Macromolecules **2006,** *39,* 4361−4365

Synthesis of Well-Defined Second (G-2) and Third (G-3) Generation Dendritic Polybutadienes

Katerina Orfanou,[†] Hermis Iatrou,[†] David J. Lohse,*[,‡] and Nikos Hadjichristidis*[,†]

Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece, and
Corporate Strategic Research Labs, ExxonMobil Research & Engineering Co.,
Annandale, New Jersey 08801

Received January 30, 2006; Revised Manuscript Received April 19, 2006

ABSTRACT: A series of well-defined second (G-2) and third (G-3) generation dendritic polybutadienes (PBd) were synthesized by the coupling of the living G-2 and G-3 dendrons with methyltrichlorosilane, using anionic polymerization high-vacuum techniques. The synthetic approach of the living G-2 dendrons involves (a) the synthesis of an in-chain double-bond PBd by selective replacement of the two chlorines of 4-(dichloromethylsilyl)-diphenylethylene (DCMSDPE), a novel linking reagent with dual functionality, with PBd by titration with PBdLi, (b) addition of *s*-BuLi to the double bond, and finally (c) polymerization of butadiene from the newly created anionic site. The synthesis of the G-3 dendrons requires the repetition of the aforementioned procedure with the exception of the addition of the living G-2 dendron, instead of PBdLi, to DCMSDPE. Intermediate and final products were characterized via size exclusion chromatography, membrane osmometry, size exclusion chromatography equipped with a two-angle laser light scattering detector, and proton nuclear magnetic resonance. The combined characterization results indicate that the dendritic PBds synthesized have high molecular and structural homogeneity.

Introduction

The synthesis of polymers with highly controlled molecular architectures has gained increased importance due to the rising demand for specialty polymers that possess novel properties. Among these, dendrimers and dendritic polymers form the newest class of macromolecules,[1] with a cascade-branched, three-dimensional architecture, which are of academic interest due to their complexity and synthetic challenge[2,3] and have found increased attention for their industrial applications.[4−7] Dendrimers are megamolecules with regularly branched repeat units with short spacers between neighboring branch points, usually of two to eight bonds. The dendritic or dendrimer-like polymers are structurally analogous to regular dendrimers but contain polymer chains of variable length between each branching unit rather than short spacers. Because of their unique physical and chemical properties, dendrimers and dendritic polymers have found use in areas such as catalysis,[8] biomimetics,[9] supramolecular chemistry,[10] surface chemistry,[11] light-harvesting materials,[12] and medicine.[13]

Six and Gnanou[14] synthesized second generation (G-2) dendritic poly(ethylene oxide) (PEO) with the following three-step strategy: (a) anionic ring-opening polymerization of ethylene oxide (EO) with a trifunctional alkoxide initiator to produce a 3-arm star PEO, (b) transformation of the living end of each arm into two hydroxyl groups, through reaction with a chloro, iodo, or tosyl derivative of 2,2-dimethyl-5-ethyl-5-hydroxymethyl-1,3-dioxane, followed by hydrolysis, and (c) polymerization of EO at the newly formed living sites. The same group[15] has also prepared G-2 dendritic copolymers of EO and styrene based on the same synthetic strategy. However, in this case each of the hydroxyl end groups of the PEO stars was transformed into two 2-bromopropionate groups that served as initiating sites for the subsequent atom transfer radical polymerizations (ATRP) of styrene.

Hedrick et al.[16] synthesized G-2 and G-3 dendrimer-like (dendritic) block copolymers of ϵ-caprolactone and methacrylate-based monomers. A hexahydroxyl functional core was used as initiator for the ring-opening polymerization of ϵ-caprolactone in the presence of $Sn(Oct)_2$ to produce a hydroxyl-terminated 6-arm star polymer. Capping the chain ends with activated bromo functional dendrons produced macroinitiators for the ATRP of methyl methacrylate and related monomers to form the dendritic block copolymers. This methodology is a general one and can be applied to the synthesis of other dendritic systems.[17−19]

Knauss and co-workers[20] have proposed a methodology based on convergent living anionic polymerization for the synthesis of hyperbranched polystyrenes (PS) structurally analogous to the above-mentioned dendritic or dendrimer-like star-branched polymers. The methodology involved the one-pot successive linking reaction and living anionic polymerization between polystyryllithium, 4-(chlorodimethylsilyl)styrene (CDMSS), and styrene. The resulting dendritic PSs have a less than perfect structure but offer the advantage of a convenient and simple one-pot synthesis.

The preparation of well-defined G-2 dendritic homo- and copolymers of isoprene and styrene was reported by Chalari and Hadjichristidis[21] via stepwise convergent anionic polymerization. The success of the synthesis relies on the selective reaction between living chains and the dual-functionality compound CDMSS. This stepwise synthesis provides excellent control over the reaction, leading to dendritic polymers with structural and compositional homogeneity.

Recently, Hirao et al.[22,23] prepared a series of well-defined architecture and precisely controlled in chain length G-7 dendritic star-branched poly(methyl methacrylate)s (PMMA)s based on an iterative divergent approach. The synthesis involved a coupling reaction of a functionalized living anionic PMMA with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups

---

[†] University of Athens.

[‡] ExxonMobil Research & Engineering Co.

* To whom correspondence should be addressed: E-mail hadjichristidis@chem.uoa.gr; david.j.lohse@exxonmobil.com.

10.1021/ma060231b CCC: $33.50

with chain-end-functionalized PMMA with benzyl bromide (BnBr) functionalities and a transformation reaction of the introduced SMP groups into BnBr functionalities. The dendrimer-like PMMAs up to the seventh generation have been successfully synthesized by repeating these two reactions seven times. With use of the same methodology, the synthesis of a structurally similar dendrimer-like star-branched block copolymer consisting of PMMA and poly(2-hydroxyethyl methacrylate) segments was also successfully achieved.

In this report we describe the convergent synthesis of well-defined G-2 and G-3 dendritic polybutadienes (PBd) by anionic polymerization high-vacuum techniques with the use of a novel dual-functional linking agent 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE), which is similar to the 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene used by Hirao et al. for the synthesis of functionalized asymmetric miktoarm star polymers.[24]

Experimental Section

Materials. Butadiene (Aldrich, >99%) was distilled twice from *n*-BuLi until final distillation at −78 °C in calibrated ampules along with a 2-fold excess of benzene. All of the solvents (tetrahydrofuran, benzene, and hexane, all reagent grade), the terminating agent (methanol), and trichloromethylsilane (Aldrich, >99%) were purified with high-vacuum techniques and procedures described in detail elsewhere.[25] *sec*-Butyl chloride (99.9%, Aldrich), dried over CaH_2 overnight, degassed, and distilled in a vacuum line, was reacted in a suitable high-vacuum apparatus, with excess Li (99% high sodium, Aldrich) in hexane to produce the initiator, *s*-BuLi.[25]

4-(Dichloromethylsilyl)diphenylethylene (DCMSDPE) was prepared from the Grignard reagent of 4-bromodiphenylethylene and trichlorodimethylsilane using high-vacuum techniques. 4-Bromodiphenylethylene was obtained from the Wittig reaction of 4-bromobenzophenone and methyltriphenylphosphonium iodide in the presence of *n*-BuLi. Details of this procedure have already been given in a very recent paper.[26]

Polymer Synthesis. All synthetic manipulations were conducted with classic high-vacuum techniques. The polymerization and linking reactions were carried out in evacuated, *n*-BuLi washed and solvent-rinsed glass reactors, at room temperature. Reagents were added via break-seals, and aliquots for characterization were removed by heat-sealing of constrictions. Full details of the apparatuses and techniques used are given elsewhere.[25]

Synthesis of G-2 Dendritic Polybutadienes. The synthetic approach involves the selective replacement of the two chlorines of DCMSDPE with PBd by titration with PBdLi, addition of *s*-BuLi to the in-chain double bond linear intermediate (G2DBL), polymerization of Bd from the newly created anionic site to produce the third living arm, and finally coupling with trichloromethylsilane. As an example, the synthesis of the G-2 dendritic PBd G2(19,23) is given below. In this paper we use names indicating the generation number and in parentheses the approximate molecular weights, in kg/mol, of the first, second, and third generation.

The living polybutadiene (PBdLi) was obtained by polymerization of butadiene (10 g, 0.185 mol) with *s*-BuLi (0.53 mmol, titer obtained by double titration of 1,2-dibromobutane[27]) in benzene (150 mL) at room temperature for 24 h. It was collected in a precalibrated ampule equipped with break-seal and connected to the apparatus shown in Figure 1. The PBdLi (M_w = 19 kg/mol, 0.53 mmol) was added dropwise to the reactor F5 containing DCMSDPE (0.062 g, 0.21 mmol) in benzene (100 mL) under continuous and vigorous stirring. The reaction was followed by taking samples in F tubes and analyzing them with size exclusion chromatography (SEC). After ∼2 equiv of PBdLi (∼8 g, 0.42 mmol) relative to DCMSDPE had been added to the reactor and when the end point was determined by SEC, the titration was stopped. The addition was carried out over a period of ∼24 h, and finally a permanent pale yellow color appeared. The color is due to the reaction with the double bond, indicating the end point of the titration. The excess PBdLi (2 g, 0.11 mmol) was removed from the apparatus by heat-sealing the constriction of the corresponding ampule. The solution of the G2DBL was transferred into the flask F6 and connected to a second apparatus (Figure 2) where the appropriate amount of initiator *s*-BuLi (0.21 mmol, titer obtained by double titration of 1,2-dibromobutane[27]) was added. The solution color immediately turned from pale yellow to deep red, indicating the opening of the double bond of the diphenylethylene moiety. The solution was left to stir for 48 h to ensure that all the DPE groups react with the *s*-BuLi. Subsequently, a new amount of butadiene (5 g) was added, and after complete polymerization (∼24 h) an aliquot was taken from the reactor for characterization and the linking agent, trichloromethylsilane (0.056 mmol), was introduced. The reaction was monitored by removing small aliquots for SEC analysis. The linking reaction was completed in 25 days. The reaction product, after neutralization of the excess of the living species with degassed methanol, was fractionated by the toluene/methanol system. The fractionated G-2 dendritic polymer was precipitated into an excess of methanol and dried under vacuum, until constant weight.

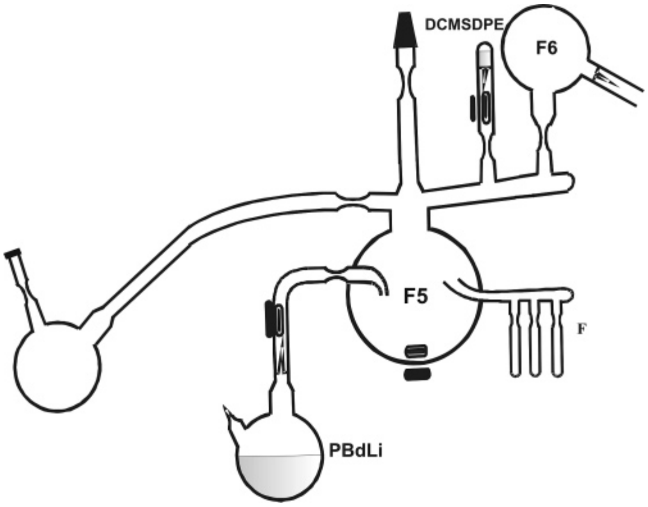


Figure 1. Apparatus for the synthesis of the in-chain double-bond polybutadiene 1,4 (PBd) homopolymers.

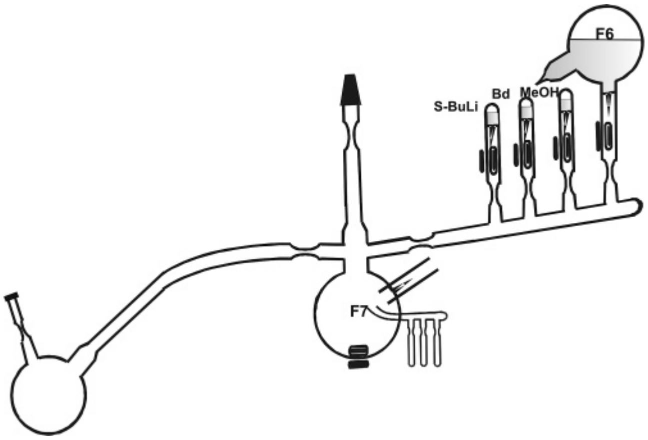


Figure 2. Apparatus for the synthesis of the dendritic polymers.

Synthesis of G-3 Dendritic Polybutadienes. The synthesis of G3(5,11,8) is described here as a representative example. The preparation, first of the linear living polybutadiene branch (8 g, M_w = 4.8 kg/mol, 1.7 mmol) and then of the living G-2 dendron PBd_3Li (13.8 g, 0.68 mmol), is similar to the previously described for the synthesis of the G-2 dendritic polymers. The produced living G-2 dendron was collected into the flask F7 and connected to a new apparatus similar to the one in Figure 1, where a second titration took place. PBd_3Li was added dropwise to the reactor containing DCMSDPE (0.08 g, 0.27 mmol) in benzene (100 mL) under stirring. This titration was also monitored by removing small aliquots and analyzing them with SEC. After $\sim$2 equiv of PBd$_3$Li ($\sim$0.54 mmol), relative to DCMSDPE, had been added to the reactor and when the end point was judged by SEC, the titration was stopped. The titration lasted $\sim$36 h. The excess of PBd$_3$Li ($\sim$2.5 g, 0.14 mmol) was removed and kept for characterization, and the in-chain double-bond G-2 dendron (G3DBD) was transferred into another apparatus (Figure 2) where the appropriate amount of initiator *s*-BuLi (0.27 mmol) was initially added. The color immediately turned from pale yellow to deep red, and after 48 h under stirring a new amount of butadiene (2 g) was introduced. An aliquot was taken from the reactor for characterization, and trichloromethylsilane (0.07 mmol) was finally added. After the completion of the linking reaction ($\sim$30 days), the excess of the living species was neutralized with degassed methanol, and the product was fractionated by the toluene/methanol system. The fractionated G-3 dendritic copolymer was precipitated into an excess of methanol and dried under vacuum until constant weight.

Molecular Characterization. Two SEC instruments were used, the first one to monitor the reactions and the second one to precisely characterize the intermediate and final fractionated products. The first instrument was a Waters HPLC system equipped with a Waters 501 high-pressure liquid chromatographic pump, four Waters Styragel columns having a porosity range of 10^2-10^6 Å, a Waters 410 differential refractometer detector, and a UV detector. Tetrahydrofuran was the eluent at a rate of 1 mL/min at 35 °C. Calibration was performed with standard PBd samples covering the molecular weight range from 1.5×10^3 to 9×10^5 g/mol.

The second instrument, a multidetector SEC system [size exclusion chromatography/refractive index (at 633 nm) and size exclusion chromatography/two-angle laser light scattering (SEC-TALLS) with laser power at 10 mW], running at 35 °C, with a flow rate of 1 mL/min was used to characterize the intermediate and final products. This system featured a Waters 1525 high-pressure liquid chromatography pump, Waters Ultrastyragel columns (HR-2, HR-4, HR-5E, and HR-6E with pore of sizes 10^3, 10^4 and 10^5 Å), a Waters 2410 differential refractometer detector (at 633 nm), and a Precision PD 2020 two-angle (15°, 90°) light scattering detector. The software of Precision Detectors "Discovery32" was used to calculate the M_w values by SEC-TALLS. The d*n*/d*c* value obtained by the multidetector system was 0.132 mL g^{-1} and was verified using the Chromatics KMX-16 differential refractometer, operated at 35 °C in THF.

The number-average molecular weights (M_n) of the dendritic macromolecules were obtained by membrane osmometry (MO) at 37 °C in toluene with a Knauer model A0330, equipped with A0545 membranes. Toluene was used as a solvent and distilled over CaH$_2$ before use. The M_n values from MO were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots, in which π is the osmotic pressure and c is the concentration in g/mL. In all cases, the correlation coefficient was better than 0.98.

NMR spectra were generated with a Bruker 400 MHz instrument with CDCl$_3$ as a solvent, at 25 °C.

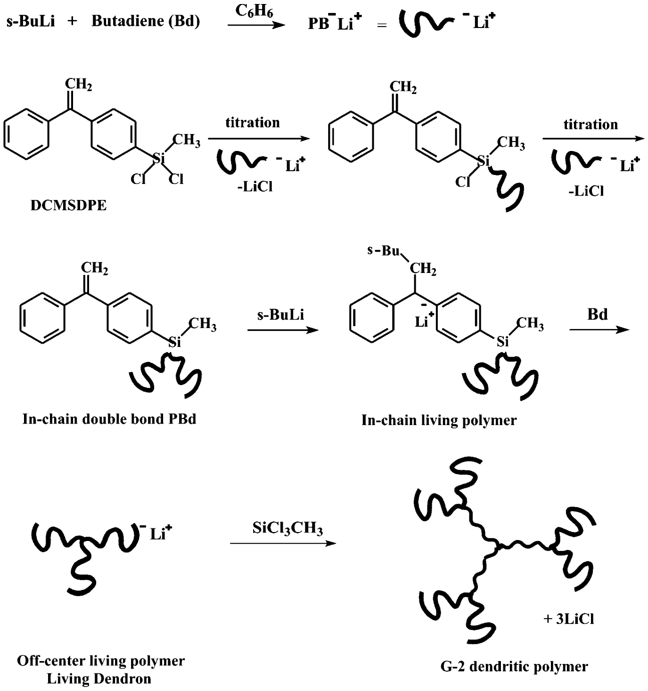
Results and Discussion

Synthesis of G-2 Dendritic Polymers. The synthesis of the G-2 dendritic polybutadiene was achieved according to the general reactions given in Scheme 1.

The initial step of the synthesis involved the titration of the two chlorines of DCMSDPE with PBdLi. The linking agent is a compound with three functional groups, two chlorosilyl groups, and a double bond. The success of the in-chain double-bond PBd synthesis depends on the selective reaction of the living chain with the chlorosilyl group rather than the double bond as shown in a previous work involving linking agent *p*-(chlorodimethylsilyl)styrene.[28,29] In the present case, the steric hindrance of the two phenyl groups of the DPE rendered the reaction of PBdLi with the chlorosilyl bond even more selective.

A relatively fast rate of addition to the solution, in the beginning, was possible, since PBdLi reacts selectively with the chlorosilane groups and not with the nonhomopolymerizable DPE double bond. As the titration continued, the rate of addition was decreased to control the stoichiometry. This is critical because (a) if SiCl groups remain they will react with the *s*-BuLi added at the next stage and (b) if PBLi is present it will initiate the polymerization of butadiene, added in the next step. Both cases lead to undesirable products.

Scheme 1. General Reaction Scheme for the Synthesis of Second-Generation Dendritic Polymers (G-2)



The linking reaction was monitored by removing samples from the reactor and analyzing them by SEC (Figure 3, sample G2(19,23)). Initially, there is only one peak on the SEC chromatogram, attributing to the end double-bond PBd with one chlorine (I). As the titration proceeds, this peak decreases while that of G2DBL (II) increases. The disappearance of the peak corresponding to (I) indicated the end of the titration. By careful addition of PBdLi near the end point, 99% substitution of both chlorines was achieved.

The reaction of *s*-BuLi with the double bond of the diphenylethylene was confirmed by the immediate change of the solution color from pale yellow to deep red, indicative of the living DPELi. It is very important to control the stoichiometry as mentioned above. It can thus be concluded that strictly preserving the stoichiometry of each reaction step is of great importance; otherwise, the byproducts formed would greatly complicate the synthesis since they are not isolated (one-pot procedure). In the case of inappropriate stoichiometric amounts of the reagents, the synthetic procedure was interrupted. A new experiment was subsequently started with fresh reagents.

After the synthesis of the in-chain living polymer, a new amount of Bd was added and the polymerization was allowed to proceed for 24 h. The desired molecular weight of the new PBd branch was estimated from the moles of DPELi and the grams of the monomer, and its actual molecular weight was found indirectly from the characterization of the dendron (off-center living polymer), since the branch could not be isolated. In some cases (Figure 4c), traces of G2DBL that remained after the polymerization of Bd may be a species that contained two $-$SiCl groups, but no double bond, since it remained unreacted throughout the rest of the synthetic procedure. Finally, an excess

Table 1. Molecular Characteristics of G-2 and G-3 Dendritic Polybutadienes

sample	M_w(arm)^a G-3 (kg/mol)	M_w(arm)^a G-2 (kg/mol)	M_w(arm)^a G-1 (kg/mol)	M_w(dendr)^c (kg/mol)	M_w(dendr)^a (kg/mol)	M_n(dendr)^b (kg/mol)	$(M_w/M_n)^{d,e}$ (dendr)
G2(4,3)		3.7	3	31.2	29.1	26.9	1.08
G2(3,6)		3.3	5.6	36.6	34.7	33.1	1.05
G2(5,14)		4.8	14	70.8	65.3	60.9	1.07
G2(14,12)		14.3	12.2	122.4	115.4	108	1.05
G2(19,23)		19	23.2	183.6	173	162.6	1.05
G2(25,21)		25.1	21.4	214.8	242.7	218.6	1.11
G2(36,49)		36	48.8	362.4	437.6	387.3	1.13
G3(5,11,8)	4.8	11.1	8.2	148.8	148.9	135.8	1.09
G3(5,6,5)	4.7	5.8	5.4	107.4	113.8	99	1.15
G3(5,6,32)$_{2br}$	4.7	6.1	32.2	126.4	126.1	112.6	1.12
G3(5,6,32)	4.7	6.1	32.2	189.6	189.1	164.4	1.15
G3(8,8,24)	7.7	7.7	24.4	211.8	202.4	185.7	1.09
G3(14,15,1)	13.8	15	1.1	258.9	222	198.2	1.12
G3(14,18,40)	13.8	18.1	39.7	393.3	380.2	347.8	1.09

[a] Obtained by SEC-TALLS in THF at 35 °C. [b] MO in toluene at 37 °C. [c] Calculated from the molecular weights of the arms. [d] Calculated from the M_w (size exclusion chromatography (SEC)−two-angle laser light scattering detector) and M_n (membrane osmometry). [e] All indices determined by SEC were lower than 1.05.

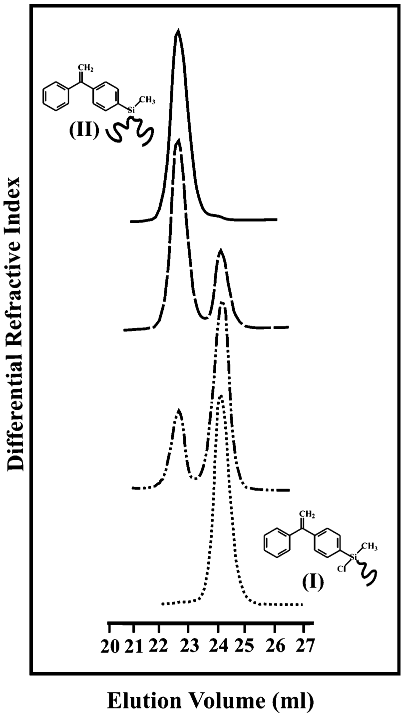


Figure 3. SEC chromatograms during the linking reaction between linear living PBd 19.0 × 10^3 precursor of the G-2(19,23) and DCMSDPE, in tetrahydrofuran (THF) at 35 °C, with a flow rate of 1 mL/min.

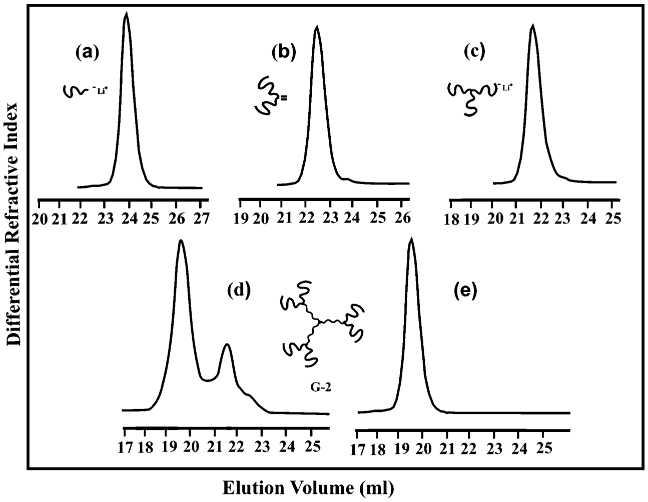
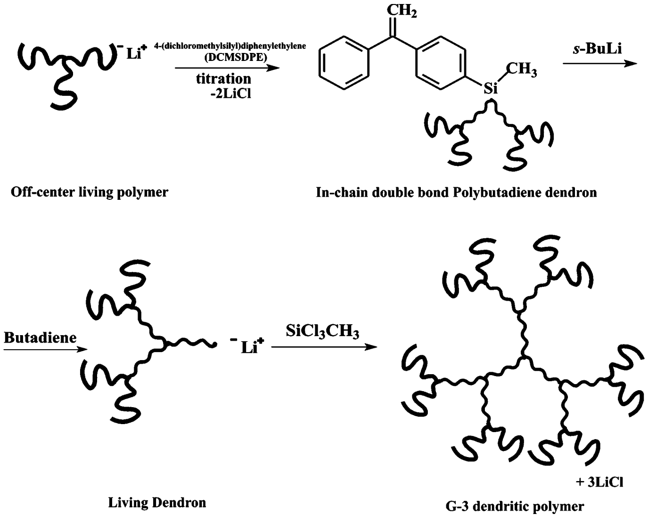


Figure 4. Monitoring the synthesis of G-2 dendritic polymer G2(19,23) by SEC: (**a**) living PBdLi, (**b**) macromonomer, (**c**) dendron, and G-2 dendritic polymer before (**d**) and after (**e**) fractionation.

Scheme 2. General Reaction Scheme for the Synthesis of Third-Generation Dendritic Polymers (G-3)



of the living dendron was added to trichloromethylsilane (3.5/1) to produce the G-2 dendritic polybutadiene.

The different steps were followed by SEC. A representative example, corresponding to G2(19,23), is given in Figure 4 and includes the SEC chromatograms of (a) PBLi, (b) the in-chain double bond PBd, (c) the dendron, and the G-2 polymer before (d) and after (e) fractionation.

Synthesis of G-3 Dendritic Polybutadienes. The synthesis of the G-3 dendritic polybutadiene is identical to that described for the G-2 polymers until the preparation of the living G-2 dendron. The general reactions for the synthesis of G-3 PBd are given in Scheme 2. In this case the necessity of preserving the stoichiometry of each reaction is more critical.

After the synthesis of the off-center living polymer a second titration took place, during which PBd_3Li was added dropwise in a solution of DCMSDPE in a molar ratio (PBd_3Li/ DCMSDPE) ~ 2/1. The reaction was monitored by SEC and was slightly slower than the first coupling of linear PBdLi on DCMSDPE due to the steric hindrance imposed by the starlike PBd_3Li.

The synthesis continued with the addition of the appropriate amount of *s*-BuLi in a molar ratio (*s*-BuLi/DCMSDPE) = 1/1,

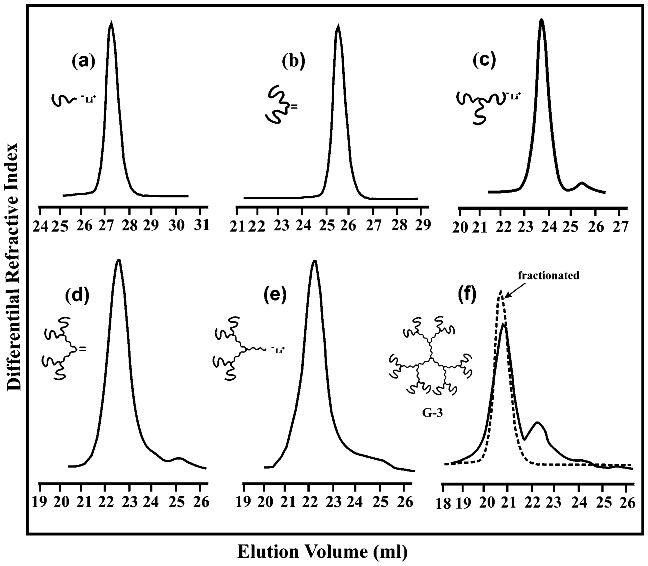


Figure 5. Monitoring the synthesis of G-3 dendritic polymer G3(5,11,8) by SEC: (**a**) living PBdLi, (**b**) first macromonomer, (**c**) off-center living polymer PBd_3Li, (**d**) second macromonomer, (**e**) dendron, and (**f**) G-3 dendritic polymer before and after fractionation.

followed by addition of a new amount of butadiene to polymerize for 24 h. The produced G-3 living dendron was coupled with trichloromethylsilane in order to create the G-3 dendritic polymer.

All steps were also followed by SEC, and a representative example, corresponding to sample G3(5,11,8), is given in Figure 5.

The molecular characteristics of the precursors and the final G-2 and G-3 denditic polybutadienes, after fractionation, are given in Table 1. The microstructure of the composed polymers was ~91 wt % 1,4 and 9 wt % 1,2, as determined by ^{1}H NMR. Only in the case of the sample G3(5,6,32) were stoichiometric amounts of trichloromethylsilane and living dendron used, resulting in the formation of a small amount of a product with two dendrons, in addition to the main product, the three-arm dendron. By fractionation of this sample, the two-arm [G3(5,6,32)$_{2br}$] and three-arm dendrons were separated.

The narrow molecular weight distribution obtained by SEC and confirmed by SEC-LALLS (M_w) and MO (M_n) as well as the agreement between the calculated and determined values of M_w for all the G-2 and G-3 dendritic polymers indicate a high degree of molecular and structural homogeneity. Rheological investigations revealed a hierarchy of relaxation times corresponding to the different generations. Only well-defined polymers could give such results, which are the subject of a forthcoming paper.[30]

Conclusions

G-2 and G-3 dendritic polybutadienes can be synthesized stepwise via convergent anionic polymerization. Their synthesis involves the use of (dichloromethylsilyl)diphenylethylene, a dual-functionality compound with two SiCl groups (linking agent) and a non-homopolymerizable double bond (diphenylethylene). This stepwise methodology and DCMSDPE provide excellent control over the reaction, leading to dendritic polymers with structural and compositional homogeneity, as indicated by the combined characterization results.

Acknowledgment. The authors thank Dr. Emmanuel N. Pitsinos (Institute of Physical Chemistry, National Center for Scientific Research (NCSR) Demokritos) for his advice on DCMSDPE synthesis and purification. The Research Committee of the University of Athens and the financial support of the Ministry of Education through the IRAKLITOS program, cofinanced from the Operational Programme and Initial Educational Vocational Training-EPEAEK and the European Social Funds, are greatly appreciated.

References and Notes

(1) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719−2728.
(2) Muscat, D.; Witte, A.; Koehler, W.; Muellen, K.; Geerts, Y. *Macromol. Rapid Commun.* **1997**, *18*, 233−241.
(3) Voegtle, F.; Duennwald, T.; Haendel, M.; Jaeger, R.; Meier, S.; Harder, G. *Chem.—Eur. J.* **1996**, *2*, 640−643.
(4) Kim, H. J.; DuPont, US Patent 485730, 1987.
(5) Hult, A.; Malmström, E.; Johansson, M.; Sörensen, K.; Perstorp AB, Eur. Patent 0630389, 1994.
(6) Sörensen, K.; Petterson, B.; Perstorp AB, World Patent 96/12754, 1996.
(7) Yeske, P. E.; Gindin, L. K.; Wicks, D. A.; Jonsson, E. H.; Bayer, Eur. Patent 0743335, 1996.
(8) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991−3023.
(9) Smith, D. K.; Diederich, F. *Chem.—Eur. J.* **1998**, *4*, 1353−1361.
(10) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681−1712.
(11) Tully, D. C.; Frechet, J. M. J. *Chem. Commun.* **2001**, 1229−1239.
(12) Adronov, A.; Frechet, J. M. J. *Chem. Commun.* **2000**, 1701−1710.
(13) Chen, C. Z.; Cooper, S. L. *Adv. Mater.* **2000**, *12*, 843−846.
(14) Six, J.-L.; Gnanou, Y. *Macromol. Symp.* **1995**, *95*, 137−150.
(15) Angot, S.; Taton, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 5418−5426.
(16) Trollsas, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644−4651.
(17) Trollsas, M.; Claesson, H.; Atthoff, B.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 3132−3136.
(18) Trollsas, M.; Kelly, M. A.; Claesson, H.; Siemens, R.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 4917−4924.
(19) Hedrick, J. L.; Trollsas, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, Ph. *Macromolecules* **1998**, *31*, 8691−8705.
(20) Knauss, D. M.; Huang, T. *Macromolecules* **2003**, *36*, 6036−6042.
(21) Chalari, I.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1519−1526.
(22) Matsuo, A.; Watanabe, T.; Hirao, A. *Macromolecules* **2004**, *37*, 6283−6290.
(23) Hirao, A.; Matsuo, A.; Watanabe, T. *Macromolecules* **2005**, *38*, 8701−8711.
(24) Zhao, Y.; Higashihara, T.; Sugiyama, K.; Hirao, A. *J. Am. Chem. Soc.* **2005**, *127*, 14158−14159.
(25) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211−3234.
(26) Mavroudis, A.; Hadjichristidis, N. *Macromolecules* **2006**, *39*, 535−540.
(27) Gilman, H.; Cartledge, F. K. J. *Organomet. Chem.* **1964**, *2*, 447−449.
(28) Vazaios, A.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym Chem.* **2005**, *43*, 1038−1048.
(29) Al-Muallem, H. A.; Knauss, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3547−3555.
(30) Orfanou, K.; Iatrou, H.; Vlassopoulos, D.; Lohse, D.; Hadjichristidis, N., to be published.

MA060231B