

Chapter 10

Synthesis, Functionalization and Characterization of Hyperbranched Poly(arylene ester)s

10.1 Introduction

Dendrimers are a group of macromolecules, regularly branched from a center core to the periphery. They have received a great deal of attention over the past ten years due to their unique properties, including monodispersity, defect free structure, low viscosity and a high degree of surface functionality.^{1,2,3,4,5} Dendrimers are synthesized in stepwise fashion by divergent methods or convergent methods. They are usually very tedious to synthesize.

Hyperbranched polymers are highly branched polymers prepared from AB_x ($x \geq 2$) type monomers by direct polymerization.⁶ Like dendrimers these materials are usually amorphous, highly soluble and they also have high degrees of functionality and low viscosities. One of the major advantages of hyperbranched polymers over dendrimers is that they can be synthesized in one step. Their properties mimic those of dendrimers. It has been reported that

¹ Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 138.

² Newkome, G. R. *Aldrichimica Acta*, **1992**, 25, 3.

³ Fréchet, J. M. J. *Science* **1994**, 263, 1710.

⁴ Tomalia, D. A. *Scientific Amer.* May **1995**, p. 62; Tomalia, D. A.; Dust, H. D. *Topics Curr. Chem.*, **1993**, 165, 193.

⁵ Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules*; VCH: Weinheim, Germany, **1996**.

⁶ Flory, P. J. *J. Am. Chem. Soc.* **1954**, 74, 2718.

functionalized dendrimers were used as tougheners for epoxy resins⁷ and silicone rubbers.⁸ Blending of immiscible hyperbranched polyester with polycarbonate was also reported to have a reinforcing effect.⁹

The focus of this research is to take advantage of the low viscosity and the high degree of surface functionality of hyperbranched polymers, functionalized with different reactive groups, and explore possible applications as crosslinkable toughening agents for composites and adhesives. The choice of using the hyperbranched poly(arylene ester)s reported by Turner *et al*^{10,11} was encouraged by the low cost of the starting materials, easy syntheses of both monomers and polymers and the good thermal properties of poly(arylene ester)s. Functionalizations of the hyperbranched polymers are simple and straightforward. Both carboxylic terminated and phenolic terminated hyperbranched poly(arylene ester)s can be directly used to modify the commercial epoxy resins. This chapter describes the synthesis, functionalization and characterization of hyperbranched poly(arylene ester)s.

⁷ Boogh, L.; Pettersson, B.; Japon, S.; Manson, J.-A. *Proced. Tenth Intern. Conf. Composit Mater.*, **1995**, vol. 4, pp. 389-396.

⁸ Muzafarov, A. M.; Gorbatshevich, O. B.; Rebrov, E. A.; Ignateva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym. Sci. (USR) Engl. Tr.*, **1993**, 35, 1575.

⁹ Massa, D. J.; Shriner, K. A.; Tunner, S. R.; Voit, B. I.; *Macromolecules* **1995**, 28, 3214.

¹⁰ Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, 27, 1611.

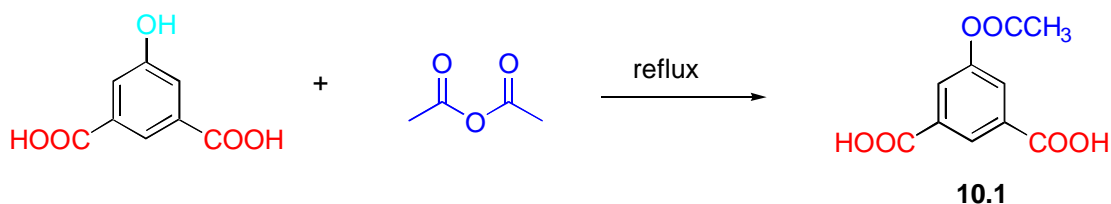
¹¹ Turner, S. R.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1993**, 26, 4617.

10.2 Results and Discussion

10.2.1 Synthesis of AB₂ and AB Monomers

5-Acetoxyisophthalic acid (**10.1**) was synthesized from 5-hydroxyisophthalic acid and an excess of acetic anhydride according to the reported procedure (Scheme 10.1).¹⁰ According to the ¹H NMR spectrum, the crude product did not contain starting material, 5-hydroxyisophthalic acid. Further purification was done by recrystallization from THF/CHCl₃ to give white crystals. Recrystallization was difficult for this compound. It took a long time to dissolve and the crystallization was very slow. The purified yield was 85%. The ¹H NMR, ¹³C NMR (Figure 10.1) and ¹H-¹³C HETCOR (Figure 10.2) agreed well with the structure.

Scheme 10.1

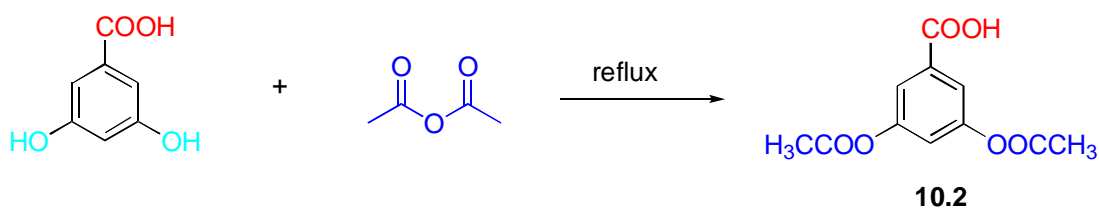


In the large scale synthesis, excess acetic anhydride has to be used to prevent the overheating problem. Once the temperature was raised, the starting material dissolved in the acetic anhydride and the mixture became homogenous. After reaction, the product was washed with a large amount of distilled water and dried under vacuum at 95 °C to remove the water and acetic acid. The ¹H NMR spectrum showed the product was pure. 309 grams (93%) of **10.1** (AB₂ monomer) was obtained and used directly for hyperbranched polymer synthesis.

Similarly, 3,5-diacetoxybenzoic acid (**10.2**) was synthesized from 3,5-dihydroxybenzoic acid and acetic anhydride (Scheme 10.2).⁹ The ¹H NMR spectrum of the

product showed no hydroxy signals of the starting material or those of the monoester. The product was recrystallized from CHCl_3 /ligroin to give a white powder. Like **10.1**, **10.2** was also difficult to recrystallize. It was difficult to dissolve and crystallize. The purified yield was 81%. The structure was further confirmed by ^1H NMR (Figure 10.3), ^{13}C NMR (Figure 10.4) and ^1H - ^{13}C HETCOR (Figure 10.5) spectra. Large scale synthesis of **10.2** was also carried out in about 350 grams scale. The yield was 95%.

Scheme 10.2



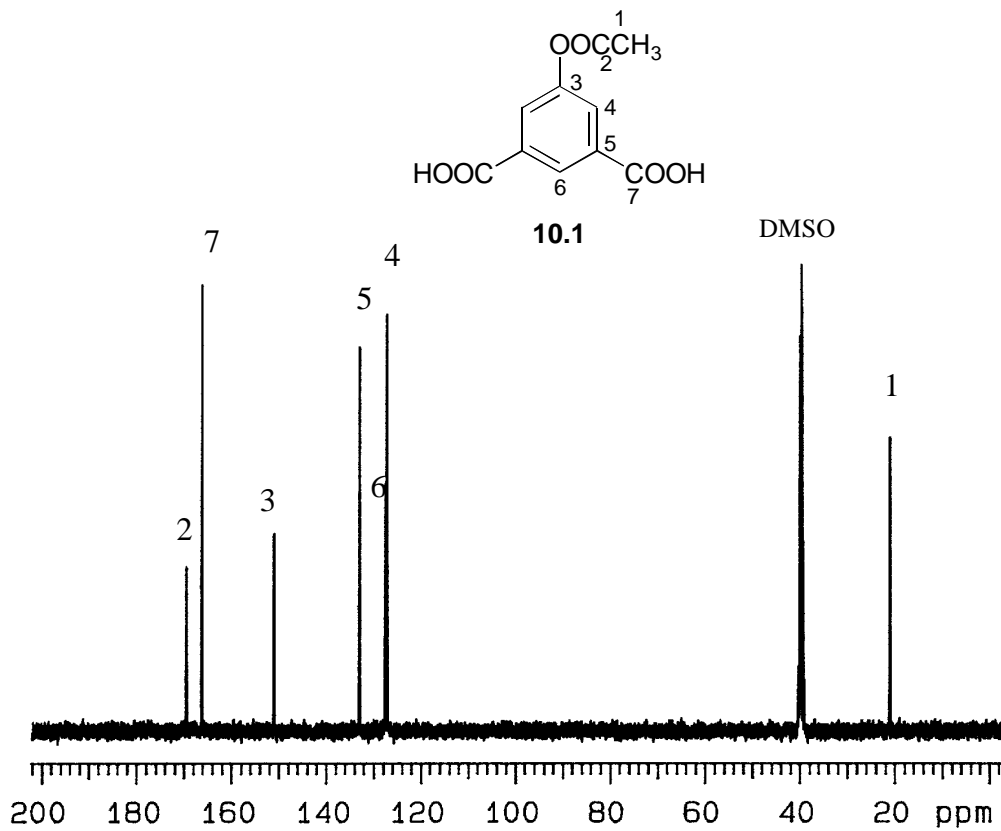


Figure 10.1 100 MHz ^{13}C NMR spectrum of compound **10.1** in DMSO-d_6 .

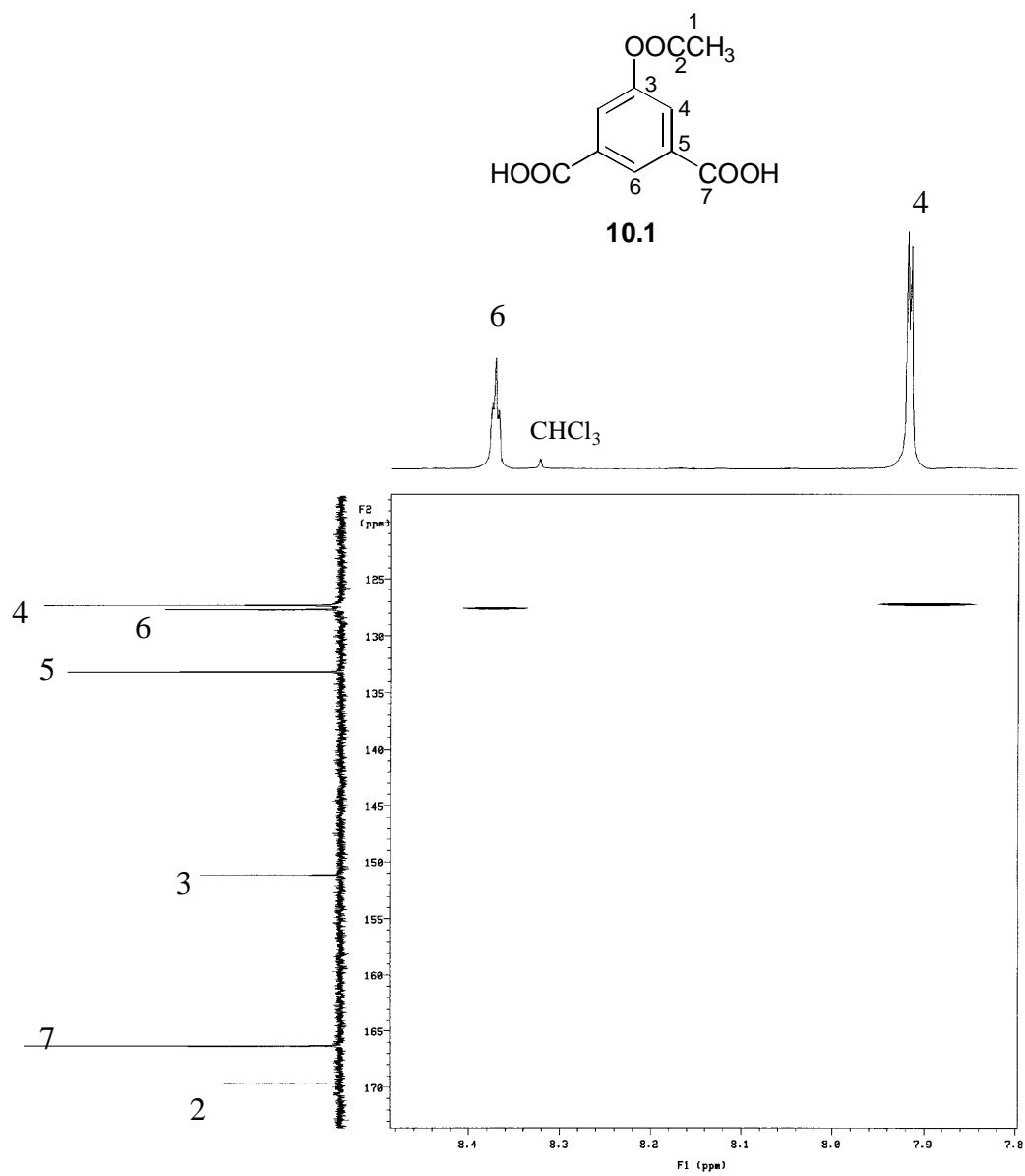


Figure 10.2 ^1H - ^{13}C HETCOR spectrum of compound **10.1** in DMSO-d_6 .

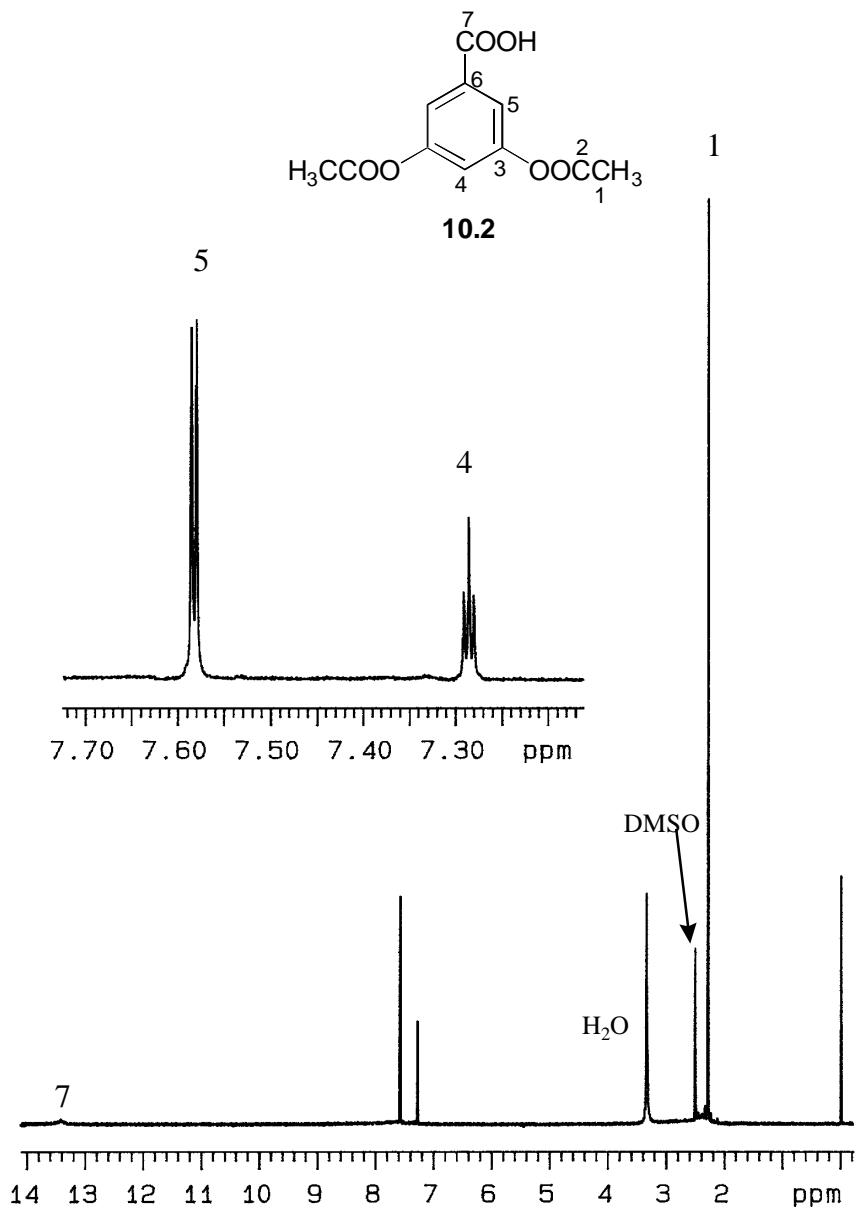


Figure 10.3 400 MHz ¹H NMR spectrum of compound **10.2** in DMSO-d₆.

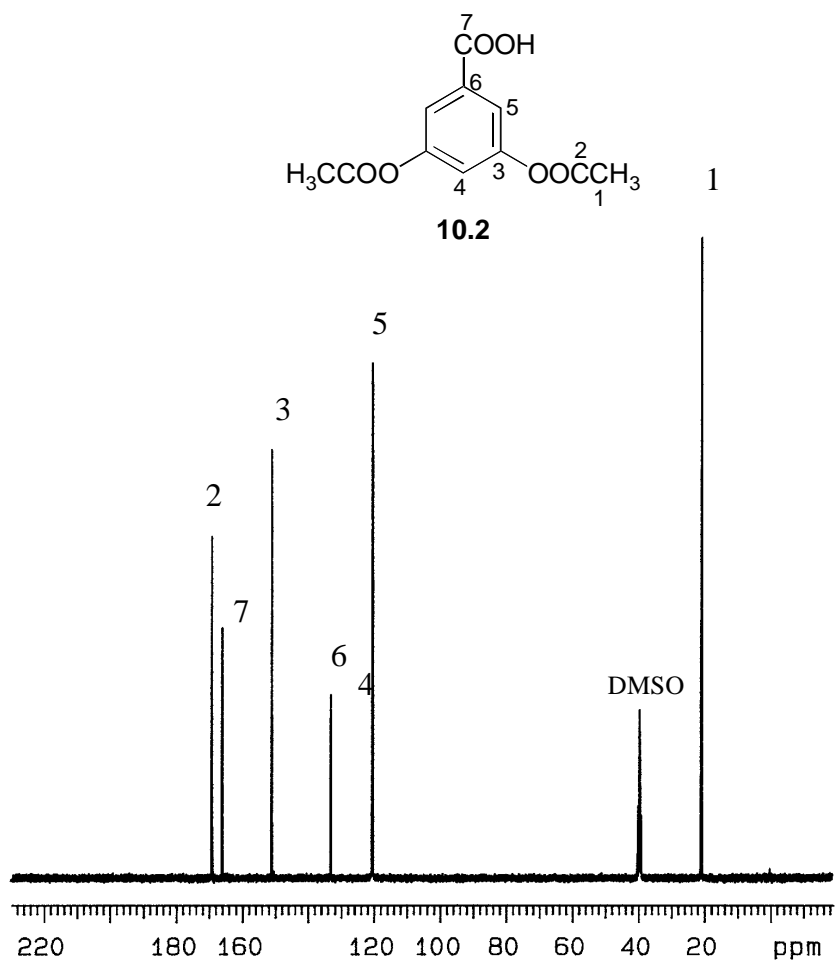


Figure 10.4 100 MHz ^{13}C NMR spectrum of compound **10.2** in DMSO-d_6 .

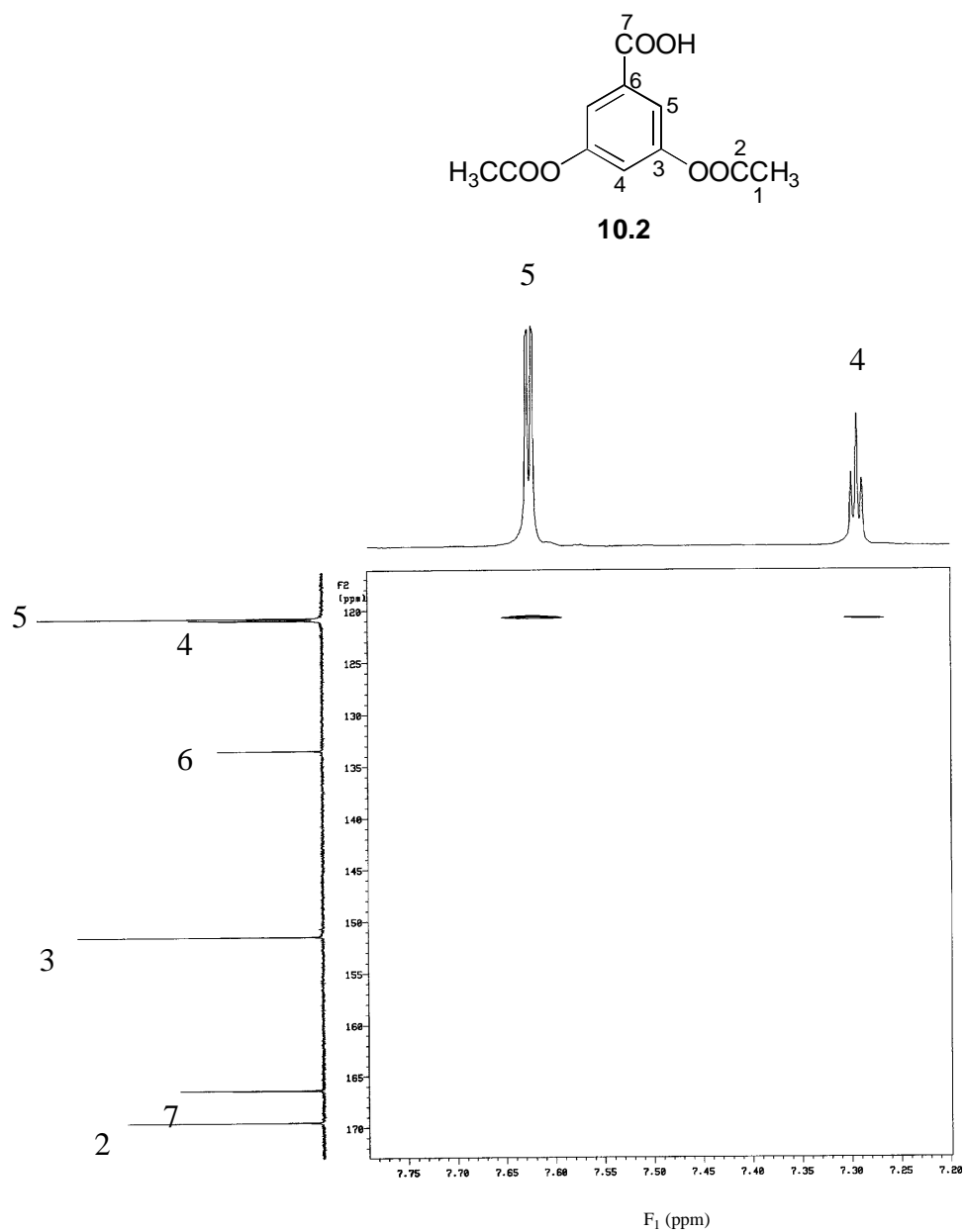
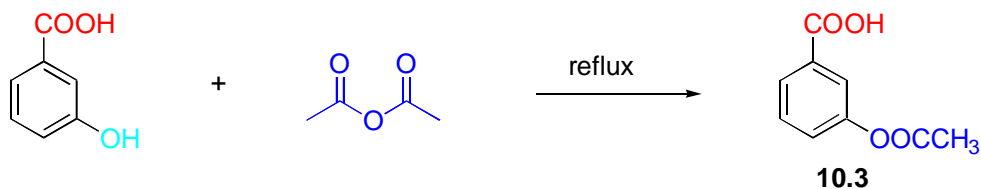


Figure 10.5 ^1H - ^{13}C HETCOR spectrum of compound **10.2** in DMSO-d_6 .

3-Acetoxybenzoic acid (**10.3**) was synthesized from 3-hydroxybenzoic acid and excess acetic anhydride (Scheme 10.3).¹⁰ The ^1H NMR and ^{13}C NMR spectra of this compound

agree well with the structure. This AB monomer was used to copolymerize with AB₂ monomer **10.1** or **10.2** to control the degree of branching.

Scheme 10.3



10.2.2 Synthesis and Characterization of Hyperbranched Poly(arylene ester)s

A. Poly(5-acetoxyisophthalic acid) (10.4, P1-COOH)

Poly(5-acetoxyisophthalic acid) (**10.4, P1-COOH**) was synthesized by bulk thermal polymerization at 255 °C for 30 minutes and then vacuum was applied to remove the condensation product, acetic acid, for 60 minutes (Scheme 10.4).⁹ The resulting brittle foamy material was crushed and refluxed in THF and H₂O to cleave the anhydride that formed during thermal polymerization. The isolated yield was 94%. Purification was done by reprecipitation from THF into ethyl ether and then from THF into H₂O. After precipitation into H₂O, it is very difficult to dissolve it in THF completely even after refluxing for 6 days. The ¹H NMR spectrum (Figure 10.6) shows a very broad signal for COOH groups at 13.0-14.2 ppm and small CH₃ signals of acetoxy groups at about 2.32 ppm. The signals in the aromatic region were very broad and complicated. They can not be used to calculate the degree of branching. This carboxylic acid terminated hyperbranched polymer, **P1-COOH**, can be directly used to modify the commercial epoxy resins. Functionalization of this hyperbranched polymer was achieved by conversion of carboxylic acid groups to acid chloride groups, and then further

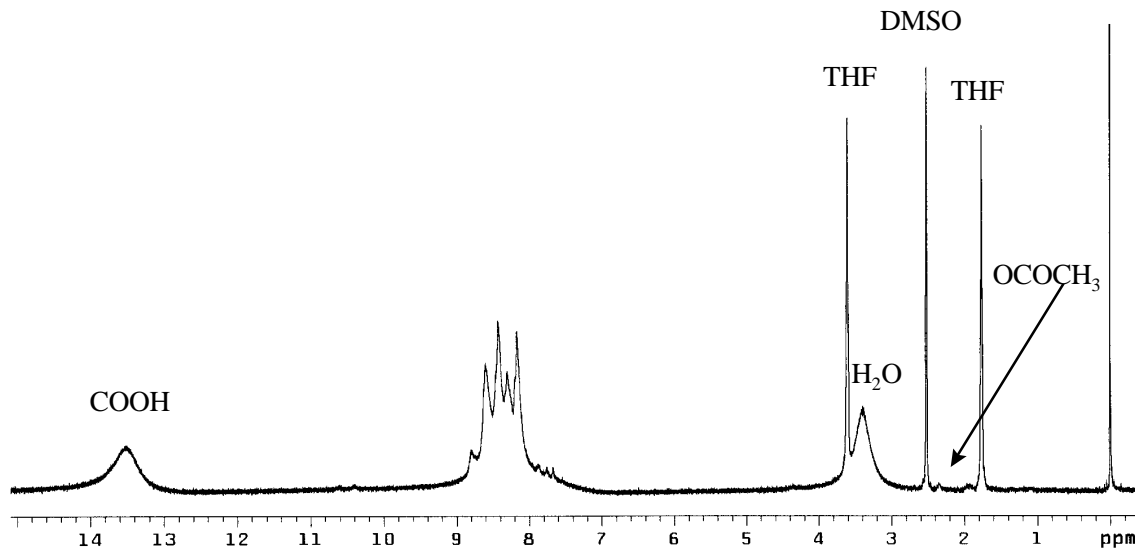


Figure 10.6 400 MHz ^1H NMR spectrum of polymer **10.4** in DMSO-d_6 .

B. Molecular weight Control

To systematically study the toughening effect of **P1-COOH** (see Chapter 11), different molecular weight **P1-COOH** samples were synthesized by controlling the reaction time and duration of the reaction performed under vacuum. The low molecular weight (LMW) **P1-COOH** was synthesized at 255 °C under argon for 30 minutes and no vacuum was applied to the system. The medium molecular weight (MMW) **P1-COOH** was synthesized at 255 °C for 20 minutes and then under vacuum for 10 minutes. The high molecular weight (HMW) **P1-COOH** was synthesized at 255 °C for 30 minutes and then under vacuum for 60 minutes. All **P1-COOH** samples were refluxed in THF/ H_2O to cleave the anhydride bonds formed during thermal polymerization. The solvents (THF and H_2O) were removed directly via rotary evaporation and the samples were dried in a vacuum oven at

95 °C for 24 hours. All samples are readily soluble in THF upon heating. The molecular weights of these **P1-COOH** were obtained from the ethyl esters (**10.6**, Scheme 10.4) measured by GPC.

C. Synthesis of Hyperbranched Copoly(arylene ester)s (10.8a-b**) from AB₂ and AB monomers**

Hyperbranched copoly(arylene ester)s synthesized from 5-acetoxyisophthalic acid (AB₂ monomer) and 3-acetoxybenzoic acid (AB monomer) can also be used to modify epoxy resins. Compared to **P1-COOH** synthesized from the AB₂ monomer, these copolyesters have the advantages of the more linear units, which could possibly contribute to the fracture toughness, and the low viscosity for better processibility. Different molar ratios of AB₂/AB can be used to synthesize branched polyesters. Two copolyester samples were prepared under reaction conditions similar to those for **P1-COOH**. The mole ratios of AB₂/AB were 2:1 (**10.8a**) and 1:1 (**10.8b**). These copolyesters were also refluxed in THF/H₂O to cleave the anhydride bond. The solvents were removed via rotary evaporation and then under vacuum. The ¹H NMR spectra of these two branched copolyesters showed the COOH signal at 13.46 ppm and acetoxy signals at about 2.3 ppm. Both **10.8a** and **10.8b** were readily soluble in THF upon heating. The molecular weights of these carboxylic terminated copolyesters were obtained from the corresponding ethyl esters (**10.9a** and **10.9b**) after reaction with thionyl chloride and then ethanol.

D. Measurements of COOH Equivalent Weights of Hyperbranched Polyesters

A key factor for proper network formation is to maintain a stoichiometric balance between the COOH, amine and epoxy groups. The COOH equivalent weights of the branched polyester can be obtained from potentiometric titration. Potentiometric titrations were performed in McGrath's laboratory using the MCI Automatic Titrator Model GT-05 which employs microprocessor control and a built-in cathode ray tube (CRT) screen. The titrator automatically allows for control of the titration, detection of the inflection points and appropriate calculation of the desired variable being measured. The commonly used titrant for polymers with phenolic or carboxylic groups is 0.025 N tetramethylammonium hydroxide (TMAH). A 0.025 N aqueous TMAH solution was prepared and standardized with potassium hydrogen phthalate (KHP) three times. The normality of TMAH solution calculated from titration was 0.02505 ± 0.00001 N. THF was initially chosen as the solvent for **P1-COOH**. The ammonium salt of **P1-COOH** precipitated out of the solution as the titration proceeded. Thus, a mixture of THF/H₂O (50/10) was then used to prevent the precipitation of ammonium salt. All the calculation results are listed in Table 10.1.

Table 10.1 The COOH equivalent weights calculated from titration
(TMAH, 0.02505 N)

Sample	Sample Weight (g)	Volume of TMAH (mL)	COOH EW (g/eq)	Average COOH EW (g/eq)
LMW #1	0.0256	7.192	142.10	
LMW #2	0.0268	7.478	143.07	142.33±0.66
LMW #3	0.0237	6.671	141.82	
MMW #1	0.0245	6.262	156.18	
MMW #2	0.0223	5.713	155.83	156.07±0.20
MMW #3	0.0269	6.875	156.20	
HMW #1	0.0237	5.898	160.42	
HMW #2	0.0259	6.467	159.89	160.53±0.70
HMW #3	0.0241	5.965	161.28	
2:1 Copolymer #1	0.0389	7.062	219.88	
2:1 Copolymer #2	0.0357	6.462	220.54	220.14±0.35
2:1 Copolymer #3	0.0362	6.568	220.01	
1:1 Copolymer #1	0.0456	6.734	270.32	
1:1 Copolymer #2	0.0423	6.274	269.14	269.66±0.60
1:1 Copolymer #3	0.0437	6.472	269.53	

The COOH equivalent weights were also calculated from ^1H NMR spectra according to the integrals COOH protons and aromatic protons. The results are listed in Table 10.2.¹ For different molecular weights of **P1-COOH**, the COOH equivalent weights calculated from ^1H NMR spectra agree very well with the results obtained for titration.

Table 10.2 The COOH equivalent weights of branched polyesters calculated from titration and ^1H NMR Spectra

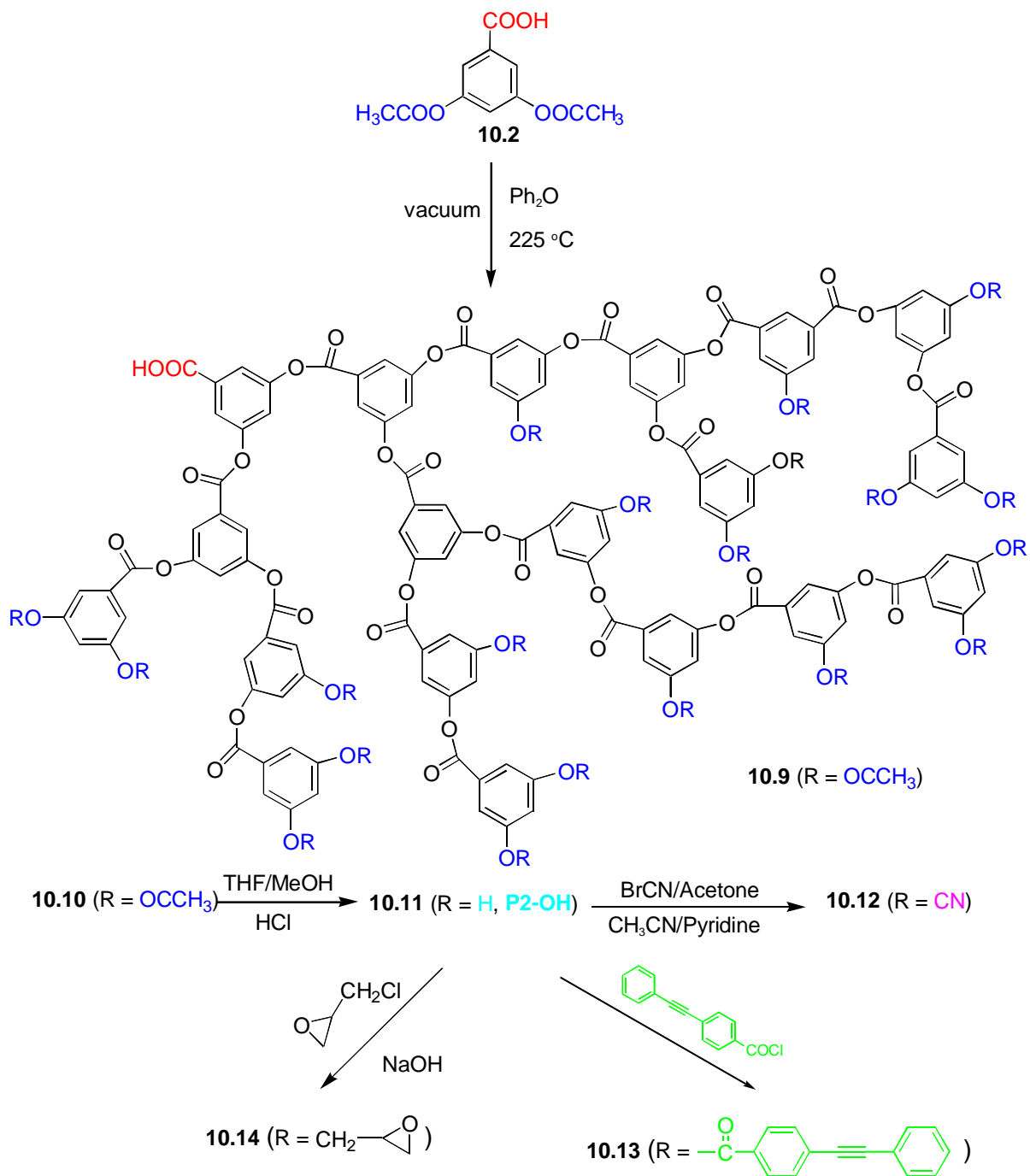
Sample	Titration (g/eq)	^1H NMR (g/eq)	M_n (kg/mol) (GPC)
P1-COOH (LMW)	142.33±0.66	145	1.33
P1-COOH (MMW)	156.07±0.20	156	3.05
P1-COOH (HMW)	160.53±0.70	167	10.50
2:1 Copolymer	220.14±0.35	238	3.48
1:1 Copolymer	269.66±0.60	262	5.04

E. Poly(3,5-diacetoxybenzoic acid) (10.10)

Poly(3,5-diacetoxybenzoic acid) (**10.10**) was synthesized by thermal polymerization in diphenyl ether as shown in Scheme 8.6.¹⁰ The polymerization was carried out at 225 °C for 60 minutes under argon. The temperature was then lowered to 180 °C to prevent evaporation of diphenyl ether at higher temperature under vacuum. Then, vacuum was applied to the system for 60 minutes to remove the condensation product, acetic acid. Purification was done by reprecipitation from THF into MeOH twice to remove the remaining diphenyl ether. The ^1H NMR spectrum (Figure 10.7) of this hyperbranched polymer showed methyl signals of the acetoxy groups at 2.10-2.40 ppm and very little COOH signal at about 13 ppm, which may

indicate that high molecular weight polymer was obtained. The TOSY spectrum (Figure 10.8) of the aromatic region showed 5 different kinds of protons (5 pairs of crosspeaks observed). The degree of branching could not be calculated according to this spectrum due to the overlapping of the peaks. The GPC trace (Figure 10.9, absolute MW, NMP, 60 °C) of **10.10** showed a very broad molecular weight distribution. The M_n and M_w calculated according to the universal calibration were 36.6 kg/mol and 707.5 kg/mol, with a polydispersity of 19.3. Functionalizations of this hyperbranched polymer were done by hydrolysis of the acetoxy groups to phenol groups, followed by further chemical modifications (Scheme 10.6).

Scheme 10.6



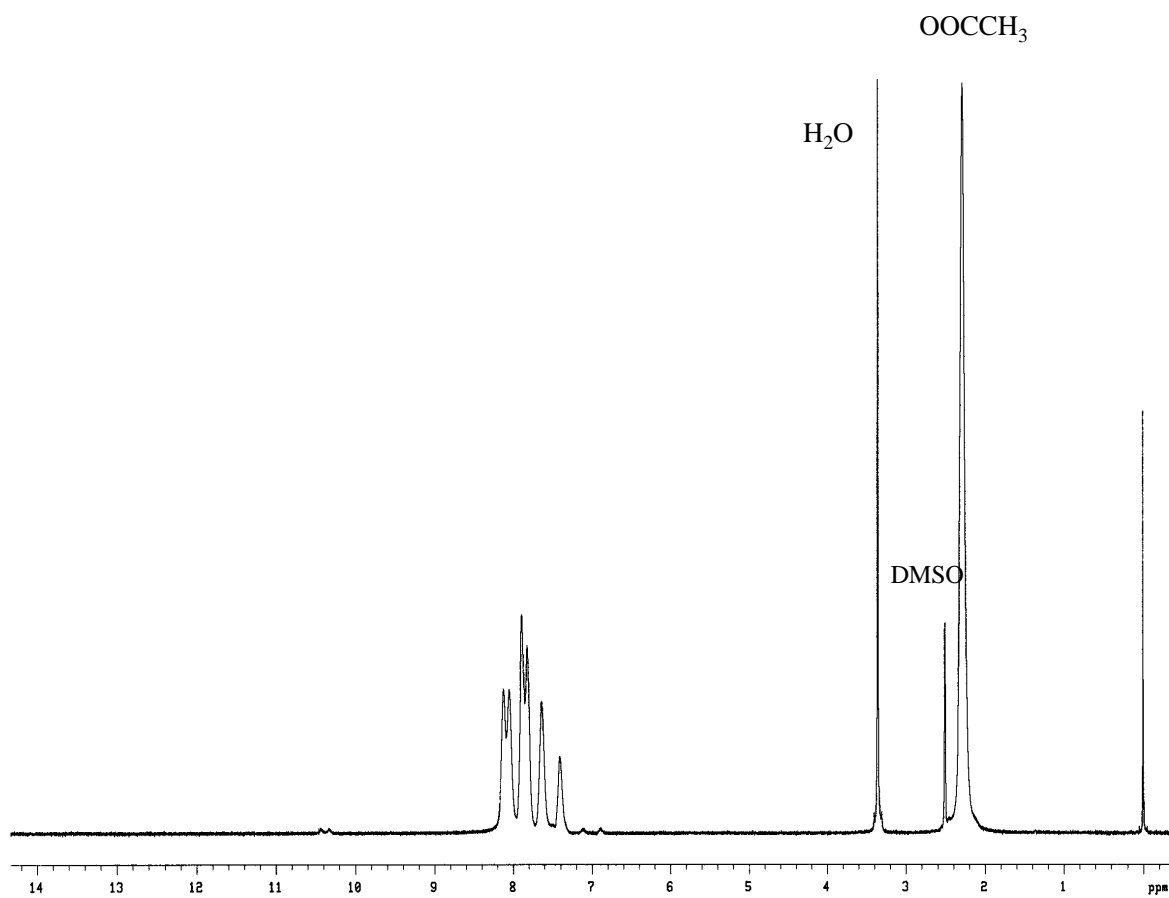


Figure 10.7 400 MHz ^1H NMR spectrum of polymer **10.10** in DMSO-d_6 .

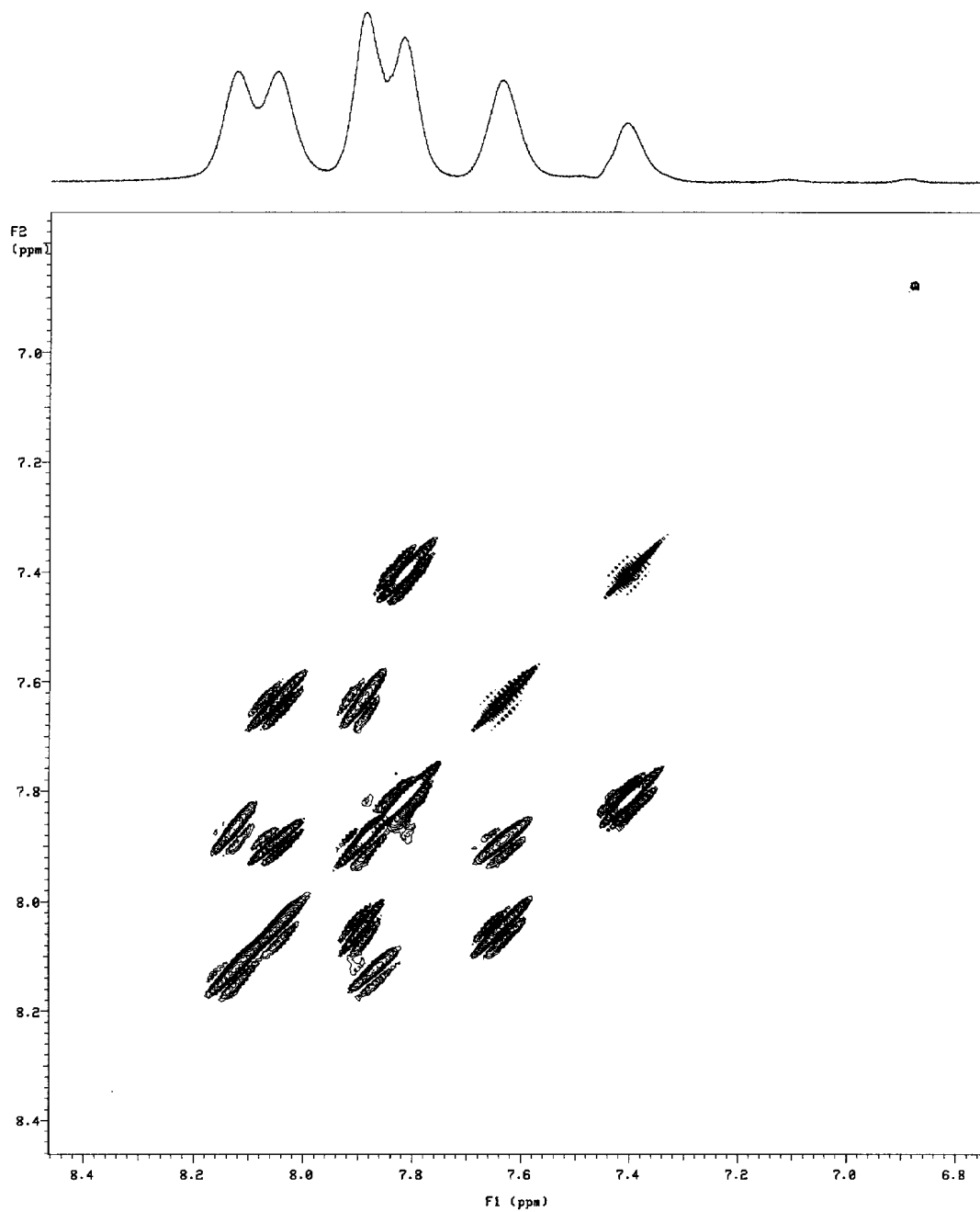


Figure 10.8 400 MHz TOSY spectrum of polymer **10.10** in DMSO-d₆.

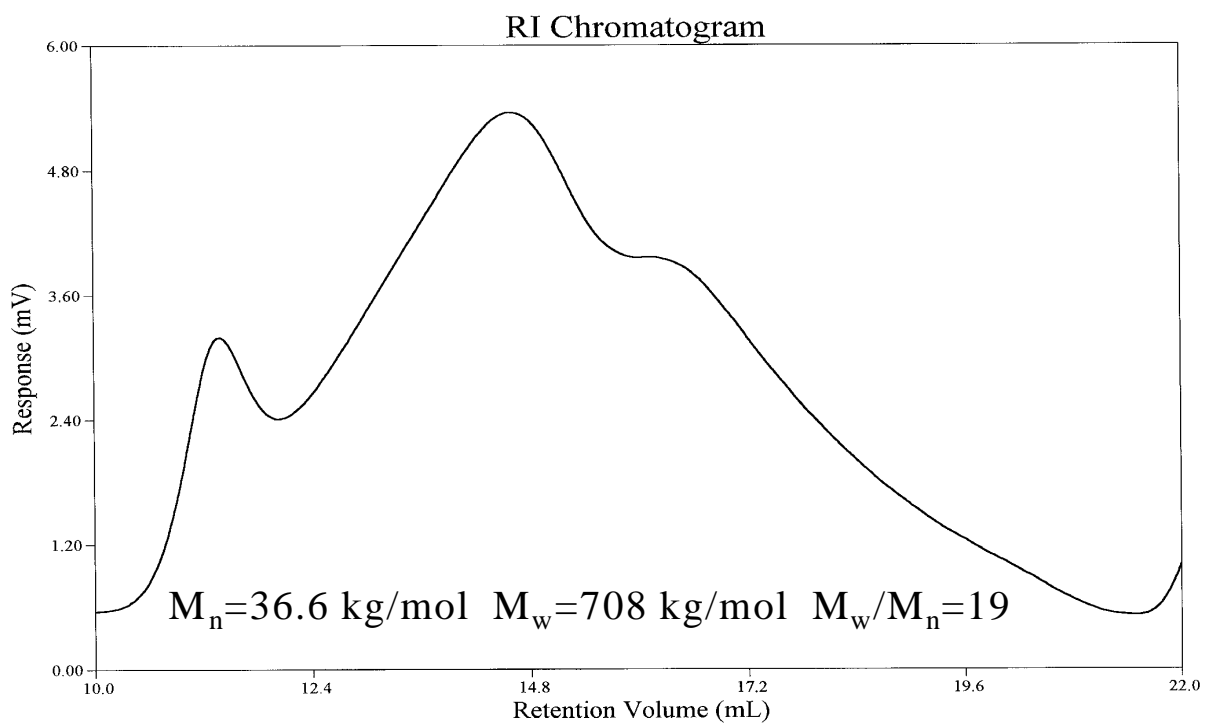


Figure 10.9 GPC trace of polymer **10.10** (NMP, 60 °C, 1 mL/min, RI detector).

10.2.3 Functionalization of Hyperbranched Poly(arylene ester)s

A. Preparation of Ethyl Ester of P1-COOH (10.6)

The ethyl esters (**10.6**) of **P1-COOH** (HMW, MMW, LMW) were prepared from the acid chloride (**10.5**) and ethanol using pyridine as base (Scheme 10.4). Light tan polymer products (**10.6**) were obtained. The ^1H NMR spectra of these ethyl ester functionalized hyperbranched poly(arylene ester)s show two signals in the aliphatic region corresponding to the ethyl groups. However, all the peaks in the aromatic region were very broad and they can not be used to calculate the degree of branching. The carboxylic acid terminated copolyesters **10.8a-b** were also converted to the corresponding ethyl esters (**10.9a-b**). The molecular weights and IV values of these polymers measured by GPC are listed in Table 10.3.

Table 10.3 The Molecular Weight Data for Ethyl Esters of Polyesters
(NMP, 60 °C, 1 mL/min, DV detector)

Polymer	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	IV (dL/g)
10.6 (HMW)	10.50	106.7	10.2	0.115
10.6 (MMW)	3.05	6.16	2.02	0.0574
10.6 (LMW)	1.33	3.33	2.50	0.0419
10.9a (AB ₂ :AB/2:1)	3.48	10.20	2.93	0.0591
10.9b (AB ₂ :AB/1:1)	5.04	11.80	2.31	0.0731

B. Vinyl functionalization of P1-COOH Using 2-Hydroxyethylmethacrylate (10.7)

Vinyl functionalization of **P1-COOH** (HMW) was done by conversion of the carboxylic groups into acid chloride groups **10.5** with thionyl chloride, followed by addition of 2-hydroxyethyl methacrylate using pyridine as base (Scheme 10.4). The excess of 2-hydroxyethyl methacrylate was removed by twice precipitation from THF into H₂O. The ¹H NMR spectrum (Figure 10.10) of **10.7** agreed well the structure. Very small COOH signals were observed in the ¹H NMR spectrum, which indicated the high conversion of the carboxylic acid groups to the vinyl ester groups. This vinyl functionalized hyperbranched polymer (**10.7**) is very soluble in vinyl monomers, such as styrene, methyl methacrylate (MMA) and acrylate monomers, and can be copolymerized with these vinyl monomers.

C. Hydrolysis of Poly(3,5-diacetoxybenzoic acid) (10.10) to Phenolic Terminal Polymer 10.11 (P2-OH)

In order to achieve functionalization of **10.10**, the acetoxy groups were converted to phenol groups by acid hydrolysis in THF and methanol (Scheme 10.6). The ¹H NMR spectrum of **10.11** shows residual signals for acetoxy groups at about 2.3 ppm and two phenolic signals at about 10.4 ppm and 9.8 ppm. The degree of hydrolysis was calculated as 99% according to the integrals of the acetoxy protons versus those of the phenolic protons.

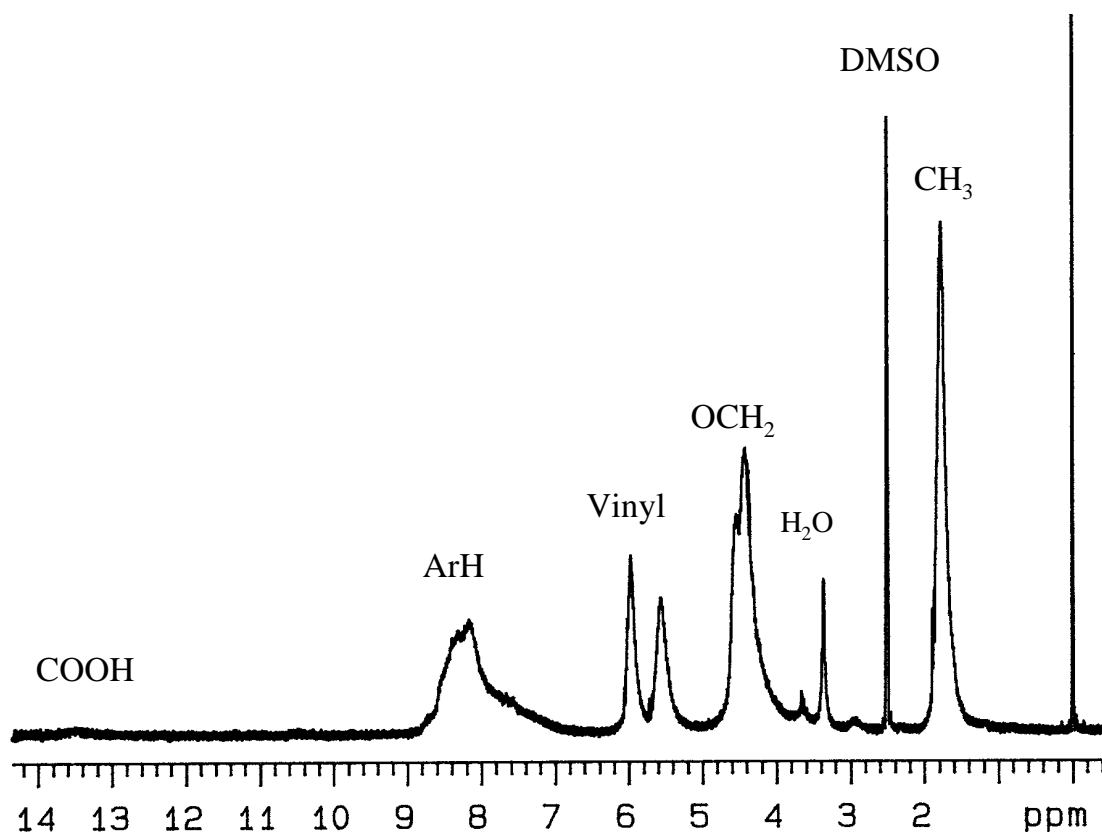


Figure 10.10 400 MHz ^1H NMR spectrum of polymer **10.7** in DMSO-d_6 .

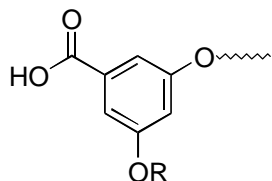
D. Degree of Branching

As discussed in Chapter 7, four different types of subunits may be present in the hyperbranched polymer structure: the unique focal point **10.15**, which has one carboxylic acid group for each molecule unless cyclization has occurred; the dendritic unit **10.16**, which has no phenolic groups; the linear unit **10.17**, which has only one phenolic group; and the terminal unit **10.18**, which has two phenolic groups. The degree of branching¹¹ is defined as

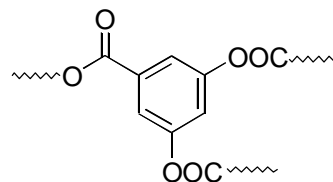
¹¹ Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, 113, 4583.

$$\text{DB (\%)} = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{(\text{total number of units})} \times 100 \quad (1)$$

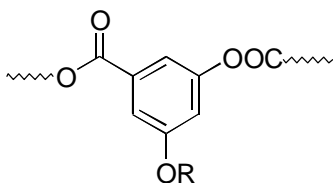
For a perfect linear molecule, the DB would be 0; and for a perfect dendritic molecule, the DB would be 100%. In all cases, DB is between 0 and 100%.



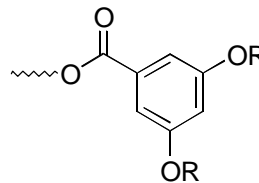
10.15: R = H or COAr~~~~
focal point



10.16
dendritic unit



10.17: R = H
linear unit



10.18: R = H
terminal unit

For hyperbranched polymer **10.11**, the TOSY spectrum (Figure 10.11) of the aromatic protons revealed three different kinds of protons, corresponding to the dendritic, the linear and the terminal protons. According to the integrals of the three different protons, the degree of branching calculated for **10.11** using equation (1) was 55.4% (Figure 10.12).

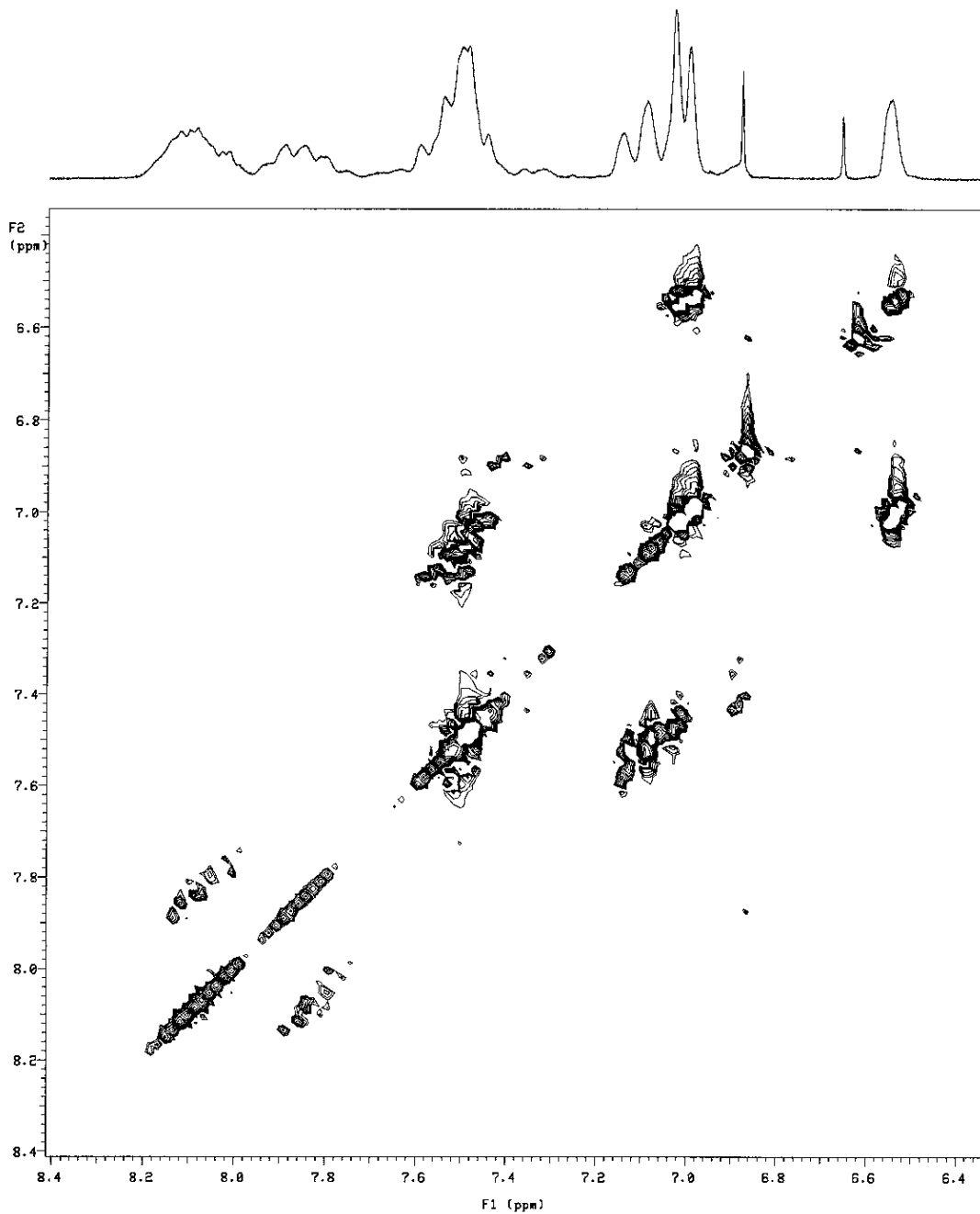


Figure 10.11 400 MHz TOSY spectrum of polymer **10.11** in DMSO-d₆.

$$\text{DB (\%)} = \frac{\text{Terminal} + \text{Dendritic}}{\text{Terminal} + \text{Dendritic} + \text{Linear}}$$

$$\text{DB (\%)} = \frac{32.78 + 35.87}{32.78 + 55.18 + 35.87} = 55.4\%$$

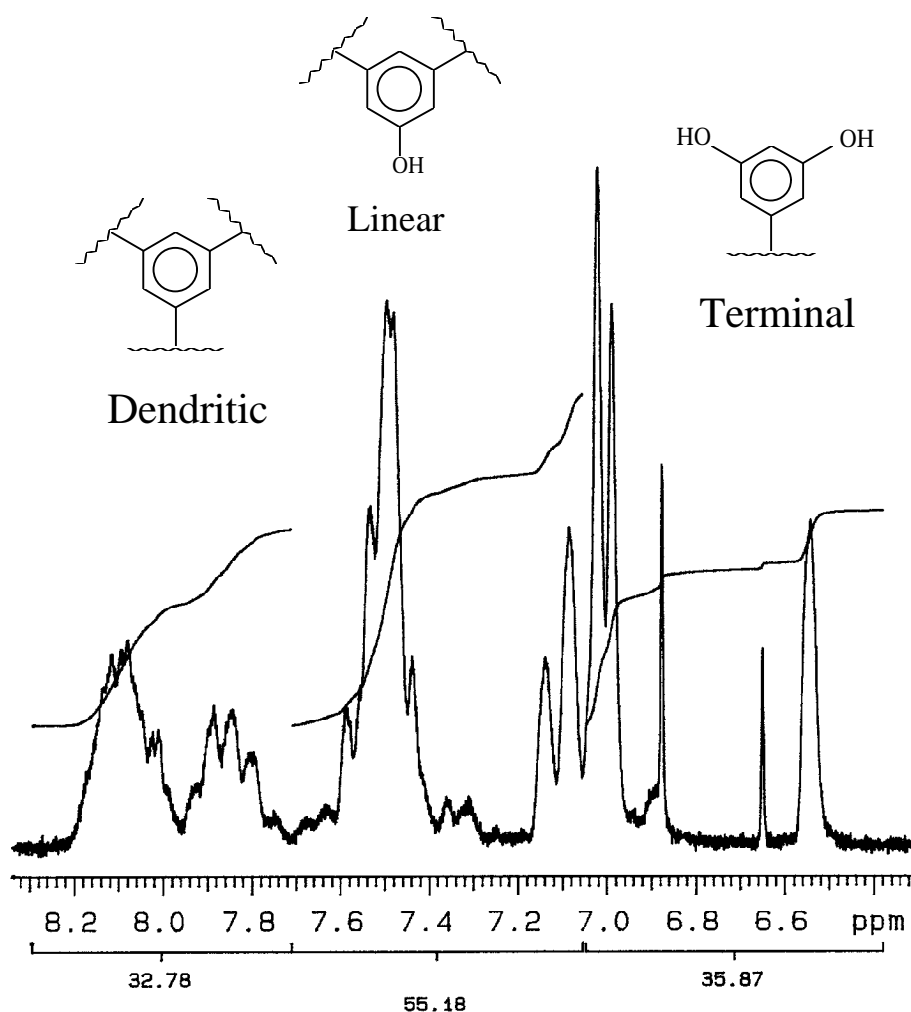


Figure 10.12 400 MHz ¹H NMR spectrum (aromatic region) of polymer **10.11** in DMSO-d₆.

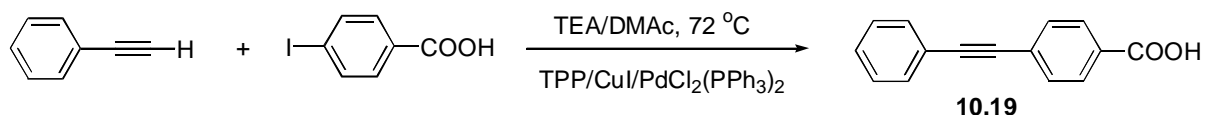
E. Attempted Cyanate Functionalization of P2-OH (10.12)

The cyanate functionalization of **10.11** was attempted with cyanogen bromide in THF and acetonitrile at room temperature (Scheme 10.6). A dark brown solid suspension was observed. No precipitation was observed when the mixture was poured into water.

F. Phenylethynyl Functionalization of 10.11 (10.13)

4-Phenylethynylbenzoic acid (**10.19**) was synthesized directly from 4-iodobenzoic acid and phenylacetylene using $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI as catalysts (Scheme 10.7).¹³ DMAc and triethylamine were used as solvents to enhance the solubility of the product **10.19**. The ^1H NMR (Figure 10.13), ^{13}C NMR (Figure 10.14) and COSY (Figure 10.15) spectra agree well with the structure of **10.19**. The yield was 87 %.

Scheme 10.7



The phenylethynyl functionalization of **10.11** was carried out in the similar fashion as polymer **10.7** (Scheme 10.4). 4-Phenylethynylbenzoic acid (**10.19**) was converted to the corresponding acid chloride with excess of thionyl chloride and then reacted with **10.11**. The functionalized polymer **10.13** precipitated out of the THF solution. The product was insoluble in hot DMSO, DMAc and NMP. One possible way to solve this problem is to use partially hydrolyzed **10.11** to react with the acid chloride of 4-phenylethynylbenzoic acid.

¹³ Stephens, C. *J. Org. Chem.* **1963**, 28, 3313.

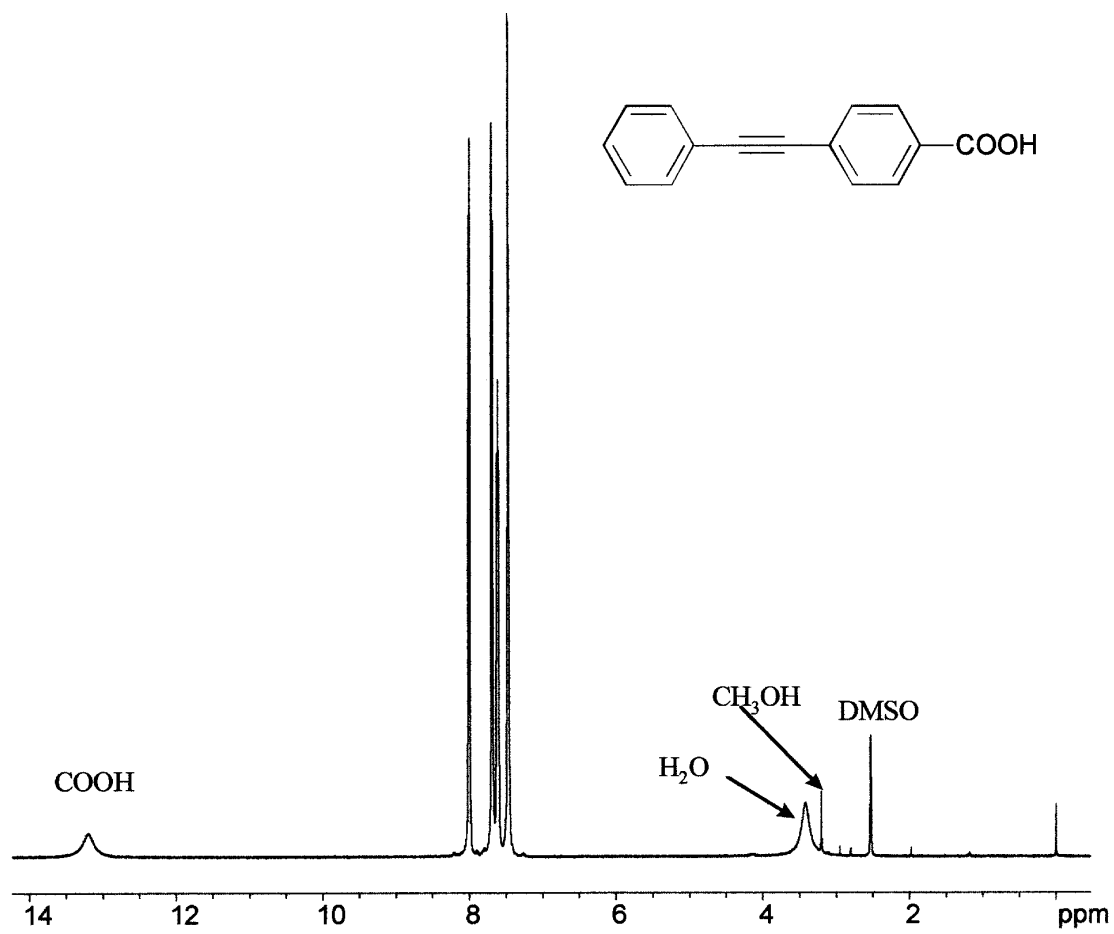


Figure 10.13 400 MHz ^1H NMR spectrum of compound **10.19** in DMSO-d_6 .

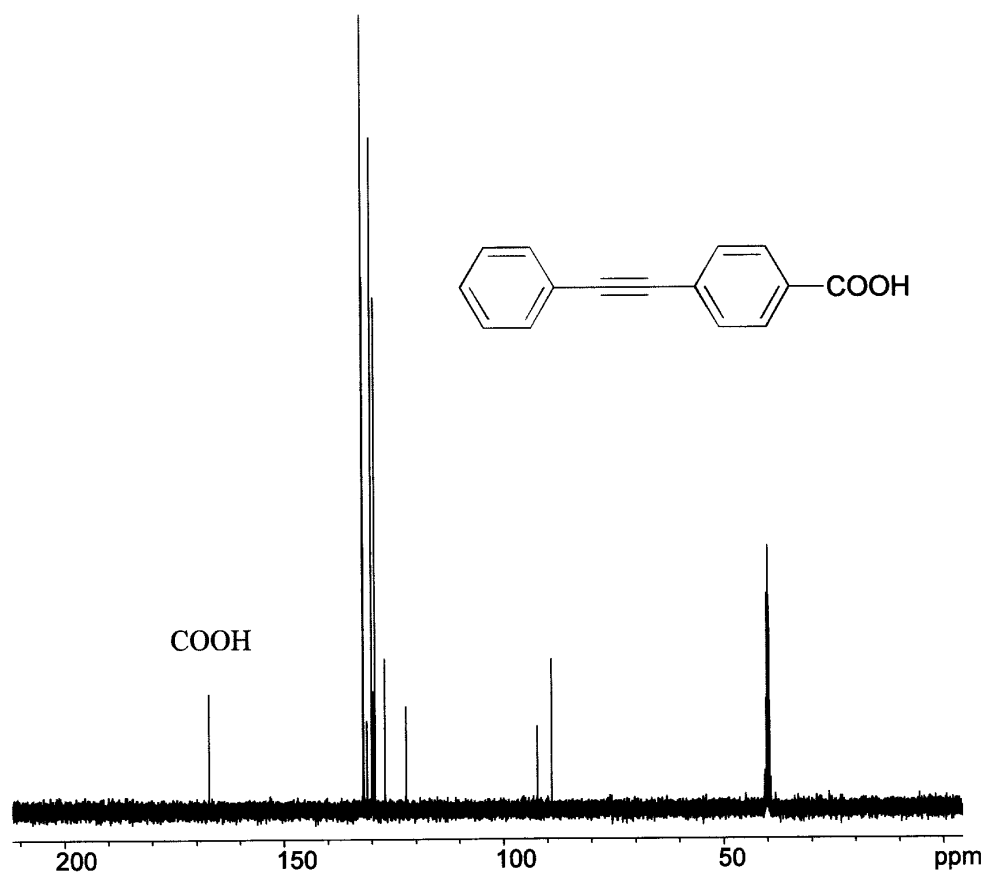
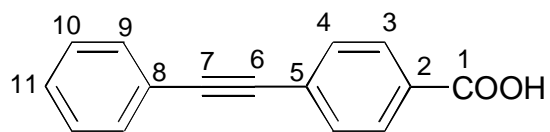


Figure 10.14 100 MHz ^{13}C NMR spectrum of compound **10.19** in DMSO-d_6 .



10.19

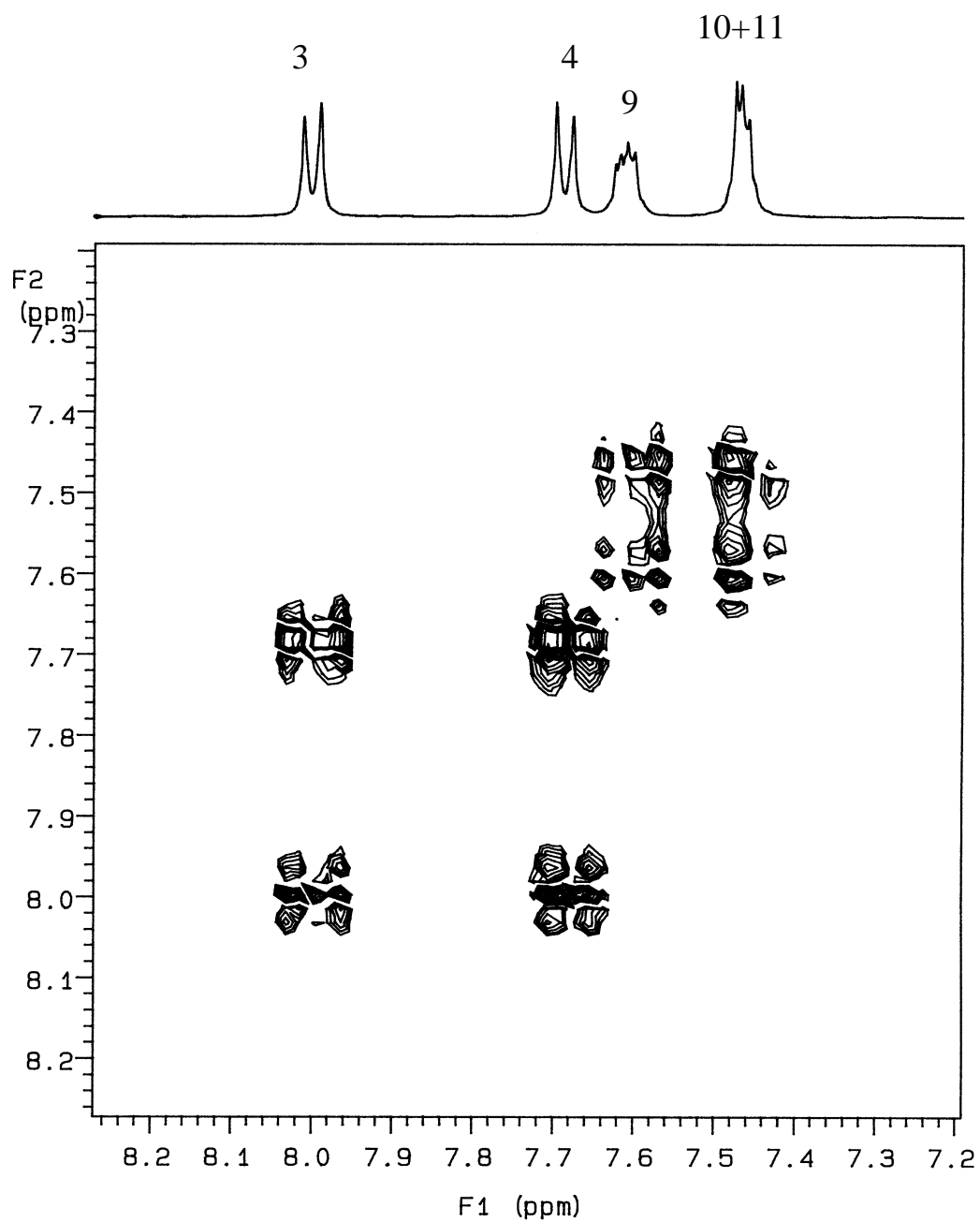


Figure 10.15 400 MHz COSY spectrum of compound **10.19** in DMSO-d₆.

G. Attempted Epoxy Functionalization of P2-OH (10.13)

In order to obtain the epoxy functionalized hyperbranched polymer, an approach was attempted by reacting the phenolic terminated polymer **10.11** with strong base, NaH, to form the sodium salt of phenolate and then reacting it with excess epichlorohydrin (Scheme 10.6). The sodium salt of the phenolic terminated polymer was expected to be insoluble in THF, but the epoxy functionalized hyperbranched polymer **10.13** should be very soluble in THF. The product was insoluble in common organic solvents such as hot DMSO, DMAc and NMP, which indicated the formation of polymeric network. A possible reason for this is the solubility of the sodium salt of **10.11** that caused the incomplete reaction between NaH and the hydroxy groups of **10.11**. Other possible reasons are the reaction conditions such as the reaction temperature and the reaction time.

10.3 Summary and Conclusions

Carboxylic terminated hyperbranched poly(arylene ester) **10.4** was synthesized by thermal polymerization of 5-acetoxyisophthalic acid (**10.1**). Different molecular weights of **P1-COOH (10.4)** were synthesized by controlling the reaction time and duration of the reaction under vacuum. Carboxylic acid terminated hyperbranched copolyesters **10.8a-b** were also synthesized by copolymerization of 5-acetoxyisophthalic acid (**10.1**) (AB₂ monomer) and 3-hydroxybenzoic acid (**8.3**) (AB monomer) using different molar ratios of two monomers. The carboxylic acid equivalent weights were estimated by titration and ¹H NMR spectroscopy and functionalized with different reactive groups. Functionalization of **P1-COOH** was done by reaction with thionyl chloride and then with alcohols bearing different reactive groups.

Phenolic terminated hyperbranched poly(arylene ester) **10.11** was synthesized by thermal polymerization of 3,5-diacetoxybenzoic acid (**10.2**) followed by acid hydrolysis. The degree of branching of this hyperbranched polymer was calculated as 55.4% according to the ^1H NMR and TOSY spectra. The phenolic terminated hyperbranched polyester **10.11** was functionalized with phenylethynyl groups.

10.4 Experimental Section

Materials and Instrumentation

Reagent grade reagents and solvents were used as received from chemical suppliers. Melting points were determined using a Haake-Buchler apparatus and are corrected. The proton NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 399.95 MHz and reported in δ units. Tetramethylsilane was used as the internal standard. All ^1H COSY (CORrelated SpectroscopY) spectra were obtained using a 16-step phase cycle. The spectral window was centered. A 90° pulse (177.5 μs) was used for both dimensions (F_1 and F_2); 128 increments of 512 point FID's (acquisition time 247 ms) with 16 scans were accumulated. Zerofilling, multiplication by sine window function, Fourier transformation and symmetrization were applied. The ^{13}C NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 100.60 MHz. Spectra were proton-decoupled and recorded in deuteriochloroform (76.9) as solvent and internal standard. FTIR spectra were recorded on a Nicolet MX-1 with KBr pellets. GPC analyses were done with a Waters 150C ALC/GPC system with permagel 10^2 - 10^6 Angstrom polystyrene-divinylbenzene columns. This instrument was equipped with a Viscotek 100 differential viscometer and differential refractive

index detectors. The viscometric data by the universal calibration yielded absolute molecular weights. Thermogravimetric analyses were carried out on a Perkin-Elmer 7700 thermal analysis system at a heating rate of 10 °C/min. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-4 at a scan rate of 10 °C/min in a nitrogen atmosphere.

Synthesis of 5-Acetoxyisophthalic Acid (10.1)⁹

To a 500 mL round bottom flask were added 5-hydroxyisophthalic acid (52.93 g, 0.2906 mol) and acetic anhydride (201.4 g, 1.970 mol). The mixture was heated at reflux and 5-acetoxyisophthalic acid dissolved during the heating. The reflux was continued for 11 h. The excess of acetic anhydride and the condensation product, acetic acid, were removed by a rotary evaporator to give a brown oil, which solidified upon adding distilled water. The white solid was filtered and washed with distilled water. It was recrystallized from THF/CHCl₃ to give white crystals, which were filtered and dried in a vacuum oven at 80 °C for 24 h, 44.18 g (85%), mp: 245 °C (monomer starts to polymerize at this temperature, lit.⁹: 235 °C) ¹H NMR (DMSO-d₆) δ 13.09 (br, H-7, 2 H), 8.36 (t, *J* = 1.6 Hz, H-6, 1 H), 7.91 (d, *J* = 1.6 Hz, H-4, 2 H), 2.31 (s, H-1, 3 H). ¹³C NMR (DMSO-d₆) d 169.58 (C-2), 166.28 (C-7), 151.10 (C-3), 133.14 (C-5), 127.63 (C-6), 127.27 (C-4), 21.25 (C-1). The ¹H-¹³C HETCOR spectrum showed two cross peaks due to the coupling of H-4 with C-4, and H-6 with C-6.

Large Scale Synthesis of 5-Acetoxyisophthalic Acid (10.1)

To a 1 L round bottom flask were added 5-hydroxyisophthalic acid (273.20 g, 1.500 mol) and acetic anhydride (306.27 g, 3.000 mol). The mixture was heated up and mechanically stirred. More acetic anhydride (150 mL) was added to the flask to prevent overheating. The mixture became homogenous after 1 hour. Some product started to precipitate out of the solution after 1/2 hour. The mixture was refluxed for another 13 h and allowed to cool to room temperature. The white solid was filtered and washed with water. Some more product which precipitated out of the filtrate was filtered and collected. The product was dried in a vacuum oven at 95 °C to remove the water and acetic acid. The total weight of the product was 309.35 g (93%).

Synthesis of 3,5-Diacetoxybenzoic Acid (10.2)¹⁰

A mixture of 3, 5-dihydroxybenzoic acid (77.06 g, 0.5000 mol) and acetic anhydride (200 mL, 2.12 mol) was heated at reflux for 11 h to give a brown solution with a small amount of solid suspension. Excess acetic anhydride and acetic acid were removed by a rotary evaporator to give a brown oil which solidified after 20 minutes. It was dried in a vacuum oven at 65 °C for 26 h. The ¹H NMR spectrum (DMSO-d₆) of this crude product showed no 3,5-dihydroxybenzoic acid. It was dissolved in 250 mL of hot CHCl₃ and the insoluble solid residue was removed by filtration. Petroleum ether (50 mL, bp 40-65 °C) was added to the solution and it was recrystallized overnight to give a fine white powder, 53.94 g (45%). It recrystallized from CHCl₃ and pet. ether again and dried in a vacuum oven at 50 °C for 36 h, 38.72 g, mp: 160.5-162.5 °C (lit.¹⁰: 157-159 °C). ¹H NMR (DMSO-d₆) δ 13.36 (br,

H-7, 1 H), 7.59 (d, $J = 2.4$ Hz, H-5, 2 H), 7.29 (t, $J = 2.4$ Hz, H-4, 1 H), 2.30 (s, H-1, 6 H). ^{13}C NMR (DMSO- d_6) δ 169.37 (C-2), 166.25 (C-7), 151.37 (C-3), 133.37 (C-6), 120.83 (C-4), 120.66 (C-5), 21.18 (C-1). The ^1H - ^{13}C HETCOR spectrum showed two cross peaks due to the coupling of H-4 with C-4, and H-6 with C-6. The gray solid recovered from the filtrate was recrystallized from CHCl_3 /ligrion (60-80 °C) to give 58.32 g of product (81% total) with melting point of 160.0-162.5 °C.

Large Scale Synthesis of 3, 5-Diacetoxybenzoic Acid (10.2)

3,5-Dihydroxybenzoic acid (231.18 g, 1.500 mol) and acetic anhydride (565.0 mL, 5.977 mol) were added to a 2 L three-necked round bottom flask. The mixture was heated at reflux for 12 h to give a brown solution with a small amount of solid suspended. It was allowed to cool to room temperature and some product precipitated as white powder. The mixture was transferred to a 1 L round bottom flask and the solvents were removed by a rotary evaporator. The brown gummy material was dried in a vacuum oven at 80 °C for 48 hours. The ^1H NMR spectrum (DMSO- d_6) of this crude product showed no starting 3,5-dihydroxybenzoic acid. It was dissolved in CHCl_3 and the small amount of suspended solid was filtered out. Upon removing the solvent, it was dried under vacuum at 95 °C for 36 hours, 339.44 g (95%), mp: 159.8-162.3 °C (lit.¹⁰: 157-159 °C).

Synthesis of 3-Acetoxybenzoic Acid (10.3)¹⁰

To a 250 mL round bottom flask were added 3-hydroxybenzoic acid (27.62 g, 0.200 mol) and acetic anhydride (40.81 g, 0.400 mol). The mixture was heated at reflux for 5 h.

Upon cooling the white product solidified. Distilled water (150 mL) was added to the flask and the product (**10.3**) was filtered and washed with water, 35.41 g (98%), mp: 127-129.9 °C (lit.¹⁰: 128-129.5 °C). . ¹H NMR (DMSO-d₆) δ 7.84 (m, 1 H, H-6), 7.66 (m, 1 H, H-8), 7.56 (m, 1 H, H-5), 7.40 (m, 1 H, H-4), 2.29 (s, 3 H, H-1). ¹³C NMR (DMSO-d₆) δ 169.68 (C-1), 166.98 (C-9), 150.94 (C), 133.74 (C), 130.30 (CH), 127.09 (CH), 126.84 (CH), 123.11 (CH), 21.30 (CH₃).

Synthesis of Poly(5-acetoxyisophthalic Acid) (10.4, P1-COOH)⁹

First a salt bath of 10 g potassium nitrate per 8.5 g of sodium nitrite was prepared. The salt bath was preheated to 260 °C. The rotary evaporator was connected to a vacuum pump and an argon inlet. The water bath was removed. 5-Acetoxyisophthalic acid monomer (13.00 g) was placed in a 250 mL round bottom flask which was connected to the rotary evaporator. Argon was allowed to flow through the system for 10 minutes. The flask was lowered into the hot salt bath with the rotary evaporator set to the maximum. speed. The temperature remained at about 255 °C through out the polymerization period. The argon was allowed to flow through the system for first 30 minutes. It was disconnected and vacuum was applied to the system to remove the condensation product, acetic acid, for 1 hour. The vacuum was disconnected and the foamy material was allowed to cooled to room temperature under argon. The brittle foam was crushed and heated at reflux in 115 mL of THF and 10 mL of distilled water until it was all dissolved (to cleave the anhydride formed during polymerization). It was precipitated into 700 mL of distilled water using a high-speed blender. The white precipitate was filtered and washed with water, and dried in a vacuum

oven at 95 °C for 24 h, 8.94 g (94%). ¹H NMR spectrum (DMSO-d₆) δ 14.2-13.0 (br, COOH), 8.8-7.4 (br, ArH), 2.32 (terminal CH₃).

Synthesis of P1-COOH (8.4, HMW)

The procedural details were the same as above. Compound **10.1** (20.00 g, 90.02 mmol) was polymerized under argon for 30 minutes and then vacuum was applied to the system for 60 minutes. The foamy material was crushed and heated at reflux in 150 mL THF and 10 mL of water until all solid was dissolved. Solvents (THF and H₂O) were removed via rotary evaporation and the product was dried in a vacuum oven at 95 °C for 24 hours, 14.39 g. It was soluble in THF upon refluxing.

Synthesis of P1-COOH (10.4, MMW)

The procedural details were about the same as above. Compound **10.1** (20.00 g, 90.02 mmol) was polymerized under argon for 20 minutes and then vacuum was applied to the system for 10 minutes. The foamy material was crushed and heated at reflux in 150 mL THF and 10 mL of water until all the solid dissolved. Solvents (THF and H₂O) were removed via rotary evaporation and the product was dried in a vacuum oven at 95 °C for 24 hours, 14.13 g. It was soluble in THF upon heating.

Synthesis of P1-COOH (10.4, LMW)

The procedural details were about the same as above. Compound **10.1** (20.00 g, 90.02 mmol) was polymerized under argon for 30 minutes and no vacuum was applied to the system. The foamy material was crushed and heated at reflux in 150 mL THF and 10 mL of water until all the solid dissolved. Solvents (THF and H₂O) were removed via rotary

evaporation and the product was dried in a vacuum oven at 95 °C for 24 hours, 14.12 g. It was soluble in THF upon refluxing.

Synthesis of Hyperbranched 2:1 Copolyester (10.8a)

The procedural details were about the same as above. Compound **10.1** (13.45 g, 60.0 mmol, AB₂ monomer) was copolymerized with **10.3** (5.40 g, 30.0 mmol, AB monomer) under argon for 20 minutes and then vacuum was applied to the system for 30 minutes. The foamy material was crushed and heated at reflux in 150 mL THF and 10 mL of water until all the solid dissolved. Some solvents (THF and H₂O) were removed via rotary evaporation and the product was dried in a vacuum oven at 110 °C for 40 hours, 13.29 g. It was soluble in THF upon refluxing.

Synthesis of Hyperbranched 1:1 Copolyester (10.8a)

The procedural details were about the same as above. Compound **10.1** (11.12 g, 50.0 mmol, AB₂ monomer) was copolymerized with compound **10.3** (9.10 g, 50.0 mmol, AB monomer) under argon for 20 minutes and then vacuum was applied to the system for 30 minutes. The foamy material was crushed and heated at reflux in 150 mL THF and 10 mL of water until all the solid dissolved. Solvents (THF and H₂O) were removed via rotary evaporation and the product was dried in a vacuum oven at 110 °C for 40 hours, 12.97 g. It was soluble in THF upon refluxing.

Preparation of Acid Chloride of P1-COOH (10.5)

To a flame dried 250 mL round bottom flask were added **10.4** (2.00 g), 80 mL of dry THF, 2.30 mL of thionyl chloride and 3 drops of anhydrous DMF. The solution was heated at reflux for 8 hours. The solvent and excess of thionyl chloride were removed by rotary evaporation. The light yellow foamy material was redissolved in 50 mL of dry THF and stored under N₂. The next functionalization reaction was carried out immediately.

General Procedure for Potentiometric Titration

Potentiometric titrations were performed in McGrath's laboratory using the MCI Automatic Titrator Model GT-05 which employs microprocessor control and a built-in cathodes ray tube (CRT) screen.¹⁴ The titrator automatically allows for control of the titration, detection of the inflection points and appropriate calculation of the desired variable being measured. The commonly used titrant for polymers with phenolic or carboxylic groups is 0.025 N tetramethylammonium hydroxide (TMAH). A 0.025 N aqueous TMAH solution was prepared and standardized with potassium hydrogen phthalate (KHP) three times. The normality of the TMAH solution calculated from titration was 0.02505±0.00001N. Into a 100 mL beaker, a branched polyester sample (about 0.02-0.05 g) was accurately weighed and dissolved in 50 mL of THF. Distilled water (10 mL) was then added to the beaker. A clear solution was observed. The solution was then titrated with TMAH solution until the end point was observed.

¹⁴ Wnuk, A. J. Thesis, VPI&SU, **1978**.

Preparation of Ethyl Ester of P1-COOH (10.6)

The poly(acid chloride) (**10.5**) solution in THF was prepared as described above using 1.00 g of P1-COOH (**10.4**). A solution of 1.0 mL of ethanol and 1.0 mL of pyridine in 30 mL of dry THF was added dropwise to the poly(acid chloride) solution. The mixture was stirred for 10 hours and precipitated into aqueous NaCl solution. HCl was added to neutralize the excess pyridine. The light tan solid (**10.6**) was filtered and dried. ^1H NMR (DMSO- d_6) δ 1.34 (br, CH_3), 3.46 (br, CH_2), 6.80-8.64 (br, ArH).

Vinyl Functionalization of P1-COOH using 2-Hydroxyethyl Methacrylate (10.7)

A solution of 2-hydroxyethyl methacrylate (4.48 mL, 0.036 mol), 3.0 mL of anhydrous pyridine and 30 mL of dry THF was added to an addition funnel. It was added dropwise to stirring **10.5** (from **10.4**, 2.00 g, 0.012 mol)in THF solution under N_2 . A white precipitate was observed due to the formation of the insoluble pyridine salt. The mixture was stirred overnight (12 hours). Part of the solvent was removed by rotary evaporation and the remaining solution was precipitated into distilled water. The product was precipitated from THF into water to remove excess 2-hydroxyethyl methacrylate. It was then dried in a vacuum oven at room temperature for 60 hours, 2.77 g. ^1H NMR spectrum (DMSO- d_6) δ 8.8-7.4 (br, ArH), 6.17-5.78 (br, vinyl, 1 H), 5.78-5.36 (br, vinyl, 1 H), 4.66-4.07 (br, OCH_2 , 4 H), 1.88-1.45 (br, CH_3 , 3 H).

Synthesis of Poly(3, 5-diacetoxybenzoic acid) in Diphenyl Ether (10.10)¹⁰

3,5-Diacetoxybenzoic acid **10.2** (20.01 g) and diphenyl ether (30.00 g) were added to a 250 mL round bottom flask. The flask was flushed with N₂ for 15 minutes. The salt bath (same composition as above) was preheated to 240 °C. The flask was connected to a rotary evaporator and the system was flushed with argon for 10 min. The flask was lowered into the salt bath with the rotary evaporator set to the maximum speed. The temperature dropped to 225 °C and was maintained there for 60 minutes. The temperature was then lowered to 180 °C. Vacuum was applied to the system to remove acetic acid and diphenyl ether for 60 minutes. The flask was allowed to cool to room temperature under argon. The brittle foamy polymer was crushed and dissolved in hot THF and precipitated into MeOH. It was reprecipitated from THF into MeOH again to remove the diphenyl ether. It was dried at 81 °C for 24 h, 14.54 g (99%). ¹H NMR (DMSO-d₆) δ 7.6-8.4 (br, ArH), 2.10-2.40 (br, OCH₃). The GPC trace (NMP, 60°C) of this hyperbranched polymer showed a broad molecular weight distribution. The M_n and M_w calculated according to the universal calibration were 36.6 kg/mol and 707.5 kg/mol respectively.

Hydrolysis of 10.10 to Phenolic Terminal groups (10.11, P2-OH)¹⁰

To a 500 mL round bottom flask were added 2.00 g of polymer **10.10**, 300 mL of THF, 45 mL of MeOH and 1.5 mL of concentrated HCl. The mixture was heated at reflux for 18 hours. The solvents were removed by a rotary evaporator to give a light yellow solid. It was reprecipitated from THF into water twice and dried in a vacuum oven at 80 °C for 36 h, 1.62 g. ¹H NMR (DMSO-d₆) δ 10.5-10.3 (br, phenol), 9.9-9.7 (br, phenol), 8.22-7.65 (br,

dendritic protons), 7.63-7.38, 8.18-7.60 (br, linear protons), 7.06-6.50 (terminal protons), 2.38-2.18 (br, CH₃). The TOSY spectrum showed 3 different kinds of protons corresponding to the dendritic, terminal and linear protons.

Attempted Cyanate Functionalization of 10.11 (10.12)

To a flame dried 250 mL round bottom flask were added **10.11** (1.00 g) and 80 mL of acetone (HPLC grade). The polymer dissolved immediately under nitrogen. Cyanogen bromide (6.0 mL, 30.0 mmol, 0.5 M in acetonitrile) was added to the reaction flask. Pyridine (10.0 mL) was added dropwise to the stirring solution. The color of the solution changed to yellow, orange and then dark brown. The stirring was continued for 5 hours. A solid suspension was observed. However, no precipitation was obtained when it was poured into water.

Phenylethynyl Functionalization of 10.11 (10.13)

To a flame dried 250 mL round bottom flask equipped with a condenser and a nitrogen inlet, 4-phenylethynylbenzoic acid (1.787 g, 8.40 mmol) was dissolved in 80 mL of dry THF. Thionyl chloride (1.46 mL, 20.0 mmol) and two drops of anhydrous DMF were added to the flask. The solution was heated at reflux for 10 hours. It was allowed to cool to room temperature. The solvent and the excess of thionyl chloride were removed by rotary evaporation. The resulting light yellow solid was dissolved in 60 mL of dry THF. A solution of **P2-OH** (1.362 g, 10.00 mmol) in 40 mL dry THF and 1.02 mL of anhydrous pyridine was added dropwise to the acid chloride solution. Precipitation of a light yellow was observed

after a few drops of **P2-OH** solution were added. The stirring was continued for another 12 hours. The mixture was diluted with 600 mL of water and neutralized with HCl to remove excess pyridine. The light yellow solid was collected by suction filtration and washed with distilled water. It was dried in a vacuum oven at 95 °C for 36 hours, 2.67 g. The product was not soluble in hot NMP, DMSO and DMAc.

Attempted Epoxy Functionalization of 10.11 (10.14)

Into a flame dried 250 mL round bottom flask were added **10.11** (2.04 g, 15.0 mmol), NaH (0.66 g, 16.5 mmol, 60% in mineral oil) and 100 mL of dry THF. Hydrogen gas bubbling was observed. The stirring was continued for 30 minutes. Epichlorohydrin (20.82 g, 176.0 mmol) and tetraethylammonium bromide (0.0047 g, 0.023 mmol) were then added to the reaction flask and the mixture was refluxed under nitrogen for 12 hours. A yellow precipitate was observed. The yellow solid was insoluble in hot NMP, DMSO and DMAc.

Synthesis of 4-Phenylethynylbenzoic Acid (10.19)¹²

To a flame dried three neck 250 mL round bottom flask equipped with a reflux condenser, 4-iodobenzoic acid (6.20 g, 25.0 mmol), phenylacetylene (fresh distilled, 4.12 mL, 50.0 mmol) and triphenyl phosphine (0.065 g, 0.25 mmol) were added. The mixture was warmed to 40 °C. In the dark, PdCl₂(PPh₃)₂ (0.024 g, 3.4×10⁻⁵ mol) and triethylamine (15.0 mL) were added and the mixture was warmed up to 60 °C. Copper iodide (0.010 g, 5.3×10⁻⁵ mol), triethylamine (10 mL) and DMAc (25 mL) were added and the temperature was raised to about 70 °C. The reaction was carried out in the dark at about 70 °C for 12 h. The

mixture was cooled to room temperature, diluted with 100 mL of THF and the solvents were removed by rotary evaporation to give a brown oil which solidified after 10 min. The light gray solid was washed with methanol and a few drops of HCl, 3.10 g (87%), mp: 222.1-228.1 °C (lit. ¹² mp: 221-222 °C). ¹H NMR (DMSO-d₆) δ 13.20 (s, br, 1 H, H-1), 8.00 (d, *J* = 8.4 Hz, 2 H, H-3), 7.69 (d, *J* = 8.4 Hz, 2 H, H-4), 7.62 (m, 2 H, H-9), 7.47 (m, 3 H, H-10 and H-11). ¹³C NMR (DMSO-d₆) δ 167.13 (C-1), 131.97 (CH), 131.94 (CH), 130.99 (C), 129.99 (CH), 129.67 (C), 129.24 (CH), 127.03 (C), 122.22 (C), 92.39 (C), 89.02 (C-7).