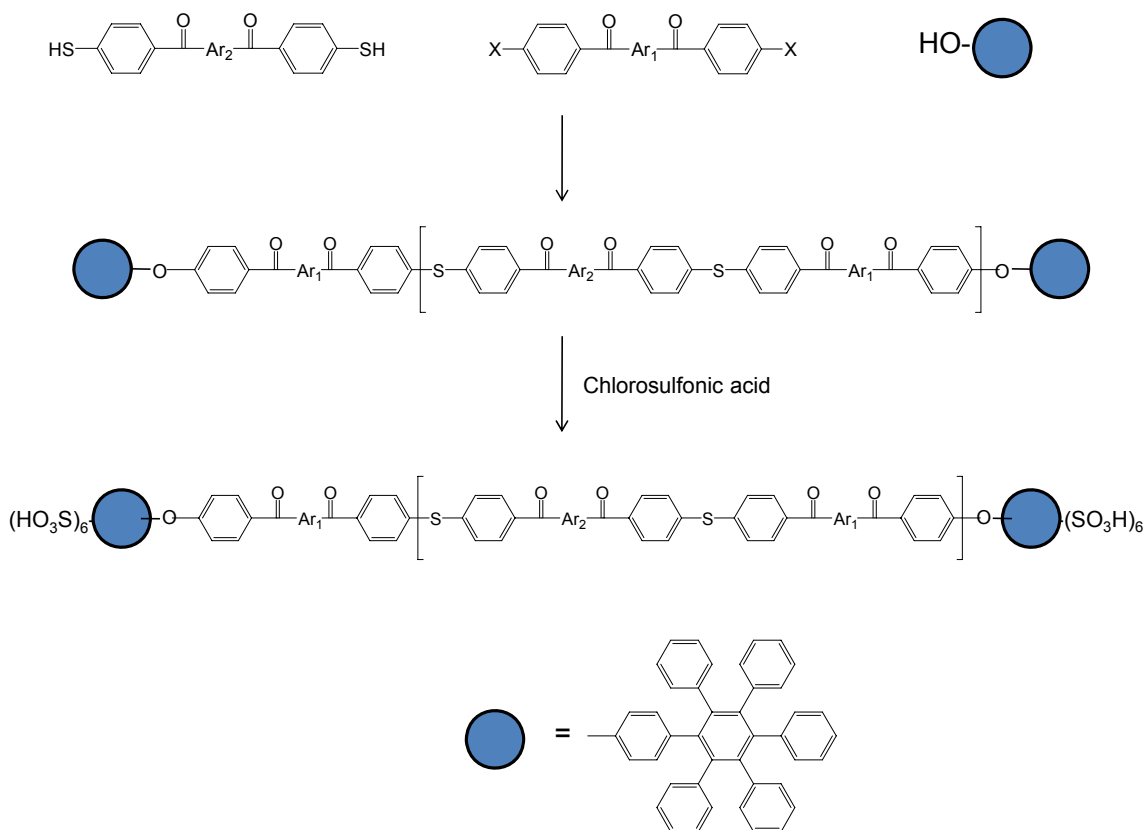
**Figure 2.14** Ionic channels in PEM.

One of the simplest methods may be the sulfonation of commercially available polymers via electrophilic addition by fuming sulfuric acid and chlorosulfonic acid.<sup>212</sup> Commercial polysulfones, such as Udel and Radel, are among non-fluorinated aromatic polymers that are being the most extensively investigated commercial polymers.<sup>208</sup>

Sulfonation reactions on these polymers take place selectively on electron-rich sites, usually ortho to the ether linkages, due to the electron-donating nature of the oxygen atoms by resonance.<sup>208</sup> Although simple, this method gives sulfonic acid units randomly distributed along the polymer backbone since the electron-rich reactive sites are located on every repeat unit. Such randomly sulfonated polymers lose their dimensional stabilities in water when certain extents of sulfonation have been reached because of swelling and these polymers become even water soluble with high degrees of sulfonation.<sup>213</sup> Also, it is thought that such random placements of sulfonic acid groups on polymer backbones lead to inefficient formation of ionic channels.<sup>214</sup> In order to avoid these complications caused by post-sulfonation, the use of sulfonated monomer has been currently investigated.<sup>214, 215</sup> One of the most significant advantages of this method over post-sulfonation is that the degree of sulfonation can be precisely controlled by simply selecting a desired feed ratio of the sulfonated monomer.<sup>214, 215</sup>

In order to improve the formation of ionic channels in PEMs, concentrating sulfonic acid groups at specific sites on polymer backbones by introducing branching have also been attracting much attention.<sup>216-218</sup> Hay et al. prepared a series of linear poly(arylene ether)s bearing multi-armed terminal groups and tested these materials as PEMs.<sup>216</sup> These polymers were synthesized by step-growth polymerizations of difunctional monomers in the presence of monofunctional end-cappers capable of undergoing postpolymerization sulfonation to give linear poly(arylene ether)s with sulfonated branched terminal groups (Figure 2.15).<sup>216</sup> To the best of our knowledge, this work was the first example of placing multiple sulfonic acid groups onto the ends of linear polymers for PEM applications. Although the authors expected to observe high

proton conductivity for these membranes because this architecture might facilitate the formation of ionic channels through which protons could travel, conductivities were quite low apparently due to the limited number of sulfonate groups that can be placed on the polymer chain ends. The maximum number of sulfonate groups per chain for these systems is 12. To increase the number of sulfonate groups, Hay et al. incorporate a trifunctional comonomer in the polymerization so that there are more than two chain ends per polymer.<sup>217</sup> These polymers indeed exhibited improved conductivities due to the larger number of sulfonic acid groups.<sup>217</sup> A further effort to increase the number of sulfonic acids per chain was reported by the same authors.<sup>218</sup> In this work, multifunctional dendritic units were incorporated into the polymer backbones to give dendritic multi-block copolymers which still maintained the blockiness of sulfonic acid regions because the sulfonic acid units were only on the dendritic repeat units. These polymers, however, did not possess sufficient mechanical properties for PEM applications apparently due to the large number of dendritic units along the polymer backbones hindering interchain entanglements. Figure 2.16 summarizes three types of hybrid linear-dendritic structures used by Hay et al. Kakimoto et al. prepared hyperbranched-linear multi-block copolymers by linking linear and hyperbranched blocks by FeCl<sub>3</sub>-catalyzed sulfonylation between sulfonyl chlorides and electron-rich phenyl rings.<sup>219</sup> These polymers could be useful for PEM applications because the unreacted sulfonyl chloride terminal groups might be able to get hydrolyzed to give polymers with sulfonic acids on chain ends although the authors did not mention this possibility in the paper.

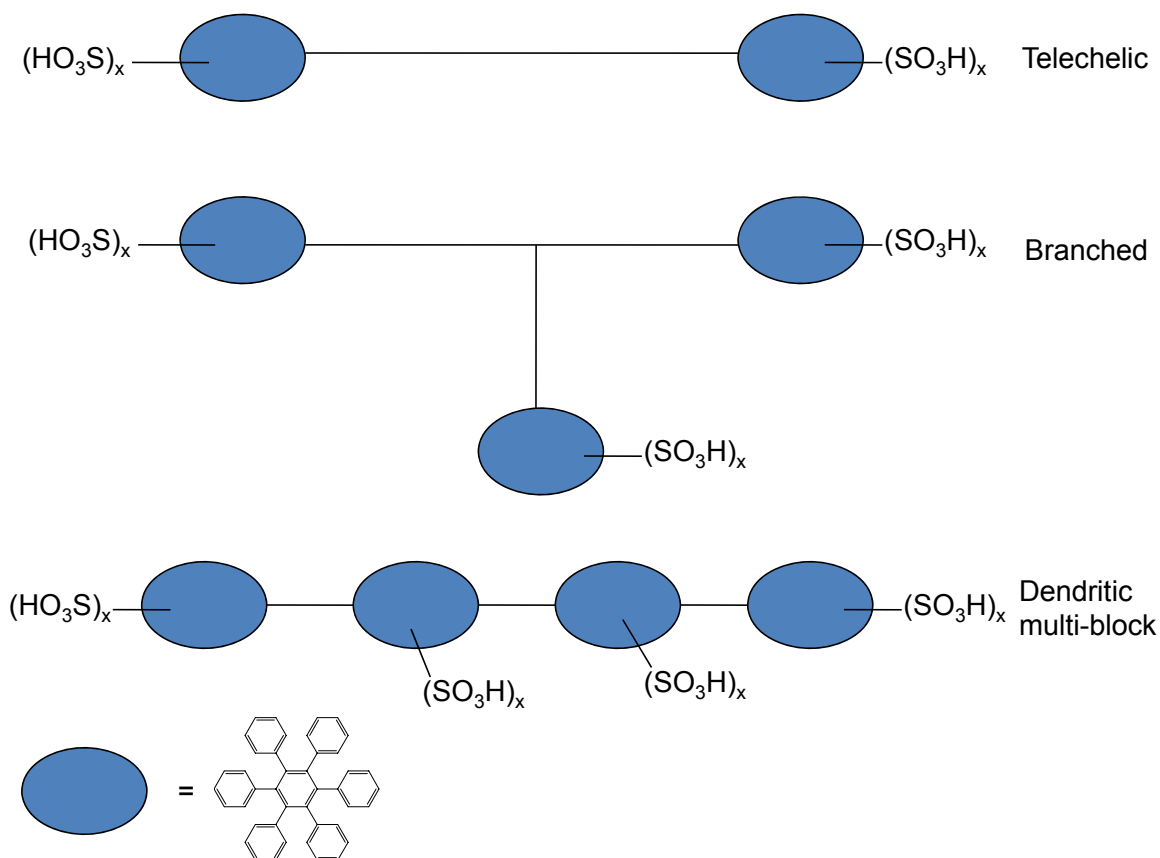


**Figure 2.15** Telechelic sulfonated poly(arylene ether)s.<sup>216</sup>

Another method of making the use of branching for PEM applications is to graft sulfonated groups from polymer backbones.<sup>208, 220</sup> This may be one of the most versatile ways to tune the properties of parent polymers in that many structures and functional groups can be introduced onto the parent polymer backbones. Deprotonation of the acidic protons, which are ortho to the sulfone units, by a strong base, such as butyllithium, followed by the reaction with an electrophile of choice is one of the most widely used procedures to graft functional groups from the polymer backbones.<sup>220</sup> The significant advantage of the grafting strategy over random placements of functional groups on polymer backbone is that functional groups are only on the side chains, not on the polymer backbones, which is considered to lead to better formation of ionic channels in

the membranes.<sup>208</sup> A wide variety of structures have been successfully grafted from polysulfones by this method.<sup>221, 222</sup> This method is summarized in Figure 2.17 where X is any electrophile of choice. Lafitte prepared polysulfones carrying sulfonic acids by reacting lithiated polysulfones with 4-fluorobenzoyl chloride and sulfonated phenols.<sup>220, 223</sup> Reaction of lithiated polysulfones with sulfuryl or sulfur dioxide is another way of introducing sulfonic acid units.<sup>224</sup> Instead of sulfonic acid units, carboxylates have also been introduced by the lithiation route by using carbon dioxide as the electrophile although the performance of this material as PEM is quite limited because of the low acidity of the carboxylic acid.<sup>225</sup> Recently, phosphonic acid units have been attached to polysulfone backbones by the reaction of lithiated polysulfones with chlorophosphonic acid esters, followed by the hydrolysis of the esters.<sup>226</sup> Although the acidity of phosphonic acid units are not as high as sulfonic acids, phosphonic acids have higher hydrolytic stability than sulfonic acids.<sup>226, 227</sup>

The lithiation method was also used to introduce crosslinking in polysulfones in order to minimize swelling and improve solvent resistance.<sup>228-230</sup> These polymers were synthesized by the reaction of lithiated polysulfones with difunctional haloalkanes. Ionically crosslinked polysulfones have also been synthesized by blending acid- and base-functionalized polymers with each other.<sup>231, 232</sup>

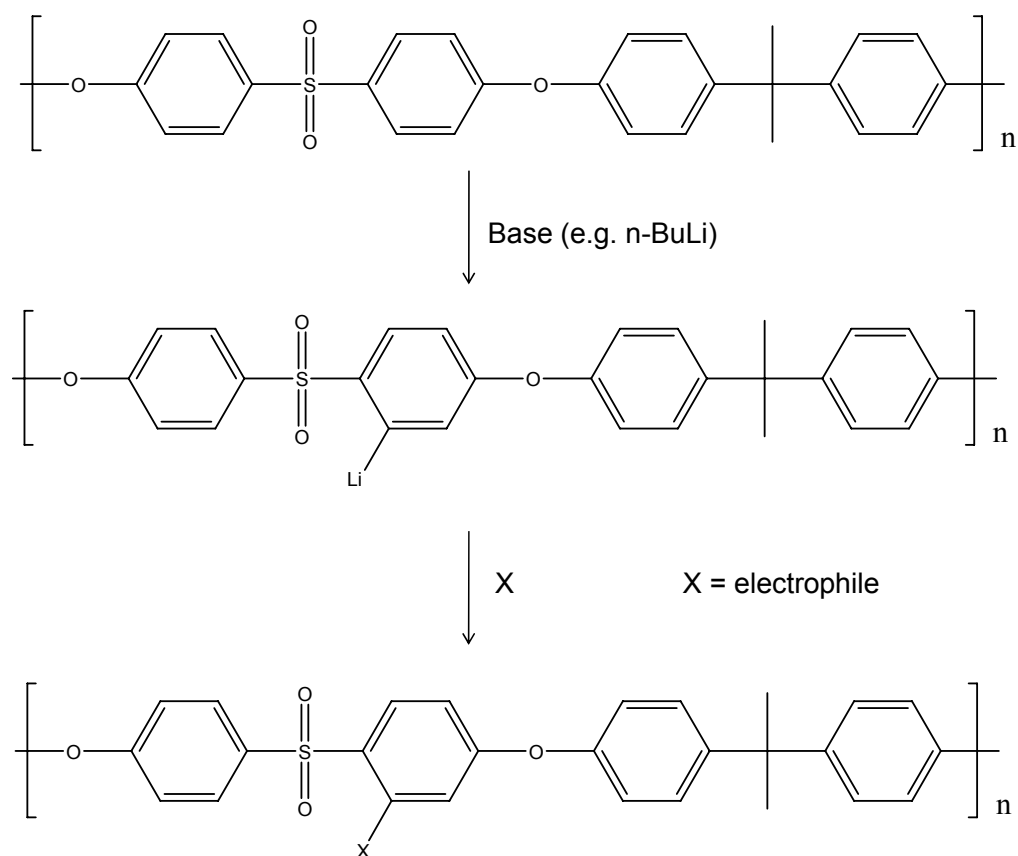


**Figure 2.16** Hybrid linear-dendritic polymers.<sup>216-218</sup>

## 2.7 Summary

Reviewing the literature in the fields of dendritic polymers reveals that a large number of dendritic and hyperbranched polymers have been synthesized using various types of monomers and functional terminal groups. Dendritic polymers possess low viscosities and poor mechanical properties because of their branch structures preventing interchain entanglements. One of the most distinguishing features of dendritic polymers is that they possess large number of terminal groups that can be used to place functional groups as opposed to linear polymers, in which there are only two chain ends and the concentration of chain ends decrease with increasing chain length.

Unlike pure dendrimers and hyperbranched polymers, linear-dendritic hybrids such as the ones covered in this review exhibit unique behaviors, such as changes in rheology and formation of micelles, which are difficult to predict just by knowing the properties of pure dendrimers and linear polymers alone. Also, one could tune the properties of linear polymers by introducing branching with various functional groups. Poly(arylene ether)s with branched structures, for example, are attracting much attention for PEM applications.



**Figure 2.17** Grafting of functional groups from polysulfones via lithiation chemistry.

## 2.8 References

1. Flory, P. J., Molecular size distribution in three-dimensional polymers. VI. Branched polymer containing A-R-Bf-l-type units. *J. Am. Chem. Soc.* **1952**, *74*, 2718-2723.



2. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kalos, F.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P., A new class of polymers: starburst-dendritic macromolecules. *Polym. J.* **1985**, *17* (1), 117-132.
3. Buhleier, E.; Wehner, W.; Vögtle, F., "Cascade"- and "nonskid-chain-like" syntheses of molecular cavity topologies. *Synthesis* **1978**, (2), 155-158.
4. Newkome, G. R.; Shreiner, C. D., Poly(amidoamine), polypropylenimine, and related dendrimers and dendrons possessing different 1 ® 2 branching motifs: An overview of the divergent procedures. *Polymer* **2008**, *49* (1), 1-173.
5. Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K., Micelles. Part 1. Cascade molecules: a new approach to micelles. A [27]-arborol. *J. Org. Chem.* **1985**, *50* (11), 2003-2004.
6. Hawker, C. J.; Fréchet, J. M. J., Preparation of polymers with controlled molecular architecture. a new convergent approach to dendritic macromolecules. *J. Am. Chem. Soc.* **1990**, *112* (21), 7638-7647.
7. Grayson, S. M.; Fréchet, J. M. J., Convergent dendrons and dendrimers: from synthesis to applications. *Chem. Rev.* **2001**, *101* (12), 3819-3867.
8. Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S., Phenylacetylene dendrimers by the divergent, convergent, and double-stage convergent methods. *J. Am. Chem. Soc.* **1994**, *116* (11), 4537-4550.
9. Miller, T. M.; Neenan, T. X., Convergent synthesis of monodisperse dendrimers based upon 1,3,5-trisubstituted benzenes. *Chem. Mater.* **1990**, *2* (4), 346-349.
10. Brouwer, A. J.; Mulders, S. J. E.; Liskamp, R. M. J., Convergent synthesis and diversity of amino acid based dendrimers. *Eur. J. Org. Chem.* **2001**, (10), 1903-1915.
11. Mulders, S. J. E.; Brouwer, A. J.; Kimkes, P.; Sudholter, E. J. R.; Liskamp, R. M. J., Molecular diversity of novel amino acid based dendrimers. *Tetrahedron Lett.* **1997**, *38* (17), 3085-3088.
12. Mulders, S. J. E.; Brouwer, A. J.; van der Meer, P. G. J.; Liskamp, R. M. J., Synthesis of a novel amino acid based dendrimer. *Tetrahedron Lett.* **1997**, *38* (4), 631-634.
13. Voit, B. I.; Wolf, D., Perfectly branched polyamide dendrons based on 5-(2-aminoethoxy)-isophthalic acid. *Tetrahedron* **1997**, *53* (45), 15535-15551.
14. Washio, I.; Shibasaki, Y.; Ueda, M., Facile synthesis of polyamide dendrimers from unprotected AB<sub>2</sub> building blocks: dumbbell-shaped dendrimer, star-shaped dendrimer, and dendrimer with carboxylic acid at core. *Macromolecules* **2005**, *38* (6), 2237-2246.
15. Zhou, L.-L.; Roovers, J., Synthesis of novel carbosilane dendritic macromolecules. *Macromolecules* **1993**, *26* (5), 963-968.
16. Morikawa, A.; Kakimoto, M.; Imai, Y., Convergent synthesis of starburst poly(ether ketone) dendrons. *Macromolecules* **1993**, *26* (24), 6324-6329.
17. Morikawa, A.; Ono, K., Preparation of poly(ether ketone) dendrons with graded structures. *Macromolecules* **1999**, *32* (4), 1062-1068.
18. Morikawa, A.; Ono, K., Preparation of poly[(ether)-(ether ether ketone)] dendrimers by the convergent method. *Polym. J.* **2000**, *32* (3), 255-262.

19. Morikawa, A., Preparation of poly(ether ketone) dendrimers, dendrons, and hyperbranched polymers by aromatic nucleophilic substitution reactions. *Kobunshi Ronbunshu* **2007**, *64* (10), 627-642.
20. Killops, K. L.; Campos, L. M.; Hawker, C. J., Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "click" chemistry. *J. Am. Chem. Soc.* **2008**, *130* (15), 5062-5064.
21. Kwock, E. W.; Neenan, T. X.; Miller, T. M., Convergent synthesis of monodisperse aryl ester dendrimers. *Chem. Mater.* **1991**, *3* (5), 775-777.
22. Miller, T. M.; Kwock, E. W.; Neenan, T. X., Synthesis of four generations of monodisperse aryl ester dendrimers based on 1,3,5-benzenetricarboxylic acid. *Macromolecules* **1992**, *25* (12), 3143-3148.
23. Hirayama, Y.; Nakamura, T.; Uehara, S.; Sakamoto, Y.; Yamaguchi, K.; Sei, Y.; Iwamura, M., Synthesis and characterization of polyester dendrimers from acetoacetate and acrylate. *Org. Lett.* **2005**, *7* (4), 525-528.
24. Potluri, S. K.; Ramulu, A. R.; Pardhasaradhi, M., Synthesis of new unsymmetrical optically active (s)-(+)-naproxen dendrimers. *Tetrahedron* **2004**, *60* (48), 10915-10920.
25. Parrott, M. C.; Benhabbour, S. R.; Saab, C.; Lemon, J. A.; Parker, S.; Valliant, J. F.; Adronov, A., Synthesis, radiolabeling, and bio-imaging of high-generation polyester dendrimers. *J. Am. Chem. Soc.* **2009**, *131* (8), 2906-2916.
26. Parrott, M. C.; Marchington, E. B.; Valliant, J. F.; Adronov, A., Synthesis and properties of carborane-functionalized aliphatic polyester dendrimers. *J. Am. Chem. Soc.* **2005**, *127* (34), 12081-12089.
27. Malkoch, M.; Malmstroem, E.; Hult, A., Rapid and efficient synthesis of aliphatic ester dendrons and dendrimers. *Macromolecules* **2002**, *35* (22), 8307-8314.
28. Shi, D.; Sha, Y.; Wang, F.; Tian, Q., Synthesis and photophysical properties of poly(ester-amine) dendrimers with focal 4-amino-N-benzylphthalimide, as sensitive media probes and switchable proton sensors. *Macromolecules* **2008**, *41* (20), 7478-7484.
29. Lee, J.-S.; Huh, J.; Ahn, C.-H.; Lee, M.; Park, T. G., Synthesis of novel biodegradable cationic dendrimers. *Macromol. Rapid Commun.* **2006**, *27* (18), 1608-1614.
30. Spindler, R.; Frechet, J. M. J., Two-step approach towards the accelerated synthesis of dendritic macromolecules. *J. Chem. Soc. Perkin Trans. 1* **1993**, *1* (8), 913-918.
31. Taylor, R. T.; Puapaboon, U., Polyurethane dendrimers via Curtius reaction. *Tetrahedron Lett.* **1998**, *39* (44), 8005-8008.
32. Newkome, G. R.; Weis, C. D.; Moorefield, C. N.; Baker, G. R.; Childs, B. J.; Epperson, J., Isocyanate-based dendritic building blocks: combinatorial tier construction and macromolecular-property modification. *Angew. Chem., Int. Ed.* **1998**, *37* (3), 307-310.
33. Feast, W. J.; Rannard, S. P.; Stoddart, A., Selective convergent synthesis of aliphatic polyurethane dendrimers. *Macromolecules* **2003**, *36* (26), 9704-9706.
34. Shen, X.; Liu, H.; Li, Y.; Liu, S., Click-together azobenzene dendrons: synthesis and characterization. *Macromolecules* **2008**, *41* (7), 2421-2425.

35. Shi, Z.-F.; Zhou, Z.-L.; Cao, X.-P., An efficient synthesis of new polyether dendrimers based on the A2B type monomer from 5-hydroxyisophthalic acid. *Chin. J. Chem.* **2006**, *24* (1), 103-108.
36. Cao, X.; Wang, F.; Guo, S., A new convergent approach to dendritic macromolecules. *Synth. Commun.* **2002**, *32* (20), 3149-3158.
37. Rannard, S. P.; Davis, N. J., A highly selective, one-pot multiple-addition convergent synthesis of polycarbonate dendrimers. *J. Am. Chem. Soc.* **2000**, *122* (47), 11729-11730.
38. Liao, Y.-H.; Moss, J. R., Organoruthenium dendrimers. *Organometallics* **1996**, *15* (20), 4307-4316.
39. Waybright, S. M.; McAlpine, K.; Laskoski, M.; Smith, M. D.; Bunz, U. H. F., Organometallic dendrimers based on (tetraphenylcyclobutadiene)cyclopentadienylcobalt modules. *J. Am. Chem. Soc.* **2002**, *124* (29), 8661-8666.
40. Onitsuka, K.; Shimizu, A.; Takahashi, S., A divergent approach to the precise synthesis of giant organometallic dendrimers using platinum-acetylides as building blocks. *Chem. Commun.* **2003**, (2), 280-281.
41. Liao, Y. H.; Moss, J. R., Ruthenium-containing organometallic dendrimers. *J. Chem. Soc., Chem Commun.* **1993**, (23), 1774-1777.
42. Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S., Synthesis of a novel organometallic dendrimer with a backbone composed of platinum-acetylide units. *Chem. Lett.* **1996**, (10), 871-872.
43. Hurst, S. K.; Cifuentes, M. P.; Humphrey, M. G., A rapid convergent approach to organometallic dendrimers : sterically controlled dendron synthesis. *Organometallics* **2002**, *21* (12), 2353-2355.
44. Bourrier, O.; Kakkar, A. K., Dendritic polymers containing a dimethylsilyl linked dihydroxybenzyl alcohol backbone: divergent synthesis, aggregation, functionalization, and an evaluation of their applications in catalysis. *J. Mater. Chem.* **2003**, *13* (6), 1306-1315.
45. Onitsuka, K.; Kitajima, H.; Fujimoto, M.; Iuchi, A.; Takei, F.; Takahashi, S., Platinum-acetylide dendrimers possessing a porphyrin core. *Chem. Commun.* **2002**, (21), 2576-2577.
46. Onitsuka, K.; Iuchi, A.; Fujimoto, M.; Takahashi, S., Synthesis of organometallic dendrimers by ligand exchange reactions: reversible bonding of dendrons to a core in transition metal acetylide dendrimers. *Chem. Commun.* **2001**, (8), 741-742.
47. Rodriguez, L.-I.; Rossell, O.; Seco, M.; Grabulosa, A.; Muller, G.; Rocamora, M., Carbosilane Dendrimers Peripherally Functionalized with P-Stereogenic Monophosphines. Catalytic Behavior of Their Allylpalladium Complexes in the Asymmetric Hydrovinylation of Styrene. *Organometallics* **2006**, *25* (6), 1368-1376.
48. Ghorai, S.; Bhattacharyya, D.; Bhattacharjya, A., The first examples of anthracene capped chiral carbohydrate derived dendrimers : synthesis, fluorescence and chiroptical properties. *Tetrahedron Lett.* **2004**, *45* (32), 6191-6194.

49. Liu, P. N.; Chen, Y. C.; Li, X. Q.; Tu, Y. Q.; Deng, J.-G., Dendritic catalysts for asymmetric transfer hydrogenation based (1S,2R)-norephedrine derived ligands. *Tetrahedron: Asymmetry* **2003**, *14* (46), 2481-2485.
50. Ma, L.; Lee, S. J.; Lin, W., Synthesis, characterization, and photophysical properties of chiral dendrimers based on well-defined oligonaphthyl cores. *Macromolecules* **2002**, *35* (16), 6178-6184.
51. Pu, L., Novel chiral conjugated macromolecules for potential electrical and optical applications. *Macromol. Rapid Commun.* **2000**, *21* (12), 795-809.
52. Sato, I.; Shibata, T.; Ohtake, K.; Kodaka, R.; Hirokawa, Y.; Shirai, N.; Soai, K., Synthesis of chiral dendrimers with a hydrocarbon backbone and application to the catalytic enantioselective addition of dialkylzincs to aldehydes. *Tetrahedron Lett.* **2000**, *41* (17), 3123-3126.
53. Ashton, P. R.; Shibata, K.; Shipway, A. N.; Stoddart, J. F., Polycationic dendrimers. *Angew. Chem., Int. Ed. Engl.* **1997**, *36* (24), 2781-2783.
54. Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J., Unimolecular micelles and globular amphiphiles: dendritic macromolecules as novel recyclable solubilization agents. *J. Chem. Soc., Perkin Trans. 1* **1993**, (12), 1287-1297.
55. Kim, T. H.; Webster, O. W., Water soluble hyperbranched polyphenylene: "a unimolecular micelle?". *J. Am. Chem. Soc.* **1990**, *112* (11), 4592-4593.
56. Unal, S.; Oguz, C.; Yilgor, E.; Gallivan, M.; Long, T. E.; Yilgor, I., Understanding the structural development in hyperbranched polymers prepared by ligomeric A2+B3 approach: comparison of experimental results and simulations. *Polymer* **2005**, *46* (13), 4533-4543.
57. Kim, J.; Pawlow, J. H.; Wojcinski, L. M., II; Murtuza, S.; Kacker, S.; Sen, A., Novel nickel(II)- and palladium(II)-based catalytic systems for the synthesis of hyperbranched polymers from ethene. *J. Am. Chem. Soc.* **1998**, *120* (8), 1932-1933.
58. Ishizu, K.; Takahashi, D.; Takeda, H., Novel synthesis and characterization of hyperbranched polymers. *Polymer* **2000**, *41* (16), 6081-6086.
59. Ishizu, K.; Mori, A., Synthesis of hyperbranched polymers by self-addition free radical vinyl polymerization of photo functional styrene. *Macromol. Rapid Commun.* **2000**, *21* (10), 665-668.
60. Gao, C.; Yan, D., Synthesis of hyperbranched polymers from commercially available A2 and BB'2 type monomers. *Chem. Commun.* **2001**, (1), 107-108.
61. Gao, C.; Yan, D.; Zhu, X.; Huang, W., Preparation of water-soluble hyperbranched poly(sulfone-amine)s by polyaddition of N-ethylethylenediamine to divinyl sulfone. *Polymer* **2001**, *42* (18), 7603-7610.
62. Gao, C.; Yan, D.; Tang, W., Hyperbranched polymers made from A2- and BB2'-type monomers, 3. Polyaddition of N-methyl-1,3-propanediamine to divinyl sulfone. *Macromol. Chem. Phys.* **2001**, *202* (12), 2623-2629.
63. Ambade, A. V.; Kumar, A., An efficient route for the synthesis of hyperbranched polymers and dendritic building blocks based on urea linkages. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39* (9), 1295-1304.
64. Yoo, S. H.; Lee, J. H.; Lee, J.-C.; Jho, J. Y., Synthesis of hyperbranched polyacrylates in emulsion by atom transfer radical polymerization. *Macromolecules* **2002**, *35* (4), 1146-1148.

65. Kim, Y. H., Lyotropic liquid crystalline hyperbranched aromatic polyamides. *J. Am. Chem. Soc.* **1992**, *114* (12), 4947-4948.
66. Russo, S.; Boulares, A.; Mariani, A., Synthesis of hyperbranched aromatic polyamides by direct polycondensation. *Macromol. Symp.* **1998**, *128*, 13-20.
67. Kricheldorf, H. R.; Bolender, O.; Stukenbrock, T., New polymer syntheses. Part 91. Hyperbranched poly(ester amide)s derived from 3,5-dihydroxybenzoic acid and 3,5-diaminobenzoic acid. *Macromol. Chem. Phys.* **1997**, *198* (9), 2651-2666.
68. Yang, G.; Jikei, M.; Kakimoto, M., Successful thermal self-polycondensation of AB<sub>2</sub> monomer to form hyperbranched aromatic polyamide. *Macromolecules* **1998**, *31* (17), 5964-5966.
69. Yang, G.; Jikei, M.; Kakimoto, M., Synthesis and properties of hyperbranched aromatic polyamide. *Macromolecules* **1999**, *32* (7), 2215-2220.
70. Brenner, A. R.; Schmaljohann, D.; Wolf, D.; Voit, B. I., Hyperbranched polyesters and polyamides by the AB<sub>x</sub> polycondensation process. *Macromol. Symp.* **1997**, *122*, 217-222.
71. Chao, D.; Ma, X.; Lu, X.; Cui, L.; Mao, H.; Zhang, W.; Wei, Y., Electroactive hyperbranched polyamide synthesized by oxidative coupling polymerization within an A<sub>2</sub> + B<sub>3</sub> strategy. *Macromol. Chem. Phys.* **2007**, *208* (6), 658-664.
72. Jikei, M.; Fujii, K.; Kakimoto, M.-a., Synthesis and characterization of hyperbranched aromatic polyamide copolymers prepared from AB<sub>2</sub> and AB monomers. *Macromol. Symp.* **2003**, *199*, 223.
73. Hong, L.; Cui, Y.; Wang, X.; Tang, X., Synthesis of a novel one-pot approach of hyperbranched polyurethanes and their properties. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *40* (3), 344-350.
74. Davis, N.; Rannard, S., Synthesis of hyperbranched polymers using highly selective chemical reactions. *Polym. Mater. Sci. Eng.* **1997**, *77*, 158-159.
75. Burgath, A.; Hanselmann, R.; Holter, D.; Frey, H., Hyperbranched polyesters and polyurethanes prepared via the core-dilution method. *Polym. Mater. Sci. Eng.* **1997**, *77*, 166-167.
76. Shanmugam, T.; Nasar, A. S., Novel hyperbranched poly(aryl ether urethane)s using AB<sub>2</sub>-type blocked isocyanate monomers and copolymerization with AB-type monomers. *Macromol. Chem. Phys.* **2008**, *209* (6), 651-665.
77. Morita, A.; Kudo, H.; Nishikubo, T., Synthesis of hyperbranched polymers by the anionic ring-opening polymerization of 3,3-bis(hydroxymethyl)oxetane. *Polym. J.* **2004**, *36* (5), 413-421.
78. Li, J.; Sun, M.; Bo, Z., Synthesis of hyperbranched polymers with precise conjugation length. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45* (6), 1084-1092.
79. Luston, J.; Kronek, J., Synthesis and polymerization reactions of cyclic imino ethers. II. Preparation of novel hyperbranched polymers from AB<sub>2</sub> monomers of 2-oxazoline type with nonequivalent B units. *Polym. Eng. Sci.* **2007**, *47* (8), 1272-1280.
80. Hawker, C. J.; Lee, R.; Fréchet, J. M. J., One-step synthesis of hyperbranched dendritic polyesters. *J. Am. Chem. Soc.* **1991**, *113* (12), 4583-4588.
81. Santimukul, S.; Anil, K., Facile synthesis of aliphatic hyperbranched polyesters based on diethyl malonate and their irreversible molecular encapsulation. *Chem. Commun.* **2004**, (18), 2126-2127.

82. Kricheldorf, H. R.; Stukenbrock, T., New polymer syntheses. 85. Telechelic, star-shaped and hyperbranched polyesters of *b* -(4-hydroxyphenyl)propionic acid. *Polymer* **1997**, *38* (13), 3373-3383.
83. Malmström, E.; Trollsas, M.; Hawker, C. J.; Johansson, M.; Hult, A., Accelerated synthesis of hyperbranched polyesters based on bis-MPA. *Polym. Mater. Sci. Eng.* **1997**, *77*, 151-152.
84. Feast, W. J.; Keeney, A. J.; Kenwright, A. M.; Parker, D., Synthesis, structure and cyclic content of hyperbranched polyesters. *Chem. Commun.* **1997**, (18), 1749-1750.
85. Kricheldorf, H. R.; Stukenbrock, T., New polymer syntheses XCIII. Hyperbranched homo- and copolyesters derived from gallic acid and *b* -(4-hydroxyphenyl)-propionic acid. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36* (13), 2347-2357.
86. Parker, D.; Feast, W. J., Synthesis, structure, and properties of hyperbranched polyesters based on dimethyl 5-(2-Hydroxyethoxy)isophthalate. *Macromolecules* **2001**, *34* (7), 2048-2059.
87. Choi, S.-H.; Lee, N.-H.; Cha, S. W.; Jin, J.-I., Hyperbranched thermotropic liquid crystalline polyesters composed of aromatic ester type mesogens and polymethylene spacers. *Macromolecules* **2001**, *34* (7), 2138-2147.
88. Parker, D.; Feast, W. J., Synthesis, structure, and properties of core-terminated hyperbranched polyesters based on dimethyl 5-(2-hydroxyethoxy)isophthalate. *Macromolecules* **2001**, *34* (17), 5792-5798.
89. Kricheldorf, H. R.; Behnken, G., Biodegradable hyperbranched polyesters derived from 1,1,1-tris(hydroxymethyl)ethane. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *47* (1), 231-238.
90. Schallausky, F.; Erber, M.; Komber, H.; Lederer, A., An easy strategy for the synthesis of well-defined aliphatic-aromatic hyperbranched polyesters. *Macromol. Chem. Phys.* **2008**, *209* (22), 2331-2338.
91. Sato, M.; Nakashima, A.; Sato, Y.; Yamaguchi, I., Linear and A<sub>2</sub>+B<sub>3</sub>-type hyperbranched polyesters comprising phenylbenzothiazole unit: preparation, liquid crystalline, and optical properties. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (20), 6688-6702.
92. Ikladios, N. E.; Mansour, S. H.; Rozik, N. N.; Dirnberger, K.; Eisenbach, C. D., New aliphatic hyperbranched polyester polyols based on 1,3,5-tris(2-hydroxyethyl) cyanuric acid as a core. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (16), 5568-5579.
93. Kricheldorf, H. R.; Behnken, G., Biodegradable hyperbranched aliphatic polyesters derived from pentaerythritol. *Macromolecules* **2008**, *41* (15), 5651-5657.
94. Sato, M.; Matsuoka, Y.; Yamaguchi, I., Preparation and properties of novel thermotropic liquid crystalline hyperbranched polyesters composed of five-membered heterocyclic mesogen by A<sub>2</sub> + B<sub>3</sub> approach. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45* (14), 2998-3008.
95. Parzuchowski, P. G.; Grabowska, M.; Tryznowski, M.; Rokicki, G., Synthesis of glycerol based hyperbranched polyesters with primary hydroxyl groups. *Macromolecules* **2006**, *39* (21), 7181-7186.

96. Mansour, S. H.; Rozik, N. N.; Dirnberger, K.; Ikladios, N. E., Hyperbranched polyesters based on polycondensation of 1,3,5-tris(2-hydroxyethyl) cyanuric acid and 3,5-dihydroxybenzoic acid. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (15), 3278-3288.
97. Lin, Q.; Long, T. E., Polymerization of A<sub>2</sub> with B<sub>3</sub> monomers: A facile approach to hyperbranched poly(aryl ester)s. *Macromolecules* **2003**, *36* (26), 9809-9816.
98. Yamaguchi, N.; Wang, J.-S.; Hewitt, J. M.; Lenhart, W. C.; Mourey, T. H., Acid chloride-functionalized hyperbranched polyester for facile and quantitative chain-end modification: one-pot synthesis and structure characterization. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40* (16), 2855-2867.
99. Turner, S. R.; Voit, B. I.; Mourey, T. H., All-aromatic hyperbranched polyesters with phenol and acetate end groups: synthesis and characterization. *Macromolecules* **1993**, *26* (17), 4617-4623.
100. Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H., Hyperbranched aromatic polyesters with carboxylic acid terminal groups. *Macromolecules* **1994**, *27* (6), 1611-1616.
101. Brenner, A. R.; Voit, B. I.; Massa, D. J.; Turner, S. R., Hyperbranched polyesters: end group modification and properties. *Macromol. Symp.* **1996**, *102*, 47-54.
102. Feast, J. W.; Stainton, N. M., Synthesis, structure and properties of some hyperbranched polyesters. *J. Mater. Chem.* **1995**, *5* (3), 405-411.
103. Malmström, E.; Hult, A., Kinetics of formation of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid. *Macromolecules* **1996**, *29* (4), 1222-1228.
104. Malmström, E.; Johansson, M.; Hult, A., Hyperbranched aliphatic polyesters. *Macromolecules* **1995**, *28* (5), 1698-1703.
105. Fréchet, J. M. J.; Hawker, C. J., Hyperbranched polyphenylene and hyperbranched polyesters: new soluble, three-dimensional, reactive polymers. *React. Func. Polym.* **1995**, *26* (1-3), 127-136.
106. Kricheldorf, H. R.; Stöber, O. L., D., New Polymer Syntheses. 78. Star-Shaped and Hyperbranched Polyesters by Polycondensation of Trimethylsilyl 3,5-Diacetoxybenzoate. *Macromolecules* **1995**, *28* (7), 2118-2123.
107. Hawker, C. J.; Chu, F.; Pomery, P. J.; Hill, D. J. T., Hyperbranched poly(ethylene glycol)s: a new class of ion-conducting materials. *Macromolecules* **1996**, *29* (11), 3831-3838.
108. Chu, F. K.; Hawker, C. J.; Pomery, P. J.; Hill, D. J. T., Intramolecular cyclization in hyperbranched polyesters. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35* (9), 1627-1633.
109. Shanmugam, T.; Sivakumar, C.; Nasar, A. S., Hydroxyl-terminated hyperbranched aromatic poly(ether-ester)s: synthesis, characterization, end-group modification, and optical properties. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (16), 5414-5430.
110. Unal, S.; Long, T. E., Highly branched poly(ether ester)s via cyclization-free melt condensation of A<sub>2</sub> oligomers and B<sub>3</sub> monomers. *Macromolecules* **2006**, *39* (8), 2788-2793.
111. Lin, Y.; Dong, Z.; Li, Y., One-pot synthesis and characterization of hyperbranched poly(ester-amide)s from commercially available dicarboxylic

- acids and multihydroxyl secondary amines. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (15), 5077-5092.
112. Li, X.; Zhan, J.; Lin, Y.; Li, Y.; Li, Y., Facile synthesis and characterization of aromatic and semiaromatic hyperbranched poly(ester-amide)s. *Macromolecules* **2005**, *38* (20), 8235-8243.
  113. Bolton, D. H.; Wooley, K. L., Synthesis and characterization of hyperbranched polycarbonates. *Macromolecules* **1997**, *30* (7), 1890-1896.
  114. Parzuchowski, P. G.; Jaroch, M.; Tryznowski, M.; Rokicki, G., Synthesis of new glycerol-based hyperbranched polycarbonates. *Macromolecules* **2008**, *41* (11), 3859-3865.
  115. Scheel, A.; Komber, H.; Voit, B., Hyperbranched thermolabile polycarbonates derived from a A2+B3 monomer system. *Macromol. Symp.* **2004**, *210*, 101-110.
  116. Hawker, C. J.; Chu, F., Hyperbranched poly(ether ketones): manipulation of structure and physical properties. *Macromolecules* **1996**, *29* (12), 4370-4380.
  117. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M., Dendritic analogs of engineering plastics: A general one-step synthesis of dendritic polyaryl ethers. *J. Am. Chem. Soc.* **1993**, *115* (1), 356-357.
  118. Chu, F.; Hawker, C. J., A versatile synthesis of isomeric hyperbranched poly(ether ketones). *Polym. Bull.* **1993**, *30* (3), 265-272.
  119. Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Kruger, R.-P., Cyclic hyperbranched poly(ether ketone)s derived from 3,5-bis(4-fluorobenzoyl)phenol. *Macromolecules* **2003**, *36* (15), 5551-5558.
  120. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stien, S. M., Dendritic analogs of engineering plastics - A general one-step synthesis of dendritic polyaryl ethers. *Macromol. Symp.* **1994**, *77*, 35-42.
  121. Shu, C.-F.; Leu, C.-M., Hyperbranched poly(ether ketone) with carboxylic acid terminal groups: synthesis, characterization, and derivatization. *Macromolecules* **1999**, *32* (1), 100-105.
  122. Wang, D.; Liu, Y.; Hong, C.-Y.; Pan, C.-Y., Preparation and characterization of novel hyperbranched poly(amido amine)s from michael addition polymerizations of trifunctional amines with diacrylamides. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (21), 5127-5137.
  123. Martinez, C. A.; Hay, A. S., Preparation of hyperbranched macromolecules with aryl fluoride and phenol terminal functionalities using new monomers and Cs<sub>2</sub>CO<sub>3</sub> or Mg(OH)<sub>2</sub> as the condensation agent. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35* (10), 2015-2033.
  124. Himmelberg, P.; Fossum, E., Development of an efficient route to hyperbranched poly(arylene ether sulfone)s. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (14), 3178-3187.
  125. Sun, Q.; Xu, K.; Peng, H.; Zheng, R.; Haeussler, M.; Tang, B. Z., Hyperbranched organometallic polymers: synthesis and properties of poly(ferrocenylenesilyne)s. *Macromolecules* **2003**, *36* (7), 2309-2320.
  126. Kambouris, P.; Hawker, C. J., A versatile new method for structure determination in hyperbranched macromolecules. *J. Chem. Soc., Perkin Trans. 1* **1993**, (22), 2717-2721.



127. Malmström, E.; Hult, A., Hyperbranched aliph. polyesters based on bis-MPA and various polyol cores. *Polym. Mater. Sci. Eng.* **1995**, 73, 349-350.
128. Malmström, E.; Johansson, M.; Hult, A., The effect of terminal alkyl chains on hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid. *Macromol. Chem. Phys.* **1996**, 197 (10), 3199-3207.
129. Suzuki, M.; Ili, A.; Saegusa, T., Multibranching polymerization: palladium-catalyzed ring-opening polymerization of cyclic carbamate to produce hyperbranched dendritic polyamine. *Macromolecules* **1992**, 25 (25), 7071-7072.
130. Reichert, V. R.; Mathias, L. J., Tetrahedrally-oriented four-armed star and branched aramids. *Macromolecules* **1994**, 27 (24), 7024-7029.
131. Kricheldorf, H. R.; Löhden, G. J., New polymer syntheses. 80. Linear, star-shaped, and hyperbranched poly(ester-amide)s from silicon-mediated one-pot condensations of 3-acetoxy-, 3,5-bisacetoxybenzoic acid, and 3-aminobenzoic acid. *Macromol. Sci. Chem.* **1995**, A32 (11), 1915-1930.
132. Kricheldorf, H. R.; Löhden, G., New polymer syntheses. 79. Hyperbranched poly(ester-amide)s based on 3-hydroxybenzoic acid and 3,5-diaminobenzoic acid. *Macromol. Chem. Phys.* **1995**, 196 (6), 1839-1854.
133. Luciani, A.; Plummer, C. J. G.; Nguyen, T.; Garamszegi, L.; Månson, J.-A. E., Rheological and physical properties of aliphatic hyperbranched polyesters. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, 42 (7), 1218-1225.
134. Hult, A.; Johansson, M.; Malmström, E., Dendritic resins for coating applications. *Macromol. Symp.* **1995**, 98, 1159-1161.
135. Johansson, M.; Hult, A., Synthesis, characterization, and UV curing of acrylate functional hyperbranched polyester resins. *J. Coat. Technol.* **1995**, 67 (849), 35-39.
136. Johansson, M.; Malmström, E.; Hult, A., Synthesis, characterization, and curing of hyperbranched allyl ether-maleate functional ester resins. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, 31 (3), 619-624.
137. Gopala, A.; Wu, H.; Xu, J.; Heiden, P., Investigation of readily processable thermoplastic-toughened thermosets: iv. BMIs toughened with hyperbranched polyester. *J. Appl. Polym. Sci.* **1999**, 71 (11), 1809-1817.
138. Schmaljohann, D.; Voit, B.; Jansen, J.; Hedriks, P.; Loontjens, A., New coating systems based on vinyl ether- and oxetane-modified hyperbranched polyesters. *Macromol. Mater. Eng.* **2000**, 275, 31-41.
139. Jikei, M.; Kakimoto, M.-A., Hyperbranched polymers: a promising new class of materials. *Prog. Polym. Sci.* **2001**, 26 (8), 1233-1285.
140. Bosman, A. W.; Janssen, H. M.; Meijer, E. W., About dendrimers: structure, physical properties, and applications. *Chem. Rev.* **1999**, 99 (7), 1665-1688.
141. Voit, B. I., New developments in hyperbranched polymers. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38 (14), 2505-2525.
142. Aulenta, F.; Hayes, W.; Rannard, S., Dendrimers: a new class of nanoscopic containers and delivery devices. *Eur. Polym. J.* **2003**, 39 (9), 1741-1771.
143. Stiriba, S.-E.; Frey, H.; Haag, R., Dendritic polymers in biomedical applications: From potential to clinical use in diagnostics and therapy. *Angew. Chem., Int. Ed.* **2002**, 41 (8), 1329-1334.

144. Kunamaneni, S.; Buzza, D. M. A.; Luca, E. D.; Richards, R. W., Rheology of fractionated and unfractionated hyperbranched polyesters. *Macromolecules* **2004**, *37* (24), 9295-9297.
145. Lederer, A.; Voigt, D.; Clausnitzer, C.; Voit, B. I., Structure characterization of hyperbranched poly(ether amide)s and preparative fractionation. *J. Chromatogr. A.* **2002**, *976* (1-2), 171-179.
146. Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L., Unique behavior of dendritic macromolecules: intrinsic viscosity of polyether dendrimers. *Macromolecules* **1992**, *25* (9), 2401-2406.
147. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III., Starburst dendrimers: control of size, shape, surface chemistry, topology and flexibility in the conversion of atoms to macroscopic materials. *Angew. Chem.* **1990**, *102* (2), 119-157.
148. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III., Starburst dendrimers: molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter. *Angew. Chem., Int. Ed. Engl.* **1990**, *29* (2), 138-175.
149. Sendijarevic, I.; McHugh, A. J., Effects of molecular variables and architecture on the rheological behavior of dendritic polymers. *Macromolecules* **2000**, *33* (2), 590-596.
150. Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Fréchet, J. M. J., Molecular ball bearings: the unusual melt viscosity behavior of dendritic macromolecules. *J. Am. Chem. Soc.* **1995**, *117* (15), 4409-4410.
151. Farrington, P. J.; Hawker, C. J.; Fréchet, J. M. J.; Mackay, M. E., Melt viscosity of dendritic poly(benzyl ether) macromolecules. *Macromolecules* **1998**, *31*, 5043-5050.
152. Uppuluri, S.; Morrison, F. A.; Dvornic, P. R., Rheology of dendrimers. 2. bulk polyamidoamine dendrimers under steady shear, creep, and dynamic oscillatory shear. *Macromolecules* **2000**, *33*, 2551-2560.
153. Kricheldorf, H. R.; Zang, Q.-Z.; Schwarz, G., New polymer syntheses. 6. Linear and branched poly(3-hydroxybenzoates). *Polymer* **1982**, *23* (12), 1821-1829.
154. Hudson, N.; MacDonald, W. A.; Neilson, A.; Richards, R. W.; Sherrington, D. C., Synthesis and characterization of nonlinear PETs produced via a balance of branching and end-capping. *Macromolecules* **2000**, *33* (25), 9255-9261.
155. Plummer, C. J. G.; Luciani, A.; Nguyen, T.-Q.; Garamszegi, M. R.; Manson, J.-A. E., Rheological characteristics of hyperbranched polyesters. *Polym. Bull.* **2002**, *49* (1), 77-84.
156. Nunez, C. M.; Chiou, B.-S.; Andradý, A. L.; Khan, S. A., Solution rheology of hyperbranchedpolyesters and their blends with linear polymers. *Macromolecules* **2000**, *33* (5), 1720-1726.
157. Ahn, D. U.; Kwak, S.-Y., Details of dynamic mechanical properties of dendritic poly(ether ketone)s in conjunction with their highly branched structure and degree of branching. *Macromol. Mater. Eng.* **2001**, *286* (1), 17-25.
158. Magnusson, H.; Malmström, E.; Hult, A.; Johansson, M., The effect of degree of branching on the rheological and thermal properties of hyperbranched aliphatic polyethers. *Polymer* **2001**, *43* (2), 301-306.

159. Pettersson, B., Hyperbranched polymers: unique design tools for multi-property control in resins and coatings. *Pigm. Resin Technol.* **1996**, *25* (4), 4-14.
160. Wooley, K. L.; Fréchet, J. M. J.; Hawker, C., Influence of shape on the reactivity and properties of dendritic, hyperbranched and linear aromatic polyesters. *Polymer* **1994**, *35* (21), 4489-4495.
161. Shu, C.-F.; Leu, C.-M.; Huang, F.-Y., Synthesis, modification, and characterization of hyperbranched poly(ether ketones). *Polymer* **1999**, *40* (23), 6591-6596.
162. Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J., Physical properties of dendritic macromolecules: a study of glass transition temperature. *Macromolecules* **1993**, *26* (7), 1514-1519.
163. Jang, J.; Oh, J. H.; Moon, S. I., Crystallization behavior of poly(ethylene terephthalate) blended with hyperbranched polymers: the effect of terminal groups and composition of hyperbranched polymers. *Macromolecules* **2000**, *33* (5), 1864-1870.
164. Kim, Y. H.; Webster, O. W., Hyperbranched polyphenylenes. *Macromolecules* **1992**, *25* (21), 5561-5572.
165. Hong, Y.; Cooper-White, J. J.; Mackay, M. E.; Hawker, C. J.; Malmström, E.; Rehnberg, N. J., A novel processing aid for polymer extrusion: Rheology and processing of polyethylene and hyperbranched polymer blends. *Rheol.* **1999**, *43* (3), 781-793.
166. Schmaljohann, D.; Pötschke, P.; Hässler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A., Blends of amphiphilic, hyperbranched polyesters and different polyolefins. *Macromolecules* **1999**, *32* (19), 6333-6339.
167. Huber, T.; Pötschke, P.; Pompe, G.; Häßler, R.; Voit, B.; Grutke, S.; Gruber, F., Blends of hyperbranched poly(ether amide)s and polyamide-6. *Macromol. Mater. Eng.* **2000**, *280/281*, 33-40.
168. Mulkern, T. J.; Beck, T. N. C., Processing and characterization of reactive polystyrene/hyperbranched polyester blends. *Polymer* **2000**, *41* (9), 3193-3203.
169. Böhme, F.; Clausnitzer, C.; Gruber, F.; Grutke, S.; Huber, T.; Pötschke, P.; Voit, B., Hyperbranched poly(ether amide)s via nucleophilic ring opening reaction of oxazolines. *High Perform. Polym.* **2001**, *13* (2), S21-S31.
170. Voit, B., Hyperbranched polymers-all problems solved after 15 years of research? *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (13), 2679-2699.
171. Turner, S. R.; Voit, B. I., Unpublished results.
172. Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I., Novel blends of hyperbranched polyesters and linear polymers. *Macromolecules* **1995**, *28* (9), 3214-3220.
173. Nunez, C. M.; Andraday, A. L.; Guo, R. K.; Baskir, J. N.; Morgan, D. R., Mechanical properties of blends of PAMAM dendrimers with poly(vinyl chloride) and poly(vinyl acetate). *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36* (12), 2111-2117.
174. Carr, P. L.; Davies, G. R.; Feast, W. J.; Stainton, N. M.; Ward, I. M., Dielectric and mechanical characterization of aryl ester dendrimer/PET blends. *Polymer* **1996**, *37* (12), 2395-2401.

175. Gitsov, I.; Wooley, K. L.; Hawker, C. J.; Ivanova, P. T.; Fréchet, J. M. J., Synthesis and properties of novel linear-dendritic block copolymers. Reactivity of dendritic macromolecules toward linear polymers. *Macromolecules* **1993**, *26* (21), 5621-5627.
176. Gitsov, I.; Fréchet, J. M. J., Solution and solid-state properties of hybrid linear-dendritic block copolymers. *Macromolecules* **1993**, *26* (24), 6536-6546.
177. Yu, D.; Vladimirov, N.; Fréchet, J. M. J., MALDI-TOF in the characterizations of dendritic-linear block copolymers and stars. *Macromolecules* **1999**, *32* (16), 5186-5192.
178. Gitsov, I.; Fréchet, J. M. J., Novel nanoscopic architectures. Linear-globular ABA copolymers with polyether dendrimers as A blocks and polystyrene as B block. *Macromolecules* **1994**, *27* (25), 7309-7315.
179. Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J., Well-defined triblock hybrid dendrimers based on lengthy oligothiophene cores and poly(benzyl ether) dendrons. *J. Am. Chem. Soc.* **1998**, *120* (42), 10990-10991.
180. Leduc, M. R.; Hawker, C. J.; Dao, J.; Fréchet, J. M. J., Dendritic initiators for "living" radical polymerizations: a versatile approach to the synthesis of dendritic-linear block copolymers. *J. Am. Chem. Soc.* **1996**, *118* (45), 11111-11118.
181. Emrick, T.; Hayes, W.; Fréchet, J. M. J., A TEMPO-mediated "living" free-radical approach to ABA triblock dendritic linear hybrid copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37* (20), 3748-3755.
182. Mecerreyes, D.; Dubois, P.; Jerome, R.; Hedrick, J. L.; Hawker, C. J., Synthesis of dendritic-linear block copolymers by living ring-opening polymerization of lactones and lactides using dendritic initiators. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37* (13), 1923-1930.
183. Froimowicz, P.; Gandini, A.; Strumia, M., New polyfunctional dendritic-linear hybrids from terminal amine polyether oligomers (Jeffamine®): synthesis and characterization. *Tetrahedron Lett.* **2005**, *46* (15), 2653-2657.
184. Namazi, H.; Adeli, M., Synthesis of barbell-like triblock copolymers, dendritic triazine-block-poly(ethylene glycol)-block-dendritic triazine and investigation of their solution behaviors. *Polymer* **2005**, *46* (24), 10788-10799.
185. Namazi, H.; Adeli, M., Solution properties of dendritic triazine/poly(ethylene glycol)/ dendritic triazine block copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (1), 28-41.
186. Mackay, M. E.; Hong, Y.; Jeong, M.; Tande, B. M.; Wagner, N. J.; Hong, S.; Gido, S. P.; Vestberg, R.; Hawker, C. J., Microphase separation of hybrid dendron-linear diblock copolymers into ordered structures. *Macromolecules* **2002**, *35* (22), 8391-8399.
187. Duan, X.; Yuan, F.; Wen, X.; Yang, M.; He, B.; Wang, W., Alternating crystalline-amorphous layers in hybrid block copolymers of linear poly(ethylene glycol) and dendritic poly(benzyl ether). *Macromol. Chem. Phys.* **2004**, *205*, 1410-1417.
188. Heuer, H.-W.; Wehrmann, R.; Meyer, A.; Pielartzik, H.; Bruder, F.-K.; Paulusse, J. M. J. Polycarbonates, polyester carbonates and polyesters having branched terminal groups. U.S. Patent 6,784,278 B2, August 31, 2004.

189. Jeong, M.; Mackay, M. E.; Vestberg, R.; Hawker, C. J., Intrinsic variation in different solvents for dendrimers and their hybrid copolymers with linear polymers. *Macromolecules* **2001**, *34* (14), 4927-4936.
190. Gitsov, I.; Fréchet, J. M. J., Stimuli-responsive hybrid macromolecules: novel amphiphilic star copolymers with dendritic groups at the periphery. *J. Am. Chem. Soc.* **1996**, *118* (15), 3785-3786.
191. Fréchet, J. M. J.; Gitsov, I.; Monteil, T.; Rochat, S.; Sassi, J.-F.; Vergelati, C.; Yu, D., Modification of surfaces and interfaces by non-covalent assembly of hybrid linear-dendritic block copolymers: poly(benzyl ether) dendrons as anchors for poly(ethylene glycol) chains on cellulose or polyester. *Chem. Mater.* **1999**, *11* (5), 1267-1274.
192. Gitsov, I.; Lambrych, K. R.; Remnant, V. A.; Pracitto, R., Micelles with highly branched nanoporous interior: solution properties and binding capabilities of amphiphilic copolymers with linear dendritic architecture. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38* (15), 2711-2727.
193. Kwak, S.-Y.; Ahn, D. U.; Choi, J.; Song, H. J.; Lee, S.-H., Amelioration of mechanical brittleness in hyperbranched polymer. 1. Macroscopic evaluation by dynamic viscoelastic relaxation. *Polymer* **2004**, *45* (20), 6889-6896.
194. Santini, C. M. B.; Hatton, T. A.; Hammond, P. T., Solution behavior of linear - dendritic rod diblock copolymers in methanol. *Langmuir* **2006**, *22* (18), 7487-7498.
195. Zhu, L.; Tong, X.; Li, M.; Wang, E., Synthesis and solution properties of anionic linear-dendritic block amphiphiles. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38* (23), 4282-4288.
196. Liu, D.; Zhong, C., Dissipative particle dynamics simulation of microphase separation and properties of linear - dendritic diblock copolymer melts under steady shear flow. *Macromol. Rapid Commun.* **2005**, *26* (24), 1960-1964.
197. Iyer, J.; Fleming, K.; Hammond, P. T., Synthesis and solution properties of new linear - dendritic diblock copolymers. *Macromolecules* **1998**, *31* (25), 8757-8765.
198. Sill, K.; Emrick, T., Bis-dendritic polyethylene prepared by ring-opening metathesis polymerization in the presence of bis-dendritic transfer agents. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (22), 5429-5439.
199. Zhu, L.; Zhu, G.; Li, M.; Wang, E.; Zhu, R.; Qi, X., Thermosensitive aggregates self-assembled by an asymmetric block copolymer of dendritic polyether and poly(N-isopropylacrylamide). *Eur. Polym. J.* **2002**, *38* (12), 2503-2506.
200. Chapman, T. M.; Hillyer, G. L.; Mahan, E. J.; Shaffer, K. A., Hydraamphiphiles: novel linear dendritic block copolymer surfactants. *J. Am. Chem. Soc.* **1994**, *116* (24), 11195-11196.
201. Marcos, A. G.; Pusel, T. M.; Thomann, R.; Pakula, T.; Okrasa, L.; Geppert, S.; Gronski, W.; Frey, H., Linear-hyperbranched block copolymers consisting of polystyrene and dendritic poly(carbosilane) block. *Macromolecules* **2006**, *39* (3), 971-977.
202. Passeno, L. M.; Mackay, M. E.; Baker, G. L.; Vestberg, R.; Hawker, C. J., Conformational changes of linear-dendrimer diblock copolymers in dilute solution. *Macromolecules* **2006**, *39* (2), 740-746.

203. Gillies, E. R.; Jonsson, T. B.; Fréchet, J. M. J., Stimuli-responsive supramolecular assemblies of linear-dendritic copolymers. *J. Am. Chem. Soc.* **2004**, *126* (38), 11936-11943.
204. Fréchet, J. M. J., Dendritic macromolecules at the interface of nanoscience and nanotechnology. *Macromol. Symp.* **2003**, *201*, 11-22.
205. Roziere, J.; Jones, D. J., Non-fluorinated polymer materials for proton exchange membrane fuel cells. *Annu. Rev. Mater. Res.* **2003**, *33*, 503-555.
206. Winter, M.; Brodd, R. J., What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* **2004**, *104* (10), 4245-4269.
207. Kreuer, K. D., On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.* **2001**, *185* (1), 29-39.
208. Jannasch, P., Fuel cell membrane materials by chemical grafting of aromatic main-chain polymers. *Fuel Cells* **2005**, *5* (2), 248-260.
209. Zaluski, C.; Xu, G., Blends of nafion and dow perfluorosulfonated ionomer membranes. *Macromolecules* **1994**, *27* (23), 6750-6754.
210. Won, J.; Park, H. H.; Kim, Y. J.; Choi, S. W.; Ha, H. Y.; Oh, I.-H.; Kim, H. S.; Kang, Y. S.; Ihn, K. J., Fixation of nanosized proton transport channels in membranes. *Macromolecules* **2003**, *36* (9), 3228-3234.
211. Iojoiu, C.; Marechal, M.; Chabert, F.; Sanchez, J.-Y., Mastering sulfonation of aromatic polysulfones: crucial for membranes for fuel cell application. *Fuel Cells* **2005**, *5* (3), 344-355.
212. Dyck, A.; Fritsch, D.; Nunes, S. P., Proton-conductive membranes of sulfonated polyphenylsulfone. *J. Appl. Polym. Sci.* **2002**, *86* (11), 2820-2827.
213. Nolte, R.; Ledjeff, K.; Bauer, M.; Muelhaupt, R., Partially sulfonated poly(arylene ether sulfone) - a versatile proton conducting membrane material for modern energy conversion technologies. *J. Membr. Sci.* **1993**, *83* (2), 211-220.
214. Hickner, M.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E., Alternative polymer systems for proton exchange membranes (PEMs). *Chem. Rev.* **2004**, *104* (10), 4587-4612.
215. Harrison, W. L.; Hickner, M. A.; Kim, Y. S.; McGrath, J. E., Poly(arylene ether sulfone) copolymers and related systems from disulfonated monomer building blocks: synthesis, characterization, and performance - a topical review. *Fuel Cells* **2005**, *5* (2), 201-212.
216. Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Hay, A. S., Ionomers for proton exchange membrane fuel cells with sulfonic acid groups on the end groups: novel linear aromatic poly(sulfide-ketone)s. *Macromolecules* **2008**, *41* (2), 277-280.
217. Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z.; Holdcroft, S.; Hay, A. S., Ionomers for proton exchange membrane fuel cells with sulfonic acid groups on the end groups: novel branched poly(ether-ketone)s. *Macromolecules* **2008**, *41* (2), 281-284.
218. Matsumura, S.; Hlil, A. R.; Hay, A. S., Synthesis, properties, and sulfonation of novel dendritic multiblock copoly(ether-sulfone). *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (19), 6365-6375.

219. Grunzinger, S. J.; Hayakawa, T.; Kakimoto, M.-A., Synthesis of multiblock hyperbranched-linear poly(ether sulfone) copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (14), 4785-4793.
220. Lafitte, B.; Puchner, M.; Jannasch, P., Proton conducting polysulfone ionomers carrying sulfoaryloxybenzoyl side chains. *Macromol. Rapid Commun.* **2005**, *26* (18), 1464-1468.
221. Lafitte, B.; Karlsson, L. E.; Jannasch, P., Sulfo-phenylation of polysulfones for proton-conducting fuel cell membranes. *Macromol. Rapid Commun.* **2002**, *23* (15), 896-900.
222. Karlsson, L. E.; Jannasch, P., Polysulfone ionomers for proton-conducting fuel cell membranes: sulfoalkylated polysulfones. *J. Membr. Sci.* **2004**, *230* (1-2), 61-70.
223. Lafitte, B.; Jannasch, P., Proton-conducting aromatic polymers carrying hypersulfonated side chains for fuel cell applications. *Adv. Funct. Mater.* **2007**, *17* (15), 2823-2834.
224. Kerres, J.; Cui, W.; Reichle, S., New sulfonated engineering polymers via the metalation route. I. sulfonated poly(ether sulfone) PSU Udel via metalation-sulfination-oxidation. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34* (12), 2421-2438.
225. Guiver, M. D.; Apsimon, J. W.; Kutowy, O., The modification of polysulfone by metalation. *J. Polym. Sci. Part C: Polym. Lett.* **1988**, *26* (2), 123-127.
226. Lafitte, B.; Jannasch, P., Phosphonation of polysulfones via lithiation and reaction with chlorophosphonic acid esters. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *43* (2), 273-286.
227. Lafitte, B.; Jannasch, P., Polysulfone ionomers functionalized with benzoyl(difluoromethylenephosphonic acid) side chains for proton-conducting fuel-cell membranes. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *45* (2), 269-283.
228. Kerres, J.; Cui, W.; Disson, R.; Neubrand, W., Development and characterization of crosslinked ionomer membranes based upon sulfinated and sulfonated PSU Crosslinked PSU blend membranes by disproportionation of sulfinic acid groups. *J. Membr. Sci.* **1998**, *139* (2), 211-225.
229. Kerres, J.; Cui, W.; Junginger, M., Development and characterization of crosslinked ionomer membranes based upon sulfinated and sulfonated PSU Crosslinked PSU blend membranes by alkylation of sulfinic groups with dihalogenoalkanes. *J. Membr. Sci.* **1998**, *139* (2), 227-241.
230. Kerres, J.; Zhang, W.; Cui, W., New sulfonated engineering polymers via the metalation route. II. Sulfinated/sulfonated poly(ether sulfone) PSU Udel and its crosslinking. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36* (9), 1441-1448.
231. Kerres, J.; Ullrich, A.; Hein, M., Preparation and characterization of novel basic polysulfone polymers. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39* (17), 2874-2888.
232. Kerres, J.; Ullrich, A.; Meier, F.; Haring, T., Synthesis and characterization of novel acid-base polymer blends for application in membrane fuel cells. *Solid State Ionics* **1999**, *125* (1-4), 243-249.

## Chapter 3: Synthesis, Characterization and Properties of Linear Poly(ether sulfone)s with Dendritic Terminal Groups

(Published as: Osano, K.; Turner, S. R. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 958-969)

### 3.1 Abstract

Hybrid linear-dendritic ABA polymers, where A and B are dendritic and linear polymers respectively, were synthesized in a single step via step-growth polymerization of 4,4'-difluorodiphenylsulfone (DFDPS) and bisphenol-A (BPA) using arylene ether ketone dendrons of first and second generations (G1-OH and G2-OH) as monofunctional end-cappers. These G1 and G2-terminated poly(ether sulfone)s (G1-PESs and G2-PESs) were characterized by  $^1\text{H}$  NMR, SEC, DSC, TGA, melt rheology, and tensile tests. The comparison of the glass transition temperatures ( $T_g$ s) of these polymers with those of t-butylphenoxy-terminated polysulfones (T-PESs) reveals that the G1- and G2-PESs have lower  $T_g$ s at all molecular weights investigated. However, a plot of  $T_g$  versus  $1/M_n$  shows that the difference between the three series becomes negligible at infinite molecular weight and agrees with the chain end free volume theory. The melt viscosities of G1-PES and G2-PES with high molecular weights do not show a Newtonian region and in the high frequency region, their viscosities are lower than that of the control while the stress-strain properties are comparable to those of the control, suggesting that it is possible to reduce the high shear melt viscosity of a PES without affecting the stress-strain properties by introducing bulky dendritic terminal groups.



### 3.2 Introduction

Linear-dendritic ABA copolymers, where A and B are dendritic and linear polymers respectively, are known to possess properties different from their linear non-dendronized analogues. There are a number of reports of attaching dendritic structures to the ends of linear polymers to form linear-dendritic ABA copolymers.<sup>1-14</sup> Unusual solution properties have been observed in some cases.<sup>2, 4, 6, 10</sup> One recent patent claims the attachment of bulky structures to the terminal ends of thermoplastics, such as bisphenol A-based polycarbonate, leads to a decreased zero shear melt viscosity without a significant reduction in  $T_g$ .<sup>15</sup> As widely known, the molecular weights of many common commercial polymers are only slightly higher than the entanglement molecular weights owing to the familiar problems with the processing of highly viscous polymers. A reduction in melt viscosity of polymers with no or little alteration of other physical properties, if possible, would facilitate the polymer processing. Our objectives are to synthesize linear-dendritic ABA copolymers via step-growth polymerization involving two difunctional monomers and preformed monofunctional dendrons as end-cappers, the motivation being the investigation of the effects of bulky terminal groups on the rheological and mechanical properties as well as the fundamental structure-property relationship of this dumbbell-like architecture. Arylene ether ketone dendrons and a polysulfone backbone were chosen for our first investigation because of their high chemical and thermal stabilities. Although several researchers<sup>1-14</sup> have built this dumbbell-like architecture, little work has been reported on the synthesis of this architecture using engineering thermoplastics via one-pot step-growth polymerization, apparently due to exchange reactions, such as transesterification and transesterification,

which would destroy the dumbbell-like architecture. Controlling the physical properties of polymers by modification of the end groups rather than the polymer backbone, if possible, could be also economical since the end group concentrations in polymers are relatively low. In this paper, we report the synthesis of our linear-dendritic ABA copolymers and the side reactions associated with it as well as measurements of some of the physical properties.

### **3.3 Experimental**

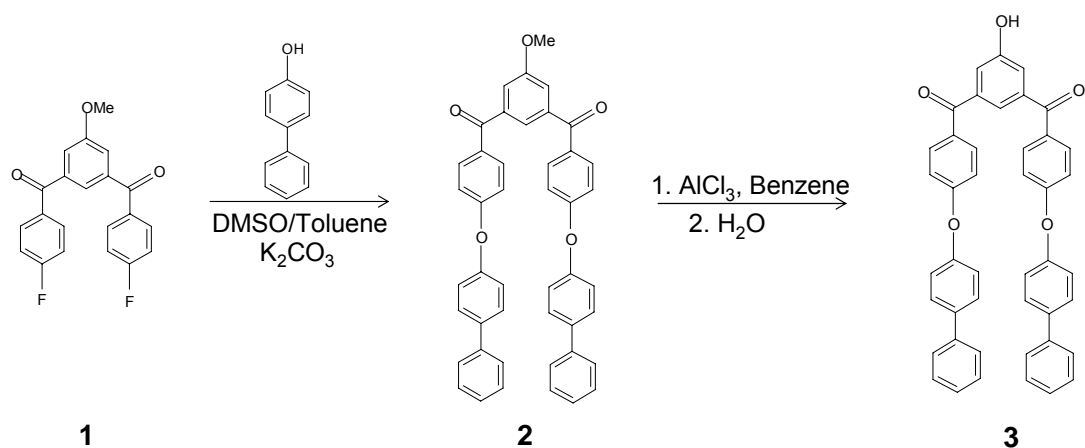
#### **3.3.1 Materials**

4,4'-Dichlorodiphenyl sulfone (Solvay) was dried under vacuum overnight before use. Dimethylsulfate (Acros Organic) was used as received. All the other reagents were purchased from Aldrich and used as received.

#### **3.3.2 Synthesis**

**Synthesis of G1 and G2 Dendrons.** The syntheses of our novel dendrons started with the preparation of 3,5-bis(4-fluorobenzoyl)anisole (**1**), the building block of the Morikawa dendrimer, from 5-hydroxyisophthalic acid using the method reported by Morikawa et al.<sup>16</sup> The crude product **1** obtained was used for the preparation of G1 dendrons (Scheme 3.1). For the synthesis of G2 dendrons (Scheme 3.2), pure **1** was used as the starting material. 9.30 g of pure **1** was obtained by performing silica gel column chromatography on 10.0 g of crude product **1** using 1:9 ethyl acetate / hexane. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of pure **1** matched those reported by Morikawa.<sup>16</sup>

**Preparation of G1-OMe (2).** The crude product containing **1** (34.05 g), 4-phenylphenol (41.27 g, 242.5 mmol), potassium carbonate (40.21 g, 291.0 mmol), DMSO (200 ml), and toluene (100 ml) were placed in a flask equipped with an Ar inlet. The mixture was stirred for 1 hr at 130 °C where water was removed by azeotropic distillation. Then the temperature was raised to 150 °C and the mixture was stirred for 2 hrs. After cooling, the bulk of the solvent was evaporated by rotary evaporator to give a yellow solid. Water was added to the solid and the excess potassium carbonate was hydrolyzed. This mixture was extracted with methylene chloride three times. The combined extracts were dried over MgSO<sub>4</sub> and filtered. The solution was then poured into ethanol to give a white precipitate, which was collected by vacuum filtration. This white powder was dissolved in methylene chloride and precipitated from ethanol again and dried under high vacuum at 80 °C overnight to give **2** (49.88 g, 79.0 mmol) as a white powder. Yield: 85% (calculated on the assumption that the crude product **1** is 93 % pure). mp 152 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.85 (m, 4H), 7.67 (t, 1H), 7.62 (m, 4H), 7.58 (m, 4H), 7.53 (d, 2H), 7.43 (m, 4H), 7.35 (m, 2H), 7.16 (m, 4H), 7.14 (m, 4H), 3.92 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ194.5, 162.2, 159.9, 155.0, 140.5, 139.5, 138.0, 132.8, 131.6, 129.1, 129.0, 127.5, 127.2, 123.7, 120.7, 118.7, 117.5, 56.0. Elemental analysis: calculated C, 82.80; H, 4.94. found: C, 82.20; H, 4.86.

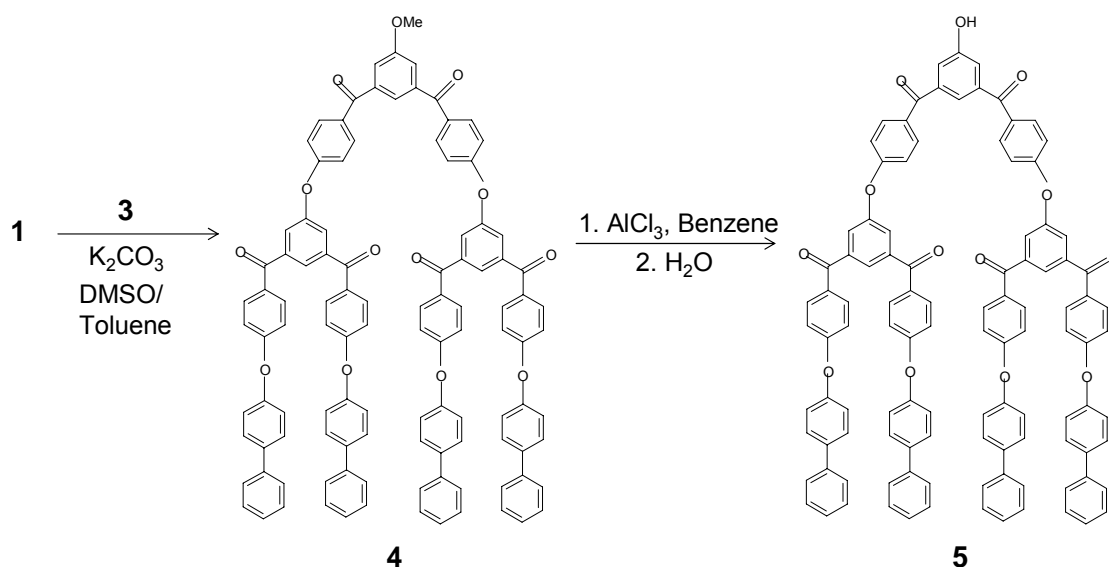


**Scheme 3.1** Synthesis of G1 dendrons.

**Preparation of G1-OH (3).** G1-OMe (**2**) (49.85 g, 76.38 mmol),  $\text{AlCl}_3$  (101.84 g, 763.8 mmol), and benzene (300 ml) were placed in a flask equipped with a reflux condenser and an Ar inlet. The mixture was stirred at reflux temperature for 1 hr. After cooling, the mixture was poured into ice-water slowly and transferred into a separatory funnel. The organic phase was collected and the aqueous phase was extracted with methylene chloride twice. The combined extracts were dried over  $\text{MgSO}_4$ . After the  $\text{MgSO}_4$  was filtered out, the solution was passed through silica gel by continuously feeding methylene chloride. After the eluent became colorless, ethyl acetate was flushed through the silica gel and the eluent was collected. The bulk of the solvent was removed by a rotary evaporator and the white solid obtained was dried under high vacuum at 80 °C overnight to give **3** (36.59 g, 57.29 mmol) as a white powder. Yield: 75%. mp 186 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.85 (m, 4H), 7.64 (t, 1H), 7.60 (m, 4H), 7.56 (m, 4H), 7.54 (d, 2H), 7.43 (m, 4H), 7.34 (m, 2H), 7.14 (m, 4H), 7.07 (m, 4H), 6.37 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  194.7, 162.1, 156.3, 154.7, 140.1, 139.3, 137.8, 132.6, 131.1, 128.8,

128.7, 127.3, 126.9, 123.4, 120.4, 120.2, 117.3. Elemental analysis: calculated C, 82.74; H, 4.73. found: C, 82.16; H, 4.76.

**Preparation of G2-OMe (4).** Pure **1** (5.00 g, 14.2 mmol), **3** (19.04 g, 29.81 mmol), potassium carbonate (4.94 g, 35.8 mmol), DMSO (30 ml) and toluene (15 ml) were added to a round bottom flask equipped with an Ar inlet. The mixture was stirred at 130 °C for 2 hrs to remove water by azeotropic distillation and at 150 °C for 2 hrs. After cooling, the crude product was precipitated in ethanol and collected by vacuum filtration. The isolation of the product was achieved by silica gel column chromatography using 1:9 ethyl acetate / methylene chloride, giving **4** (19.24 g, 12.10 mmol) as a slightly yellow powder Yield. 85 %. No melting point was detected by DSC, which is consistent with the observation made by Morikawa et al.<sup>16</sup> that his similar G2 and higher generation dendrons do not have melting points. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ7.95-7.82 (m, 14H), 7.73 (d, 4H), 7.58-7.70 (m, 17H), 7.52 (d, 2H), 7.45 (m, 8H), 7.36 (m, 4H), 7.14-7.21 (m, 12H), 7.11 (m, 8H), 3.91 (s, 3H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ194.2, 193.5, 162.3, 160.9, 159.8, 156.2, 155.0, 140.3, 139.4, 137.9, 132.8, 132.7, 132.6, 131.3, 129.1, 128.9, 127.5, 127.1, 124.1, 123.4, 120.7, 118.6, 118.1, 117.5, 56.1. Elemental analysis: calculated C, 82.35; H, 4.57. found: C, 82.43; H, 4.50.

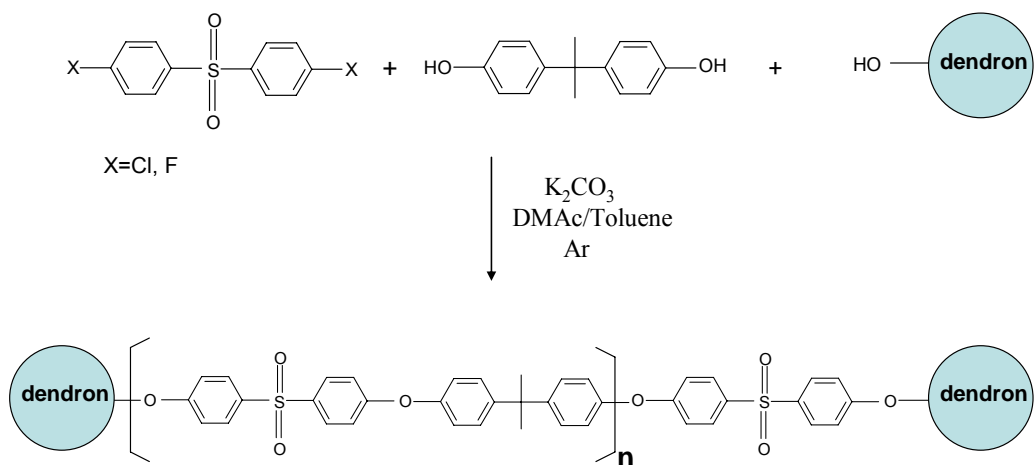


**Scheme 3.2** Synthesis of G2 dendrons.

**Preparation of G2-OH (5).** G2-OMe (**4**) (15.00 g, 9.436 mmol), aluminum chloride (12.58 g, 94.35 mmol), and benzene (70 ml) were placed in a flask equipped with an Ar inlet and stirred at 80 °C for 1 hr. After cooling, the mixture was poured into ice water slowly and transferred into a separatory funnel. The organic phase was collected and the aqueous phase was extracted twice with methylene chloride. The combined extracts were dried over MgSO<sub>4</sub>. After the MgSO<sub>4</sub> was filtered out, the solvent was removed by a rotary evaporator. The isolation of the product was carried out by silica gel column chromatography using 1:9 ethyl acetate / methylene chloride. The white powder obtained was dried under high vacuum at 80 °C overnight to give **5** (10.71 g, 6.797 mmol) as a white powder. Yield: 72%. No melting point was detected by DSC. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ7.88 (m, 2H), 7.86-7.78 (m, 12H), 7.68 (d, 4H), 7.65-7.53 (m, 17H), 7.46 (m, 10H), 7.32 (m, 4H), 7.16-7.09 (m, 12H), 7.06 (m, 8H), 6.44 (s, 1H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ194.1, 193.6, 162.3, 160.9, 156.3, 156.2, 155.0, 140.3, 139.6,

137.9, 132.8, 132.7, 132.5, 131.3, 129.1, 128.9, 127.5, 127.1, 124.1, 123.3, 120.7, 120.2, 118.2, 117.5. Elemental analysis: calculated C, 82.32; H, 4.48. found: C, 82.23; H, 4.41.

**Polymerization.** G1-PESs were synthesized from 4,4'-difluorodiphenylsulfone (DFDPS) and bisphenol-A (BPA) and the preformed G1-OH (Scheme 3.3). Molecular weight control was achieved by stoichiometric imbalance according to the Carothers equation. The following is a detailed procedure for one of the polymers; DFDPS (4.411 g, 17.35 mmol), BPA (3.846 g, 16.85 mmol), G1-OH (0.638 g, 0.9986 mmol), potassium carbonate (6.50 g, 47.0 mmol), DMAc (30 ml), and toluene (15 ml) were placed in a flask equipped with an Ar inlet and mechanical stirrer. The mixture was stirred at 130-140 °C for 5 hrs to remove water by azeotropic distillation and at 155 °C for 15 hrs. After cooling, the mixture was diluted with THF and filtered to remove KF and K<sub>2</sub>CO<sub>3</sub>. The polymer was then precipitated in 800 ml dilute aqueous HCl. The polymer was collected by vacuum filtration and redissolved in THF and reprecipitated in EtOH. The polymer was dried under vacuum at 120-130 °C overnight before characterization. G2-PESs were prepared in a similar fashion using G2-OH as the end-capper. T-PESs were synthesized from DCDPS, BPA, and 4-tert-butylphenol using the same procedure except that the polymerization time employed was 24 hrs. For the investigation of transesterification, G1-PESs and G2-PESs were also synthesized from DCDPS using the same procedure as T-PESs. In this paper, we refer these G1-PESs and G2-PESs that were made from DCDPS as C-G1-PESs and C-G2-PESs, respectively, in order to avoid confusion and distinguish these polymers from those made from DFDPS.

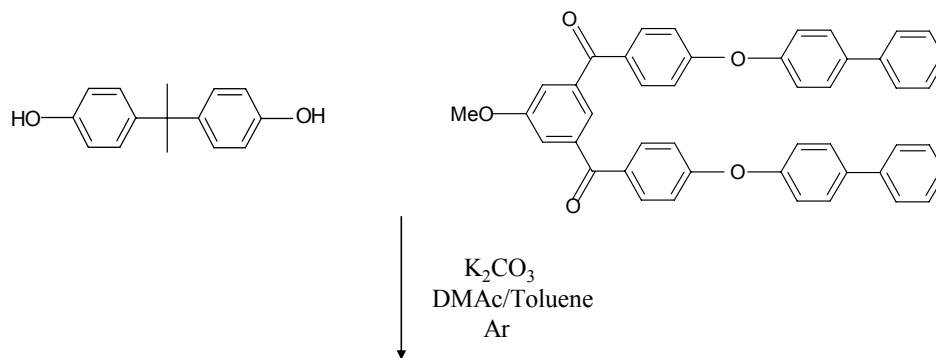


**Scheme 3.3** Preparation of ABA copolymers.

**Preparation of polymers with dendritic additives.** T-PES c with 7 wt % G1-OMe was prepared by dissolving T-PES c (4.65 g) and G1-OMe (0.35 g) in methylene chloride and the bulk of solvent was removed on a rotary evaporator. Then the mixture was dried at 130 °C under vacuum for 2 days. All other additive-containing polymers were made by this method using calculated amounts of parent polymers and dendritic additives.

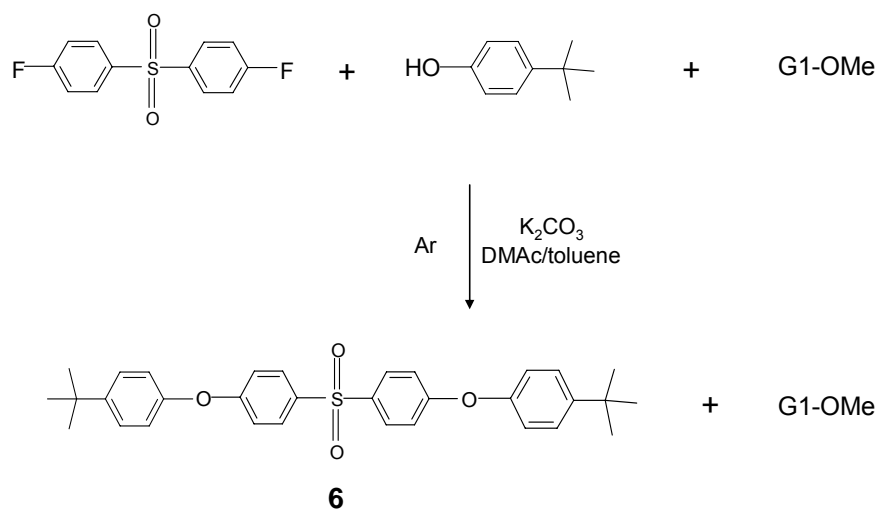
**Model reactions investigating transesterification.** G1-OMe (1.00 g, 1.53 mmol) and BPA (3.80 g, 16.6 mmol), potassium carbonate (6.50 g, 47.0 mmol), DMAc (25 ml), and toluene (15 ml) were placed in a flask equipped with an Ar inlet and exposed to the same condition as the polymerization procedure. After the reaction, the mixture was poured into ethanol to check whether or not G1-OMe precipitated (Scheme 3.4). Another mixture was made simply by dissolving BPA and G1-OMe in DMAc followed by no heating. This mixture was also poured into ethanol to check the formation of precipitates.





**Scheme 3.4** Model reaction investigating ether cleavage of G1 dendron by BPA.

DFDPS (0.50 g, 2.0 mmol), TBP (0.59 g, 3.9 mmol), G1-OMe (0.20 g, 0.31 mmol) and potassium carbonate (0.58 g, 4.2 mmol) were placed in a flask containing DMAc (5 ml) and toluene (3 ml). After exposing this mixture to the same condition as the polymerization procedure and the similar work-up, the product was dried under high vacuum (Scheme 3.5). The crude product was analyzed by FAB-MS.



**Scheme 3.5** Model reaction investigating ether cleavage of G1 dendron by TBP.

4,4'-Di(*t*-butylphenoxy)diphenylsulfone (**6**) was synthesized from DFDPS (0.50 g), *t*-butylphenol (0.59 g) and potassium carbonate (0.58 g) and isolated by silica gel column chromatography using methylene chloride as the mobile phase. The purity of this product was confirmed by  $^1\text{H}$  NMR and it was analyzed by FAB-MS.

### 3.3.3 Characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Differential Scanning Calorimetry (DSC) was run from 40 °C to 230 °C by Perkin Elmer Pyris1 under nitrogen with a flow rate of 20 ml/min and a heating rate of 10 °C/min.  $T_g$  was determined from the mid-point of an endothermic shift of the second heating cycle. In the case of G1-OMe (**2**), the sample was heated to 180 °C and rapidly (80 °C/min) cooled down to 25 °C. Then the second cycle was scanned at 10 °C/min to determine the  $T_g$ . The same procedure was used to measure the  $T_g$  of G2-OMe.  $T_m$  was determined from the melting peak of the first heating cycle under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out by TA Instruments TGA2950 from 25 °C to 800 °C under nitrogen at a heating rate of 10 °C/min. Size Exclusion Chromatography (SEC) was recorded in THF with a flow rate of 1.00 ml/min at 40 °C by Waters 717 Autosampler with 3 in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The  $dn/dc$  values were calculated on-line using the calibration constant for the RI detector and for the mass of the polymer samples assuming 100% mass recovery of the samples. Elemental

analysis was done by Atlantic Microlab, Inc (Norcross, Georgia). Melt viscosities was measured by TA Instrument G2 rheometer with a 25 mm steel parallel plate using frequency sweep mode at 4 % strain at 280 °C under nitrogen. Mass spectrometry was recorded by JMS-HX110 dual focusing mass spectrometer with Fast Atomic Bombardment (FAB) using nitrobenzyl alcohol as the matrix. Tensile tests were performed on an Instron Model 4400 Universal Testing System controlled by Series IX software. Dog-bone shaped samples (10 mm gauge length and 2.91 mm width) were cut by a standard bench-top die from compression molded films (0.5 mm thickness). Compression molding was done on Teflon sheets at 230 °C. Samples were deformed under ambient conditions at a cross-head speed of 25 mm/min until failure occurred.

### **3.4 Results and Discussion**

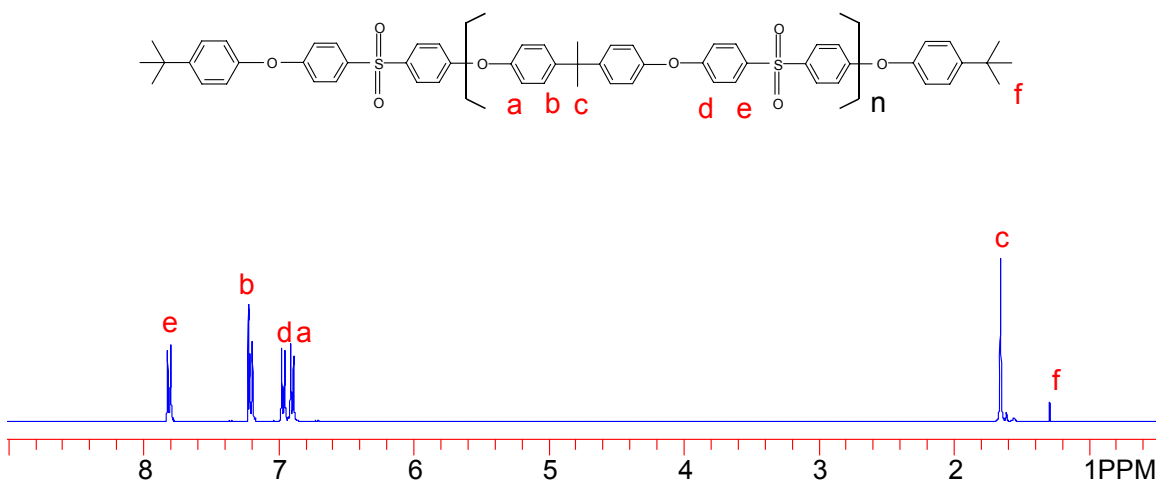
G1-PESs and G2-PESs were made from DFDPS, instead of the less expensive analogous monomer DCDPS, in order to minimize the arylene ether exchange on the dendrons. T-PESs were made from DCDPS because TBP does not possess an exchangeable ether linkage. The molecular weights of all the polymers were obtained by <sup>1</sup>H NMR end group analysis and SEC and are summarized in Table 3.1. Figure 3.1- Figure 3.3 show the <sup>1</sup>H NMR spectra of the polymers. For T-PESs, the <sup>1</sup>H NMR molecular weight determination was done by comparing the tert-butyl peak at 1.29 ppm to the isopropylidene signal of the polymer backbone at 1.66 ppm. For G1-PESs and G2-PESs, the dendrons' biphenyl peak at 7.3 ppm was compared to that of the isopropylidene signal. As shown in Table 3.1, the molecular weights were successfully controlled using

calculated amounts of reactants according to the Carothers equation, indicating that the dendrons can serve as end-cappers to build this dumbbell-like architecture.

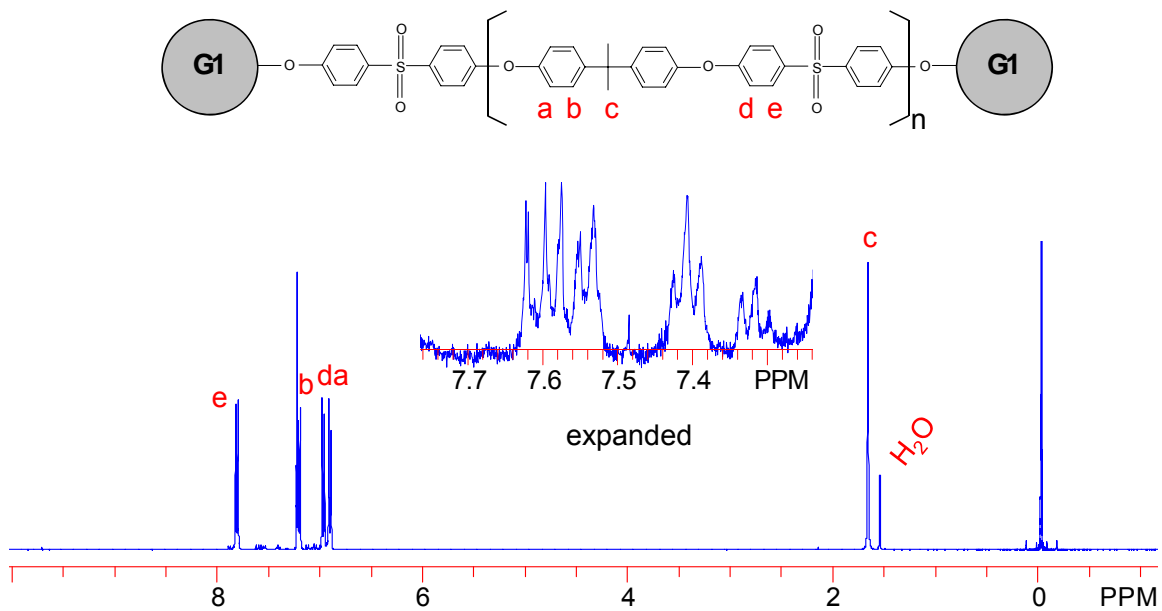
**Table 3.1** Molecular weights of PESs prepared with different end-cappers.

Polymer name	End-capper	Target $M_n$ (g/mol)	$^1\text{H}$ NMR $M_n$ (g/mol)	SEC $M_n$ (g/mol)	SEC $M_w$ (g/mol)	PDI <sup>a</sup>
T-PES a	TBP	$6.9 \times 10^3$	$6.9 \times 10^3$	$5.7 \times 10^3$	$1.0 \times 10^4$	1.8
T-PES b	TBP	$1.1 \times 10^4$	$1.1 \times 10^4$	$9.2 \times 10^3$	$1.8 \times 10^4$	2.0
T-PES c	TBP	$1.6 \times 10^4$	$1.9 \times 10^4$	$1.7 \times 10^4$	$2.9 \times 10^4$	1.7
T-PES d	TBP	$2.2 \times 10^4$	$2.5 \times 10^4$	$2.0 \times 10^4$	$3.6 \times 10^4$	1.8
T-PES e	TBP	$3.3 \times 10^4$	$3.8 \times 10^4$	$2.6 \times 10^4$	$6.0 \times 10^4$	2.3
G1-PES f	G1	$1.7 \times 10^4$	$1.8 \times 10^4$	$1.8 \times 10^4$	$3.5 \times 10^4$	1.9
G1-PES g	G1	$2.3 \times 10^4$	$2.4 \times 10^4$	$2.3 \times 10^4$	$4.7 \times 10^4$	2.0
G1-PES h	G1	$3.4 \times 10^4$	$3.8 \times 10^4$	$3.2 \times 10^4$	$6.9 \times 10^4$	2.2
G2-PES i	G2	$1.9 \times 10^4$	$2.0 \times 10^4$	$1.7 \times 10^4$	$4.1 \times 10^4$	2.4
G2-PES j	G2	$2.5 \times 10^4$	$2.9 \times 10^4$	$2.3 \times 10^4$	$7.0 \times 10^4$	3.0
G2-PES k	G2	$3.6 \times 10^4$	$3.9 \times 10^4$	$3.0 \times 10^4$	$7.6 \times 10^4$	2.5

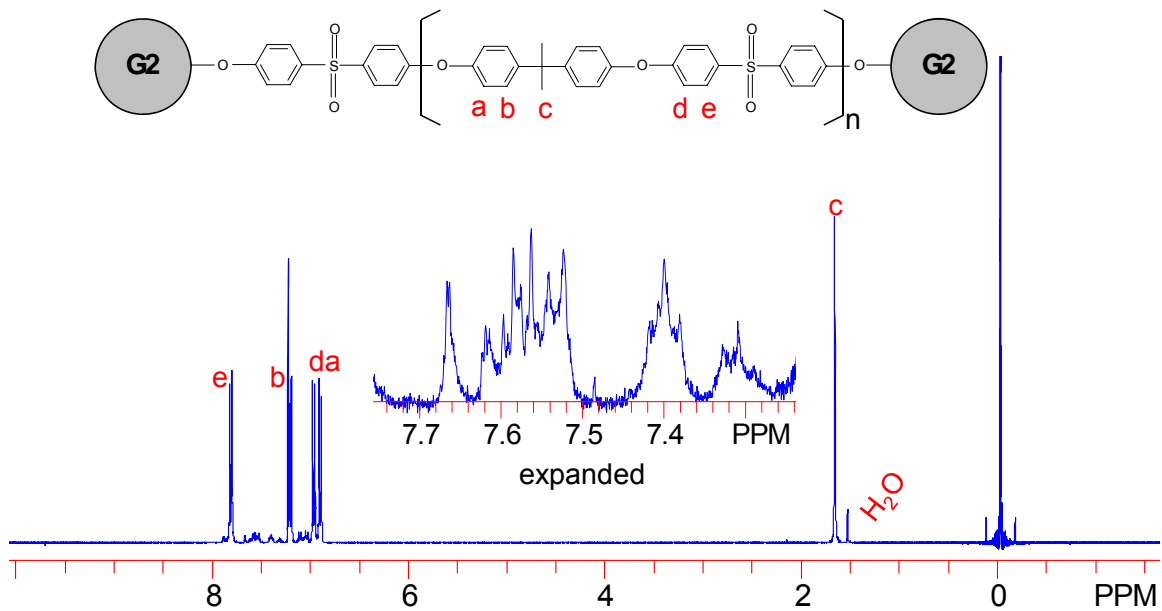
<sup>a</sup> PDI = SEC  $M_w$  / SEC  $M_n$



**Figure 3.1**  $^1\text{H}$  NMR spectrum of T-PES e in chloroform-*d*.



**Figure 3.2**  $^1\text{H}$  NMR spectrum of G1-PES h in chloroform-*d*.



**Figure 3.3**  $^1\text{H}$  NMR spectrum of G2-PES k in chloroform-*d*.

Table 3.2 shows the intrinsic viscosities and thermal properties of the polymers. The TGA analyses show that the  $T_d$ s of G1-PESs and G2-PESs are not significantly affected by molecular weights, suggesting that the thermal stabilities of the terminal dendrons and the polysulfone backbone are comparable. T-PESs, however, increase their thermal stability with increasing molecular weight because of the relatively low thermal stability of TBP on the chain ends. Mark-Houwink constants for all the polymers are about 0.5-0.6, a typical range for a polymer with random coil conformation. The DSC traces of all the polymers showed only a single  $T_g$ , indicating the absence of phase separation.

**Table 3.2** Intrinsic viscosities and thermal properties of end-capped PESs.

<b>Polymer name</b>	<b>IV (dl/g)</b>	<b>M-H constant</b>	<b><math>T_d^a</math> (°C) TGA</b>	<b><math>T_g</math> (°C) DSC</b>
T-PES a	0.14	0.52	450	169
T-PES b	0.19	0.61	458	176
T-PES c	0.22	0.64	463	183
T-PES d	0.28	0.63	465	185
T-PES e	0.36	0.61	482	191
G1-PES f	0.28	0.66	493	179
G1-PES g	0.33	0.64	490	181
G1-PES h	0.34	0.54	497	186
G2-PES i	0.29	0.67	483	175
G2-PES j	0.35	0.54	489	179
G2-PES k	0.36	0.56	477	184

<sup>a</sup> 5 % weight loss under nitrogen

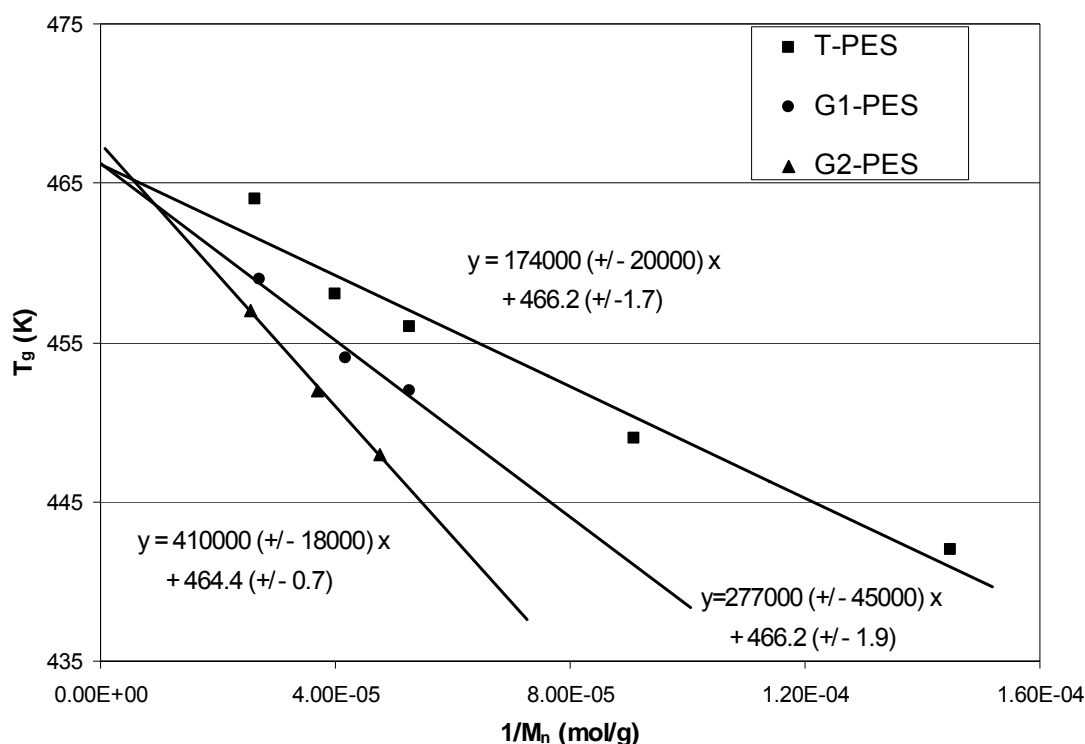
A plot of  $T_g$  versus  $1/M_n$ , with  $M_n$  determined by  $^1H$  NMR, for the three series is shown in Figure 3.4a and that with  $M_n$  determined by SEC is shown in Figure 3.4b. In

Figure 3.4a, the slopes for T-PESs, G1-PESs and G2-PESs are -174000 (+/- 20000) g/mol K, -277000 (+/- 45000) g/mol K, and -410000 (+/- 18000) g/mol K whereas their y-intercepts are 466.2 (+/-1.7) K, 466.2 (+/-1.9) K and 464.4 (+/-0.7) K. The slopes in Figure 3.4b are -145000 (+/-22000) g/mol K, -288000 (+/-70000) g/mol K, and -346000 (+/- 63000) g/mol K and the y-intercepts are 466.3 (+/-2.2) K, 467.5 (+/-3.1) K, and 468.0 (+/-2.9) K. Both plots indicate that G1-PESs and G2-PESs have lower  $T_g$ s than T-PESs at all molecular weights investigated. But the y-intercepts of all the three lines are essentially the same which is consistent with the chain end free volume theory which states that the effects of chain ends should decrease with increasing molecular weight and eventually become negligible at infinite molecular weight. The slopes of the three lines in Figure 3.4a are all close to the corresponding values in Figure 3.4b, implying that the molecular weight determinations by NMR and SEC are consistent with each other, although the data points from SEC are somewhat more scattered than those from NMR as can be seen from the magnitudes of the errors. The slightly more scattered SEC data points for G2-PESs than the other two series are probably the result of transesterification that can happen on the dendrons. NMR end group analysis, however, is not affected by ether exchange reactions because it only gives the ratio of dendron to backbone repeat unit concentrations and contains no information on where the dendrons are located on the polymer chains. It has been known in the literature that transesterification of activated arylene ether linkages readily happens during polymerization.<sup>17-20</sup> Such side reactions, if taking place on our dendrons, would lead to defect structures in the target dumbbell-like architecture and broaden the PDI because the polymer chains can grow from the internal ether linkages of the dendrons. In our cases, transesterification should not cause a major

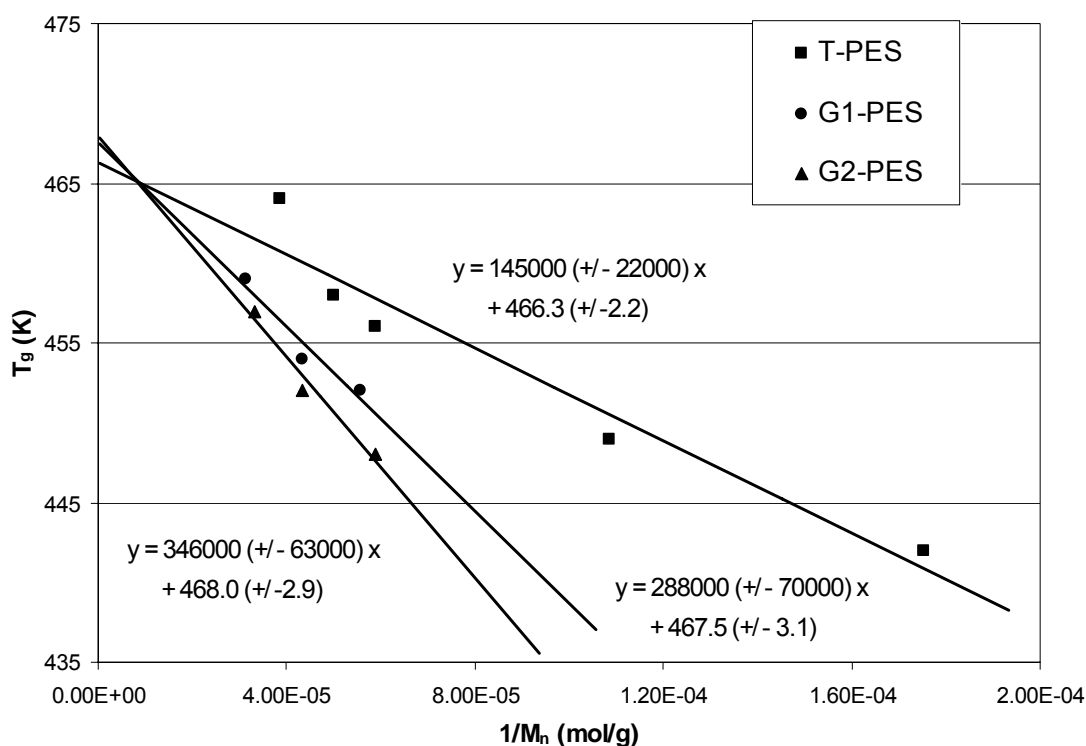
problem because the highly reactive nature of DFDPS prevents the phenolate from attacking the arylene ether linkages of the dendrons. But in fact, the PDIs of all the G2-PESs are slightly higher than G1-PESs and T-PESs. This observation is consistent with what we speculate based on the fact that the G2 dendron has a larger number of exchangeable ether linkages than G1 dendron and suggests that transesterification, although to a small extent, happened on G2 dendron. A few sets of model experiments were conducted to study the arylene ether cleavage on our dendrons. BPA and G1-OMe were exposed to the same condition as the polymerization procedure. After work-up, the mixture was poured into ethanol, which is a selective solvent for BPA. However, no precipitates were formed, suggesting that one or both legs of G1-OMe might be replaced by BPA. In order to exclude the possibility of BPA preventing the precipitation of G1-OMe, a mixture of BPA and G1-OMe were made by dissolving them in DMAc and poured into ethanol without heating. As expected, a white precipitate formed and the  $^1\text{H}$  NMR spectrum of the precipitates confirmed the structure of intact G1-OMe. This set of experiment suggests that BPA attacks the ether linkages of G1-OMe if there are no other electrophiles in the reaction mixture. In order to simulate the ether cleavage in the actual polymerization, DFDPS, TBP, and G1-OMe were exposed to the same condition. TBP was used as the monofunctional analog of BPA to prevent the formation of polymeric species and to simplify the analysis of the products. After similar work-up, the product mixture was analyzed by FAB-MS, showing peaks for the intact G1-OMe at 652 m/z, **6** at 515 m/z, and two more peaks at 500 and 1030 m/z, which presumably were formed from either G1-OMe or **6** during ionization. In order to confirm that the peaks at 500 and 1030 m/z really came from either **6** or G1-OMe, FAB-MS was run on pure **6**. This FAB-



MS spectrum of pure **6** gave three peaks at 500, 515 and at 1030 m/z. The peak at 515 m/z is from **6**, but those at 500 and 1030 m/z probably resulted from the formations of a fragment and dimerization during ionization. This implies that no peaks from ether cleavage of G1-OMe were detected from the model reaction mixture. This result supports our initial assumption that the aryether linkages in G1-OMe does not experience transesterification to a significant extent due to the much higher reactivity of DFDPS which prevents a nucleophile from attacking aryether linkages of G1-OMe. The same experiment was attempted on G2-OMe. However, G2-OMe, due to its large molecular weight, only gave a weak signal on FAB-MS spectrum which made it difficult for us to distinguish expected peaks from noise. Thus it was not investigated further.



**Figure 3.4a**  $T_g$  versus  $1/M_n$  for T-PESs, G1-PESs, and G2-PESs.  $M_n$  determined from  $^1\text{H}$  NMR.



**Figure 3.4b**  $T_g$  versus  $1/M_n$  for T-PESs, G1-PESs, and G2-PESs.  $M_n$  determined from SEC.

C-G1-PESs and C-G2-PESs were made from DCDPS and their molecular weights are shown in Table 3.3. The molecular weights of C-G1-PESs were successfully controlled and their PDIs are approximately two whereas G2-PESs showed PDIs of around six, abnormally high for a step-growth polymer, suggesting that G2 dendron experienced more ether exchange reactions than G1 dendron due to its larger number of ether linkages. This observation is consistent with our explanation on the slightly higher PDIs of G2- PESs shown in Table 3.1. Also, it indicates that the use of DFDPS is effective in minimizing transesterification.

**Table 3.3** Molecular weights of C-G1-PESs and C-G2-PESs.

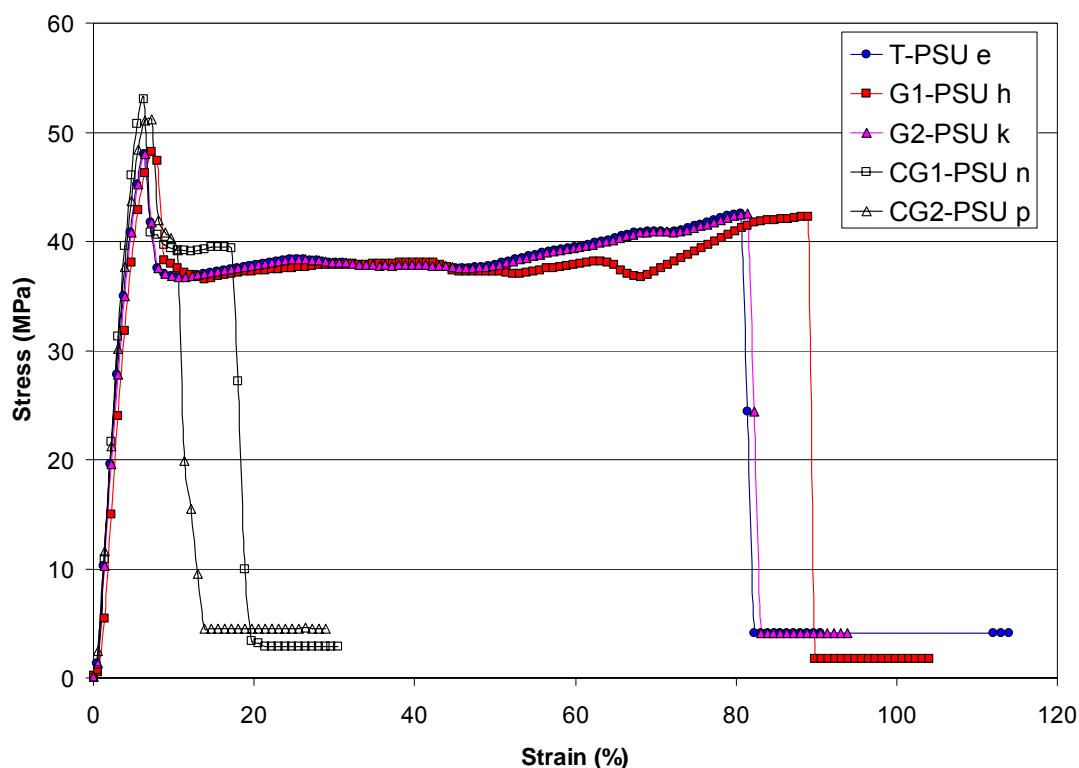
Polymer name	End-capper	Target $M_n$ (g/mol)	$^1\text{H}$ NMR $M_n$ (g/mol)	SEC $M_n$ (g/mol)	SEC $M_w$ (g/mol)	PDI <sup>a</sup>
C-G1-PES l	G1	$1.7 \times 10^4$	$1.7 \times 10^4$	$1.4 \times 10^4$	$2.5 \times 10^4$	1.8
C-G1-PES m	G1	$2.3 \times 10^4$	$2.7 \times 10^4$	$1.7 \times 10^4$	$3.9 \times 10^4$	2.3
C-G1-PES n	G1	$3.4 \times 10^4$	$3.4 \times 10^4$	$3.1 \times 10^4$	$6.7 \times 10^4$	2.2
C-G2-PES o	G2	$2.5 \times 10^4$	$2.9 \times 10^4$	$7.8 \times 10^4$	$4.6 \times 10^5$	5.9
C-G2-PES p	G2	$3.6 \times 10^4$	$3.8 \times 10^4$	$3.6 \times 10^4$	$2.2 \times 10^5$	6.1

<sup>a</sup> PDI = SEC  $M_w$  / SEC  $M_n$

Figure 3.5 shows stress-strain plot of T-PES e, G1-PES h, G2-PES k, C-G1-PES n, and C-G2-PES p. As Figure 3.5 shows, T-PES, G1-PES, and G2-PES have comparable moduli and ductilities, indicating that the mechanical properties of the polysulfones were not negatively affected by the attachment of the bulky dendritic end groups. However, C-G1-PES n and C-G2-PES p, which were prepared from DCDPS, exhibited lower ductilities. This is probably because these polymers are randomly branched due to the dendrons participating in transesterification. In addition, these randomly branched polymers are likely to contain more cyclics as described by Kricheldorf.<sup>21</sup> The linear segments of such defect-containing polymer chains are not as long as those in G1-PES h and G2-PES k, making them unable to have as much interchain entanglement.

In order to see whether there is a significant difference in  $T_g$  between having the dendrons covalently attached to the polymer chain ends and having them as additives with no covalent bonds to the polymer backbone, G1-OMe and G2-OMe were added to the T-PESs such that the weight fractions of the dendrons in the mixtures would be approximately the same as those of the dendrons in G1-PESs and G2-PESs. Assuming that the size of t-butyl group is very small compared to the dendrons, these additive-

containing T-PESs differ from the G1-PESs and G2-PESs only in that the dendrons are not covalently attached to the polymer backbones. The DSC traces of all the additive-containing polymers showed only a single  $T_g$ , indicating the absence of phase separation. Table 3.4 shows the  $T_g$ s of these additive-containing mixtures and those calculated by Fox equation. The comparisons of the  $T_g$ s of the G1-PESs and G2-PESs in Table 3.1 with those of the corresponding additive-containing T-PESs in Table 3.4 reveal that having dendrons covalently attached to the polymer backbone leads to slightly higher  $T_g$ s, suggesting that polymers with these bulky dendrons on the chain ends have lower segmental mobility.



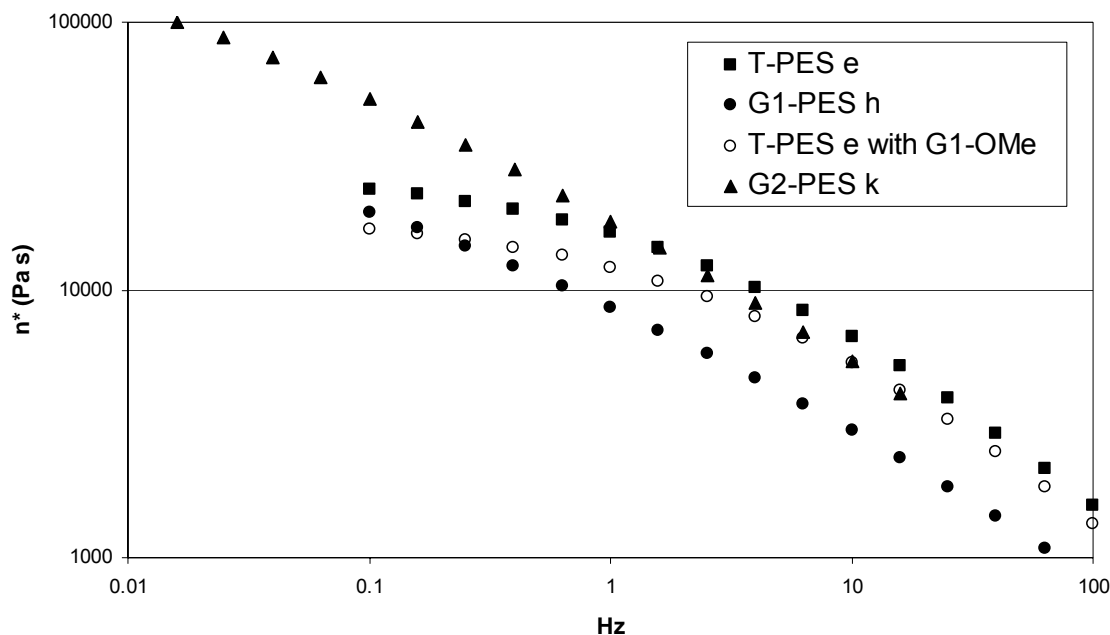
**Figure 3.5** Stress-strain plots of PESs with different end-groups.

**Table 3.4**  $T_g$ s of mixtures of T-PESs and dendritic additives.

Parent Polymer	Dendritic additive	$T_g$ dendritic additive	Wt. % dendritic additive	$T_g$ Fox eq. (°C)	$T_g$ DSC (°C)
T-PES c	G1-OMe	66	7	172	165
T-PES d	G1-OMe	66	5	177	171
T-PES e	G1-OMe	66	4	184	179
T-PES c	G2-OMe	104	17	167	163
T-PES d	G2-OMe	104	12	173	166
T-PES e	G2-OMe	104	9	182	176

Figure 3.6 shows melt viscosity versus frequency plot for T-PES e, G1-PES h, G2-PES k and T-PES e with G1-OMe. Although a direct comparison of T-PES e, G1-PES h and G2-PES k is difficult because of the differences in molecular weight and  $T_g$ , one significant observation is that G1-PES h and G2-PES k do not have a Newtonian region and show greater shear thinning than T-PES e, implying that the processing of polysulfones with these dendritic end groups at a high shear rate may be easier than that with no dendritic end groups. These data in conjunction with the tensile tests suggest that it is possible to decrease the high shear viscosity with no significant reduction in stress-strain properties. As far as our polysulfone systems are concerned, the advantage of introducing bulky terminal groups can be best seen at high shear rates in contrast to the recent patent<sup>15</sup> claiming that dendritic end-capped polycarbonates possess lowered zero shear viscosity than the non-branched analog. Also, the viscosity of T-PES e with G1-OMe is lower than that of the corresponding G1-PES h in the low shear rate region, but the greater shear thinning of G1-PES h makes its viscosity lower than that of T-PES e with G1-OMe at high shear rates, meaning that having G1 dendron covalently attached to

the polymer backbone is more advantageous than having the dendron as an additive at high shear rates.



**Figure 3.6** Melt viscosity versus frequency at 280 °C under nitrogen.

### 3.5 Conclusions

In summary, we have described the synthesis of linear-dendritic ABA copolymers, where A is either G1 or G2 aryether ketone dendron and B is a PES, via step-growth polymerization and characterized some of the physical properties. The  $T_g$ s of these polymers were lower than those of T-PESs. But the difference becomes smaller with increasing molecular weight and essentially negligible at infinite molecular weight, which is consistent with the chain end free volume theory. The  $T_g$ s of G1-PESs and G2-PESs were higher than those of the corresponding additive-containing T-PESs. Transesterification of the dendrons was successfully minimized by the use of DFDPS, the more reactive analog of DCDPS. Melt rheology showed that G1-PES and G2-PES

with high molecular weights exhibited greater shear thinning than the control whereas their mechanical properties were not significantly affected. These results indicate that it is possible to reduce the high shear viscosity without negatively affecting the stress-strain properties by introducing dendritic terminal groups. C-G1-PES and C-G2-PES, which were prepared from DCDPS, possess poor mechanical properties, implying that polymers with branch points randomly distributed along the polymer chains have inferior mechanical properties presumably due to a reduction in interchain entanglement. We are currently working on the attachment of dendritic structures to the ends of other types of polymer backbones and hope to report the results in the near future.

### 3.6 Acknowledgements

This work was supported by the U.S. Army Research Laboratory and U.S. Army Research Office under grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. We thank Professor Timothy Long's group for allowing us to use their SEC, TGA, and DSC. We are also grateful to Dr. Garth Wilkes' group for performing tensile tests for us.

### 3.7 References

1. Gitsov, I.; Wooley, K. L.; Hawker, C. J.; Ivanova, P. T.; Fréchet, J. M. J., Synthesis and properties of novel linear-dendritic block copolymers. Reactivity of dendritic macromolecules toward linear polymers. *Macromolecules* **1993**, *26* (21), 5621-5627.
2. Gitsov, I.; Fréchet, J. M. J., Solution and solid-state properties of hybrid linear-dendritic block copolymers. *Macromolecules* **1993**, *26* (24), 6536-6546.
3. Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J., Well-defined triblock hybrid dendrimers based on lengthy oligothiophene cores and poly(benzyl ether) dendrons. *J. Am. Chem. Soc.* **1998**, *120* (42), 10990-10991.

4. Fréchet, J. M. J.; Gitsov, I.; Monteil, T.; Rochat, S.; Sassi, J.-F.; Vergelati, C.; Yu, D., Modification of surfaces and interfaces by non-covalent assembly of hybrid linear-dendritic block copolymers: poly(benzyl ether) dendrons as anchors for poly(ethylene glycol) chains on cellulose or polyester. *Chem. Mater.* **1999**, *11* (5), 1267-1274.
5. Emrick, T.; Hayes, W.; Fréchet, J. M. J., A TEMPO-mediated "living" free-radical approach to ABA triblock dendritic linear hybrid copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37* (20), 3748-3755.
6. Gitsov, I.; Lambrych, K. R.; Remnant, V. A.; Pracitto, R., Micelles with highly branched nanoporous interior: solution properties and binding capabilities of amphiphilic copolymers with linear dendritic architecture. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38* (15), 2711-2727.
7. Sill, K.; Emrick, T., Bis-dendritic polyethylene prepared by ring-opening metathesis polymerization in the presence of bis-dendritic transfer agents. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (22), 5429-5439.
8. Lambrych, K. R.; Gitsov, I., Linear-dendritic poly(ester)-*block*-poly(ether)-*block*-poly(ester) ABA copolymers constructed by a divergent method. *Macromolecules* **2003**, *36* (4), 1068-1074.
9. Namazi, H.; Adeli, M., Synthesis of barbell-like triblock copolymers, dendritic triazine-block-poly(ethylene glycol)-block-dendritic triazine and investigation of their solution behaviors. *Polymer* **2005**, *46* (24), 10788-10799.
10. Namazi, H.; Adeli, M., Solution properties of dendritic triazine/poly(ethylene glycol)/ dendritic triazine block copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (1), 28-41.
11. Froimowicz, P.; Gandini, A.; Strumia, M., New polyfunctional dendritic-linear hybrids from terminal amine polyether oligomers (Jeffamine®): synthesis and characterization. *Tetrahedron Lett.* **2005**, *46* (15), 2653-2657.
12. Kwak, S.-Y.; Ahn, D. U.; Choi, J.; Song, H. J.; Lee, S.-H., Amelioration of mechanical brittleness in hyperbranched polymer. 1. Macroscopic evaluation by dynamic viscoelastic relaxation. *Polymer* **2004**, *45* (20), 6889-6896.
13. Gitsov, I.; Fréchet, J. M. J., Novel nanoscopic architectures. Linear-globular ABA copolymers with polyether dendrimers as A blocks and polystyrene as B block. *Macromolecules* **1994**, *27* (25), 7309-7315.
14. Ge, Z.; Chen, D.; Zhang, J.; Rao, J.; Yin, J.; Wang, D.; Wan, X.; Shi, W.; Liu, S., Facile synthesis of dumbbell-shaped dendritic-linear-dendritic triblock copolymer via reversible addition-fragmentation chain transfer polymerization. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45* (8), 1432-1445.
15. Heuer, H.-W.; Wehrmann, R.; Meyer, A.; Pielartzik, H.; Bruder, F.-K.; Paulusse, J. M. J. Polycarbonates, polyester carbonates and polyesters having branched terminal groups. U.S. Patent 6,784,278 B2, August 31, 2004.
16. Morikawa, A.; Kakimoto, M.; Imai, Y., Convergent synthesis of starburst poly(ether ketone) dendrons. *Macromolecules* **1993**, *26* (24), 6324-6329.
17. Johnson, R. N.; Farnham, A. G., Poly(aryl ethers) by nucleophilic aromatic substitution. III. Hydrolytic side reactions. *J. Polym. Sci. Part A-1* **1967**, *5* (9), 2415-2427.



18. Wang, Y.-F.; Chan, K. P.; Hay, A. S., Ring-opening polymerization of macrocyclic aryl ether ketone oligomers containing the 1,2-dibenzoylbenzene moiety. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34* (3), 375-85.
19. Ben-Haida, A.; Baxter, I.; Colquhoun, H. M.; Hodge, P.; Kohnke, F. H.; Williams, D. J., Ring-closing depolymerization of aromatic polyethers. *Chem. Commun.* **1997**, (16), 1533-1534.
20. Newton, A. B.; Rose, J. B., Relative reactivities of the functional groups involved in synthesis of poly(phenylene ether sulfones) from halogenated derivatives of diphenyl sulfone. *Polymer* **1972**, *13* (10), 465-74.
21. Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Kruger, R.-P., Cyclic hyperbranched poly(ether ketone)s derived from 3,5-bis(4-fluorobenzoyl)phenol. *Macromolecules* **2003**, *36* (15), 5551-5558.

## **Chapter 4: Synthesis of Linear Poly(ether sulfone)s with Hyperbranched Terminal Groups**

(Manuscript in preparation)

### **4.1 Abstract**

In the previous chapter, we have reported hybrid linear-branched ABA polymers where A and B are dendrons and linear polymers respectively. In this chapter, we report the synthesis of the same ABA architecture with hyperbranched polymers as the A segments. This architecture was constructed by growing hyperbranched poly(ether ketone)s onto the ends of fluoro-terminated polysulfones. The unreacted fluoro-terminal groups of the hyperbranched polymers were capped by tert-butylphenol. The reactions were carried out at 90 °C to suppress ether cleavage. The results from NMR and SEC showed that up to eleven tert-butylphenol units were successfully attached to the terminal segments per chain.

### **4.2 Introduction**

Linear-dendritic ABA copolymers, where A and B are dendritic and linear polymers respectively, have been known in the literature for more than a decade and a wide variety of polymers with this ABA architectures have been investigated.<sup>1-16</sup> Previously, we published a report on linear-dendritic ABA architecture consisting of step-growth polymers by attaching preformed arylene ether ketone dendrons onto the ends of linear poly(ether sulfone)s.<sup>16</sup> In this report, we extend this work by utilizing hyperbranched polymers as the A segments of ABA architecture. As widely known, one

of the most important advantages of hyperbranched polymers over monodisperse dendrons and dendrimers is that the synthesis is much less laborious due to the fact that hyperbranched polymers are constructed in fewer synthetic steps (often one pot), although defect structures are always contained in these polymers. Constructing ABA architectures from step-growth polymers often requires the suppression of reversible reactions such as transesterification and transetherification. Here, we report the synthesis of ABA linear-hyperbranched ABA copolymers, where A and B are hyperbranched polyketones and linear polysulfones respectively. We have chosen  $AB_2$  monomer to construct the hyperbranched segments because this approach does not lead to crosslinking as opposed to  $A_2 + B_3$  method described in Chapter 2 of this thesis.

## **4.3 Experimental**

### **4.3.1 Materials**

All reagents were purchased from Aldrich and used as received except that 4,4'-difluorodiphenyl sulfone (DFDPS) and bisphenol-A (BPA) were dried under vacuum overnight before use.

### **4.3.2 Synthesis**

**Preparation of  $AB_2$  Monomer (1).** This compound was synthesized according to a published procedure.<sup>17</sup>

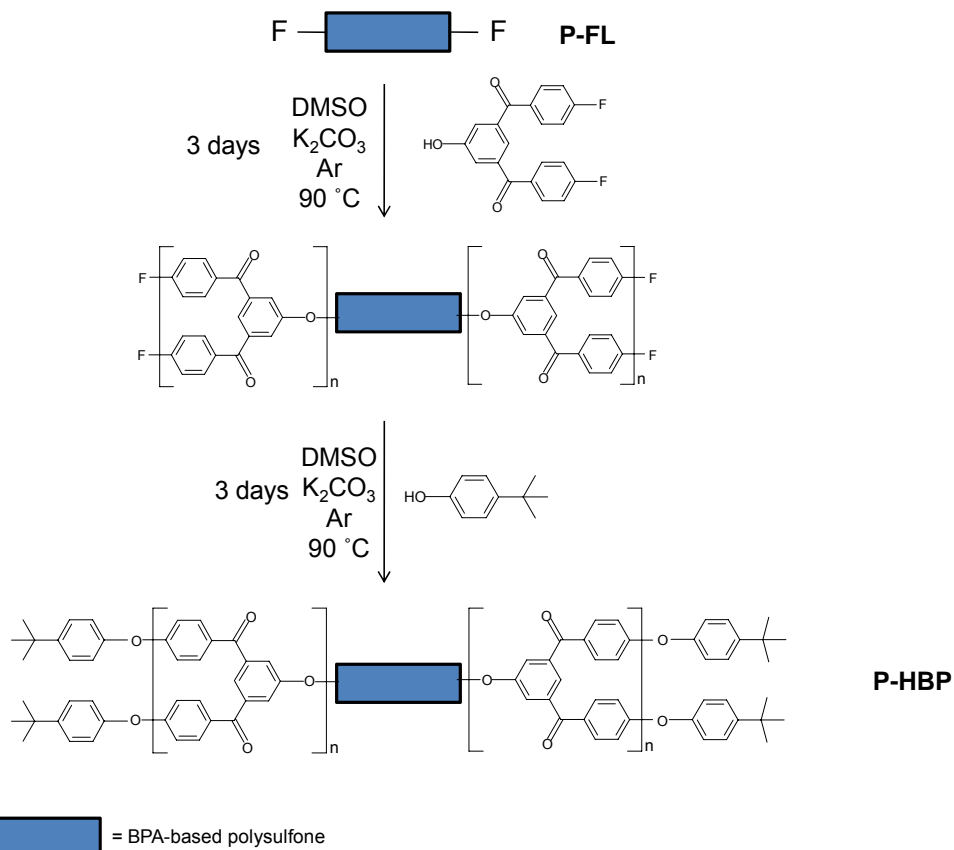
**Preparation of Protected  $AB_2$  Monomer (2).** This compound was prepared by the method described in Chapter 3 of this thesis.

**Polymerization.** Fluoro-terminated polysulfone (**P-FL**) was synthesized from 4,4'-difluorodiphenylsulfone (DFDPS) and bisphenol A (BPA). Molecular weight control was achieved by stoichiometric imbalance with a calculated amount of DFDPS in excess. DFDPS (4.411 g, 17.35 mmol), BPA (3.881 g, 17.00 mmol), K<sub>2</sub>CO<sub>3</sub> (4.930 g, 35.67 mmol), DMAc (25 ml), and toluene (15 ml) were placed in a flask equipped with an Ar inlet and mechanical stirrer. The mixture was stirred at 130-140 °C for 3 hrs to remove water by azeotropic distillation and at 155 °C for 3 hrs. After cooling, the mixture was diluted with THF and filtered to remove KF and K<sub>2</sub>CO<sub>3</sub>. The polymer was then precipitated in 800 ml dilute aqueous HCl. The polymer was dried under vacuum at 120-130 °C overnight, giving 7.1 g of **P-FL**.

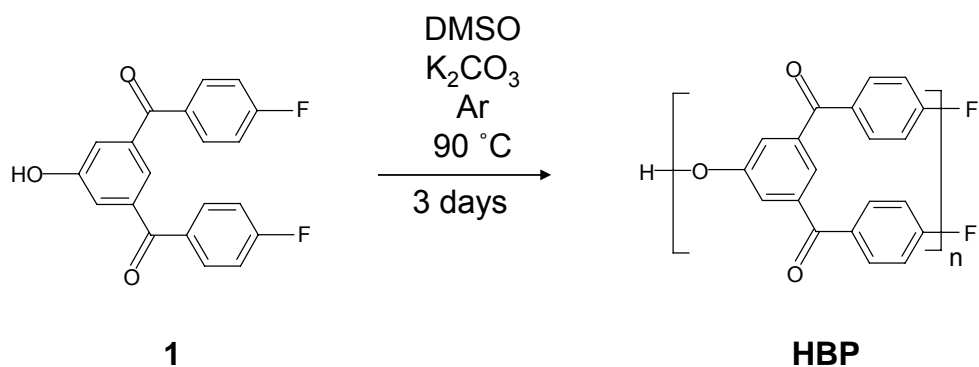
**Preparation of Polysulfones with Hyperbranched Terminal Groups (P-HBP).** **P-FL** (1.00 g,  $3.33 \times 10^{-2}$  mmol), the AB<sub>2</sub> monomer (0.56 g, 1.7 mmol), K<sub>2</sub>CO<sub>3</sub> (0.69 g, 5.0 mmol) and DMSO (10 ml) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 90 °C with a stream of Ar. After 3 days of reaction, *tert*-butylphenol (0.37 g, 2.5 mmol) was added to the flask and the mixture was allowed to react for 3 more days. After cooling, the mixture was poured into 300 ml of dilute aqueous HCl to precipitate the crude product. The product was washed with water to remove any trapped inorganic salts. The product was dissolved in methylene chloride and precipitated in acetone 4 times to remove any free hyperbranched polymers. The polymer was dried under vacuum at 120 °C overnight, giving 0.22 g of **P-HBP**.

**Model Reaction by Homopolymerization of AB<sub>2</sub> Monomer at 90 °C.** **1** (0.50 g, 1.5 mmol), DMSO (10 ml), and K<sub>2</sub>CO<sub>3</sub> (0.25 g, 1.8 mmol) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 90 °C under Ar for 3 days. After

cooling, the mixture was poured into 200 ml of dilute aqueous HCl. The white precipitate was collected by vacuum filtration and dried under high vacuum overnight to give **HBP**.

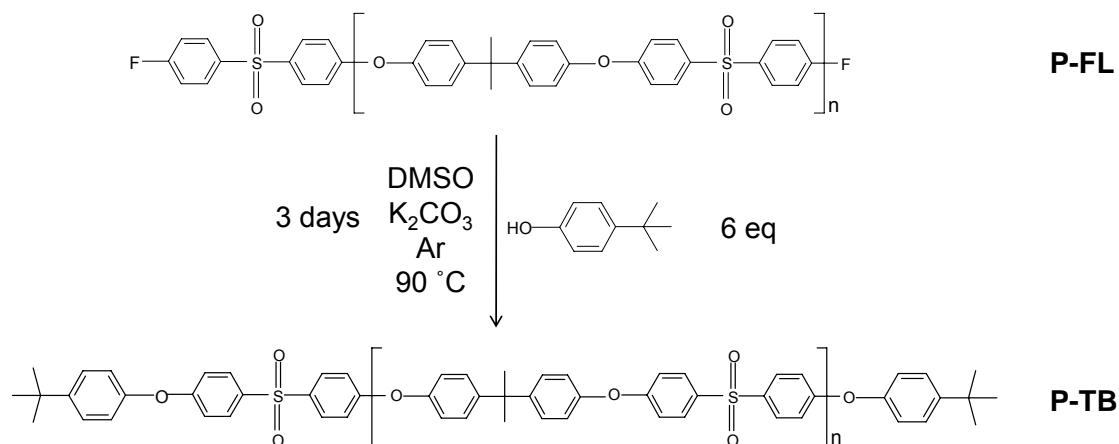


**Scheme 4.1** Synthesis of polysulfones with hyperbranched terminal groups.



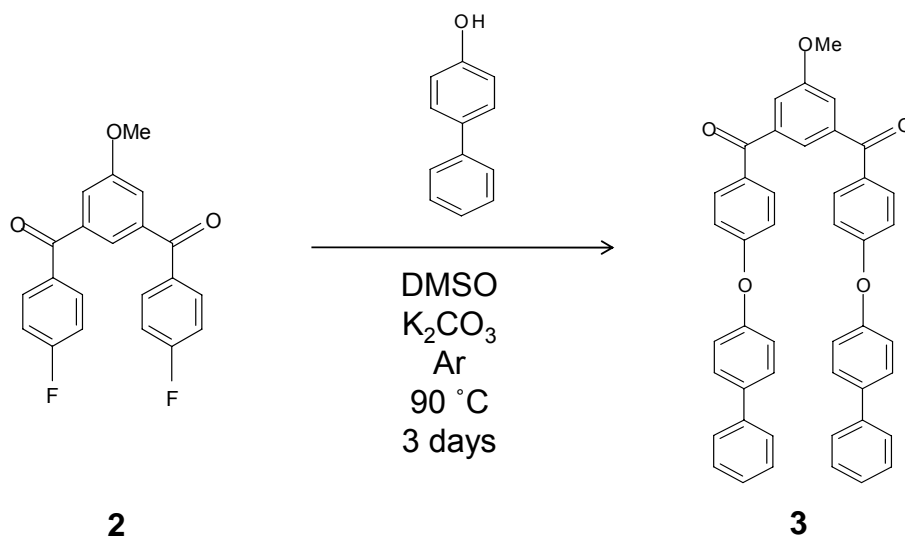
**Scheme 4.2** Model study for the formation of HBP from **1** at 90 °C.

**Model Reaction of P-FL with *tert*-butylphenol at 90 °C.** P-FL (0.50 g,  $1.7 \times 10^{-2}$  mmol), *tert*-butylphenol (0.015 g, 0.10 mmol), DMSO (10 ml), and K<sub>2</sub>CO<sub>3</sub> (0.017 g, 0.12 mmol) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 90 °C under Ar for 3 days. After cooling, the mixture was poured into 200 ml of dilute aqueous HCl. The white precipitate was collected by vacuum filtration, washed with EtOH to remove free *tert*-butylphenol and dried under high vacuum overnight to give 0.45 g of P-TB.



**Scheme 4.3** Model reaction of P-FL with *tert*-butylphenol.

**Model Reaction of 2 with 4-Phenylphenol at 90 °C.** 2 (0.50 g, 1.4 mmol), 4-phenylphenol (0.73 g, 4.3 mmol), DMSO (10 ml) and K<sub>2</sub>CO<sub>3</sub> (0.69 g, 5.0 mmol) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 90 °C under Ar for 3 days. After cooling, the mixture was poured into 100 ml of ethanol. The white precipitate was washed with water and dried under vacuum overnight to give 0.76 g (1.2 mmol) of 3 in 83% yield. The <sup>1</sup>H NMR spectrum matched that reported in Chapter 3.



**Scheme 4.4** Model reaction of **2** with 4-phenylphenol.

#### 4.3.3 Characterization

NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Size Exclusion Chromatography (SEC) was recorded in THF with a flow rate of 1.00 ml/min at 40 °C by Waters 717 Autosampler with 3 in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The  $d\eta/dc$  values were calculated on-line using the calibration constant for the RI detector and for the mass of the polymer samples assuming 100% mass recovery of the samples.

#### 4.4 Results and Discussion

Our synthetic strategy to construct the ABA architecture was by the reaction of a fluoro-terminated polysulfone chain with an arylene ether ketone AB<sub>2</sub> monomer (Scheme

4.1). A fluoro-terminated chain was chosen for the synthesis because we would need the AB<sub>2</sub> monomer to react with the polysulfone chain ends, not with itself preferentially. The analogous chloro-terminated chain would not be our choice because of its much lower reactivity, which would cause the AB<sub>2</sub> monomer to react preferentially with itself.

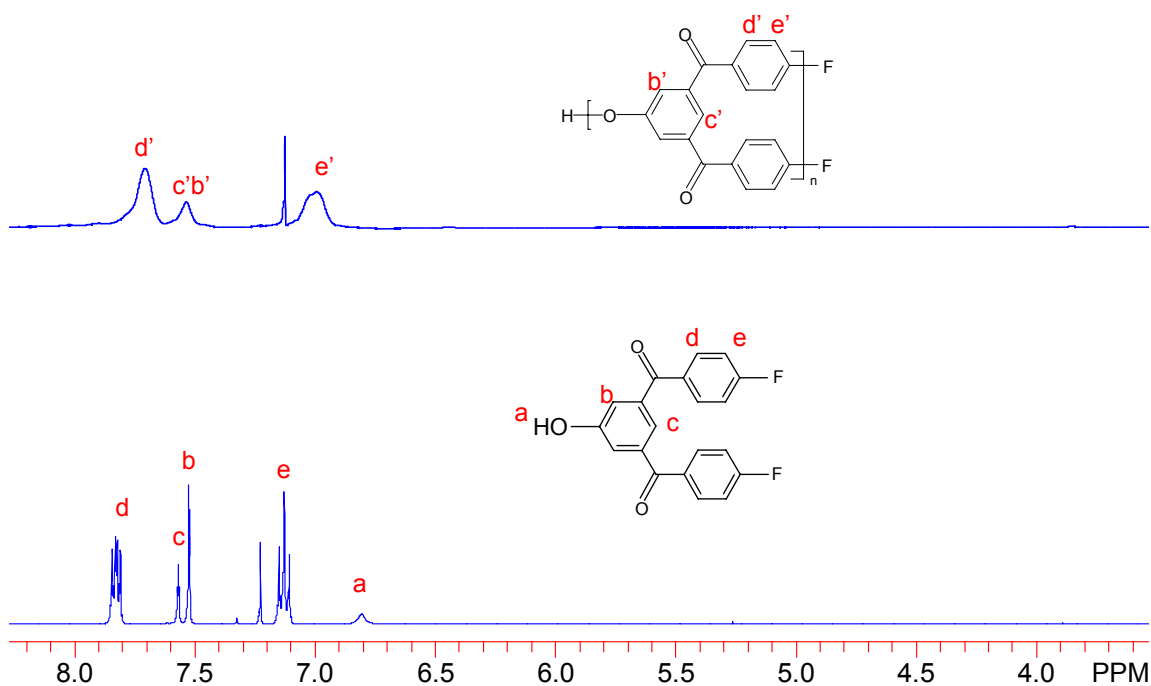
In order to construct polysulfones with hyperbranched terminal groups by S<sub>N</sub>Ar, it is necessary to suppress ether cleavage. Jannasch successfully suppressed ether cleavage by carrying out S<sub>N</sub>Ar at 90 °C to attach pendant sulfonate units onto the sides of polysulfone backbones.<sup>18</sup> To confirm that this particular reaction condition would be suitable for our system as well, a few model reactions were carried out.

The first model reaction was carried out by homopolymerizing **1** at 90 °C for 3 days (Scheme 4.2). The molecular weight determined by SEC-LS is shown in Table 4.1. As can be seen, the M<sub>n</sub> of this polymer was 8.2 x 10<sup>3</sup> g/mol with a PDI of 1.8. The <sup>1</sup>H NMR spectrum of this product showed broad peaks (Figure 4.1), which is an indicative of a successful polymerization of the monomer. This monomer was first reported by Miller, who homopolymerized it in DMAc at 150 °C to give a M<sub>n</sub> of up to 1.6 x 10<sup>4</sup> g/mol.<sup>19</sup> In our model reaction, **1** could successfully homopolymerize to give a hyperbranched polymer at 90 °C.

**Table 4.1** Molecular weight of **HBP**.

Polymer	M <sub>n</sub> SEC-LS (g/mol)	M <sub>w</sub> SEC-LS (g/mol)	PDI
<b>HBP</b>	8.2 x 10 <sup>3</sup>	1.5 x 10 <sup>4</sup>	1.8





**Figure 4.1**  $^1\text{H}$  NMR spectra of **1** before and after polymerization in chloroform-*d*.

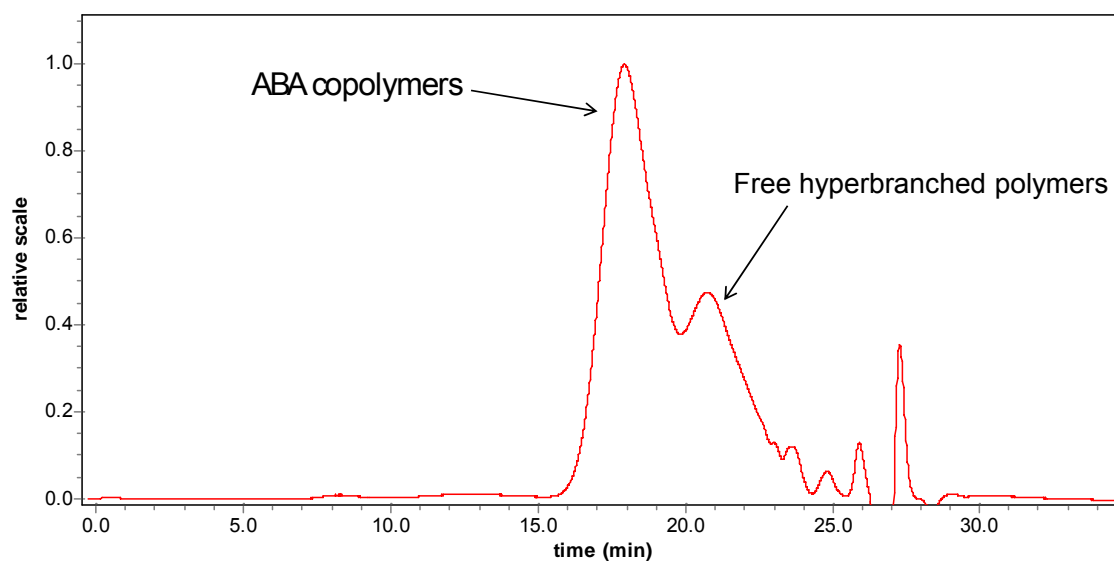
The second model reaction (Scheme 4.3) was performed by allowing **P-FL** to react with an excess of tert-butylphenol at 90 °C for 3 days. Here, t-butylphenol was used as a model for any nucleophile capable of causing ether cleavage. After the reaction, the molecular weight was determined by SEC-LS and  $^1\text{H}$  NMR. These results are summarized in Table 4.2. The  $M_n$  and  $M_w$  determined by SEC-LS before the reaction were  $3.0 \times 10^4$  g/mol and  $4.5 \times 10^4$  g/mol, respectively. After the reaction, these values were  $3.0 \times 10^4$  g/mol and  $4.5 \times 10^4$  g/mol and that determined by  $^1\text{H}$  NMR end group analysis was  $2.6 \times 10^4$  g/mol. These observations indicate that the end-capping with a large excess of phenol at 90 °C was almost complete with a minimum decrease in molecular weight.

**Table 4.2** Molecular weights of **P-FL** and **P-TB**.

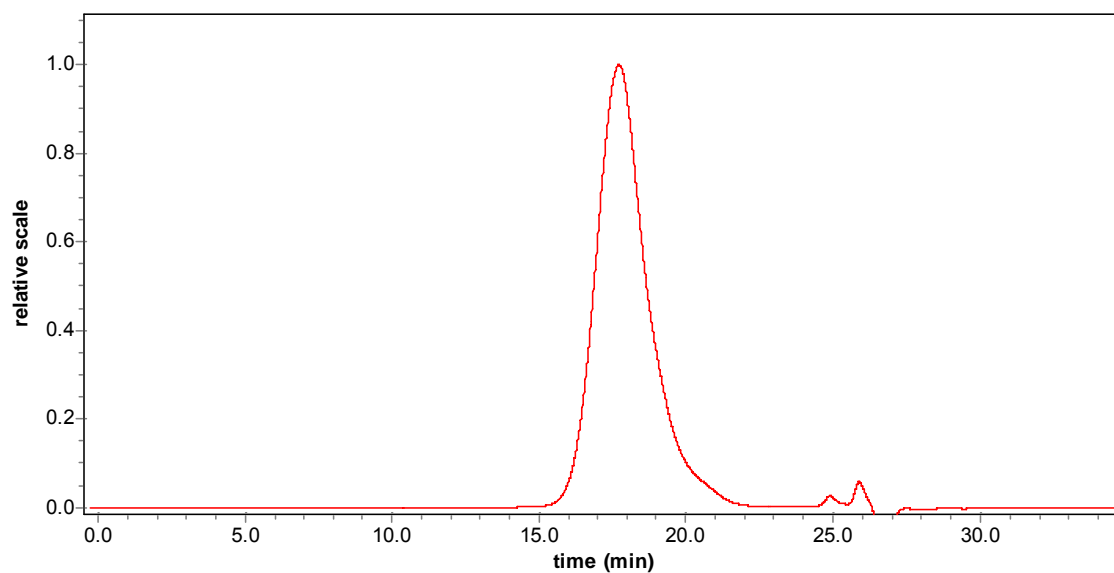
Polymer	M <sub>n</sub> <sup>1</sup> H NMR (g/mol)	M <sub>n</sub> SEC-LS (g/mol)	M <sub>w</sub> SEC-LS (g/mol)	PDI
<b>P-FL</b>	-	3.0 x 10 <sup>4</sup>	4.5 x 10 <sup>4</sup>	1.5
<b>P-TB</b>	2.6 x 10 <sup>4</sup>	2.5 x 10 <sup>4</sup>	4.5 x 10 <sup>4</sup>	1.8

The third model reaction was carried out by reacting **2** with 4-phenylphenol in DMSO containing K<sub>2</sub>CO<sub>3</sub> at 90 °C for 3 days (Scheme 4.4). **2** was used as a model for the hyperbranched polymer and 4-phenylphenol for any phenol. After the work-up, product **3** was obtained in 83 % yield. The fact that we obtained 83 % isolated yield without further purification indicates that this particular reaction gave a high conversion with no significant side reactions. Thus this model study suggests that the terminal fluoro groups of the hyperbranched polymer could be displaced with high conversion by a phenol under this reaction condition.

A few linear-hyperbranched ABA polymers were synthesized by reacting **P-FL** with the AB<sub>2</sub> monomer. *Tert*-butylphenol was added to the product mixture to cap the unreacted fluoro terminal groups of the polymer. The SEC traces of the crude products showed bimodal peaks because of free hyperbranched polymers. The free hyperbranched polymers were removed from the product polymers by repeated precipitation in acetone. Acetone was chosen because it was a selective solvent for free hyperbranched polymers. After the repeated fractionations, the SEC traces of the samples showed unimodal peaks, indicating that the free hyperbranched polymers were successfully removed. Figure 4.2a and Figure 4.2b show the SEC traces of one of the samples before and after the fractionation.



**Figure 4.2a** SEC trace before fractionation in acetone.



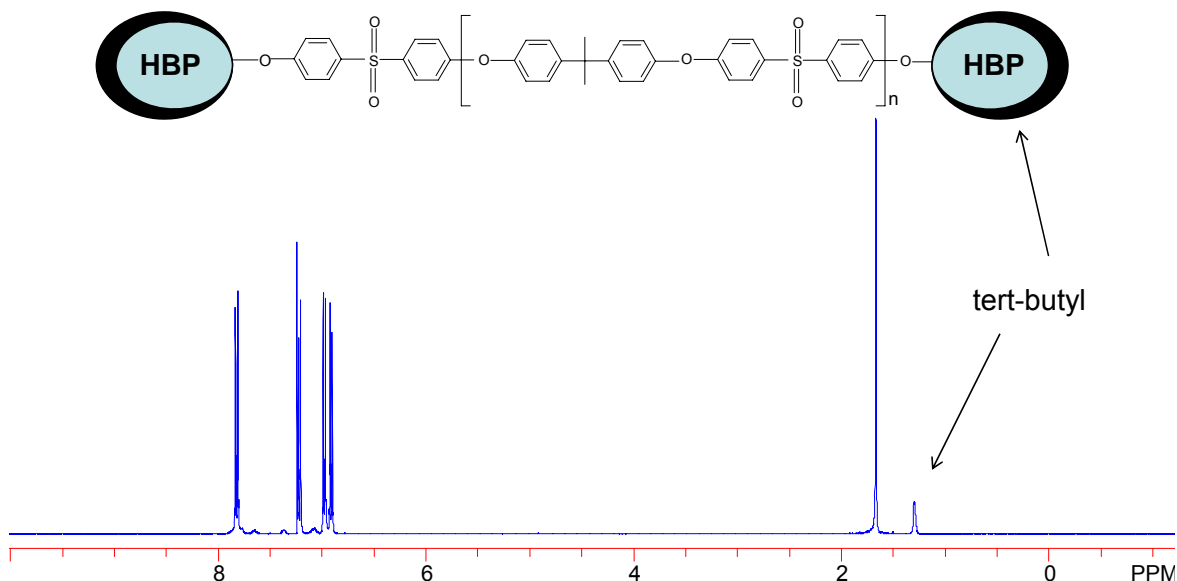
**Figure 4.2b** SEC trace after fractionation in acetone.

The molecular weight determined by SEC-LS and the number of *tert*-butyl terminal units of each of the samples measured by  $^1\text{H}$  NMR are summarized in Table 4.3. To calculate the number of *tert*-butyl units per chain, the integration values of the *tert*-butyl units were compared to those of the isopropylidene units of the polymer backbones.

The maximum number of *tert*-butyl groups per chain was calculated assuming that all monomers attached onto the chain ends. For example, sample 3 should have 25 monomer units on each of the polysulfone chain ends. Since the number of terminal groups of an AB<sub>2</sub>-type hyperbranched polymer with N repeat units is N+1, each polysulfone chain end should possess 26 *tert*-butyl groups and one chain should have 52 (26 x 2) *tert*-butyl groups. The solution cast films of these samples made self-standing films and were all creasible.

**Table 4.3** Molecular weights and numbers of *tert*-butyl terminal units for ABA copolymers.

	Sample 1	Sample 2	Sample 3
<b># of AB<sub>2</sub> monomers (feed) / chain</b>	15	30	50
<b>Max # of <i>tert</i>-butyl groups /chain (assume no free HBPs)</b>	17	32	52
<b>Exp. # of <i>tert</i>-butyl groups / chain (by <sup>1</sup>H NMR)</b>	4	8	11
<b>Solution-cast film</b>	Creasible	Creasible	Creasible
<b>M<sub>n</sub> (SEC in THF)</b>	3.2 x 10 <sup>4</sup>	3.7 x 10 <sup>4</sup>	3.7 x 10 <sup>4</sup>
<b>PDI (M<sub>w</sub>/M<sub>n</sub> from SEC)</b>	1.4	1.5	1.5



**Figure 4.3**  $^1\text{H}$  NMR spectrum of Sample 3 after end-capping with *tert*-butylphenol in chloroform-*d*.

#### 4.5 Conclusions

Polysulfones with hyperbranched terminal groups were synthesized by reacting fluoro-terminated polysulfones with an arylene ether ketone  $\text{AB}_2$  monomer. Unreacted terminal groups of the product polymers were capped by *tert*-butylphenol. The final products were isolated by repeated precipitation in acetone. The films prepared from these polymers were creasible and self-standing. This synthetic method can be a versatile way to place functional hyperbranched polymers on the ends of poly(arylene ether)s simply by changing R groups on the end-capping phenols.

#### 4.6 Acknowledgements

We are grateful to Dr. Timothy Long's group for allowing our group to use their SEC.

## 4.7 References

1. Grayson, S. M.; Fréchet, J. M. J., Convergent dendrons and dendrimers: from synthesis to applications. *Chem. Rev.* **2001**, *101* (12), 3819-3867.
2. Gitsov, I. W., K. L.; Hawker, C. J.; Ivanova, P. T.; Fréchet, J. M. J., Synthesis and properties of novel linear-dendritic block copolymers. Reactivity of dendritic macromolecules toward linear polymers. *Macromolecules* **1993**, *26* (21), 5621-5627.
3. Gitsov, I. F., J. M. J., Solution and solid-state properties of hybrid linear-dendritic block copolymers. *Macromolecules* **1993**, *26* (24), 6536-6546.
4. Malenfant, P. R. L. G., L.; Fréchet, J. M. J. , Well-Defined Triblock Hybrid Dendrimers Based on Lengthy Oligothiophene Cores and Poly(benzyl ether) Dendrons. *J. Am. Chem. Soc.* **1998**, *120*, 10990-10991.
5. Fréchet, J. M. J. G., I.; Monteil, T.; Rochat, S.; Sassi, J.-F.; Vergelati, C.; Yu, D., Modification of Surfaces and Interfaces by Non-covalent Assembly of Hybrid Linear-Dendritic Block Copolymers: Poly(benzyl ether) Dendrons as Anchors for Poly(ethylene glycol) Chains on Cellulose or Polyester. *Chem. Mater.* **1999**, *11* (5), 1267-1274.
6. Emrick, T. H., W.; Fréchet, J. M. J., A TEMPO-mediated "living" free-radical approach to ABA triblock dendritic linear hybrid copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37* (20), 3748-3755.
7. Gitsov, I. L., K. R.; Remnant, V. A.; Pracitto, R., Micelles with highly branched nanoporous interior: solution properties and binding capabilities of amphiphilic copolymers with linear dendritic architecture. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38* (15), 2711-2727.
8. Sill, K. E., Todd., Bis-Dendritic Polyethylene Prepared by Ring-Opening Metathesis Polymerization in the Presence of Bis-Dendritic Transfer Agents. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5429-5439.
9. Lambrych, K. R. G., I., Linear-Dendritic Poly(ester)-*block*-poly(ether)-*block*-poly(ester) ABA Copolymers Constructed by a Divergent Method. *Macromolecules* **2003**, *36* (4), 1068-1074.
10. Namazi, H. A., M., Synthesis of barbell-like triblock copolymers, dendritic triazine-block-poly(ethylene glycol)-block-dendritic triazine and investigation of their solution behaviors. *Polymer* **2005**, *46* (24), 10788-10799.
11. Namazi, H. A., Mohsen., Solution Properties of Dendritic Triazine/Poly(ethylene glycol)/ Dendritic Triazine Block Copolymers. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43* (1), 28-41.
12. Froimowicz, P. G., A.; Strumia, M., New polyfunctional dendritic-linear hybrids from terminal amine polyether oligomers (Jeffamine®): synthesis and characterization. *Tetrahedron* **2005**, *46*, 2653-2657.
13. Kwak, S.-Y. A., D. U.; Choi, J.; Song, H. J. ; Lee, S.-H., Amelioration of mechanical brittleness in hyperbranched polymer. 1. Macroscopic evaluation by dynamic viscoelastic relaxation. *Polymer* **2004**, *45* (20), 6889-6896.
14. Gitsov, I. F., J. M. J., Novel nanoscopic architectures. Linear-globular ABA copolymers with polyether dendrimers as A blocks and polystyrene as B block. *Macromolecules* **1994**, *27* (25), 7309-7315.

15. Ge, Z. C., Daoyong; Zhang, Jingyan; Rao, Jingyi; Yin, Jun; Wang, Di; Wan, Xuejuan; Shi, Wenfang; Liu, Shiyong., Facile synthesis of dumbbell-shaped dendritic-linear-dendritic triblock copolymer via reversible addition-fragmentation chain transfer polymerization. *J. Polym. Sci. Part A.: Polym. Chem.* **2007**, *45* (8), 1432-1445.
16. Osano, K.; Turner, R., Synthesis, characterization, and properties of linear poly(ether sulfone)s with dendritic terminal groups. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (3), 958-969.
17. Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Kruger, R.-P., Cyclic hyperbranched poly(ether ketone)s derived from 3,5-bis(4-fluorobenzoyl)phenol. *Macromolecules* **2003**, *36* (15), 5551-5558.
18. Lafitte, B.; Jannasch, P., Proton-conducting aromatic polymers carrying hypersulfonated side chains for fuel cell applications. *Adv. Funct. Mater.* **2007**, *17* (15), 2823-2834.
19. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M., Dendritic analogs of engineering plastics: A general one-step synthesis of dendritic polyaryl ethers. *J. Am. Chem. Soc.* **1993**, *115* (1), 356-357.

## **Chapter 5: Synthesis of Dendritic End-Cappers for Poly(arylene ether sulfone)s**

### **5.1 Abstract**

Various dendritic end-cappers for poly(arylene ether sulfone)s were investigated in attempts to find convenient and inexpensive synthetic methods for these end-cappers. Although these methods were not as convenient as those reported in Chapter 3 and Chapter 4, some of these attempts opened up new areas, which we would like to investigate in the future.

### **5.2 Introduction**

In this chapter, we report the synthesis of functional and non-functional dendritic end-cappers for poly(arylene ether sulfone)s. The results shown in this chapter came from the experiments that were carried out as a part of the work discussed in Chapter 3 and Chapter 4 to try to find convenient and inexpensive synthetic methods for dendritic end-cappers which would allow us to prepare 5-10 grams of the final products in a timely fashion. These results were, however, not included in these chapters. The results of these experiments will be of value to others who may continue research in this area.

### **5.3 Experimental**

#### **5.3.1 Materials**

All reagents were purchased from Aldrich and used as received.



### 5.3.2 Synthesis

**Preparation of 5-acetoxyisophthalic acid (3).** 5-Hydroxyisophthalic acid (4.85 g, 26.6 mmol) was placed in a 100 ml round bottom containing a magnetic stirring bar. To this flask, acetic anhydride (26 ml) and fuming sulfuric acid (2 drops) were added and the mixture was stirred at 60 °C for 24 hrs. After cooling to room temperature, the mixture was poured into ice water. The white precipitate was collected by vacuum filtration and recrystallized from 1:1 ethanol/water mixture. The white solid was collected by vacuum filtration and washed with hexane three times. The solid was dried under vacuum at room temperature overnight to yield 5.03 g (22.4 mmol) of **3** as a white solid. Yield: 84%. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>1</sup>

**Preparation of 5-acetoxyisophthaloyl chloride (4).** **3** (4.93 g, 22.0 mmol) was placed in a 100 ml round bottom flask with a magnetic stirring bar. To this flask, thionyl chloride (25 ml, 345 mmol) and DMF (2 drops) were added. The mixture was stirred at 60 °C for 10 hrs to give a clear yellow solution. The excess thionyl chloride was distilled off with the use of an argon stream. The solid was then washed with hexane and dried under vacuum overnight to give 4.32 g (16.6 mmol) of **4** as a pale yellow solid. Yield: 75%. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>1</sup>

**Preparation of AB<sub>2</sub> monomer (1) via acetic anhydride route.** **4** (4.31 g, 16.5 mmol) and fluorobenzene (15 ml, 160 mmol) were placed in a dropping funnel. To a 100 ml round bottom flask containing a magnetic stirring bar,  $\text{AlCl}_3$  (9.10 g, 68.2 mmol) and fluorobenzene (10 ml, 107 mmol) were added. This flask was immersed in an ice-water bath and the acylchloride solution was added dropwise to this flask. After the addition was completed, the ice-water bath was removed and the mixture was stirred at room

temperature for 24 hrs. The solution was poured into crashed ice to terminate the reaction. The mixture was extracted with dichloromethane three times and the combined organic solvents were evaporated on a rotary evaporator to yield brown solid. To this brown solid, a solution of KOH (5.20 g, 9.27 mmol) in a mixture of 10 ml of water and 65 ml of ethanol was added. The mixture was stirred at reflux temperature under argon for 1.5 hrs. After the reaction, the mixture was cooled to room temperature and poured into 300 ml of dilute aqueous HCl. The brown precipitate was collected by vacuum filtration and recrystallized from toluene three times to 1.95 g (5.77 mmol) of **1** as a white solid. Yield: 35%. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>1</sup>

**Preparation of 1,3-bis(tert-butyl dimethylsilyl)-5-(tert-butyl dimethyl siloxy) isophthalate (5).** 5-Hydroxyisophthalic acid (5.00 g, 27.5 mmol), imidazole (11.0 g, 162 mmol), and anhydrous DMF (40 ml) were placed in a flask equipped with an Ar inlet. To this mixture, a solution of TBDMSCl (16.3 g, 109 mmol) in 90 ml of anhydrous DMF was added dropwise. The mixture was heated at 60 °C for 12 hrs. After cooling, the precipitated crystals were collected by vacuum filtration and dissolved in hexane. The solution was washed with 0.5 M aqueous NaOH and then with water in a separatory funnel. The solution was dried over  $\text{MgSO}_4$  and dried under vacuum overnight to give 10.2 g (19.5 mmol) of **5** as a white solid. Yield: 74 %. The  $^1\text{H}$  NMR spectrum of this compound matched that reported in the paper.<sup>2</sup>

**Preparation of 5-(tert-butyl dimethyl siloxy) isophthalic acid (6).** **5** (10.1 g, 19.2 mmol), water (40 ml), glacial acetic acid (40 ml) and THF (40 ml) were placed in a flask with a magnetic stirring bar. The mixture was stirred at room temperature for 3 hrs and 200 ml water was added. The mixture was cooled to 0 °C in an ice bath, giving a

precipitate. The precipitate was collected by vacuum filtration and dried under vacuum overnight to give 3.97 g (13.4 mmol) of **6** as a white solid. Yield: 70 %. The  $^1\text{H}$  NMR spectrum of this compound matched that reported in the paper.<sup>2</sup>

**Preparation of 5-(tert-butyl dimethyl siloxy) isophthaloyl chloride (7).** **6** (3.95 g, 13.3 mmol), and thionyl chloride (35 ml, 482 mmol) were placed in a flask with a magnetic stirring bar under Ar. The mixture was stirred at 75 °C for 12 hrs. The excess thionyl chloride was distilled off with a stream of Ar. The light yellow solid was dried under vacuum overnight to give 3.19 g (9.58 mmol) of **7** as a light yellow solid. Yield: 72 %. The  $^1\text{H}$  NMR spectrum of this compound matched that reported in the paper.<sup>2</sup>

**Preparation of 5-nitroisophthaloyl chloride (10).** 5-Nitroisophthalic acid (**9**) (10.0 g, 47.4 mmol) was placed in a 100 ml round bottom flask containing a magnetic stirring bar. To this flask, thionyl chloride (50 ml, 690 mmol) and DMF (3 drops) were added. The mixture was stirred at 40-50 °C for 5 hrs to give a clear yellow solution. The excess thionyl chloride was distilled off with a stream of argon. The yellow solid was washed with hexane and dried under vacuum overnight to give 10.3 g (41.7 mmol) of **10** as a pale yellow solid. Yield: 88 %. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>3</sup>

**Preparation of 3,5-bis(4'-fluorobenzoyl)nitrobenzene (11).** **10** (10.2 g, 41.1 mmol) was dissolved in fluorobenzene (30 ml, 320 mmol) and placed in a dropper funnel.  $\text{AlCl}_3$  (12.3 g, 92.5 mmol) and fluorobenzene (10 ml, 106 mmol) were placed in a 250 ml round bottom flask containing a magnetic stirring bar. The flask was cooled to 0 °C by immersing it in an ice-water bath. To the flask, the solution of **10** was added dropwise under argon. After the addition was completed, the ice-water bath was removed and the

mixture was stirred at room temperature for 12 hrs. The mixture was poured into crushed ice to terminate the reaction. The mixture was extracted with dichloromethane and the combined organic solvents were evaporated on a rotary evaporator. The solid was recrystallized from toluene to give 8.31 g (22.6 mmol) of **11** as a white solid. Yield: 55%. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>3</sup>

**Preparation of 3,5-bis(4'-fluorobenzoyl)aniline (12).** **11** (0.50 g, 1.36 mmol) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (1.54 g, 6.82 mmol) were placed in a 50 ml round bottom flask containing a magnetic stirring bar under argon. DMF (7 ml) was added to the flask and the solution was stirred at 70 °C for 2.5 hrs. After the reaction, the mixture was poured into water and  $\text{NaHCO}_3$  (2.0 g, 24 mmol) was added. The aqueous phase was extracted with dichloromethane three times. The product was purified by recrystallization from toluene to give 0.33 g (0.979 mmol) of **12** as a white solid. Yield: 72 %. The  $^1\text{H}$  NMR spectrum matched that reported in the literature.<sup>3</sup>

**Preparation of 3,5-bis(4'-fluorobenzoyl)anisole (13).** **13** was synthesized by the method described in Chapter 3.

**Preparation of 3,5-bis(2',6'-dimethyl-4'-fluorobenzoyl)anisole (15).** **13** (0.50 g, 1.42 mmol), 2,6-dimethylphenol (0.44 g, 3.55 mmol),  $\text{K}_2\text{CO}_3$  (0.59 g, 4.26 mmol), DMSO (8 ml), and toluene (5 ml) were placed in a flask with a magnetic stirring bar under Ar. The mixture was heated at 140 °C for 1 hr and at 150 °C for 2 hrs. After cooling, the mixture was poured into water and extracted with methylene chloride three times. The product was isolated by silica gel column chromatography using 80/20 methylene chloride/hexane to give 0.28 g (0.69 mmol) of **15** as a green oil. Yield: 48 %.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$ 7.82 (m, 4H), 7.65 (t, 1H), 7.51 (d, 2H), 7.14 (m, 6H), 6.86 (m, 4H),

3.91 (s, 3H), 2.14 (s, 12H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$ 194.2, 161.9, 159.8, 150.7, 139.8, 132.9, 131.3, 130.7, 129.7, 123.4, 118.8, 115.8, 56.0.

**Preparation of hydroxyl-terminated polysulfone (P-OH).** P-OH was synthesized from 4,4'-dichlorodiphenylsulfone (DCDPS) and bisphenol-A (BPA). Molecular weight control was achieved by stoichiometric imbalance with a calculated amount of BPA in excess. DCDPS (4.84 g, 16.8 mmol), BPA (3.78 g, 17.1 mmol), potassium carbonate (2.40 g, 17.4 mmol), DMAc (30 ml), and toluene (20 ml) were placed in a flask equipped with an Ar inlet and mechanical stirrer. The mixture was stirred at 130-140 °C for 3 hrs to remove water by azeotropic distillation and at 155 °C for 3 hrs. After cooling, the mixture was diluted with THF and filtered to remove KF and  $\text{K}_2\text{CO}_3$ . The polymer was then precipitated in 800 ml dilute aqueous HCl washed with water. The polymer was dried under vacuum at 120-130 °C overnight to give 6.8 g of P-OH as a white solid. Yield: 92 %.

**Preparation of end-capped polysulfone (P-Cap).** P-OH (0.30 g,  $1.1 \times 10^{-2}$  mmol), 1-chloro-2-phenoxyethane (0.025 g, 0.16 mmol), DMAc (8 ml), benzene (5 ml), and  $\text{K}_2\text{CO}_3$  (0.0020 g,  $1.5 \times 10^{-2}$  mmol) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 100 °C for 12 hrs. After cooling, the mixture was filtered into 200 ml of MeOH to give a white precipitate. The white polymer was dried under vacuum at 120-130 °C overnight to give 0.27 g of P-Cap as a white solid. Yield: 90 %.

**Preparation of AB<sub>2</sub> monomer with hydroxyethoxy focal point (20).** 1 (1.28 g, 3.80 mmol), chloroethanol (1.53 g, 19.0 mmol),  $\text{K}_2\text{CO}_3$  (0.63 g, 4.56 mmol) and DMSO (10 ml) were placed in a flask with a magnetic stirring bar. The mixture was stirred at 90 °C under Ar for 24 hrs. The mixture was poured into water and extracted with methylene

chloride three times. The product was then isolated by silica gel column chromatography using 10/90 ethylacetate/methylene chloride to give 0.97 g of **20** as a yellow oil. Yield: 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.84-7.89 (m, 4H), 7.53-7.54 (t, 1H), 7.48-7.49 (d, 2H), 7.13-7.19 (m, 4H), 4.17 (t, 2H), 3.97 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ194.2, 165.8 (d, *J* = 255.3 Hz), 159.9, 139.3, 133.3, 132.9, 123.9, 119.5, 116.0, 70.1, 61.4.

**Preparation of G1-dendron with hydroxyethoxy focal point (24).** **23** (0.50 g, 0.78 mmol), K<sub>2</sub>CO<sub>3</sub> (5.4 mg, 3.9 x 10<sup>-2</sup> mmol), ethylene carbonate (75.7 mg, 0.86 mmol) and DMAc (15 ml) were placed in a flask with a magnetic stirring bar. The mixture was stirred at 150 °C for 5 hrs. The mixture was poured into water and extracted with methylene chloride three times. The product was isolated by silica gel column chromatography using 10/90 ethylacetate/methylene chloride to give 0.22 g (0.33 mmol) of **24** as a white solid. Yield: 42 %. mp: 122 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.85 (m, 4H), 7.67 (t, 1H), 7.62 (m, 4H), 7.58 (m, 4H), 7.53 (d, 2H), 7.43 (m, 4H), 7.35 (m, 2H), 7.16 (m, 4H), 7.14 (m, 4H), 3.92 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ194.5, 162.2, 159.9, 155.0, 140.5, 139.5, 138.0, 132.8, 131.6, 129.1, 129.0, 127.5, 127.2, 123.7, 120.7, 118.7, 117.5, 69.8, 61.2.

**Preparation of G1-dendron with *tert*-butylphenol terminal groups (25).** **13** (1.00 g, 2.84 mmol), *tert*-butylphenol (0.90 g, 5.97 mmol), K<sub>2</sub>CO<sub>3</sub> (0.91 g, 6.58 mmol), DMAc (10 ml) and toluene (5 ml) were placed in a flask with a magnetic stirring bar. The mixture was stirred at 130 °C for 1 hr and at 150 °C for 2 hrs. The mixture was poured into water, extracted with methylene chloride three times and dried under MgSO<sub>4</sub>. The product was isolated by silica gel column chromatography using 15/85

ethylacetate/hexane to give 1.46 g (2.39 mmol) of **25** as colorless oil. Yield: 84 %. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of this compound matched those reported in the literature.<sup>4</sup>

**Preparation of HBP (by NaH route).** NaH (0.0864 g, 3.60 mmol) was placed in a flask under Ar. **1** (0.8950 g, 2.648 mmol) was dissolved in anhydrous THF (10 ml) in another flask under Ar and poured into the NaH. The THF was removed under vacuum and anhydrous DMAc (16 ml) was added to the flask. The mixture was heated at 150 °C for 2 hrs under Ar and poured into 500 ml of dilute aqueous HCl. The white precipitate was collected by vacuum filtration and dried under vacuum overnight to give 0.81 g of **HBP** as a white solid. Yield: 92 %.

**Preparation of HBP (by K<sub>2</sub>CO<sub>3</sub> route).** **1** (1.00 g, 2.96 mmol), K<sub>2</sub>CO<sub>3</sub> (0.44 g, 3.20 mmol), DMAc (18 ml), and toluene (10 ml) were placed in a flask equipped with an Ar inlet and mechanical stirrer. The mixture was stirred at 130-140 °C for 1 hrs to remove water by azeotropic distillation and at 150 °C for 2 hrs. After cooling, the mixture was poured into 500 ml dilute aqueous HCl. The polymer was collected by vacuum filtration and dried under vacuum overnight to give 0.92 g of **HBP** as a white solid. Yield: 93 %.

### 5.3.3 Characterization

NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Size Exclusion Chromatography (SEC) was recorded in THF with a flow rate of 1.00 ml/min at 40 °C by Waters 717 Autosampler with 3 in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The  $\text{dn/dc}$  values

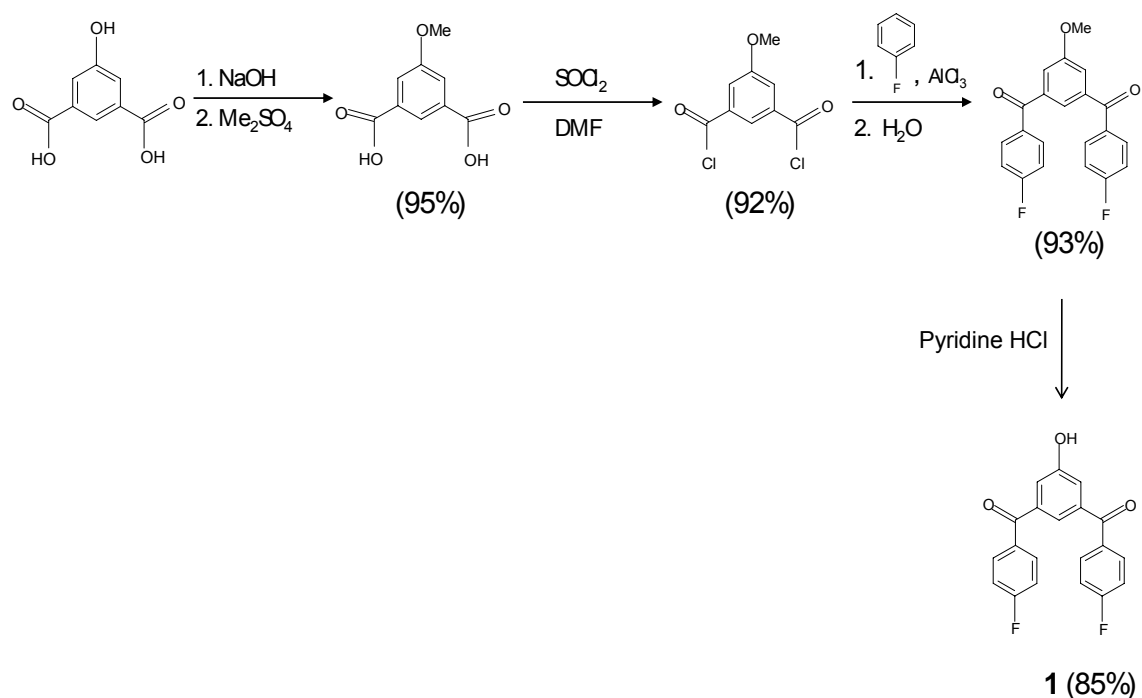
were calculated on-line using the calibration constant for the RI detector and for the mass of the polymer samples assuming 100% mass recovery of the samples.

## **5.4 Results and Discussion**

### **5.4.1 Synthesis of AB<sub>2</sub> Monomer with Various Synthetic Routes**

In Chapter 4, we described the use of AB<sub>2</sub> monomer (**1**) to attach and grow hyperbranched polymers onto the ends of polysulfones. For the work described in Chapter 4, this AB<sub>2</sub> monomer was synthesized from 5-hydroxyisophthalic acid using dimethylsulfate as the protecting agent (Scheme 5.1). As shown in Scheme 5.1, four steps are required to obtain **1** from 5-hydroxyisophthalic acid. All the steps were high yielding and the overall yield (from 5-hydroxyisophthalic acid to **1**) was almost 70 %. Furthermore, none of the reagents used in this synthetic route is expensive. Although we are now aware that this synthetic method is the most economical, a few other synthetic routes were tested in our lab to try to prepare this monomer in a safer (without the use of dimethylsulfate) and more economical way. In this section, we report our efforts on the other synthetic routes to the monomer.

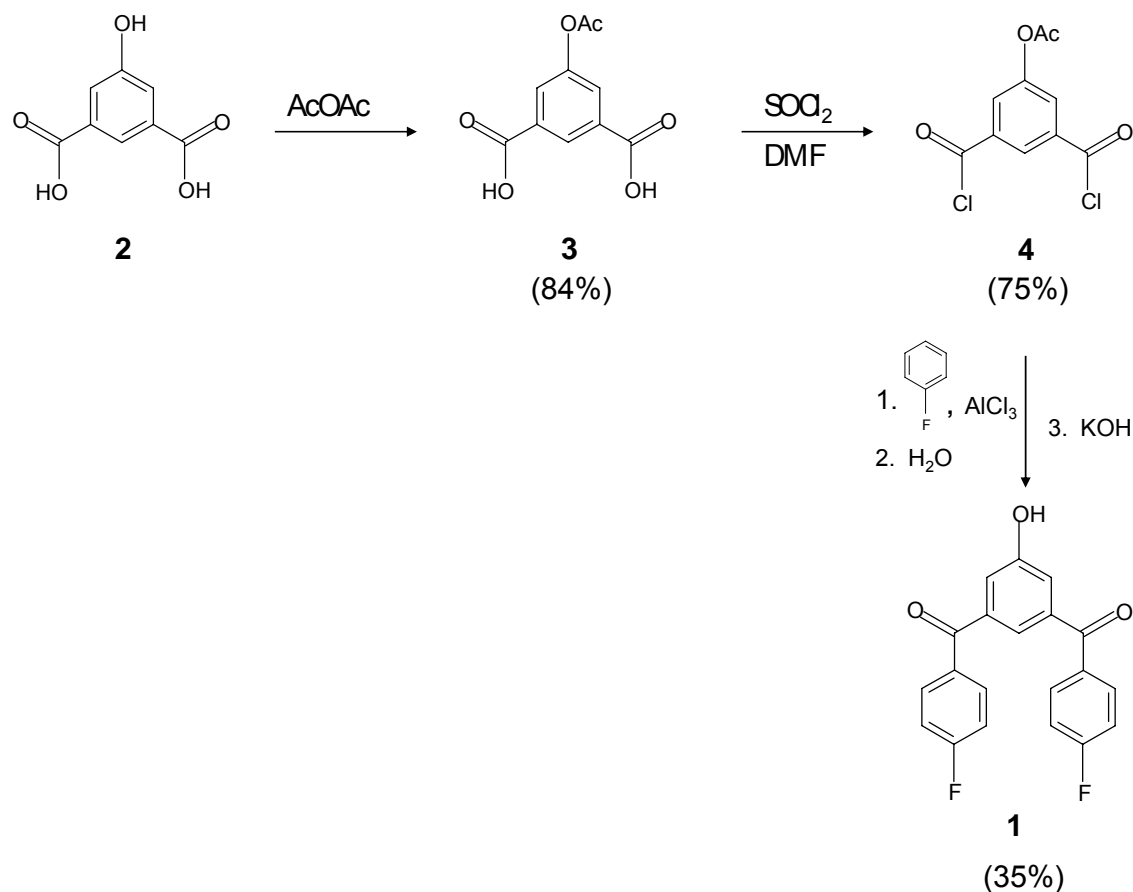




**Scheme 5.1** Synthetic procedure utilized to obtain **1** in Chapter 4.

#### 5.4.1.1 Acetic Anhydride Route

An attempt was made to prepare **1** using acetic anhydride as the protecting group instead of dimethylsulfate because of the safety concerns regarding dimethylsulfate. The first step was the reaction of 5-hydroxyisophthalic acid (**2**) with acetic anhydride to protect the phenolic hydroxyl group to give the corresponding protected dicarboxylic acid (**3**) in 84 % yield, followed by the treatment with thionylchloride to give the diacylchloride (**4**) in 75 % yield. The acetoxy group of the product of Friedel-Craft acylation was hydrolyzed by KOH without isolating the acetoxy-protected intermediate. This acetic anhydride route has been described by Baek<sup>1</sup> and reported to give **1** from **4** in 85 % yield. The first two steps of this route gave satisfactory yields as described in the paper. Although we followed the same procedure, we only obtained 35 % yield for the last step (Scheme 5.2). No more effort was made on this synthetic route.

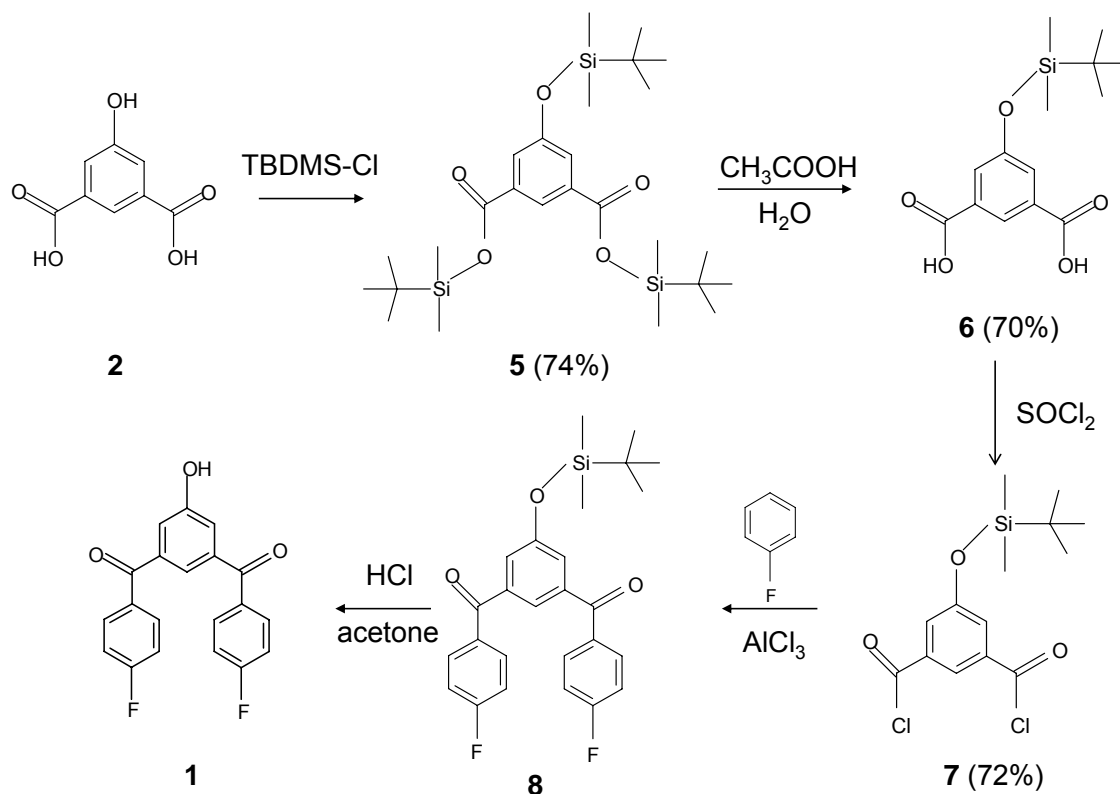


**Scheme 5.2** Synthetic route utilizing acetic anhydride as a protecting agent.

#### 5.4.1.2 *Tert*-Butyldimethylsilyl Chloride (TBDMS-Cl) Route

TBDMS-Cl was also studied as a protecting reagent according to the method reported by Heuer.<sup>2</sup> This synthetic route is shown in Scheme 5.3. The first step was the reaction of **2** with TBDMSi-Cl to give intermediate **5** in 74 % yield. Since silylchloride does not react selectively with phenolic hydroxyl groups, the carboxylic acid units were also inevitably protected. The next step was the hydrolysis of the protected carboxylic acid units to give **6** in 70 % yield. The conversion of the carboxylic acid groups into the corresponding acylchloride was achieved by thionylchloride to give **7** in 72 % yield. Friedel-Crafts acylation, however, gave a mixture of several compounds making the

isolation of the desired intermediate difficult. Moreover, the significantly high cost of TBDMS-Cl and the extra step (intermediate **5**) needed to get to diacylchloride **7** discouraged further investigation of this synthetic route.



**Scheme 5.3** Synthetic route utilizing TBDMS-Cl as a protecting agent.

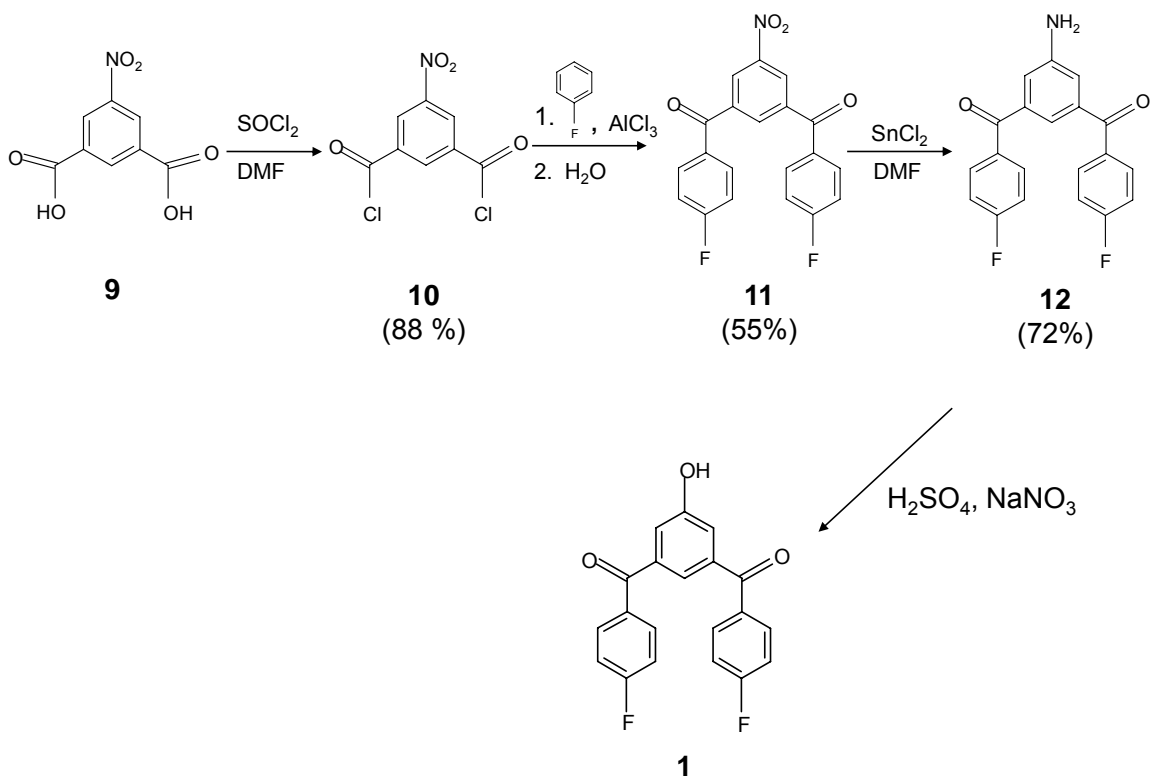
#### 5.4.1.3 5-Nitroisophthalic Acid Route

An effort was made to synthesize **1** using another route. This synthetic route was reported by Miller.<sup>5</sup> 5-nitroisophthalic acid (**9**) was used as the starting material (Scheme 5.4). The first step of the synthesis was the reaction of **9** with thionylchloride to give diacylchloride **10** in 88 % yield, followed by Friedel-Crafts acylation to give intermediate **11** in 55 % yield. The nitro group was then reduced to amine by  $\text{SnCl}_2$  to give intermediate **12** in 72 % yield. The percent yield of the Friedel-Crafts acylation in this

synthesis was only about 55 % and that of the reduction step was 75%. This synthetic route was therefore not investigated further. However, this synthetic route is interesting in that one could prepare dendrons with amino focal points from **12**. In Chapter 3, we described the attachment of G1-OH onto the ends of polysulfones. Dendrons with amino focal points could be attached to the ends of other types of polymer backbones such as polyamides. This synthetic route may be worth revisiting if one wishes to prepare dendrons with such amino focal points. Also, **12** is interesting in that it could be used as a difunctional monomer to make poly(arylene ether ketone)s if polymerized with suitable bisphenols. This will be discussed in detail in Chapter 6.

#### **5.4.2 Synthesis of Sulfonated End-Cappers for Polysulfones**

In the previous chapters, we described the successful synthesis of polysulfones with dendritic terminal groups. In addition to the dendritic terminal groups described in those chapters, synthesis of various dendritic end groups was attempted in our lab. Our initial plan was to prepare dendrons with functional groups (mainly ionic sulfonates). In this section, we report our synthetic attempts to prepare these end cappers although we realized that the preparation of analogous hyperbranched end cappers as described in Chapter 4 would be much more facile and decided not to investigate these functionalized dendrons further because we would need a synthetic method that would allow us to obtain ~10 grams of final products at a reasonable cost and time.

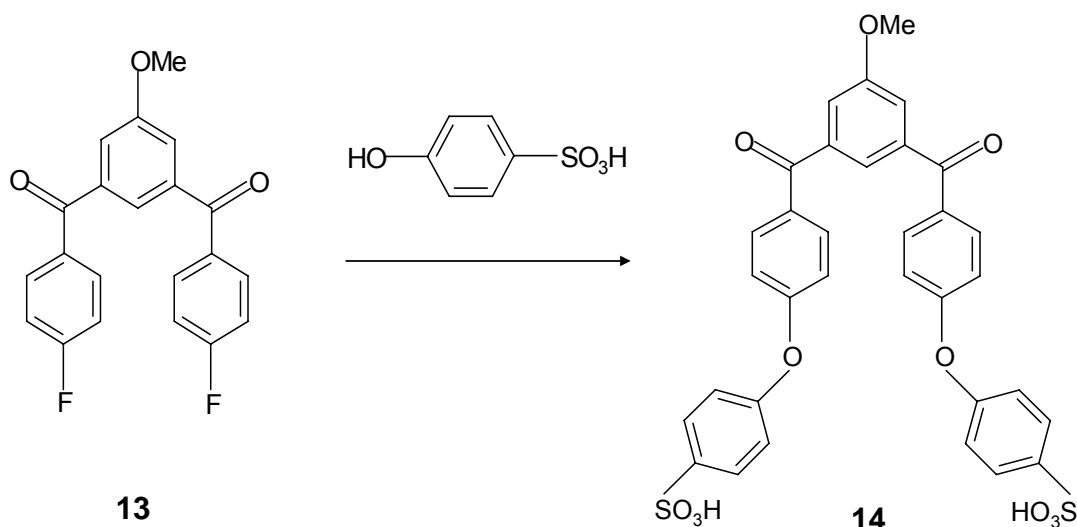


**Scheme 5.4** Synthesis of AB<sub>2</sub> monomer by 5-nitroisophthalic acid route.

#### 5.4.2.1 Methoxy Protective Group Route

Compound **13**, which was used to prepare dendrons in Chapter 3, could react with 4-hydroxybenzene sulfonic acid to give a dendron (**14**) with two sulfonate arms as shown in Scheme 5.5. It was thought that demethylation of **14** would give a dendron with phenolic hydroxyl focal point, which could be attached to the ends of polysulfones. Morikawa, who reported **13** for the first time in 1993, apparently tried to demethylate the methoxy-protected dendrons after placing various functional groups on the arms of this compound.<sup>6-8</sup> The dendrimers carrying functional groups reported by this author used different building blocks probably due to strenuous conditions required for demethylation

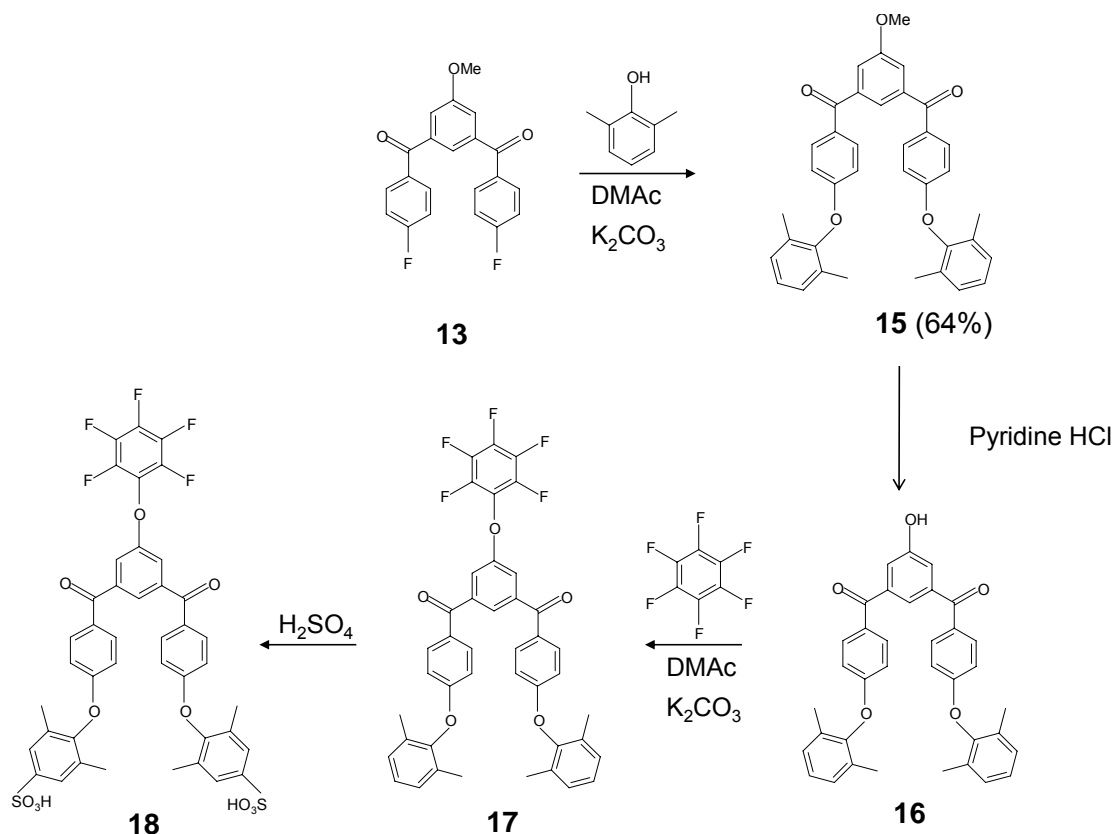
which would cause degradations of functional groups.<sup>8</sup> Thus a different method would be needed to prepare arylene ether ketone dendrons with functional groups.



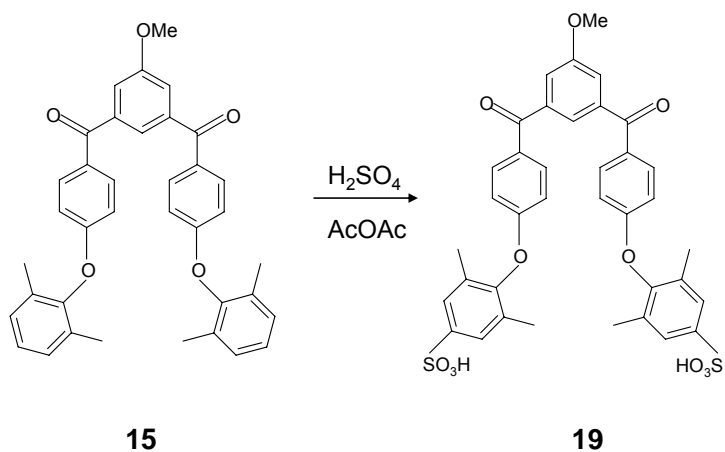
**Scheme 5.5** Synthesis of **14** from **13** by  $\text{S}_{\text{N}}\text{Ar}$  with 4-hydroxybenzene sulfonic acid.

Our first approach to a sulfonated dendron was to sulfonate an end-capper after demethylation. This would avoid undesirable desulfonation in the demethylation step. The first step of our proposed synthetic route was the reaction of **13** with 2,6-dimethylphenol to give intermediate **15**. These methyl groups could direct sulfonation onto the para-positions of the terminal phenyl rings by blocking ortho substitutions. The second step is demethylation by pyridine hydrochloride to give deprotected dendron **16**, followed by the reaction with excess hexafluorobenzene to give intermediate **17**. If a selective sulfonation could occur on **17**, the final end-capper (**18**) should be obtained, which could be attached to the ends of polysulfones by the reaction with OH-terminated polysulfones. The most important key to obtain **18** would be the selective sulfonation of **17** on the para positions of the terminal phenyl rings. In order to estimate the selectivity of sulfonation on **17**, a model reaction was carried out by sulfonating **15** with

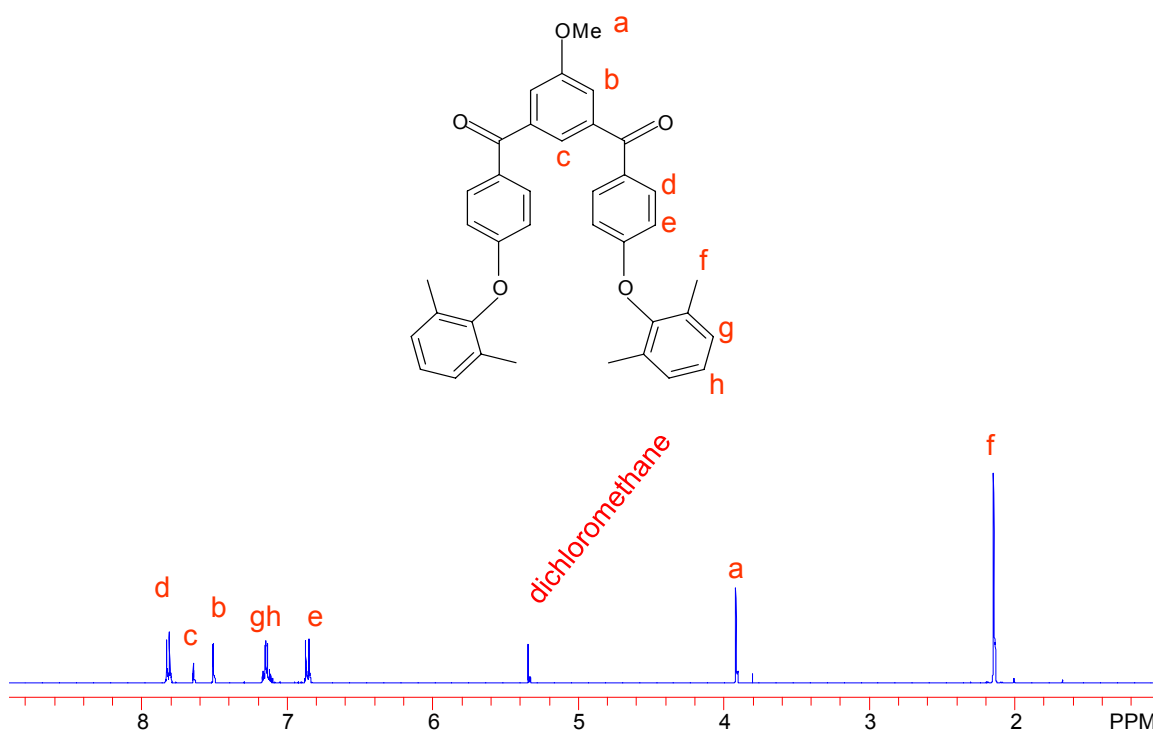
acetylsulfate. It turned out, however, that the reaction mixture contained a large number of impurities apparently because sulfonation took place not only on the terminal phenyl rings but also on the ones in the center. This may be explained by the  $^1\text{H}$  NMR spectrum of the precursor **15** (Figure 5.1). As the spectrum shows, proton e is more electron-rich than proton h. Also, proton g has essentially the same electron density as proton h. Thus, in terms of electron density, the electrophilic addition should not take place preferentially on position h. Although, h is sterically less hindered than e and g, it is outnumbered by e and g. Similar results were reported by Lambrechts<sup>9</sup>, who obtained a mixture of meta and para substituted products by the sulfonation of 2,6-dimethylphenol with  $\text{H}_2\text{SO}_4$ . Due to this complication, this synthetic route was abandoned.



**Scheme 5.6** Synthetic route to sulfonated dendritic end-capper.



**Scheme 5.7** Model reaction of sulfonation using **15**.

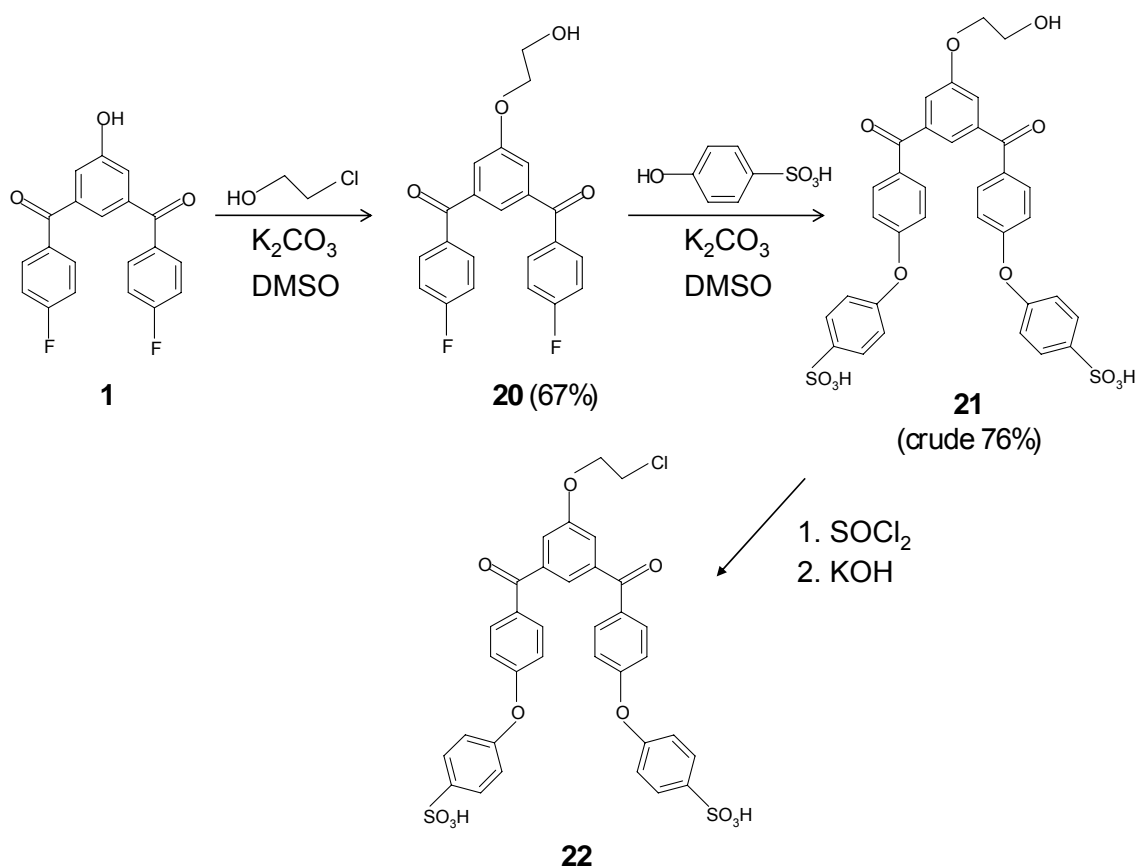


#### 5.4.2.2 Hydroxyethoxy Protective Group Route

Another synthetic approach that was tested was to introduce a hydroxyethoxy unit as a protecting group. The advantage of utilizing a hydroxyethoxy unit as a protecting



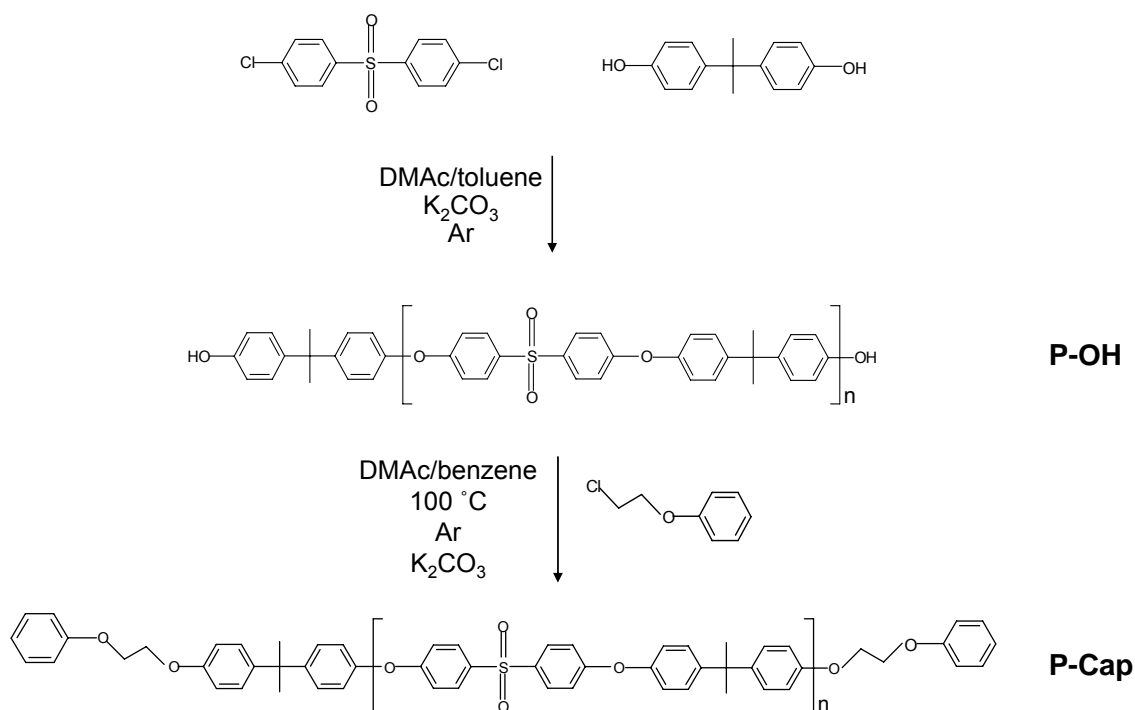
group is that a deprotecting step is not needed after the attachment of sulfonate groups. The primary hydroxyl group of hydroxyethoxy unit is not acidic enough to be deprotonated by  $K_2CO_3$  and does not participate in  $S_NAr$  reactions to a significant extent. In fact, Morikawa successfully used this protection method to build arylene ether ketone dendrimers.<sup>8</sup> Our target was **22**, which could react with an OH-terminated polysulfone to place sulfonates on polysulfone chain ends (Scheme 5.8). Such primary aliphatic alcohol could also be used for polyesters or polyurethanes.



**Scheme 5.8** Synthetic route to sulfonated G1 dendritic end-capper **22**.

In order to confirm that the reaction of an OH-terminated polysulfone with a primary alkyl chloride could lead to a complete end-capping, a model study was

performed by reacting 1-chloro-2-phenoxyethane with an OH-terminated polysulfone (**P-OH**) before attempting to synthesize **22** (Scheme 5.9). The product polymer (**P-Cap**) was precipitated in methanol, which is a selective solvent for any unreacted 1-chloro-2-phenoxyethane. The molecular weights of this polymer determined by SEC before and after the end-capping reaction were essentially the same, suggesting that no significant side reactions occurred during the end-capping reaction (Table 5.1). Also, the  $M_n$  of the final polymer determined by  $^1\text{H}$  NMR is very close to the SEC result. These results indicate that complete end-capping was achieved and that end-capper **22** should work as well.



**Scheme 5.9** End-capping of phenolate-terminated polysulfone with 1-chloro-2-phenoxyethane.

**Table 5.1** Molecular weights of polysulfone before and after end-capping with 1-chloro-2-phenoxyethane.

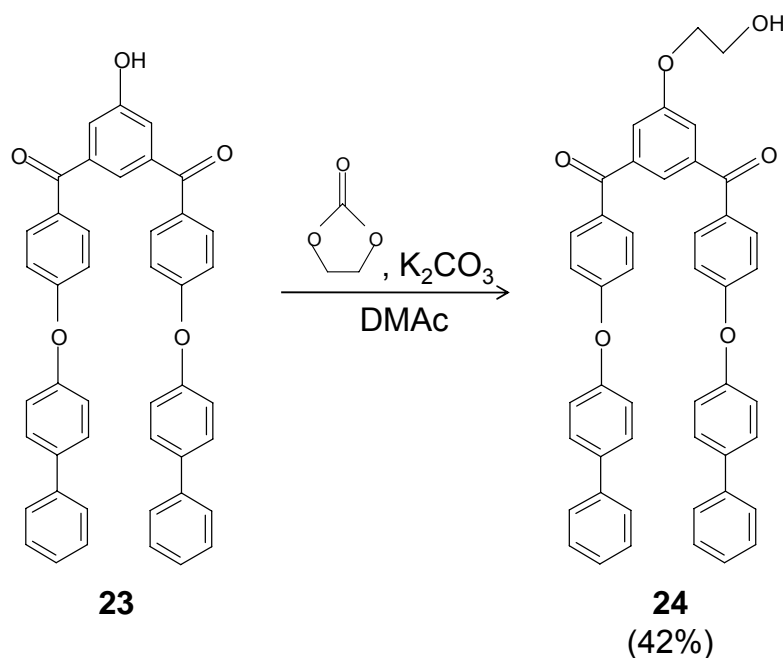
Polymer	$^1\text{H}$ NMR $M_n$ (g/mol)	SEC $M_n$ (g/mol)	SEC $M_w$ (g/mol)	PDI
P-OH	-	$2.7 \times 10^4$	$5.4 \times 10^4$	2.0
P-Cap	$3.0 \times 10^4$	$2.7 \times 10^4$	$5.1 \times 10^4$	1.9

Motivated by the model reaction mentioned above, the introduction of hydroxyethoxy unit by chloroethanol was attempted and it successfully gave the product (**20**) in 67 % yield after isolation by silica gel column chromatography. The  $S_NAr$  of **20** with 4-hydroxybenzenesulfonic acid, followed by precipitation in saturated aqueous NaCl solution containing 1 M HCl gave a mixture of products in 76 % (crude yield). This product showed unidentifiable peaks on its  $^1\text{H}$  NMR spectrum. Since the isolation of this precursor called for column chromatography, no effort was made to isolate this product and thus this synthetic route was abandoned.

#### 5.4.3 Synthesis of G1 Dendron with Hydroxyethoxy Focal Point

In Chapter 3, we reported the attachment of non-functional dendritic end-cappers onto the ends of polysulfones. These end-cappers possessed phenolic hydroxyl focal points. In addition to this end-capper, an analogous end-capper with hydroxyethoxy focal point (**24**) was successfully prepared by the reaction of G1-OH (**23**) with ethylene carbonate as shown in Scheme 5.10. Because of the hydroxyethoxy unit, this end-capper would be suitable to be attached onto the ends of polyesters. Our group may revisit this compound to work on polyester backbones in the future. The low percent yield for the preparation of **24** by this method would probably be improved by using chloroethanol or

bromoethanol instead of ethylene carbonate because we believe that ether cleavage was the main cause of the low percent yield. Chloroethanol and bromoethanol call for much lower reaction temperatures than ethylene carbonate.

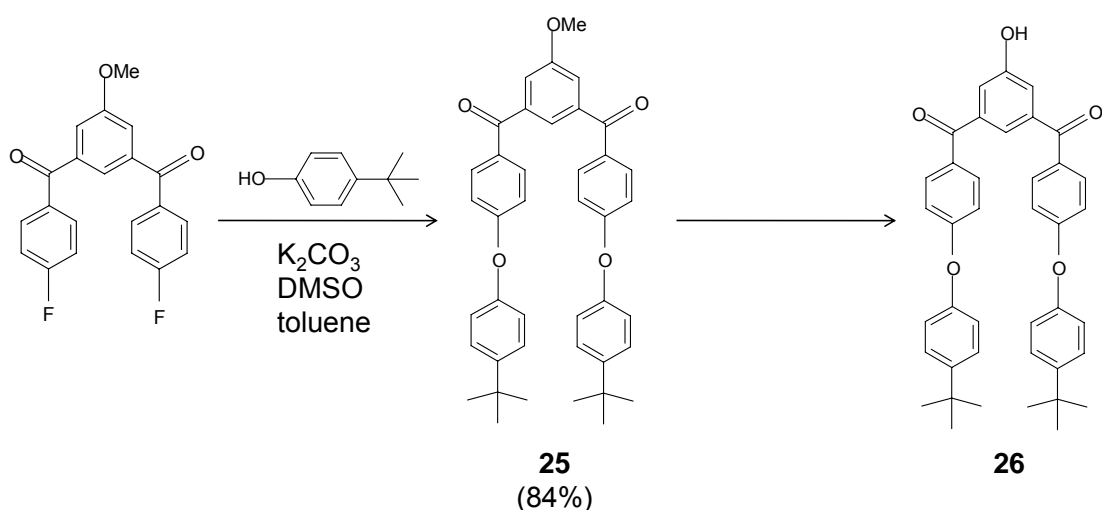


**Scheme 5.10** Preparation of non-functional dendritic end-capper with hydroxyethoxy focal point.

#### 5.4.4 Synthesis of G1 Dendron with *Tert*-Butylphenol Terminal Groups

In Chapter 3, dendrons with 4-phenylphenol terminal groups were described. The synthesis of analogous dendrons with *tert*-butylphenol end-groups was also investigated as shown in Scheme 5.11. Although intermediate **25** was successfully isolated in 84 % yield, silica gel column chromatography was required for the isolation whereas the analogous dendron with 4-phenylphenol was conveniently isolated by a simple precipitation in ethanol.

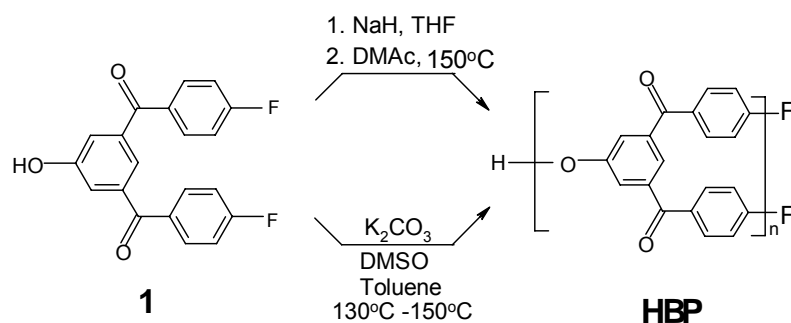
In the literature, demethylation of **25** by  $\text{BBr}_3$  was reported to give **26** in 92 % yield after column chromatography. Although this was high yielding, the cost of  $\text{BBr}_3$  was significantly higher than  $\text{AlCl}_3$  which was used to demethylate the analogous dendron with 4-phenylphenol terminal groups. Also, demethylation of **25** by  $\text{AlCl}_3$  was unsuccessful because of the cleavage of *tert*-butyl groups. For these reasons, this synthetic route was not investigated further.



**Scheme 5.11** Preparation of G1 dendron with *tert*-butylphenol terminal groups.

#### 5.4.5 Synthesis of Hyperbranched End-Capper

Homopolymerization of  $\text{AB}_2$  monomer **1** to give hyperbranched polymers (HBPs) was described in the literature (Scheme 5.11).<sup>5, 10</sup> Either  $\text{K}_2\text{CO}_3$  or  $\text{NaH}$  could be used to deprotonate the phenolic hydroxyl group. The synthesis of these hyperbranched polymers was investigated in our lab and we obtained results consistent with the literature. The molecular weights of these HBPs are summarized in Table 5.2.



**Scheme 5.12** Synthesis of HBP.

**Table 5.2** Molecular weights of HBPs.

	SEC-LS		
	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
Method 1 (via NaH)	$6.5 \times 10^3$	$1.0 \times 10^4$	1.6
	$1.2 \times 10^4$	$3.0 \times 10^4$	2.5
Method 2 (via $K_2CO_3$ )	$1.1 \times 10^4$	$1.6 \times 10^4$	2.5

An attempt was made to convert the phenolic hydroxyl groups into hydroxyethoxy units by reacting HBP with chloroethanol. The  $^1\text{H}$  NMR spectrum of the product did not show the ethylene unit. A reaction of HBP with acetic anhydride was carried out to check the accessibility or the presence of phenolic hydroxyl groups on this polymer. The  $^1\text{H}$  NMR spectrum of the product, however, did not show acetoxy groups on this polymer. This may be because the phenolic hydroxyl groups of the focal point is either inaccessible due to the steric congestion or does not exist because of the formation

of cyclic species as described by Kricheldorf.<sup>10</sup> Therefore, no more efforts were made on the conversion of the phenolic hydroxyl units of HBPs into hydroxyethoxy units.

## **5.5 Conclusions**

We have described our efforts on various synthetic routes to dendritic terminal groups for polysulfones, all of which was a part of the experiments reported in the previous chapters.

For the synthesis of the AB<sub>2</sub> monomer, the dimethylsulfate route found to be a better method than any of the alternative synthetic routes that were investigated.

A hydroxyethoxy unit was introduced as a protective group for the phenolic hydroxyl group of our arylene ether ketone dendron. Although the hydroxyethoxy unit was successfully introduced, the isolation of the product required column chromatography, which discouraged further investigation of this strategy.

The focal points of hyperbranched polymers based on our AB<sub>2</sub> monomer were difficult to be used for further chemical modification. This suggests that attachment of preformed hyperbranched polymers to the ends of poly(arylene ether sulfone)s has difficulties and may not be a good strategy.

## **5.6 Acknowledgements**

We are grateful to Dr. Timothy Long's group for allowing our group to use their SEC.

## 5.7 References

1. Baek, J.-B.; Tan, L.-S., Linear-hyperbranched copolymerization as a tool to modulate thermal properties and crystallinity of a para-poly(ether-ketone). *Polymer* **2003**, *44* (12), 3451-3459.
2. Heuer, H.-W.; Wehrmann, R.; Meyer, A.; Pielartzik, H.; Bruder, F.-K.; Paulusse, J. M. J. Polycarbonates, polyester carbonates and polyesters having branched terminal groups. 6,784,278 B2, 2004.
3. Yu, Z.; Fossum, E.; Wang, D. H.; Tan, L.-S., Alternative approach to an AB2 monomer for hyperbranched poly(arylene ether ketone imide)s. *Synth. Commun.* **2008**, *38* (3), 419-417.
4. Abramov, M. A.; Shukla, R.; Amabilino, D. B.; Dehaen, W., New accelerated strategy for the synthesis of poly(Ether Ketone) dendrons. *J. Org. Chem.* **2002**, *67* (3), 1004-1007.
5. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M., Dendritic analogs of engineering plastics: A general one-step synthesis of dendritic polyaryl ethers. *J. Am. Chem. Soc.* **1993**, *115* (1), 356-357.
6. Morikawa, A.; Kakimoto, M.; Imai, Y., Convergent synthesis of starburst poly(ether ketone) dendrons. *Macromolecules* **1993**, *26* (24), 6324-6329.
7. Morikawa, A.; Ono, K., Preparation of poly(ether ketone) dendrons with graded structures. *Macromolecules* **1999**, *32* (4), 1062-1068.
8. Morikawa, A.; Ono, K., Preparation of poly[(ether)-(ether ether ketone)] dendrimers by the convergent method. *Polym. J.* **2000**, *32* (3), 255-262.
9. Lambrechts, H. J. A.; Schaasberg-Nienhuis, Z. R. H.; Cerfontain, H., Aromatic sulfonation. Part 92. Sulfonation of the three methylphenols and the six dimethylphenols in concentrated aqueous sulfuric acid: and the isomerization of some of the resulting sulfonic acids and of m-xylene-2- and o-xylene-3-sulfonic acid. *J. Chem. Soc., Perkin Trans. II* **1985**, (5), 669-675.
10. Kricheldorf, H. R.; Vakhtangishvili, L.; Schwarz, G.; Kruger, R.-P., Cyclic hyperbranched poly(ether ketone)s derived from 3,5-bis(4-fluorobenzoyl)phenol. *Macromolecules* **2003**, *36* (15), 5551-5558.



## Chapter 6: Synthesis and Characterization of Cyclohexyl-Containing Poly(ether ketone sulfone)s

(Published as: Osano, K.; Das, S.; Turner, S. R. *Polymer* **2009**, *50*, 1144-1149)

### 6.1 Abstract

A series of poly(ether ketone sulfone)s were synthesized from 1,4-di(fluorobenzoyl)cyclohexane, difluorodiphenyl sulfone and bisphenol-A. These polymers were characterized by NMR, IR, SEC, DSC, TGA, tensile tests and DMA. The results from NMR, IR, and SEC indicated that essentially no side reactions, such as crosslinking, associated with enolate chemistry take place during the polymerizations although *cis/trans* stereochemical isomerization was observed. Comparison of the  $T_g$ s of the polymers with 1,4-cyclohexyl units to those of the terephthaloyl analogs suggested that the *trans*-1,4-cyclohexyl unit imparts slightly higher  $T_g$  than the terephthaloyl moiety. Tensile tests and DMA revealed that polymers with 1,4-cyclohexyl units have essentially the same storage moduli as the corresponding aromatic analogs despite the inherent flexibility of the cyclohexyl unit. DMA also showed that the cyclohexyl unit imparts a larger magnitude of sub- $T_g$  motion than terephthaloyl unit while maintaining high modulus.

### 6.2 Introduction

Poly(arylene ether ketone)s and poly(arylene ether sulfone)s, or simply polyketones and polysulfones, are widely known as high- $T_g$  engineering thermoplastics

with excellent hydrolytic and thermal stabilities.<sup>1, 2</sup> Although there are several synthetic methods for these polymers, they are mainly synthesized in solution by the nucleophilic aromatic substitution ( $S_NAr$ ) between bisphenols and aromatic dihalides, which requires high reaction temperatures (typically  $>150\text{ }^{\circ}\text{C}$ ) in the presence of weak bases such as  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ .<sup>1, 2</sup> A large number of polysulfones and polyketones have been reported and several amorphous polysulfones and semi-crystalline polyketones are commercially available today.<sup>1, 2</sup> There remain, however, some structural modifications of these polymer classes that have not been explored. Previously, our research group has reported polysulfones with biphenyl and terphenyl segments in search of novel high performance materials.<sup>3</sup> Another intriguing and unexplored modification is to incorporate cyclohexyl groups. Cyclohexyl groups have been incorporated into a wide variety of polyesters and poly(ester carbonate)s to impart desirable physical properties.<sup>4-13</sup> Polyesters based on 1,4-cyclohexanedimethanol (CHDM) are perhaps the most well-known examples of polymers containing 1,4-cyclohexyl groups in the backbone. The incorporation of CHDM into a polymer backbone is known to enhance impact performance and can have a major influence on crystallization rate.<sup>12</sup> Many examples of polyesters containing CHDM are commercial products.<sup>12</sup> Although incorporation of such aliphatic groups into polysulfones and polyketones would probably lower the thermal stabilities of the polymers, the fundamental structure-property relationships of such cyclohexyl-containing polyketones and polysulfones are of interest. We recently prepared 1,4-di(4-fluorobenzoyl)cyclohexane (**3**) conveniently in two steps from commercially available 1,4-cyclohexanedicarboxylic acid (CHDA, **1**). This monomer can be incorporated into either polyketones or polysulfones by the common  $S_NAr$  route. To the

best of our knowledge, very little work has been reported to investigate the effects of the 1,4-cyclohexyl unit on the mechanical and thermal properties of polysulfones and polyketones. In this paper, we report the synthesis and characterization of bisphenol-A (BPA)-based poly(ether ketone sulfone)s containing 1,4-cyclohexyl groups. We compare the properties of these 1,4-cyclohexyl-containing polymers with analogous polymers containing terephthaloyl groups. BPA was chosen as the bisphenol for our first investigation because its structure imparts high solubility to the polymers, which allows for important solution characterizations such as NMR and SEC.

## 6.3 Experimental

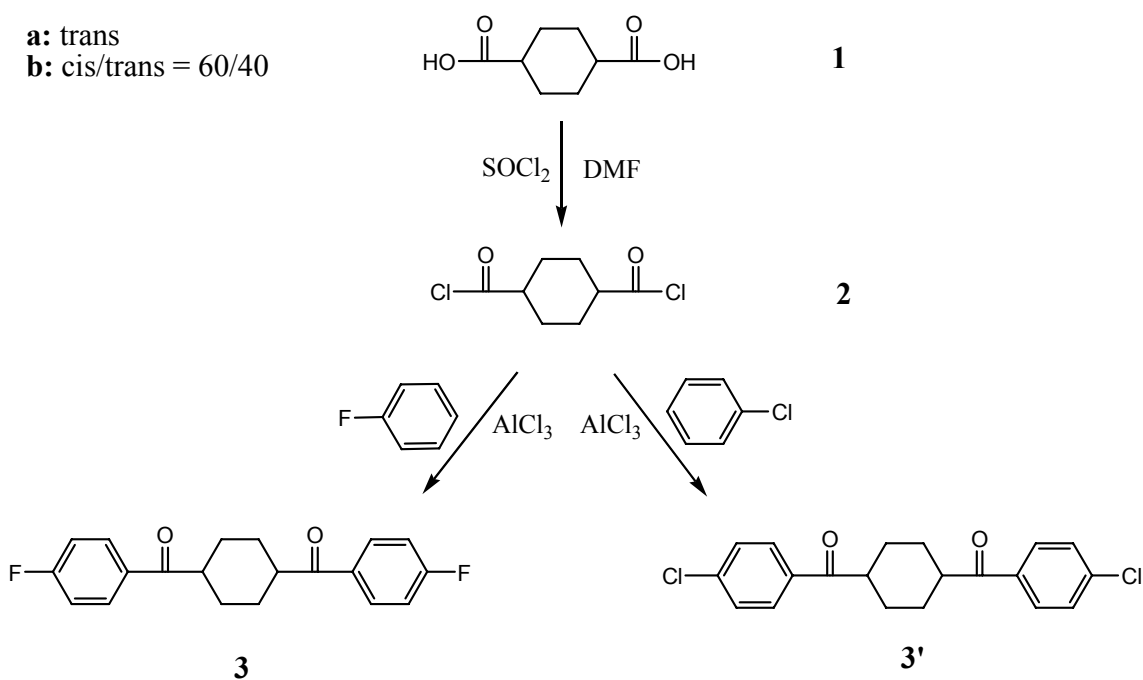
### 6.3.1 Materials

All chemicals were purchased from Aldrich and used as received with an exception of *trans*-1,4-CHDA which was a gift from Eastman Chemical Company.

### 6.3.2 Synthesis

**Preparation of *trans*-1,4-di(4-fluorobenzoyl)cyclohexane (3a).** **3a** was prepared by Friedel-Craft acylation of fluorobenzene with 1,4-cyclohexanedicarbonyl chloride<sup>14</sup> (**2a**) (Scheme 6.1). AlCl<sub>3</sub> (27.5 g, 0.206 mol) was placed in a flask containing 100 ml fluorobenzene and a magnetic stirring bar. This mixture was cooled under argon in an ice-water bath. To this mixture, **2a** (19.5 g, 0.0933 mol) dissolved in 50 ml fluorobenzene was added dropwise through a dropper. After the addition, the ice-water bath was removed and the mixture was stirred at room temperature for 8 hrs. The mixture was then

poured into crushed ice to terminate the reaction and stirred overnight. The aqueous phase was decanted by the use of a separatory funnel. Fluorobenzene was evaporated on a rotary evaporator and the mixture was dried under high vacuum at 40 °C for 5 hrs. The crude product was recrystallized from DMAc twice. The white crystalline solid was dried under vacuum at 80 °C overnight to give 18.55 g of **3a**. Yield: 61%. mp: 210 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.97 (m, 4H), 7.15 (m, 4H), 3.29 (m, 2H), 2.01 (m, 4H), 1.64 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ201.8, 165.6 (d, *J* = 253.8 Hz), 132.6, 131.1 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 22.1 Hz), 45.0, 28.8. Elemental analysis: calculated C, 73.16; H, 5.53. found: C, 72.93; H, 5.45.



**Scheme 6.1** Synthesis of 1,4-di(4-fluorobenzoyl)cyclohexane (**3**) and 1,4-di(4-chlorobenzoyl)cyclohexane (**3'**).

**Preparation of a *cis/trans* (60/40) mixture of 1,4-di(4-fluorobenzoyl)cyclohexane (3b).** **3b** was prepared from **2b** (18.5 g, 0.0885 mol) using the same procedure as above except that toluene was used as a recrystallization solvent, giving 21.3 g of **3b** as a white crystalline solid. Yield: 73%. mp: 156 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.97 (m, 4H), 7.92 (m, 6H), 7.15 (m, 4H), 7.14 (m, 6H), 3.40 (m, 3H), 3.29 (m, 2H), 2.01 (m, 4H), 1.95 (m, 6H), 1.77 (m, 6H), 1.64 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ201.5, 165.7 (d, *J* = 254.8 Hz), 165.4 (d, *J* = 254.3 Hz), 132.6, 132.3, 130.8 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 9.0 Hz), 115.8 (d, *J* = 22.2 Hz), 115.5 (d, *J* = 21.8 Hz), 44.7, 42.7, 28.6, 26.1. Elemental analysis: calculated C, 73.16; H, 5.53. found: C, 72.98; H, 5.43.

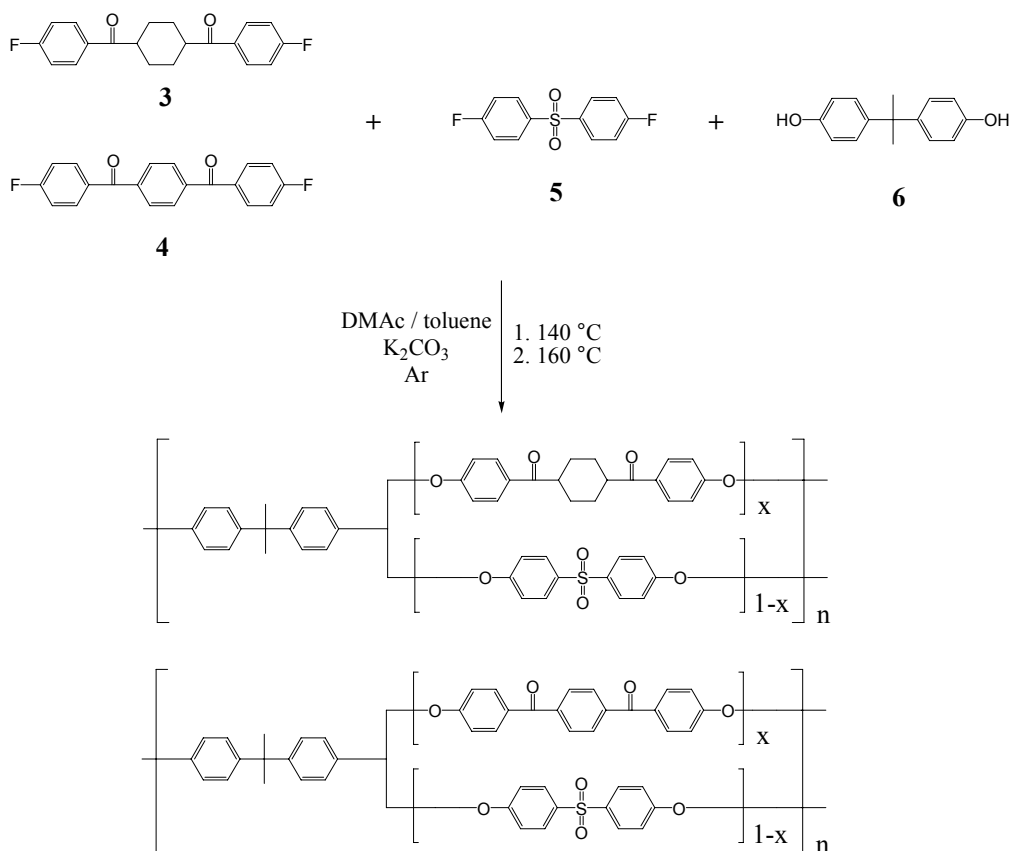
**Preparation of *trans*-1,4-di(4-chlorobenzoyl)cyclohexane (3'a).** **3'a** was prepared from 20.0 g of **2a** using the same procedure as **3a** except that chlorobenzene was used in Friedel-Crafts acylation, giving 11.20 g of **3'a** as a white crystalline solid. Yield: 32%. mp: 230.6 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ7.87 (m, 4H), 7.42 (m, 4H), 3.25 (m, 2H), 2.01 (m, 4H), 1.64 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ201.9, 139.5, 134.2, 129.6, 129.0, 44.8, 28.5. Elemental analysis: calculated C, 66.49; H, 5.02. found: C, 66.42; H, 5.03.

**Synthesis of 1,4-di(4-fluorobenzoyl)benzene (4).** **4** was prepared from terephthaloyl chloride as described by Zhao.<sup>15</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of this compound matched those reported in their paper.

**Polymer acronyms.** In this paper, we give polymer samples descriptive acronyms. For a polymer made from 100 % **3a** and 0 % 4,4'-difluorodiphenylsulfone (DFDPS, **5**), for example, the name is P-C100S0. The letters, C and S, stand for cyclohexyl and sulfone and the numbers indicate mol % of cyclohexyl and sulfone units, respectively.

For samples made from the *cis/trans* mixture (**3b**), the first letter used is P' (e.g. P'-C100S0). For terephthaloyl-containing controls, we use the letter T in place of C (e.g. P-T100S0).

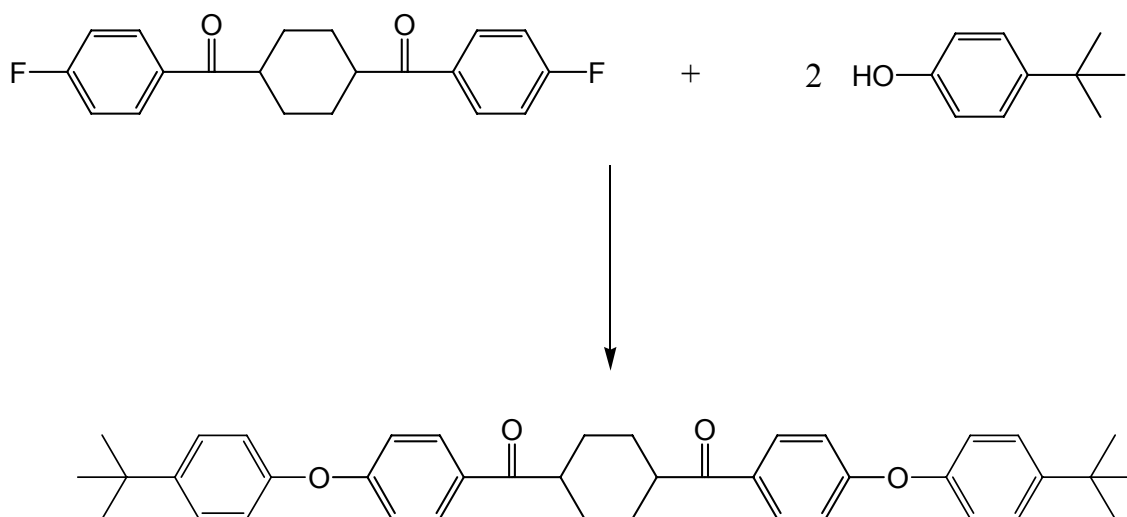
**Synthesis of cyclohexyl-containing poly(ether ketone sulfone)s.** Polymers were synthesized from **3**, **5**, and BPA (**6**) (Scheme 6.2). The detailed procedure for P-C100S0 is as follows. **6** (2.885 g, 0.01264 mol), **3a** (4.149 g, 0.01264 mol), K<sub>2</sub>CO<sub>3</sub> (3.50 g, 0.0253 mol), DMAc (30 ml) and toluene (15 ml) were added to a flask equipped with a mechanical stirrer and argon inlet. Water was removed by azeotropic distillation at 140 °C for 3 hrs. Then toluene was distilled out by increasing the temperature to 160 °C. The polymerization was allowed to continue until a highly viscous mixture was obtained (3-5 hrs). The mixture was transferred into a beaker containing 800 ml dilute aqueous HCl and allowed to stand overnight. The water was decanted and the white solid was washed with hot water to remove any trapped salts and was dried under high vacuum at 130 °C overnight to give 6.3 g of a white polymer. The same procedure was employed to prepare other polymer samples.



**Scheme 6.2** Synthesis of poly(ether ketone sulfone)s.

**Synthesis of terephthaloyl-containing poly(ether ketone sulfone)s.** Polymers were prepared by the same procedure as the cyclohexyl-containing polymers except that **4** was used in place of **3**.

**Model reactions for *cis-trans* isomerization.** **3a** (1.000 g, 3.046 mmol) and *tert*-butylphenol (0.915 g, 6.09 mmol) were exposed to the same condition as the polymerization procedure in DMAc (Scheme 6.3). After the reaction, the mixture was cooled to room temperature and filtered to remove inorganic salts. The solvent was evaporated under high vacuum at 80 °C overnight. The white solid was analyzed by  $^1\text{H}$  NMR. The same experiment was performed on **3b** as well.



**Scheme 6.3** Model reaction for *cis-trans* isomerization of 1,4-cyclohexyl unit.

### 6.3.3 Characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Differential Scanning Calorimetry (DSC) data were obtained with a Perkin Elmer Pyris1 under nitrogen with a flow rate of 20 ml/min and a heating rate of 10 °C/min.  $T_g$  was determined from the mid-point of an endothermic shift of the second heating cycle.  $T_m$  was determined from the melting peak of the first heating cycle under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out by a TA Instruments TGA2950 from 25 °C to 800 °C under nitrogen at a heating rate of 10 °C/min. Size Exclusion Chromatograms (SEC) were recorded in chloroform at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5 + HR 2 + HR 3 + HR 4 styragel column set. A Viscotek refractive index detector and a viscometer were used for molecular weight determination. Polystyrene standards were utilized to construct



a universal molecular weight calibration curve. Elemental analysis was done by Atlantic Microlab, Inc (Norcross, Georgia). Tensile tests were performed on an Instron Model 4400 Universal Testing System with Series IX software. Samples (10 mm gauge length and 2.91 mm width) were cut by a standard bench-top die from compression molded films (0.5 mm thickness). A Seiko DMS 210 with an attached auto-cooler was used in tension mode. Dynamic mechanical spectra of samples were recorded at a heating rate of 2°C/min while they were deformed (10 micrometer amplitude) in the tension mode at a frequency of 1 Hz under nitrogen. A Zeiss Polarizing Optical Microscope (POM) and a LEO 1550 Field Emission Scanning Electron Microscope (SEM) with 5kV accelerating voltage were used to investigate the presence of any crystallinity in films cast from chlorobenzene onto glass plates. The solvent was evaporated over 72 hrs at ambient condition and then in a vacuum oven overnight.

#### **6.4 Results and Discussion**

An attempt to synthesize a high molecular weight polymer from BPA and **3'a**, which is a much more economical monomer than either **3a** or **3b** due to the lower cost of chlorobenzene than fluorobenzene, was unsuccessful apparently because of the much lower reactivity of the chloride than the analogous fluoride. The reaction mixture never became viscous after 72 hours of reaction and even started to take on dark brown color due to the prolonged reaction time. The resultant product was, therefore, not investigated any further and we focus our attention on the polymers made from the fluoro monomers.

**Table 6.1** Molecular weights of soluble poly(ether ketone sulfone)s by SEC.

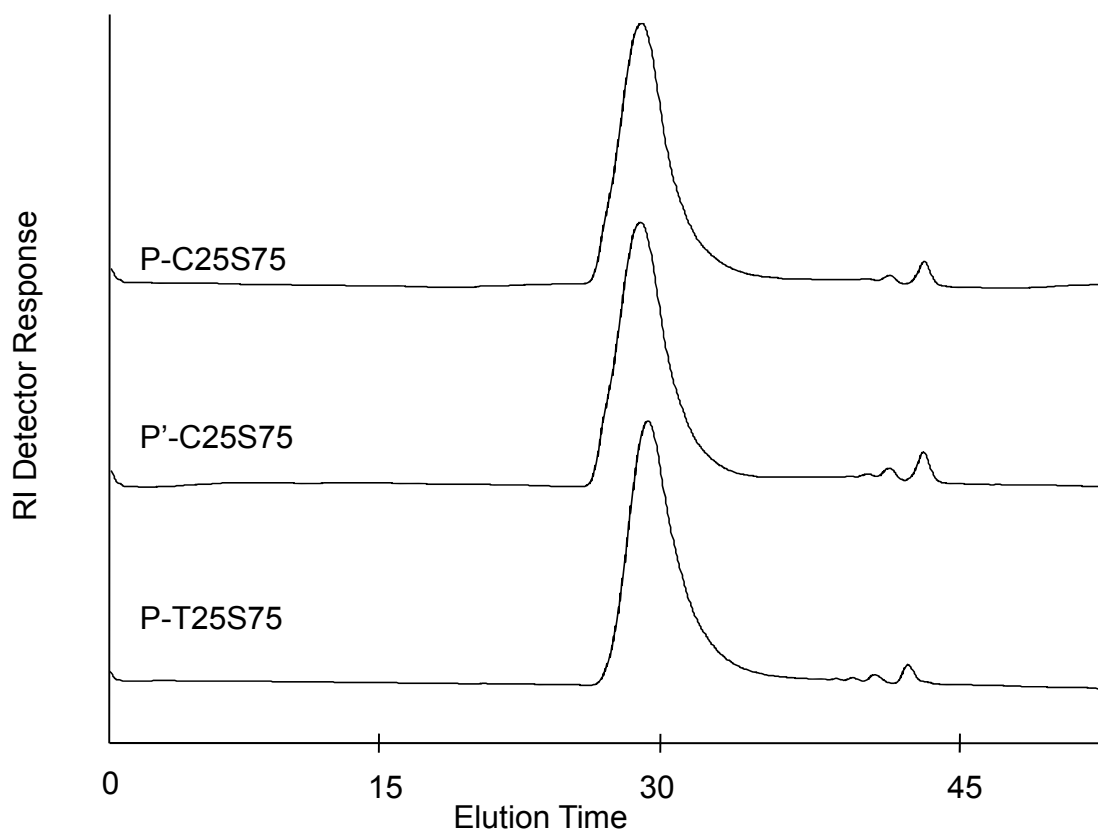
ID	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI ( $M_w/M_n$ )
P-C25S75	$4.0 \times 10^4$	$6.1 \times 10^4$	1.5
P-C50S50	$3.6 \times 10^4$	$5.3 \times 10^4$	1.5
P-C75S25	$3.0 \times 10^4$	$4.5 \times 10^4$	1.5
P'-C25S75	$5.2 \times 10^4$	$7.3 \times 10^4$	1.4
P'-C50S50	$3.1 \times 10^4$	$5.8 \times 10^4$	1.9
P'-C75S25	$4.3 \times 10^4$	$7.9 \times 10^4$	1.8
P-T25S75	$3.8 \times 10^4$	$6.5 \times 10^4$	1.7
P-T50S50	$2.7 \times 10^4$	$4.9 \times 10^4$	1.8
P-T75S25	$3.4 \times 10^4$	$5.4 \times 10^4$	1.6
P-T100S0	$2.3 \times 10^4$	$4.6 \times 10^4$	2.0

All polymerizations utilizing the fluoro-monomers (**3a**, **3b** and **4**) yielded highly viscous mixtures as the polymerization proceeded to high conversion, which typically took less than 5 hrs. The samples containing sulfone groups were soluble in common chlorinated solvents at room temperature, such as dichloromethane and chloroform, as expected from the highly kinked structure of sulfone. The molecular weights of the soluble polymers were determined by SEC and are summarized in Table 6.1. These samples displayed high molecular weights as well as PDIs of equal to or less than 2 with unimodal traces, suggesting the absence of side reactions during polymerizations. The SEC traces of a few of these samples are shown in Figure 6.1 as representatives of these samples. The  $^1\text{H}$  NMR spectrum of each of these polymers showed that its composition was in good agreement with the initial monomer feed ratio. Also, the fact that none of these  $^1\text{H}$  NMR spectra showed any vinyl peaks eliminated our concern that side reactions associated with enolate chemistry might happen. In contrast, the polymers with the highest percentage of cyclohexyl unit (P-C100S0 and P'-C100S0) were insoluble in any

common organic solvent at room temperature and only soluble in hot (>100 °C) chlorinated and polar aprotic solvents whereas the corresponding terephthaloyl control, P-T100S0, was soluble in chlorinated solvents at room temperature. The solubility differences between the 1,4-cyclohexyl-containing polymers and the 1,4-phenyl-containing polymers were surprising. The IR spectra of the poorly soluble cyclohexyl-containing polymers did not show the presence of vinyl groups or any other difference that could lead to branching or ultimately crosslinked structures. It is possible that this difference in solubility results from the cyclohexyl polymer chains packing more tightly than the aromatic counterparts. Ridgway reported that an increase in  $T_m$  brought about by a partial replacement of adipic acid units in nylon-6,6 by CHDA was larger than that caused by terephthalic acid.<sup>16</sup> Although our polymers are not semi-crystalline, the cyclohexyl units may play a role in minimizing the interaction with solvents.

The  $T_g$ s,  $T_m$ s, and  $T_d$ s of the cyclohexyl-containing polymers and of the corresponding terephthaloyl analogs as well as the *cis/trans* ratios of the cyclohexyl after the polymerizations are shown in Table 6.2. As can be seen, the *cis/trans* ratios of the cyclohexyl groups in the polymers changed after the polymerization reactions and very similar *cis/trans* ratios were observed for polymers made from **3a** and **3b**. The *cis/trans* ratios were determined by comparing the  $\alpha$ -hydrogens on the *cis* and *trans* isomers. The  $^1\text{H}$  NMR spectrum of P-C50S50 is shown in Figure 6.2 as a representative of the cyclohexyl-containing polymers. In order to verify the *cis-trans* isomerization in the polymerization reactions, a model study was carried out using the all-*trans* monomer (**3a**) and tert-butylphenol (Scheme 6.3). The product obtained showed a *cis/trans* ratio of 15/85. The same experiment performed using **3b** (*cis/trans* = 60/40) in place of **3a**

displayed a *cis/trans* ratio of 14/86. These observations suggest that *cis-trans* isomerization readily occurs in the polymerizations apparently due to the formation of enolates during the reaction and are consistent with the *cis/trans* ratios of the final polymers shown in Table 6.1. A *cis/trans* ratio of 15/85 has been observed in a CHDA-based polyamide<sup>17</sup> which was synthesized via high-temperature polycondensation.



**Figure 6.1** SEC traces of P-C25S75, P'-C25S75 and P-T25S75.

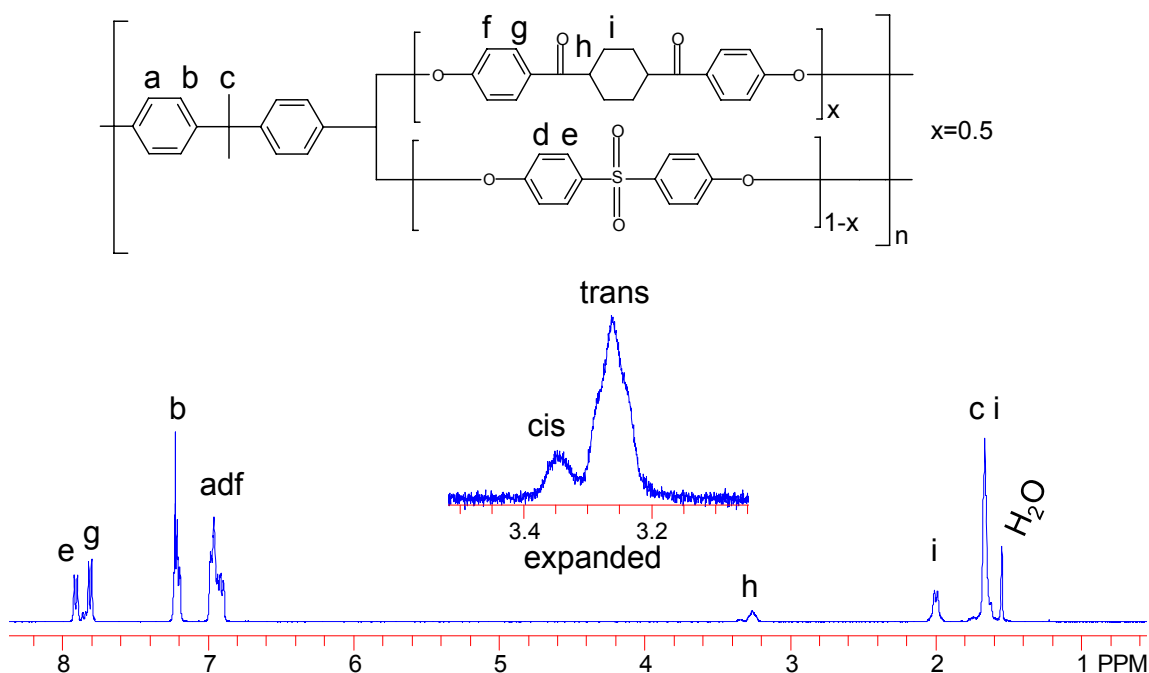
The comparison of the cyclohexyl-containing polymers with the terephthaloyl-containing controls revealed that all the cyclohexyl-containing polymers had slightly higher  $T_g$ s than those of the controls despite the flexibility of the cyclohexyl units. These observations, however, are consistent with the results reported by Yee<sup>10</sup> who compared *trans*-1,4-cyclohexyl-containing poly(ester carbonate)s to terephthalate-containing

analogues and argued that *trans*-1,4-cyclohexyl units impart  $T_g$ s slightly higher than or equal to terephthalate because its spatial conformation is very similar to that of 1,4-phenylene linkage which makes the persistence lengths of the polymers essentially the same as those with terephthalate analogues. Yee also reported that poly(ester carbonate)s containing 1,4-cyclohexyl units with a *cis/trans* ratio of 72/28 displayed  $T_g$ s remarkably lower than those of all-*trans* analogues and those of the terephthalate controls because of the much shorter persistent length of the *cis* isomer.<sup>10</sup> In our case, however, all polymers showed slightly higher  $T_g$ s than the corresponding terephthaloyl controls probably because our final polymers have low *cis* percentages.

**Table 6.2** Thermal properties and *cis/trans* ratios of BPA-based poly(ether ketone sulfone)s.

ID	Final c/t	mol% 3a	mol% 3b	mol% 4	mol% 5	$T_g$ (°C)	$T_m$ (°C)	$T_d^*$ (°C)
P-C25S75	15/85	25	0	0	75	185	-	450
P-C50S50	14/86	50	0	0	50	178	216	445
P-C75S25	18/82	75	0	0	25	176	-	440
P-C100S0	-	100	0	0	0	173	-	437
P'-C25S75	17/83	0	25	0	75	180	-	416
P'-C50S50	18/82	0	50	0	50	174	-	436
P'-C75S25	17/83	0	75	0	25	169	-	399
P'-C100S0	-	0	100	0	0	178	-	390
P-T25S75	-	0	0	25	75	181	-	486
P-T50S50	-	0	0	50	50	172	-	497
P-T75S25	-	0	0	75	25	166	-	496
P-T100S0	-	0	0	100	0	164	205	504

\* 5% weight loss under nitrogen

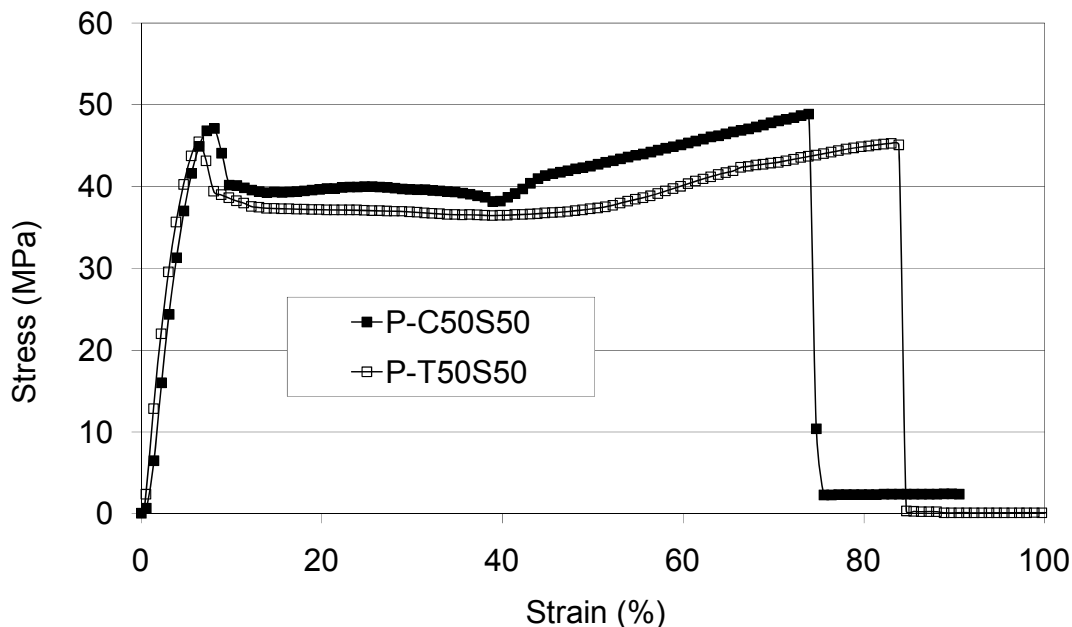


**Figure 6.2**  $^1\text{H}$  NMR spectrum of P-C50S50 in chloroform- $d$ .

As shown in Table 6.2, P-C50S50 and P-T100S0 exhibited melting transitions. However, these melting transitions were very small and only visible on the first heating cycle in DSC, suggesting that these two samples are not semi-crystalline polymers in a practical sense. In fact, P-T100S0 has been reported as an amorphous polymer in the literature.<sup>18, 19</sup> All polymers in Table 6.1, except for the ones containing 75% or higher cyclohexyl (P-C75S25, P-C100S0, P'-C75S25 and P'-C100S0), were compression moldable at 230 °C. Compression molding on P-C75S25, P-C100S0, P'-C75S25 and P'-C100S0, however, gave inhomogeneous films. No melting transitions were observed for these samples by DSC. Nor was any crystallinity detected in their solvent-cast films by POM and SEM, suggesting that the inhomogeneity in these compression molded samples

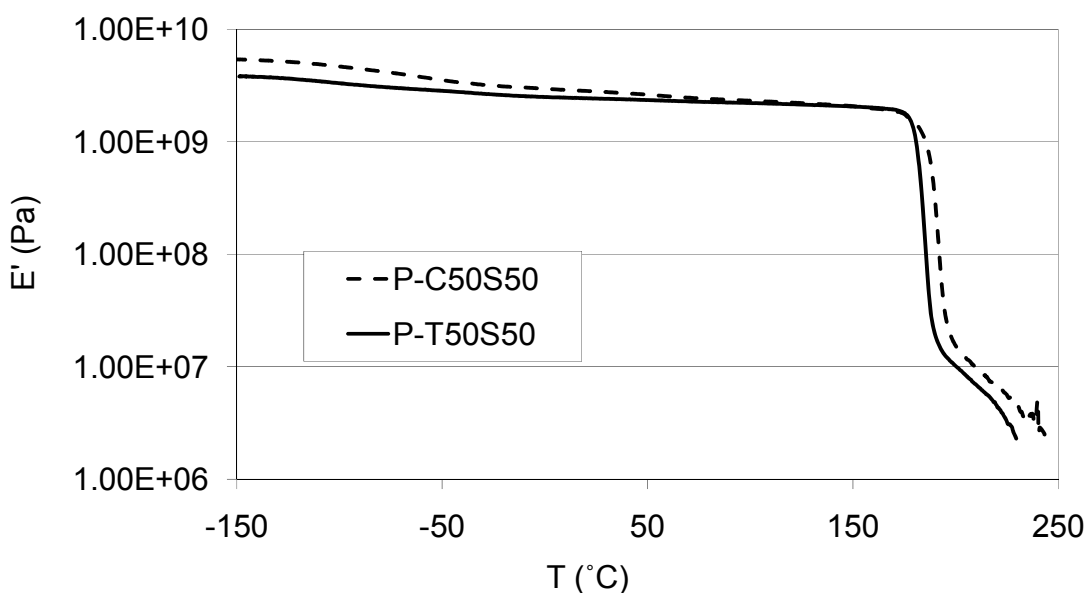
is likely the result of some thermal degradation during the compression molding process due to the large percentages of the cycloaliphatic groups. In fact, the PDI of P-C75S25 increased from 1.5 to 2.5 after the compression molding at 230 °C whereas no significant difference was observed for P-C50S50.

As shown in Table 6.2, the  $T_d$ s for the cyclohexyl-containing polymers were all lower than those of the corresponding terephthaloyl analogs as expected from the aliphatic structure. P-C25S75, for example, showed a  $T_d$  of 450 °C whereas its control, P-T25S75, displayed a  $T_d$  of 486 °C. The same trend was observed for all the other samples. However, the  $T_d$ s of P' series were lower than those of P series. One possible explanation is that P and P' series may have slightly different monomer sequences because of the difference in reactivity between the cis and trans isomers.



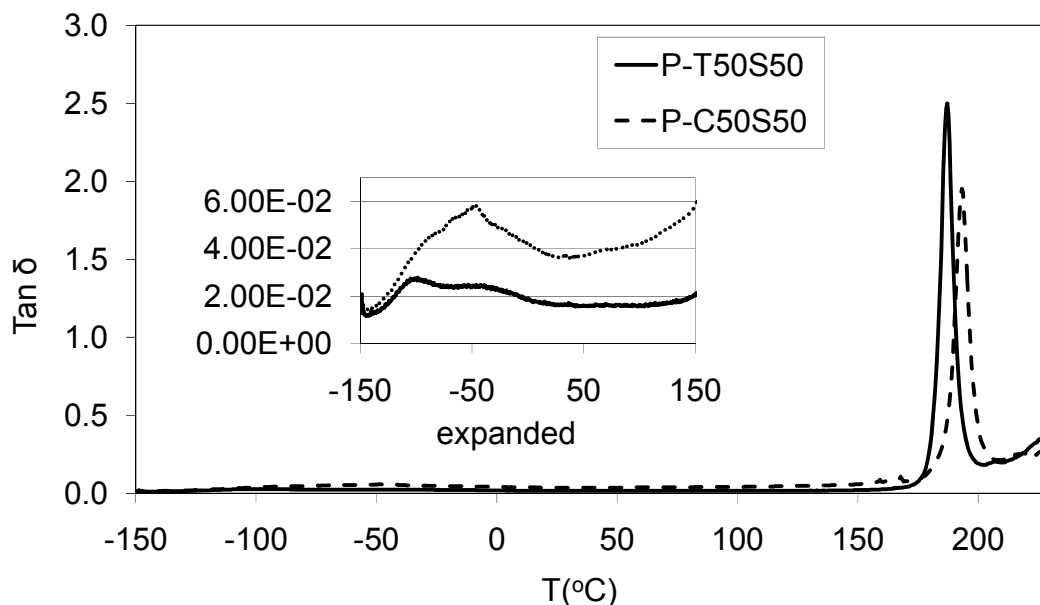
**Figure 6.3** Stress-strain properties of P-C50S50 and P-T50S50.

Tensile tests by Instron revealed that P-C50S50 has essentially the same modulus, yield stress, strain to yield and strain to failure as P-T50S50 (Figure 6.3). This was further supported by a plot of storage modulus,  $E'$ , versus temperature measured by DMA (Figure 6.4a), which showed that the modulus of P-C50S50 is the same as or slightly higher than that of P-T50S50 at all temperatures investigated. It has also been reported in the literature that no significant change in modulus was observed upon partial substitutions of terephthalate units in PETs by CHDA.<sup>5</sup> Interestingly, a plot of  $\tan \delta$  versus temperature (Figure 6.4b) showed that the magnitude of the secondary relaxation for P-C50S50 is larger than that for P-T50S50, meaning that the cyclohexyl units lead to a higher magnitude of sub- $T_g$  motion than the terephthaloyl units apparently due to the flexibility of the cyclohexyl units while maintaining the high modulus.



**Figure 6.4a**  $E'$  versus temperature for P-C50S50 and P-T50S50 by DMA.





**Figure 6.4b** Tan  $\delta$  versus temperature for P-C50S50 and P-T50S50 by DMA.

## 6.5 Conclusions

In summary, we have described the synthesis of 1,4-cyclohexyl-containing poly(ether ketone sulfone)s and characterized some of the properties. Despite the relatively low thermal stability of cyclohexyl, it was successfully incorporated into poly(ether ketone sulfone)s by  $S_NAr$  without any detrimental side reactions. In spite of its perceived flexibility, the 1,4-cyclohexyl was found to impart slightly higher  $T_g$  than the terephthaloyl analog. The results from tensile testing and DMA revealed that the cyclohexyl units lead to essentially the same stress-strain properties as the terephthaloyl control. Also significant was that the cyclohexyl groups lead to a larger magnitude of sub- $T_g$  relaxation than the terephthaloyl control apparently due to their flexibility, suggesting that an incorporation of this cyclohexyl-containing monomer into poly(ether

ketone sulfone)s may be a way of improving the impact strength without a loss of modulus.

## 6.6 Acknowledgements

We are grateful to Dr. Timothy Long's group for allowing our group to use their SEC, TGA, and DSC. We would also like to thank Eastman Chemical Company for donating CHDA to us. We would also like to acknowledge Dr. Garth Wilkes for analyzing the morphology of our samples by POM and SEM.

## 6.7 References

1. Cotter, R. J., *Engineering plastics: a handbook of polyarylethers*. Gordon and Breach Science Publishers: Basel, 1995.
2. Olabisi, O., *Handbook of thermoplastics*. Marcel Dekker: New York, 1997.
3. Mao, M.; Das, S.; Turner, S. R., Synthesis and characterization of poly(aryl ether sulfone) copolymers containing terphenyl groups in the backbone. *Polymer* **2007**, *48* (21), 6241-6245.
4. Jeong, Y. G.; Jo, W. H.; Lee, S. C., Synthesis and crystallization behavior of poly(m-methylene 2,6-naphthalate-co-1,4-cyclohexylenedimethylene 2,6-naphthalate) copolymers. *Macromolecules* **2003**, *36* (11), 4051-4059.
5. Sanchez-Arrieta, N.; Martinez de Ilarduya, A.; Alla, A.; Munoz-Guerra, S., Poly(ethylene terephthalate) copolymers containing 1,4-cyclohexane dicarboxylate units. *Eur. Polym. J.* **2005**, *41* (7), 1493-1501.
6. Johnson, A. H.; Wegner, J.; Soucek, M. D., Hydrolytic stability of oligoesters: comparison of steric with anchimeric effects. *Eur. Polym. J.* **2004**, *40* (12), 2773-2781.
7. Lee, S.-S.; Yee, A. F., Temperature-dependent transition of deformation mode in poly(1,4-cyclohexylenedimethylene terephthalate)/poly(ethylene terephthalate) copolymers. *Macromolecules* **2003**, *36* (18), 6791-6796.
8. Iijima, T.; Hamakawa, S.; Tomoi, M., Preparation of poly(1,4-cyclohexylenedimethylene phthalate)s and their use as modifiers for aromatic diamine-cured epoxy resin. *Polym. Int.* **2000**, *49* (8), 871-880.
9. Polk, M. B.; Bota, K. B.; Akubuiro, E. C.; Phingbodhipakkiya, M., Liquid crystal block copolyesters. 2. Preparation and properties of block copolyesters containing cyclohexane and benzene rings. *Macromolecules* **1981**, *14* (6), 1626-1629.

10. Li, X.; Yee, A. F., Design of mechanically robust high-Tg polymers: physical properties of glassy poly(ester carbonate)s with cyclohexylene rings in the backbone. *Macromolecules* **2003**, *36* (25), 9421-9429.
11. Li, X.; Yee, A. F., Design of mechanically robust high-Tg polymers: mechanical properties of glassy poly(ester carbonate)s with cyclohexylene rings in the backbone. *Macromolecules* **2004**, *37* (19), 7231-7239.
12. Turner, S. R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42* (23), 5847-5852.
13. Brenner, A. R.; Voit, B. I.; Massa, D. J.; Turner, S. R., Hyperbranched polyesters: end group modification and properties. *Macromol. Symp.* **1996**, *102*, 47-54.
14. Dang, T. D.; Dalton, M. J.; Venkatasubramanian, N.; Johnson, J. A.; Cerbus, C. A.; Feld, W. A., Synthesis and characterization of polyaryleneetherketone triphenylphosphine oxides incorporating cycloaliphatic/cage hydrocarbon structural units. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42* (23), 6134-6142.
15. Zhao, W.; Carreira, E. M., Synthesis and photochromism of novel phenylene-linked photochromic bispyrans. *Org. Lett.* **2006**, *8* (1), 99-102.
16. Ridgway, J. S., Structure-property relationships of ring-containing nylon 66 copolyamides. *J. Polym. Sci. Part A-1: Polym. Chem.* **1970**, *8* (11), 3089-3111.
17. Vanhaecht, B.; Teerenstra, M. N.; Suwier, D. R.; Willem, R.; Biesemans, M.; Koning, C. E., Controlled stereochemistry of polyamides derived from cis/trans-1,4-cyclohexanedicarboxylic acid. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39* (6), 833-840.
18. Herold, F.; Schneller, A., High-performance polymers. *Adv. Mater. (Weinheim, Ger)* **1992**, *4* (3), 143-152.
19. Walker, K. A.; Markoski, L. J.; Moore, J. S., Processible poly(arylene ether ketones) that can be crosslinked to high-performance networks. *Macromolecules* **1993**, *26* (14), 3713-3716.

## **Chapter 7: Synthesis of Cyclohexyl-Containing Poly(arylene ether ketone sulfone)s with Different Bisphenols**

### **7.1 Abstract**

Various bisphenols were incorporated into poly(arylene ether ketone sulfone)s containing cyclohexyl units via  $S_NAr$  reactions in attempts to find novel, high performance materials. These polymers were characterized with DSC and TGA. Although some of these polymers showed premature precipitation and low thermal stabilities, these experiments helped us optimize synthetic procedures for polymers containing the cyclohexyl units.

### **7.2 Introduction**

In Chapter 6, the synthesis and characterization of bisphenol-A (BPA) based poly(arylene ether ketone sulfone)s containing cyclohexyl units were described. In addition to these BPA-based poly(arylene ether ketone sulfone)s, polymers based on a few other bisphenols were synthesized to try to find novel, high performance materials. The results discussed in this chapter came from the experiments that were carried out as a part of the work discussed in Chapter 6. The results of these experiments will be of value to others who may continue research in this area.

Another motivation for investigating this area was to try to prepare semi-crystalline poly(arylene ether ketone sulfone)s. Poly(arylene ether ketone)s, or simply polyketones, are widely known for their excellent thermal and chemical stabilities due to their semi-crystalline nature. The semi-crystallinity is responsible for their higher use temperatures and better chemical and solvent resistance than the poly(arylene ether

sulfone) analogs. Because of these superior properties, polyketones find their applications in aggressive environments such as automotive piston parts and aerospace structural components.<sup>1,2</sup> The  $T_g$ s of polyketones, however, are typically in the 135-165 °C range, which is significantly lower than the 180-230 °C range for polysulfones. Although the semi-crystalline nature of polyketones makes their maximum use temperatures higher than those of polysulfones, their dimensional stabilities, due to their lower  $T_g$ s, are relatively poor around 180 °C, a use temperature often desired in aerospace applications.<sup>2</sup> For this reason, there has been a need for high performance materials possessing the  $T_g$ s of polysulfones and crystallinity of polyketones.<sup>3</sup> An ideal polymer would have a  $T_g$  greater than 200 °C for dimensional stability and  $T_m$  lower than 400 °C for melt processing as well as a sufficiently broad  $T_g - T_m$  window for a reasonable rate of crystallization. Our research group has recently prepared semi-crystalline segmented polysulfones by copolymerizing biphenyl and terphenyl-based polysulfones.<sup>4</sup> This block copolymer, however, did not crystallize fast enough to show crystallization peak on DSC apparently due to the narrow  $T_g - T_m$  window. It has been widely known in the literature that 1,4-disubstituted cyclohexanes, especially the *trans* isomers, are highly crystalline.<sup>5,6</sup> Incorporation of the cyclohexyl-containing monomer into polyketones and polysulfones would be of interest in terms of how the  $T_g$  and  $T_m$  are affected. In this chapter, we report the synthesis of cyclohexyl-containing poly(arylene ether ketone sulfone)s as well as measurements of their thermal properties.

## 7.3 Experimental

### 7.3.1 Materials

All reagents were purchased from Sigma-Aldrich and used as received.

### 7.3.2 Synthesis

**Synthesis of triptycene precursor (2).** Anthracene (54.0 g, 0.303 mol) and 1,4-benzoquinone (37.0 g, 0.342 mol) were placed in an 1000 ml round bottom flask with a magnetic stirring bar. To this flask, 300 ml of xylene was added and the mixture was stirred and heated at 140-145 °C for 2 hrs under nitrogen. The mixture was allowed to cool to room temperature and the brown solid was collected by vacuum filtration. The solid was thoroughly washed with hot water and finally recrystallized from 1:10 chlorobenzene/xylene mixture. The solid was collected by vacuum filtration and dried under vacuum at 60 °C overnight to yield 73.9 g (0.258 mol) of **2** as a brown solid. Yield: 85 %. The <sup>1</sup>H NMR spectrum of this product matched those reported in the literature.<sup>7</sup>

**Synthesis of triptycene (3).** **2** (73.8 g, 0.258 mol) was placed in an 1000 ml round bottom flask equipped with a reflux condenser. Acetic acid (300 ml) was added to the flask and the mixture was heated to refluxed temperature with stirring under nitrogen. Concentrated hydrobromic acid (10 drops) was added to the flask and stirring was continued for 1.5 hrs. After cooling to room temperature, the mixture was filtered by vacuum filtration to collect the white precipitate. The precipitate was washed with hexane twice and dried under vacuum at 60 °C overnight to yield to 53.3 g (0.186 mol) of **2** as a

light brown solid. Yield: 72 %. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of this product matched those reported in the literature.<sup>7</sup>

**Synthesis of *trans*-1,4-cyclohexane dicarbonylchloride (5).** *Trans*-1,4-cyclohexanedicarboxylic acid (3.00 g, 0.0172 mol) was placed in a 50 ml round bottom flask containing a magnetic stirring bar. Thionyl chloride (20 ml) and DMF (2 drops) were added to the flask and the mixture was stirred at 50 °C for 5 hrs to give a clear yellow solution. The excess thionyl chloride was distilled off with a stream of argon. The solid was then washed with hexane and collected by vacuum filtration to give a 3.13 g of *trans*-1,4-cyclohexanedicarbonyl chloride as a pale yellow solid. Yield: 86%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$ 2.75 (m, 2H), 2.32 (m, 4H), 1.60 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$ 176.3, 53.9, 27.9. The  $^{13}\text{C}$  NMR spectrum of this product matched those reported in the literature.<sup>8</sup>

**Synthesis of *trans*-1,4-di(4-methoxybenzoyl)cyclohexane (6).** *Trans*-1,4-cyclohexanedicarbonyl chloride (3.10 g, 0.0148 mol) was dissolved in anisole (10 ml) and placed in a dropper.  $\text{AlCl}_3$  (4.80 g, 36.0 mmol) and anisole (10 ml) were placed in a 50 ml round bottom flask. This flask was immersed in an ice-water bath. To the flask, the solution of the acylchloride was added dropwise under argon. After the addition was completed, the ice-water bath was removed and the mixture was stirred at room temperature overnight to give a red solution. The mixture was poured into crashed ice to terminate the reaction. The white solid was collected by vacuum filtration and washed with water and methanol. The solid was recrystallized from 70:30 toluene/DMAc, washed with MeOH and dried under high vacuum at 60 °C overnight to yield 5.02 g of **6**

as a white crystalline solid. Yield: 96%. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of this product matched those reported in the literature.<sup>9</sup>

**Synthesis of *trans*-1,4-di(4-hydroxybenzoyl)cyclohexane (7).** *Trans*-1,4-di(4-methoxybenzoyl)cyclohexane (5.015 g, 14.23 mol) and pyridine hydrochloride (16.4 g, 0.142 mol) were placed in a 50 ml round bottom flask equipped with a mechanical stirring rod. The mixture was stirred at 225 °C under argon for 3 hrs. After the reaction, the mixture was poured into 150 ml of 0.5 M aqueous HCl to give a white precipitate. The precipitate was collected by vacuum filtration and washed with fresh water. The white solid was then recrystallized from methanol and dried under vacuum at 60 °C overnight to yield 3.36 g of **7** as a white needle-like solid. Yield: 73%. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of this product matched those reported in the literature.<sup>8</sup>

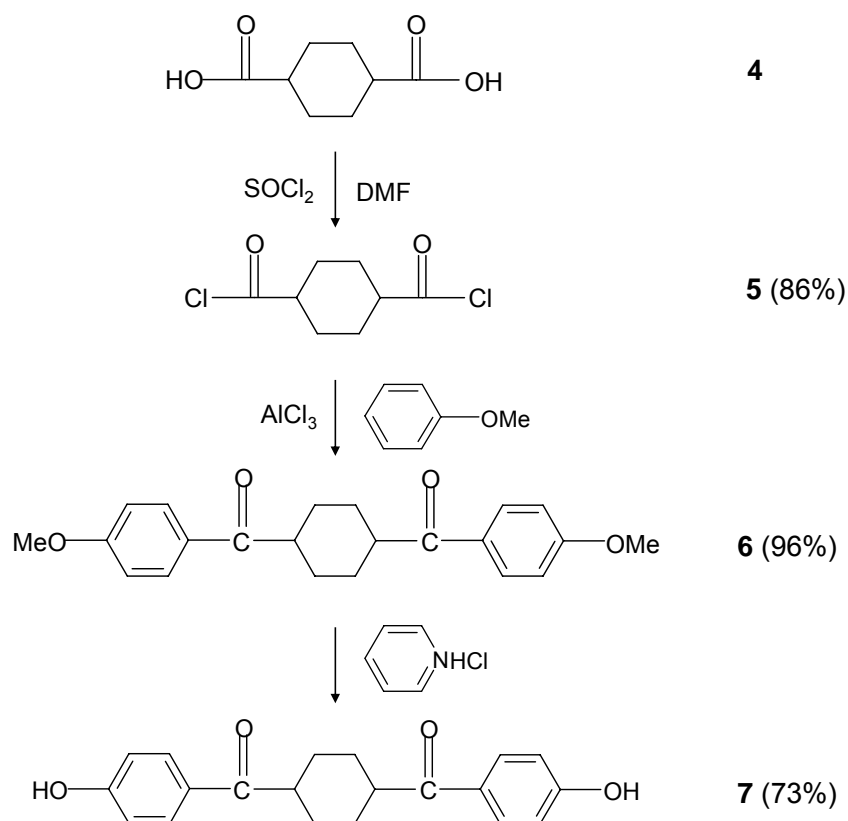
**Synthesis of *trans*-1,4-di(4-fluorobenzoyl)cyclohexane (8).** **7** was synthesized according to the method described in Chapter 5.

**Polymerization.** Polymers were synthesized from **8**, 4,4'-difluorodiphenylsulfone (DFDPS, **11**), and various bisphenols (Scheme 7.3). The detailed procedure for one of the polymers is as follows. Bisphenol-F (4.250 g, 12.64 mmol), **7** (4.149 g, 12.64 mmol),  $\text{K}_2\text{CO}_3$  (3.50 g, 25.3 mmol), DMAc (30 ml) and toluene (15 ml) were added to a flask equipped with a mechanical stirrer and argon inlet. Water was removed by azeotropic distillation at 140 °C for 3 hrs. Then toluene was distilled out by increasing the temperature to 160 °C. The polymerization was allowed to continue until a highly viscous mixture was obtained (~5 hrs). The mixture was transferred into a beaker containing 800 ml dilute aqueous HCl and allowed to stand overnight. The water was decanted and the



white solid was washed with hot water to remove any trapped salts and was dried under high vacuum at 130 °C overnight to give 6.3 g of a white polymer.

All polymers were first synthesized in DMAc. For the cases where premature precipitation was observed, diphenylsulfone was used as the solvent and the reaction temperature was increased to 200-280 °C to dissolve the polymers.

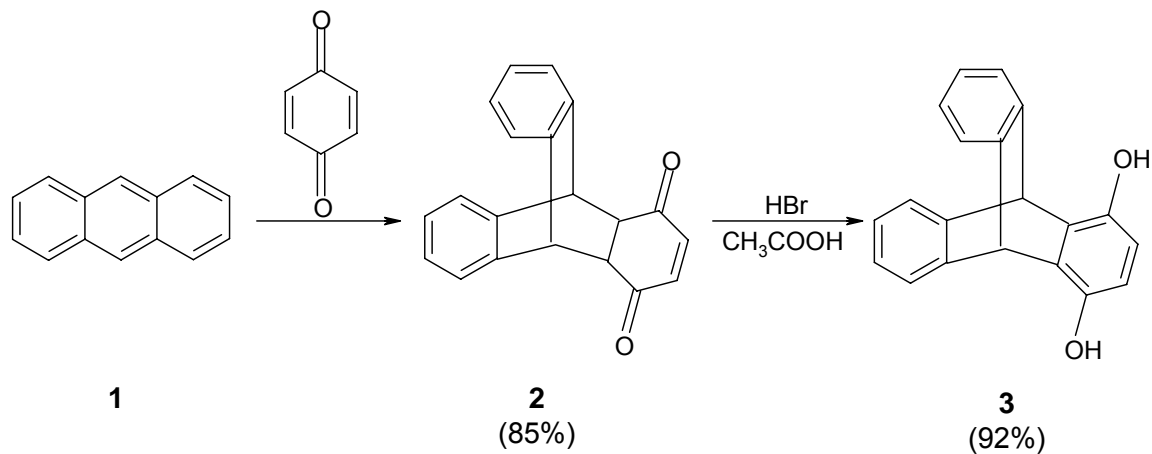


**Scheme 7.1** Synthesis of 1,4-di(4-hydroxybenzoyl)cyclohexane (**7**).

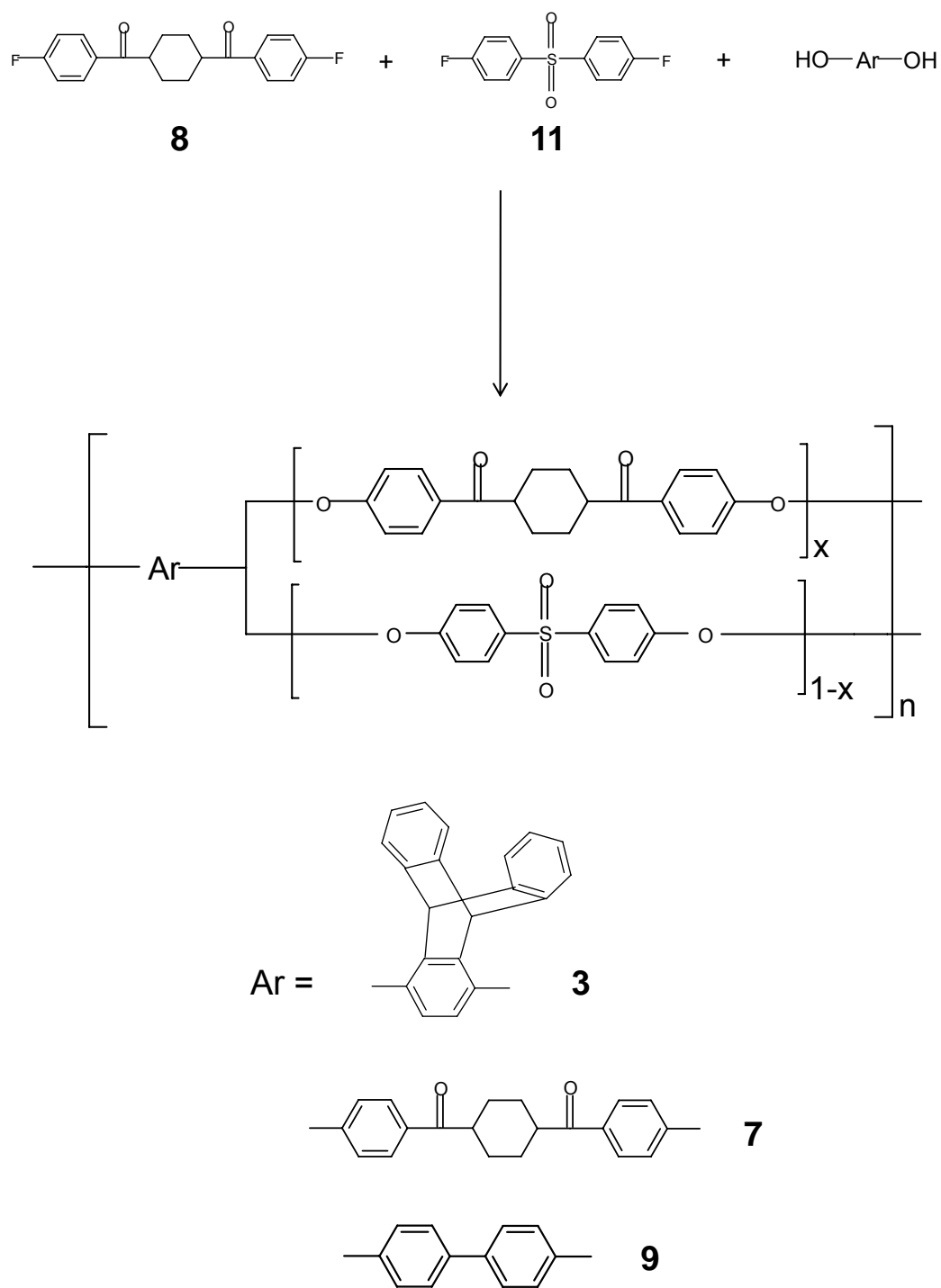
### 7.3.3 Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Differential Scanning Calorimetry (DSC) was run by Perkin Elmer Pyris1 under nitrogen with a flow rate of 20 ml/min and a heating rate of 10 °C/min. T<sub>g</sub> was

determined from the mid-point of an endothermic shift of the second heating cycle.  $T_m$  was determined from the melting peak of the first heating cycle under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out by TA Instruments TGA2950 from 25 °C to 800 °C under nitrogen at a heating rate of 10 °C/min.



**Scheme 7.2** Synthesis of triptycene (**3**).



**Scheme 7.3** Synthesis of cyclohexyl-containing poly(arylene ether ketone sulfone)s.

## 7.4 Results and Discussion

Monomer **3** was polymerized with triptycene (**3**) and cyclohexyl-bisphenol (**7**) as well as commercially available biphenol (**9**). These bisphenols were chosen because of their linear linkages, which we thought would lead to crystallinity. **3** was synthesized conveniently in two steps from anthracene according to the literature procedure.<sup>7</sup> A remarkably high  $T_g$  (265 °C) was observed when this triptycene was incorporated into a polysulfone backbone due to the extremely rigid structure of the triptycene.<sup>10</sup> It is of interest to incorporate this monomer in polyketone backbones because the drastic increase in  $T_g$  that would result could be useful. **7** was chosen because polymerization of **3** and **7** would give a polymer with a cyclohexyl unit in every repeat unit. **9** was chosen for its high linearity and commercial availability.

All polymerizations were first carried out in DMAc containing  $K_2CO_3$ . The  $T_g$ s,  $T_m$ s, and  $T_d$ s of these polymers are summarized in Table 7.1. Polymers with 100 mol % of **7**, 75 mol % of **9** and 100 mol % of **9** led to premature precipitation during the synthesis apparently due to their high linearity. In attempts to keep these polymers in solution, diphenylsulfone was also used as the solvent so that the reactions could be carried out at higher temperatures. Heating these polymer solutions above 200 °C for 30-60 min led to decomposition of the polymers, giving black mixtures apparently due to the degradation of the cyclohexyl units in the basic reaction medium at these high temperatures. Polymers, except for C, F and G, gave highly viscous mixtures (climbed up on the stirring rod) after about 5 hrs of reactions. These polymers, however, were insoluble in any common organic solvent at room temperature. Also significant was that

none of the polymers was melt processible at 50 °C above their  $T_g$ , giving brown inhomogeneous films.

These results suggest that cyclohexyl units must be polymerized well below 200 °C to avoid any degradation and that preparing high melting semi-crystalline polymers from this monomer may be difficult because of the limited thermal stability of the cyclohexyl units.

**Table 7.1** Thermal properties of poly(arylene ether ketone sulfone)s.

ID	Ar	mol% <b>8</b>	mol% <b>11</b>	$T_g$ (°C)	$T_m$ (°C)	$T_d$ (°C)
A	<b>3</b>	75	25	251	-	448
B	<b>3</b>	100	0	244	-	433
C	<b>7</b>	100	0	Premature precipitation		
D	<b>10</b>	25	75	223	-	450
E	<b>10</b>	50	50	210	-	428
F	<b>10</b>	75	25	Premature precipitation		
G	<b>10</b>	100	0	Premature precipitation		

## 7.5 Conclusions

A cyclohexyl-containing aromatic difluoride monomer was polymerized with various bisphenols. Biphenol and cyclohexyl-containing bisphenol led to premature precipitation apparently due to their high linearity. Cyclohexyl units degraded in diphenyl sulfone around 200 °C, indicating that polymerization of this monomer must be carried out well below 200 °C in order to avoid any degradation during the synthesis and that

preparing semi-crystalline poly(arylene ether)s with this monomer may be difficult to achieve due to the low thermal stability.

## 7.6 Acknowledgements

We would like to thank Professor Timothy Long's group for allowing us to use their TGA and DSC.

## 7.7 References

1. Cotter, R. J., *Engineering plastics: a handbook of polyarylethers*. Gordon and Breach Science Publishers: Basel, 1995.
2. Olabisi, O., *Handbook of thermoplastics*. Marcel Dekker: New York, 1997.
3. Carlier, V.; Devaux, J.; Legras, R.; McGrail, P. T., The percentage of rigid chain length, (PRCL), a new concept for predicting glass transition temperatures and melting points of poly(aryl ether ketones) and poly(aryl ether sulfones). *Macromolecules* **2002**, 25 (24), 6646-6650.
4. Mao, M.; Das, S.; Turner, S. R., Synthesis and characterization of poly(aryl ether sulfone) copolymers containing terphenyl groups in the backbone. *Polymer* **2007**, 48 (21), 6241-6245.
5. Burdett, K. A., An improved acid chloride preparation via phase transfer catalysis. *Synthesis* **1991**, (6), 441-442.
6. Turner, S. R., Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42 (23), 5847-5852.
7. Bartlett, P. D.; Ryan, M. J.; Cohen, S. G., Triptycene (9,10-o-Benzenoanthracene). *J. Am. Chem. Soc.* **1942**, 64 (11), 2649-2653.
8. Dang, T. D.; Dalton, M. J.; Venkatasubramanian, N.; Johnson, J. A.; Cerbus, C. A.; Feld, W. A., Synthesis and characterization of polyaryleneetherketone triphenylphosphine oxides incorporating cycloaliphatic/cage hydrocarbon structural units. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42 (23), 6134-6142.
9. Zhao, W.; Carreira, E. M., Synthesis and photochromism of novel phenylene-linked photochromic bispyrans. *Org. Lett.* **2006**, 8 (1), 99-102.
10. Rifai, S.; Breen, C. A.; Solis, D. J.; Swager, T. M., Facile in situ silver nanoparticle formation in insulating porous polymer matrices. *Chem. Mater.* **2006**, 18 (1), 21-25.

## Chapter 8: Preliminary Results for Future Work

### 8.1 Introduction

In this chapter, strategies and preliminary results on the placements of functional groups on the sides and ends of poly(arylene ether)s that are currently investigated in our lab is reported. Also, possible future work for building ABA architectures with polymer backbones other than poly(arylene ether)s is discussed.

### 8.2 Experimental

#### 8.2.1 Materials

All reagents were purchased from Aldrich and used as received.

#### 8.2.2 Synthesis

**Preparation of P-1.** 3,5-bis(4'-fluorobenzoyl)nitrobenzene (**1**) (4.3344 g, 12.30 mmol), bisphenol-A (BPA) (2.8084 g, 12.30 mmol), K<sub>2</sub>CO<sub>3</sub> (1.8658 g, 13.53 mmol), DMAc (25 ml), and toluene (20 ml) were placed in a flask equipped with an Ar inlet and mechanical stirrer. The mixture was stirred at 130-140 °C for 5 hrs to remove water by azeotropic distillation and at 150 °C for 12 hrs. After cooling, the mixture was diluted with THF and filtered to remove KF and K<sub>2</sub>CO<sub>3</sub>. The polymer was then precipitated in 800 ml dilute aqueous HCl. The polymer was collected by vacuum filtration and dried under vacuum at 120-130 °C overnight.

**Preparation of P-HBP.** P-FL (1.00 g,  $3.33 \times 10^{-2}$  mmol), the AB<sub>2</sub> monomer (0.090 g, 0.27 mmol), K<sub>2</sub>CO<sub>3</sub> (0.040 g, 2.9 mmol) and DMSO (10 ml) were placed in a flask equipped with an Ar inlet. The mixture was stirred at 90 °C under Ar. After 3 days of reaction, 4-hydroxybenzenesulfonic acid was added to the flask and the mixture was allowed to react for 3 more days. After cooling, the mixture was poured into 200 ml of water and 15 g of NaCl was added to precipitate the product. The product was collected by vacuum filtration and washed with water to remove any trapped inorganic salts and dried under vacuum at 120 °C overnight.

### 8.2.3 Characterization

NMR spectra were obtained by a Varian Inova 400 (400 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Size Exclusion Chromatography (SEC) was recorded in THF with a flow rate of 1.00 ml/min at 40 °C by Waters 717 Autosampler with 3 in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The  $dn/dc$  values were calculated on-line using the calibration constant for the RI detector and for the mass of the polymer samples assuming 100% mass recovery of the samples. Differential Scanning Calorimetry (DSC) was run from 40 °C to 230 °C by Perkin Elmer Pyris1 under nitrogen with a flow rate of 20 ml/min and a heating rate of 10 °C/min.  $T_g$  was determined from the mid-point of an endothermic shift of the second heating cycle. A Solartron 1252A+1287 impedance/gain-phase was used to determine the proton



conductivities in the range of 10Hz-1MHz. Sample membranes were under fully hydrated conditions in DI water at 30 °C.

#### 8.2.4 Preparation of Films

Polymer samples in the base form were dissolved in DMAc (7 wt%) and cast onto a smooth glass substrate and dried at 50-60 °C for 3 days with a glass cover and placed in a vacuum oven at 120 °C overnight.

Films were converted into the acid form by immersing in 1 M aqueous HCl solution for 3 days. Ion Exchange Capacities (IECs) of the films in the acid form were measured by acid-base titration. The films were immersed in 2 M NaCl solution for 3 days and the solutions were titrated by 0.010 KOH solution. Water uptake (WU) was calculated according to the following equation:

$$WU = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \%$$

$W_{\text{wet}}$  was the mass of a sample film measured after immersing it in DI water for 3 days and immediately drying the film surface by Kimwipe.  $W_{\text{dry}}$  is the mass of the sample film after drying at 50 °C under vacuum overnight. Hydration number ( $\lambda$ ) is defined as the number of water molecules per sulfonic acid and was calculated by the following equation:

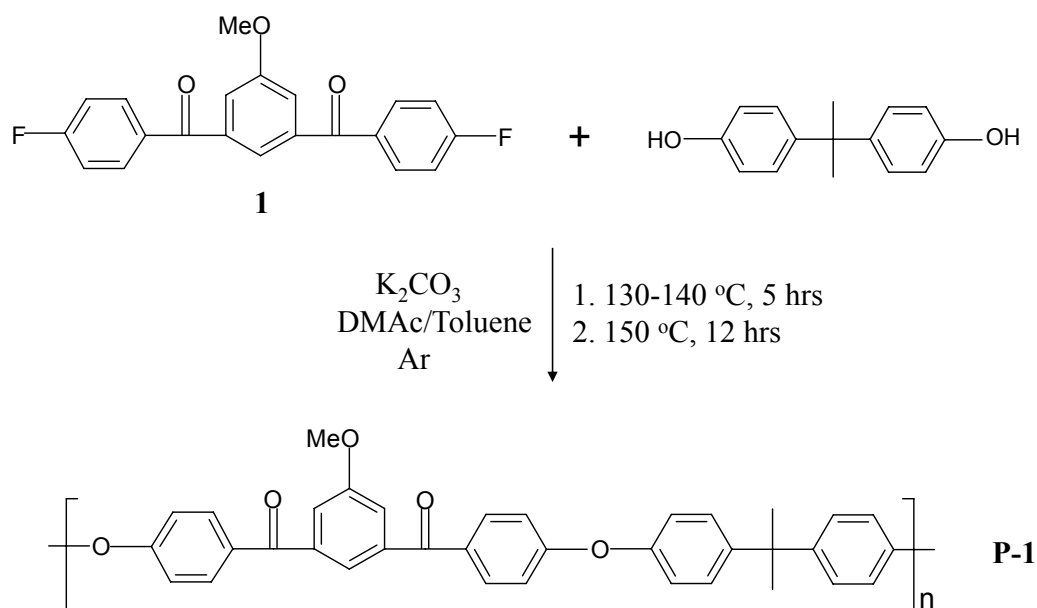
$$\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}}) / MW_{\text{H}_2\text{O}}}{\text{IEC} \times W_{\text{dry}}} \times 1000$$

where  $MW_{\text{H}_2\text{O}}$  is the molecular weight of water, 18.02 g/mol.

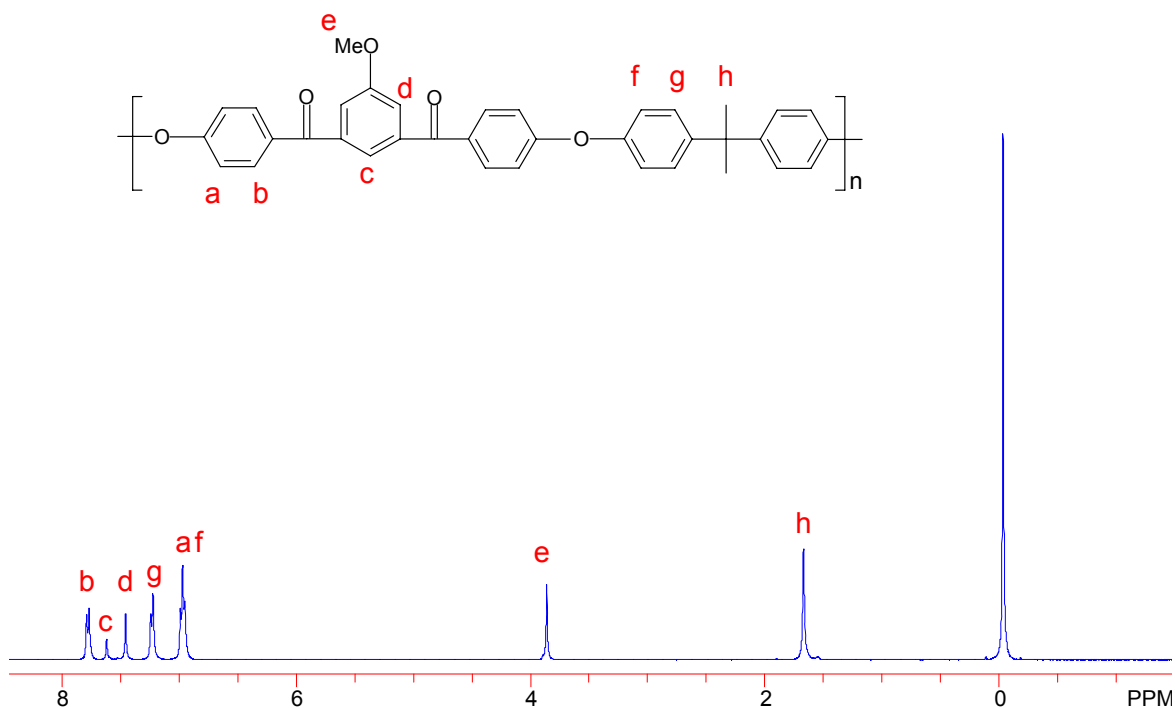
## 8.3 Preliminary Results and Possible Future Work

### 8.3.1 Polyketones with Pendant Functional Groups

Protected difluoride monomer **1**, one of the intermediates discussed in the previous chapters, is difunctional as shown in Scheme 8.1. Our preliminary results showed that this monomer was polymerizable with BPA to give a high molecular weight polymer (**P-1**) with a  $T_g$  of 150 °C. The solution casting of this polymer gave a self-standing creasible film. The molecular weight and  $T_g$  of this polymer are shown in Table 8.1. The  $^1\text{H}$  NMR spectrum of **P-1** is shown in Figure 8.1.



**Scheme 8.1** Successful polymerization of **1** with BPA.



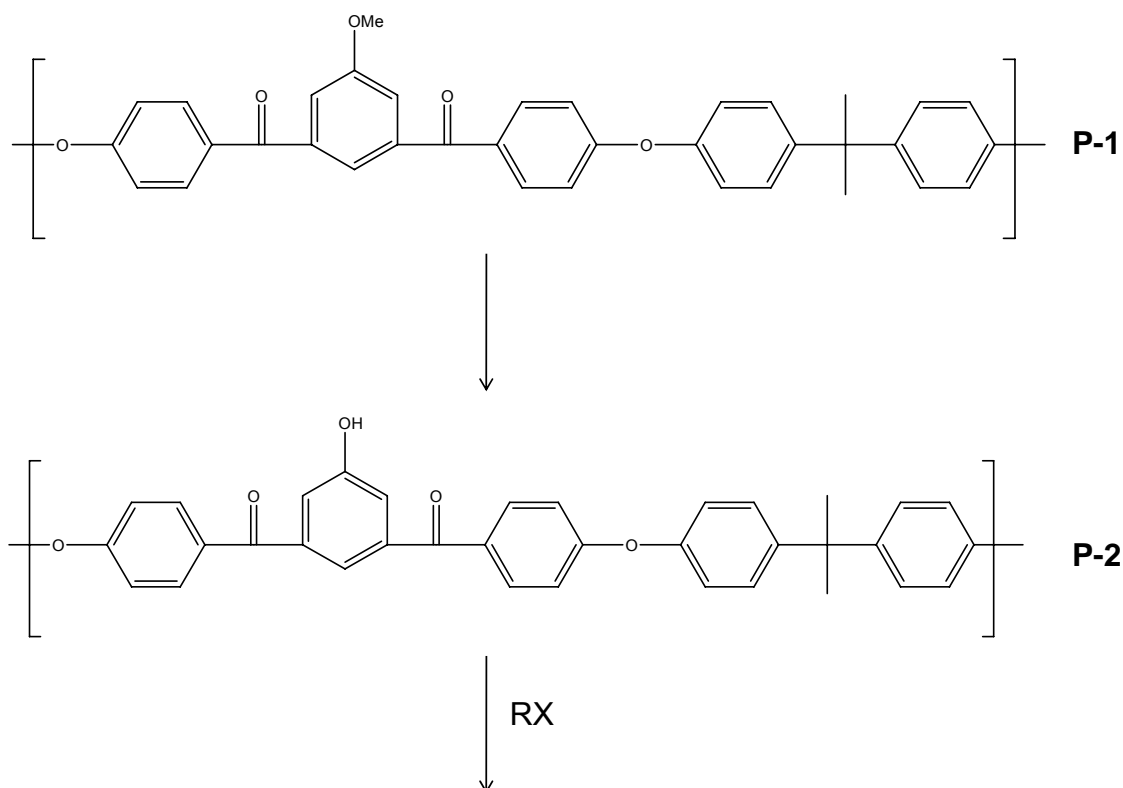
**Figure 8.1** <sup>1</sup>H NMR spectrum of **P-1** in chloroform-*d*.

**Table 8.1** Molecular weight of **P-1** determined by SEC-LS and *T<sub>g</sub>* determined by DSC.

	<b>M<sub>n</sub></b> <b>(g/mol)</b>	<b>M<sub>w</sub></b> <b>(g/mol)</b>	<b>PDI</b>	<b>T<sub>g</sub></b> <b>(°C)</b>
<b>P-1</b>	3.0 x 10 <sup>4</sup>	1.2 x 10 <sup>5</sup>	4.0	150

It is of interest to demethylate the methoxy units of the polymer to give a phenol-containing polymer because such phenol units may be used to react with a wide variety of electrophiles to attach functional groups to the polymer (Scheme 8.2). Boron tribromide is one candidate for the demethylation step because the reaction can be done at low temperatures (often at -78 °C) which could suppress any side reactions. As shown in Figure 8.1, the methoxy units of P-1 are clearly visible and one should be able to confirm the disappearance of methoxy units simply by <sup>1</sup>H NMR spectrum if demethylation is

successful. One member in our group is now planning to work on these chemistries to synthesize poly(arylene ether ketone)s with pendant sulfonic acid units for applications in Proton Exchange Membranes (PEMs).

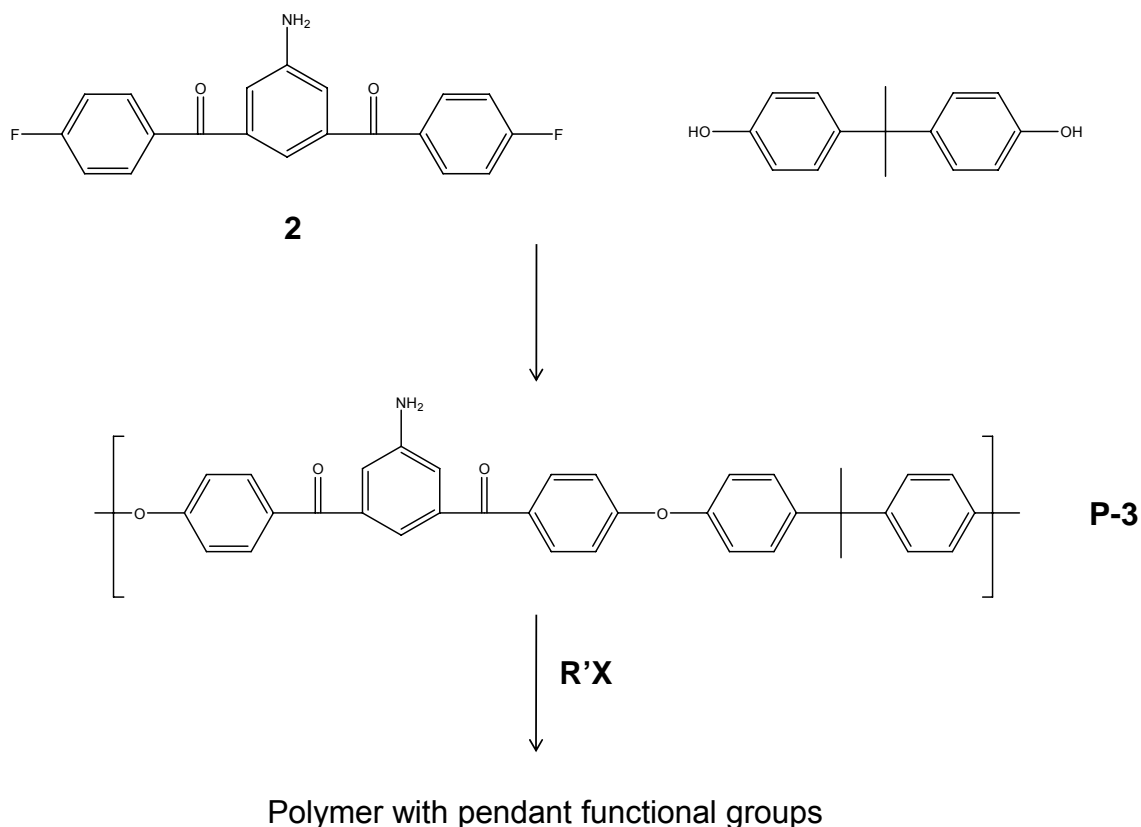


Polymer with pendant R groups

**Scheme 8.2** Demethylation of **P-1** and introduction of pendant functional group R.

One of the intermediates discussed in Chapter 6, an amino analog of **1**, could also be used to introduce pendant groups to poly(arylene ether ketone) backbones because this monomer (**2**) is difunctional as shown in Scheme 8.3. An amino group on an strongly electron-deficient site of a phenyl ring is known to be inactive in  $S_NAr$  reactions.<sup>1, 2</sup> 3-aminophenol was also successfully used as a mono-functional end-capper for polysulfones.<sup>3</sup> In fact, **2** was successfully polymerized with bisphenol A to study

intermolecular hydrogen bonding.<sup>1, 2</sup> A significant advantage of this method over that shown in Scheme 8.2 is that deprotection is not needed after polymerization.

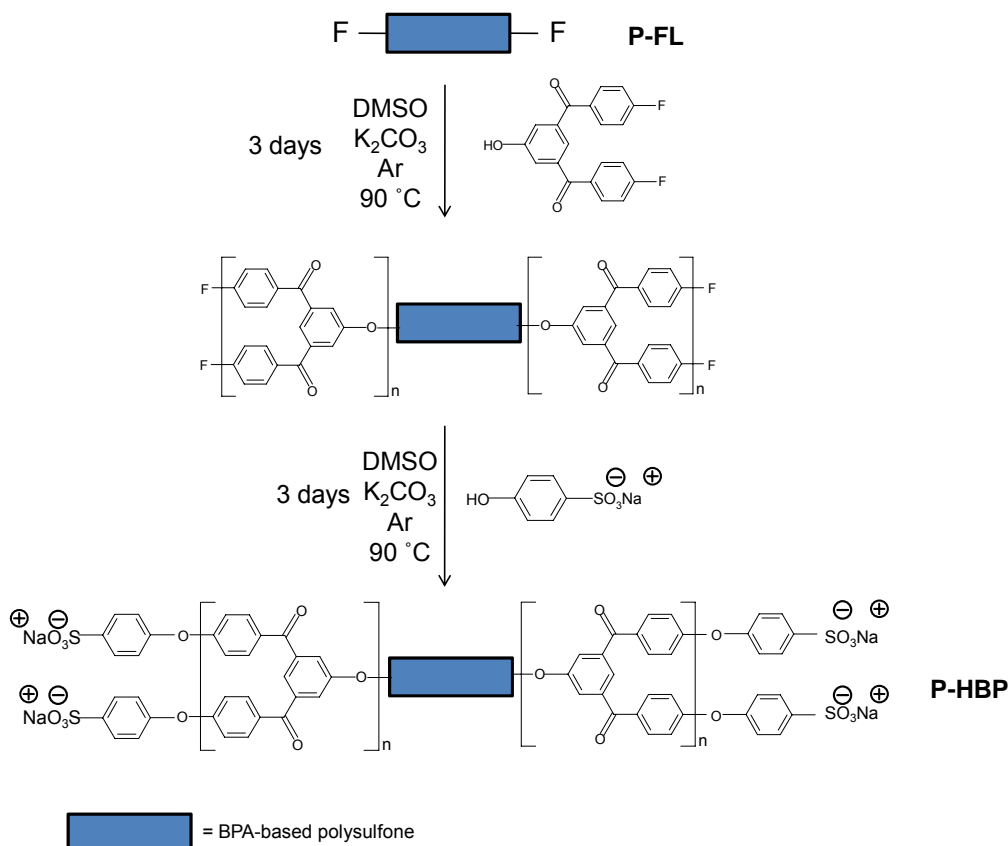


**Scheme 8.3** Polymerization **2** with BPA, followed by reaction of amino units with an electrophile.

### 8.3.2 Polysulfones with Sulfonated Hyperbranched Terminal Groups

In Chapter 4, the synthesis of polysulfones with hyperbranched terminal groups possessing tert-butyl end groups was described. One of the most distinguishing features of this system is that it is versatile in that the tert-butyl terminal groups of the polymers can be replaced by other functional groups simply by replacing tert-butylphenol with other functionalized phenols in the last part of the synthetic step.

As discussed in Chapter 2, the poly(arylene ether)s have been attracting much attention as alternative materials for PEMs because of the drawbacks of Nafion. Because the high proton conductivity of Nafion is ascribed to the microphase separations between hydrophilic and hydrophobic segments forming continuous ionic channels through which protons can travel, a considerable amount of research focuses on the placements of sulfonic acid groups on specific sites of polymer chains in order to assist the formation of ionic channels. Linear poly(arylene ether)s with multiple sulfonate groups on the chain ends have been reported by Hay et al.<sup>4</sup> Our system, if sulfonated phenols are used to cap the reactive end groups, would lead to polymers with multiple sulfonated groups on the chain ends as shown in Scheme 8.4. These polymers are currently being investigated for PEM applications.



**Scheme 8.4** Synthesis of polysulfones with sulfonated hyperbranched terminal groups.

Preliminary investigation of this synthesis was carried out. The synthetic method used was the same as that described in Chapter 4, except that sodium 4-hydroxybenzenesulfonate was used instead of tert-butylphenol. A few samples were prepared and preliminary results of water uptake (WU), Ion Exchange Capacity (IEC), hydration number ( $\lambda$ ) and proton conductivity ( $\sigma$ ) are summarized in Table 8.2.

**Table 8.2** IEC, WU and  $\lambda$  for PAESs with sulfonated dendritic terminal groups.

	Sample 1	Sample 2	Sample 3	Nafion112 <sup>5</sup>
Target # sulfonates/chain	8	22	50	-
Exp. # sulfonates/chain*	4.5	9.8	-	-
IEC (mequiv/g)	0.15	0.34	-	0.90
WU (%)	5	7	-	25
$\lambda$ (H <sub>2</sub> O/SO <sub>3</sub> H)	17	11	-	15
$\sigma$ (mS/cm)	4.0	5.3	-	90
Film	Creasible	Creasible	-	-

\*Calculated from IEC values

As shown in Table 8.2, Sample 1 and Sample 2 made self-standing creasible films and have proton conductivities of 4.0 and 5.3, respectively. As a reference, the conductivity of Nafion112 reported in the literature is 90 mS/cm.<sup>5</sup> The WU values and  $\lambda$  values of these polymers were 5 % and 7%, and 17 and 11, respectively. Although the proton conductivities of these polymers were significantly lower than that of Nafion, this is most likely due to the lower number of sulfonic acid groups on these polymers. Sample 3 which has a larger number of sulfonic acid units, however, showed a partial solubility in water. We are currently in the process of optimizing the synthetic condition to

minimize the water solubility of the polymers (e.g., by using other bisphenol monomers and different feed ratios of reactants).

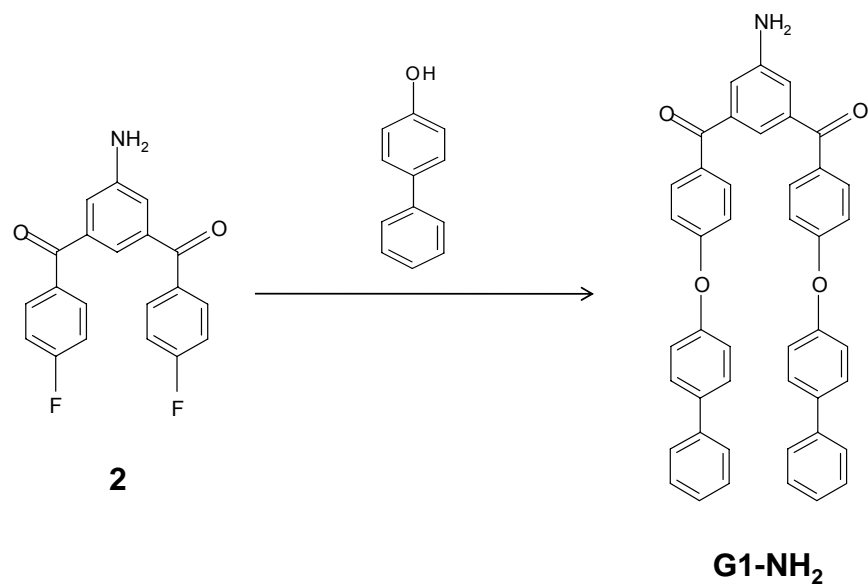
Another possible future effort is to place other functional groups on the polymer chain ends because one of the most distinguishing features of our systems is that the terminal groups can be replaced by other functional groups, such as perfluorinateds, phosphates, long alkyl chains, and carboxylates, simply by replacing the functional group on the phenol in the last synthetic step.

### **8.3.3 Dendritic End Groups on Other Types of Polymer Backbones**

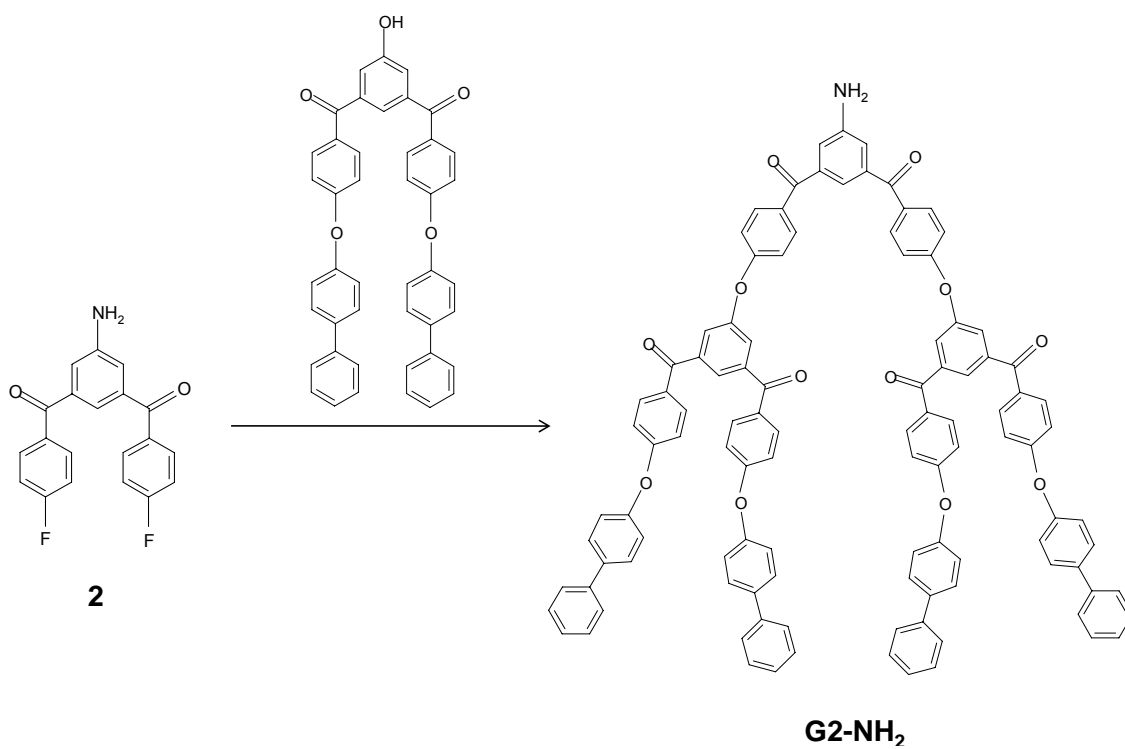
In Chapter 3, we reported the synthesis and characterization of polysulfones with arylene ether ketone dendritic terminal groups. The focal points of the dendrons used in this work were phenolic hydroxyl groups. In Chapter 6, the synthesis of the corresponding hydroxyethoxy analog of the dendron was described.

The combination of the dendrons reported in Chapter 3 and intermediate **2** would make analogous dendrons with amino focal points, which could be attached to other types of polymer backbones such as polyamides and polyimides. The synthetic procedures for the dendrons reported in Chapter 3 were all high yielding with relatively convenient isolation procedure. An advantage of this method would be that deprotection is not needed before being used as end-cappers as shown in Scheme 8.5 and Scheme 8.6. Reaction and isolation of dendrons become harder with increasing generation. Thus, the absence of the need for deprotection after going up to the higher generation could allow for the facile preparation of dendritic end-cappers.





**Scheme 8.5** Proposed synthesis of G1 dendron with amino focal point.



**Scheme 8.6** Proposed synthesis of G2 dendron with amino focal point.

Chemical reaction scheme showing the synthesis of HBP-amine:

Structure 2 (4-amino-2,6-bis(4-fluorophenyl)benzoic acid) reacts with Structure 3 (4-hydroxy-2,6-bis(4-fluorophenyl)benzoic acid) to form HBP-amine (H<sub>2</sub>N-oval-HBP).

## 8.4 Acknowledgements

## 8.5 References

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- membrane fuel cells. I. Copolymer synthesis and fundamental properties. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45* (21), 4879-4890.
4. Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Hay, A. S., Ionomers for proton exchange membrane fuel cells with sulfonic acid groups on the end groups: novel linear aromatic poly(sulfide-ketone)s. *Macromolecules* **2008**, *41* (2), 277-280.
  5. Lee, H.-S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E., Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low-temperature coupling reactions for proton exchange membrane fuel cells. *Polymer* **2008**, *49* (3), 715-723.

## Chapter 9: Summary and Conclusions

Synthesis and characterization of polysulfones with novel structures and architectures were described.

Poly(arylene ether sulfone)s with arylene ether ketone dendritic terminal groups were reported in the initial chapter. Synthesis of these polymers required a careful suppression of transesterification. These polymers showed superior stress-strain properties than the analogous randomly branched polymers. Also, the melt viscosities of these polymers in the high frequency region were lower than the control, suggesting that it is possible to reduce the high shear melt viscosities of this type of polymers without affecting the stress-strain properties by introducing bulky dendritic terminal groups.

In the subsequent chapter, the synthesis of poly(arylene ether sulfone)s with hyperbranched terminal groups was described. These polymers were synthesized by reacting fluoro-terminated poly(arylene ether sulfone) chains with an arylene ether ketone AB<sub>2</sub> monomer. Multiple *tert*-butylphenol units were successfully attached to the polymer chain ends, suggesting that this synthetic method could be useful for introducing multiple functional groups onto the polymer chain ends in fewer synthetic steps than an analogous method using preformed dendritic end-cappers.

Lastly, the incorporation of a novel cyclohexyl-containing monomer into poly(arylene ether sulfone) backbones was described. Tensile tests and DMA showed the cyclohexyl units impart a higher magnitude of secondary relaxation than the terephthaloyl units while maintaining high modulus, suggesting that incorporating

cyclohexyl units in poly(arylene ether sulfone) backbones could improve the impact strengths of the polymers.