Functional, Hyperbranched Polyesters Via Baylis–Hillman Polymerization

Sanhao Ji,[1] Bernd Bruchmann,[2] Frederik Wurm,[1] Harm-Anton Klok[1]

[1]École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, Bâtiment MXD, Station 12, CH-1015 Lausanne, Switzerland
[2]Polymer Research, BASF SE, D-67056 Ludwigshafen, Germany
Correspondence to: H.-A. Klok (E-mail: harm-anton.klok@epfl.ch)

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ABSTRACT: Hyperbranched polyesters are among the most common hyperbranched polymers. One of the interesting features of hyperbranched polyesters is that they contain unreacted hydroxyl and carboxylic acid groups at the linear and terminal structural units, which can be postmodified to adjust thermal, solubility, or mechanical properties, or to prepare core–shell type architectures. This article reports on the synthesis of a novel class of hyperbranched polyesters via an $A_2 + B_3$ type Baylis–Hillman polymerization of 2,6-pyridinedicarboxaldehyde and trimethylolpropane triacrylate. Baylis–Hillman polymerization generates highly functional polyesters that contain not only unreacted aldehyde and/or acrylate groups at the linear and terminal structural units but also chemically orthogonal vinyl and hydroxyl groups along the polymer backbone. Using 3-hydroxyquinuclidine as the catalyst, hyperbranched polymers with number-average molecular weights up to 7500 g/mol and degrees of branching up to 0.81 were obtained. To demonstrate the versatility of these hyperbranched polyesters to act as platforms for further derivatization, the orthogonal postpolymerization modification of the hydroxyl, vinyl, and pyridine functional moieties with phenyl isocyanate, methyl-3-mercaptopropionate, and methyl iodide is presented. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 25–34, 2012

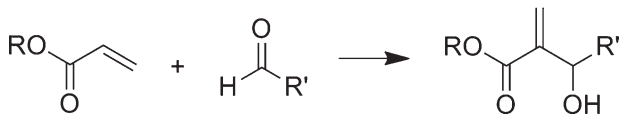
KEYWORDS: $A_2 + B_3$ approach; Baylis Hillman reaction; functionalization of polymers; hyperbranched; polyesters

INTRODUCTION Hyperbranched polymers are an attractive class of materials that possess some of the properties that are characteristic for highly branched polymer architectures, such as high functionality, enhanced solubility, low viscosity, and low crystallinity, while obviating the tedious, stepwise synthetic protocols that are required for the synthesis of dendrimers.[1–4] Over the past decades, a broad variety of hyperbranched polymers has been synthesized. Among the many types of hyperbranched polymers that have been reported, hyperbranched polyesters are one of the most dominating representatives.[5]

Hyperbranched polyesters can be synthesized via various approaches but are most often prepared via AB_2 or $A_2 + B_3$ type step polymerizations.[6–11] The resulting hyperbranched polymers contain hydroxyl and/or carboxylic acid functional groups at the linear and terminal structural units, which are amenable to postpolymerization modification and can be used to tune the thermal, solubility, and mechanical properties of these materials or to prepare core–shell type architectures. Access to hyperbranched polymers that contain multiple, chemically orthogonal functional groups, which can be regioselectively addressed would enable enhanced control of the properties of these macromolecules and further expand their scope of applications.

This contribution explores the feasibility of the Baylis–Hillman reaction for the synthesis of hyperbranched polyesters. The Baylis–Hillman reaction involves the base-catalyzed reaction of an α,β-unsaturated carbonyl compound with an aldehyde to form an α-methylene-β-hydroxycarbonyl compound (Scheme 1).[12–14] This reaction has attracted interest in organic synthesis as it is an atom-economical carbon–carbon bond forming reaction that can be carried out with control over stereochemistry and generates a polyfunctional scaffold that can be converted to a variety of other products. Very recently, also first examples of the use of the Baylis–Hillman reaction for the synthesis of linear side-chain functional polyesters were reported.[15,16] Two characteristics that make this reaction an attractive tool in polymer synthesis include: (i) Baylis–Hillman polymerization results in polyesters with two chemically orthogonal side-chain functional groups, *viz*. a vinyl group and an hydroxyl group, which can subsequently be selectively modified via an appropriate postpolymerization modification reaction; (ii) as the vinyl and hydroxyl groups are generated during the C—C bond forming process, Baylis–Hillman polymerization allows the preparation of side-chain functional polyesters without the need for laborious protective group chemistry. While the previous

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Baylis-Hillman reaction.

published reports exclusively focused on the synthesis of linear polymers, this contribution investigates the $A_2 + B_3$ type Baylis–Hillman polymerization of 2,6-pyridinedicarboxaldehyde and trimethylolpropane triacrylate (TMPTA) to generate highly functional, hyperbranched polyesters and explores the postpolymerization modification of the vinyl, hydroxyl, and pyridine moieties of these materials.

EXPERIMENTAL

Materials

All reagents and solvents were of commercial grade and used as received. TMPTA was purified by flash column chromatography on silica gel using hexane and ethyl acetate (4:1, v/v) as the eluent. 2,6-Pyridinedimethanol was obtained from Acros. All other chemicals and reagents were acquired from Sigma–Aldrich (Buchs, Switzerland). Deuterated solvents for NMR spectroscopy were acquired from Armar Chemicals (Döttigen, Switzerland).

Analytical Methods

Gel permeation chromatography (GPC) was performed on a Waters Alliance GPCV 2000 system equipped with refractive index, differential viscometer, and light scattering detectors. Separation was carried out at 60 °C with TSK-Gel Alpha 2500 + 3000 + 4000 columns, using vacuum distilled High-performance liquid chromatography (HPLC) grade N,N-dimethylformamide (DMF) + 0.5 g/L LiCl as eluent and a flow rate of 0.6 mL/min. Molecular weights were determined using conventional and universal calibration curves, which were created with narrow polydispersity poly(methyl methacrylate) standards. Mark–Houwink α parameters were determined by universal calibration. Results were calculated with the Empower Pro multidetection GPC software (Version 5.00). The interdetector volume was adjusted from the peak position of uniform poly(ethylene glycol) (PEG) oligomers. The volume of the injected loop was 0.214 mL, and the polymer concentration was calculated to give a viscometric signal less than 0.5% of the baseline level. NMR spectra were recorded on Bruker ARX-400 and ARX-600 spectrometers. $CDCl_3$ was used as the solvent. For ^{1}H NMR spectroscopy, chemical shifts are reported in ppm relative to the solvent's residual ^{1}H signal ($CDCl_3$: 7.25 ppm). Coupling constants J are given in Hz. ^{13}C NMR spectra were recorded at 101 MHz. The ^{13}C signal of the solvent ($CDCl_3$: 77 ppm) was used as internal reference. Coupling constants J are given in Hz. ^{13}C NMR spectra of hyperbranched polymer **6** were recorded at 150.9 MHz. To allow integration, inverse gated proton decoupled ^{13}C NMR spectra were recorded with a pulse interval of 10 s to allow complete recovery of all carbons. Electrospray ionization-mass spectrometry (ESI-MS) analysis was performed on a single quadrupole mass spectrometer Finnigan SSQ 710C (Finnigan-MAT, Bremen, Germany) equipped with an ESI interface. Data were acquired using the ICIS software running on a Digital Unix workstation. Fourier transform reflectance infrared spectra were acquired using a nitrogen-purged Nicolet Magna-IR 560 spectrometer equipped with a Micro Specular Reflectance accessory (Specac) and processed using the OMNIC ESP 5.1 software.

Procedures

2,6-Pyridinedicarboxaldehyde (2)

In a 500 mL round bottom flask equipped with a condenser, 2,6-pyridinedimethanol (5 g, 37 mmol) was dissolved in hot $CHCl_3$ (250 mL). The flask was cooled to room temperature, and activated manganese oxide (60 g, 20 equiv) was added as a solid. The mixture was vigorously stirred under reflux for 4 days until most of the starting material was consumed. After cooling to room temperature, the suspension was filtered over Celite. The oxidized products were purified by flash column chromatography on silica gel, eluting with ethyl acetate and dichloromethane (1:1, v/v), which afforded **2** as a white, pure solid (2.1 g, yield 42%).

^{1}H NMR (400 MHz, $CDCl_3$): 10.16 (s, 2H, HC=O), 8.16 (d, J = 7.8 Hz, 2H, pyridine-H), 8.07 (t, J = 7.8 Hz, 1H, pyridine-H). ^{13}C NMR (101 MHz, $CDCl_3$): 192.34, 152.98, 138.37, 125.32. MS (ESI): 136.96 $[M+H]^+$. ^{1}H NMR, ^{13}C NMR, and ESI-MS spectra are included in Supporting Information (Figs. S1–S3).

Mono(β-hydroxy-α-methylene-2-pyridinepropanoic acid)-diacryloyl Trimethylolpropane (3)

To a stirred mixture of 2-pyridinecarboxaldehyde (164 μL, 1.68 mmol) and TMPTA (500 mg, 1.68 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (180 mg, 1.6 mmol) and methanol (120 μL, 3 mmol) were added. DMF (0.2 mL) was added to help dissolve the reactants. The brown, homogeneous reaction mixture was stirred at ambient temperature for 5 h, and the progress of the reaction was monitored by thin layer chromatography (TLC) (solvent: ethyl acetate). On completion, the reaction mixture was purified by flash column chromatography on silica gel, eluting with ethyl acetate to give the desired product **3** as light yellow oil (545.6 mg, yield 80.5%).

^{1}H NMR (400 MHz, $CDCl_3$): 8.53 (d, J = 2 Hz, 1H, pyridine-H), 7.65 (t, J = 2 Hz, 1H, pyridine-H), 7.38 (d, J = 2 Hz, 1H, pyridine-H), 7.18 (t, J = 2 Hz, 1H, pyridine-H), 6.34 (t, J = 3.6 Hz, 3H, =C$\underline{H}_2$), 6.07 (m, J = 3.8 Hz, 2H, —C$\underline{H}$=CH$_2$), 5.96 (s, 1H, =C$\underline{H}_2$), 5.83 (d, 2H, C$\underline{H}$=CH$_2$), 5.56 (s, 1H, —C$\underline{H}$—OH), 4.82 (s, 1H, —O$\underline{H}$), 4.03 (s, —O—C$\underline{H}_2$—, 6H), 1.43 (m, J = 6.2 Hz, 2H, —C$\underline{H}_2$—CH$_3$), 0.84 (t, J = 6.2 Hz, 3H, —CH$_2$—C$\underline{H}_3$). ^{13}C NMR (101 MHz, $CDCl_3$): 165.6, 159.24, 148.18, 141.33, 136.87, 131.21, 127.81, 122.65, 120.93, 72.25, 63.91, 40.79, 22.95, 7.22. MS (ESI): 404.66 $[M+H]^+$. ^{1}H NMR, ^{13}C NMR, and ESI-MS spectra are included in Supporting Information (Figs. S4–S6).

2-((Acryloyloxy)methyl)-2-ethylpropane-1,3-diyl Bis(2-(hydroxy(pyridin-2-yl)methyl)acrylate) (4)

To a stirred mixture of 2-pyridinecarboxaldehyde (328 μL, 3.36 mmol) and TMPTA (500 mg, 1.68 mmol), DABCO (240 mg, 2.1 mmol) and methanol (120 μL, 3 mmol) were added. DMF (0.2 mL) was added to help dissolve the reactants. The

brown, homogeneous reaction mixture was stirred at ambient temperature for 5 h, and the progress of the reaction was monitored by TLC (solvent: ethyl acetate). On completion, the reaction mixture was purified by flash column chromatography on silica gel, eluting with ethyl acetate to give the desired product **4** as light yellow oil (643.3 mg, yield 75%).

^{1}H NMR (400 MHz, $CDCl_3$): 8.51 (d, J = 2 Hz, 2H, pyridine-H), 7.65 (t, J = 2 Hz, 2H, pyridine-H), 7.36 (d, J = 2 Hz, 2H, pyridine-H), 7.18 (t, J = 2 Hz, 2H, pyridine-H), 6.34 (d, J = 3.6 Hz, 3H, $=CH_2$), 6.07 (m, J = 3.8 Hz, 1H, $-CH=CH_2$), 5.93 (s, 2H, $-CH=CH_2$), 5.82 (d, 1H, $-CH=CH_2$), 5.50 (s, 2H, $-CH-OH$), 4.84 (s, 2H, $-OH$), 3.98 (m, $-O-CH_2-$, 6H), 1.29 (m, J = 6.2 Hz, 2H, $-CH_2-CH_3$), 0.77 (t, J = 6.2 Hz, 3H, $-CH_2-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): 165.51, 159.28, 148.17, 141.3, 136.9, 131.21, 127.75, 122.65, 120.94, 72.24, 64.07, 40.77, 22.77, 7.14. MS (ESI): 511.63 $[M+H]^+$. ^{1}H NMR, ^{13}C NMR, and ESI-MS spectra are included in Supporting Information (Figs. S7–S9).

2-Ethyl-2-(((2-(hydroxy(pyridin-2-yl)methyl)acryloyl)oxy)-methyl)propane-1,3-diyl Bis(2-(hydroxy(pyridin-2-yl) methyl)acrylate) (5)

To a stirred mixture of 2-pyridinecarboxaldehyde (530 μL, 5.57 mmol) and TMPTA (487 mg, 1.64 mmol), DABCO (360 mg, 3.2 mmol) and methanol (180 μL, 4.5 mmol) were added. DMF (0.2 mL) was added to help dissolve the reactants. The brown, homogeneous reaction mixture was stirred at ambient temperature for 5 h, and the progress of the reaction was monitored by TLC (solvent: ethyl acetate). On completion, the reaction mixture was purified by flash column chromatography on silica gel, eluting with ethyl acetate to give the desired product **5** as a light yellow oil (780 mg, yield 77%).

^{1}H NMR (400 MHz, $CDCl_3$): 8.42 (d, J = 2 Hz, 3H, pyridine-H), 7.59 (t, J = 2 Hz, 3H, pyridine-H), 7.31 (d, J = 2 Hz, 3H, pyridine-H), 7.11 (t, J = 2 Hz, 3H, pyridine-H), 6.25 (s, 3H, $=CH_2$), 5.88 (s, 3H, $=CH_2$), 5.55 (s, 3H, $-CH-OH$), 5.04 (br, 3H, $-OH$), 3.8 (m, $-O-CH_2-$, 6H), 1.08 (m, J = 6.2 Hz, 2H, $-CH_2-CH_3$), 0.64 (t, J = 6.2 Hz, 3H, $-CH_2-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$):165.38, 159.32, 148.12, 141.28, 136.86, 127.58, 122.58, 120.9, 72.19, 63.87, 40.72, 22.56, 7.02. MS (ESI): 618.56 $[M+H]^+$. ^{1}H NMR, ^{13}C NMR, and ESI-MS spectra are included in Supporting Information (Figs. S10–S12).

Polymer 6

Procedure 1. To a stirred mixture of 2,6-pyridinedicarboxaldehyde **2** (195.4 mg, 1.4 mmol) and TMPTA **1** (390 μL, 1.4 mmol), 3-hydroxyquinuclidine (3-HQD; 100 mg, 0.8 mmol) was added. DMF (1 mL) was added to help dissolve the reactants, and the homogeneous reaction mixture was stirred at ambient temperature. The course of the reaction was followed by ^{1}H NMR spectroscopy and GPC. To this end, 450 μL aliquots were taken from the reaction mixture at defined time intervals. These samples were diluted with chloroform (50 mL) and then washed with a saturated solution of aqueous $NaHCO_3$, filtered and concentrated under reduced pressure. The resulting material was dissolved in chloroform (2 mL) and precipitated in diethyl ether (100 mL). The precipitated hyperbranched polyester was isolated by centrifugation and obtained as a white powder. The molecular weights of the polymer samples analyzed at different reaction times are summarized in Table 1.

^{1}H NMR (400 MHz, $CDCl_3$): 9.96 ($HC=O$), 7.82 (pyridine-H), 7.61 (pyridine-H), 7.2 (pyridine-H), 6.31 ($=CH_2$), 6.13 ($=CH_2$), 5.47 ($-CH-OH$), 4.84 ($-OH$), 3.78 ($-O-CH_2-C-$), 1.23 ($-CH_2-CH_3$), 0.77 ($-CH_2-CH_3$). ^{13}C NMR (150.9 MHz, $CDCl_3$): 192.43, 165.65, 158.68, 151.36, 140.94, 138.25, 127.72, 125.12, 120.34, 72.5, 64.07, 40.67, 22.85, 7.52. ^{1}H NMR is included in Supporting Information (Fig. S13).

Procedure 2. TMPTA **1** (408 μL, 1.5 mmol) was dissolved in 0.5 mL DMF and added dropwise over 30 min into a mixture of 2,6-pyridinedicarboxaldehyde **2** (204.7 mg, 1.5 mmol) and 3-HQD (100 mg, 0.8 mmol), which was dissolved in 0.5 mL DMF. The homogeneous reaction mixture was stirred at ambient temperature. The course of the reaction was followed by ^{1}H NMR spectroscopy and GPC. To this end, aliquots were withdrawn from the reaction mixture, and polymer samples were isolated as described in *Procedure 1*.

Procedure 3. To a stirred mixture of 2,6-pyridinedicarboxaldehyde **2** (256.1 mg, 1.9 mmol) and TMPTA **1** (334 μL, 1.2 mmol), 3-HQD (99 mg, 0.8 mmol) was added. DMF (1.0 mL) was added to help dissolve to reactants, and the homogeneous reaction mixture was stirred at ambient temperature. The course of the reaction was followed by ^{1}H NMR spectroscopy and GPC. To this end, aliquots were withdrawn from the reaction mixture, and polymer samples were isolated as described in *Procedure 1*.

Procedure 4. TMPTA **1** (342 μL, 1.3 mmol) was dissolved in 0.5 mL DMF and added dropwise over 30 min into a mixture of 2,6-pyridinedicarboxaldehyde **2** (257.9 mg, 1.9 mmol) and 3-HQD (105.4 mg, 0.8 mmol), which was dissolved in 0.5 mL DMF. The homogeneous reaction mixture was stirred at ambient temperature. The course of the reaction was followed by ^{1}H NMR spectroscopy and GPC. To this end, aliquots were withdrawn from the reaction mixture, and polymer samples were isolated as described in *Procedure 1*.

Postpolymerization Modification of 6 with Methyl 3-Mercaptopropionate (7). Polymer **6** (120 mg, Table 1, *Procedure 3* after 2 h) was dissolved in dry THF (0.2 mL), and pyridine (0.2 mL) was added to the mixture. Then, a large excess of methyl 3-mercaptopropionate (56 μL mL, 10 mmol) was added. The solution was stirred overnight at ambient temperature. The postmodified polymer was precipitated by addition of cold diethyl ether (100 mL) and isolated by centrifugation to afford **7** as a white powder (93.5 mg). M_n = 15,400; M_w/M_n = 2.58. The GPC elugram is included in Supporting Information (Fig. S14). ^{1}H NMR spectroscopy indicated quantitative conversion of the double bonds.

^{1}H NMR (400 MHz, $CDCl_3$): 9.99 ($HC=O$), 7.72, 7.32 (pyridine-H), 5.04 ($-CH-OH$), 4.45 ($-OH$), 3.88 ($-O-CH_2-C-$), 3.61 ($-OCH_3$, 6H), 3.15 ($-CH-CH_2-S-$), 2.84 ($-CH_2-S-CH_2-CH_2$), 2.6 ($-S-CH_2-CH_2-$), 2.42 ($-S-CH_2-CH_2-$), 1.32 ($-CH-CH_3$), 0.76 ($-CH-CH_3$).

TABLE 1 Summary of Reaction Conditions Evaluated for the Baylis–Hillman Polymerization of **1** and **2** and Molecular Characterization Data of the Resulting Polymers

Procedure	Monomer Molar Ratio (A_2:B_3)	Polymerization Time (h)	Addition Mode	M_w[a] (g/mol)	M_n[b] (g/mol)	M_n[c] (g/mol)	M_w/M_n[b] (–)	α[c]	DB[d]
1	1:1	1	One-pot	6,800	3,700	3,600	1.9	0.26	0.57
1	1:1	2	One-pot	8,500	4,200	4,200	1.9	0.25	0.66
1	1:1	3	One-pot	7,200	2,600	2,300	2.6	0.24	0.36
2	1:1	1	Slow monomer addition	13,400	5,000	5,400	3.3	0.31	0.65
2	1:1	2	Slow monomer addition	27,100	7,300	9,300	4.1	0.35	0.72
2	1:1	3	Slow monomer addition	28,100	7,500	9,700	4.0	0.36	0.68
3	3:2	1	One-pot	11,600	2,800	4,200	2.3	0.30	0.79
3	3:2	2	One-pot	19,700	5,100	8,700	2.2	0.29	0.61
3	3:2	3	One-pot	17,300	3,300	5,700	3.1	0.27	0.63
4	3:2	1	Slow monomer addition	8,800	4,300	4,500	2.7	0.30	0.81
4	3:2	2	Slow monomer addition	20,300	5,200	6,100	4.6	0.33	0.72
4	3:2	3	Slow monomer addition	Gelation	–	–	–	–	–

[a] Determined by GPC with a laser light scattering detector.
[b] Measured by GPC using a conventional calibration curve, which was created with PMMA standards.
[c] From GPC determined using universal calibration.
[d] Calculated from eq 1.

Postpolymerization Modification of 6 with Phenyl Isocyanate (8). To polymer **6** (96.2 mg, Table 1, *Procedure 3* after 2 h) dissolved in chloroform (1.2 mL), phenyl isocyanate (120 μL, 1.1 mmol) was added, and the solution was stirred for 6 h at ambient temperature. The postmodified product was precipitated by the addition of cold diethyl ether (100 mL) and isolated by centrifugation. Polymer **8** was obtained as a transparent oil (103.3 mg). $M_n = 3900$; $M_w/M_n = 11.6$. The GPC elugram is included in Supporting Information (Fig. S14). ^{1}H NMR spectroscopy indicated 83% conversion of the hydroxyl groups.

^{1}H NMR (400 MHz, $CDCl_3$): 6.5–8.0 (aromatic ring), 6.26 (=C$\underline{H}_2$), 5.82 (=C$\underline{H}_2$), 5.31 (—C$\underline{H}$—OH), 3.9 (—O—C$\underline{H}_2$—C—), 1.25 (—C$\underline{H}_2$—CH$_3$), 0.77 (—CH$_2$—C$\underline{H}_3$).

Postpolymerization Modification of 6 with Methyl Iodide (9). To the polymer **6** (40 mg, Table 1, *Procedure 3* after 2 h) dissolved in DMF (0.1 mL), methyl iodide (50 μL, 0.8 mmol) was added, and the solution was stirred for 1 h at ambient temperature. The removal of methyl iodide and DMF *in vacuo* gave the postmodified product **8** as yellow transparent oil (52 mg). $M_n = 10{,}200$; $M_w/M_n = 6.5$. ^{1}H NMR spectroscopy indicated 47% conversion of the pyridine residues. The GPC elugram is included in Supporting Information (Fig. S14).

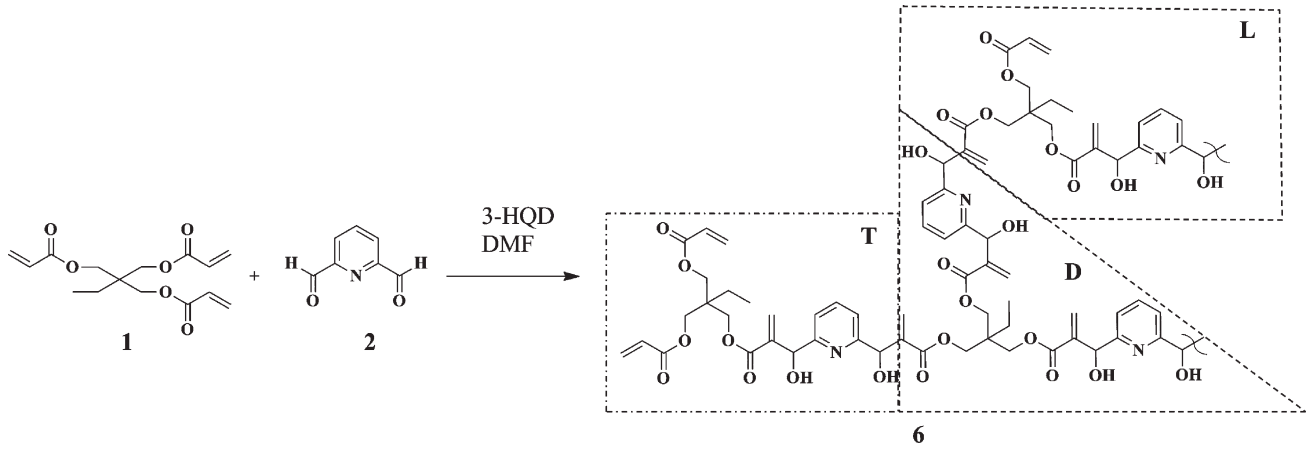
^{1}H NMR (400 MHz, $CDCl_3$): 9.91 (H$\underline{C}$=O), 7.75 (pyridine-H), 7.4 (pyridine-H), 7.32 (pyridine-H), 6.25 (=C$\underline{H}_2$), 6.03 (=C$\underline{H}_2$), 5.9 (—C$\underline{H}$—OH), 5.56 (—O$\underline{H}$), 3.95 (—O—C$\underline{H}_2$—C—), 1.39 (—C$\underline{H}_2$—CH$_3$), 0.79 (—CH$_2$—C$\underline{H}_3$).

RESULTS AND DISCUSSION

Polymerization

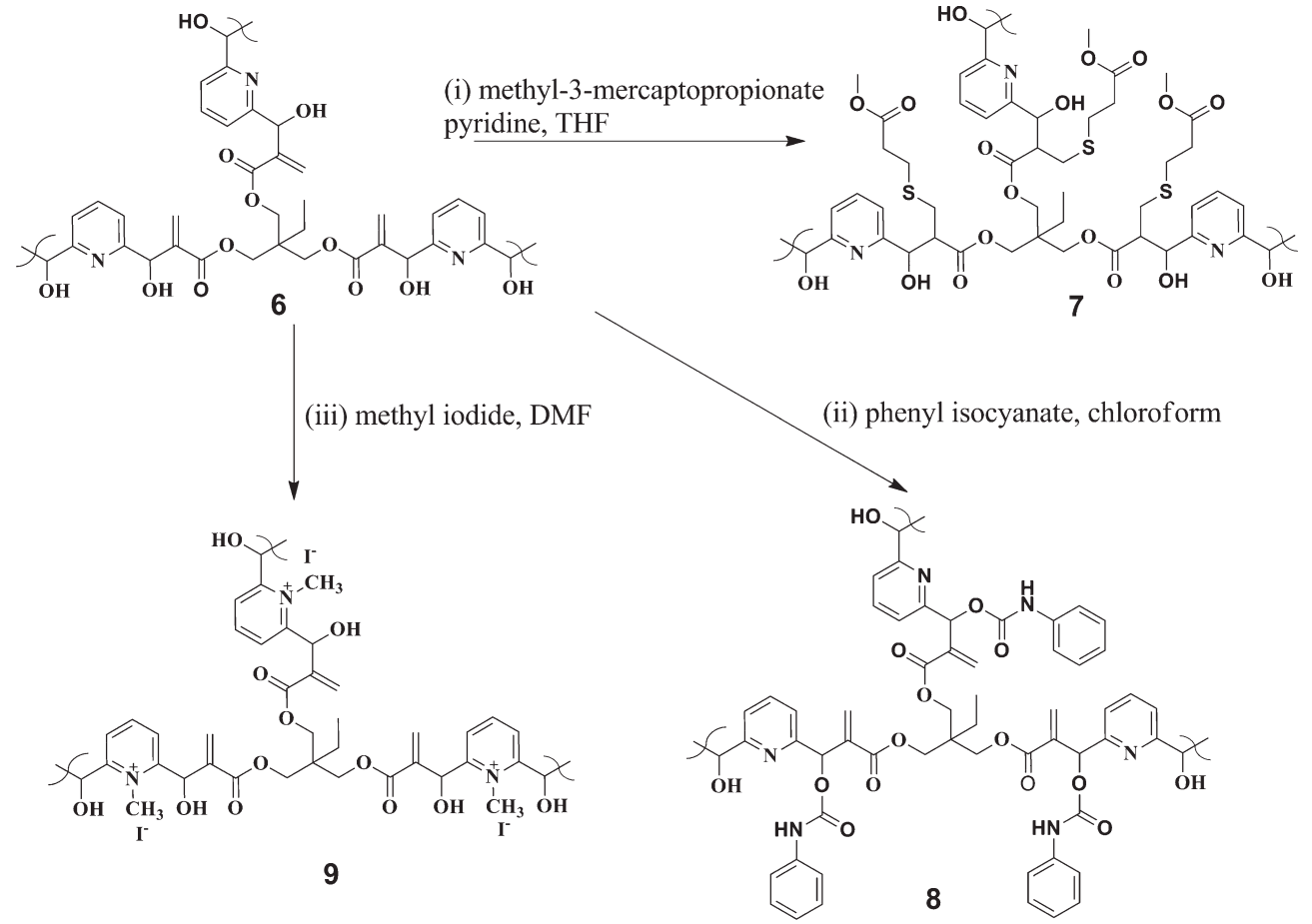
To evaluate the feasibility of the Baylis–Hillman reaction for the synthesis of hyperbranched polyesters, this report investigates the $A_2 + B_3$ polymerization of 2,6-pyridinedicarboxaldehyde (**2**) and TMPTA (**1**) (Scheme 2). These monomers were chosen as the Baylis–Hillman reactions between 2,6-pyridinedicarboxaldehyde and methyl acrylate[17] and 2-pyridinecarboxaldehyde and methyl acrylate[18] have been reported to proceed with 93–100% yield, which is an important requirement to obtain high molecular weight polymers in a step-type polymerization. All polymerizations of **1** and **2** were carried out in DMF, which was found to be a good solvent for both the monomers and the polymer and ensured homogeneous reaction conditions, and used 3-HQD as the catalyst. A number of polymerization procedures were evaluated, which differed with respect to the molar ratio of monomers used, the mode of monomer addition as well as reaction time. The resulting polymers were analyzed with GPC and NMR. Table 1 summarizes the reaction conditions that were evaluated and the characteristics of the final polymers.

In a first series of polymerization experiments, monomers **1** and **2** were mixed in a 1:1 molar ratio and polymerized at room temperature in the presence of 3-HQD as the catalyst (Table 1, *Procedure 1*). Using this protocol, polymers were obtained with a number-average molecular weight (M_n) of 4200 after 2 h of reaction time. Longer reaction times (3 h) did not result in an increase, but rather in a decrease of



SCHEME 2 Synthesis of hyperbranched polyesters via Baylis-Hillman polymerization.

molecular weight, pointing toward a possible depolymerization, which would be consistent with the potential reversible character of the Baylis–Hillman polymerization (as long as catalyst is present). Instead of feeding polymerization reaction with a mixture of both monomers, a second series of experiments explored the slow addition of **1** to a solution containing **2**. This approach has been frequently explored for the synthesis of hyperbranched polymers via the $A_2 + B_3$ strategy.[19–23] Slow addition of **1** to a DMF solution containing **2** and 3-HQD indeed afforded polymers with significantly increased molecular weights, for example 7300 g/mol instead of 4200 g/mol after 2 h (Table 1, *Procedure 2*). Instead of polymerizing **1** and **2** at an equimolar monomer ratio, the polymerization can also be carried out at



SCHEME 3 Postpolymerization modification of hyperbranched polyesters prepared via Baylis-Hillman polymerization.

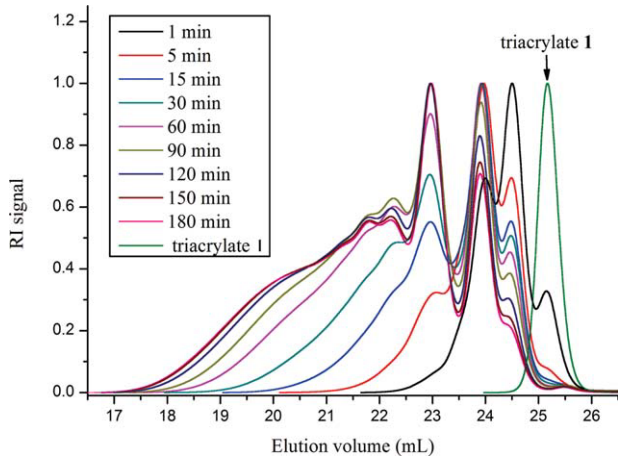


FIGURE 1 GPC elugrams of samples taken at regular time intervals during the Baylis–Hillman polymerization of **1** and **2** (*Procedure 3*).

stoichiometric concentration of acrylate and aldehyde groups, that is at a 3:2 molar ratio of the A_2 and B_3 monomers. One-pot polymerization of **2** and **1** at a 3:2 molar monomer ratio afforded polymers with slightly lower molecular weights after 1 h and slightly increased molecular weights after 2 and 3 h as compared to the analogous 1:1 $A_2 + B_3$ polymerization (Table 1, *Procedure 3* and *Procedure 1*). As was observed above (cf. *Procedure 1* and *Procedure 2*, Table 1), slow addition of 2 equiv of **1** to a solution of 3 equiv **2** resulted in polymers with increased molecular weights as compared to the one-pot polymerization at equivalent reaction times (*Procedure 4*, Table 1). However, whereas the one-pot procedure afforded a soluble polymer even after 3 h, gelation was observed after 3 h when **1** is slowly added to **2**.

GPC was used to investigate the kinetics of the hyperbranched polymerization of **1** and **2**. As a typical example, Figure 1 shows a series of GPC traces that were taken over a period of 3 h, and which allow to monitor monomer consumption and the evolution of polymer molecular weight (see also Supporting Information Figs. S15–S20). The results in Figure 1 were obtained by a one-pot polymerization of **1** and **2** using stoichiometric amounts of acrylate and aldehyde groups (*Procedure 3*). With increasing polymerization time, the GPC traces in Figure 1 broaden and shift to smaller

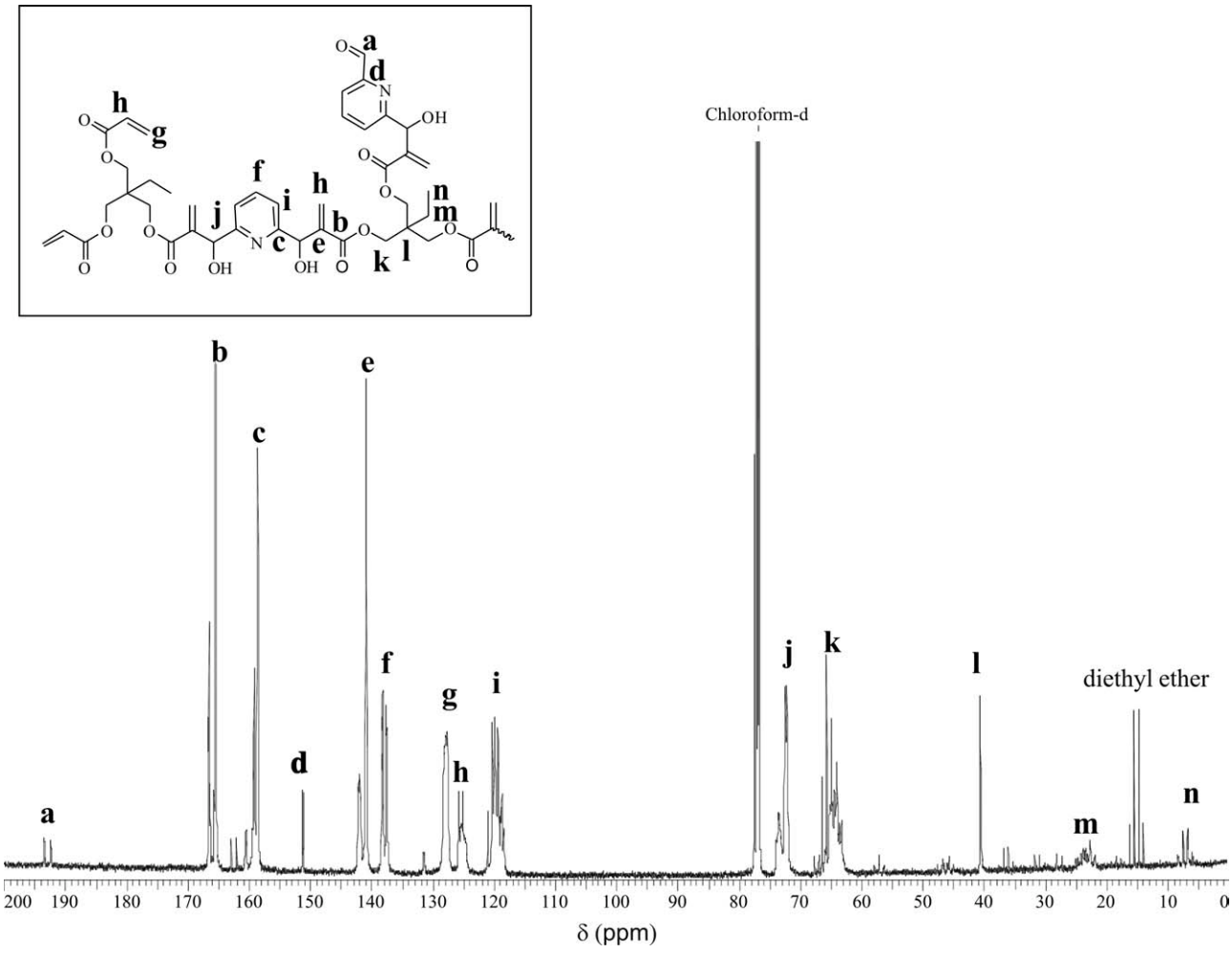


FIGURE 2 ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$) of hyperbranched polyester **6** (*Procedure 3*, Table 1, polymerization time 1 h).

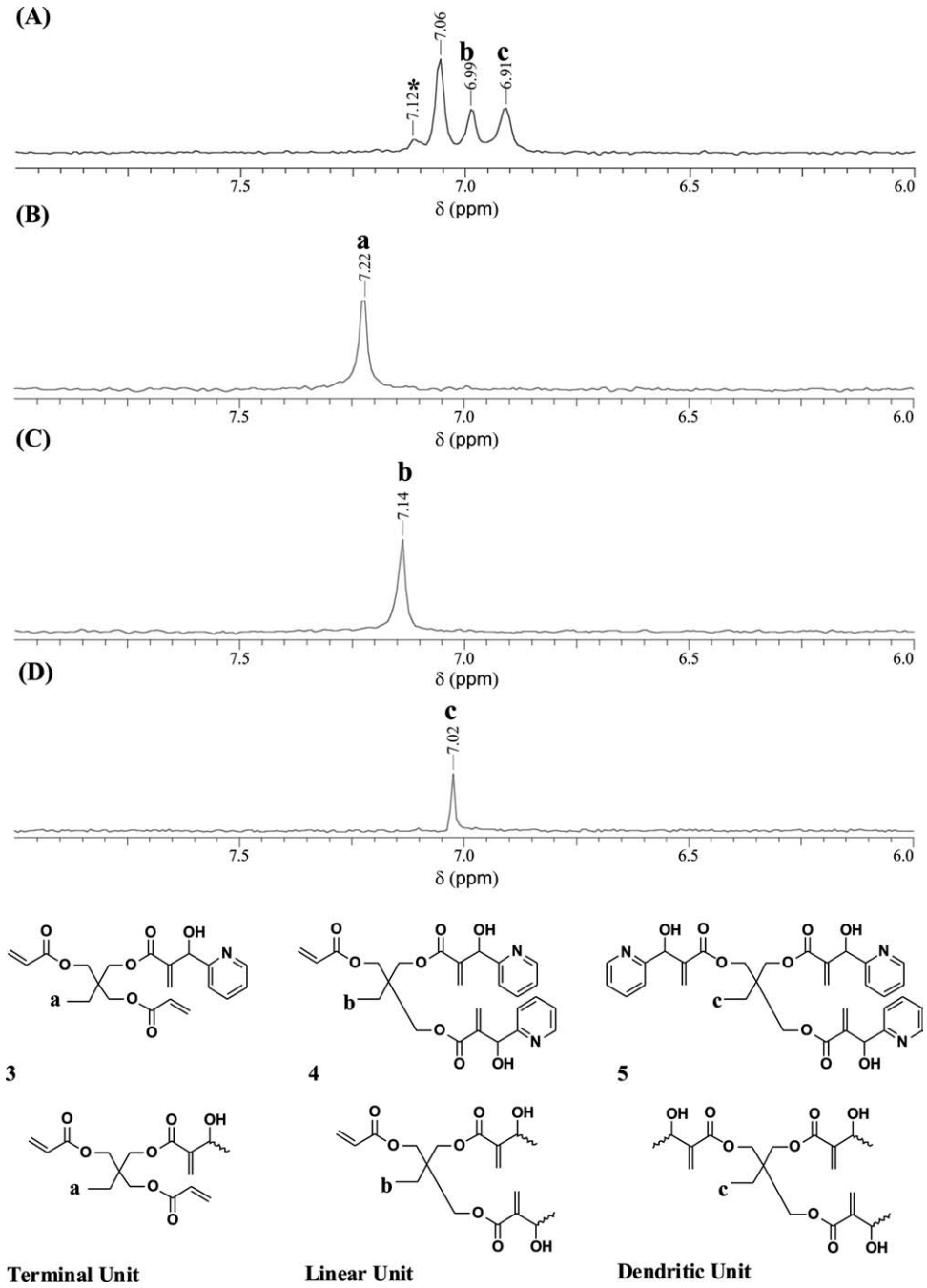


FIGURE 3 ^{13}C NMR spectra of (A) hyperbranched polymer **6** (*Procedure 3*, after a polymerization time of 1 h), (B) model compound **3**, (C) model compound **4**, and (D) model compound **5**.

elution volumes, which is consistent with the formation of hyperbranched polymer **6**. Furthermore, monitoring the intensity of the peak corresponding to **1** reveals that monomer consumption is quantitative after 15 min.

Structural Characterization

In addition to providing insight into polymerization kinetics, GPC experiments were also used to obtain information about the molecular architecture of polymers obtained by polymerization of **1** and **2**. A first indication comes from the relatively broad polydispersities (M_w/M_n) at the end of the polymerization reaction, which are characteristic of many hyperbranched polymers.[1] Furthermore, the use of triple detection GPC allowed to determine Mark–Houwink α parameters, which give information about the solution structure of the polymers. Typical values for a linear, statistical coil in a good solvent are $0.5 < \alpha < 1$, whereas for hyperbranched polymers usually smaller values of $0.2 < \alpha < 0.5$ are reported.[3,5,19,21] For polymers obtained from **1** and **2**, α parameters were found that ranged from 0.24 to 0.36 (Table 1), indicating a compact

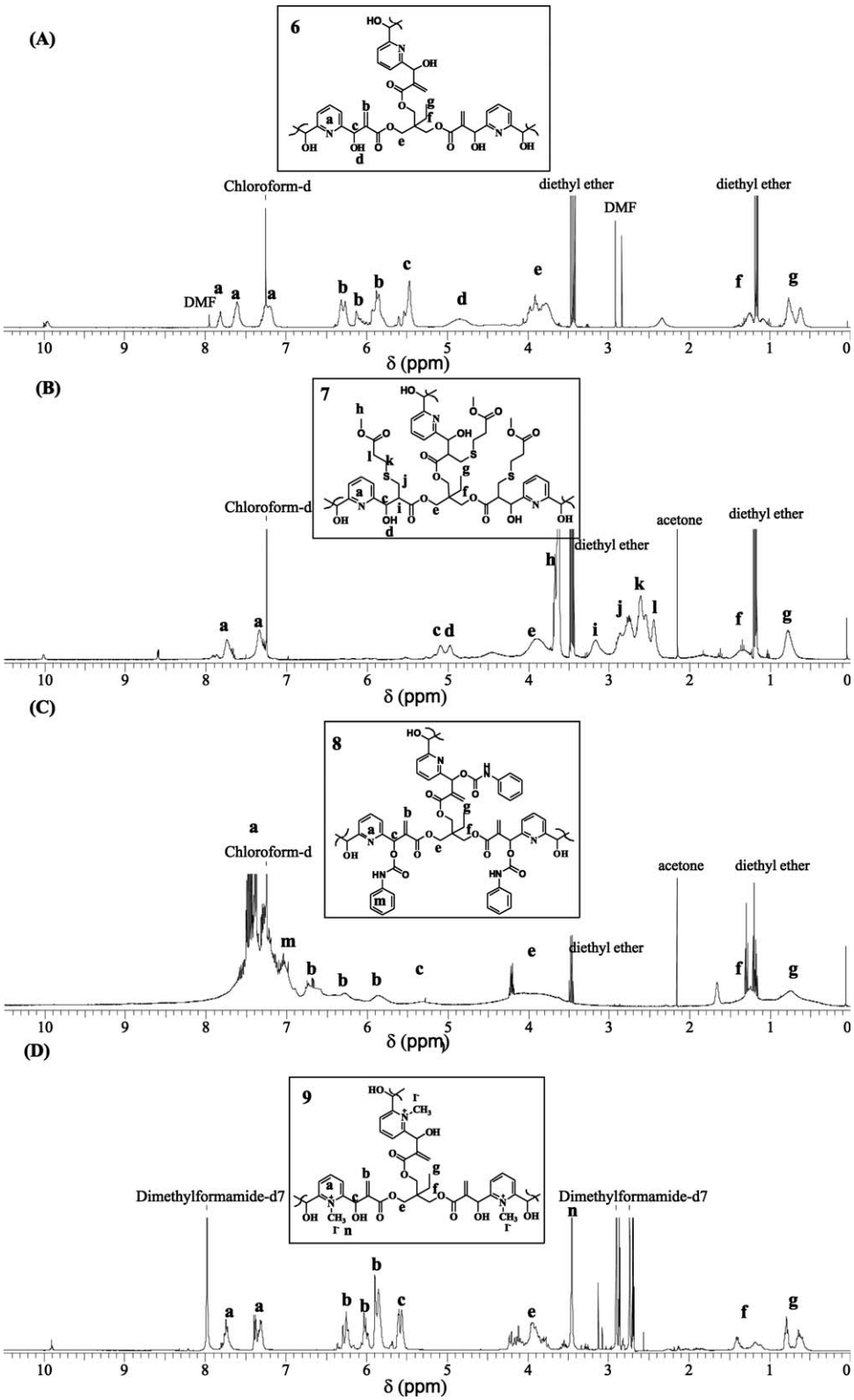


FIGURE 4 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (A) polymer **6** (*Procedure 3*, after a polymerization time of 1 h), (B) polymer **7**, (C) polymer **8**, and (D) polymer **9** (in d_6-DMF).

solution structure as would be expected for a hyperbranched polymer. No significant dependence of the α parameter either on the molecular weight of the polymer or on the synthetic strategy was observed.

Further information about the architecture of hyperbranched polymer **6** was obtained from NMR experiments. Polymerization of **1** and **2** results in polymers with an irregular, hyperbranched structure, which are composed of three different structural units, that is linear (L), dendritic (D), and terminal (T) units (Scheme 2). Estimation of the relative amounts of these three different structural units allows to calculate the degree of branching (DB), which provides a quantitative approach to assess and compare the architectures of hyperbranched polymers produced in different polymerization experiments. The relative amounts of D, L, and T units could be determined using ^{13}C NMR spectroscopy. As a typical example, Figure 2 shows the full ^{13}C NMR spectrum of a hyperbranched polyester prepared from **1** and **2**, whereas Figure 3 represents a magnification of the 6–8 ppm region, which shows the methyl (—CH_3) resonances of the TMPTA units. The methyl region of the ^{13}C NMR spectrum shows three major and one smaller resonances. The three major resonances could be assigned using model compounds **3**, **4**, and **5**, which, respectively, represent the T, L, and D units. The minor, low field shifted resonance at 7.12 ppm is tentatively ascribed to result from intramolecular cyclization or other intermolecular side reactions. Experimental evidence that would allow an unambiguous assignment of this signal, however, is lacking at the moment. As this signal is relatively small compared with the other three resonances, it was not further taken into account for the determination of the DB. The use of an inversed gated, proton decoupled ^{13}C NMR protocol allowed to integrate the different methyl resonances and subsequently estimate the fractions of T, L, and D units. From these numbers, the DB was calculated using:[24]

$$\mathrm{DB} = 2\mathrm{D}/(2\mathrm{D} + \mathrm{L}) \quad (1)$$

For the hyperbranched polyesters **6** prepared in this contribution, DBs ranging from 0.36 to 0.81 were determined (Table 1). Samples that were prepared via slow monomer addition seemed to show a tendency toward slightly higher DB values.

Postpolymerization Modification

Hyperbranched polymer **6** contains three chemically orthogonal functional groups, *viz*. hydroxyl, vinyl, and pyridine moieties that are amenable to further functionalization via postpolymerization modification. As a first proof-of-concept, the modification of **6** with methyl-3-mercaptopropionate, phenyl isocyanate, and methyl iodide was investigated (Scheme 3). These postpolymerization modification reactions were monitored with ^{1}H NMR and FTIR spectroscopy.

Postpolymerization modification of **6** with methyl-3-mercaptopropionate proceeded with quantitative conversion of the vinyl groups, as evidenced by the disappearance of the double bond resonances in the ^{1}H NMR spectrum (Fig. 4) as well as the disappearance of the C=C vibration at 1631 cm^{-1} in the FTIR spectrum (Fig. 5). Reaction of **6** with phenyl isocyanate results in the appearance of aromatic resonances in the ^{1}H NMR spectrum as well as two new C—H vibrations at 906 and 725 cm^{-1} in the FTIR spectrum, which reflect the introduction of the carbamate groups. Comparison of the ^{1}H NMR integrals of peak "*m*" (6.9–7.1 ppm, aromatic protons of the carbarate side chain) with that of peak "*c*" (tertiary C—H proton) allowed to estimate a 83% hydroxyl group conversion. Finally, quaternization of the pyridine groups with methyl iodide afforded a water-soluble hyperbranched polyester. Quaternization is evident from the signal at 3.5 ppm in the ^{1}H NMR spectrum of **9** and is also supported by a new FTIR band at 1629 cm^{-1}, which is due to the new C—N bond.[25] The conversion of pyridine groups was estimated to 47% based on comparison of the ^{1}H NMR integrals of signals "*n*" and "*c*."

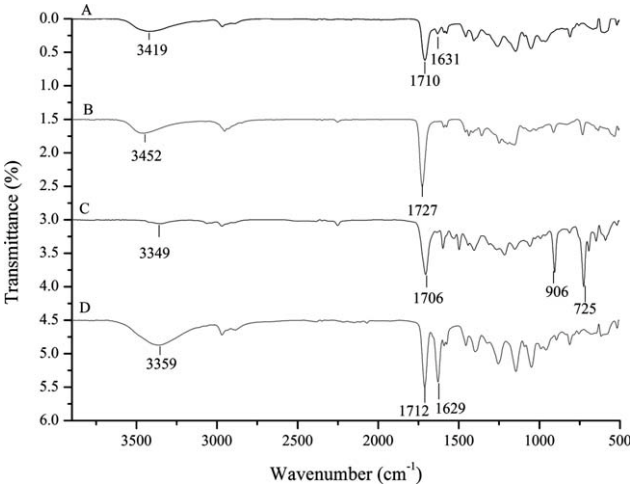


FIGURE 5 FTIR spectra of (A) polymer **6** (*Procedure 3*, after a polymerization time of 1 h), (B) polymer **7**, (C) polymer **8**, and (D) polymer **9**.

CONCLUSIONS

This manuscript has investigated the feasibility of the Baylis–Hillman reaction for the synthesis of hyperbranched polymers. Using 2,6-pyridinedicarboxaldehyde and TMPTA as monomers and 3-HQD as catalyst, hyperbranched polyesters with number-average molecular weights of up to 7500 g/mol were obtained via an $A_2 + B_3$ type approach. Carrying out these polymerizations following a slow monomer addition protocol resulted in increased molecular weights as compared to materials that were obtained in a one-pot polymerization. Also the DB of the polymers prepared via slow monomer addition seemed to be slightly increased as compared to polymers obtained via one-pot $A_2 + B_3$ hyperbranched polymerization. The Baylis–Hillman reaction is an attractive tool for the synthesis of functional hyperbranched polyesters as it generates functional groups that are amenable to further postpolymerization modification. The hyperbranched polyesters prepared in this contribution contain three orthogonally

reactive functional groups, *viz*. hydroxyl, vinyl, and pyridine moieties, and in first proof-of-concept experiments, the successful postpolymerization modification of these groups was demonstrated. The presence of multiple, orthogonal function groups make these polyesters of interest, for example as precursors for dual cure coatings as well as a variety of other applications.

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