DendriMacs. Well-Defined Dendritically Branched Polymers Synthesized by an Iterative Convergent Strategy Involving the Coupling Reaction of AB_2 Macromonomers

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Received December 8, 2005; Revised Manuscript Received January 28, 2006

ABSTRACT: We describe here the first example of an iterative convergent strategy for the synthesis of dendritically branched polymers involving condensation coupling reactions of AB_2 macromonomers. The macromonomers were synthesized by living anionic polymerization, initiated with 3-*tert*-butyldimethylsiloxy-1-propyllithium and end capped with 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl) ethylene. Following a deprotection reaction, the macromonomer, functionalized with two phenol groups and one primary alcohol group, can be built up into a dendritic structure by a series of Williamson coupling reactions and subsequent end group modification reactions. Since the *dendri*tic structures are built up from *mac*romonomers we have coined the term "DendriMac" to describe these branched polymers. In this paper, we will discuss the synthesis of the macromonomer, the iterative reaction sequence and merits of a convergent strategy. Some preliminary characterization data will also be reported.

Introduction

The physical properties of branched polymers differ significantly from linear polymers of equivalent molecular weight. The design and synthesis of new, well-defined molecular architectures, such as star branched polymers,[1,2] mikto star polymers,[3−5] and H-shaped polymers,[6,7] has contributed much to understanding and prediction of the relationship between structure and properties. More recently numerous strategies have been devised to synthesize more complex branched architectures with various resulting structures and differing degrees of control, including syntheses of dendrigraft, dendritically branched, and arborescent[8−13] polymers, much of this work has recently been reviewed by Gauthier and Teertstra.[14] A number of examples of well-defined dendritically branched polymers, essentially analogues of classical dendrimers with an additional polymer chain between branch points have also been reported, notably by Hadjichristidis,[15] Gnanou,[8,16] Hedrick[17] and Hirao.[18,19] Hadjichristidis describes the synthesis of well-defined second generation dendritic polymers based on stepwise convergent anionic polymerization and chlorosilane coupling reactions and while the resulting polymers are undoubtedly well-defined, the nature of the chemistry, requiring multiple reaction steps to be carried out under high vacuum conditions means that attaining higher generations is likely to be challenging. Gnanou,[16] has most recently reported the synthesis of dendrimer-like polystyrene by atom transfer radical polymerization (ATRP) by a divergent methodology. Using multifunctional calixarene-based initiators for ATRP of styrene and end group modification reactions, third generation dendrimer-like structures were obtained. However, the polymerizations had to be stopped at low monomer conversions to prevent irreversible coupling reactions between growing species and the polydispersity values of the resulting structures were not narrow, in the region of 1.25−1.4. Hedrick followed a similar divergent approach by living ring-opening polymerization of ϵ-caprolactone followed by functionalization and deprotection. The polydispersity of the resulting structures remained relatively narrow with values in the range 1.06−1.16. Hirao also adopted a divergent strategy to synthesize dendrimer-like poly(methyl methacrylate) (PMMA). In this case a series of iterative steps involving a coupling reaction of α-functionalized living anionic PMMA with benzyl bromide moieties was carried out. Up to seven generations of branching was attained with narrow molecular weight distributions (polydispersities of less than 1.05) although detecting imperfections in the structure would become a near impossibility at higher generations, an inherent problem with divergent strategies. Furthermore, it is likely that this methodology could not produce such well-defined structures from other monomers such as styrene or dienes because of less favorable rates of initiation in these cases. The motivation for much of the above work is to provide "model" long chain branched materials to help elucidate the relationship between molecular architecture and the physical properties of polymers, specifically the effect of long-chain branching on rheology. Indeed the theoretical prediction of the rheological properties of such structures has already been undertaken.[20] To facilitate the experimental validation (or otherwise) of the developed theories, structures with the highest degree of control over, not only the molecular weight and polydispersity of the final structure but also the molecular weight and polydispersity between branch points and degree of branching is desired. Imperfections in any of these parameters must be minimized.

To try to meet this challenge, we have adopted a different approach to those described above and have adhered more closely to the original concept of dendrimers as our model. Dendrimers were first synthesized in the 1980s via a step growth condensation reaction of AB_x monomers and numerous examples have been reported including aliphatic[21] and aromatic polyesters,[22,23] aliphatic[24] and aromatic polyethers,[25−27] polyalkanes,[28,29] polysilanes,[30] and many more. The synthesis of dendrimers aims to produce perfectly monodisperse molecules and while we cannot hope to produce perfectly monodisperse

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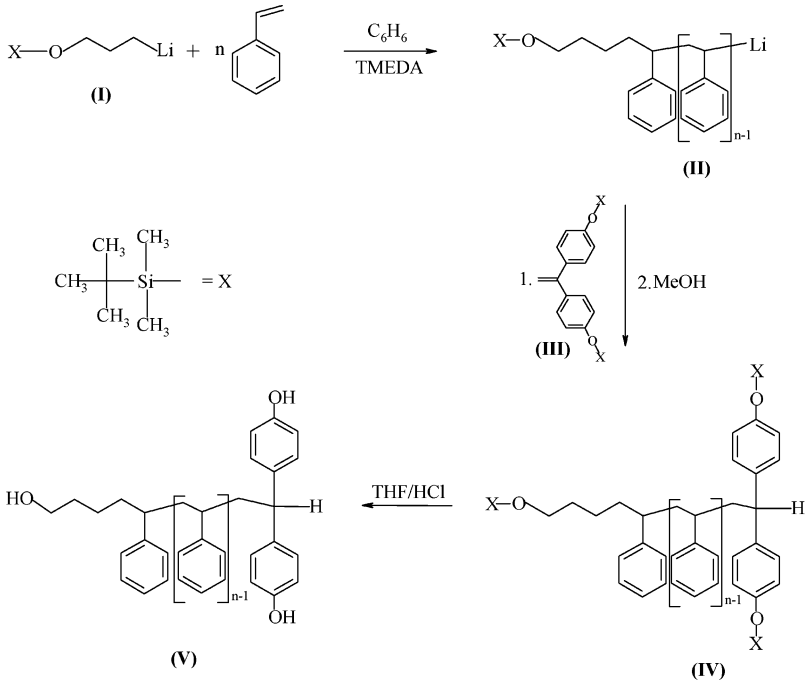
10.1021/ma052627d CCC: $33.50
Published on Web 02/21/2006

Scheme 1. Synthesis of AB_2 Macromonomer-$(OH)_3$



dendritically branched long chain polymers, adapting the synthetic strategies adopted to synthesize dendrimers should serve to minimize imperfections and polydispersity.

We describe here a strategy to synthesize long-chain *dendri*tically branched polymers by the condensation coupling of an AB_2 *mac*romonomer and coin the term DendriMacs to describe them. While the resulting structures are similar to many described above, the nature of the synthetic strategy sets them apart. The macromonomers are synthesized by living anionic polymerization and as such are well-defined in terms of both molecular weight and polydispersity and the DendriMacs are produced in an iterative convergent approach via a series of condensation coupling reactions. There are numerous examples in the literature of coupling reactions that could be exploited to synthesize DendriMacs: for example, esterification;[21−23] Williamson reaction between an alkoxide and a halide to yield an ether linkage;[24−27] Suzuki coupling reaction between a boronic acid and a halide.[31−33] We have used a Williamson coupling reaction to yield an ether linkage in a fashion similar to that used by Fréchet in the synthesis of classical hyperbranched and dendritic polyethers.[25,26,34] This has been shown to be viable by Fréchet who used this coupling reaction to successfully prepare a sixth generation dendrimer with a nominal molecular weight of 13 542 Da and hyperbranched polyethers with molecular weights (by light scattering) in excess of 100 000 Da. Furthermore, we have recently exploited this reaction to successfully synthesize a series of highly but less well-defined (hyper)branched polystyrenes, HyperMacs, in a "one-pot" polycondensation of analogous AB_2 macromonomers.[35] The ether linkage is stable and the functionalities required on the macromonomer can be readily introduced with the aid of some simple protection/deprotection and end group modification chemistry. The use of anionic polymerization for the synthesis of the condensation macromonomers in the present work allows the synthesis of macromonomers with molecular weights from a few hundred to tens of thousands of grams per mole, offering the possibility of varying the molecular weight between branch points from below the entanglement molecular weight, M_e, to many times M_e thereby enabling a "tuning" of the molecular parameters of the branched polymers to facilitate their use in structure−property correlation studies. The iterative nature of the methodology coupled with the prepolymerization of the macromonomers means that in theory (but not yet in reality) the molecular weight might be varied from generation to generation and furthermore the type of polymer may be varied from generation to generation making this a very versatile methodology.

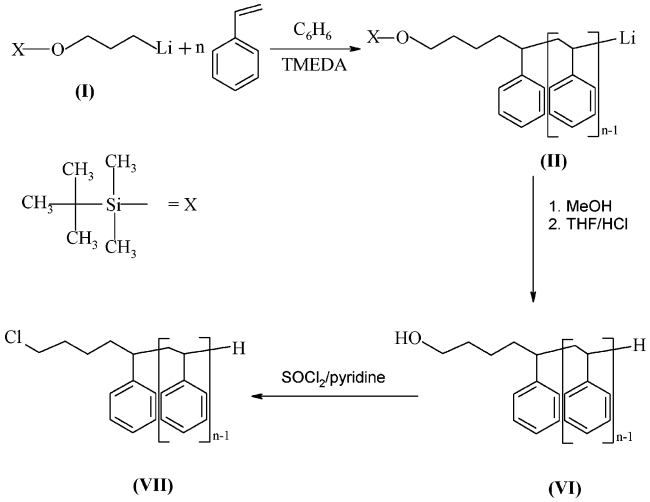
In outline the approach described involves the synthesis of well-defined AB_2 macromonomers by anionic polymerization using a lithium initiator containing a protected primary alcohol functionality. The living polymer is then end capped with a diphenylethylene derivative containing two protected phenol groups. Following deprotection of the functional groups and conversion of the primary alcohol group into an alkyl chloride, the macromonomer can be built up into a DendriMac via a convergent strategy.

Experimental Section

Materials. Benzene (HPLC grade, Aldrich) and styrene (Aldrich) were both dried and degassed over CaH_2 (Aldrich), styrene was further purified with dibutylmagnesium immediately prior to use. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (Aldrich) and 3-*tert*-butyldimethylsiloxy-1-propyllithium, 0.7 M in cyclohexane (InitiaLi 103, FMC Corporation) were used as received. 1,1-Bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene was synthesized in two steps from dihydroxybenzophenone according to the procedure of Quirk and Wang.[36] Thionyl chloride (99+%, Aldrich) and pyridine (anhydrous, Aldrich) were used as received. THF was purified by passing the solvent through a system of columns designed to remove both protic impurities and oxygen.[37] 18-Crown-6-ether and potassium carbonate powder, 325 mesh (both Aldrich) were dried in a vacuum oven and stored in a vacuum desiccator.

Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity and light scattering detectors. A value of 0.185 (obtained from Viscotek) was used for the d*n*/d*c* of polystyrene. 2 × 300 mm PLgel 5 μm mixed C columns (with a linear range of molecular weight from 200 to 2 000 000 g mol^{-1}) were employed; THF was used as the eluent with a flow rate of 1.0 mL/min at a temperature of 30 °C. The coupling reactions were monitored and further analyzed by SEC using a Viscotek 200 with

Scheme 2. Synthesis of Alkyl Chloride End Functionalized Polystyrene, the Peripheral Macromonomer



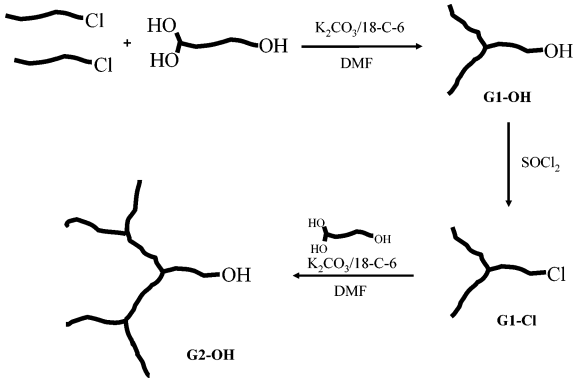
a refractive index detector and 3 × 300 mL PLgel 5 μm 10^4 Å high-resolution columns (with an effective molecular weight range of 10 000−600 000 g mol^{-1}), THF was used as the eluent at a flow rate of 1.0 mL/min. ^{1}H NMR analysis was carried out on either a Varian Inova-500 MHz or Mercury-400 MHz spectrometer using C_6D_6 as a solvent. Spectra were referenced to the trace of C_6H_6 (7.2 ppm) present in the C_6D_6.

Synthesis of Protected AB$_2$ Macromonomer-(OH)$_3$ (IV, Scheme 1). Anionic polymerizations were carried out using standard high vacuum techniques, at room temperature with benzene as the solvent and a typical reaction was as follows; benzene (500 mL) and styrene (50 g, 0.48 mol) were distilled, under vacuum, into a 1-liter reaction flask. To the monomer solution was added tetramethylethylenediamine (TMEDA) 1 mol equiv with respect to lithium initiator and then 3-*tert*-butyldimethylsiloxy-1-propyllithium, 0.7 M in cyclohexane (**I**) as the initiator, the latter being injected through a septum. For a target M_n of 15 000 g mol^{-1} we used 0.5 mL (3.3 mmol) TMEDA and 4.8 mL initiator (3.3 mmol). Upon addition of the initiator to the reaction mixture, the orange/red color of living polystyryllithium was observed. The solution was stirred for 1 h to allow complete conversion before a small sample of polymer solution (for molecular weight/nmr analysis) was removed and terminated with nitrogen sparged methanol. To the remaining living polymer solution was added 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (**III**) (1.5 mol equiv with respect to lithium) as a solution in benzene. The reaction was stirred at room temperature for 5 days before the reaction was terminated with nitrogen sparged methanol. The polymer was recovered by precipitation in methanol, redissolved in benzene, reprecipitated once more into methanol and dried in vacuo. Yield: >95%. M_n = 15 900 g mol^{-1}; M_w = 16 700 g mol^{-1}; PDI = 1.05. ^{1}H NMR (C_6D_6): CH_2OSi δ 3.36, $HC(Ph)_2$ δ 3.5, $Si(CH_3)_2C(CH_3)_3$ δ 1.0, $ArOSi(CH_3)_2C(CH_3)$ δ 0.1, $CH_2OSi(CH_3)_2C(CH_3)_3$ δ 0.0.

Synthesis of AB$_2$ Macromonomer-(OH)$_3$ (V). The AB$_2$ macromonomer with all three alcohol groups protected by *tert*-butyldimethylsilyl (TBDMS) groups was dissolved in THF (10% w/v solution). To the solution was added dropwise, concentrated HCl (37 wt %), mole ratio of acid:protected alcohol was 5:1. The solution was then warmed to reflux and stirred at reflux overnight. The solution was cooled and the polymer recovered by precipitation into methanol, redissolved in benzene, reprecipitated once more into methanol and dried in vacuo at 50 °C for 2 days. Yield: >95%. ^{1}H NMR (C_6D_6): CH_2OH δ 3.15, HO−Ph δ 3.7−3.8.

Synthesis of Alkyl Chloride End-Functionalized Polystyrene (VII, Scheme 2). Polystyrene was synthesized as described above, initiated with 3-*tert*-butyldimethylsiloxy-1-propyllithium in the presence of TMEDA. After 1 h, the living polymer (**II**) was terminated with nitrogen sparged methanol. The polymer was recovered by precipitation in methanol, redissolved in benzene, reprecipitated once more into methanol and dried in vacuo. Yield: >95%. M_n = 10 900 g mol^{-1}; M_w = 11 500 g mol^{-1}; PDI = 1.05. ^{1}H NMR (C_6D_6): CH_2OSi δ 3.36, $Si(CH_3)_2C(CH_3)_3$ δ 1.0, $CH_2OSi(CH_3)_2C(CH_3)_3$ δ 0.0.

Scheme 3. Convergent Approach for the Synthesis of Dendritically Branched Polystyrene.

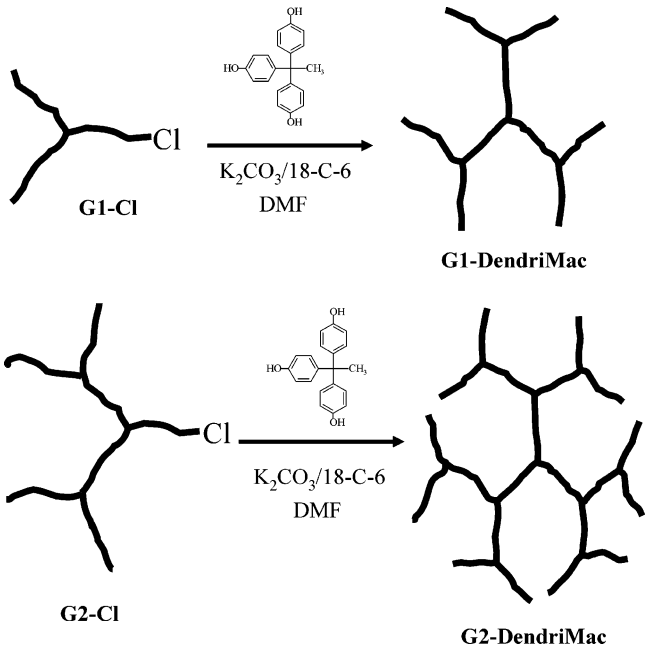


Following deprotection with HCl in THF, as described above, the primary alcohol group was converted into an alkyl chloride according to the general procedure described below.

Chlorination of Primary Alcohol Group. In a 500 mL round-bottom flask, 10 g of the deprotected macromonomer (10 900 g mol^{-1}, 9.2 × 10^{-4} mol) was dissolved in 100 mL of benzene under an inert atmosphere of nitrogen gas. To this solution was added 0.58 g (7.4 × 10^{-3} mol) pyridine and the mixture stirred for 15 min before cooling to 0 °C with an ice/water bath. To the stirring solution was added 1.1 g (9.2 × 10^{-3} mol) of thionyl chloride over a period of 5 min before allowing the reaction mixture to rise to room temperature over an hour. The mixture was then warmed to 55 °C and stirred at this temperature overnight. A small aliquot was then removed for ^{1}H NMR analysis (in C_6D_6) which confirmed that the signal for the CH_2−OH (3.15 ppm) had been completely replaced by a new signal for CH_2−Cl at 2.9 ppm. The remaining polymer was recovered in quantitative yield by precipitation into methanol. The product was collected by filtration, redissolved in toluene, and passed through a column of alumina to remove any residual traces of pyridine or thionyl chloride. The purified material was precipitated into methanol, collected by filtration and dried to constant mass in vacuo at 50 °C for several days.

Synthesis of G1-Branched Polystyrene. A G1-branched polystyrene was synthesized by reacting alkyl chloride end functionalized polystyrene, PS-Cl (**VII**, Scheme 2) with the AB$_2$ polystyrene condensation macromonomer PS-(OH)$_3$ (**V**, Scheme 1) in a Williamson coupling reaction. The polymer chains being joined through an aryl−alkyl ether linkage formed by the reaction of the alkyl chloride with the phenol functionalities (Scheme 3). The synthetic procedure is as follows: All coupling reactions were carried out under an inert atmosphere of either argon or nitrogen. PS-Cl (M_n 10 900 g mol^{-1}, 30.3 g, 2.8 × 10^{-3} mol), PS-(OH)$_3$ (M_n 16 200 g mol^{-1}, 20.0 g, 1.2 × 10^{-3} mol), potassium carbonate (0.68 g, 4.9 × 10^{-3} mol), and 18-crown-6-ether (1.3 g, 4.9 × 10^{-3} mol) were dissolved in 250 mL of DMF. The solution temperature was raised to reflux using an oil bath and the reaction mixture was stirred vigorously. The progress of the reaction was followed by extracting small samples periodically and subjecting the sample to size exclusion chromatography analysis. The reaction was complete after 2 h. The mixture was then cooled and the polymer recovered by precipitation into methanol. The product was redissolved in benzene and reprecipitated once again into methanol before drying in vacuo. The G1-OH (Scheme 3) branched polymer was isolated from the excess PS-Cl and any partially coupled polymer by fractionation using toluene/methanol as the solvent/nonsolvent combination. Yield: 26.0 g (56%). M_n = 38 900 g mol^{-1}; M_w = 41 300 g mol^{-1}; PDI = 1.06. The G1-OH was converted to G1-Cl (Scheme 3) by transformation of the primary alcohol group to an alkyl chloride moiety using thionyl chloride according to the

Scheme 4. Synthesis of G1 and G2 DendriMacs by coupling reaction of G1-Cl and G2-Cl Dendritically Branched Polymers to 1,1,1-Tris(4-hydroxyphenyl)ethane



procedure described above. Following purification a portion of G1-Cl was used for the synthesis of G2-branched polystyrene.

Synthesis of G2-Branched Polystyrene. G1-Cl (M_n 37 300 g mol^{-1}, 9.0 g, 2.4 × 10^{-4} mol), PS-(OH)$_3$ (M_n 16 200 g mol^{-1}, 1.6 g, 9.8 × 10^{-5} mol), potassium carbonate (0.055 g, 3.9 × 10^{-4} mol), and 18-crown-6-ether (0.10 g, 3.9 × 10^{-4} mol) were dissolved in 50 mL of DMF. The solution temperature was raised to reflux using an oil bath, and the reaction mixture was stirred vigorously overnight. The mixture was then cooled and the polymer recovered by precipitation into methanol. The product was redissolved in benzene and reprecipitated once again into methanol before drying in vacuo. The G2-OH (Scheme 3) branched polymer was isolated from the excess G1-Cl and any partially coupled polymer by fractionation using toluene/methanol as the solvent/nonsolvent combination. Yield: 3.5 g (37.2%). M_n = 95 100 g mol^{-1}; M_w = 97 600 g mol^{-1}; PDI = 1.03. The G2-OH was converted to G2-Cl by transformation of the primary alcohol group to an alkyl chloride moiety using thionyl chloride according to the procedure described above.

Synthesis of G1 DendriMac. G1-Cl (M_n 37 300 g mol^{-1}, 2.0 g, 5.4 × 10^{-5} mol), 1,1,1-tris(4-hydroxyphenyl)ethane (4.6 mg, 1.5 × 10^{-5} mol), potassium carbonate (0.012 g, 8.9 × 10^{-5} mol), and 18-crown-6-ether (0.24 g, 8.9 × 10^{-5} mol) were dissolved in 10 mL of DMF. The solution temperature was raised to reflux using an oil bath and the reaction mixture was stirred vigorously for 4 h. The mixture was then cooled and the polymer recovered by precipitation into methanol. The product was redissolved in benzene and reprecipitated once again into methanol before drying in vacuo. The G1-DendriMac (Scheme 4) polymer was isolated from the excess G1-Cl and any partially coupled polymer by fractionation using toluene/methanol as the solvent/nonsolvent combination. Yield: 0.3 g (15%). M_n = 119 300 g mol^{-1}; M_w = 123 700 g mol^{-1}; PDI = 1.04.

Synthesis of G2 DendriMac. G2-Cl (M_n 95 100 g mol^{-1}, 3.5 g, 3.7 × 10^{-5} mol), 1,1,1-tris(4-hydroxyphenyl)ethane (4.6 mg, 1.5 × 10^{-5} mol), potassium carbonate (0.012 g, 8.9 × 10^{-5} mol), and 18-crown-6-ether (0.24 g, 8.9 × 10^{-5} mol) were dissolved in 10 mL of DMF. The solution temperature was raised to reflux using an oil bath and the reaction mixture was stirred vigorously overnight. The mixture was then cooled and the polymer recovered by precipitation into methanol. The product was redissolved in benzene and reprecipitated once again into methanol before drying in vacuo. The G2-DendriMac (Scheme 4) polymer was isolated from the excess G1-Cl and any partially coupled polymer by fractionation using toluene/methanol as the solvent/nonsolvent combination. Yield: 0.25 g (7%). M_n = 284 900 g mol^{-1}; M_w = 298 700 g mol^{-1}; PDI = 1.05

Results and Discussion

In a recent publication,[35] we discussed the synthesis of HyperMacs, long chain branched polymers prepared by the coupling of AB_2 condensation macromonomers in a one-pot polycondensation. The resulting polymers are highly but irregularly branched architectures, polydisperse in both molecular weight and degree of branching; essentially HyperMacs are long chain branched analogues of hyperbranched polymers. In the present publication we describe the synthesis of well-defined, low polydispersity dendrimer-like branched polymers, only differing from dendrimers by the presence of a well-defined polystyrene chain between branch points.

Anionic polymerization is a living polymerization technique with no intrinsic termination reaction and results in polymers of well-defined molecular weight and narrow polydispersity. The living nature of the polymerization also allows for the introduction of functional groups at either end of the polymer chain by using suitable initiators and terminating agents. AB_2 condensation macromonomers have been prepared using a commercially available lithium initiator (containing a protected primary alcohol functionality). The living polymerization was end capped with a readily synthesized diphenylethylene derivative containing two protected phenol groups in a controlled termination reaction. Following deprotection of the alcohol groups, the AB_2 macromonomers can be used to build up dendritically branched polymeric architectures. The macromonomers are joined together by via an ether linkage formed by a Williamson coupling reaction.

Synthesis of Macromonomers. When considering not only the design but also the synthesis of the macromonomer building blocks, our prime objectives were to quantitatively introduce the relevant functionalities that would facilitate subsequent Williamson coupling reactions but also to retain good control over both the molecular weight and the polydispersity of the macromonomers. Since we have adopted a convergent approach to the synthesis of the DendriMacs, the macromonomer forming the peripheral generation, only requires a single "A" functionality rather than the AB_2 functionality of the other macromonomers. The synthetic outline for the synthesis of both the AB_2 macromonomer and the peripheral macromonomer are shown in Schemes 1 and 2. A full account of the synthesis of the macromonomers is discussed elsewhere.[35]

Synthesis of DendriMacs. There are essentially two general strategies for the synthesis of dendrimers; a divergent and convergent approach. The earliest examples[38,39] of dendrimer synthesis were carried out via a divergent approach in which the molecule is built from the inside out. As the number of generations increases there is a rapid increase in the number reactive sites at the chain ends and with each reaction step potential problems increase. First, any incomplete reaction of these terminal groups leads to imperfections in the subsequent generation and the probability of these occurring increases as the growing molecule increases in generations. Furthermore, as the number of reactive groups increase it can become progressively more difficult to detect any possible imperfections, especially in the case of the macromolecular dendritically branched polymer of the type described here, where the concentration of chain ends is very low with respect to the molecular mass. An alternative convergent approach for dendrimer synthesis was first reported by Hawker and Fréchet in

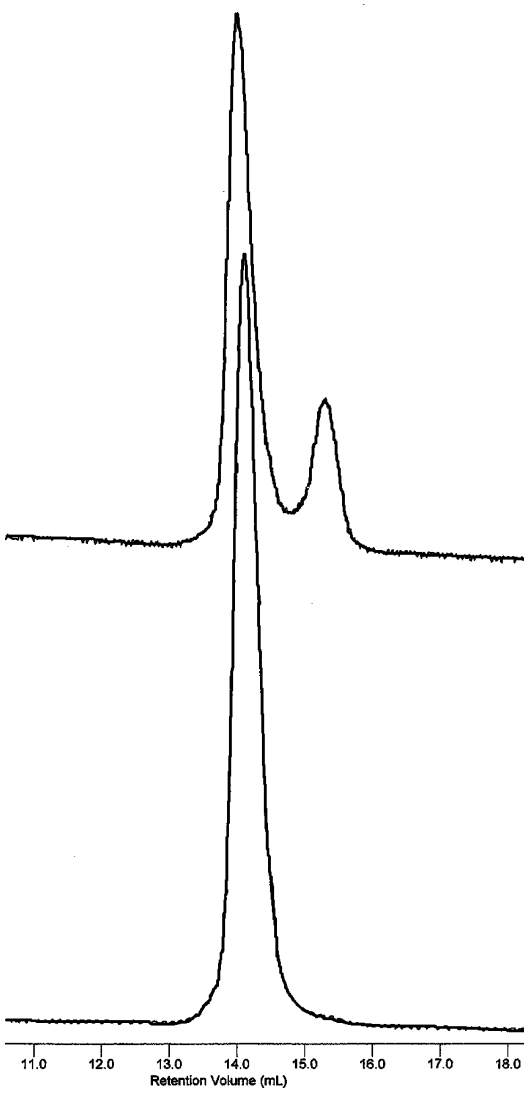


Figure 1. SEC chromatogram of GI−OH before and after fractionation.

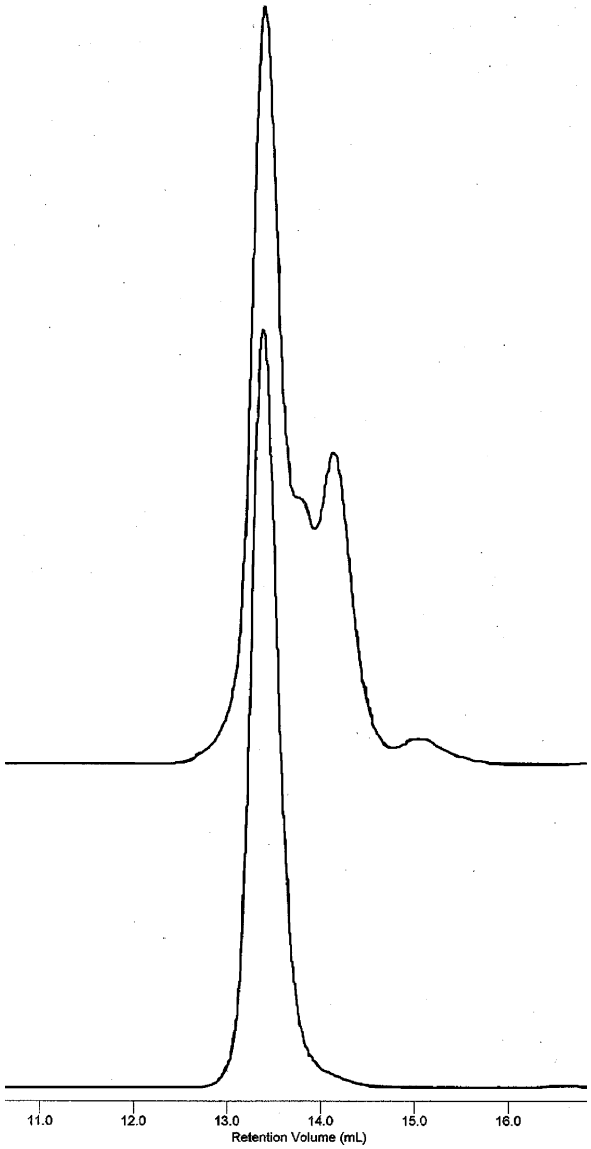


Figure 2. SEC chromatogram of G2-OH before and after fractionation.

1990.[25] This approach offers distinct advantages in that the molecule is built from what will ultimately become the periphery and, at each step, growth is designed to occur via few reaction steps. Furthermore, in the case of long chain branched analogues of dendrimers, each coupling reaction can be followed by size exclusion chromatography. Incomplete reaction results in partially coupled material which is easily detected and imperfectly branched material can be removed by fractionation. We have adopted a convergent strategy analogous to that of Hawker and Fréchet to construct dendritically branched polystyrene by an iterative series of Williamson coupling reactions and end group modification reactions (Scheme 3).

The Williamson coupling reactions occur between the alkyl chloride functionality present on one macromonomer and the phenol functionalities present on the other macromonomer. Under the mild basic conditions no reaction occurs with the primary alcohol group which after coupling and fractionation can be converted to an alkyl chloride for the subsequent coupling reaction. In each coupling reaction a small excess of the alkyl chloride functionalized polymer is used with respect to the AB_2 macromonomer and this excess and any partially coupled polymer can be separated from the desired product by fractionation of a 1−2% w/v toluene solution of the polymer mixture using methanol as the nonsolvent. SEC chromatograms (RI detector response) of the G1-OH and G2-OH polymers before and after fractionation are shown in Figures 1 and 2, respectively.

C-alkylation is a well-known potential side reaction to the ether formation of a Williamson Coupling reaction and the choice of solvent is very important in achieving efficiency of reaction and a low level of C-alkylation. Since the macromonomer coupling reaction will be promoted when carried out in a good solvent for the polymer and Feuer and Hooz[40] suggest that ether formation is favored (and C-alkylation minimized) by the use of aprotic solvents with a high dielectric constant we concluded that solvents such as THF and DMF would be suitable candidates and the use of both has been investigated. The coupling reactions proceed very rapidly in refluxing DMF, reaching completion in a matter of a few hours but the extent of reaction is, we believe, somewhat limited by side reactions between the macromonomer and impurities generated by heating DMF. In work carried out in parallel to this on the synthesis of HyperMacs, and previously reported[35] it was concluded that heating DMF to reflux results in its partial degradation and one of the well-known products of this degradation,[41] dimethylamine, could react with the alkyl chloride functionality of the macromonomer. The Williamson polycondensation reactions resulting in the formation of polystyrene HyperMacs were similarly rapid when carried out in DMF but in all cases the

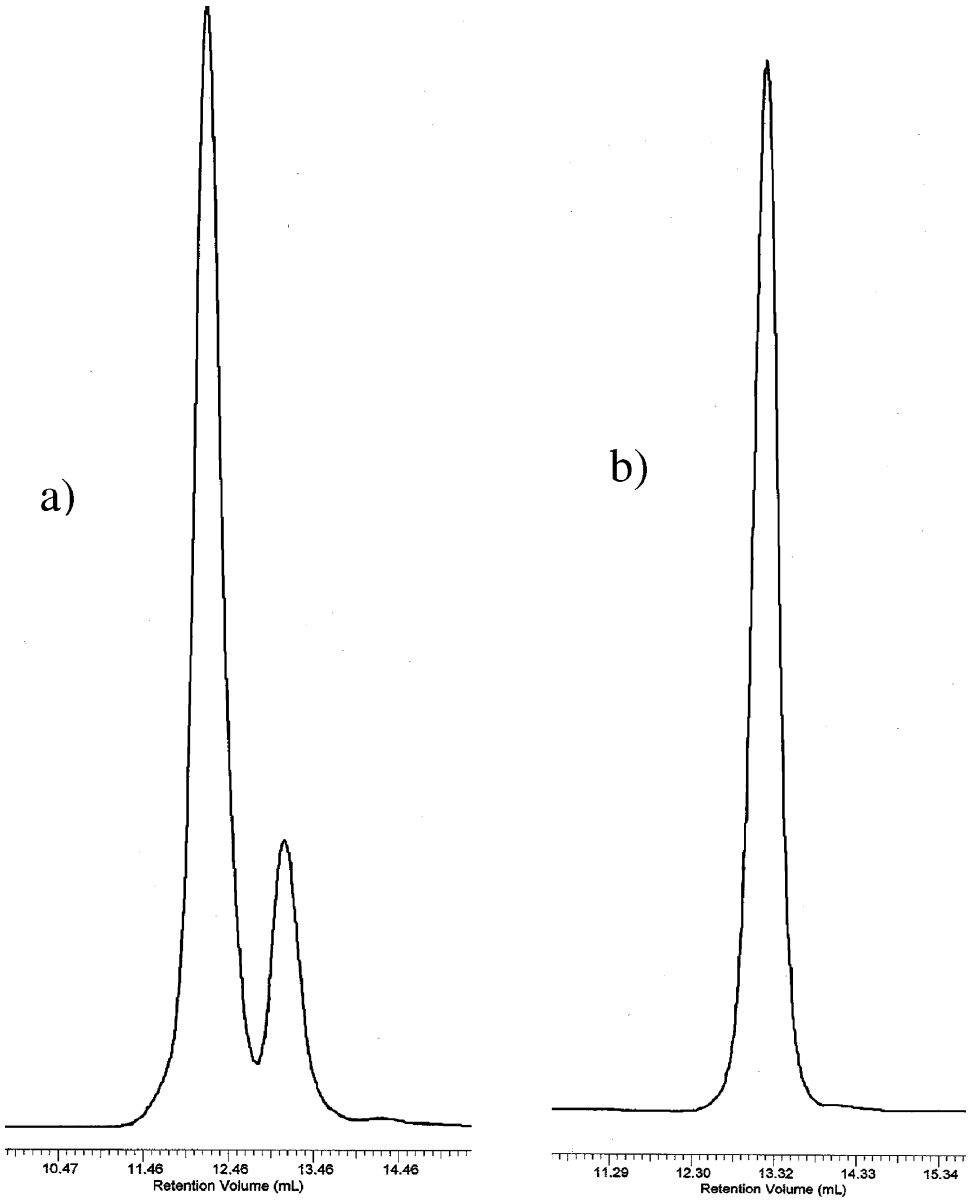


Figure 3. SEC chromatogram of G1 DendriMac (a) before and (b) after fractionation.

extent of reaction was limited by side reactions. ^{1}H NMR analysis of one of the HyperMac reaction products showed that despite the presence of "unreacted macromonomer" , there was no evidence of residual alkyl chloride functionality. It is apparent that in the present work, the extent to which the coupling reactions proceed may be similarly limited by deleterious reactions with impurities generated by thermal decomposition of DMF. In Figure 2, the SEC chromatogram of unfractionated G2-OH, we can see that although the major component of this mixture is the desired product, confirmed by molecular weight analysis following purification, there is also present unreacted starting material, both G1-Cl (at retention volume c. 14.25 mL) and macromonomer-(OH_3) (at retention volume 15 mL) as well as partially coupled product evident as a shoulder to the main peak. However, one of the principal advantages of the convergent methodology is that after each coupling reaction the crude product mixture can be readily analyzed and purified and after fractionation the desired materials are obtained with narrow molecular weight distributions as evidenced by the SEC chromatograms in Figures 1 and 2. It should also be noted that while the fractionation process is very good at purifying the product of the coupling reactions, this process results in the loss of material and in relatively modest yields. The yield of G1-OH after fractionation is 56%, and the yield of G2-OH is 37%. The lower yield of G2-OH is due to greater quantities of unreacted starting materials and partially coupled polymer in the reaction mixture, almost certainly the result of a higher degree of side reaction because of a lower concentration (cf. DMF) of reactive functionalities on the higher molecular weight starting materials. With this in mind, we considered alternative solvents. As previously mentioned the two principal requirements for a solvent for this reaction is that (a) the solvent is a good solvent for polystyrene and (b) that the solvent is aprotic with a high dielectric constant. These constraints somewhat limit the choice. Other solvents that meet requirement b include acetone, acetonitrile, and dimethyl sulfoxide all of which are non solvents for polystyrene. The "textbook" good solvents for polystyrene, toluene and benzene, both have very low dielectric constants, and therefore, the only other viable solvent we could investigate was tetrahydrofuran (THF). We found not surprisingly that the rate of reaction in refluxing DMF was far higher than in refluxing THF, not only because of the difference in boiling point (153 °C for DMF and 67 °C for THF) but also because of the difference in dielectric constant (7.58 and 36.71

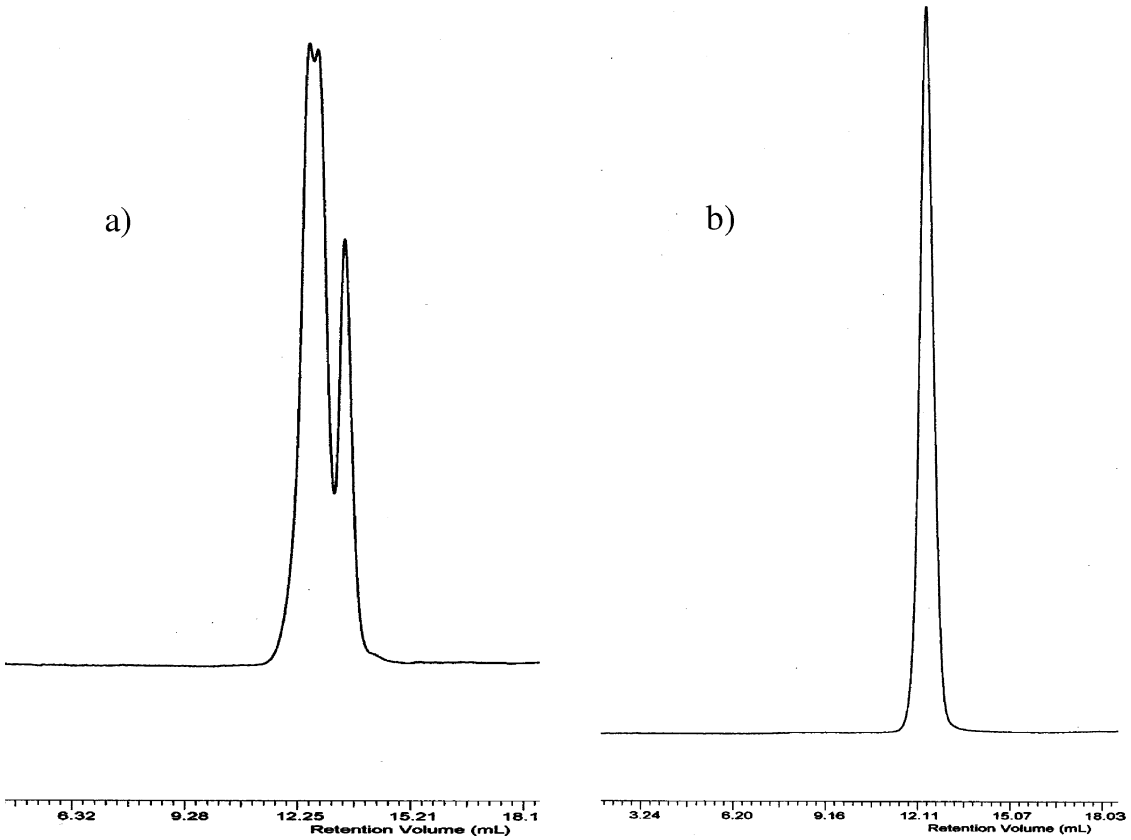


Figure 4. SEC chromatogram of G2- DendriMac (a) before and (b) after fractionation.

Table 1. Theoretical and Actual Molecular Weight Data for Starting Materials, Dendritically Branched Polystyrenes, G1-OH and G2-OH, and Polystyrene G1 and G2 DendriMacs

		SEC data		
	theoretical M_n/gmol^{-1}	M_n/gmol^{-1}	M_w/gmol^{-1}	PDI
macromonomer-$(OH)_3$	-	15 900	16 700	1.05
macromonomer-Cl	-	10 900	11 500	1.05
G1-OH	37 700	38 900	41 300	1.06
G1-DendriMac	117 000	119 000	124 000	1.04
G2-OH	94 000	96 000	98 000	1.03
G2-DendriMac	287 000	285 000	299 000	1.05

Table 2. Intrinsic Viscosity and Branching Factor, g', Values for Dendritically Branched Polystyrenes G1-OH, G2-OH, and G1- and G2-DendriMac

	$[\eta]_{br}$/dL g^{-1} [a]	$[\eta]_{lin}$/dL g^{-1} [b]	g'[c]
G1-OH	0.191	0.248	0.77
G1-DendriMac	0.379	0.541	0.70
G2-OH	0.344	0.457	0.75
G2-DendriMac	0.563	1.013	0.55

[a] Measured by SEC viscometry. [b] Calculated using the Mark−Houwink equation $[\eta] = KM^a$. [c] $g' = [\eta]_{br}/[\eta]_{lin}$.

for THF and DMF at 25 °C respectively), the coupling reaction being favored by solvents with high dielectric constants.[40] In contrast to DMF, the reaction in THF proceeded very slowly, after 150 min at reflux there was no apparent reaction and even after 5 days at reflux the extent of reaction was only a fraction of that observed in DMF.

The dendritically branched polymers G1-Cl and G2-Cl can be coupled to a multifunctional core, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) by the same coupling reaction to give dendrimer like branched polymers, DendriMacs, Scheme 4. Hence, a 2 g sample of G1-Cl was coupled to THPE via a Williamson coupling reaction in DMF in the presence of potassium carbonate and 18-crown-6-ether. Although once again the reaction was hampered to a certain extent by side reactions the major product was the desired G1-DendriMac, which was subsequently purified by fractionation using toluene as the solvent and methanol as the nonsolvent. The G2-Cl was similarly reacted with THPE to form a G2-DendriMac, the SEC chromatograms of the G1-DendriMac and G2-DendriMac before and after fractionation are shown in Figures 3 and 4. It can be seen that with the molecular weight of the polymer to be coupled having increased, the efficiency of the reaction decreases. This is undoubtedly due to undesirable side reactions between impurities (generated from degrading DMF) and the alkyl chloride functionality, as alluded to earlier. In the case of the coupling of G2-Cl with THPE the crude product of the reaction is a mixture of the desired product and partially coupled material, with the desired product formed in less than 50% yield. In turn this means that, although pure product can be obtained via fractionation, the yields become very low. In the earliest reactions, that is the synthesis of G1-OH and G2-OH, the yields after fractionation are very respectable, 56% for G1-OH and nearly 40% for G2-OH. However, in the synthesis of G1 and especially G2 DendriMac, the efficiency of the reaction did fall away quite sharply.

We did consider increasing the amount of dendron with respect to THPE but since the major loss of material is due to the fractionation process we felt that while we might increase the efficiency of the reaction, overall yields were unlikely to be much improved because of a greater proportion of contaminant to be removed by fractionation. It should be noted however that in purifying (by fractionation) the G1 and G2 DendriMacs, our primary aim was to obtain sufficient pure DendriMac to allow characterization of the material rather than to maximize the yield. The molecular weights of both the dendritically branched polystyrenes (G1-OH and G2-OH) and the G1 and

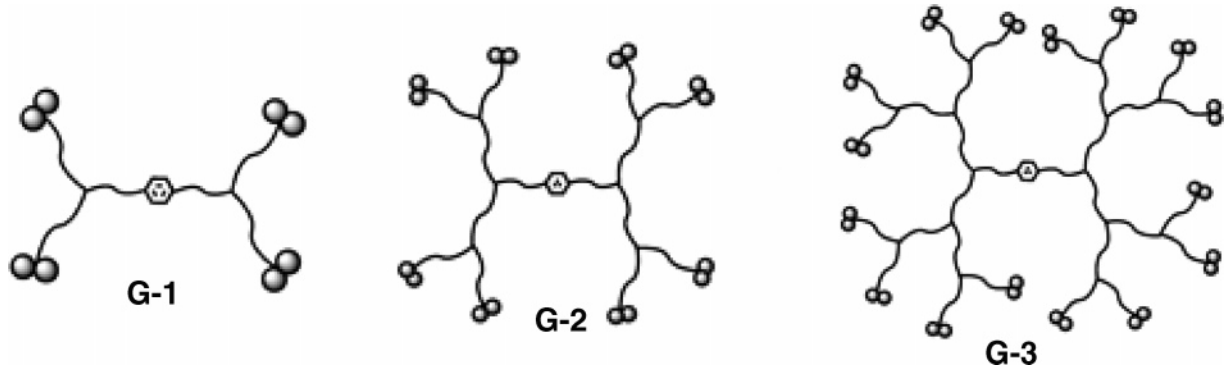


Figure 5. Dendrimer-like PMMA branched polymers reported by Hirao et al.[18]

G2 DendriMacs are shown in Table 1 and are in excellent agreement with the theoretical values based on the starting materials. To further investigate the branched nature of the molecular architectures, the branching factor g' was calculated, g' being given by the ratio of the intrinsic viscosity of the branched polymer $[\eta]_{br}$ to the intrinsic viscosity of a linear polymer $[\eta]_{lin}$ of the same molecular weight.[19,42] Shown in Table 2 are the intrinsic viscosity values of the branched polymers, obtained by SEC viscometry, the intrinsic viscosity of linear polymers of identical molecular weight, calculated using the Mark−Houwink equation with values of $a = 0.712$ and $K = 12.8 \times 10^{-5}$dL/g (supplied by American Polymer Standards Corporation) and g'. Unsurprisingly as the degree of branching increases the value of g' decreases, but it is a little surprising that there is only a modest difference between G1-OH and G2-OH. However, the value of g' for G1 DendriMac falls to 0.7 and for G2-DendriMac to 0.55, demonstrating the increasingly branched, compact structure.

For comparison we similarly obtained g' values for a series of 4-arm polystyrene star branched polymers with molecular weights from 52 000 to 830 000 g mol^{-1}. The values of g' were all in the region of 0.72 (±0.02). Dendrimer-like branched polymers synthesized by Hirao et al.[18] with PMMA chains of approximately 11 000 g mol^{-1} between branch points but a slightly different structure (see Figure 5) had a branching factor, g' of 0.80, 0.59, and 0.46 for G-1, G-2, and G-3, respectively. Although it is not possible to make a direct comparison between the DendriMacs synthesized in this paper with Hirao's materials, we can see that similar trends exist as the number of generations of branching increases.

Conclusions

We have synthesized polystyrene condensation macromonomers by living anionic polymerization using an initiator with a protected alcohol functionality and a diphenylethylene derivative containing two protected phenol groups as an end capping agent. Following deprotection and end group modification we have demonstrated for the first time that it is possible to convert these macromonomers into dendritically branched polymers, DendriMacs, via a stepwise, convergent strategy. The resulting branched polymers were purified by fractionation and have been characterized by size exclusion chromatography which showed that the molecular weights are in excellent agreement with predicted values. Furthermore, the branching factor g' was obtained by the ratio of the intrinsic viscosity of the branched polymer (from SEC viscometry) to the intrinsic viscosity of a linear polymer of the same molecular weight; as expected, as the degree of branching increased, the value of g' fell, indicating a more compact structure.

However, although we have demonstrated that the concept of synthesis of dendritically branched polymers via a convergent strategy is feasible, the coupling reactions are hampered by (probable) deleterious side reactions between the alkyl chloride functionality on the polymer and impurities generated by heating DMF (the reaction solvent). The effect of these side reactions becomes more serious as the molecular weight of the polymer increases due to the reduced concentration of halide with respect to DMF. Work is ongoing to try and overcome this problem which will be vital if useful amounts of these materials are to be made for rheological investigations.

Acknowledgment. We thank Dr. Alan Kenwright for his assistance with NMR experiments. This research was funded by the Engineering and Physical Sciences Research Council (GR/R02412/01) and we gratefully acknowledge their financial support.

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MA052627D