

Notes

SYNTHESIS OF AN EPOXY-TERMINATED HYPERBRANCHED AROMATIC POLYESTER*

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Abstract An epoxy-terminated hyperbranched aromatic polyester (P3) was synthesized from a hyperbranched aromatic polyester containing carboxylic acid end groups (P1), which was derived from the condensation polymerization of the AB₂ monomer, 5-acetoxisophthalic acid. Polymer P1 was converted into the polymeric acid chloride by reaction with thionyl chloride. The acid chloride was reacted with ethanol and glycidol to form a poly(ethyl ester) (P2) and an epoxy terminated material (P3), respectively. The reaction conditions in each step of these processes had to be controlled very carefully to avoid unwanted cross-linking reactions. The characterization of products and intermediates, including molecular weight distributions and thermal properties, are reported.

Keywords Hyperbranched polymer, Hyperbranched aromatic polyester, Epoxy-terminated hyperbranched aromatic polyester

INTRODUCTION

Hyperbranched polymers (HBPs) possess some of the structural and physical properties of dendrimers, such as a high degree of branching and a large number of end groups, but they are much more readily accessible synthetically^[1]. HBPs are generally prepared from AB_x monomers, where *x* is usually 2 or 3, in a one-step polymerization. While the degree of branching and the structural precision obtained in HBPs are both lower than in dendrimers, HBPs possess a practical competitive advantage for potential commercialization, because of their inherently lower cost than dendrimers.

HBPs have low melt viscosity, high solubility and large number of end groups. These properties make such materials potentially useful as the tougheners for thermosets. HBPs were first studied as the tougheners for thermosets by Boogh and coworkers^[2]. They reported that with the appropriate choice of matrix, hyperbranched starting materials and end groups, the fracture toughness of the modified system could be increased, for example, by a factor of 6 from 120 J/m² to 720 J/m² when using only a 5% loading of modifier and without affecting either *T_g* or modulus. The epoxy terminated HBPs they studied were derived from the hydroxy terminated aliphatic HBPs first described by Hult and co-workers^[3] and marketed by Perstorp under the Boltorn TradeMark; the HBP used by Boogh and coworkers was a G3 material based on a tetrafunctional core and with hydroxyl and secondary epoxy end groups.

In this work, the synthesis of an epoxy-terminated hyperbranched aromatic polyester (P3) from a HBP containing carboxylic acid end groups (P1) is described. The acid functionalised HBP was derived from the condensation polymerization of the AB₂ monomer, 5-acetoxisophthalic acid, and the isolation, purification and characterization of all intermediates and products are described; including the molecular weight distribution and thermal analysis of the epoxy functionalised HBP (P3).

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EXPERIMENTAL

All chemicals, except where noted below, were purchased from the Aldrich Chemicals Company Ltd and used without further purification.

Monomer Synthesis

5-Acetoxyisophthalic acid

5-Hydroxyisophthalic acid (0.25 mol) was heated in 1.00 mol of acetic anhydride (Ac_2O) to reflux. The acid was dissolved after about 0.5 h and refluxing was continued for 6 h. After cooling to room temperature, the product was precipitated and was collected by filtration. The crude product was recrystallized from ethanol (m.p. 243°C , yield 89%). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 2.31 (s, 3H), 7.91 (s, 2H) and 8.39 (s, 1H).

Polymerization

Polymerization of 5-acetoxyisophthalic acid to prepare P1

5-Acetoxyisophthalic acid (30 g, 0.13 mol) was charged into a cylindrical glass reactor designed for efficient mixing, heated in a thermostated oil bath and equipped with a helical mechanical stirrer, gas inlet and outlet and attached to a vacuum line. The oil bath temperature was kept at 245°C . Within a short time an isotropic melt was obtained. In the first stage of polycondensation a rapid stream of dry nitrogen was passed through the system. Then vacuum was applied to drive the reaction to high conversion. At the end of the reaction, stirring with the mechanical stirrer was no longer possible due to the increased melt viscosity of the product. The product was heated in a mixture of 50 mL THF/5 mL water at reflux until a homogeneous solution was obtained. The polymer was then precipitated by pouring into 500 mL of hot toluene, recovered by filtration and redissolved in hot THF, reprecipitated in hot toluene and dried in a vacuum oven at 80°C for 24 h. The yield of white solid was 78%. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7–9 (Ar H).

Preparation of the acid chloride of P1

A sample of P1 (1.0 g, 0.006 mol) was dissolved in dry THF and 2 mL (0.01 mol) of thionyl chloride and 20 mg benzyltriethylammonium chloride were added. A clear solution was obtained after about 10 min. The reaction mixture was refluxed for 20 h. The solvent and the excess thionyl chloride were removed in a rotary evaporator, and the product dried under vacuum (*ca.* 0.13 Pa). The polymeric acid chloride was redissolved in 20 mL dry THF and used directly for subsequent modification reactions.

Preparation of the ethyl ester of P1 (P2)

A mixture of dry ethanol (0.8 mL), triethylamine (1.3 mL) and 20 mL dry THF was added to the THF solution of the polymeric acid chloride slowly under the protection of nitrogen. The reaction mixture was stirred for 18 h at room temperature, filtered and then precipitated from THF solution by adding methanol. A few drops of HCl were added to improve the polymer precipitation. The polymer (P2) was recovered by filtration and washed with methanol, dried in a vacuum oven at 80°C for 24 h. The yield was 0.98 g of white solid. $^1\text{H-NMR}$ (CDCl_3 , δ): 1.41 (b, CH_3), 4.41 (b, CH_2), 8.10, 8.22, 8.30, 8.42, 8.62, 8.80 and 8.99 (Ar).

Preparation of epoxy-terminated hyperbranched polymer (P3)

A mixture of glycidol (1.2 mL), triethylamine (2.2 mL) and 20 mL dry THF was added to the THF solution of the polymeric acid chloride slowly under nitrogen. The reaction mixture was stirred for 18 h at room temperature. The reaction mixture was filtered, the crude P3 was precipitated from THF solution by adding methanol, recovered by filtration, dissolved in chloroform and reprecipitated into methanol, dried in a vacuum oven at 40°C for 24 h. The yield was 0.78 g of cream-colored solid. The $^1\text{H-NMR}$ (CDCl_3) spectrum of the polymer P3 is shown in Fig. 1, along with the assignment of the glycidyl signals. The epoxy equivalent weight of P3 was 215 g/eqv.

Characterization

The NMR studies were carried out using a Varian Unity 200 spectrometer at 200 MHz and a Varian Unity 300

spectrometer at 300 MHz. Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer Pyris at a heating rate of 20 K/min or 25 K/min in Al pans under argon. Melting points were obtained using an Electrothermal IA92000 series digital melting point apparatus. Molecular weight distributions were obtained using size exclusion chromatography (SEC) in chloroform using three 5 μm columns of PLgel beads with pore sizes of 10, 10^2 and 10^4 nm (Polymer Labs) and both the Viscotek triple detection system and conventional RI detection with PS calibration (see below).

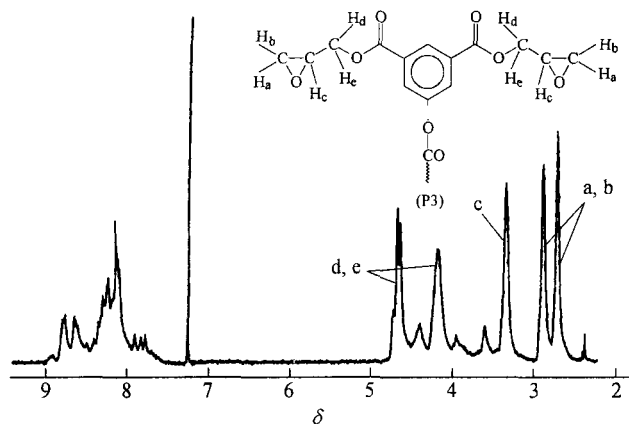


Fig. 1 300 MHz ^1H -NMR spectrum of the polymer P3

RESULTS AND DISCUSSION

Synthesis of Epoxy-terminated Hyperbranched Aromatic Polyester

The structure of the epoxy-terminated hyperbranched aromatic polyester made in this work is shown in Fig. 2. The synthesis route is shown in Scheme 1. The hyperbranched polymer P1, formed by melt condensation polymerization of the AB_2 monomer, 5-acetoxyisophthalic acid, was found to be readily converted into the polymeric acid chloride by reaction with thionyl chloride. The acid chloride was treated with alcohol to form the esters (Scheme 1) as a check that simple soluble and uncrosslinked HBPs could be prepared by this procedure. The condensation of 5-acetoxyisophthalic acid to P1 proceeded as reported by Turner^[4]. The product P1 was converted to the polymeric acid chloride with thionyl chloride by heating under reflux in dry THF. Excess of thionyl chloride (SOCl_2) and THF were removed by rotary evaporation, and the product was dried under vacuum. The polymeric acid chloride, a light yellow viscous liquid, was reacted with glycidol in the presence of triethylamine (Et_3N) as an acceptor for HCl to form P3. Each step in this synthesis has to be conducted with some care and under as mild conditions as possible in order to avoid cross-linking and the formation of an insoluble intractable product. Epoxy groups are more reactive than ordinary ethers and give products in which the ring has opened. They undergo acid-catalyzed ring opening to form a cross-linked polymer with water or acid. Because of the liberation of HCl during the reaction and the fact that excess Et_3N may decompose the epoxy ring, excess SOCl_2 should be avoided and the amount of Et_3N should be regulated carefully. Despite these restrictions soluble uncrosslinked products were obtained.

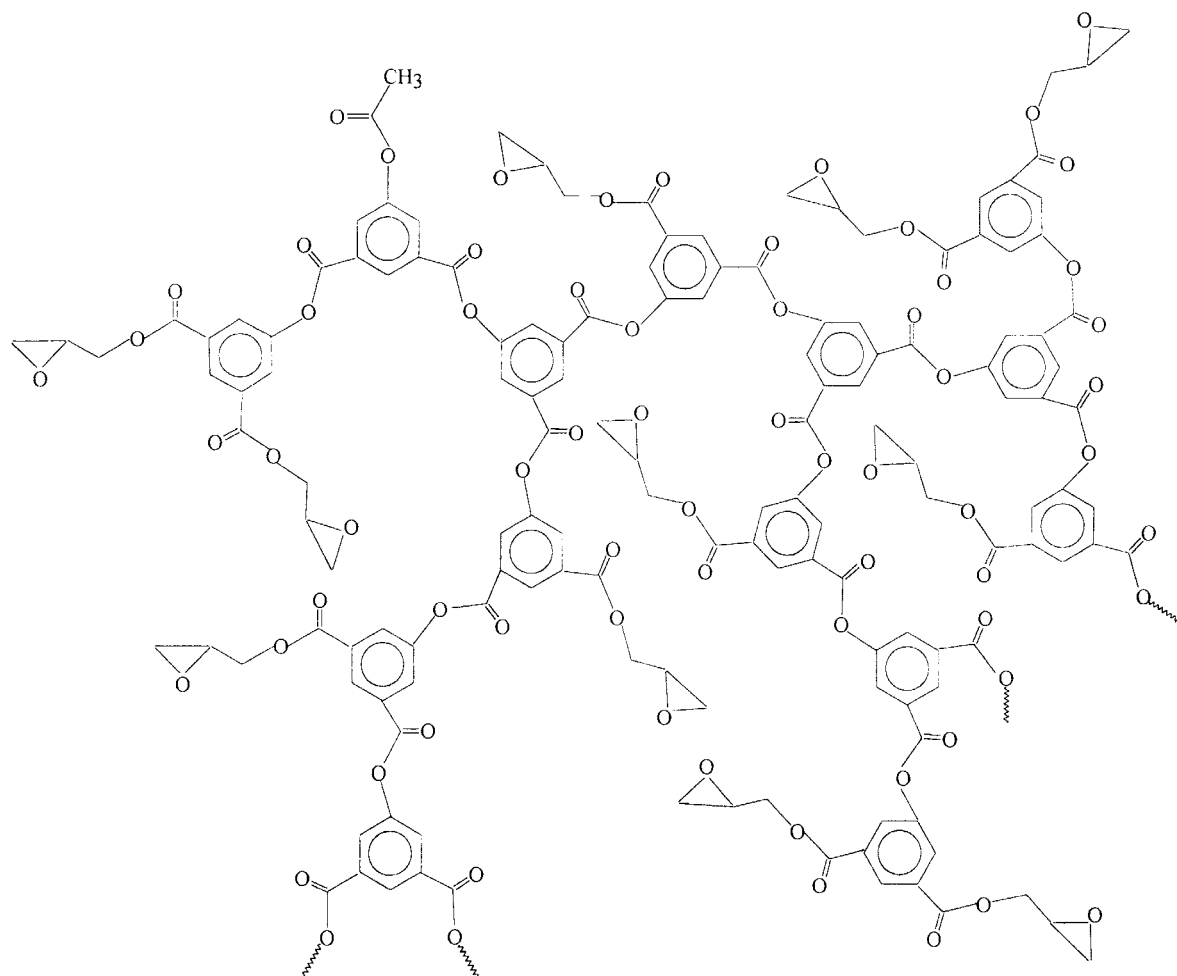
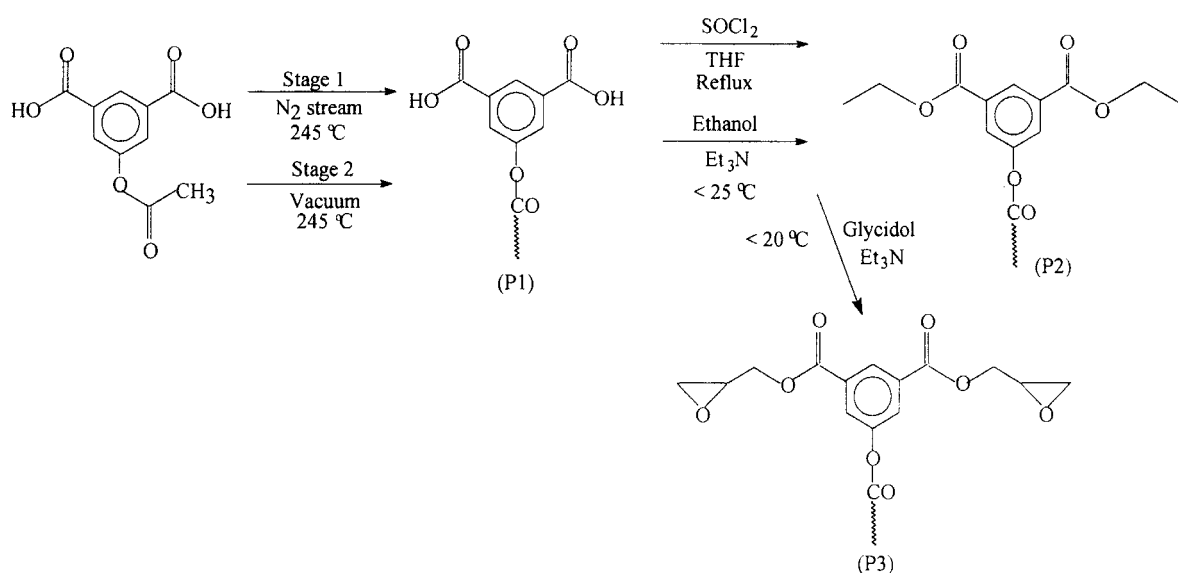


Fig. 2 The structure of the epoxy-terminated hyperbranched aromatic polyester (P3)



Scheme 1 The synthesis route to P3

Molecular Weight and Degree of Branching

The characterization of the hyperbranched polymer with epoxy end groups was attempted using SEC in chloroform, using a Viscotek triple detection system (RI-DV-RALLS) and conventional SEC with a RI detector and polystyrene calibration. The results obtained for three separate syntheses are summarized in Table 1. The characterization of hyperbranched polymers is fraught with difficulties and uncertainties and these materials were no exception to this generalization. According to the predictions of Flory^[5] we should expect, in the absence of cyclisation or other growth terminating side reactions, increasing molecular weight and increasing molecular weight distribution (M_w/M_n) with increasing reaction conversion. Indeed, Flory teaches that for AB_x polymerization as conversion tends towards 100% the molecular weight distribution tends towards infinity. The data presented in Table 1, while they are consistent with the hypothesis that we have successfully prepared hyperbranched polymers, illustrate the difficulty encountered in characterizing size and size distribution in these kinds of system. Thus, whatever set of data is considered, we see that the molecular weight observed for each P3 sample depended on the duration of the polymerization leading to the formation of the P1 sample from which the P3 sample was prepared; this is reasonable, longer reaction duration leading to higher molecular weight in P1 and hence in P3.

Table 1. The SEC analysis of P3 in chloroform

Sample	Time of vacuum applied for P1 (min)	SEC Data					
		Conventional Calibration			Triple Detector System		
		M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
P3-1	30	3,420	1,190	2.87	9,690	6,360	1.52
P3-2	60	4,300	880	4.89	21,000	11,300	1.86
P3-3	90	6,110	870	7.02	61,500	34,900	1.91

The actual values for the weight and number average molecular weights recorded by the two analyses are not in good agreement, those obtained from the triple detection system, are appreciably higher than the polystyrene equivalent molecular weights obtained from a conventional polystyrene calibration. The difference may reflect the fact that the RI detector is relatively insensitive to the high mass end of the distribution in this case; however, the conventional polystyrene calibration analysis displays the expected increase in M_w/M_n with reaction conversion whereas the triple detector suggests a M_w/M_n tending to two. Thus, the SEC analysis is consistent with the formation of highly branched polymers but can not be taken as unambiguous proof thereof.

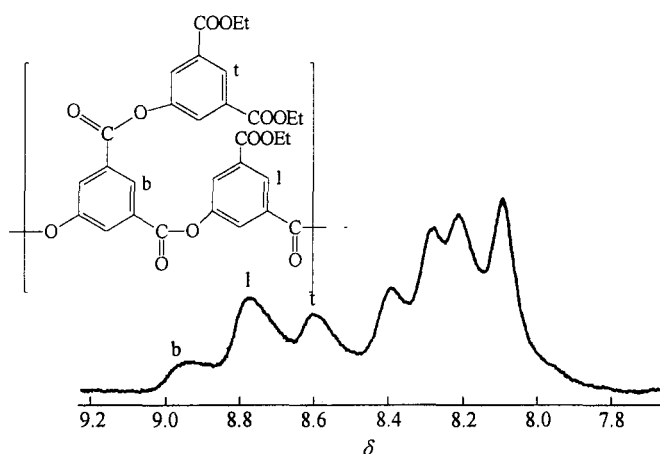


Fig. 3 300 MHz ¹H-NMR spectrum of P2

In order to obtain information about the degree of branching (DB), the analytical strategy of Turner *et al.*^[4] was followed. The DB for P1 and P3 could not be determined directly from their ¹H-NMR spectra because the

chemical shifts of the aromatic protons are not well enough resolved for this determination. However, the ^1H -NMR spectrum of the hyperbranched ethyl esters (P2) shows sufficient differences in the chemical shifts and line widths of the aromatic protons to allow the degree of branching to be determined (Fig. 3). Using the ^1H -NMR signals of the aromatic H between the ester units on each ring it is possible to make the assignments shown in Fig. 3. The signals arising from the hydrogen in a fully branched unit (b) display the broadest line consistent with the longest relaxation time, the signal associated with a linear (l) unit is intermediate in width and the rapidly relaxing terminal units (t) display the narrowest line. Deconvoluting these three signals allows us to establish that the degree of branching is 0.5, *i.e.* is that branching is statistical as predicted by Flory.

Thermal Properties of P1, P2, P3

As expected the glass transition temperatures (T_g), as revealed by differential scanning calorimetry (DSC), of the three hyperbranched polymers prepared in this study are very strongly dependent on the nature of the end groups (Table 2).

Table 2. The relation between T_g of hyperbranched aromatic polyester and the nature of the end groups

Sample	P1	P2	P3
T_g ($^{\circ}\text{C}$)	257	155	183

CONCLUSIONS

Sets of three hyperbranched aromatic polyesters having acid, ethyl ester and glycidyl terminal groups have been prepared and characterized. The characterization data, SEC, NMR and DSC, are consistent with the formation of hyperbranched polymers according to the proposed reaction scheme, although some uncertainties in the absolute values of molecular weight and molecular weight distributions remain it is clear that the polymerizations proceed with statistical branching and that the glass transition temperatures of the resultant polymers are dependent on the nature of the terminal groups.

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