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Synthesis and characterization of hyperbranched polyesters incorporating the AB_2 monomer 3,5-bis(3-hydroxylprop-1-ynyl)benzoic acid

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Abstract

The AB_2 monomer, 3,5-bis(3-hydroxylprop-1-ynyl)benzoic acid **1**, has been synthesized using a Sonogashira cross-coupling with a palladium catalyst system developed for use with deactivated aryl halides. Numerous condensation methods have then been assessed in the homopolymerization of the acid-diol monomer **1** to afford hyperbranched polyesters. However, as a result of the thermal instability of the monomer, direct thermal polymerizations could not be employed. Alternative approaches using carbodiimide-coupling reagents enabled the production of soluble polyesters possessing molecular weights and degrees of branching ranging from 2500 to 11,000 and 0.22 to 0.33, respectively.

Keywords: Hyperbranched polymer; Polyester; Coupling reagents; MALDI-TOF MS

1. Introduction

The controlled synthesis of hyperbranched macromolecules has proven to be a significant challenge to polymer chemists in recent years [1]. A variety of acetylenic monomers have been synthesized using Sonogashira cross-coupling methodologies and subsequently polymerized in order to construct either unsaturated macrocyclic, linear or hyperbranched polymers. For example, Moore and coworkers have used bis-acetylenic containing AB monomers [2,3] in a step-wise approach to synthesize highly rigid macrocycles consisting of between 4 and 12 acetylene groups. Moore and coworkers have also utilized Sonogashira methodologies to construct dendrimers [4–6] comprised of triacetylenic aryl components. In addition, linear diacetylenes [7–10] have been synthesized by the oxidative polycoupling of bis-acetylenes and possess the ability to undergo topochemical cross-polymerization either via irradiation or heating. The result is a polydiacetylene network that can be stretched at room temperature to give strong, transparent anisotropic photosensitive materials, with possible applications in second and third-order nonlinear optics [11,12]. We hereby report the synthesis of a novel hyperbranched polyester system that incorporates the rigid bis-acetylenic monomer **1** as part of our program developing new macromolecular systems at Reading.

2. Results and discussion

2.1. Synthesis of 3,5-bis(3-hydroxylprop-1-ynyl)benzoic acid *1*

The acid-diol acetylenic AB_2 monomer **1** has been synthesized (Scheme 1) in a modification of a three-step process [13] from commercially available 3,5-dibromobenzoic acid in an overall yield of 69%. Initial protection

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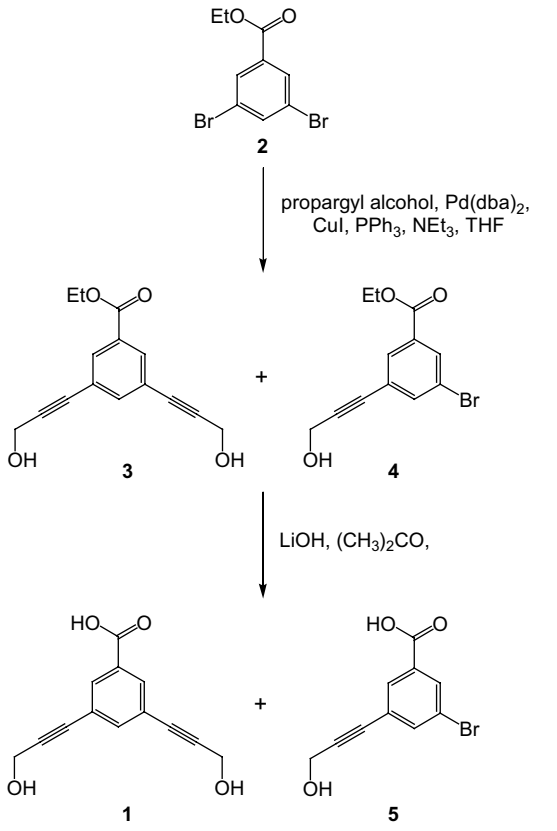


Scheme 1. Synthesis of the AB_2 monomer **1** and AB monomer **5**.

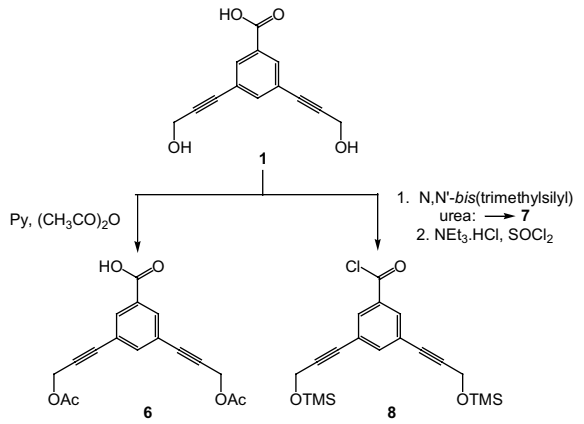
of the carboxylic function was achieved using ethanol in conjunction with the coupling reagent (DCC) to afford the ethyl 3,5-dibromobenzoate **2** as a cream solid [14]. Use of the original coupling conditions employed by Sonogashira et al. [15] with the ethyl 3,5-dibromobenzoate **2** and propargyl alcohol only led to formation of the mono-substituted product **4** as a result of the deactivation of the aromatic ring by the ethyl ester functionality. This effect was also observed by Thorland and Krause [16] in the coupling of trimethylsilylacetylene to methyl bromobenzoate and higher catalyst loadings were employed in this case to increase the cross-coupling efficiencies. However, when this approach was applied to the coupling of ethyl 3,5-dibromobenzoate **2** and propargyl alcohol, it proved ineffective. Consequently, Hayes and co-workers screened [13] a range of palladium catalysts and ligand combinations in order to optimize the production of the bis-acetylenic ethyl ester **3**. The result of this screen afforded a modified Sonogashira cross-coupling procedure with a palladium catalyst system [triethylamine/bis(dibenzylideneacetone)palladium/triphenylphosphine/copper iodide/THF] that produced the bis-acetylenic ester **3** in an acceptable yield of 70%. Subsequent base catalyzed hydrolysis of the bis-acetylenic ethyl ester **3** furnished the desired acid-diol acetylenic monomer **1** as a white powder in an improved yield of 91%. Also isolated in the above reaction sequence were the mono-acetylenic ester **4** and acid **5** in yields of 10% and 32%, respectively.

2.2. Polyester synthesis

A wide range of methodologies for constructing hyperbranched polyesters from AB_x monomers ($x \geqslant 2$), where A or B are hydroxyl or carboxylic acid moieties, have been reported [17–22]. These routes involve generally either thermally driven homopolymerization or activation of either A or B functionalities, and more recently organometallic reagents that act as *trans*-esterfication catalysts have been utilized. Thermally driven homopolycondensation of AB_2 monomers have been employed infrequently and the presence of a catalyst has also proved necessary, such as *p*-toluene sulfonic acid [17] or an organometallic reagent. The organometallic catalysts employed include $Co(OAc)_2$ [18], $Bu_2Sn(OAc)_2$ [19], $Sn(Oct)_2$ [20,22], $Mn(OAc)_2$ and Sb_2O_3 [21] in combination with reduced pressure and high temperatures. Attempts to melt-polymerize the acid-diol acetylenic AB_2 monomer **1** using $Bu_2Sn(OAc)_2$ or $Co(OAc)_2$ under similar conditions employed by Hawker and coworkers [18,22] afforded insoluble materials. Detailed investigations of the thermal characteristics of the acid-diol acetylenic AB_2 monomer **1** by differential scanning calorimetry (DSC) revealed that as the acid-diol was heated above its melting point (≈160 °C), decomposition of the monomer and, to a certain extent, uncontrolled homopolymerization occurred. In the light of these results, it was therefore decided that high temperature polymerizations of the AB_2 monomer **1** were unsuitable.

Consequently, alternative methods based upon either hydroxyl acetylation [22,23] or acid activation [22–26] via acid chloride formation were investigated (Scheme 2). Using a procedure adapted from Turner et al. [23], the hydroxyl functions of the monomer **1** were acetylated using acetic anhydride and pyridine to afford the 3,5-bis(3-acetyloxyprop-1-ynyl)benzoic acid **6** as a cream solid. However, in a similar fashion to the acid-diol precursor **1**, the acetylated AB_2 monomer **6** proved to be unstable at high temperatures and therefore melt polymerizations under reduced pressures resulted in total sample decomposition.

In an alternative approach, activation of the acid moiety was attempted. Silylated derivatives of **1** were thus constructed followed by selective formation of an acid chloride at the carboxylic function to afford AB_2 monomer **8** (Scheme 2). Initial attempts to silylate the monomer using the procedure described by Fréchet and coworkers [24] afforded only a silylester diol benzoate



Scheme 2. Synthesis of acetylated and silylated AB_2 monomers **6** and **8**.

derivative. In an alternative approach, *N*,*N*′-(trimethylsilyl)urea was employed [27] to construct the required *tris*-silylated intermediate as a clear oil. The *tris*-silylated derivative **7** was then converted to the desired acid chloride **8** by treatment with thionyl chloride [24]. Attempts to purify the acid chloride **8** prior to polymerization by reduced pressure distillation resulted in the formation of an insoluble material. Therefore, the solvent and excess thionyl chloride was removed carefully under reduced pressure and the crude acid chloride **8** was polymerized in situ by gradually increasing the temperature to 145 °C. This process affords a shiny brown solid and GPC analysis revealed the presence of low molecular weight oligomers (ranging between 500 and 2000 amu). The purity of the acid chloride proved to be crucial in this polymerization—a result that is consistent with the observations of Fréchet and co-workers [28].

In the light of the moderate progress towards hyperbranched polyesters using direct thermal polymerizations or activated acid derivatives, the use of coupling reagents to mediate polyesterification was examined.

2.3. Polymerization studies using coupling reagents

Commercially available coupling reagents 1,1-carbonyldiimidazole (CDI), 1,3-dicyclohexylcarbodiimide (DCC), 1,3-diisopropylcarbodiimide (DIC) and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI) were all studied in the homopolymerization of the AB_2 monomer **1**.

Homopolymerizations using either CDI or EDCI as the condensation reagent resulted in insoluble, low molecular weight oligomers that featured between 4 and 6 monomer units. Although CDI has been applied [29] successfully in the synthesis of aromatic polyesters from 3,5-dihydroxybenzoic acid and 3-hydroxyisophthalic acid, the polymerization of lactic acid has also proved difficult using this coupling reagent [30]. Initial polymerization studies using CDI and monomer **1** were conducted by stirring a mixture of the two components at room temperature for 16 h and then at 90 °C for 20 h. A cream solid was produced following precipitation into methanol. ^1H and ^{13}C NMR spectroscopic analyses revealed the presence of numerous methylene carbons, which indicated the presence of a variety of anhydride, carbamate and ester linkages. MALDI-TOF mass spectrometric analysis served to reaffirm this conclusion, several discrete series were evident in the mass spectra and the value of the observed mass ions corresponded to oligomeric esters, carbamates and carboxy-imidazolides. In an attempt to increase the selectivity of CDI towards polyesterification, the reaction was carried out at −78 °C, however, with little effect.

The coupling reagent EDCI was selected since its urea by-product is water-soluble enabling facile purification of esters. However, in this study this property also resulted in the production of insoluble materials. A solution of monomer **1**, EDCI and 4-dimethylaminopyridine (DMAP) were stirred in dry THF at room temperature for periods up to 60 h. A brown resinous material was formed on the vessel walls and was dissolved in DMSO and purified by precipitation into deionized water to afford a dark brown solid **9edci.1**. MALDI-TOF MS analyses of the solids revealed signals separated by regularly repeating intervals (∼211 m/z) that corresponded to progressive monomer units that emanated from a residue possessing a molecular weight of 173 m/z. This peak corresponds to a protonated molecule of EDCI (Fig. 1) that is bound to the focal point of each hyperbranched macromolecule. A consequence of which is the materials poor solubility and precipitation from the reaction solution, preventing the continuation of polymerization events and resulting in low molecular weight polyesters.

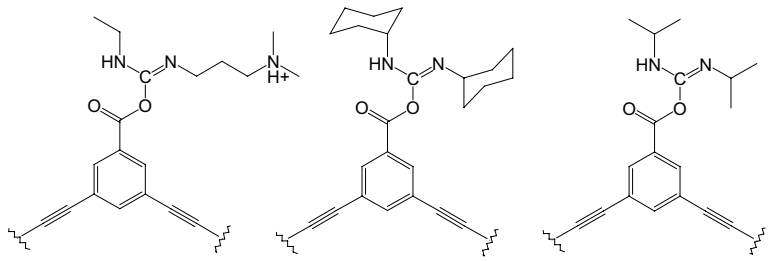
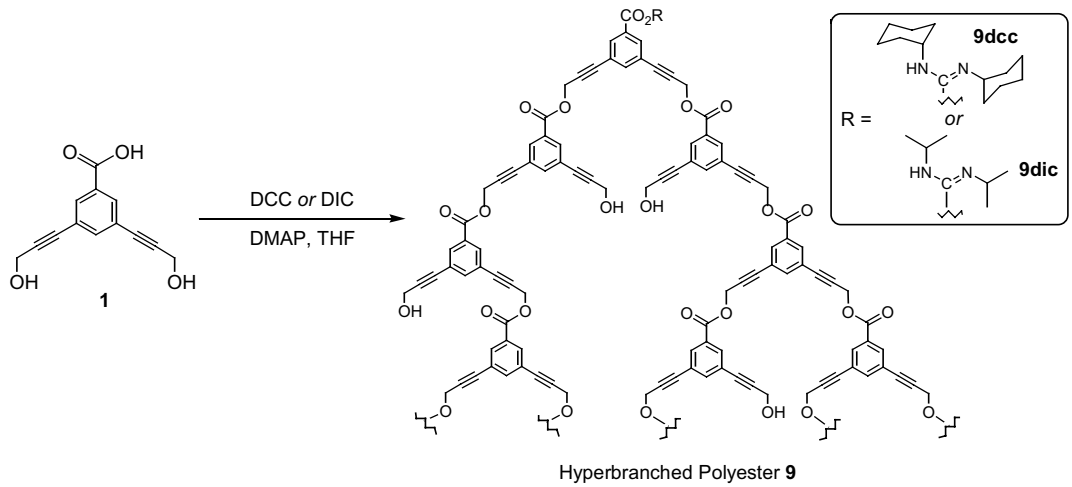


Fig. 1. The first monomer unit in the hyperbranched polyesters **9** complete with the focal point bearing the coupling reagent residue.



Scheme 3. Hyperbranched polymerization of the acid-diol AB_2 monomer **1** via a coupling reagent approach.

Variation of the reagent concentrations and reaction solvent failed to have any significant influence upon the resulting polyesters molecular weight and DB.

In the light of the low polymerization efficiency of EDCI, the studies focused on the use of carbodiimide reagents DCC and DIC. In contrast to the use of CDI and EDCI, the polyesterifications mediated by DCC and DIC afforded hyperbranched polyesters with molecular weights and degrees of polydispersity ranging between 2500 and 11,000, and 1.5 and 2.5, respectively and these polymers were soluble in organic solvents such as THF. Carbodiimide reagents of this type have been utilized in peptide and step-wise dendrimer synthesis [31], in addition to the polymerization [30,32] of AB_x monomers ($x \geqslant 1$). Generally, a suspension of DCC or DIC was stirred at room temperature in a dry THF solution of monomer **1** and DMAP for a period of 1 h to 3 days. The resulting solid dicyclohexylurea (DCU) or diisopropylurea (DIU) by-products were removed by filtration and the reaction mixtures concentrated to afford solids that were re-precipitated from cyclohexane or diethyl ether to afford white solids **9dcc.*x*** and **9dic.*x*** ($x = 1$–7), respectively (Scheme 3 and Table 1).

Purity of the crude polyesters was a critical issue as DCU or DIU by-products were retained in the polymeric architecture after re-precipitation. The urea by-products are insoluble in most common organic solvents, however it was found that urea molecules associated with the polymeric material were partially soluble in the solvents used to dissolve the polyesters. A comprehensive examination of the ureas solubilities revealed that they were partially soluble in diethyl ether. As a result the crude polyesters **9dcc.*x*** and **9dic.*x*** ($x = 1$–7) were stirred in diethyl ether for up to 24 h, thereby separating the urea and DMAP by-products, as well as unreacted monomer **1** and other low molecular weight oligomers ($\leqslant$4 monomer units). Using this method the percentage conversion of monomer **1** was usually in the region 55–80%.

To assess the scope of the polycondensation the reaction conditions and reagent concentrations were varied. Table 1 shows the various conditions employed and

Table 1
Polymerization of the AB_2 monomer **1** using coupling reagents to afford polyesters **9**

Polyester	CR[a]	Reaction time (h)	[**1**] (mol/l)	[CR] (mol/l)	Feed ratio [**1**]:[CR]	M_w[b]	M_n[b]	PD	DB[c]
9dcc.1	DCC[d]	60	0.20	0.20	1:1	3229	1879	1.72	0.23
9dcc.2	DCC	24	0.30	0.50	2:3	9600	4144	2.32	0.28
9dcc.3	DCC	30	2.00	3.00	2:3	10,996	5264	2.09	0.27
9dcc.4	DCC	60	0.20	0.40	1:2	5358	2137	2.51	0.23
9dcc.5	DCC	24	0.50	1.50	1:3	2602	1619	1.61	0.22
9dcc.6	DCC	1	0.50	0.75	2:3	9417	6172	1.52	0.26
9dcc.7	DCC	2	0.50	0.75	2:3	10,396	5700	1.82	0.28
9dic.1	DIC[e]	45	0.20	0.50	1:3	4635	2408	1.92	0.31
9dic.2	DIC	1	0.50	0.75	2:3	7633	4300	1.78	0.33
9dic.3	DIC	3	0.50	0.75	2:3	8085	4698	1.72	0.31
9dic.4	DIC	4.5	0.50	0.75	2:3	8345	4779	1.75	0.30
9dic.5	DIC	9	0.50	0.75	2:3	8435	4748	1.78	0.30
9dic.6	DIC	15	0.50	0.75	2:3	9371	5354	1.75	0.27
9dic.7	DIC	45	0.50	0.75	2:3	9257	5392	1.72	0.28

[a] CR = coupling reagent.
[b] Determined by GPC measurements with THF as the eluent using polystyrene standards.
[c] Determined by ^{13}C NMR spectroscopic analysis.
[d] DCC = 1,3-dicyclohexylcarbodiimide.
[e] DIC = 1,3-diisopropylcarbodiimide.

ratio of the reagents, in addition to the characteristics of the resulting polyester.

The optimum concentration of coupling reagent was found to be approximately 1.5 equivalents as the molecular weight of the polyesters decreased significantly when the concentration of coupling reagent to monomer was equal, doubled or tripled. The concentration of the monomer in solution and reaction time had little effect on the molecular weight or DB of the polyesters. In fact the maximum molecular weight material was usually obtained within the first hour of the reaction, with it then only increasing slightly over a further 1–15 h. For example the polyester **9dic.2** was synthesized in an hour and has a M_w of ~7600, whereas **9dic.6** was synthesized over 15 h and has a M_w of ~9400. In all cases the polyesters **9dcc.*x*** and **9dic.*x*** ($x = 1$–7) were white or off-white solids, soluble in THF with similar DB ranging from 0.22 to 0.33. The PDs of the polyesters **9dcc.*x*** were found to vary considerably, although that was found to be the opposite for the polyesters **9dic.*x***, which generally had PDs of ~1.7.

DSC analysis of the polyesters **9dcc.*x*** and **9dic.*x*** ($x = 1$–7) were hampered initially as a result of the poor thermal stability of the materials. Upon heating, most of the polyesters melted in the range 180–210 °C, which was accompanied by discolouration and almost instantaneous decomposition. Heating the polyesters **9dcc.*x*** and **9dic.*x*** ($x = 1$–7) to just below their melting points and then cooling and re-heating enabled their T_g values to be recorded as approximately 140 and 135 °C, respectively.

The polyesters **9dcc.*x*** and **9dic.*x*** ($x > 1$) were isolated as diethyl ether insoluble fractions and identified and characterized by their respective MALDI-TOF MS, ^1H and ^{13}C NMR spectra. The molecular weight of the polyesters was determined by GPC measurements with THF as eluent using polystyrene standards. The ^1H NMR spectrum of a DCC coupled polyester **9dcc.2** (entry 2 in Table 1) obtained using a monomer: coupling reagent feed ratio of 2:3 is shown in Fig. 2. The two broad singlet resonances ***a*** and ***b*** at δ_H 4.31 and 5.23 ppm, respectively, are assigned to methylene protons adjacent to a hydroxyl and ester functions. The broad resonance ***c*** at δ_H 5.39 ppm is attributed to the terminal hydroxyl protons of the hyperbranched polyester and is suppressed upon treatment of the solution with the addition of D_2O. The two broad resonances ***d*** and ***e*** at 7.70 and 7.87 ppm in the spectrum correspond to the sum of the aromatic protons of the branched, linear and terminal aromatic residues. In addition, a broad set of proton resonances at high field between δ_H 0.6 and 1.8 ppm correspond to the aliphatic protons of the DCC moiety located at the focal point of each hyperbranched macromolecule and enabled differentiation of the polyesters. For example, when DIC was used instead of DCC in the polymerization, the aliphatic proton resonances of the *iso*-propyl fragments were clearly evident between 0.80 and 1.20 ppm. Further evidence for the different coupling reagent residues at the focal point of the resulting hyperbranched polyesters was provided by detailed MALDI-TOF MS analyses in which regular repeating series of mass ions were present that corresponded

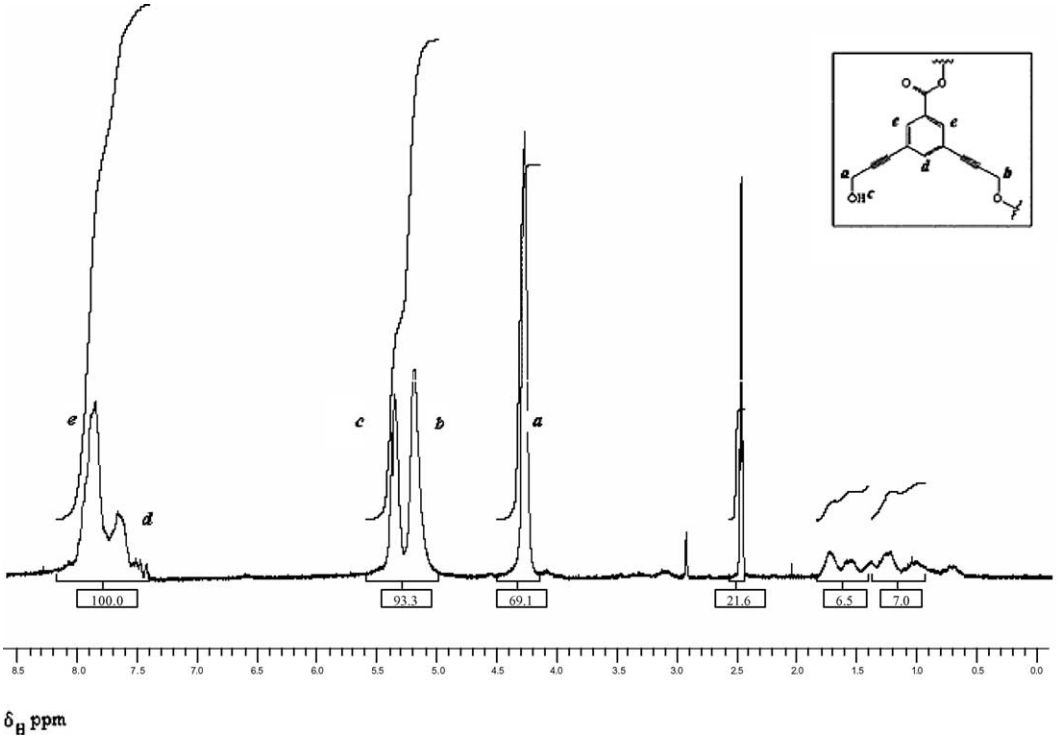


Fig. 2. The ^{1}H NMR spectrum of the Polyester **9dcc.2**.

to the proposed hyperbranched macromolecules. However, cyclized products were not detected using this analytical technique.

GPC analysis of the polyesters **9dcc.*x*** and **9dic.*x*** ($x > 1$) revealed broad molecular weight distributions (Fig. 3) under all conditions employed, which included polyesters possessing molecular weights $\geqslant$1,000,000. For all of the hyperbranched polyesters in this study, the degree of branching obtained was significantly lower than that the statistical value of 0.5 calculated by Frey and coworkers [33], for the direct homopolymerization of AB_2 monomers. It is proposed that the lower degrees of branching factors obtained for this type of polyester arise as a consequence of the rigid conformation of the monomer **1** that in turn produces considerable steric hindrance during the polymerization. Consequently, hyperbranched polyesters possessing a high proportion of linear units are produced.

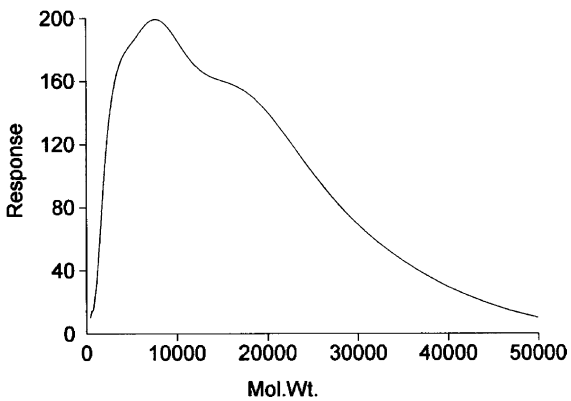


Fig. 3. The GPC chromatogram of polyester **6dic.3**.

3. Experimental

3.1. Materials

Reagents were purchased from the Aldrich Chemical Company or Acros Chimica, and were used as received without purification with the exception of triethylamine and thionyl chloride which were distilled from 4 Å molecular sieves. Solvents were used as supplied with the exception of the following: THF was distilled under argon from sodium benzophenone.

3.2. 3,5-Bis(3-hydroxyprop-1-ynyl)benzoic acid ethyl ester **3** [12]

To a rapidly stirring solution of 3,5-dibromobenzoic acid ethyl ester **2** (8.00 g, 26 mmol) and triethylamine (24

ml) in anhydrous THF (130 ml), under an inert N_2 atmosphere, was added, bis(dibenzylideneacetone) palladium (0.62 g, 0.98 mmol), triphenylphosphine (1.40 g, 4.9 mmol) and copper iodide (0.24 g, 1.1 mmol). The mixture was stirred for 1 h and then propargyl alcohol (4.40 g, 79 mmol) was added continuously over a period of 3 h, after which time the mixture was heated to and maintained under reflux for 40 h. Upon cooling to room temperature, the mixture was filtered and the filtrate concentrated in vacuo. The resultant oil was dissolved in chloroform (100 ml), then washed with 1 M HCl (50 ml) and water (2×100 ml). The organic phase was then dried ($MgSO_4$), filtered at the pump and the filtrate concentrated in vacuo. The resulting oil was purified by flash column chromatography (SiO_2; 4:1 v:v, CH_2Cl_2:EtOAc) to afford **3** as a pale yellow solid. The solid was then dissolved in the minimum volume of diethyl ether and precipitated into cyclohexene (300 ml), to afford **3** as a cream solid (4.7 g, 70%); melting point 90–92 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS) δ_H 1.35 (t, 3H, $J = 14.3$, CH_3), 4.34 (q, 2H, $J = 21.4$, CH_2), 4.43 (s, 4H, $2CH_2$), 7.52 (t, 1H, $J = 3.2$, ArH), 7.94 (d, 2H, $J = 1.6$, 2ArH); ^{13}C NMR (62.8 MHz, $CDCl_3$, TMS) δ_C 14.6 (CH_3), 51.8 (CH_2), 62.0 (CH_2), 84.2 (2C≡C), 89.3 (2C≡C), 123.7 (2ArC–C), 131.4 (ArC–CO_2Et), 132.9 (2ArCH), 138.7 (ArCH), 165.7 (C=O); IR: ν_{max} cm^{-1}: 666, 723, 1414, 1462, 1585, 1735, 2354, 2856, 2923; *m/z* (desorption chemical ionization, NH_3) 276[$(MNH_4)^+$, 80%], 258[100%], 213[28%], 185[29%], 128[20%] and 49[19%].

3.3. 3,5-Bis(3-hydroxyprop-1-ynyl)benzoic acid *1* [12]

To a stirred solution of **3** (1.90 g, 7.4 mmol) in acetone (50 ml) was added 1 M lithium hydroxide (50 ml) and the mixture was heated under reflux for 4.5 h. Upon cooling the solution was concentrated in vacuo and the acidity of the remaining aqueous solution was adjusted to pH 2 with 1 M HCl, after which a light brown precipitate formed. Filtration of this solid yielded a brown/gold product that was dissolved in the minimum volume of ethyl acetate, dried ($MgSO_4$), filtered and the filtrate concentrated in vacuo to afford the AB_2 monomer **1** as a cream solid (1.6 g, 91%); melting point 162–164 °C; ^{1}H NMR (250 MHz, d_6-DMSO, TMS) δ_H 4.33 (d, 4H, $J = 5.6$, $2CH_2$), 5.43 (t, 2H, $J = 11.8$, 2OH), 7.65 (t, 1H, $J = 3.2$, ArH), 7.88 (d, 2H, $J = 1.6$, 2ArH); ^{13}C NMR (62.8 MHz, d_6-DMSO, TMS) δ_C 49.7 ($2CH_2$), 82.1 (2C≡C), 92.0 (2C≡C), 123.9 (2ArC–C), 131.9 (2ArCH), 132.4 (ArC–CO_2Et), 137.4 (ArCH), 166.1 (C=O); IR: ν_{max} cm^{-1}: 670, 723, 971, 1309, 1591, 1710, 2295, 2725, 3172, 3421; *m/z* (desorption chemical ionization, NH_3) 248[$(MNH_4)^+$, 9%], 230[100%], 213[33%], 185[32%], 128[28%].

3.4. 3,5-Bis(3-acetyloxy prop-1-ynyl)benzoic acid *6*

To freshly distilled pyridine (20 ml) under argon was added 3,5-bis(3-hydroxyprop-1-ynyl)benzoic acid **1** (234 mg, 1 mmol) and acetic anhydride (300 mg, 3 mmol). The reaction mixture was heated under reflux for 4 h, cooled to room temperature and then filtered. The solution was then concentrated in vacuo to afford a solid residue that was purified via column chromatography (SiO_2; 4:1 v:v, EtOAc:CH_2Cl_2) to afford **6** as a pale yellow solid. The solid was dissolved in EtOAc, dried ($MgSO_4$), filtered and the filtrate concentrated in vacuo to afford the acetylated monomer **6** as a cream solid (0.158 g, 49%); melting point 100–102 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS) δ_H 2.08 (s, 6H, $2CH_3$), 4.83 (s, 4H, $2CH_2$), 7.67 (t, 1H, $J = 3.2$, ArH), 8.06 (d, 2H, $J = 1.6$, 2ArH); ^{13}C NMR (62.8 MHz, $CDCl_3$, TMS) δ_C 19.7 ($2CH_3$), 51.5 ($2CH_2$), 83.2 (2C≡C), 83.9 (2C≡C), 122.2 (2ArCC), 129.0 (ArC–CO_2Et), 132.4 (2ArCH), 138.5 (ArCH), 168.7 (2C=O), 169.3 (C=O); IR: ν_{max} cm^{-1}: 1032, 1066, 1229, 1267, 1451, 1589, 1691, 1745, 2235, 3408; *m/z* (desorption chemical ionization, NH_3) 332-[$(MNH_4)^+$, 58%], 79[100%].

3.5. Trimethylsilyl-3,5-bis(3-(trimethylsilyloxy)prop-1-ynyl)benzoate *7*

To a rapidly stirred suspension of 3,5-bis(3-hydroxyprop-1-ynyl)benzoic acid **1** (255 mg, 1.1 mmol) in dry dichloromethane under an inert atmosphere was added *N*,*N*′-bis(trimethylsilyl) urea (487 mg, 2.4 mmol). The mixture was heated under reflux for 4 h and then filtered under argon. The filtrate was then concentrated in vacuo to afford a white solid that was not soluble in hexane and a clear oil. The oil component was dissolved in hexane and filtered under argon through a pad of $MgSO_4$. The filtrate was then concentrated to afford the trimethylsilyl-3,5-bis(3-(trimethyl silyloxy)prop-1-ynyl)benzoate **7** as a clear oil (0.398 g, 80%); ^{1}H NMR (250 MHz, $CDCl_3$, TMS) δ_H 0.00 (s, 18H, $6CH_3$), 0.17 (s, 9H, $3CH_3$), 4.30 (s, 4H, $2CH_2$), 7.41 (t, 1H, $J = 3.0$, ArH), 7.79 (d, 2H, $J = 1.5$, 2ArH); ^{13}C NMR (62.8 MHz, $CDCl_3$, TMS) δ_C 0.00 ($6CH_3$), 0.06 ($3CH_3$), 51.8 ($2CH_2$), 83.6 (2C≡C), 89.3 (2C≡C), 123.8 (2ArC–C), 132.3 (ArC–CO_2Et), 133.2 (2ArCH), 138.6 (ArCH), 165.5 (C=O); IR: ν_{max} cm^{-1}: 846, 1002, 1090, 1253, 1341, 1366, 1441, 1594, 1708, 2958; *m/z* (desorption chemical ionization, NH_3) 447[(M + 1), 40%], 375[21%], 279[36%], 90[92%], 74 [100%].

3.6. 3,5-Bis(3-(trimethylsilyloxy)prop-1-ynyl)benzoyl chloride *8*

The acid chloride **8** was synthesized using a procedure adapted from [24]. To a solution of the silylated monomer **7** (362 mg, 0.8 mmol) in dry CH_2Cl_2 (40 ml)

containing triethylammonium chloride (11 mg, 0.08 mmol) was added freshly distilled thionyl chloride (0.1 ml, 1.1 mmol) drop-wise under nitrogen. After the addition was complete the mixture was heated to reflux for 4.5 h, cooled and then the excess thionyl chloride and solvent removed in situ by gradual heating to afford the acid chloride **10** as a dark yellow oil.

3.7. General procedure for polymerization of monomer *1* using coupling reagents

To a stirred solution of 3,5-bis(3-hydroxyprop-1-ynyl)benzoic acid 1, in anhydrous THF was added coupling reagent (DCC or DIC) and DMAP (a catalytic amount). The reaction vessel was then fitted with a calcium chloride guard tube and stirred at room temperature for 24 h. The mixture was then filtered and the filtrate concentrated in vacuo. The resulting crude product was dissolved in THF and added drop-wise into cyclohexene to afford a cream precipitate. The mixture was then filtered and the solid was stirred in Et_2O and then filtered to afford the polyester as a white solid (yields obtained: 55–90%); ^{1}H NMR (250 MHz, d_6-DMSO, TMS) δ_H 4.31 (broad band, CH_2), 5.23 (broad band, CH_2), 5.39 (broad band, OH), 7.70 (broad band, ArH), 7.87 (broad band, ArH); ^{13}C NMR (62.8 MHz, d_6-DMSO, TMS) δ_C 49.7 (CH_2), 53.8 (CH_2), 81.7 (C≡C), 84.4 (C≡C), 86.1 (C≡C), 92.4 (C≡C), 123.0 (ArC–C), 124.1 (ArC–C), 130.4 (ArCH), 131.9 (ArC–CO_2), 138.0 (ArCH), 138.4 (ArCH), 163.9 (C=O): DB = 20–40%; IR: ν_{max} cm^{-1}: 722, 766, 896, 944, 1034, 1062, 1112, 1224, 1335, 1376, 1456, 1593, 1641, 1728, 2724, 2924, 3378; GPC: M_w = 2500–11,000.

3.8. Analytical methods

Thin layer chromatography was performed on aluminum sheets coated with Merck 5735 Kieselgel 60F. Sorbsil 60 (0.040–0.063 mm mesh, Merck 9385) was used to perform column chromatography. Mass spectra were obtained from a VG Autospec instrument operating in chemical ionization (CI) mode employing ammonia as the impact gas and MALDI-TOF MS spectra were recorded on a SAI Ltd LaserToF LT3 instrument. In the case of MALDI-TOF MS, α-cyano-4-hydroxycinnamic acid was employed as the matrix. A typical sample preparation is described as follows: 3 μl of a solution of the analyte in THF (1–10 mg/ml) was combined with 10–20 μl of the freshly prepared matrix (0.1 or 0.2 M in THF) in a mini-vial, and from the mixture was taken a 2 μl aliquot which was transferred onto a sample plate and left to air dry prior to analysis. ^{1}H and ^{13}C NMR spectra were recorded at 250 and 62.8 MHz, respectively, on a Bruker AC250 spectrometer (using the deuterated solvent as lock and residual solvent or tetramethylsilane as an internal reference). Infrared (IR) spectra were recorded as KBr discs on a Perkin Elmer 1720-× infrared Fourier Transform spectrometer. GPC was performed on a PL-GPC 220 coupled with a refractive index detector, with THF as the eluent at a flow rate of 1.0 ml/min and temperature of 40 °C. Differential scanning calorimetry (DSC) was performed using a Mettler DSC 20 system.

4. Conclusions

As a result of the thermal instability of the acid-diol AB_2 monomer **1**, it was impossible to perform direct thermally driven polyesterifications to generate the desired hyperbranched polymers. Consequently, milder conditions, such as those employing reagents such as DCC or DIC were used successfully to afford a variety of different polyesters. As predicted, these polyesters were found to possess low branching factors as determined using ^{13}C NMR spectroscopic analysis. The DB values range between 0.22 and 0.33 as a direct result of the highly rigid conformation of the monomer **1** and the use of bulky coupling reagents, which in turn creates steric hindrance during the coupling steps. The molecular weight of the polyesters obtained via this approach were comparable to related studies on hyperbranched polyesters and varied between 2500 and 11,000 and the hyperbranched materials exhibited excellent solubility characteristics in aprotic solvents such as THF. Detailed thermal analysis of the resultant polyesters revealed T_g values in the range 135–145 °C, however, these polymers could not be heated above ~180 °C as this resulted in rapid decomposition or cross-linking to generate intractable materials.

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