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Hyperbranched Aromatic Polyesters with Carboxylic Acid Terminal Groups

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ABSTRACT: Melt condensation of 5-acetoxyisophthalic acid (1) and 5-(2-hydroxyethoxy)isophthalic acid (4) yielded hyperbranched aromatic polyesters with carboxylic acid terminal groups. The polymer of 1 has a T_g of 239 °C and thus required melt acidolysis polymerization temperatures of 240–260 °C to obtain M_ws in the 20 000 to 80 000 range. The polyester based on 4, with a lower T_g, was obtained at around 190 °C using standard polycondensation techniques. Comparisons of Mark–Houwink plots of these polyesters with linear polystyrene were consistent with the expected highly branched structures. NMR studies revealed the degree of branching to be about 50%, similar to what has been observed in other hyperbranched polyester systems. The hyperbranched polyesters were easily converted to the ammonium or sodium salts and the viscosity behavior of these water-soluble hyperbranched polyelectrolytes was investigated.

Introduction

Hyperbranched polymers are highly branched non-cross-linked polymers prepared by the condensation of A_xB monomers where x is generally 2 or 3. Such materials were described by Flory[1] in 1952, but only in recent years has purposeful synthesis and characterization of this class of polymers been undertaken. Consideration of these hyperbranched structures as "imperfect" dendrimers arising from a one-step polymerization, contrasted to the multistep syntheses described for dendrimers,[2–4] has stimulated much of this work. Numerous examples of hyperbranched polymers have been described,[5–11] including our description of the synthesis and characterization of all-aromatic polyesters with acetate or phenolic terminal groups.[12]

The preparation of dendritic and hyperbranched polymers with carboxylic acid terminal groups has been pursued vigorously. Such materials are in the size regime of micelles, and this similarity has been expressed by referring to these structures as unimolecular micelles.[5] In addition, the properties of the water-soluble salts of these dense molecules and their comparison to conventional linear polyelectrolytes is of interest.

Tomalia[2] reported a divergent growth method for the preparation of polyamidoamines with terminal carboxyl groups. Newkome et al. have reported a divergently grown carboxylic acid terminated polyamide[13] and a hydrocarbon core terminal acid structure[14] that has been given the trivial name of "micellanoic" acid. Fréchet et al. have used the convergent approach to prepare carboxylic acid terminated polyesters[15] and polyethers.[16] Kim and Webster[5] have prepared a carboxylic acid terminated all-aromatic hyperbranched polyphenylene by modification of the dibromoaryl hyperbranched polymer prepared from the condensation of (3,5-dibromophenyl)boronic acid. Kim[17] has also prepared hyperbranched aromatic polyamides with terminal carboxylic acid groups via intramolecular amine acid chloride condensations. We report here the synthesis, characterization, and some properties of hyperbranched polyesters based on the melt condensation of 5-acetoxyisophthalic acid and 5-(2-hydroxyethoxy)isophthalic acid. These melt condensations have the advantage of directly yielding hyperbranched polyesters with carboxylic acid end groups.

Experimental Section

General Procedures. All solvents were reagent grade unless otherwise indicated. 5-Hydroxyisophthalic acid was purchased from Aldrich. Other reagents were purchased from either Eastman Laboratory Chemicals or Aldrich. All products and intermediates were dried at 60 °C under house vacuum of about 30 Torr.

The polycondensations were carried out in a rotary evaporator at the highest possible rotation speed, using a salt bath, which was a mixture of potassium nitrate and sodium nitrite in the ratio of 10 g to 8.5 g, respectively, as the heat source. This method provides good heat transfer by maximizing the amount of polymer in contact with the flask surface. It also eliminates problems with removing mechanical stirrers from the solid polymers, which are brittle foams that fill the entire flask. The rotary evaporator and reaction flask were evacuated and flushed with argon twice before heat was applied.

Monomer Synthesis. 5-Acetoxyisophthalic Acid (1). 5-Hydroxyisophthalic acid (0.25 mol, 45.5 g) was heated in 102 g of acetic anhydride (Ac$_2$O) (1 mol) to reflux. The acid dissolved after about 0.5 h of reflux and the reflux was continued for 5 h. The excess Ac$_2$O was removed in vacuum and the crude white product was recrystallized twice from a chloroform/toluene mixture and yielded 48 g (86%) with a melting point of about 235 °C (compound starts to lose acetic acid and polymerize at this temperature). ^{1}H NMR (DMSO-d_6), δ in ppm: 2.25 (s, 3 H), 7.8 (s, 2 H), 8.2 (s, 1 H), 13.4 (br, 2 H, COOH).

Dimethyl 5-Hydroxyisophthalate (2). Anhydrous HCl (13 g, 0.356 mol) was bubbled into 700 mL of methanol in a 1000-mL round-bottomed 3-necked flask equipped with a stirrer and reflux condenser. 5-Hydroxyisophthalic acid (100 g, 0.55 mol) was added. A clear solution was obtained after 10 min. The mixture was heated to reflux to 2 h and then filtered hot. The product crystallized out of the solution overnight and was collected and washed carefully with water and dried. A white solid (104 g, 90%), mp 158–59 °C, was obtained. ^{1}H NMR (DMSO-d_6), δ in ppm: 3.8 (s, 6 H), 7.48 (M, 2 H), 7.87 (s, 1 H), 10.3 (b, 1 H).

Dimethyl 5-(2-Hydroxyethoxy)isophthalate (3). A pressure reactor was charged with 100 g of 2, 56 g (1.27 mol) of ethylene oxide, and 700 mL of 2-propanol and heated to 95 °C. The vessel

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was charged to 75 psi with nitrogen and the reaction was continued under stirring at 95 °C for 4 h. The pressure was released and the reaction mixture cooled to room temperature. 2-Propanol was removed by rotary evaporation. The crude mixture was purified by column chromatography (solvent: ethyl acetate: hexane:acetic acid 3:6:0.5). The yield was 64% with evidence of partial hydrolysis (methyl proton integration less than theoretical) of the ester during the reaction. ^{1}H NMR (DMSO-d_6), δ in ppm: 3.7 (2 H), 3.84 (COOMe, <6), 4.05 (2 H), 5.1 (OH, 1 H), 7.6 (2H), 8.0 (1 H).

5-(2-Hydroxyethoxy)isophthalic Acid (4). A reaction flask was charged with 20 g of **3** and 150 mL of THF. After the solid was dissolved, 7 g of sodium hydroxide dissolved in 100 mL of water was added. The mixture was refluxed for 72 h and then cooled to room temperature. The pH was adjusted with hydrochloric acid to 2–3 and then the solvent was partially removed. The product precipitated and was collected by filtration, washed with water, and dried. A white solid (9.6 g, 54%) was obtained, mp 170–75 °C dec. ^{1}H NMR (DMSO-d_6), δ in ppm: 3.7 (2 H), 4.05 (2 H), 4.9 (1 H), 7.65 (2 H), 8.05 (1 H), 13.2 (2 H).

3-(4-Acetoxyphenyl)propionic Acid (5). 3-(4-Hydroxyphenyl)propionic acid (50 g, 0.31 mol) and acetic anhydride (100 g, 0.98 mol) were brought to reflux in a 500-mL round-bottomed flask for 1 h. The mixture was cooled and 300 mL of cold toluene was added. A colorless solid was formed which was collected by filtration, washed several times with heptane, and dried. The yield was 46 g (73%), mp 95 °C. ^{1}H NMR (DMSO-d_6), δ in ppm: 2.2 (s, 3 H), 2.47 (t, 2 H), 2.75 (t, 2 H), 6.48, 6.50, 7.20, 7.22 (4 H), 12.1 (s, <1 H).

Polymerization. Polymerization of 5-Acetoxyisophthalic Acid (1) to P1. 5-Acetoxyisophthalic acid (1) (20 g, 0.089 mol) was charged into a 250-mL round-bottomed flask that was connected to a rotary evaporator as described above. The salt bath temperature was 250 °C and for the first 20 min a strong argon stream was passed through the system. Within 4 min an isotropic melt was obtained. After 20 min the argon was shut off and vacuum (5 × 10^{-3} Torr) was applied for another 20 min. During this time the polymer formed a brittle foam filling the flask entirely. The foam was crushed and a mixture of 100 mL of THF/10 mL water was added. The water was necessary to cleave the anhydride bonds that form during the polymerization. The mixture was heated to reflux until a homogeneous solution was obtained (4 h). The polymer was then precipitated from water, collected, dried, taken up in hot THF, and reprecipitated from ether. The solid polymer (14.1 g, 96%) was slightly cream colored to colorless. ^{1}H NMR (DMSO-d_6), δ in ppm: 7–9 (br, Ar H), 13.4 (br, COOH).

Polymerization of 5-Acetoxyisophthalic Acid (1) to P1 in a Nonreactive Diluent. A 100-mL round-bottomed flask was charged with **1** (2.85 g, 0.0127 mol) and 2.85 g of phenyl sulfone. The mixture was stirred for 40 min at 250 °C while a slow argon stream was applied. After about 20 min a precipitate was observed that increased in volume with time. Then a vacuum of 4.5 × 10^{-2} Torr was applied for 3 h which removed the phenyl sulfone. The resulting solid was heated to reflux in THF/water (50 mL/5 mL) and the precipitated into 500 mL of hot toluene and dried. The yield of solid polymer was 1.88 g (90%). The ^{1}H NMR spectrum was identical to that from the polycondensation of neat **1** and no residual phenyl sulfone was detected.

Polymerization of 5-(2-Hydroxyethoxy)isophthalic Acid (4) to P2. A 50-mL round-bottomed flask was charged with 3 g (0.013 mol) of **4** and purged on the rotary evaporator as described above. The solid was heated to 190 °C under an argon stream and after 3 min an isotropic melt was obtained. Dibutyltin diacetate (3 drops) was added and the reaction was continued for 30 min. Vacuum (8 × 10^{-3} Torr) was applied to drive the condensation to higher conversion. The polymerization was continued for an additional 30 min with observation of brittle foam formation after approximately 10 min. The solid dissolved readily in hot THF and was recovered by precipitation into ether, yielding a cream-colored solid (2.5 g, 90.5%). ^{1}H NMR (DMSO-d_6), δ in ppm: 4.36 (b, 2 H), 4.52 (b, 2 H), 7.56 (b, 2 H), 7.94 (b, 1 H), 13.2 (b, 1 H).

Copolymerization of 1 and 3-(4-Acetoxyphenyl)propionic Acid (5). A 100-mL round-bottomed flask was charged with 6 g (0.0268 mol) of **1** and 2 g (0.0096 mol) of 3-(4-acetoxyphenyl)-propionic acid (**5**), and after the standard purging was reacted at 250 °C. An isotropic melt was observed after 3 min. The argon was shut off after about 20 min and the reaction was continued under vacuum (1.1 × 10^{-2} Torr) for another 20 min. A brownish, glassy-looking foam was obtained. A refluxing mixture of water and THF was necessary to dissolve the copolymer. It was precipitated from ether and 5.7 g (98%) of an orange-brown solid was obtained. ^{1}H NMR (DMSO-d_6), δ in ppm: 2.95 (b, 4 H), 6.7–7.5 (b m, Ar H from **4**), 7.5–8.8 (b m, Ar H from **1**), 13.4 (b, COOH).

Preparation of the Ammonium Salt of P1. A slow stream of anhydrous ammonia was bubbled through a dilute THF solution (1 g/100 mL) of **P1**. After the first precipitation occured (2 min), the ammonia stream was left on for another 5 min. The precipitated polysalt was collected by filtration, washed with THF several times, and dried. Anal. (corrected for residual THF) Calcd for C: C, 53.3; H, 3.9; N, 7.8. Found: C, 53.9; H, 3.9; N, 7.1.

Preparation of the Acid Chloride of P1. A sample of **P1** (1 g, 0.006 mol) was dissolved in anhydrous THF and 0.95 mL (0.01 mol) of thionyl chloride was added along with 3 drops of DMF. A clear solution was obtained after about 10 min. The reaction mixture was refluxed for 6 h. The solvent and excess of thionyl chloride were removed by rotary evaporation, and the polymeric acid chloride was redissolved in 30 mL of THF and used directly for modification reactions.

Preparation of the Ethyl Ester of P1. The polymeric acid chloride from above was converted to the ethyl ester by adding 0.58 mL (0.01 mol) of ethanol and 1.3 mL of triethylamine in 30 mL of THF slowly to the THF solution of the acid chloride under nitrogen. A small amount of precipitation (Et$_3$NHCl) could be observed. The mixture was stirred at room temperature overnight, filtered, and then precipitated into water. A few drops of HCl were added to improve the polymer precipitation. The yield was 1.1 g of white solid. ^{1}H NMR (CDCl$_3$), δ in ppm: 1.4 (b, CH$_3$), 4.4 (b, CH$_2$), 8.23, 8.43, 8.62, 8.8, 8.98 (Ar). The extent of reaction determined by integration showed that 85–90% of the carboxylic acid groups were converted into the ethyl ester.

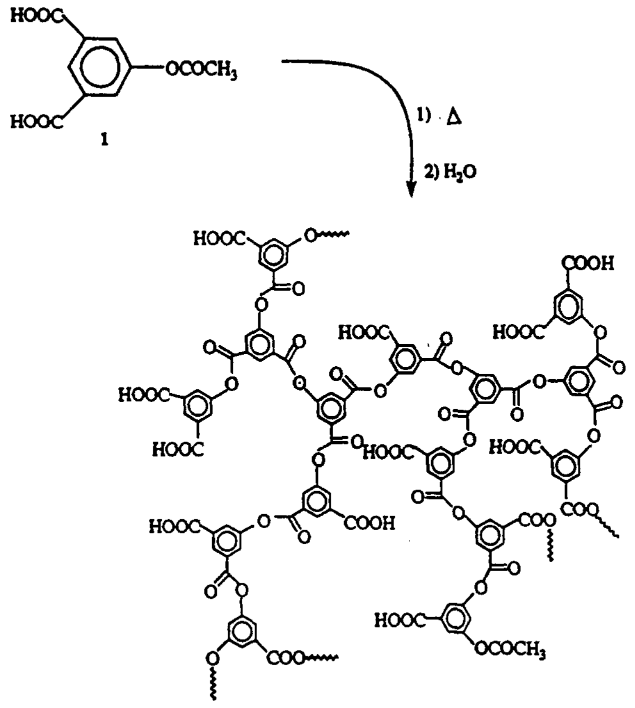
Preparation of the *p*-Methoxyanilide of P1. A solution of 0.376 g (0.003 mol) of *p*-methoxyaniline and 0.4 mL of Et$_3$N in 30 mL of THF was prepared and slowly added to a solution of the polymeric acid chloride from **P1** (0.003 mol) in 30 mL of THF. The mixture was stirred overnight at room temperature. The hydrochloride salt was filtered off, the polymer was recovered by precipitation into water, and after drying 0.4 g of an off-white solid was obtained. ^{1}H NMR (DMSO-d_6), δ in ppm: (b, 3.65 CH$_3$), 6.8, 7.6, 8.0–8.8 (Ar), 10.3 (NH). Integration indicated that about 96% of the carboxylic acid groups were converted into the amide.

Characterization. The NMR studies were done on a QE 300 General Electric instrument, the IR analysis on a Perkin-Elmer 1430, thermal analysis data were obtained from Du Pont-TA-Instrument 912, Perkin-Elmer DSC 7, and TGA 7. Molecular weight distributions were obtained by size-exclusion chromatography (SEC) in THF using three PLgel mixed-bed 7.5 mm i.d. × 300 mm 10 μM particle diameter columns (Polymer Laboratories, Amherst, MA). The system consisting of coupled differential viscometry (DV), low-angle laser light scattering (LALLS), and differential refractive index (DRI) detection has been described previously.[18] Absolute molecular weights were obtained by universal calibration using the DV, or directly from LALLS. Samples with free carboxylic groups were protected with a silylating agent, bis(trimethylsilyl)trifluoroacetamide (BSTFA), to prevent absorption to the SEC columns. Typically 100 μL of BSTFA was added to 5 mg of sample dissolved in 10 mL of THF. This solution was allowed to sit for 1 h before injection into the SEC chromatograph. Capillary viscosity measurements were made with Ubbelohde viscometers.

Results and Discussion

Polymerization. The direct thermal condensation of 5-hydroxyisophthalic acid is not possible since this compound decomposes before melting. Thus 5-acetoxyisophthalic acid (**1**) was prepared by acetylation of the phenolic group with acetic anhydride. The noncatalyzed acidolysis

Scheme 1

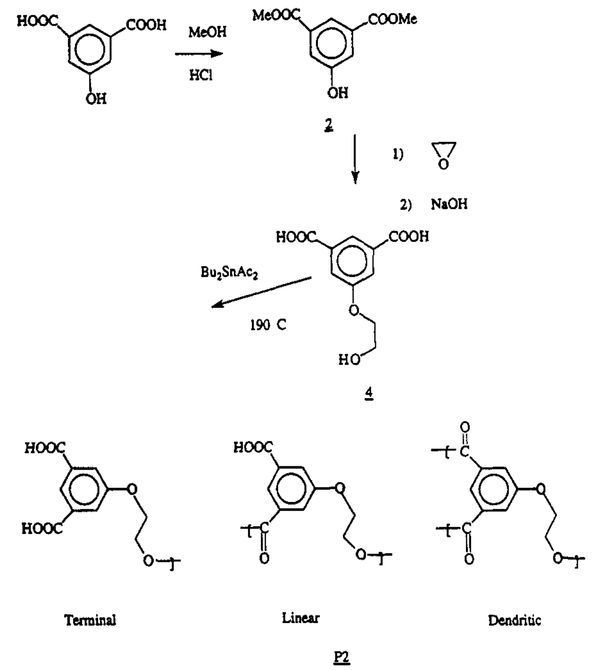


polymerization of 1 is a two-stage polymerization reaction. At first the monomer melts at 250 °C and acetic acid is removed at this temperature with the assistance of an inert gas purge. The melt quickly advances to the solid state and at this time a vacuum is applied and a foam results. The reaction is held at 250 °C for 0.5 h. The solid polymer was found to be insoluble in THF and other organic solvents. IR analysis showed the presence of strong anhydride bonds at 1800 cm^{-1}. The formation of anhydrides at these elevated temperatures is known,[19,20] and thus this leads to the cross-linked nature of the polymer. This solid is easily converted quantitatively to a carboxylic acid terminated soluble polyester by refluxing it in a THF/water mixture. No anhydride absorption was observed by IR after this treatment. The structure for **P1** and general reaction are shown in Scheme 1.

It was also possible to carry out the polymerization in an inert diluent. Phenyl sulfone was found to be a solvent at elevated temperature for the monomer. Even though the polymer precipitated over the course of the polymerization, a polymer with an identical chemical structure and similar molecular weight to that from the neat polymerizations was obtained. The phenyl sulfone provided the advantage of improving heat transfer and reducing the foam formation on application of vacuum. The phenyl sulfone was completely removed during the vacuum part of the polymerization process.

Another carboxylic acid terminated hyperbranched polymer was prepared from 5-(2-hydroxyethoxy)isophthalic acid (4). This monomer was readily prepared by ethoxylating the phenolic OH of 1 with ethylene oxide. Anhydride formation was avoided in this polymerization since it was possible to do this condensation at a lower temperature than that needed for the all-aromatic polymer, since the glass transition temperature of the hyperbranched polyester is much lower than that of the all-aromatic polymer. The polymerization of 4 was accomplished at 190 °C using Bu_2SnAc_2 as catalyst. The polymerizing mixture again formed a solid foam but the solid was found to be readily soluble in organic solvents and showed no anhydride bond formation. This synthesis and polymerization are shown in Scheme 2.

Scheme 2



Copolymerization. Flory[1] predicted that A_2B monomers can be copolymerized with AB monomers to form soluble branched systems. We observed facile copolymer formation of 1 from various AB monomers with the copolymerization conditions and results dependent on the comonomer charge and copolymer composition. For example, for the copolymerization of 1 with 3-(4-acetoxyphenyl)propionic acid (5), at a 75/25 charge ratio of 1/5, a temperature of 250 °C was needed for good conversion. At this composition the copolymerization was principally a solid-state reaction with anhydride formation. However, a melt polymerization was achieved at 230 °C with no anhydride formation by raising the amount of the flexible AB monomer so that a 50/50 charge ratio was used. Precise control of the reaction temperature is important in this case since a lower temperature decreases the acidolysis rate considerably, whereas higher temperature leads to anhydride formation.

Degree of Branching. The degree of branching could not be determined directly from ^1H NMR spectra obtained in DMSO for the acid terminated polymers because the chemical shifts of the aromatic protons were not well enough resolved for this determination. However, the ^1H NMR spectrum of the ethyl ester of the hyperbranched carboxylic acid showed sufficient differences in the chemical shifts of the aromatic protons to allow the degree of branching to be determined. Using the definition of degree of branching[4] as

$$DB = \frac{\text{dendritic units} + \text{terminal units}}{\text{dendritic units} + \text{terminal units} + \text{linear units}}$$

a degree of branching of approximately 50% was obtained. This value is similar to what we observed for the melt polymerization of 3,5-diacetoxybenzoic acid[11] and observed by Fréchet for the melt polymerization of trimethylsilyl 3,5-bis(trimethylsiloxy)benzoate.[4] A DB of approximately 60% was obtained for the methyl ester of the copolymer 1 and 5 by integrating only the proton resonances from the A_2B comonomer and neglecting the AB comonomer.

Molecular Weight. The carboxylic acid terminated hyperbranched polyesters could not be analyzed directly by size exclusion chromatography (SEC) because the polymer absorbed to the column. This problem was

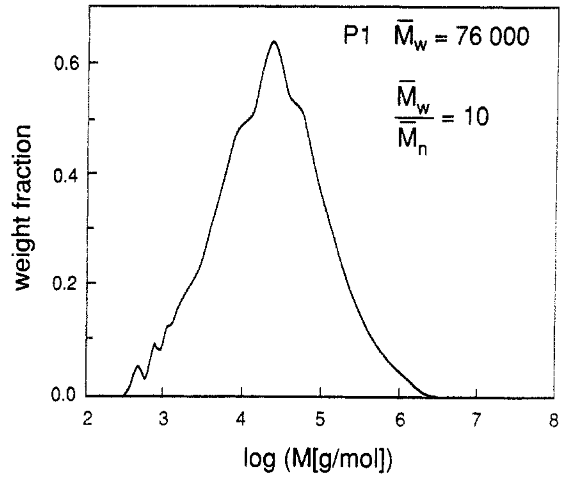


Figure 1. SEC trace of **P1** in THF using column sets and instrument described in the Experimental *Section.*

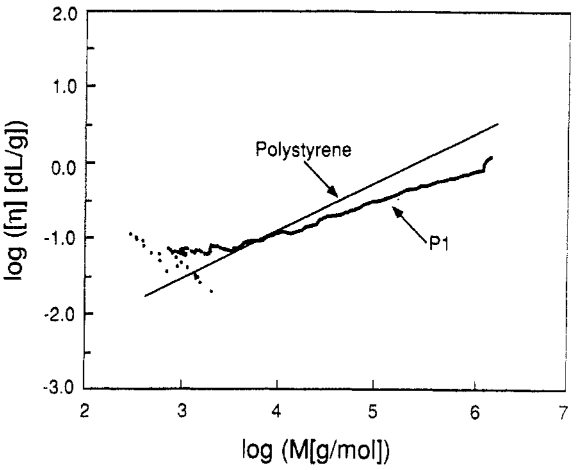
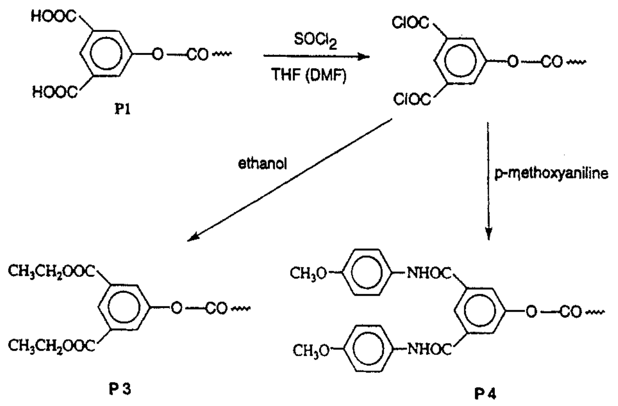


Figure 2. Plot, of log[η] vs log [M] for polystyrene and **P1** as obtained from SEC.

Scheme 3



overcome by protection of the carboxylic acid groups with trimethylsilyl groups. Silylation was accomplished by reacting the polymer with BSTFA (bis(trimethylsilyl)-trifluoroacetamide). For characterization of these hyperbranched polyesters dn/dc was determined from the differential refractive index (DRI) detector and $\bar{M}_w$ was measured by low-angle laser light scattering (LALLS). Universal calibration using coupled differential viscometry (DV) was used to obtain molecular weight distributions. Molecular weights obtained from LALLS and DV agreed, and because of better sensitivity across the broad distributions, we primarily used the DV results. The molecular weight distributions of these polyesters are broad, multimodal (Figure 1), and broaden with increasing conversion, similar to what we reported previously for hyperbranched polyesters derived from 3,5-diacetoxybenzoic acid and consistent with the predictions of Flory.[1] It was possible to compare the SEC results on the TMS protected polymers with other polymers derived from **P1**. **P1** was found to be readily converted to the polymeric acid chloride with thionyl chloride. The acid chloride was easily reacted with ethanol to form the ethyl ester or *p*-methoxyaniline to form the amide (Scheme 3). ^{1}H NMR analysis confirmed that at least 90% of the carboxylic acids were esterified in both cases. SEC analysis of a sample of **P1** protected with BSTFA, gave $\bar{M}_n$ of 8530 and $\bar{M}_w$ of 42 900 ($\bar{M}_w/\bar{M}_n$ = 5.03). Conversion of this polymer to the ethyl ester (**P3**) via the acid chloride gave $\bar{M}_n$ of 3060 and $\bar{M}_w$ of 11 300 ($\bar{M}_w/\bar{M}_n$ = 3.69). Thus it appears that there is some degradation during this conversion and some fractionation during the workup.

Viscosities were obtained from SEC–DV measurements and by conventional capillary viscometry. The relationship between [η] and molecular weight can be measured across the molecular weight distribution in the SEC experiment and is described by the Mark–Houwink equation [η] = KM^a. Comparison of log[η]–log MW plots of the TMS protected carboxylic acid terminated hyperbranched polymer with polystyrene standards (Figure 2) (the linear pendant carboxylic acid polyester is not available and would be very difficult if not impossible to prepare) indicates that these polyesters are highly branched. The slopes of the hyperbranched structure were always considerably less than those for the linear polystyrene standard. The values of the slope, which is *a* in the Mark–Houwink equation, were all less than 0.5 and are consistent with our previous results on hyperbranched polyesters prepared from 1,3-diacetoxybenzoic acid. The value of *a* approaches 0.5 at θ conditions and is generally between 0.65 and 0.75 for a linear random coil polymer in a good solvent. These small *a* values are consistent with a highly branched, compact structure.

Polyelectrolyte Properties. Capillary viscosity measurements were made in aqueous salt free and aqueous salt solutions for the ammonium and sodium salts of **P1**. Polyelectrolytes exhibit a phenomenon called the "polyelectrolyte effect" in salt free solutions. In the typical plot of reduced viscosity, η_{sp}/c versus concentration, *c* is not linear as for uncharged polymers and shows an upward curvature with decreasing concentration. This effect is suppressed at high ionic strength, i.e., at concentrations of low molecular weight electrolytes of 0.05–0.5 mol/L. A linear plot for polyelectrolytes is expected in salt free solutions, when $c^{0.5}$ versus c/η_{sp} is plotted according to the empirical Fuoss equation.[21] The viscosity result for an ammonium salt of **P1** is shown in Figure 3 where η_{sp} versus *c* plots in salt free and 0.4 M NaCl solution are shown. The Fuoss plot is shown in Figure 4. The behavior is that of a classic polyelectrolyte. The polyelectrolyte effect has been traditionally explained to arise from increasing coil expansion from charge repulsions along the polymer backbone as the solution is diluted. Therefore, the existence of the polyelectrolyte effect in **P1** could be indicative that these hyperbranched structures are quite flexible and can expand much like a linear random coil polymer. However, this may not be the case since recent publications have questioned the traditionally accepted concept of polyelectrolyte behavior and attribute the upswing in reduced viscosities at low concentrations to domain phenomena.[22,23]

Treatment of **P1** with an aqueous base can result in degradation of the polymer as well as salt formation. For example, when a sample of **P1-NH$_4$** is dissolved in a sodium

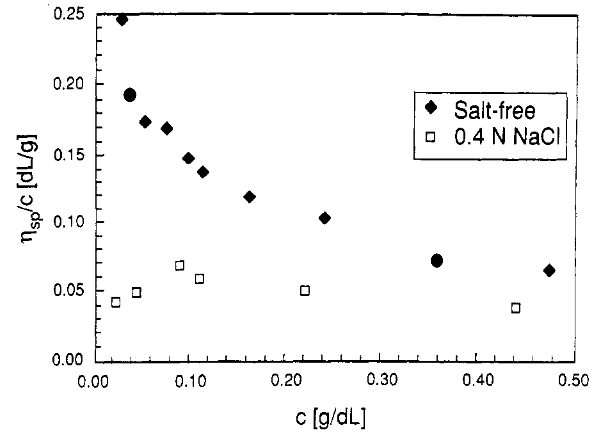


Figure 3. Reduced viscosity η_{sp}/c versus c plot for an ammonium salt of **P1** in salt free and 0.4 M NaCl solutions.

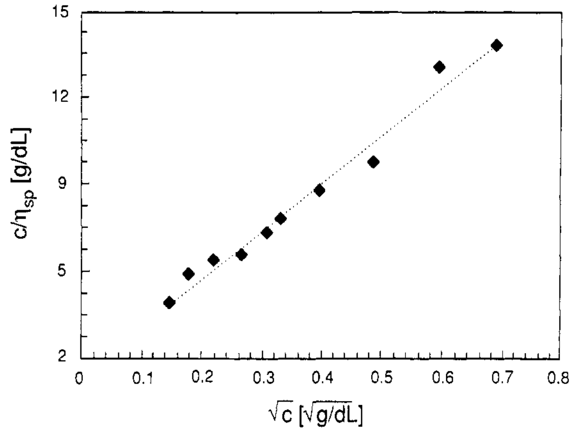
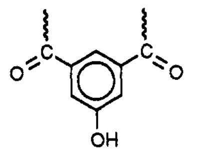


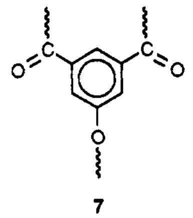
Figure 4. Fuoss plot (*c* versus c/η_{sp}) for an ammonium salt of **P1**.

carbonate/bicarbonate buffer at pH 10, the degradation (decrease in molecular weight) can be followed directly by capillary viscometry. This result is shown in Figure 5. The degradation can also be followed by UV spectroscopy since the hydrolysis of the ester linkages results in the formation of phenols. It was established with model compounds that a free phenol moiety (**6**) has E_{max} at 327 nm while the esterified phenol **7** has an E_{max} at 292 nm.



6

λ_{max} = 327 nm



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λ_{max} = 292 nm

In order to minimize this rapid degradation, the ammonium salt was used since it could be prepared by bubbling anhydrous ammonia through a THF or NMP solution of the acid polymer. The salt was observed to precipitate from solution as if formed.

Thermal Properties. **P1** is an amorphous polymer with a T_g observed at 250 °C by DSC and decomposition onset observed at 480–490 °C by TGA for a sample with $\bar{M}_w$ = 76 000 and $\bar{M}_w/\bar{M}_n$ = 10. In the TGA analysis these polymers lose about 4 wt % due to remaining solvent below 150 °C and an additional 6 wt % between 200 and 350 °C, due to loss of acetic acid and continued polymerization, before the decomposition that starts above 450 °C.

Addition of the ethoxy unit into the chain lowers the T_g of **P2** in comparison to **P1**. For a sample with $\bar{M}_w$ = 20 100 and $\bar{M}_w/\bar{M}_n$ = 2.0, we observed a T_g after three heating cycles at 150 °C. It is noted here that several samples of **P2** yielded large differences in T_g with the 150 °C value close to a maximum. It is possible that this polymer continues to react due to the presence of unremoved catalyst, even after reprecipitations. Incorporation of 25 mol % of **5** into a copolymer with **1** decreased the T_g to 183 °C while a 50 mol % copolymer showed a T_g of 129 °C.

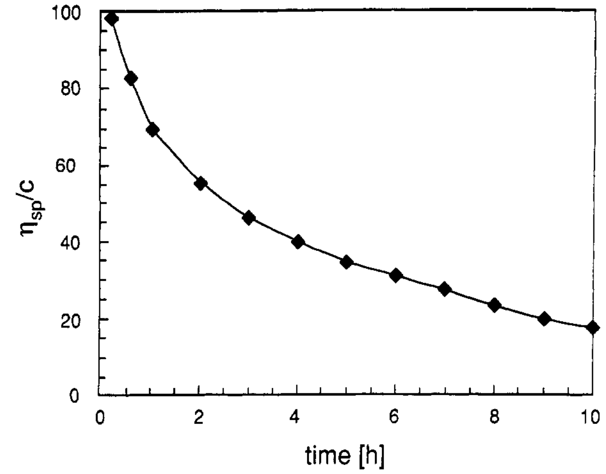

Figure 5. Reduction of viscosity with time for an ammonium salt of **P1** in sodium carbonate/bicarbonate buffer at pH 10.

Summary and Conclusions

Hyperbranched polyesters with terminal carboxylic acid groups were readily prepared by conventional condensation techniques. Both an all-aromatic polymer based on 5-acetoxyisophthalic acid (**1**) and an alkyaryl polyester based on 5-(2-hydroxyethoxy)isophthalic acid (**4**) were prepared and studied. For the all-aromatic polymerization the desired acidolysis step-growth reaction was accompanied by some anhydride formation. Destruction of this cross-linking reaction was necessary in order to dissolve and study these polymers. Characterization of these all-aromatic polymers showed that they have degrees of branching similar to that observed for the acetate terminated polymers prepared previously. The acid terminated polymers were readily converted into water-soluble salts and exhibited dilute solution polyelectrolyte effects that could be suppressed by added salt. The all-aromatic polyesters exhibited T_gs around 250 °C. A decrease in T_g was observed with the insertion of the ethoxy group. **1** was also found to readily copolymerize with 3-(4-acetoxyphenyl)propionic acid (**5**) to give soluble, highly branched copolymers that showed lower T_gs than the all-aromatic A_2B structure.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(2) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein.
(3) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichimica Acta* **1992**, *25*, 31 and references therein.
(4) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(5) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592; *Macromolecules* **1992**, *25*, 5561.
(6) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(7) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583.
(8) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843.
(9) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.
(10) Mathias, L.; Carothers, T. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(11) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356.

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

(13) Newkome, G. R.; Lin, X. *Macromolecules* **1991**, *24*, 1443.

(14) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Bechera, R. K.; Johnson, A. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178.

(15) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2459.

(16) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin. Trans. 1*, in press.

(17) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.

(18) Mourey, T. H.; Miller, S. M.; Balke, S. T. *J. Liq. Chrom.* **1990**, *13*, 435.

(19) Kricheldorf, H. R.; Lübbers, D. *Eur. Polym. J.* **1991**, *27*, 1937.

(20) Huang, J.; Leblanc, J.-P.; Hall, H. K., Jr. *J. Polym. Sci. Part A* **1992**, *30*, 345. Huls, R.; Hubert, A. *Bull. Soc. Chim. Belg.* **1956**, *65*, 596.

(21) Fuoss, R. M. *J. Polym. Sci.* **1948**, *3*, 603.

(22) Cohen, J.; Priel, Z.; Rabin, Y. *J. Chem. Phys.* **1988**, *88*, 7111.

(23) Sedlak, M.; Amis, E. J. *J. Chem. Phys.* **1992**, *96*, 826. Sedlak, M. *Macromolecules* **1993**, *26*, 1158.