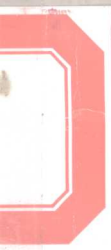


Dendrimers and Dendrons

Concepts, Syntheses, Applications

(2)

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6 Hyperbranched Materials

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6.1 General Concepts

Whereas the well-characterized, perfect (or nearly so) structures of dendritic macromolecules constructed by discrete stepwise procedures have been illustrated in the preceding chapters, this Chapter describes the related, less-than-perfect, hyperbranched polymers, which can be synthesized by means of a direct, one-step polycondensation of AB_x monomers where $x \geq 2$. Flory's prediction and subsequent demonstration^[1, 2] that AB_x monomers can generate highly branched polymers heralded advances in the creation of idealized dendritic systems; thus, the desire for simpler, and in most cases more economical (one-step), procedures for obtaining the hyperbranched relatives became more attractive. However, it was not until three decades later, led by the efforts of Professor H. R. Kricheldorf,^[3] that synthetic protocols aimed at the investigation of these unique polymers began to evolve.

Such one-step polycondensations afford products possessing a high degree of branching (DB), but which are not as faultless as the stepwise constructed dendrimers; for reviews, see refs.^[4-9] The supramolecular assemblies and micellar properties of these hyperbranched polymers offer synthetic and physical insights as well as noteworthy comparative relationships to the monomolecular dendritic analogues. The DB of these hyperbranched polymers generally ranges from 55–70% and is independent of their molecular weights. For an extensive presentation of DB and average number of branches (ANB) per non-terminal monomer moiety, Frey and Hölder^[10] considered the copolymerization of AB_x monomers with AB and AB_y monomers.

Synthetic high molecular weight polymers with spherical symmetry have also been created^[11] by a graft-on-graft procedure (chloromethylation, followed by anionic grafting), which results in tree-like structures, analogous to these hyperbranched materials. These have been termed "arborescent graft polymers".^[12-14] Control of structural rigidity in these materials has been investigated.^[15] In general, grafting side chains of comparable molecular weight on a linear core forms "comb-branched" structures, ultimately leading to materials with increasing globular or spherical shape as generations increase. Such polymers are obtained with molecular weights ideally increasing geometrically as expressed by:

$$M = M_b + M_b f + M_b f^2 + \dots = \sum_{x=0}^{G+1} M_b f^x, \quad (6.1)$$

where M_b is the molecular weight per branch, and f is the branching functionality, which remains constant for each generation G . For the graft-on-graft procedure, high molecular weights ($> 10^6$) were realized after three graftings with $M_w/M_n \approx 1.1-1.3$ at each generation. Monolayer films of arborescent polystyrene-based grafts have been created,^[16] and SANS studies of arborescent graft polystyrenes have been published.^[17, 18] The synthesis^[19] of poly(ethylene imine)-based comb-burst dendrimers, their Monte Carlo simulations,^[20] and density profiles from simulated comb-burst molecules^[21] have appeared. A similar all-hydrocarbon, hyperbranched polyethene has also been reported.^[22] Schultz and Wilks^[23] addressed registration of hyperbranched polymers possessing symmetrical I-shaped structural repeat units with the Chemical Abstracts Registry Service as well as nomenclature and structural representation of asymmetrical I-shaped hyperbranched polymers.^[24] Möller et al.^[25] considered and discussed the conversion dependence of the polycondensation branching density for AB_x monomers. Polycondensation kinetic formulae were derived, thereby affording the time-dependent degree of polymerization and conversion. Other Monte Carlo simulations of hyperbranched reactions are known.^[25a]

Mansfield^[26] examined molecular weight distributions of imperfect dendrimers. Fourier analysis of the products revealed that essentially monodisperse molecular weight

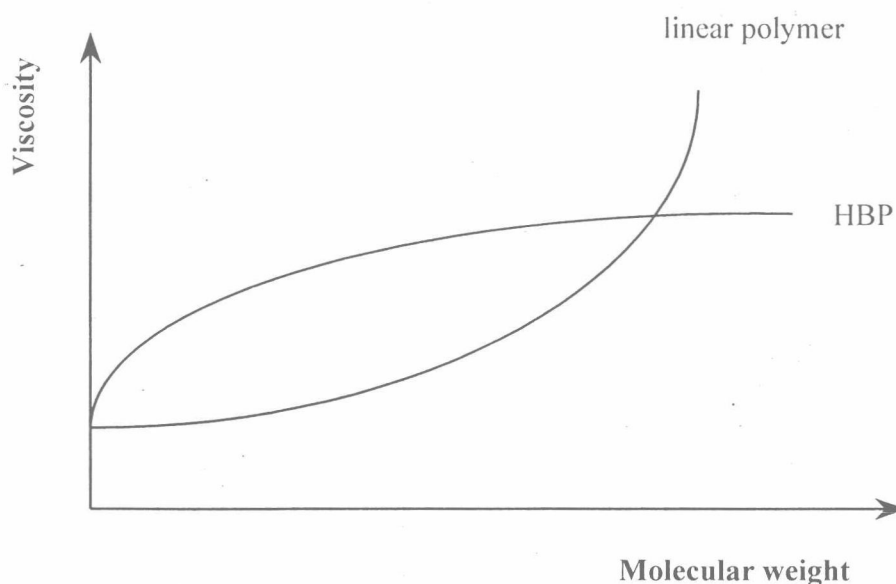


Figure 6.1 Viscosity behavior as related to molecular weight of linear and hyperbranched polymers. Reproduced by permission of Elsevier Science.^[32]

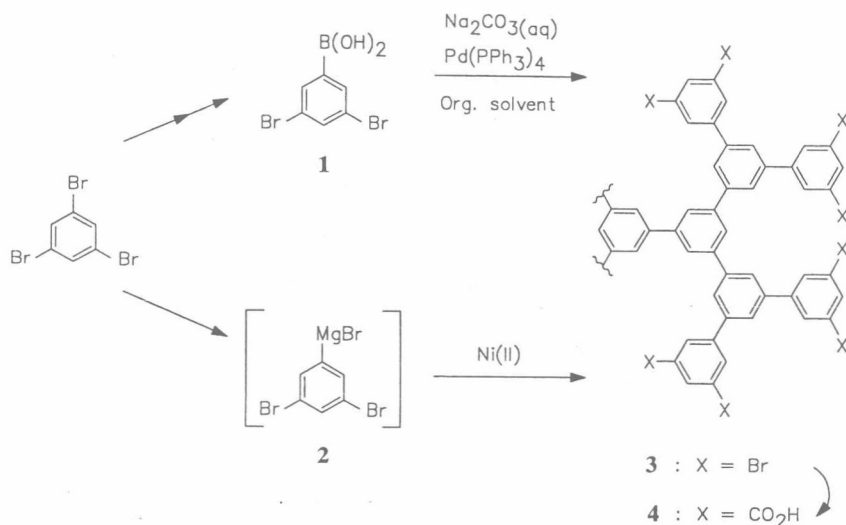
ranges could be obtained (for divergent growth) if, in the early stages of growth, perfection was maintained, or nearly so, while later generations inevitably possess arbitrary amounts of defects. Hanselmann, Hölter, and Frey^[27, 28] used computer simulation to model the kinetics of a novel core dilution/slow addition protocol for hyperbranched polymer preparation. Essentially, the technique consists of the slow addition of AB_x monomers to a B_f core with rapid and quantitative reaction ($x = 2$ or 3 ; $f = 2-12$). This method was shown to control resultant molecular weights, lower polydispersity, and enhance DB. McCoy^[29] later presented an analytical solution for the growth of hyperbranched polymers; distribution kinetics of branched growth was addressed. A report on the kinetics of reactions with non-uniform reaction rate constants leading to hyperbranched materials has recently appeared,^[30] in which three situations for AB_2 systems and the kinetics of self-condensing vinyl polymerization for the ABB' system are considered. It was found^[30] that the influence of the first B substituent on the reactivity with the second B group has the greatest effect on structural outcome. The competition between hyperbranched growth and cyclization that can occur with flexible AB_x ($x = 2$ or 4) monomers in a step growth process has been simulated with a three-dimensional lattice model.^[31] Two mean-field kinetic models have also been considered.^[31a] Phase behavior has been addressed.^[31b]

In general, the comparative viscosity behavior for linear vs. hyperbranched macromolecules plotted against M_w is as shown in Figure 6.1.^[32] Spherical dendritic materials also exhibit^[33] a similar property for equivalent molecular weights; their mechanical properties are, for the most part, delineated by the core, whereas the chemical properties are determined by the shell, thus controlling the phase-separation processes. Thus, hyperbranched polymers have been shown to instill outstanding performance as tougheners in epoxy resins and do not lead to decreased resin stiffness or T_g s.

6.2 1 → 2 Aryl-Branched

6.2.1 1 → 2 Aryl-Branched and Connectivity

Kim and Webster reported,^[34-36] patented,^[37] and reviewed^[38-42] the facile one-step conversion^[38] of 3,5-dibromophenylboronic acid^[43] (**1**) in the presence of a catalyst [$Pd(PPh_3)_4$] under reflux conditions in aqueous carbonate to give the hyperbranched polyphenylene **3** (Scheme 6.1).^[44, 45] An alternative route to **3** utilized the mono-Grignard^[34] (**2**), prepared from 1,3,5-tribromobenzene with activated magnesium,^[46] and $Ni(PPh_3)_2Cl_2$; this method proved advantageous in large-scale runs. Based on ^{13}C NMR



Scheme 6.1 Transition metal mediated preparation of polyphenylene macromolecules.^[44, 45]

spectroscopy, the DB was estimated to be ca. 70 %, while the molecular weight of **3** was qualitatively found to be a function of the organic solvent employed. Polymerization with Ni(II) gave polymers of \overline{M}_n in the 2,000 to 4,000 amu range, often with greater polydispersity than those obtained by the boronic acid route. Molecular weight limitations may result from steric hindrance at the organometallic center and/or intramolecular cyclization(s). The effect of different terminal groups on the T_g of these polyphenylenes and triphenylbenzenes has been studied.^[47]

Diverse derivatives have been prepared from polythio-polyphenylene, which, due to instability, was generated in less than quantitative yields by a metal-halogen exchange process. Electrophiles used to quench the polythiated polyphenylene included CO_2 , $\text{CH}_3\text{OCH}_2\text{Br}$, Me_2CO , DMF, $\text{C}_6\text{H}_5\text{C(O)Me}$, MeOH , Me_2SO_4 , and Me_3SiCl .

Reaction of the polybromide **3** with the anion of 2-methyl-3-buten-2-ol was examined. In this case, "polymer reactivity seems to be enhanced when a small amount of the bromide groups had reacted with the reagent." It was speculated^[35] that "accelerated reactivity of a partially converted polymer could be one characteristic of highly branched materials." Wooley et al.^[48] supported this supposition with the finding that the convergent coupling of dendritic wedges to a hexavalent core proceeded to completion with no evidence of partially substituted cores based on GPC experiments, thus indicating an accelerated reactivity of partially transformed branched macromolecules. The phenomenon was attributed to "localized polarity or microenvironmental effects" favoring monomer connectivity. These observations lend support to the assertion of complete surface transformation for many *divergently* constructed dendrimers.

When biphenyl ether or 1-methylnaphthalene was used as solvent, the polyphenylenes were determined to possess higher M_n values than in xylene solution. No molecular weight increase was obtained by the addition of further monomer at or toward the end of the polymerization. The highest molecular mass was obtained using nitrobenzene as solvent. In order to investigate the unimolecular micellar behavior of the water-soluble lithium salt of polycarboxylic acid **4**, its ^1H NMR spectrum in the presence of an NaOAc solution of *p*-toluidine was recorded. Signals associated with the guest molecule(s) were shifted upfield and dramatically broadened.

Webster et al.^[49] expanded on the preparation of the polyphenylenes to develop the one-pot synthesis of hyper-cross-linked poly(triphenylcarbinol); thus, reaction ($-80 \rightarrow 25^\circ\text{C}$, THF) of 4,4'-dilithiobiphenyl with Me_2CO_3 afforded trityl alcohol based polymer. The absence of carbonyl or methoxycarbonyl NMR resonances led to speculation that the polymer grows via a branched convergent process.

6.2.2 1 \rightarrow 2 Aryl-Branched, Ester Connectivity

Kricheldorf et al.^[3] laid the very early synthetic foundation for their, as well as others', hyperbranched efforts. Branched polycondensations were achieved by the copolymerization of 3-acetoxybenzoic acid and 3,5-bis(acetoxy)benzoic acid (**5**) or [3-(trimethylsiloxy)benzoyl chloride] and 3,5-bis(trimethylsiloxy)benzoyl chloride (**6**). Formulae for the most probable branching units (**a-c**) derived from the copolymerizations (Scheme 6.2) are depicted in Figure 6.2. The \bar{M}_n using the trimethylsiloxy-based monomers ranged from 10,000 to 29,000 amu, while that for the acetoxy-based building blocks varied slightly from 3,300 to 3,700 amu.

In this series, a relatively clean condensation process was demonstrated^[50-55] by reactions of the silylated carboxylic acids with acetylated phenol moieties. This procedure avoids acidic protons as well as reduces the effects of acid-catalyzed side reactions.

Fréchet et al.^[56] reported the high-yielding, reproducible preparation of the hyperbranched aromatic polyester (**7**) with controllable molecular weight by the self-condensation of **6**, which was synthesized from 3,5-dihydroxybenzoic acid by silylation (Me_3SiCl , Et_3N) followed by treatment with SOCl_2 and a catalyst (Me_4NCl). Polymerization^[56, 57] of acid chloride **6** (Scheme 6.2) was effected thermally; a polystyrene-equivalent M_w of 184,000 amu for the polyester was obtained using a reaction temperature of 200 °C and a catalyst (DMF or $\text{Me}_3\text{N}\cdot\text{HCl}$). The thermal stability was reported to be analogous to that of similar linear materials, whereas solubility was found to be enhanced. The DB was determined to be between 55 and 60 %, the branches bearing a large number of both internal and external free phenolic groups, functionalization of which was possible. The molecular weight was found to increase with higher reaction temperatures, longer reaction times, and increased quantities of catalyst.

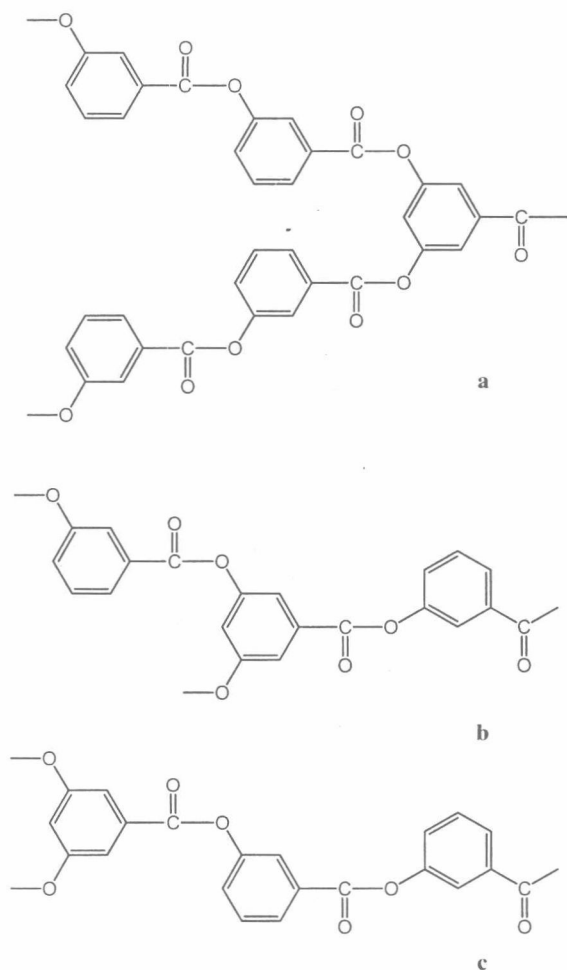
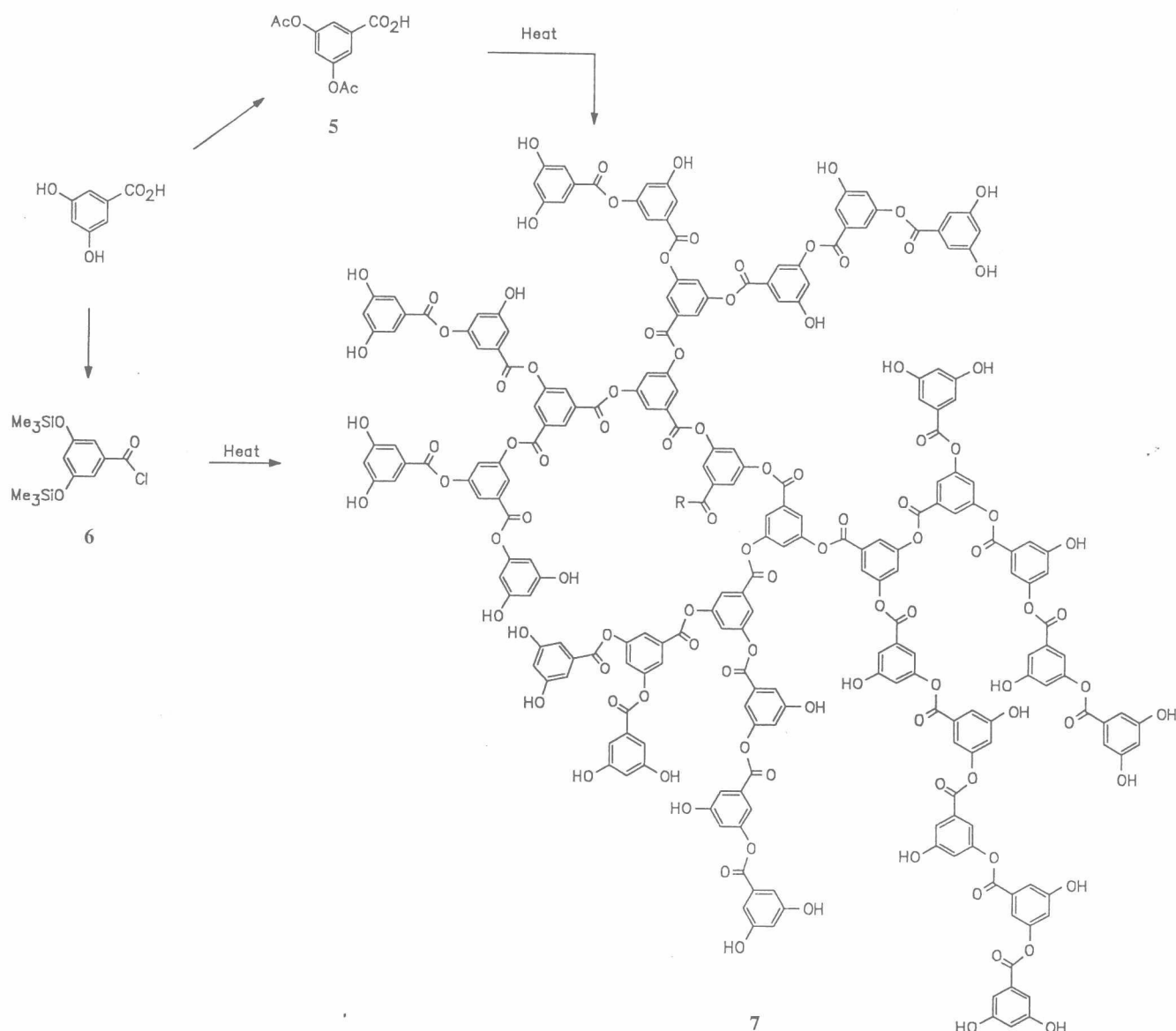


Figure 6.2 Branching unit formulae for Kricheldorf's pioneering hyperbranched polymers.^[3]



Scheme 6.2 Thermolysis of AB₂-type monomers affords high molecular weight polyesters.^[57]

Fréchet and Hawker^[58] employed a step-growth polymerization for the preparation of hyperbranched aromatic polyesters based on 3,5-dihydroxybenzoic acid derived monomers. The physical properties of these dendrimers were compared and contrasted to those of Kim and Webster's polyphenylenes^[44] and those of Kambouris and Hawker's partially aliphatic polyesters.^[59] Interesting comparisons have been made^[33] between dendritic and hyperbranched structures; the thermal properties (T_g s and thermogravimetric analysis) were found to be independent of architecture, while their solubilities proved comparable, but greater than those of their linear counterparts. Analogous hyperbranched poly(silyl ester)s have been prepared.^[59a]

Turner, Voit, and Mourey^[60, 61] later reported analogous hyperbranched polyester macromolecules (7) obtained by the thermal polymerization (Scheme 6.2) of AB₂ diacetate 5, prepared (Ac₂O) from 3,5-dihydroxybenzoic acid. Polymer structures derived from 5 were supported by similar spectral characterization as that described for polymers obtained from 6. Condensation of 5 below 170 °C was found to be "slow", whereas at 250 °C the rate was substantially increased. Products (possessing $\bar{M}_w > 1,000,000$ amu) were much less sensitive to purity of the starting material (i.e., 5) than those synthesized employing TMS monomer 6. When monomer 5 was heated *in vacuo*, it was the quality and duration of the vacuum that had the largest effect on the resultant weight; the \bar{M}_w ranged from 5,000 to 800,000 amu depending on the temperature, time, and vacuum.

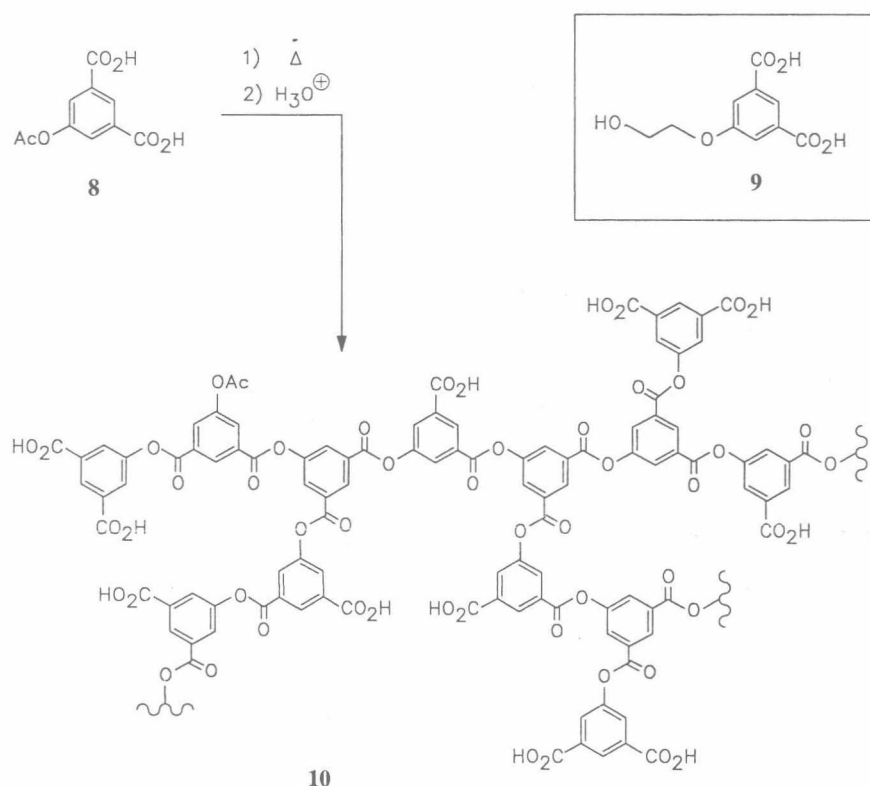
Catalysts (Mg° or $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$) did not improve the reaction course. These materials^[60, 62] have been characterized by their molecular weights, viscosities, and rheology; the influence on the properties of different terminal groups as well as blend behavior have also been discussed.^[63]

Massa, Voit, et al.^[64] conducted a survey of the phase behavior of blends of these polyester hyperbranched polymers with linear polymers. Blend miscibility of a hydroxy-terminated polyester was found to be comparable to that of poly(vinylphenol), indicating strong *H*-bonding interactions, whereas miscibility of an acetoxy-terminated analogue decreased relative to the hydroxy derivative.

Kumar and Ramakrishnan^[65] prepared hyperbranched polyesters by subjecting 3,5-dihydroxybenzoic acid and its derivatives to standard self-condensation conditions (i.e., transesterification). Spacer lengths between branching centers were varied using mesogenic segments and the resulting products were studied by DSC. These hyperbranched materials were found to be amorphous with no liquid-crystalline phases. This was postulated as being attributable to a "random distribution of the mesogenic segments."

A related series of hyperbranched polymers possessing high molecular weights (20,000–50,000 amu) was created^[62, 66] by melt condensation of either 5-acetoxy- (8) or 5-(2-hydroxyethoxy)isophthalic acid (9) (Scheme 6.3). Polymerization of diacid 8 was effected in two stages: (1) melting at 250 °C combined with removal of AcOH with the aid of an inert gas, and (2) application of a vacuum at the onset of solid-state formation. Refluxing the resultant acid-terminated, ester-linked polymer 10 in THF/ H_2O decomposed the labile anhydride cross-links that were generated under the reaction conditions. The DB^[56] was determined to be ca. 50 %. The acetoxy monomer was also copolymerized with various AB-type monomers, e.g., 3-(4-acetoxyphenyl)propionic acid. Isophthalic acid 9, prepared from 5-hydroxyisophthalic acid with ethylene oxide, was polymerized at 190 °C using a catalyst $[\text{Bu}_2\text{Sn}(\text{OAc})_2]$. The resulting carboxylic acid terminated hyperbranched polymer (not shown) proved to be readily soluble in common organic solvents. Due to a lower condensation temperature than that employed for the polymerization of diacid 8, evidence of anhydride bond formation was not observed.

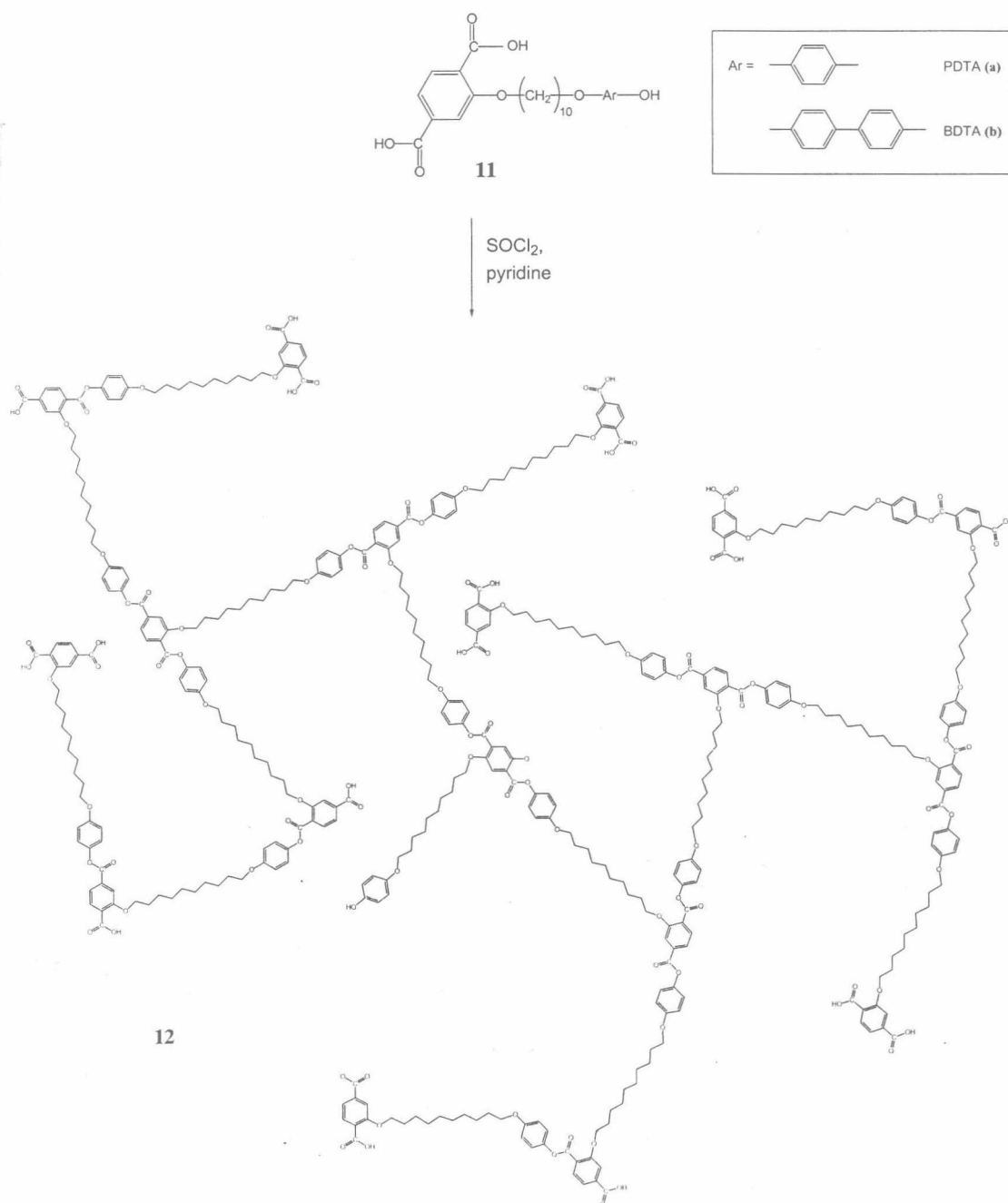
Feast et al.,^[67, 67a] in their continuing study of the polymerization of dimethyl hydroxyalkoxyisophthalates,^[68] reported step-growth polymerization of these AB_2 monomers



Scheme 6.3 Melt condensation of isophthalic acid derivatives affording polyesters.^[62, 66]

possessing alkyloxy methylene chain lengths of 2 to 6 units. Polymerization was effected by heating (210 to 240 °C) under nitrogen in the presence of a transesterification catalyst $[\text{Mn}(\text{OAc})_2/\text{Sb}_2\text{O}_3]$ and a thermal degradation suppressant $[(\text{PhO})_3\text{PO}]$. For polymers obtained using the monomer with the shortest chain length, molecular weight and polydispersity increased with increasing reaction time up to a maximum molecular weight of 107,000 amu and an M_w/M_n of 15. Similar behavior for the higher chain length polymeric homologues was not observed, although an “odd-even effect” was noted in that alkene lengths of 2, 4, or 6 methylene units produced higher molecular weight polymers than the monomers possessing an odd number (3 or 5) methylenes.

Kricheldorf et al.^[69] prepared two classes of liquid-crystalline hyperbranched copolymers by copolymerization of silylated **5** with difunctional mesogenic monomers. One class was prepared from a binary mesogen mixture comprised of silylated derivatives of β -(4-acetoxyphenyl)propionic acid and 4-acetoxybenzoic acid, while the other class was obtained from a ternary mixture that also incorporated silylated 6-acetoxy-2-naphthoic acid. It was found that, in this case, at least a six-difunctional monomer segment length



Scheme 6.4 Thermotropic, liquid-crystalline hyperbranched polymers based on terephthalate derivatives.^[72]

between branch junctures was required in order to obtain a nematic phase. Melt rheology was used to further characterize the binary-based polymers. Additional poly(ester)s prepared by Kricheldorf et al. included liquid-crystalline poly(ester)s based on β -(4-hydroxyphenyl)propionic acid and either 4-hydroxybenzoic^[70] or gallic^[71] acids.

Jin et al.^[72] reported the preparation of thermotropic, liquid-crystalline hyperbranched polymers (e.g., **12** in Scheme 6.4) based on terephthalic acid derivatives **11** possessing either phenyl (a) or biphenyl (b) moieties. Monomer preparation was effected by methoxy-*para*-xylene oxidation (KMnO_4) to give the diacid, phenol liberation (HBr), esterification, phenol alkylation [$\text{Br}(\text{CH}_2)_{10}\text{Br}$], aryl diol (or biphenyl diol) chain attachment, and finally ester hydrolysis. Polymerization was brought about by polycondensation in the presence of SOCl_2 in pyridine. The \bar{M}_n s were found to be 6,970 and 15,050 amu for the phenyl- and biphenyl-based polymers, respectively. Each was observed to form nematic liquid crystals, although this property was not exhibited by the corresponding methyl ester terminated polymers; the DB for both materials was determined to be ca. 40 %.

Voit et al.^[73] examined blends of amphiphilic polyesters and polyolefins. Polyesters, prepared by polycondensation of 3,5-dihydroxybenzoyl chloride, in turn obtained by hydrolysis of the corresponding bis(TMS) derivative, were surface-modified with dodecanoyl chloride to afford amphiphilic globular polymers. The ability to incorporate organic dyes was demonstrated. Blends with polypropylene or polyethylene were prepared, with the polymer content ranging from 0.05 to 20 wt %. The dye-hosting potential facilitated homogeneous dye distribution in the polyolefin matrices.

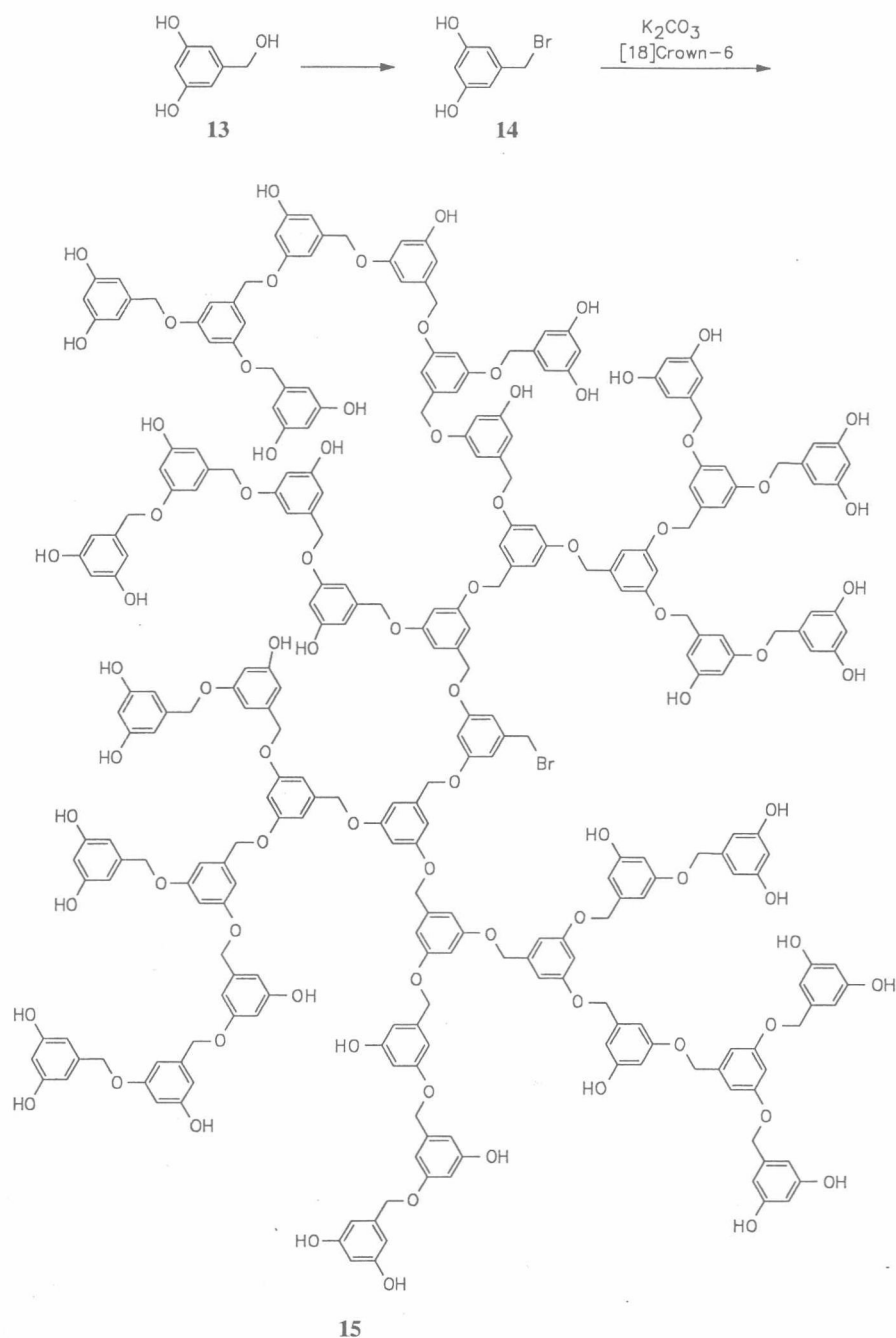
Kricheldorf, Bolender, and Wollheim^[74] also reported the polycondensation of bisilylated acid chloride **6** (see Scheme 6.2) as well as its co-polycondensation with 3-trimethylsiloxybenzoyl chloride or *N,N'*-bis(trimethylsilyl)bis(aniline-P). Terminal group modification with acetyl, chloroacetyl, undecanoyl, stearoyl, 4-methoxycinnamoyl, and perfluorooctanoyl acid chlorides was also reported; solubilities and T_g s were found to vary greatly with end group. Films cast from 4-methoxycinnamoyl-coated polymers were cross-linked by UV irradiation.

6.2.3 1 \rightarrow 2 Aryl-Branched, Ether Connectivity

A one-step synthesis (Scheme 6.5) of the hydroxy-terminated, dendritic polyether **15** from 5-(bromomethyl)-1,3-dihydroxybenzene (**14**), prepared (PPh_3 , CBr_4) from 1,3-dihydroxy-5-(hydroxymethyl)benzene (**13**), has been reported.^[75, 76] Bromomethyl monomer **14** was polymerized upon addition to an acetone suspension of K_2CO_3 and 18-crown-6 (an ubiquitous method of connectivity in convergent, iterative sequences).^[77] The rate of monomer addition did not significantly affect the polymer characteristics and \bar{M}_w exceeded 10^5 . ^1H NMR spectroscopic analysis indicated that *C*- as well as *O*-alkylation occurred during polymerization, to varying degrees ranging from 11 to 32 %, when parameters such as reaction time, concentration, and solvent were varied; the least amount of *O*-alkylation occurred utilizing prolonged reaction times (92 h) with acetone as the solvent. Polymer characterization also included molecular weight determinations by SEC and low-angle laser light scattering.

Wooley and coworkers^[78] prepared similar perfluorinated materials using a pentafluorinated aryl-terminated 1st generation Fréchet-type monomer (**16**; Scheme 6.6). Treatment of monomer **16** with Na metal afforded the hyperbranched material **17** through benzyloxy anion substitution of the terminal *p*-fluoro moieties. These polymers were derivatized with lithium trifluoroethoxide, lithium perfluorodecanoxide, and *p*-iodophenol. AFM revealed a significant decrease (2-fold) in the friction coefficient of films of the perfluoroalkyl-substituted material relative to the unsubstituted polymers. Analysis (MALDI-TOF MS) of the cyclization that occurred during this hyperbranched synthesis has been reported.^[79]

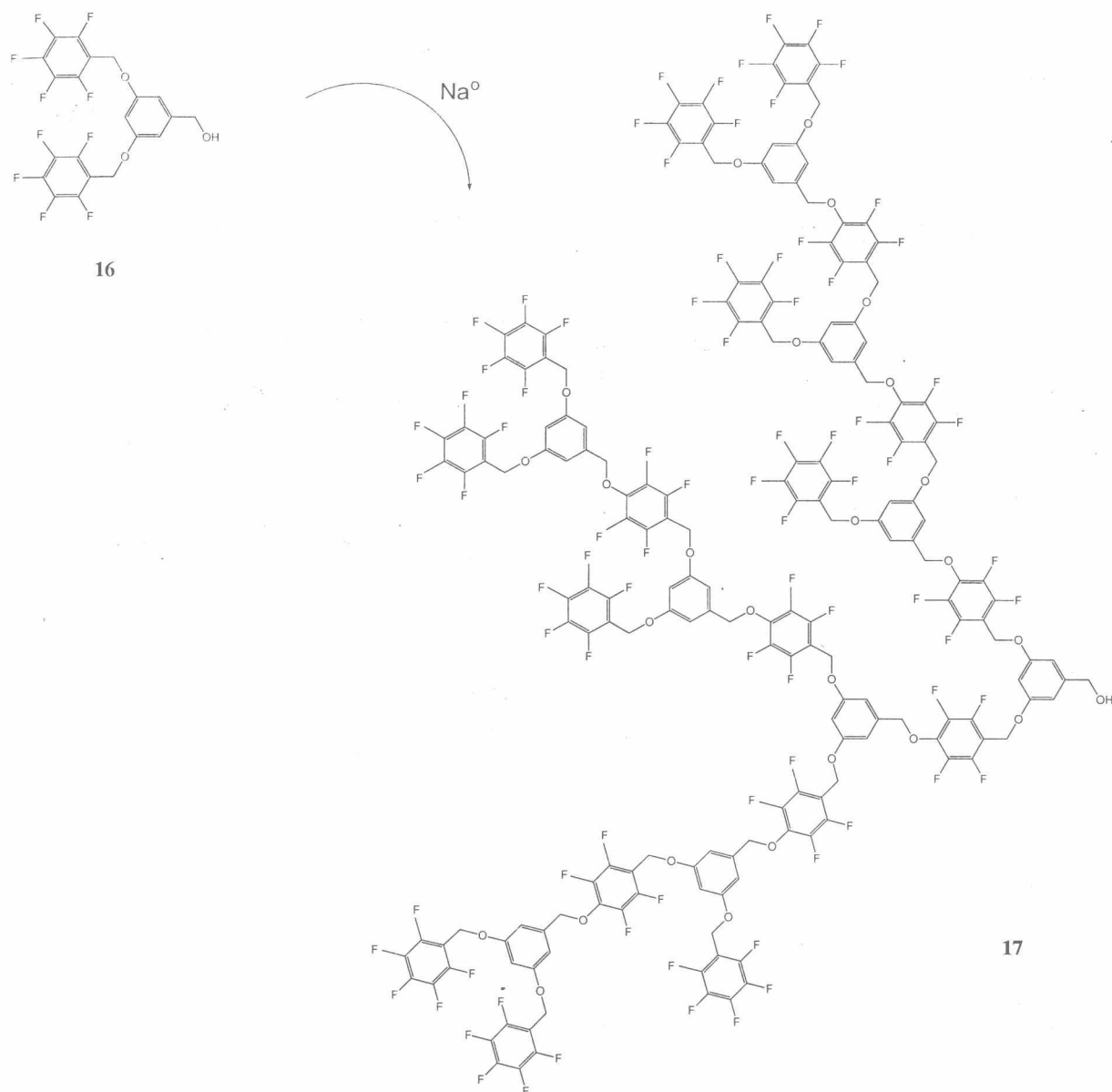
Miller, Neenan, et al.^[80, 81] reported a general single-pot method (Scheme 6.7) for the preparation of poly(aryl ether) hyperbranched macromolecules (**20a-d**) that were functionally analogous to linear poly(aryl ether) engineering plastics.^[80-82] These hyper-



Scheme 6.5 Preparation of hyperbranched analogs (**15**) of Fréchet's convergently constructed, (benzyl ether)-based dendrimers.^[73]

branched polymers were generated from phenolic A_2B -type monomers (**18a–d**), which were converted (NaH, THF) to the corresponding sodium phenoxides (**19a–d**) and subjected to polymerization. The procedure utilized phenoxide monomers possessing two carbonyl-, sulfonyl-, or tetrafluorophenyl-activated aryl fluoride moieties, which were displaced during monomer connection. Reaction conditions included a short duration (0.5–2 h) and moderate temperatures (100–180 °C). Polymerizations involving monomers **18a,b** were found to be insensitive to the reaction temperature, whereas the self-assembly of monomers **18c,d** at 140 °C afforded insoluble gels, presumably due to acetylene cross-linking, although at 100 °C completely soluble polymers were realized. A related procedure (bromide displacement by phenoxide ion) using 2,4-dibromophenol or 2,4,6-tribromophenol as the starting material has also been reported.^[36]

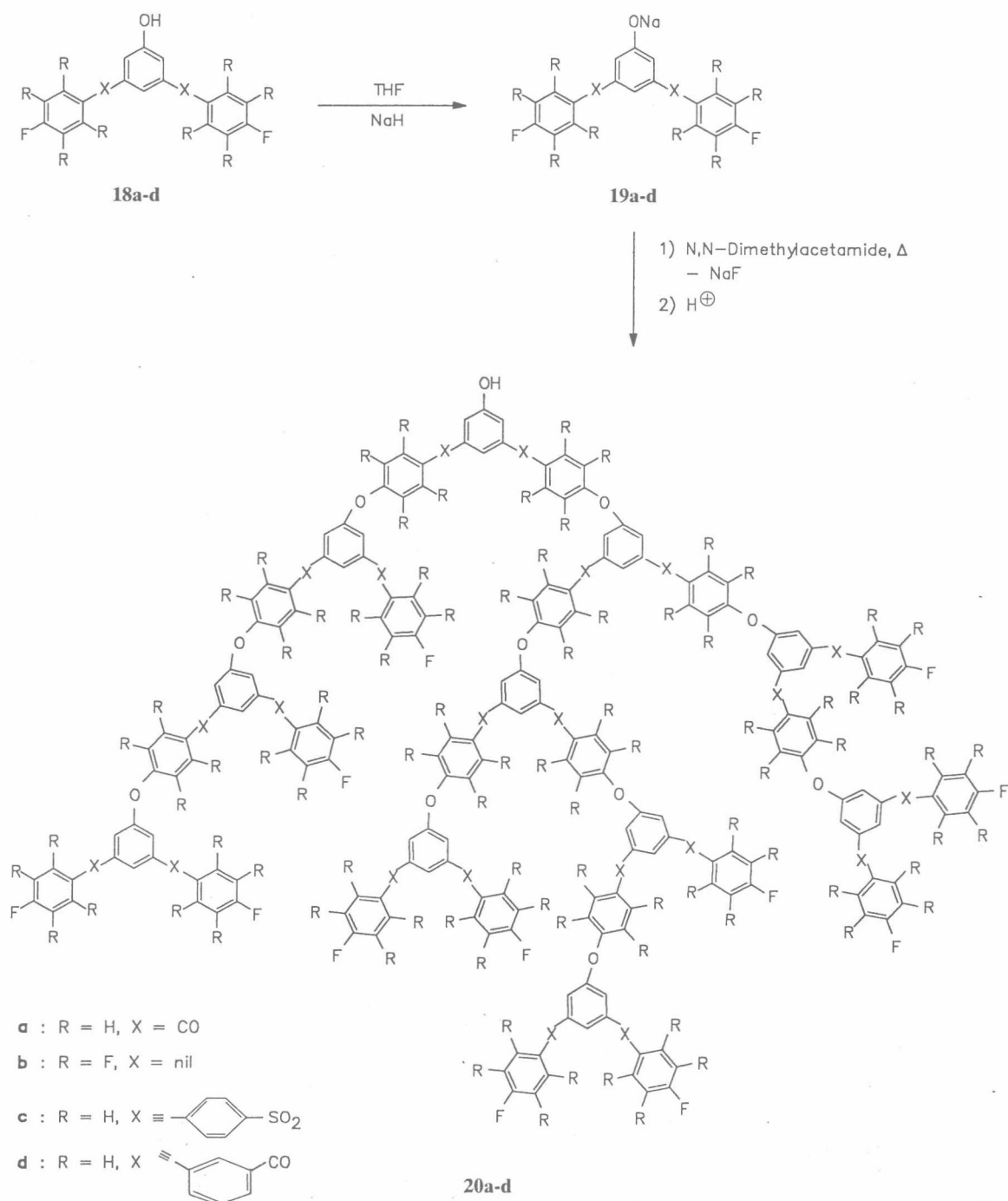
Polyhydroxylated, oxygen-organosolv lignin (also referred to as oxygen-acetone lignin) possessing a highly branched architecture has been employed as a micromonomer



Scheme 6.6 Wooley's hyperbranched perfluorinated construct.^[78]

(**21**; Figure 6.3) for polyesterification using diacyl chlorides and oligoethylene oxide glycol by Evtugin and Gandini.^[83] Notably, lignin use in the production of hyperbranched architectures is of practical concern in view of the ready availability of these abundant and renewable biomass resources.

Chang and Fréchet^[84] applied their proton-transfer polymerization approach to the construction of hyperbranched poly(aryl ether)s. Using epoxy-modified benzyl ether **22** (Scheme 6.8) under basic conditions, repetitive phenolic proton abstraction, epoxide ring-opening, and proton transfer facilitated formation of the polymer (e.g., **23**). Chemo- and regioselectivity were maintained due to the greater nucleophilicity of the phenolate compared to the secondary alkoxide; an M_w up to 206,000 amu was reported and the polymerization kinetics were also addressed.



Scheme 6.7 Preparation^[80, 81] of branched analogs of (aryl ether) engineering plastics.

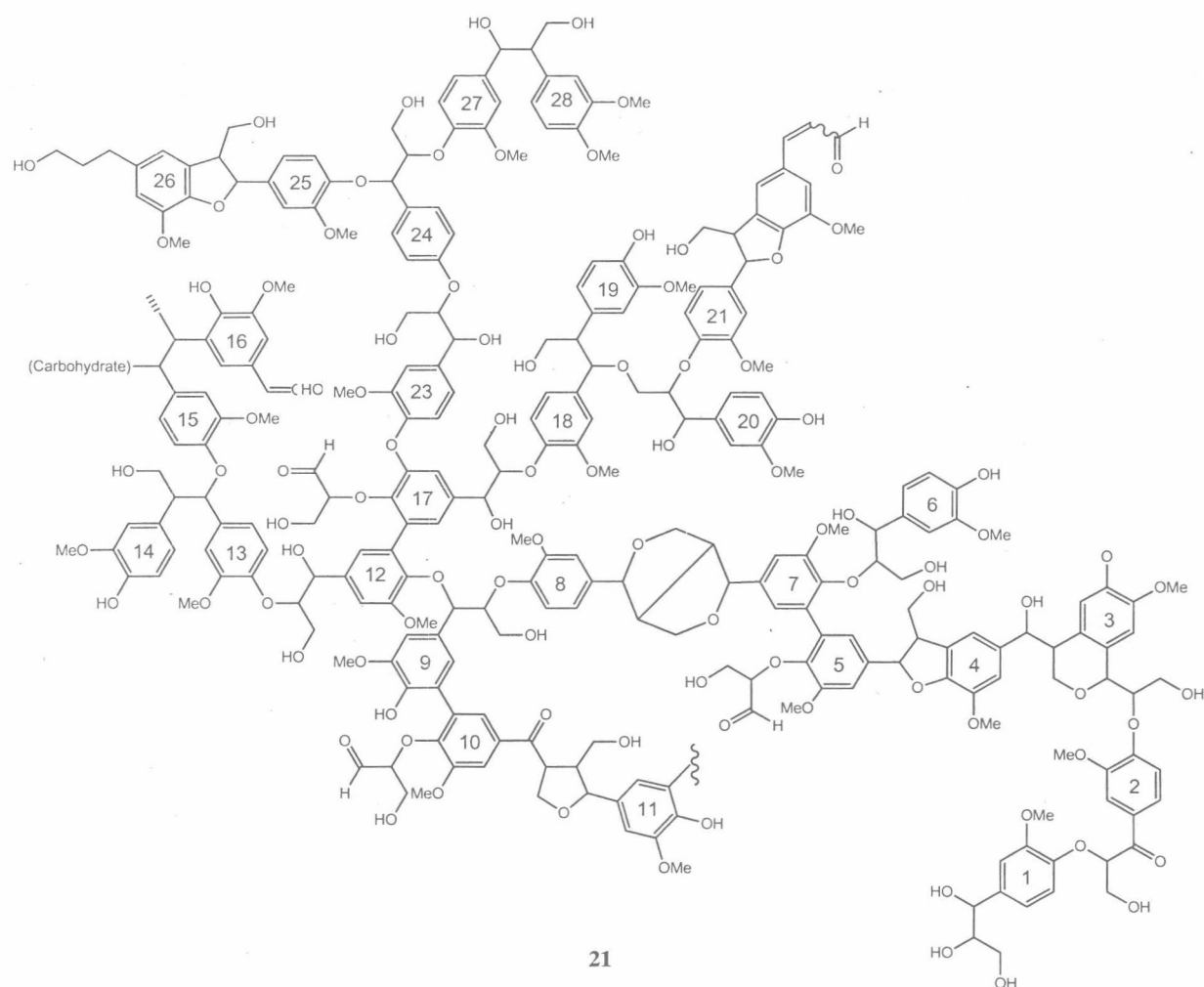


Figure 6.3 Branched lignins (21) used as “micromonomers” for hyperbranched polymers.^[83]

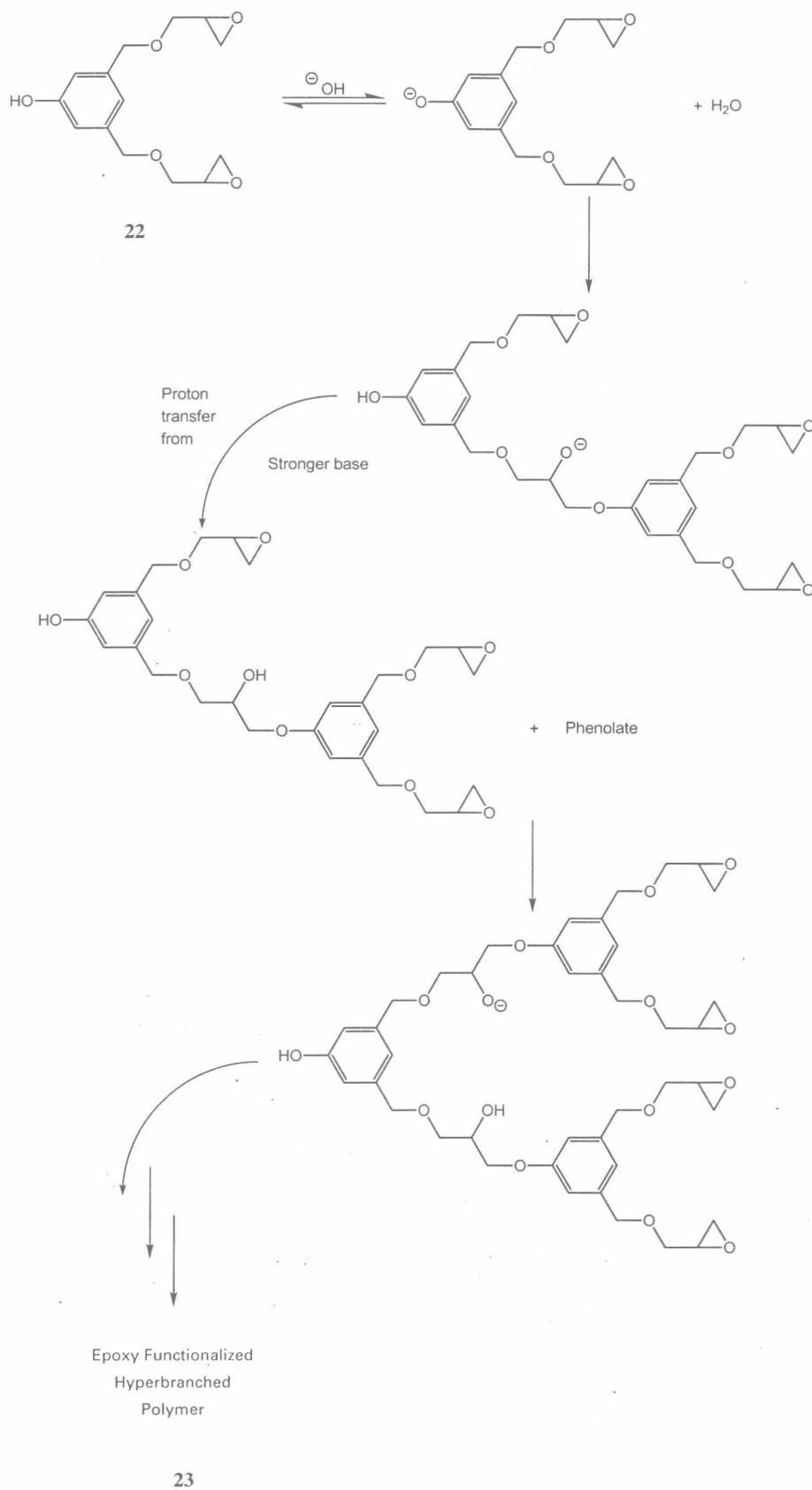
6.2.4 1 → 2 Aryl-Branched, Amine Connectivity

Hyperbranched *m*-polyanilines (25; Scheme 6.9), prepared for the study of organic magnetic systems, have been reported.^[85] Pd-catalyzed ($\text{Pd}_2\text{dba}_3/3$ equiv. BINAP) condensation of 3,5-dibromoaniline (24) yielded branched polymer 25; analogous linear materials have also been reported. Molecular weights determined for these materials ranged from 7,000 to 22,000 amu, with a DP of 50 as determined by GPC.

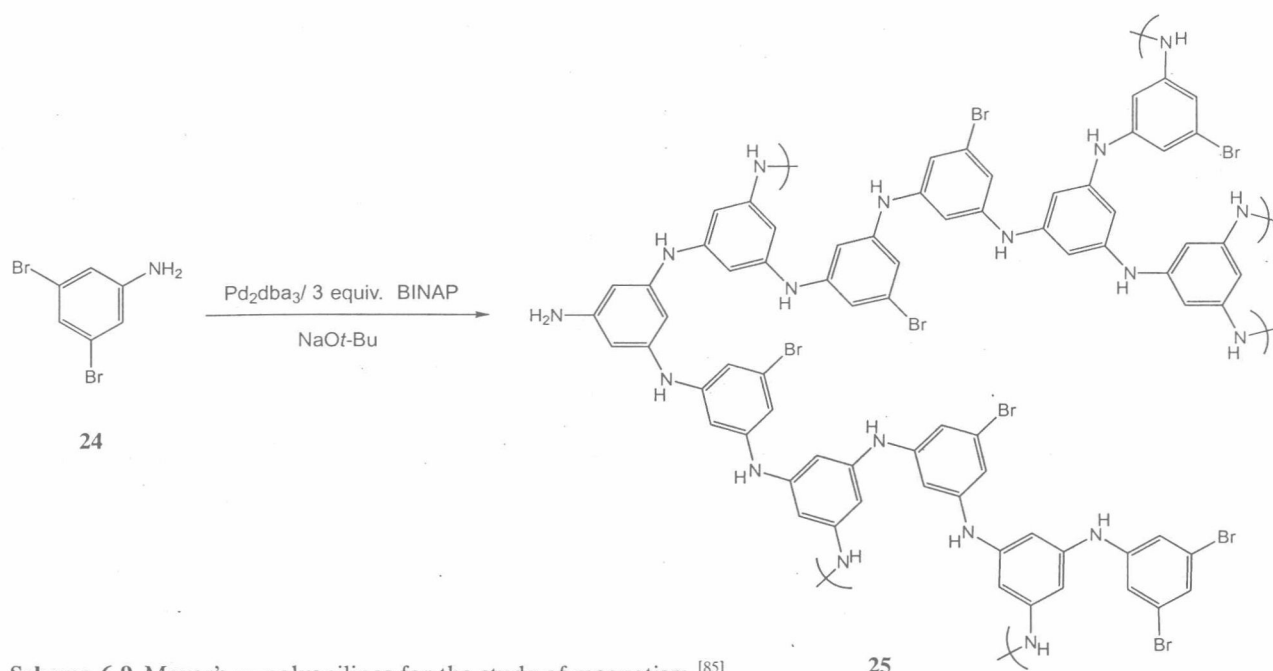
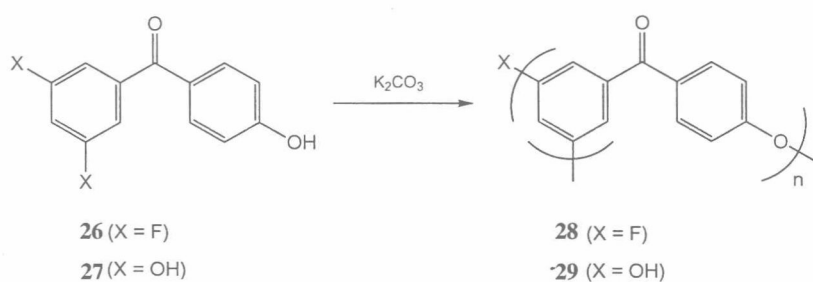
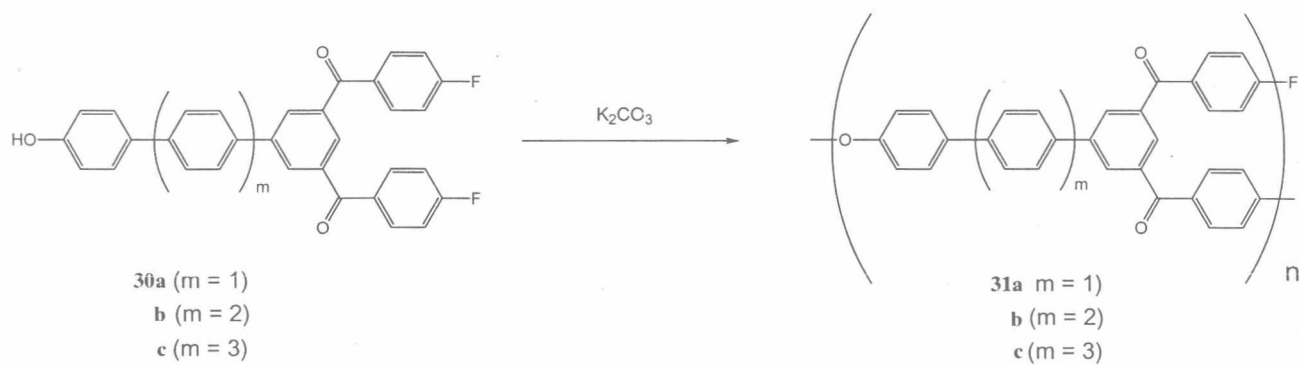
6.2.5 1 → 2 Aryl-Branched, Ether & Ketone Connectivity

Hawker et al.^[86, 87] reported the structural characterization of hyperbranched macromolecules (Scheme 6.10; 28 and 29), obtained from the polymerization of monomers related to the AB_2 systems such as 3,5-difluoro-4'-hydroxybenzophenone (26) and 3,5-dihydroxy-4'-fluorobenzophenone (27); also see.^[87a] These new related families of poly(ether ketone)s possessed the same internal linkages as well as terminal groups, but differed in the DB. Interestingly, as DB increased, the solubilities of the polymers increased, whereas their viscosities decreased; no change in the thermal characteristics was observed.

Hawker and Chu^[88] later expanded on their poly(ether ketone) hyperbranched polymers to include AB_3 - and AB_4 -type monomers. The thermal properties of these materials were shown not to depend on molecular architecture, but rather on chain end functional-

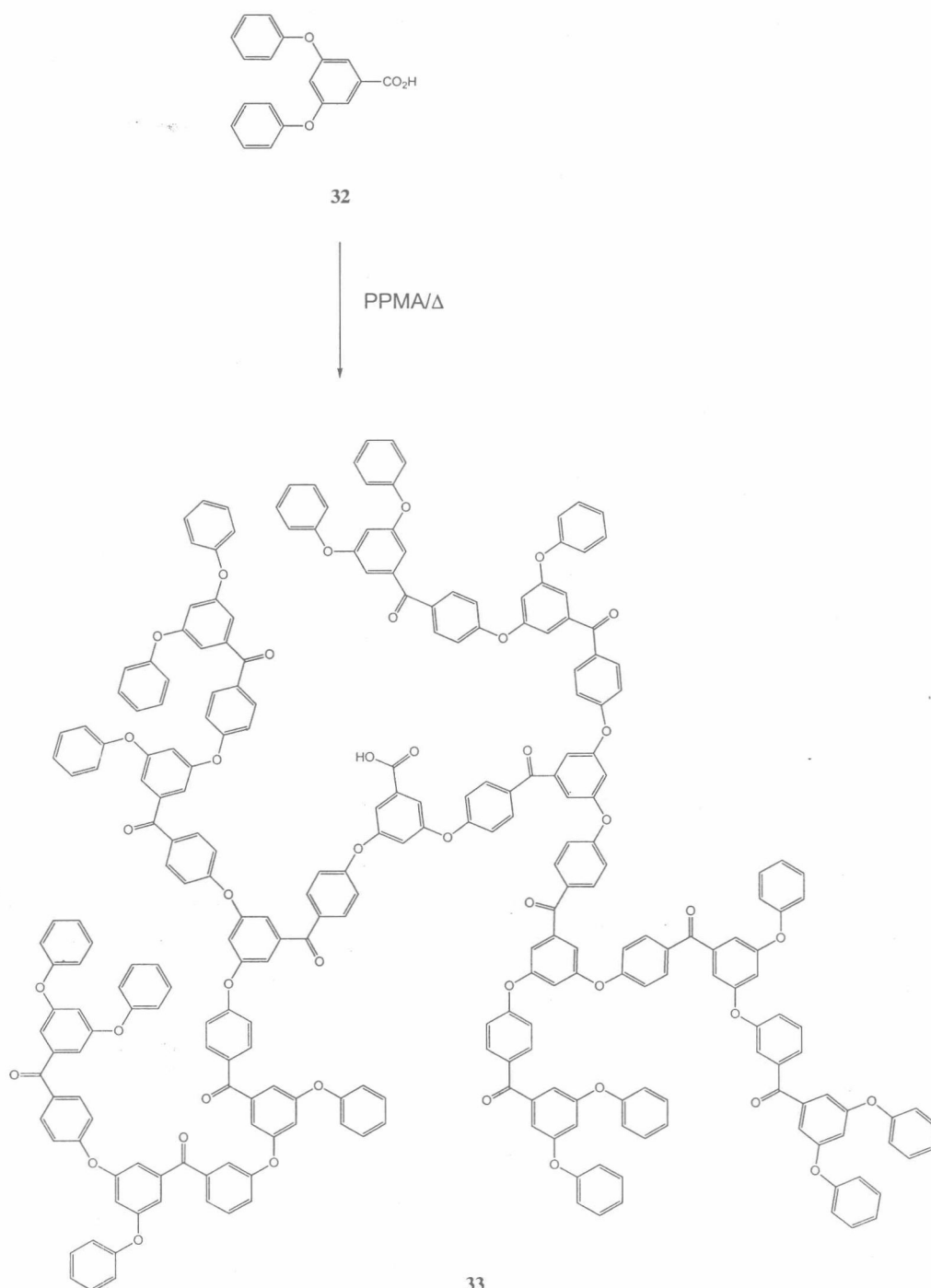


Scheme 6.8 Fréchet's poly(aryl ether)s obtained by proton-transfer polymerization.^[84]

Scheme 6.9 Meyer's *m*-polyanilines for the study of magnetism.^[85]Scheme 6.10 Preparation of hyperbranched keto aryl ether polymers.^[86,87]Scheme 6.11 Morikawa's polyphenylene polymers.^[89]

ity; the T_g s ranged from 97 to 290 °C. Imparting aqueous solubility by capping with carboxylate moieties led to the creation of unimolecular micelles, as demonstrated by the solubilization of 1,4-diaminoanthraquinone in water (40-fold increase in solubility compared to that in neat water).

Morikawa^[89] reported the use of phenolic displacement of aryl fluoro substituents to achieve hyperbranched monomer connectivity. A series of phenyl-homologated phenolic monomers (**30**; Scheme 6.11) was thus polymerized (K_2CO_3) to afford a new family of polymers (**31**) possessing thermal properties that varied in relation to the phenylene spacer length. For example, T_g s increased with increasing spacer length. The thermal properties were also compared with those of other poly(ether ketone)s. Different fluoro-terminated hyperbranched poly(ether ketone)s with varying DB and their linear counterparts have been synthesized and the effects of the DB have been evaluated.^[90]



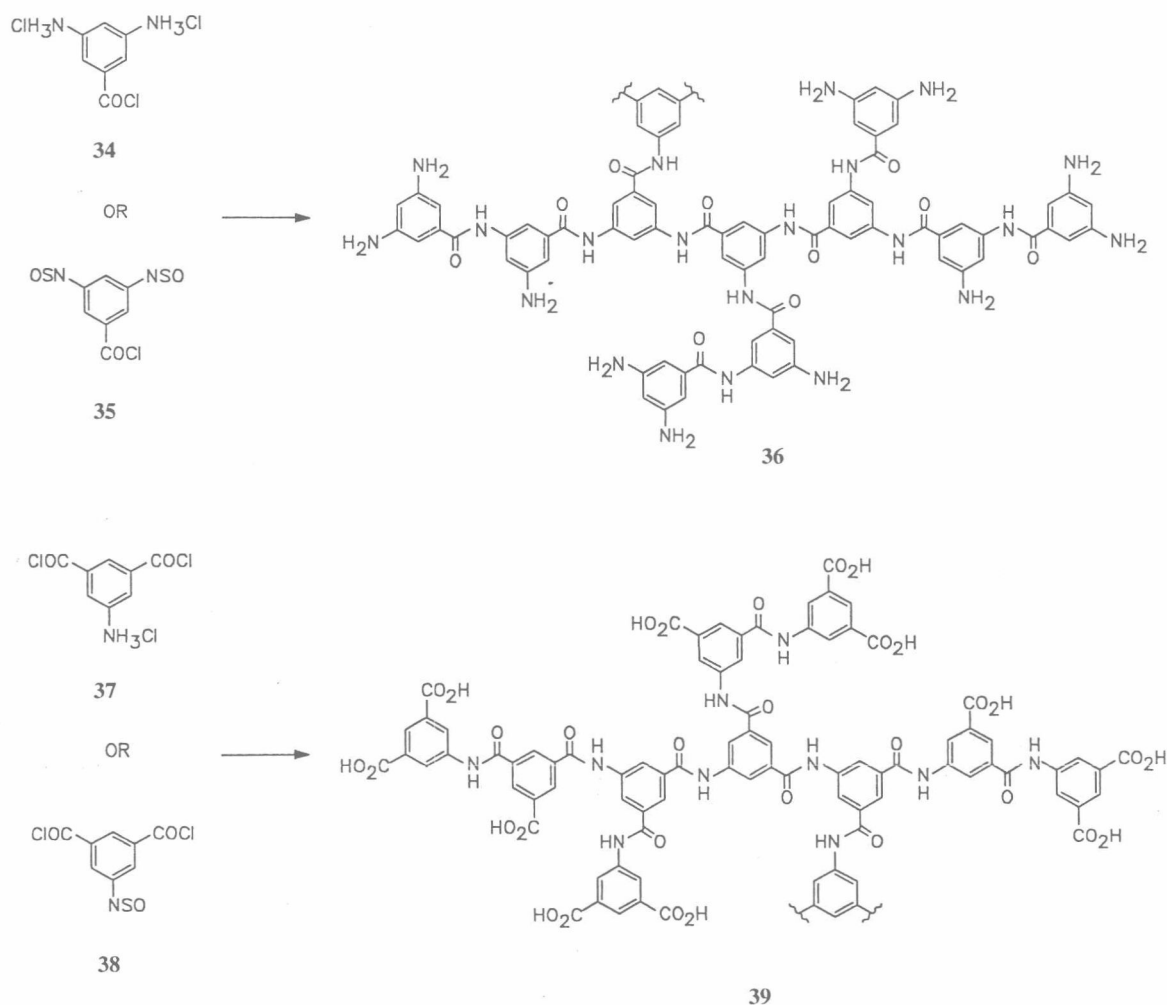
Scheme 6.12 Shu's poly(ether ketone)s.^[91]

Shu, Leu, and Huang^[91] prepared poly(ether ketone)s (**33**) by the polycondensation of 3,5-di(phenoxy)benzoic acid (**32**; Scheme 6.12) using $P_2O_5/MeSO_3H$ as both the condensing agent and solvent. These materials (e.g., **33**) were further modified with *p*-toluic, 4-*n*-octylbenzoic, or stearic acid, effectively changing the thermal and solution properties of the polymers. For example, as the length of the terminal alkyl chains was increased, the T_g of the polymer was observed to decrease. Similar poly(ether ketone)s have been constructed^[92] using 5-phenyloxyphthalic acid; the resulting polymer, possessing carboxylic acid termini, was modified with a variety of capping groups including MeOH, diphenyl ether, toluene, and NH_3 , and was found to have DBs of ca. 55%. 1,4-Diaminoanthraquinone was used to demonstrate the micellar character of the ammonium carboxylate derivative. Poly(aryl ether oxazole)s are also known.^[92a]

Telechelic oligo(ether ketone)s possessing two trimethylsiloxy end groups and one methyl moiety per repeat group were accessed by polycondensation of 4-fluoro-2'-methyl-4'-(trimethylsiloxy)benzophenone.^[93] Condensation of a small amount of bis(phenol-P) imparted the telechelic character. The oligomers were condensed with silylated 3,5-bis(acetoxy)benzoic acid to produce A-B-A triblock copolymers.

6.2.6 1 → 2 Aryl-Branched, Amide Connectivity

Kim^[36, 94, 95] reported two related types of hyperbranched aromatic polyamides; each employed amide bond formation for monomer connection and was based on three-directional, aryl branching centers (Scheme 6.13). Polymerization occurred upon neu-



Scheme 6.13 Procedures for the preparation of poly(aryl amide) polymers.^[36, 94] The carboxyl-terminated polymers exhibit lyotropic liquid-crystalline behavior.