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Catalytic Chain Transfer Mediated Autopolymerization of Divinylbenzene: Toward Facile Synthesis of High Alkene Functional Group Density Hyperbranched Materials

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Supporting Information

ABSTRACT: A facile and highly reproducible autopolymerization method, mediated by catalytic chain transfer, for the synthesis of hyperbranched materials with high alkene functional group density is reported. The rapid autopolymerization of divinylbenzene at 150 °C in the absence of any catalytic chain transfer agent was demonstrated to result in the formation of highly cross-linked networks/gels in less than 10 min. Exploitation of the extremely high chain transfer coefficient of bis[(difluoroboryl)diphenylglyoximato]cobalt-



(II) delayed gelation and produced good yields of high molecular weight hyperbranched divinylbenzene in under 1 h on a multigram scale. Gas chromatography was employed to monitor the levels of conversion over the course of the reaction. The materials produced were characterized by GPC, MALLS, and viscometry.

INTRODUCTION

Dendritic materials are three-dimensional (3D), globular macromolecules which contain regular, well-defined, and extremely high levels of branching. They are typically accessed by the application of highly controlled, very efficient, and multistage synthetic strategies.¹⁻⁵ Furthermore, the material properties associated with these highly branched macromolecular structures have generated a great deal of interest related to their potential to deliver significantly differentiated application performance in such areas as altering polymer melt flow characteristics, $^{6-8}$ improving drug/gene delivery, $^{9-12}$ and maximizing dye transport in light harvesting and light-emitting diodes.¹³ However, research into fully defining the end use performance of such dendritic materials has been hampered by the typically labor intensive and expensive routes required for their production. Consequently, this has significantly contributed to the lack of uptake of these materials into mass markets. In comparison, hyperbranched materials can be produced using relatively inexpensive, one-pot synthetic approaches and have structures similar to that of a dendrimer, only less well-defined.¹⁴⁻¹⁷ This has led to the most recent research on branched polymeric materials being dominated by the development of new hyperbranched polymers and synthetic/processing systems specifically designed to achieve such structures.¹⁸

During the formation of hyperbranched polymers, care must be taken to avoid cross-linking, which leads to the formation of an insoluble gel instead of the desired, solvent-soluble hyperbranched macromolecules. Indeed, it has been demonstrated that gelation in uncontrolled free radical systems generally occurs below 20% monomer conversion, even at very dilute monomer concentrations («10% monomer).¹⁹ In 2002, Sherrington et al.¹⁹ and Guan²⁰ independently reported the use of catalytic chain transfer²¹⁻²⁵ (CCT), an industrially viable polymerization control strategy, to control the free radical polymerization of multifunctional monomers to form hyperbranched materials. In this work it was demonstrated that soluble, highly branched methacrylic copolymers could be made in a simple, one-step, high conversion batch polymerization, where a cobalt porphyrin was successfully used to inhibit gelation provided the branching agent (a multifunctional monomer such as tripropylene glycol diacrylate) concentration was kept low (5 wt %).¹⁹ Additionally, because methacrylates are a monomer class that are particularly applicable to CCT due to the presence of an α -methyl group on the monomer from which facile hydrogen abstraction can occur to terminate growth, it was demonstrated that this control could be achieved through the use of very small amounts of CCT agent, typically between 2.5 and 10.0 ppm.¹⁹ Furthermore, the CCT hydrogen abstraction termination mechanism was demonstrated to produce macromolecules with increased concentrations of alkene chain-ends compared to those produced by the use of more conventional chain transfer agents, e.g. thiols, leaving them susceptible to postmodification.¹⁹ This is because the chain transfer mechanism employed ensures that any CCTterminated polymer has an unsaturated carbon-carbon double bond as the terminal group.^{26,27}

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Interestingly, the work conducted by Guan did not involve the inclusion of a monofunctional monomer; the reactions were homopolymerizations of a difunctional monomer.²⁰ To the best of our knowledge, this was the first report of such a monomer being successfully homopolymerized in the presence of a CCT agent and was an important step toward creating hyperbranched systems with high alkene functional group density through the application of addition polymerization. Guan also showed that ethylene glycol dimethacrylate (EGDMA) could be homopolymerized in either the bulk or a solution (1,2dichloroethane) system. In the presence of an azo-initiator and ~500 ppm of a CoBF derivative, high molecular weight, solvent soluble polymers were successfully isolated up to 70% monomer conversion.²⁰ By comparison, when no CCT agent was introduced, the solution formed a gel almost instantly.

Despite the robust and facile nature of the methods developed by Sherrington and Guan, little work has been undertaken to extend this CCT-based methodology to different divinyl species beyond methacrylate-based monomers, despite several being readily commercially available. One such monomer (divinylbenzene (DVB)) has been the subject of a number of recent developments which have enabled the homopolymerization of this monomer to yield highly branched, alkene functionality dense hyperbranched poly(divinylbenzene) (HBDVB). Baskaran demonstrated the homopolymerization of commercially obtained DVB could be achieved via anionic selfcondensing vinyl polymerization (SCVP)²⁸ with *n*-BuLi.² ′ In this synthesis, DVB containing 35% monofunctional impurities was polymerized in 10 min to produce yields in excess of 90% polymeric material. However, the materials produced in this method typically contained anywhere from 1 to 15% insoluble cross-linked material, and the molecular weights achieved were moderate ($M_w = 155\ 000\ \text{g mol}^{-1}$).²⁹ Wang et al. described the application of the deactivation enhanced atom transfer radical polymerization $(ATRP)^{30-32}$ of DVB to produce HBDVB.³³ Manipulating the polymerization in this way allowed the controlled homopolymerization of DVB to produce very high molecular weight HBDVB ($M_w = 5400000 \text{ g mol}^{-1}$) after 28 h in good yields (60%).³³ More recently, work by Perrier et al.³⁴ reported that commercially available DVB, containing a mixture of 80% m-DVB and p-DVB and 20% ethylstyrene (ES), could be homopolymerized via reversible addition-fragmentation chain transfer (RAFT) polymerization to realize moderately high molecular weight ($M_w = 233\,000 \text{ g mol}^{-1}$) highly branched materials after ~ 18 h polymerization reaction time.³

In this study, we report the first application of CCT to the homopolymerization of commercially available DVB, aimed at developing a facile methodology for the large scale production of HBDVB. In doing so, a new route to the production of hyperbranched structures with high alkene content is defined which results in the production of tens of grams of HBDVB in less than 1 h. Furthermore, we report the comparison of applying this method of creating highly branched polymer structures to both the individual homopolymerization and copolymerization of *m*-DVB and *p*-DVB.

EXPERIMENTAL SECTION

Materials. Unless otherwise stated, all reagents were used as received and without further purification, and all procedures were conducted under an inert nitrogen atmosphere using standard Schlenk line techniques. *m*-Divinylbenzene and *p*-divinylbenzene (*m*- and *p*-DVB) were synthesized individually via a Wittig reaction and purified via bulb-to-bulb distillation just before use. Styrene (99%+),

divinylbenzene 80% (DVB-80, technical grade, 80% difunctional monomer (*m*- and *p*-DVB), 20% monofuntional monomer (3- and 4ethylstyrene)), hydroquinone (99%+), cyclohexanone (99%+), potassium *tert*-butoxide (98%+), methyltriphenylphosphonium bromide (98%), isophthalaldehyde (97%), terephthalaldehyde (98%), hexane (99%+), deuterated chloroform (99.8%+), and tetrahydrofuran (THF, anhydrous, 99%+) were all purchased from Sigma-Aldrich. Tetrahydrofuran was passed through two alumina towers and collected under nitrogen to ensure exclusion of water. High-purity nitrogen was purchased from BOC gases. Chromatographic grade neutral aluminum oxide was purchased from Acros Organics. 2,2'-Azobis-(isobutyronitrile) (AIBN, 98%+) purchased from Wako Chemicals was recrystallized three times from methanol before use. Bis-[(difluoroboryl)diphenylglyoximato]cobalt(II) (CoPhBF) was obtained from DuPont.

Preparation of *m*-Divinylbenzene. *m*-DVB was synthesized according to a literature procedure via a Wittig reaction.³⁵ Potassium tert-butoxide (53.0 g, 0.47 mol) was dissolved in dry THF (750 mL) in a 2 L, three-necked flask. Methyltriphenylphosphonium bromide (160.8 g, 0.45 mol) was then added to the resulting solution in a single addition, and the resulting bright yellow solution of the resultant ylide was stirred for 20 min at room temperature. Isophthalaldehyde (25.0 g, 0.18 mol) dissolved in dry THF (250 mL) was then added dropwise to the stirring mixture, maintaining the temperature below 40 °C. The stirring was continued for 1 h at room temperature postaddition, after which ice water (400 g ice in 800 mL of water) was introduced, and the resulting organic phase was separated from the water phase in a separating funnel. The water phase was repeatedly shaken with nhexane $(3 \times 500 \text{ mL})$, and the precipitate formed was removed by filtration. Thereafter, the organic fractions were combined and dried over anhydrous magnesium sulfate. Hydroquinone (0.03 g, 2.7×10^{-4} mol) was added to inhibit polymerization, and the hexane was removed under vacuum. The crude product was vacuum distilled twice at 45 °C (0.2 mbar) to yield m-DVB as a clear liquid. 9.2 g (39% yield); purity >99% as determined by GC. ¹H NMR (CDCl₃, 400 MHz) at 25 °C: δ = 7.4 (s, 1H, aromatic), 7.3 (m, 3H, aromatic), 6.7– 6.8 (dd, 2H, -CH=CH₂), 5.7-5.8 (dd, 2H, -CH=C(H)H cis), 5.2–5.3 (dd, 2H, -CH=C(H)H trans). Mass spectrum m/z (relative intensities) 130 (M⁺, 100.0), 129 (22.7), 128 (26.5), 127 (12.3), 115 (23.5), 77 (7.2), 63 (3.9), 51 (1.7).

Preparation of *p***-Divinylbenzene.** *p*-DVB was synthesized by the same procedure as for *m*-DVB, with the exception that dialdehyde terephthalaldehyde was added to the ylide solution in this case. The crude product was vacuum-distilled twice at 45 °C (0.2 mbar) to yield *p*-DVB as a clear liquid which rapidly solidified on standing to become a sweet smelling, opaque solid. 10.5 g (45% yield); purity >99% as determined by GC. ¹H NMR (CDCl₃, 400 MHz) at 25 °C: δ = 7.4 (s, 4H, aromatic), 6.7–6.8 (dd, 2H, –CH=CH₂), 5.7–5.8 (dd, 2H, –CH=C(H)H *cis*), 5.2–5.3 (dd, 2H, –CH=C(H)H *trans*). Mass spectrum *m*/*z* (relative intensities) 130 (M⁺, 100.0), 129 (20.3), 128 (26.1), 127 (12.5), 115 (26.5), 77 (21.1), 63 (12.3), 51 (5.0).

General Polymerization Procedure. The required quantities of degassed DVB, cyclohexanone, and CoPhBF were introduced into a dry Schlenk flask equipped with a magnetic stirrer bar and containing an inert nitrogen atmosphere. The reaction vessel was then immersed in a preheated oil bath which was thermostatically controlled to remain at 150 °C. Upon completion of the reaction, the vessel was removed from the oil bath and immediately quenched in liquid nitrogen to prevent further reaction and hence gelation. The mixture was then diluted with chloroform, precipitated into cold (0 °C) methanol, and collected via filtration. The crude polymer was dissolved and reprecipitated a further two times before yields were determined gravimetrically after 48 h under vacuum at 50 °C.

Example 1: DVB-80 Polymerization. Degassed DVB-80 (30 mL, 27.6 g, 0.21 mol) and cyclohexanone (30 mL, 28.4 g) were transferred to a Schlenk flask containing CoPhBF (0.391 g, 6.18×10^{-4} mol), a magnetic stirrer bar, and an inert nitrogen atmosphere. The resulting solution was then rapidly heated to 150 °C by immersion in a preheated oil bath and held at that temperature for 45 min, after which it was immediately quenched in liquid nitrogen to prevent gelation.

Once cooled, the solution was dissolved in 30 mL of chloroform, and the subsequent solution was added dropwise to cold (0 °C) methanol. The resulting precipitate was collected via filtration to provide a fine off-white/brown powder (coloration due to CoPhBF) which was then dried to constant mass. Yield = 40%. ¹H NMR (CDCl₃, 400 MHz) at 25 °C: δ = 7.44 -5.95 (broad m, aromatic and -CH=CH₂), 5.79-5.50 (broad s, 1H, -CH=CH *cis*), 5.25-5.05 (broad s, 1H, -CH=CH *trans*), 2.65-0.64 (broad m, CH₂ (backbone) and -Ar-CH₂-CH₃). GPC: M_n = 4800, M_w = 111 200, D = 23.2. MALLS: M_n = 66 000, M_w = 742 700, D = 11.3, R_n = 50.4 nm.

Example 2: Synthesis of *p***-DVB**-*co-m***-DVB**. *p*-DVB (1.5 mL, 1.38 g, 1.05×10^{-2} mol), *m*-DVB (1.5 mL, 1.38 g, 1.05×10^{-2} mol), cyclohexanone (3 mL), and CoPhBF (0.0391 g, 6.18×10^{-5} mol) were added to a Schlenk flask equipped as described in example 1. The resulting solution was then rapidly heated to 150 °C and held at that temperature for 20 min, after which it was taken off and immediately quenched in liquid nitrogen to prevent gelation. The product was recovered as described in example 1 with a yield of 51%. ¹H NMR (CDCl₃, 400 MHz) at 25 °C: δ = 7.61–5.95 (broad m, aromatic and –*CH*=*C*H₂), 5.88–5.50 (broad s, 1H, –*C*H=*C*H *cis*), 5.35–5.01 (broad s, 1H, –0CH=*C*H *trans*), 2.83–0.59 (broad m, *CH*₂ (backbone)). GPC: M_n = 6000, M_w = 150 900, D = 25.2. MALLS: M_n = 445 000, M_w = 1725 000, D = 3.9, R_n = 62.3 nm.

Note on Gelation. Gelation was defined as the point at which the solution ceased to be a free-flowing, easily stirred liquid and became a rubbery/solidified gel. This point was a readily observable change in physical form apparent through visual inspection. However, gelation was confirmed by withdrawing a small sample and attempting to dilute it in chloroform. Where gelation had occurred, material presented as nonredissolvable translucent particles in the resulting solution. The time at which this occurred was defined as the gelation time and represented a change from an oligomeric/hyperbranched system to an extended cross-linked system.

Refractive Index Measurements. HBDVB dn/dc values were obtained using the Cirrus Multi Software and verified using a Mettler Toledo 30GS refractometer which was calibrated against deionized water. Several concentrations of HBDVB in THF (at both high and low levels of monomer conversion) were prepared and warmed to 40 °C to replicate the conditions in the GPC system. The refractive index of each solution was measured and plotted against sample concentration, yielding a straight line with a gradient equal to the dn/dc of the specific polymer sample. The dn/dc values of HBDVB-80 and HBDVB-100 were determined to be 0.215 and 0.228, respectively. Branching and molecular weight were not observed to affect the recorded dn/dc.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) was performed using a refractive index (RI) detector with HPLC THF as the eluent. Analysis was performed at 40 °C with a flow rate of 1 mL min⁻¹ through two PolarGel-M columns with a calibration range of 580–377 400 Da calibrated with 10 poly(styrene) narrow molecular weight distribution standards. All GPC equipment and standards were supplied by Polymer Laboratories (Varian). GPC data were analyzed using the Cirrus GPC offline software package.

Nuclear Magnetic Resonance. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained in CDCl₃ on a Bruker AV3500 (500 MHz) or Bruker AV3400 (400 MHz) spectrometer. Chemical shifts are referenced against residual solvent signal (¹H = 7.26 ppm, ¹³C = 77.16 ppm) and processed using the MestReC software package.

Gas Chromatography–Mass Spectroscopy. GC-MS was performed on a VG/Micromass/Waters AutoSpec in EI+ mode. A 15 m capillary column of type BP-1 with 0.25 mm thickness was employed, with helium at 80 kPa employed as the carrier gas. The parameters used for the GC analysis of compounds taken up in dichloromethane were the following: column temperature, from room temperature to 50 °C in 3 min, raised up to 280 °C by 4 °C min⁻¹; injection temperature: 250 °C; sample: 1 mL. Typically, 50 mg of sample was dissolved in 1 mL of dichloromethane for analysis.

RESULTS AND DISCUSSION

Development of the Polymerization Process and Determination of the Polymerization Kinetics. A CCT control agent was employed to control the molecular weight within the polymerizations conducted in this study to prevent gelation. The catalyst chosen in this study was bis-[(difluoroboryl)diphenylglyoximato]cobalt(II) (CoPhBF, Figure 1).



Figure 1. Molecular structures of bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (CoPhBF) (left), *m*-DVB (top right), and *p*-DVB (bottom right).

It has been shown that the purity of CoPhBF is not necessarily a good indicator of the expected activity.³⁶ Instead, the catalytic activity of the batch of CoPhBF which was used throughout this study was determined to ensure that the results could be rigorously compared with the prior literature. Determination of the chain transfer constant (C_s) of this batch of CCT agent was obtained through a combination of both Mayo plots³⁷ and chain length distribution (CLD) plots.³ In both methods, several low conversion polymerizations are conducted containing different concentrations of CTA following the methodology reported by Suddaby et al.³⁹ The resulting molecular weight distribution was subsequently analyzed by GPC and the data manipulated to yield C_s (see Supporting Information, Figures S1-S4). Styrene was chosen as a suitable monomer for the determination of C_s for the CoPhBF used in this study because it is structurally very similar to DVB and has been extensively studied, and as such direct comparison could be made to already determined literature values. At the same time it removes any potential to produce cross-linked microgels which may complicate the determination of C_s . The results of the C_s calculations conducted as part of this study are shown in Table 1.

Table 1. Values of C_s for CoPhBF/Styrene Obtained from Both Mayo and CLD Plots

	Cs			
run	Mayo $(1/M_n)$	Mayo $(2/M_w)$	CLD	
1	507	381	382	
2	467	359	367	
3	463	357	351	
average	479 ± 20	366 ± 13	367 ± 16	

The C_s was determined to be in good agreement with the reported results of Heuts et al., who reported a C_s value of 400 for CoPhBF in styrene when using the number-average molecular weight distribution (M_n) as the data for the Mayo method³⁶ and 657 and 478 for the same system when using the weight-average molecular weight (M_w) in Mayo and the CLD method analysis, respectively.⁴⁰ It is worthy of noting that they concluded greater accuracy was obtained from using the

weight-average molecular weight distributions. This is supported by the data from this study, as smaller error ranges are obtained from the application of both the Mayo and CLD methods when using $M_{\rm w}$ to analyze the GPC data (Table 1). The $M_{\rm w}$ -based $C_{\rm s}$ value obtained in this study was 366 ± 15 , indicating that the catalyst had an acceptable level of activity for the intended application and comparable with the literature.

Polymerization of Divinylbenzene. The initial polymerization of DVB-80 was attempted using 2,2'-azobis-(isobutyronitrile) (AIBN) as the source of initiating radicals (Table 2, entries A1-A3).

Table 2. Conditions and Obtained Yields for the AIBNInitiated or Autopolymerization of $DVB-80^a$

ID	AIBN (mg)	temp (°C)	CoPhBF (mg)	time (min)	yield (%)
A1	39.4	90	782	2880	
A2	39.4	90	391	1440	4.1
A3	65.7	90	391	1140	18
B1		150		10	gel
B2		150	391	30	22
B3		150	391	30	27
B4		150	391	30	17
B5		150	391	45	38
B6		150	391	45	42
B7		150	391	45	41
B8		150	391	48	Gel
^{<i>a</i>} In each case 30 mL of DVB and 30 mL of cyclohexanone were used.					

It was observed that under these conditions lengthy polymerization times were required to obtain any polymeric product. Initial CoPhBF concentrations were observed to be too high, yielding only oligomeric products that were too low in molecular weight to be isolated by filtration from the supernatant after 48 h. Reducing the catalyst concentration by 50% led to minimal improvements in yields (Table 2, A2) while increasing the AIBN concentration by 66% did improve the yields (Table 2, A3). However, this strategy was unsustainable with the level of AIBN increasing to scales large enough to render the process unsafe.

Consequently, the autopolymerization of DVB-80 was attempted at an elevated temperature of 150 °C with the target of significantly reducing reaction times. Under these conditions polymerization proceeds through either a diradicaltype mechanism as suggested by Flory or a molecule-assisted homolysis (MAH) mechanism as proposed by Mayo.41,42 Recent literature has favored the latter mechanism in which a Diels-Alder cycloaddition of two vinyl groups occurs. This leads to the formation of a cyclic intermediate; subsequent loss of a hydrogen atom from this intermediate results in the formation of the initiating radicals.⁴³ Use of autopolymerization over conventional azo-thermal radical initiators that are typically used for CCT polymerization would allow a significantly higher reaction temperature to be employed by removing the dependence on half-life temperatures. The results of the initial autopolymerization reactions are detailed in Table 2 along with lower temperature AIBN-initiated polymerizations for comparison.

Initial autopolymerizations of DVB-80 conducted in the absence of CoPhBF (Table 2, entry B1) was observed to be rapid and resulted in gelation after 10 min of reaction time. The rapid autopolymerization observed was attributed to a number of potential reasons; the presence of two vinyl units on each DVB molecule means that a greater proportion of random molecular collisions will have the correct geometry and associated energy to result in the formation of an initiating species/chain propagation, while the weakly electron-donating nature of the vinyl groups in p-DVB may enhance the reactivity of the monomer toward radical addition. If this latter factor is the dominant effect, then this increased affinity for radical addition may not be seen in m-DVB since electron donating groups tend to be ortho/para directing in aromatic benzene-type systems.

CoPhBF was reintroduced into the system, and a series of reproducibility studies were undertaken to assess the duration of polymerization required to achieve significant recoverable yields of hyperbranched materials. A typical yield of 22% was achieved in 30 min when 391 mg of CCT agent was introduced (Table 2, entries B2-B4) which is a reduction of 18 h 30 min in the reaction time compared to the previous AIBN-initiated system (Table 2, entry A3). When the reaction time was increased to 45 min, the average recoverable yield rose to 40% (Table 2, entries B5-B7). The isolated material was determined to be completely soluble in a range of organic solvents (tetrahydrofuran, ethyl acetate, dichloromethane, and chloroform). However, extending the reaction time beyond 45 min resulted in the onset of gelation (Table 2, entry B8). Repeat experiments defined that this system typically became insoluble/cross-linked in a reaction time range of 46-48 min. Therefore, where these reaction/concentration conditions were utilized, all reactions were quenched at 45 min to avoid insoluble material being present in the final product.

Determination of the Composition of DVB-80 by GC. Analysis of the composition of the DVB-80 solution was undertaken via gas chromatography (GC) to assess precisely what monomeric species were present in the polymerization mixture. Four unique compounds were identified in the GC trace of DVB-80; 3- and 4-ethylstyrene which eluted at 17.85 and 18.15 min, and *m*-DVB and *p*-DVB which eluted at 19.75 and 20.25 min, respectively (Supporting Information, Figure S5). The area under the GC peaks is a quantitative representation of the amount of compound present in the sample. However, to correctly ascertain the relative sensitivities of detection of each compound by the UV detector present in the GC instrument, it is necessary to determine the relative GC response factors (f_i) of each material. These can be calculated using eq 1.

$$f_i = \frac{A_i}{A_{\rm st}} f_{\rm st} \tag{1}$$

Where A_i is the unknown sample area, A_{st} is the standard peak area, and f_{st} is the standard response factor for the machine, in this case 1.00 and as such can be ignored. A dichloromethane solution containing 1:1 molar ratios of *m*-DVB and *p*-DVB was prepared and subjected to repeated GC analysis, and the data obtained are shown in Table 3.

Thus, an average response factor of $f_i = 1.11$ was defined for *m*-DVB where f_i for *p*-DVB was set to 1; i.e., the detector is ~10% more sensitive to *m*-DVB than to *p*-DVB. It was not possible to obtain pure samples of 3- and 4-ethylstyrene to determine their individual response factors. It was noted that the relative average f_i corrected peak area for *m*-DVB calculated to be 456 200 compared to 265 200 for *p*-DVB. From this, it was concluded that the difunctional components of the DVB-80 solution contains a mixture of 63% *m*-DVB and 37% *p*-DVB.

Table 3. Relative Peak Areas of a Dichloromethane Solution Containing 1:1 Molar Ratio of *p*-DVB:*m*-DVB As Determined by GC

	peak area		
monomer	run 1	run 2	run 3
<i>m</i> -DVB	417 600	365 700	451 400
<i>p</i> -DVB	372 800	316 800	424 400
ratio (p:m)	1:1.12	1:1.15	1:1.06

The total combined area of the monofunctional peaks was found to typically account for 22% of the total peak area, suggesting the commercially quoted 80% DVB content was valid.

Monitoring Monomer Conversion via GC. With the composition of the solution established and relative response factors determined, GC analysis of samples taken from the reaction solutions were used to follow the conversion of all the monomers present in the system with time. First, the apparent rates of polymerization (k_{app}) for *m*- and *p*-DVB in a system free of 3- and 4-ethylstyrene were determined by following the progress of an autoinitiated polymerization. The reaction medium comprised of a 1:1 ratio of pure m- and p-DVB, prepared by mixing together samples of the pure monomers synthesized following the methods detailed in the Experimental Section. This polymerization was repeated three times so that average peak areas could be used to gain an estimation of the error associated with this methodology. The polymerization reaction results are shown in Table 4, and the response factor corrected comparison of the average monomer peak areas with time is detailed in Table 5.

Table 4. Reaction Times and Polymer Yields from the Mixed m- and p-DVB Kinetics Measurements^a

ID	monomers	ratio	time (min)	yield (%)	
C1	<i>m</i> -DVB/ <i>p</i> -DVB	1:1	23.0	49	
C2	<i>m</i> -DVB/ <i>p</i> -DVB	1:1	24.0	53	
C3	<i>m</i> -DVB/ <i>p</i> -DVB	1:1	22.5	51	
^{<i>a</i>} The	reactions were quenched	d when	the viscosity	appeared t	:0

approach the point of gelation.

Table 5. Average GC Peak Area Values for Three Polymerizations of 1:1 Molar Ratios of *m*-DVB and *p*-DVB after Standardization of the Peak Areas against Residual Solvent and Being Response Factor Corrected

	standardized average peak areas		
time (min)	m-DVB	p-DVB	
0	98 692	96 446	
5	96 873	84 580	
10	94 625	54 447	
18	76 433	32 642	
20	71 246	30 471	
22	64 702	28 509	

Gelation times were found to vary between 22.5 and 24 min over the three repeats, significantly shorter than the DVB-80 reactions. This suggests that the presence of the monofunctional monomer may be retarding the overall reaction rate observed with DVB-80. Thus, 22 min was identified as the last acceptable data point when following the reaction kinetics of the 1:1 m-/p-DVB mixture polymerizations via GC. Furthermore, the GC analysis showed that the rate of consumption of *m*-DVB was observed to be significantly slower than the consumption of *p*-DVB. Analysis of the standardized, response factor corrected data set shows that the rate of consumption of *m*-DVB is only 2% after 5 min, 4% after 10 min, and a total of 34% conversion after the full 22 min reaction period. In contrast, the consumption figures for *p*-DVB were 12%, 44%, and 70%, respectively, at the same time intervals. Plotting these conversions as a $\ln(1/1 - c)$ (where *c* is the decimal monomer conversion) vs time graph yielded two straight lines with gradients equal to k_{app} as shown in Figure 2.



Figure 2. Kinetics plot detailing the relative polymerization rates of *m*-DVB and *p*-DVB. The gradient of each line is equal to k_{app} : *p*-DVB (red) 10.62 × 10⁻⁴ ± 0.75 × 10⁻⁴; *m*-DVB (black) 3.97 × 10⁻⁴ ± 0.2 × 10⁻⁴.

As shown in Figure 2, the k_{app} for *p*-DVB is over 2.5 times greater than that of *m*-DVB. Further confirmation of this trend was provided by observing the gelation times for a subsequent series of homoautopolymerizations conducted using 100% *m*-and *p*-DVB as their respective starting materials following the same standard polymerization method (Table 6).

Table 6. Conditions for the Homoautopolymerization of mor p-DVB To Determine Gelation Times^{*a*}

ID	monomer	time (min)
D1	p-DVB	16
D2	p-DVB	17
D3	<i>m</i> -DVB	33
D4	m-DVB	32

^a3 mL of DVB and 3 mL of cyclohexanone were used in each case in the presence of 39.1 mg of CoPhBF. The reaction temperature was held at a constant 150 $^{\circ}$ C until the point of gelation had occurred.

p-DVB was found to gel in half the time required for *m*-DVB, further confirming that *p*-DVB is much more susceptible to autopolymerization than *m*-DVB. This was believed to be due to a combination of differences in steric and electronic effects between the two monomers. Furthermore, the magnitude of this reduction in the gelation time is of the order that would be predicted by taking into account the difference in the k_{app} values for these monomers generated from the gas chromatogram data from the 1:1 mixed monomer kinetic experiments. These empirical data sets support the earlier proposal made on the relative reactivity of DVB and styrene by demonstrating that the weakly electron-donating effects of the vinyl groups into the electron system in *p*-DVB do indeed serve to make them more susceptible to radical attack, and since these electron-donating

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effects tend to be ortho/para directing, this effect is not observed in *m*-DVB.

Since a retardation of the observed polymerization rate had been observed with mixed monomer systems, a kinetics study was undertaken to assess the impact of the presence of both the monofunctional 3- and 4-ethylstyrene and the uneven *p*-DVB:*m*-DVB ratio found in DVB-80. The results of this kinetics study are shown in Figure 3.



Figure 3. GC generated kinetics plot detailing the polymerization rates of *m*-DVB, *p*-DVB, 3-ethylstyene, and 4-ethylstyrene in the autopolymerization of DVB-80. The gradient of each line is equal to $k_{\rm app}$: *p*-DVB (red) 7.55 × 10⁻⁴ ± 0.84 × 10⁻⁴; *m*-DVB (black) 2.89 × 10⁻⁴ ± 0.17 × 10⁻⁴; 4-ES (blue) 1.34 × 10⁻⁴ ± 0.02 × 10⁻⁴; 3-ES (green) 8.66 × 10⁻⁵ ± 0.08 × 10⁻⁵.

The data demonstrate that the $k_{\rm app}$ of *p*-DVB was still higher than that of *m*-DVB, even when $[p\text{-}DVB] \ll [m\text{-}DVB]$. This again suggests that the para isomer is more reactive toward radical addition than the meta isomer. However, while the difference between the *m*-DVB and *p*-DVB reaction ratios remains constant at 1:2.6, the $k_{\rm app}$ values of both difunctional monomers are reduced compared to the homopolymerization systems. This reduction in the $k_{\rm app}$ values was attributed to the presence of the monofunctional monomer (the ES contaminant) both further diluting the concentrations of the more reactive difunctional monomers and reducing the reactivity of any chain ends that contain ethylstyrene radicals. However, we note that it is difficult to be definitive on the exact nature of the reduction in $k_{\rm app}$ in such mixed feed systems due to the significant role that penultimate unit effects may have in such copolymerizations.⁴⁴ Further evidence that ethylstyrene led to reduced reactivity of the hyperbranched system came from comparing the polymerization of DVB-80 against a second commercially available feedstock which contained only 55% DVB, with the rest of the solution consisting of 3- and 4-ethylstyrene. As expected, a higher content of monofunctional ethylstyrene monomer led to a dramatic decrease in the poly(DVB) yield from ~40% in 45 min in DVB-80 solutions to only 12% after 60 min reaction time in DVB-55 solutions.

Gel Permeation Chromatography and Multiangle Laser Light Scattering Analysis. Both GPC and MALLS were utilized to follow the changes in molecular weight of the HBDVB materials produced via the polymerization of both the 1:1 m- and p-DVB mixture and DVB-80 over the course of the reaction, where time-related sampling was conducted as earlier described. Both the GPC (Figure 4) and the MALLS (Supporting Information, Figure S6) of the polymers isolated from the 1:1 m- and p-DVB polymerizations clearly show that as the reaction progresses, both the molecular weight increases and the molecular weight profile broadens significantly, taking on the characteristic multimodal peak shape attributed to branched structures, ³³

Furthermore, both of these data sets suggest that these reactions comply with the classical statistics of the formation of hyperbranched materials, as suggested by Flory. This states that linear polymeric structures with little or no branching will initially be formed and that branching will only occur as the polymerization progresses.⁴⁵ Both the GPC and MALLS data for the first, lowest conversion kinetic sample, taken after only 5 min, demonstrated that the polymer formed up to this point had a single distribution with a relatively narrow molecular weight profile ($\oplus(MALLS) = 1.74$, $\oplus(GPC) = 2.15$), which is characteristic of a linear polymeric material. At this stage, the M_w of the material was also relatively low (MALLS = 8900 g mol⁻¹, GPC = 5700 g mol⁻¹). As the reaction progressed, the



Figure 4. RI chromatographs of HBDVB produced from the polymerization of *m*- and *p*-DVB that has been isolated at different reaction times: 5 (black), 10 (red), 15 (blue), 18 (green), 20 (brown), and 22 min (magenta).

molecular weight and distribution profiles of the polymers started to increase dramatically, and a multimodal distribution was generated, indicating that the polymerization was producing nonlinear structures. It is proposed that gelation in this system is delayed because there are significant amounts of monomer still in the system, combined with the fact that the CCT agent ensures that the branch lengths are very short, keeping the reactive chain ends within a relatively high sterically hindered environment. These two factors combine to promote monomer-hyperbranch/oligomer-hyperbranch interaction and discourage hyperbranch-hyperbranch coupling. However, further propagation will eventually deplete the monomer to the point that the reaction balance will shift to being dominated by the combination of hyperbranched macromolecules, resulting in gelation. This highlights the reason why maximum yields for a successful hyperbranching polymerization are between 40 and 50% which typically equates to a monomer conversion of $\sim 70\%$.³⁴

Further evidence for the formation of a branched structure is provided by the fact that the molecular weight reported by the MALLS instrument is consistently higher than the molecular weight reported by GPC. This is because refractive index (RI) detectors on the GPC system used in this study are only sensitive to the relative concentration of the sample being analyzed, whereas MALLS analysis is proportional to both concentration and molecular weight. Furthermore, MALLS is typically more representative of the true M_w and dispersity values (D) values for a sample of material which contains 3D macromolecules.^{33,46} This is confirmed by the comparison of the GPC and MALLS data for polymers manufactured using 1:1 *m*- and *p*-DVB mixture (sample C3) and DVB-80 (sample B6) feedstocks (Figure 5).



Figure 5. Overlay of the MALLS and GPC chromatographs of materials C3 and B6 produced from the polymerization of a 1:1 mix of *m*- and *p*-DVB and DVB-80, respectively.

While the M_n , M_w , and D values obtained from the GPC RI detectors for the products from both feedstocks were found to be comparable (Table 7) and exhibit distributions with very similar profiles (Figure 5), the data obtained via MALLS clearly show that the sample from the DVB-80 consists of lower molecular weight material. This is reflected in Table 7, with the MALLS generated M_w of material C3 being over 3 times higher than material B6. However, D values acquired via MALLS are significantly reduced due to the MALLS under-representing the lower molar mass data.

In all cases, both MALLS and GPC analysis of the materials demonstrated that higher molecular weight hyperbranched materials were obtained through the polymerization of a

Table 7. Comparison of Data obtained via MALLS and GPC for HBDVB Samples C3 and B6 Produced from the Polymerization of a 1:1 Mix of *m*- and *p*-DVB and DVB-80, Respectively

	MALLS data				GPC RI data	a
sample ID	$M_{\rm n}$	$M_{ m w}$	Đ	$M_{\rm n}$	$M_{ m w}$	Đ
B6	76 000	602 600	7.92	4800	111 200	23.16
C3	431 000	1 929 000	4.48	6000	150 900	25.22

mixture of pure *m*- and *p*-DVB as opposed to use of the DVB-80 feedstock. There are several reasons why the exclusion of monofunctional monomer may lead to higher molecular weights. First, the introduction of monofunctional monomer will result in less vinyl functionality on the backbone of branched molecules, leading to fewer reactive centers that can propagate the structure to produce very high molecular weights. Second, as already discussed, the DVB-80 polymerization mixture contains approximately 48% m-DVB and 32% p-DVB. However, because of the differing reactivity of these two monomers, it is thought that the initial polymeric material will consist primarily of p-DVB, with m-DVB being incorporated more at the later stages of the polymerization. This will result in more *m*-DVB being incorporated toward the "surface" of the 3D macromolecule, dramatically slowing the molecular weight built from these points in the structure attributed to the reduced reactivity of the chain end.

Intrinsic Viscosity Determination and Comparison to *Poly(styrene)*. Hyperbranched/dendritic materials display markedly lower melt viscosities than corresponding linear polymers of the same molecular weight.^{47–49} As a direct result of the increased crowding in the molecular structure, entanglements both inside branched structures and between individual macromolecules are significantly reduced. This means that entanglement dominated physical properties, such as melt viscosity, should be severely affected.⁵⁰ Thus, a classical Mark–Houwink–Sakurada (MHS) plot of $log(M_w)$ vs $log(\eta)$ of linear polymer standards and the corresponding hyperbranched structure provides further evidence of the occurrence of branching in the macromolecule, since the linear polymer should have a significantly higher MHS exponent (gradient) than the hyperbranched system. In this study, poly(styrene) standards have been used as a direct comparison to HBDVB because of the unavailability of linear poly(DVB). The intrinsic viscosity of THF solutions of each molecular weight of the material was determined using a BV-400 (Polymer Laboratories) bridge viscometer attached in-line to the GPC system. In all cases, the value of M_w was determined by MALLS to provide a consistent and standardized set of results.

From the data contained in Figure 6, the MHS exponent of poly(styrene) was calculated to be ~0.74 at 40 °C, which compares well with the widely accepted literature value for the MHS exponent of 0.70 at 40 °C.⁵¹ Additionally, it was calculated through subsequent repeats that the MHS exponent determined in this study for poly(styrene) had an associated error of ~6% (0.74 ± 0.04). This level of error (both in the viscometer and in the determination of M_w) was considered acceptable for the intended purpose of demonstrating the significant difference in the MHS exponent for linear poly(styrene) and HBDVB. The MHS exponent of the HBDVB produced in this study was 0.19 ± 0.01, significantly below that of poly(styrene), and was in agreement with previously reported values.³³ This much reduced MHS

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Figure 6. Plot of $\log(\eta)$ (intrinsic viscosity) vs $\log(M_w)$ for poly(styrene) standards (×) and HBDVB (\Box). The MHS exponent (α) was shown to be approximately 0.74 for poly(styrene) and 0.19 for HBDVB.

exponent for HBDVB compared to poly(styrene) is a direct indication of a lower intrinsic viscosity and provides further evidence of high levels of branching within these macromolecules.

During the formation of highly branched polymers it is widely believed that intramolecular cyclization occurs, hence leading to a deviation from the Flory-Stockmayer theory which predicts that insoluble polymer networks would be formed at monomer conversion levels much lower than have been reported in the current literature.^{33,52–57} Direct quantification of the levels of cyclization in these species is typically difficult. To date, the only report establishing a method for quantification of cyclics in branched structures by Rosselgong and Armes relies of ¹H NMR spectroscopy.⁵⁸ Analysis of the HBDVB by ¹H NMR is complicated by signal broadening and poor peak resolution because of a decrease in molecular mobility. By virtue of the large broadening of the peaks, accurate integration of individual peaks for structural assignment was not possible with a sufficient degree of confidence, and work to improve on this is the subject of ongoing investigation.

CONCLUSIONS

This work has clearly shown that CCT polymerization can successfully be utilized to synthesize hyperbranched polymers of difunctional styrenyl monomers, in both the presence and absence of monofunctional monomers. Furthermore, this can be achieved in less than 1 h with good batch to batch reproducibility by using high reaction temperatures (150 °C) and autoinitiation as the means of radical generation. The proposed branched molecular structures of the resulting polymers was confirmed by comparison of the GPC-RI and MALLS data of the products obtained and further confirmed by comparison of intrinsic viscosity values to those of linear poly(styrene) standards and the DVB products. The former demonstrated that there is a significant difference between the data collected by these different detectors, which generally indicates 3D structure with the latter demonstrating that the MHS exponent was 0.74 for poly(styrene) and 0.19 for HBDVB, a difference which again indicated a significant level of branching in materials produced by the autopolymerization of DVB. It has also been demonstrated that the order of reactivity of the monomeric species investigated in this study is p-DVB > m-DVB > 4ES > 3ES under autopolymerization conditions as determined by monitoring changes in the composition of the polymerization system as the reaction proceeded. Consequently, the homoautopolymerization of *p*-DVB was found to reach the point of gelation in half the time of *m*-DVB. Additionally, kinetic analysis of an autoinitiated polymerization of a 1:1 mixture of *p*-DVB:*m*-DVB showed that this level of differential in reactivity was maintained when in they were used as a monomer mixture, as the ratio of their calculated k_{app} was determined to be 2.6:1. The inclusion of the monofunctional materials in DVB-80 and the disparity in the difunctional monomer concentrations was observed to result in the polymerizations taking longer to reach the gel point in the autopolymerization of DVB-80 and also in DVB-55.

ASSOCIATED CONTENT

Supporting Information

Additional GPC data detailing the determination of chain transfer constants (C_s), a GC trace of the DVB-80 solution, and MALLS traces for the copolymerization of *m*-/*p*-DVB. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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