

# Preparation of Multiallylic Dendronized Polymers via Anionic Polymerization

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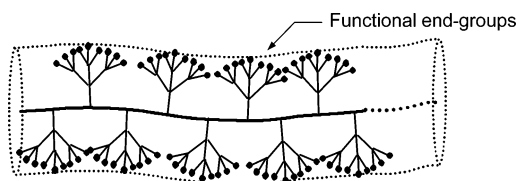
**ABSTRACT:** The anionic polymerization technique was investigated to prepare dendronized polymers (denpols) made of a polystyrene backbone and carbosilane dendrons. The monomers, namely 3,5-bis(3-triallylsilanylpropyloxy)styrene (**G1-bis**) and 3,4,5-tris(3-triallylsilanylpropyloxy) styrene (**G1-tris**), are fitted with respectively two or three allyl-terminated carbosilane dendrons of first generation. Polymers with monomodal molecular weight distribution and low polydispersity have been produced. Steric effects brought by the dendrons result in a slow polymerization rate, leading to an apparent saturation of the degree of polymerization. As a matter of fact, polymers of highest molecular weight could only be obtained from the less bulky monomer **G1-bis**. When the polymerization is complete or drastically reduced by steric factors, an intramolecular transfer reaction is suspected to take place. Finally, the solubility and thermal properties of these multiallylic denpols are discussed.

## Introduction

The dendronization of linear polymer chains by dendrons wedges on each monomer repeat unit leads to a new class of macromolecules, called linear dendronized polymers (or denpols).<sup>1</sup> The growing interest for dendronized polymers first arises from their ability to adopt a wormlike morphology;<sup>2,3</sup> a stiffening of the denpol may result from pure repulsive effect only,<sup>4</sup> when sterically demanding dendrons are tightly attached onto the polymer backbone. A second point of interest for dendronized polymers arises from their large number of terminal groups accessible to functionalization.<sup>1</sup> This peculiar feature associated with shape anisotropy allows to imagine the synthesis of nanocylinders covered with functional groups, as sketched in Figure 1. Indeed, such *surface functionalized nanocylinders* constitute an idealistic image of functional dendronized polymers. Even though stiff denpols have already been reported in the literature,<sup>2,4</sup> the functional branches at the dendron periphery may not all be distributed at the outer surface of the macromolecule but should, to some extent, fold back in the dendritic inner core.<sup>5</sup>

The synthesis of dendronized polymers is a difficult and challenging task, especially when close attachment of bulky dendrons to the backbone is concerned and when functionalization of the dendrons is targeted.<sup>1,6,7</sup> Dendronized polymers can be prepared (i) by grafting the dendron (at once or via a stepwise process) onto a preformed polymer chain ("graft-onto" route) or/and (ii) by polymerizing (or polycondensing) a dendronized monomer or a precursor ("macromonomer" route). Either of these two procedures offers advantages and drawbacks. The grafting-onto route makes possible series of dendronization starting from a well-defined polymer backbone, the main drawback usually being the large number of structural defects due to incomplete grafting.<sup>1,6</sup> The macromonomer approach allows the preparation of structurally perfect dendrons but often leads to oligomers with large polydispersities.<sup>1,6,7</sup>

The macromonomer route could be very straightforward, however. This synthetic pathway was found to yield dendronized polymers of high molecular weight, especially when the



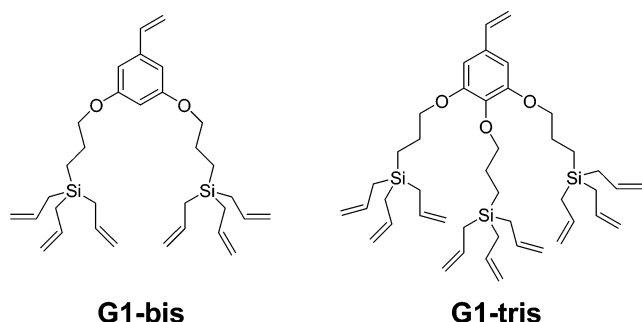
**Figure 1.** Schematic view of a surface functionalized dendronized polymer.

polymerization was run in the bulk or at least in a very concentrate media.<sup>8</sup> Percec et al. even evidenced a remarkable self-acceleration of the radical polymerization when the dendronized monomers preorganize into a self-assembly system.<sup>8a</sup> To obtain a controlled molecular weight and a low polydispersity, living (and "mediated") polymerization techniques have been used.<sup>8h–j,9–12</sup> Ring-opening metathesis polymerization (ROMP) was found to be a valuable living polymerization technique to prepare well-defined dendronized polymers.<sup>9,10</sup> Quite bulky G1 and G2 bis-dendronized norbornene monomers could thus be polymerized in a controlled fashion to lead to polymers of high molecular weights with low polydispersities.<sup>10b–e</sup> Similarly, coordination polymerization by Natta-type (Rh<sup>I</sup>-based catalyst) could be applied to highly bulky dendritic phenylacetylene to give polymers of remarkably high molecular weight.<sup>8h–j</sup> The ring-opening polymerization (ROP) technique was also reported to polymerize effectively an  $\epsilon$ -caprolactone monomer bearing G1 and G2 dendron to produce oligomers of predictable molecular weights.<sup>11</sup> Finally, cationic and anionic polymerization techniques have been used to successfully polymerize pseudo-dendritic monomers.<sup>9,12</sup> For cationic polymerization, the polymerizable unit was a vinyloxy<sup>12a,b</sup> and an oxazoline<sup>12c</sup> group, while for anionic polymerization a maleimide<sup>9</sup> group was used. The targeted oligomers were usually produced in a controlled manner to give materials of low polydispersity.<sup>12</sup> It is surprising to notice that only one attempt of using living anionic polymerization technique was reported to polymerize pseudo-dendritic monomers,<sup>9</sup> although this technique was found to be efficient to polymerize styrene macromonomers<sup>13</sup> and other monomers bearing bulky side groups.<sup>14</sup>

Recently, controlled radical polymerization techniques have been performed by some authors to polymerize dendronized

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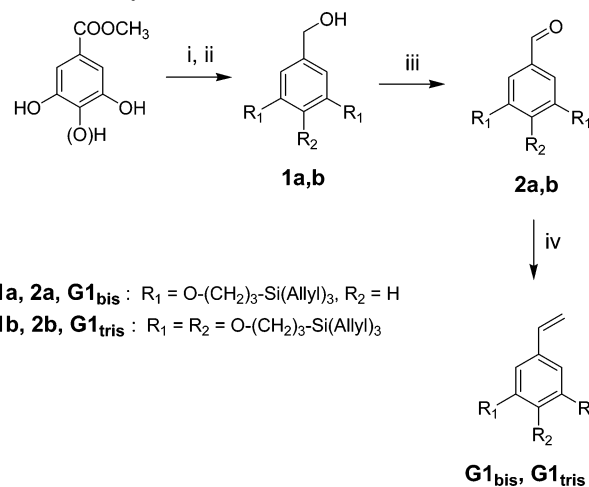
Scheme 1. Formulas of the Allylic End-Functionalized Dendritic Monomers



(meth)acrylic monomers.<sup>8g,15–17</sup> The polymerization techniques used were atom transfer radical polymerization (ATRP)<sup>8g,15,16</sup> and reversible addition fragmentation chain transfer polymerization (RAFT).<sup>17</sup> Reasonably high degrees of polymerization with narrow and monomodal distributions were obtained for dendritic monomers up to the second generation<sup>8g,15–17</sup> or else up to the third generation when a long spacer was used to space out the polymerizable site from the dendritic moieties.<sup>15b</sup> As far as molecular weight is concerned, however, Schlüter et al. found that ATRP and RAFT were much less efficient than thermally induced radical polymerization (TRP).<sup>8g,17</sup> Finally, Xi et al. synthesized different linear–dendritic block copolymers where the dendritic block is a dendronized polymer.<sup>16</sup> Such well-defined block copolymers are of course accessible only via living (or “mediated”) polymerization techniques.

As long as functional denpols are concerned, the materials have been produced both by using the graft-onto and the macromonomer routes.<sup>1</sup> So far, a large variety of functional (and functionalizable) groups have been introduced at the dendron termini, such as (protected) amines,<sup>18</sup> (protected) hydroxyls,<sup>11,15,19</sup> allyls,<sup>4,20</sup> oligo(ethylene glycol)s,<sup>21</sup> etc., or else ionic,<sup>22</sup> metallic,<sup>23</sup> or optically active species.<sup>24</sup> Among all functional denpols reported in the literature, very few of them were prepared via a controlled polymerization technique of end-functionalized dendritic monomers. Only ATRP, RAFT, and ROP techniques were used to polymerize dendritic monomers carrying protected hydroxyls<sup>10e,11,15</sup> and amines<sup>8g,17</sup> end branches. As already mentioned, these first attempts of using radically controlled polymerization could produce well-defined functional denpols of high degree of polymerization (DP) and low polydispersity only when steric hindrance was not too pronounced. So far and to our knowledge, no block copolymerization has been performed using an end-functional dendritic monomer.

The aim of this paper is to present results of living anionic polymerization applied to dendronized monomers. The monomers are styrene substituted by two (**G1-bis**) or three (**G1-tris**) carbosilane dendrons of first generation and terminated with functional allyl groups, as shown in Scheme 1. The multiple attachment of these three-armed G1 dendrons onto a styrene unit could bring enough steric hindrance not to consider the attachment of dendrons of higher generation (G2, G3, ...). The presence of the reactive allylic groups at the terminal branches of the dendrons makes possible a subsequent functionalization of the dendronized polymers. Actually, allyl groups are capable of undergoing quite efficient reactions such as radical addition of thiols,<sup>25</sup> hydrosilylation,<sup>26</sup> hydroboration,<sup>27</sup> etc., allowing a large variety of functional moieties to be subsequently grafted to. It has to be mentioned that multiallylic dendronized polymers have already been reported by us<sup>4</sup> and by Kim et al.<sup>20a,b</sup> but were prepared using the graft-onto route. Chain-growth polym-

Scheme 2. Synthesis of the Monomers **G1-bis** and **G1-tris**<sup>a</sup>

**1a, 2a, G1<sub>bis</sub>** :  $R_1 = \text{O}-(\text{CH}_2)_3\text{-Si}(\text{Allyl})_3$ ,  $R_2 = \text{H}$   
**1b, 2b, G1<sub>tris</sub>** :  $R_1 = R_2 = \text{O}-(\text{CH}_2)_3\text{-Si}(\text{Allyl})_3$

<sup>a</sup> (i)  $\text{K}_2\text{CO}_3$ , DMF,  $\text{Br}-(\text{CH}_2)_3\text{-Si}(\text{allyl})_3$ , 50 °C; (ii)  $\text{LiAlH}_4$ , THF, 0 °C; (iii)  $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , 25 °C; (iv)  $\text{Ph}_3\text{P}^+\text{CH}_3, \text{Br}^-$ , *t*-BuOK, THF, 0 °C.

erization of monomers having alkene side chains have already been reported in the literature, but the corresponding monomers did not carry more than two pendent alkene chains.<sup>28</sup> In the present paper are reported the synthesis of the dendritic monomers **G1-bis** and **G1-tris** and their anionic polymerization to prepare the corresponding multiallylic dendronized polymers **poly(G1-bis)** and **poly(G1-tris)**.

## Results and Discussion

**Monomer Synthesis.** The bis- and tris-dendronized styrene monomers (**G1-bis** and **G1-tris**) were prepared by using a four step procedure, starting from methyl 3,5-dihydroxybenzoate and methyl 3,4,5-trihydroxybenzoate, respectively (Scheme 2). The procedure starts with the Williamson etherification of the methyl di- or trihydroxybenzoate by the dendron triallyl(3-bromopropyl)silane.<sup>29</sup> The methylbenzoate derivatives were then reduced by  $\text{LiAlH}_4$  into the benzylic alcohols **1a,b**, to be further smoothly oxidized by  $\text{MnO}_2$  to give the corresponding benzaldehyde derivatives **2a,b**. By using the Wittig reaction, the latter compounds then led to the final dendritic styrene monomers **G1-bis** and **G1-tris**. Because the monomers are liquid at room temperature and have high boiling points, they unfortunately could not be purified by recrystallization or by distillation. Instead, they were recovered and carefully purified by column chromatography, freeze-dried from benzene solution several times, and then stored at −30 °C.

**Anionic Polymerization.** Anionic polymerization was applied to monomer **G1-bis**, in both apolar and polar media and with **G1-tris** in polar medium. Polymerizations using apolar solvent conditions were performed in benzene at room temperature for 1 h with *s*-BuLi as initiator. For polar conditions, polymerizations were carried out in THF or DME (1,2-dimethoxyethane) at low temperatures (−95, −78, −60, or −50 °C) for variable reaction times (from 30 to 300 min) and using *s*-BuLi, K-Naph, or Li-Naph as initiator. The polymerization conditions and the characteristics of the polymers **poly(G1-bis)** and **poly(G1-tris)** are presented in Tables 1 and 2, respectively.

For all polymerization runs, the presence of the living styryl carbanion could be deduced from the color change of the solution which instantaneously turned orange or red (for the lithium or potassium counteranion, respectively) at the initiation step and which persisted up to the addition of a few drops of methanol to quench the polymerization.

Table 1. Anionic Polymerization of Monomer G1-bis

entry	initiator (mmol)	[G1-bis] <sub>0</sub> /[I] <sub>0</sub> <sup>a</sup>	solvent	temp (°C)	time (min)	conv (%)	$\overline{M}_n^b$ (SEC)	$\overline{M}_n^c$ (MALLS)	$\overline{DP}_n$	PDI <sup>d</sup>
1	<i>s</i> -BuLi (0.22)	16	benzene	25	60	60	4300	9000	17	1.13
2	<i>s</i> -BuLi (0.21)	18	benzene	25	60	56	5600	8700	17	1.26
3	<i>s</i> -BuLi (0.30)	7	THF	-78	30	100	4100	6300	12	1.05
4	<i>s</i> -BuLi (0.26)	9	THF	-78	60	100	5000	7900	15	1.11
5	<i>s</i> -BuLi (0.29)	5	THF	-78	300	100	3200	4200	8	1.06
6	K-Naph (0.38)	8	THF	-78	30	100	4100	5900	11	1.07
7	K-Naph (0.36)	8	THF	-78	120	100	4200	5800	11	1.17
8	<i>s</i> -BuLi (0.16)	18	THF	-78	30	56	8000	14400	28	1.41
9	K-Naph (0.16)	16	THF	-78	30	77	8300	17400	33	1.18
10	K-Naph (0.12)	15	THF	-78	60	78	9500	17000	33	1.34
11	K-Naph (0.13)	21	THF	-78	60	60	9900	17200	33	1.33
12	K-Naph (0.28)	14	THF	-95	30	85	7700	13200	25	1.11
13	K-Naph (0.16)	10	THF	-95	60	83	7000	13400	26	1.12
14	K-Naph (0.13)	15	THF	-95	120	71	8100	14200	27	1.22
15	K-Naph (0.12)	17	THF	-60	60	60	11000	20900	40	1.32
16	Li-Naph (0.12)	27	THF	-95	30	20	10800	20400	39	1.50
17	K-Naph (0.12)	20	DME	-50	30	100	8700	17200	33	1.55

<sup>a</sup> Amount multiplied by two in the case of the bifunctional naphthalene initiators. <sup>b</sup> Measured by SEC with polystyrene reference. <sup>c</sup> Measured from multiangle laser light scattering (MALLS) detector. <sup>d</sup> Polydispersity calculated from SEC refractometer results.

Table 2. Anionic Polymerization of Monomer G1-tris

entry	initiator (mmol)	[G1-tris] <sub>0</sub> /[I] <sub>0</sub> <sup>a</sup>	solvent	temp (°C)	time (min)	conv (%)	$\overline{M}_n^b$ (SEC)	$\overline{M}_n^c$ (MALLS)	$\overline{DP}_n$	PDI <sup>d</sup>
18	<i>s</i> -BuLi (0.18)	6	THF	-78	30	82	3400	4600	6	1.08
19	<i>s</i> -BuLi (0.21)	14	THF	-95	90	56	3800	5700	8	1.05
20	K-Naph (0.11)	15	THF	-50	45	15	3700	5800	8	1.08
21	K-Naph (0.11)	23	THF	-50	120	28	4600	6600	9	1.11
22	K-Naph (0.18)	13	DME	-50	120	47	6800	12 500	17	1.26

<sup>a</sup> Amount multiplied by two in the case of the bifunctional naphthalene initiators. <sup>b</sup> Measured by SEC with polystyrene reference. <sup>c</sup> Measured from multiangle laser light scattering (MALLS) detector. <sup>d</sup> Polydispersity calculated from SEC refractometer results.

Let us begin with the polymerization of **G1-bis** in benzene solvent, first (Table 1, entries 1 and 2). The two polymerizations operated in benzene led to the same results. After 1 h reaction, the conversion remained incomplete (~60%), leading to polymers of low degree of polymerizations ( $\overline{DP}_n = 17$ ). This first result shows that dendronized styrene with bulky and multiallylic dendrons can be anionically polymerized but that polymerization proceeds at a very low rate, comparatively to nondendronized styrene monomer. The polymers are characterized by a quite low polydispersity (PDI ~ 1.2), but the SEC traces (not presented here) show a tailing at the high molecular weight side which indicates the formation of some chain couplings. This is the reason why the polymerization of **G1-bis** was more intensively investigated in polar medium.

Polymerization of **G1-bis** in polar medium was carried out mostly in THF solution (entries 3–16). Whatever *s*-BuLi or K-Naph initiator used, the monomer **G1-bis** was able to polymerize successfully to give polymers with a monomodal and a symmetrical molecular weight distribution with a low polydispersity (PDI < 1.2). A typical SEC trace (entry 6) is presented as an example in Figure 2. As already observed in benzene medium, the polymerizations are not always quantitative. Complete conversion is observed only for low molecular weight polymers ( $\overline{DP}_n < 20$ ). This observation brings evidence that, beyond the oligomer regime, the propagation rate drastically drops off. This phenomenon is of course related to the bulkiness of the dendritic moiety and will be widely discussed later. For one polymerization run (entry 5) performed at a prolonged reaction time (5 h), the color of the solution was found to slowly fading away, suggesting a progressive deactivation of the polystyryl carbanion with time. A SEC analysis of the resulting polymer, however, showed a symmetrical distribution of the molecular weight and a low polydispersity value (PDI ~ 1.1)

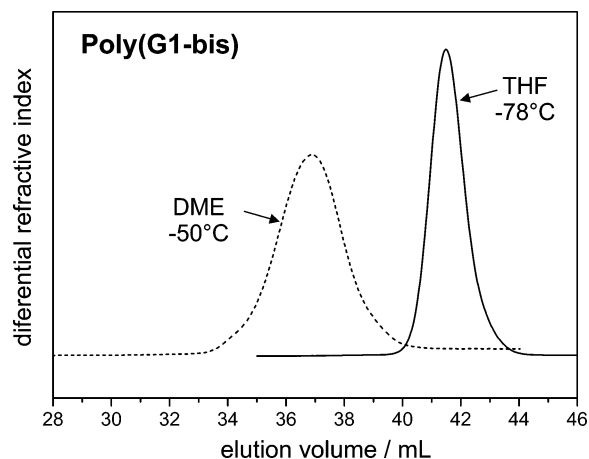


Figure 2. SEC elution traces of **poly(G1-bis)** obtained from a polymerization performed with K-Naph initiator for 30 min in THF at -78 °C (entry 6) and in DME at -50 °C (entry 17).

which proves that no significant interchain couplings occurred under these conditions (5 h at -78 °C). For polymerizations reaching full conversion (entries 3–7), one can observe a marked difference between the measured  $\overline{DP}_n$  values and the calculated ones, from the initial monomer and initiator concentration ( $\overline{DP}_{n,calc} = [G1-bis]_0/[I]_0$ ). Most probably, this difference corresponds to a fraction of initiator consumed to neutralize traces of impurities left in the monomers, which are of course very difficult to totally eliminate.  $Bu_2Mg$  (5 mol %) was used to tentatively kill the last remaining impurities in the monomer solution prior to polymerization, as shown by Hirao et al. in previous works.<sup>14a,30</sup> For our dendritic monomers, however, this action did not lead to any significant reduction of the initiator consumption and therefore was abandoned.



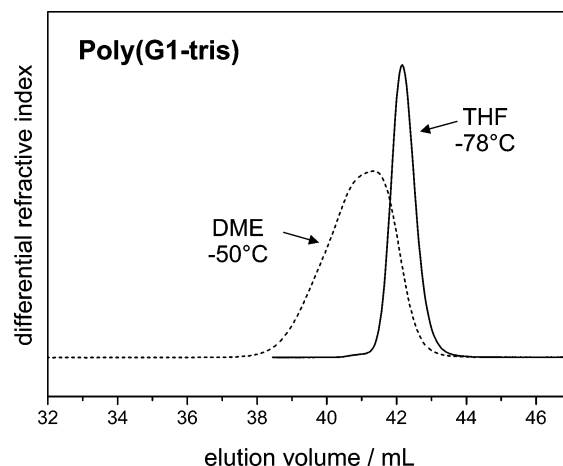
Let us examine now the polymers of higher molecular weight ( $\overline{DP}_n > 20$ ) and more specifically those initiated by K-Naph in THF. As already mentioned, conversion does not reach completion, and the propagation rate becomes so low that an apparent saturation of  $\overline{DP}_n$  is observed (entries 8–15). More surprisingly, the increase of the reaction time has nearly no effect on  $\overline{DP}_n$ . As an example, the growth of the polymers seems to levels off to  $\overline{DP}_n \sim 26$  when the polymerization is performed at  $-95^\circ\text{C}$ , whatever the reaction time (30–120 min, entries 12–14). Similarly, a “saturation” to  $\overline{DP}_n \sim 33$  is obtained at  $-78^\circ\text{C}$  (30 or 60 min, entries 9 and 10) for an equivalent targeted  $M_n$  value.

Temperature appears to be a pertinent parameter to push up the  $\overline{DP}_n$  “saturation” values. As a result,  $\overline{DP}_n$  values were found to significantly increase from about 26, 33, to 40 by raising the polymerization temperature from  $-95$ ,  $-78$ , to  $-60^\circ\text{C}$ , respectively (entries 13, 10, and 15). By increasing temperature, however, the polydispersity of the resulting polymers gets the general tendency to increase very slightly, to reach still a reasonable value ( $\text{PDI} \sim 1.3$ ) when polymerization is operated at  $-60^\circ\text{C}$ .

The nature of both the initiator and the counteranion was found to affect the polymer characteristics. Overall, the best polymerization results for **G1-bis** were obtained by using K-Naph, rather than *s*-BuLi or Li-Naph. When compared to monofunctional *s*-BuLi, bifunctional K-Naph initiator led to higher  $\overline{DP}_n$  values ( $\overline{DP}_n = 33$  vs 25; entries 8 and 9). Compared to Li-Naph, K-Naph led to lower  $\overline{DP}_n$  values, but the polydispersity was much lower ( $\overline{DP}_n = 25$  vs 39 and  $\text{PDI} = 1.11$  vs 1.50; entries 12 and 16).

A polymerization of **G1-bis** was performed by replacing THF solvent by 1,2-dimethoxyethane (DME), which is known to enhance the propagation rates by increasing the ratio of dissociated ions.<sup>31</sup> It is fair to assume that DME may act also through the polymer–solvent interaction parameter  $\chi$ .<sup>32</sup> To avoid the crystallization of DME ( $\text{mp} = -58^\circ\text{C}$ ), the polymerization was operated at  $-50^\circ\text{C}$  for 30 min. This run led to a complete conversion (100%) of the monomer. The resulting polymer was characterized by a relatively high molecular weight ( $\overline{DP}_n = 33$ ) and a symmetrical distribution of the molecular weights, although the polydispersity got slightly increased ( $\text{PDI} \sim 1.55$ ), as observed in the SEC trace presented in Figure 2 (entry 17). Nevertheless, this result shows the positive additional effect of the better solvent DME<sup>31</sup> and of a temperature increase to improve the polymerization rate of monomers **G1-bis**, while keeping moderate the transfer reactions.

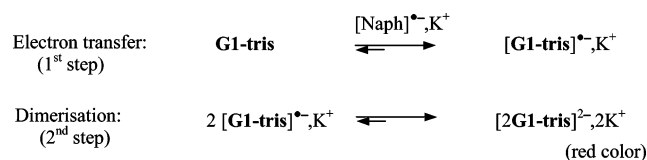
Let us examine now the second monomer **G1-tris** whose results are summarized in Table 2. This more sterically hindered monomer was also able to polymerize anionically (entries 18–22). The polymers show a quite low polydispersity with a symmetrical shape of the SEC peak, as can be seen in Figure 3 (entry 18). As compared to **G1-bis**, the polymerization of this bulkier **G1-tris** monomer leads to an apparent saturation of  $\overline{DP}_n$  to much lower values. Whatever the temperature ( $-95$  to  $-50^\circ\text{C}$ ) and time (up to 2 h) in THF solvent (entries 18–21), only oligomers are produced ( $\overline{DP}_n < 10$ ) while conversion never reaches completion. This result clearly illustrates the drastic decrease of the propagation rate when is increased the bulkiness of the dendritic moiety attached to the styrene. Contrarily to monomer **G1-bis**, no temperature effect is observed on the  $\overline{DP}_n$  “saturation” values. Higher molecular weights could only be obtained by replacing THF solvent by DME



**Figure 3.** SEC elution traces of **poly(G1-tris)** obtained from a polymerization performed with *s*-BuLi initiator in THF at  $-78^\circ\text{C}$  (entry 18) and with K-Naph initiator in DME at  $-50^\circ\text{C}$  (entry 22).

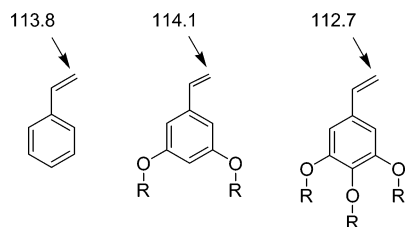
(compare entries 21 and 22). In DME, the  $\overline{DP}_n$  value could thus be doubled ( $\overline{DP}_n = 17$ ) while the distribution of the molecular weight was kept low and monomodal ( $\text{PDI} \sim 1.26$ ), as can be seen in Figure 3 (entry 22).

Another interesting finding concerns the efficiency of initiation observed between *s*-BuLi and K-Naph initiators. Polymerization of monomer **G1-tris** could be initiated (from color appearance) by K-Naph only above a critical temperature of about  $-50^\circ\text{C}$ , while *s*-BuLi was efficient already at  $-95^\circ\text{C}$  (entries 19 and 20). This observation clearly shows that the initiation step is more difficult with K-Naph than with *s*-BuLi and that it is temperature dependent. Contrarily to *s*-BuLi, initiation with K-Naph preliminary requires an electron transfer from the naphthalenide radical anion  $[\text{Naph}]^{\bullet-}, \text{K}^+$  onto the monomer **G1-tris**.<sup>33</sup> Then, the resulting monomer radical anion  $[\text{G1-tris}]^{\bullet-}, \text{K}^+$  rapidly dimerizes into a colored dianion from which the polymerization can start, as follows:<sup>14a,34</sup>



The absence of colored solution (at  $-78^\circ\text{C}$ ) in the case of K-Naph indicates that  $[\text{2G1-tris}]^{2-}, 2\text{K}^+$  does not form in these experimental conditions and that one of the two reactions cited above does not occur. Basically, it is reasonable to assume that the electron transfer should be the limiting step, rather than the radical dimerization,<sup>34</sup> as developed below. The difficulty of initiation might then be explained by the high electron density of the styryl monomer due to electron-donating effect of the three alkoxy groups connected to the benzene ring. With the hypothesis that the chemical shift of the carbone  $\beta$  ( $^{13}\text{C}$  NMR) of the vinyl group gives an estimation of the electron density at this place,<sup>28g,35</sup> the measured value for monomer **G1-tris** actually shows a significantly higher electronic density than that of monomers **G1-bis** and styrene (see Figure 4). The difference of reactivity between *s*-BuLi and K-Naph might therefore be explained by the stability of the  $[\text{Naph}]^{\bullet-}, \text{K}^+$  initiator due to the delocalization of the charge throughout the naphthalene core.

By looking through the data for polymers **poly(G1-bis)** and **poly(G1-tris)** in Tables 1 and 2, one observes a large difference between the molecular weights measured by SEC (ref PS) and by MALLS detection. It is well-known that SEC generally gives



**Figure 4.** Measured  $^{13}\text{C}$  chemical shift values  $\delta$  (in ppm) of the  $\text{C}_\beta$  styrenic double bond for monomers styrene, **G1-bis** and **G1-tris** (with  $\text{R} = -(\text{CH}_2)_3-\text{Si}(\text{allyl})_3$ ).

molecular weight values of denpols underestimated in regards to MALLS because dendronization usually brings a strong deviation of the hydrodynamic behavior by increasing the compactness and the rigidity of the whole macromolecule.<sup>1a,d</sup> In our case, the ratio  $\overline{M}_n$  (MALLS)/ $\overline{M}_n$  (SEC) increases with  $\overline{\text{DP}}_n$  to reach a value of about 2 for the highest molecular masses. A factor value of 2 still remains a moderate value as regards to few other values already reported, typically in the range from 2 to 8.<sup>2e,f,k,8b,h,11</sup>

One of the particular interests of the anionic polymerization is its living character which enables the preparation of well-defined block copolymers of narrow molecular weight distribution.<sup>14a</sup> The result of block copolymerization provides also information concerning the stability of the propagating chain end of the polymers. In this study, block copolymerizations of monomer **G1-bis** with styrene were carried out by using classical conditions (*s*-BuLi initiator in THF at  $-78^\circ\text{C}$ ). The results are gathered in Table 3, and the corresponding chromatograms of the copolymers are presented in Figure 5. Excluding steric effects, styrene and **G1-bis** monomers are expected to show alike reactivities, as supposed from the similar  $^{13}\text{C}$  NMR chemical shift of the  $\text{C}_\beta$  values of the vinyl group<sup>28g,34</sup> measured for monomer **G1-bis** ( $\text{C}_\beta = 114.1$  ppm) and styrene ( $\text{C}_\beta = 113.8$  ppm), as indicated in Figure 4. Practically, monomer **G1-bis** was taken for the first stage polymerization. This order was deliberately chosen because the opposite order would probably lead to a noticeable deactivation of the poly(styryl) chains since **G1-bis** monomer cannot be purified as well as styrene monomer. For this first stage, a low ratio  $[\text{G1-bis}]_0/[\text{I}]_0$  was used to ensure a complete polymerization at small reaction time. Two copolymerizations were carried out; the difference is the reaction time allowed for the polymerization of the first block, which is of 15 and 120 min (Table 3). Prior to addition of styrene for the second stage polymerization, a small amount of the first block **poly(G1-bis)** was cannulated out of the reactor for analysis.

For the first copolymer **poly(G1-bis-*b*-styrene)1**, a reaction time of 15 min was allowed for the polymerization of the block **poly(G1-bis)** (Table 3). As shown in the SEC trace in Figure 5, the carbanion at the **poly(G1-bis)** end chain could further initiate the second stage polymerization of styrene monomer, leading to a copolymer of increased molecular weight ( $\overline{M}_n = 16\,000$ ) and of narrow distribution ( $\text{PDI} = 1.06$ ). As previously observed, the molecular weight of the copolymer was higher than expected. Most probably, some remaining impurities in monomer **G1-bis** have consumed a small amount of initiator, thus reducing from the beginning the amount of active polymer chains. A more careful look at the chromatogram in Figure 5 shows that the copolymer **poly(G1-bis-*b*-styrene)1** contains a residual amount (7% weight amount) of homopolymer **poly(G1-bis)**, which corresponds to about 36% of deactivated chains.<sup>36</sup> The second copolymer **poly(G1-bis-*b*-styrene)2** was prepared in order to estimate the stability of the carbanion with

time. For this second copolymerization, all conditions remain unchanged except the first stage reaction time which was extended to 2 h, leaving the carbanion at the **poly(G1-bis)** end chains active for all this duration. The resulting SEC trace (Figure 5) distinctly shows the presence of two peaks of monomodal and narrow molecular weight distribution ( $\text{PDI} \sim 1.05$ ). One peak is attributed to the copolymer and the other one to deactivated homopolymer **poly(G1-bis)**. For this second copolymerization run, the amount of residual homopolymer **poly(G1-bis)** ( $\sim 37\%$  weight amount) corresponds to about 73% of deactivated chains.<sup>36</sup> Evidently, the carbanionic **poly(G1-bis)** chains are subjected to a noticeable deactivation with time.

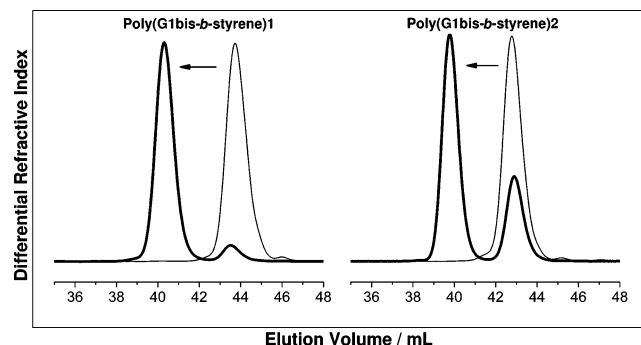
This chain deactivation seems to reflect a chain transfer process, which should take place most likely at the allylic branches. Such transfer reaction was already suggested to occur during the anionic polymerization of different *p*-alkenylstyrene by Ruckenstein et al.<sup>28d</sup> and Hirao et al.<sup>28f</sup> Actually, it is known that, in the presence of strong carbanionic species, allylsilyls can be subjected to proton abstraction<sup>37</sup> or carbanion addition<sup>38</sup> at the allylic branch. It is worth mentioning, however, that such reactions usually occur when quite activated carbanions (e.g., BuLi/TMEDA, BuLi/*t*-BuOK, or LDA) are used at elevated temperature.<sup>37,38</sup>

If deactivation is caused by such a chain transfer reaction, the narrow molecular weight distribution ( $\text{PDI} \sim 1.05$ ) measured for the copolymers necessarily implies the occurrence of intrachain couplings, which indeed is most likely to happen because of the high density of allylic branches closely located to the carbanion chain end of **poly(G1-bis)**. Moreover, the monomodal shape of the SEC peaks obtained for all polymers indicates that reactions transfer should essentially occur at the end of the polymerization. Such intrachain couplings cannot be detected by SEC analysis in the series of homopolymers of course (Table 1) because a chain deactivated by MeOH or by intramolecular reaction exhibits similar hydrodynamic behavior. Similarly, the NMR technique is not accurate enough to detect a single transfer reaction on a macromolecule. To discuss further on the possible transfer reactions, one can envisage that the polymerization of monomers **G1-bis** and **G1-tris** is competing with an intramolecular transfer reaction to lead to a deactivation of the carbanion at the polystyryl end chain. In such a case, one can reasonably assume that the transfer reaction should take place at allylic branches (via a proton abstraction<sup>37</sup> or an addition of the carbanion<sup>38</sup>) located at close vicinity of the carbanion at the **poly(G1-bis)** end chain. As long as oligomerization is concerned, the rate of the transfer reactions should remain negligible as regards to the propagation rate. The anionic polymerization should therefore be considered as quasi-living, at least at the early stage of the reaction. The intramolecular transfer reaction should start competing when the propagation is drastically slowed down by the increasing density of (allylic) branches connected to the polymer backbone which hinder the diffusion of the monomer to the carbanion at the polystyryl end chain. This competing reaction explains the tendency for PDI to increase when polymers of higher  $\overline{\text{DP}}$ s are targeted (see Table 1). This intramolecular reaction is expected to be more favored with monomer **G1-tris** which carries a greater density of allylic branches. Finally and as previously mentioned, it should also be expected to take place at the end of the polymerization, once all monomers have been consumed. The slow color fading of the polymer solution observed during the polymerization of **G1-bis** for an extended 5 h reaction time is in agreement with the presence of such a transfer reaction with time (Table 1, entry 5). The low polydispersity ( $\text{DPI} = 1.06$ ) obtained for the

Table 3. Anionic Block Copolymerization of G1-bis with Styrene

name	[G1-bis] <sub>0</sub> /[I] <sub>0</sub> <sup>a</sup>	[styrene] <sub>0</sub> /[I] <sub>0</sub> <sup>a</sup>	stage 1			stage 2			amount <sup>d</sup> (%)
			time (min)	$\overline{M}_n^b$	PDI <sup>c</sup>	time (min)	$\overline{M}_n^b$	PDI <sup>c</sup>	
<b>poly(G1-bis-<i>b</i>-styrene)1</b>	4.4	70	15	3000	1.08	15	16000	1.06	93
							(3400)	(1.08)	(7)
<b>poly(G1-bis-<i>b</i>-styrene)2</b>	4	40	120	2500	1.09	15	14700	1.05	63
							(2700)	(1.06)	(37)

<sup>a</sup> With *s*-BuLi initiator. <sup>b</sup> Measured from multiangle laser light scattering (MALLS) detector. <sup>c</sup> Polydispersity calculated from SEC refractometer results. <sup>d</sup> Estimated from SEC peak areas using UV detector at 280 nm;<sup>36</sup> in parentheses, values corresponding to deactivated poly(G1-bis).



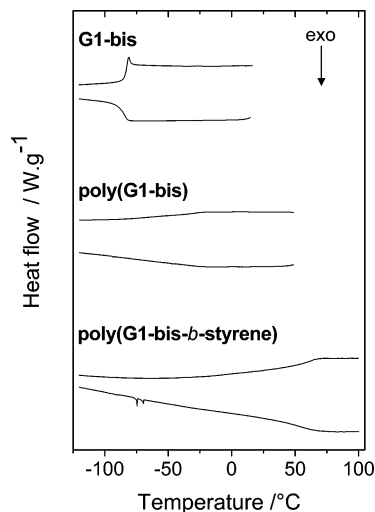
**Figure 5.** SEC elution traces of the crude copolymerization mixtures (bold line) and of the corresponding **poly(G1-bis)** recovered at the end of the first stage polymerization (plain line). The reaction time for the first stage polymerization was 15 min for **poly(G1-bis-*b*-styrene)1** and 120 min for **poly(G1-bis-*b*-styrene)2**.

resulting polymer conforms with a coupling reaction, intramolecular in nature.

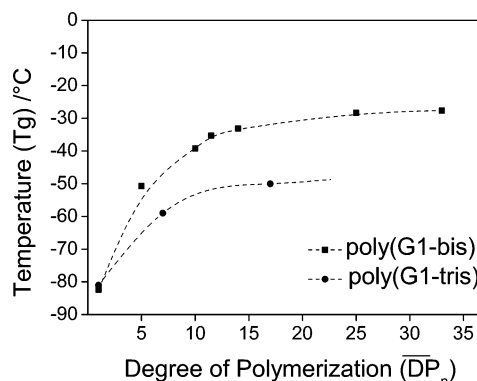
**Polymer Properties.** The dendronized homopolymers **poly(G1-bis)** and **poly(G1-tris)** look as a transparent viscous oil at room temperature, and the copolymers **poly(G1-bis-*b*-styrene)** appear as white crystals. All materials are thermally stable under air. Both homopolymers, copolymers, and monomers start decomposing at temperatures in the range 240–280 °C under air, as evidenced by thermogravimetry analysis (TGA).

A remarkable property of the dendronized polymers reported here are their extraordinary solubility in organic solvent. The homopolymers **poly(G1-bis)** and **poly(G1-tris)** are highly soluble in most organic solvents such as dichloromethane, acetone, hexane, diethyl ether, and even butanol. They are not soluble in methanol, yet. The copolymers **poly(G1-bis-*b*-styrene)** show a much better solubility character than poly(styrene) since they are soluble in acetone and diethyl ether, for instance.

As regards to thermal behavior, all dendronized homopolymers **poly(G1-bis)** and **poly(G1-tris)** exhibit a purely amorphous character. A glass transition temperature ( $T_g$ ) is observed at temperatures below –30 °C as a single transitional event, as shown in the DSC thermograms given as an example in Figure 6. Such low  $T_g$  values are not so surprising, however, since the monomers **G1-bis** and **G1-tris** are also purely amorphous, and both exhibit glass transition temperatures as low as  $T_g \sim -80$  °C (Figure 6). Figure 7 shows that  $T_g$  continuously increases with  $\overline{DP}_n$ , to level off at  $T_g \sim -30$  °C for **poly(G1-bis)** and  $T_g \sim -50$  °C for **poly(G1-tris)**. For both polymers,  $T_g$  seems to be already constant for  $\overline{DP}_n \sim 20$ . Limitation of  $T_g$  at such low DP values has already been reported for branched polymers such as poly(macromonomers)<sup>39</sup> and side-chain liquid crystal polymers.<sup>40</sup> A possible explanation for this behavior might be related to the end chain effects of the lateral branches through the excess free volume around the branch ends.<sup>39</sup> Even if there are only a few data reported for **poly(G1-tris)**, its  $T_g$  values are definitely lower than that of **poly(G1-bis)**. It shows



**Figure 6.** Low-temperature DSC traces of monomer **G1-bis** and of a typical polymer **poly(G1-bis)** and copolymer **poly(G1-bis-*b*-styrene)**.



**Figure 7.** Evolution of the  $T_g$  values as a function of  $\overline{DP}_n$  values for **poly(G1-bis)** and **poly(G1-tris)**.

that the increase of branching density further increase the plastification of the polymer, rather than its rigidity.<sup>4,25,41</sup> This observation seems to indicate that there is still some available space to fill in the dendritic coverage of **poly(G1-tris)** to further and significantly stretch out the polymer backbone by repulsive effects. The extremely low  $T_g$  values of the dendronized polymers are brought by the strong plastifying effect of the multiple allylic branches<sup>4,25,41b</sup> connected to the polystyryl backbone. It is worth comparing these  $T_g$  values with that of poly(styrene) ( $T_g \sim 100$  °C)<sup>42</sup> to better realize the huge plastifying effect induced by the dendrons.

The thermal behavior of the copolymers **poly(G1-bis-*b*-styrene)** is also worthy to comment. Both copolymers have a similar **G1-bis**/styrene block content and therefore exhibit the same behavior. Contrarily to our expectation, the copolymers exhibit a single glass transition temperature at about +60 °C, as shown in Figure 6. This result is surprising because one should expect the presence of two distinct  $T_g$  values: one at



about +100 °C corresponding to the PS block and the other one at about -50 °C corresponding to the **poly(G1-bis)** block (see Figure 7). Most likely, this result reflects a miscibility of the two blocks leading to a monophasic system. In such a case, the measured  $T_g$  value represents an intermediate  $T_g$  value of the two polymer blocks. The absence of microphase separation might be explained from the low molecular weight of the **poly(G1-bis)** block.

## Conclusions

Multiallylic dendronized monomers could be successfully polymerized by means of anionic polymerization technique. Best results were obtained when the polymerization was run in polar medium. Dendronized polymers of monomodal and low molecular weight distribution (PDI ~ 1.2) could thus be prepared. During the polymer growth, the increasing steric effects brought by the bulky dendrons attached to the styrene unit was found to drastically reduce the polymerization rate. As a result, the degree of polymerization found a limitation to  $DP_n \sim 30$  for **poly(G1-bis)** and  $DP_n \sim 10$  for **poly(G1-tris)**. Optimization of the experimental conditions (higher temperature, better solvent, etc.) could offer polymers of significantly higher molecular weights but with slightly increased polydispersities. The polymerization was suspected to compete with an intramolecular transfer reaction, most likely at the allylic branches located at the vicinity of the polystyryl carbanionic center. This side reaction appears to take place significantly when the propagation is drastically slowed down (by steric effects) or at the completion of the polymerization. Although the polymerization might not be considered as truly living, it however led to series of homopolymers and block copolymers of well-defined structure. All dendronized polymers are purely amorphous and exhibit exceptionally low glass transition temperature values. This result shows the ability of the carbosilane dendritic coverage to strongly plastify the styrene polymer backbone. Finally, the high density of allylic branches covering the surface of the denpols can be used for grafting a posteriori a large variety of functional groups. Examples of such surface functionalized denpols will be described in subsequent papers.

## Experimental Section

**Materials.** THF was dried over KOH and then distilled over sodium benzophenone. Benzene was distilled over sodium and distilled again over polystyryllithium (orange solution). Et<sub>2</sub>O was dried over CaCl<sub>2</sub> and then distilled over sodium. Other solvents were used as received. Allyl bromide (Aldrich, 97%) was distilled before use; magnesium chips (Acros) were washed with diethyl ether and dried in an oven before use. Triallyl(3-bromopropyl)silane (99.5+ % GC) was prepared from freshly distilled 3-bromopropyl(trichloro)silane (Aldrich, 96%) and allylmagnesium bromide.<sup>29</sup> Methyl 3,5-dihydroxybenzoate (Acros, 97%), methyl 3,4,5-trihydroxybenzoate (Aldrich, 98%), lithium aluminum hydride (Aldrich, 1 M in THF), manganese oxide (Merck), potassium *tert*-butoxide (Acros, 98%), and methyl triphenylphosphonium bromide (Aldrich, 98%) were used without any purification. Metal naphthalenides were prepared from the reaction of metal (lithium or potassium) with a small excess of naphthalene in dry THF. Commercially available *s*-BuLi as 1.3 M solution in cyclohexane from Aldrich was diluted with *n*-hexane.

**Instrumentation.** Isolation of the homopolymers was performed by passing the crude polymerization mixtures through a column filled with a SX1 Bio-Beads gel (Bio-Rad) and eluted with THF by gravity flow. Both <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were measured in CDCl<sub>3</sub> solvent (unless specified) using a Bruker AC300 spectrometer. Mass spectrometry analyses (FAB

technique) were performed by the Laboratory of Bio-Organic Mass Spectrometry (LSMBO) from the University Louis Pasteur in Strasbourg. Elemental analyses were carried out by the analytical department of the Institute Charles Sadron (ICS) in Strasbourg. Molecular weight determinations were performed at ICS by size exclusion chromatography (SEC) in THF on a Waters chromatograph fitted with five PLGel 10 μm Mixed B columns and by using three detection modes: a differential refractometer detector (Shimadzu RID-10A) calibrated with polystyrene standards, a UV detector (λ = 254 and 280 nm), and a multiangle laser light scattering (MALLS) detector (Wyatt DAWN DSP, λ = 632.8 nm). The  $\overline{M}_w$  (MALLS) values were determined using a  $dn/dc$  value of 0.139 for **poly(G1-bis)** and 0.136 for **poly(G1-tris)**. The reported  $M_n$  (MALLS) values were calculated from  $\overline{M}_w$  (MALLS detection) and PDI values (refractometry detection). Thermogravimetry analyses (TGA) were performed on a TA SDTQ600 instrument; the decomposition temperature values correspond to a 2% weight loss of the sample when heated at 10 °C/min under air. Differential scanning calorimetry (DSC) thermograms were recorded on a TA Instruments Q1000 fitted with a nitrogen cooling system allowing the measurements from -150 to 300 °C.

**Monomer Synthesis.** *Methyl 3,5-Bis{3-(triallylsilyl)propyloxy}benzoate*. A mixture of methyl 3,5-dihydroxybenzoate (6.8 g, 40 mmol), triallyl(3-bromopropyl)silane (25.5 g, 93 mmol), and potassium carbonate (24.8 g, 179 mmol) in 80 mL of DMF was heated at 50 °C for 24 h. The solvent was removed under reduced pressure, and the residue was portioned between water and Et<sub>2</sub>O. The aqueous layer was extracted with Et<sub>2</sub>O (three times); the combined organic phases were washed with water (three times), dried over MgSO<sub>4</sub>, concentrated in vacuo, and purified by column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>/hexane: 1/3) to give 21 g (95%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.16 (2H, d, *J* = 2.2 Hz, ArH), 6.63 (1H, t, *J* = 2.2 Hz, ArH), 5.80 (6H, m, CH=), 4.90 (12H, m, =CH<sub>2</sub>), 3.93 (4H, t, CH<sub>2</sub>O), 3.91 (3H, s, OCH<sub>3</sub>), 1.85 (4H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.64 (12H, m, SiCH<sub>2</sub>CH=), 0.72 (4H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.9 (C=O), 159.9 (C<sub>3Ar</sub>), 134.1 (CH=), 131.8 (C<sub>1Ar</sub>), 113.8 (=CH<sub>2</sub>), 107.6 (C<sub>2Ar</sub>), 106.6 (C<sub>4Ar</sub>), 70.6 (CH<sub>2</sub>O), 52.1 (OCH<sub>3</sub>), 23.2 (CH<sub>2</sub>CH<sub>2</sub>O), 19.4 and 7.4 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>32</sub>H<sub>48</sub>O<sub>4</sub>Si<sub>2</sub>: C, 69.53 (69.19); H, 8.76 (8.78); Si, 10.16 (10.03).

*Methyl 3,5-Bis{3-(triallylsilyl)propyloxy}benzyl Alcohol (1a)*. To a solution of the ester derivative (20.8 g, 37.6 mmol) in 100 mL of THF at 0 °C was added dropwise a solution (37.6 mL, 37.6 mmol) of LiAlH<sub>4</sub> in THF (1 M). After addition, the mixture was allowed to reach room temperature and stirred overnight. A concentrated solution of NH<sub>4</sub>Cl was added carefully to quench the reaction. The mixture was passed through a celite plug and the solid washed with THF until no more product could be recovered. The combined solution was dried over MgSO<sub>4</sub>, concentrated in vacuo, and purified by column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>-hexane: 1-1) to give 18.5 g (94%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.51 (2H, d, *J* = 2.2 Hz, ArH), 6.37 (1H, t, *J* = 2.2 Hz, ArH), 5.80 (6H, m, CH=), 4.9 (12H, m, =CH<sub>2</sub>), 4.63 (2H, d, *J* 4.0 Hz, CH<sub>2</sub>OH), 3.90 (4H, t, CH<sub>2</sub>O), 1.82 (4H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.63 (12H, m, SiCH<sub>2</sub>CH=), 0.70 (4H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 160.3 (C<sub>3Ar</sub>), 143.2 (C<sub>1Ar</sub>), 134.1 (CH=), 113.8 (=CH<sub>2</sub>), 105.0 (C<sub>2Ar</sub>), 100.5 (C<sub>4Ar</sub>), 70.4 (CH<sub>2</sub>O), 65.4 (CH<sub>2</sub>OH), 23.3 (CH<sub>2</sub>CH<sub>2</sub>O), 19.5 and 7.5 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>31</sub>H<sub>48</sub>O<sub>3</sub>Si<sub>2</sub>: C, 70.94 (70.42); H, 9.22 (9.20); Si, 10.70 (10.76).

*Methyl 3,4,5-tris{3-(triallylsilyl)propyloxy}benzoate* was prepared by using the same procedure as above. Starting from 2.1 g of methyl 3,4,5-trihydroxybenzoate (11.3 mmol), 11.9 g of triallyl(3-bromopropyl)silane (43.6 mmol), and 10.3 g of potassium carbonate (74.6 mmol) in DMF, 6.8 g (79%) of a colorless oil was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25 (2H, s, ArH), 5.80 (9H, m, CH=), 4.90 (18H, m, =CH<sub>2</sub>), 4.00 and 3.98 (6H, 2t, CH<sub>2</sub>O), 3.90 (3H, s, OCH<sub>3</sub>) 1.85 (6H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.64 and 1.62 (18H, m, SiCH<sub>2</sub>CH=), 0.70 (6H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.8 (C=O), 152.5 (C<sub>3Ar</sub>), 142.0 (C<sub>4Ar</sub>), 134.1 (CH=), 124.7 (C<sub>1Ar</sub>), 113.8 (=CH<sub>2</sub>), 108.0 (C<sub>2Ar</sub>), 75.8, 71.6 (CH<sub>2</sub>O), 52.1 (OCH<sub>3</sub>), 24.2 and 23.3 (CH<sub>2</sub>-

CH<sub>2</sub>O), 19.4 and 7.4 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>44</sub>H<sub>68</sub>O<sub>5</sub>-Si<sub>3</sub>: C, 69.43 (69.17); H, 9.01 (9.07); Si, 11.04 (11.19).

**Methyl 3,4,5-bis{3-(triallylsilyl)propyloxy}benzyl alcohol (1b)** was prepared by using the same procedure as for **1a**. The treatment of 6.6 g of the previously prepared ester derivative (8.7 mmol) in 60 mL of THF with 8.7 mL of a solution of LiAlH<sub>4</sub> (1 M) in THF gave 4.9 g (77%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.56 (2H, s, ArH), 5.80 (9H, m, CH=), 4.90 (18H, m, =CH<sub>2</sub>), 4.60 (2H, s, CH<sub>2</sub>OH), 3.94 and 3.92 (6H, 2t, CH<sub>2</sub>O), 1.85 (6H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.64 and 1.60 (18H, m, SiCH<sub>2</sub>CH=), 0.70 (6H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 153.0 (C<sub>3</sub>Ar), 137.2 (C<sub>1</sub>Ar), 136.1 (C<sub>4</sub>Ar), 134.1 (CH=), 113.7 (=CH<sub>2</sub>), 105.3 (C<sub>2</sub>Ar), 75.8 and 71.6 (CH<sub>2</sub>O), 65.5 (CH<sub>2</sub>OH), 24.1 and 23.4 (CH<sub>2</sub>CH<sub>2</sub>O), 19.4 and 7.4 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>43</sub>H<sub>68</sub>O<sub>4</sub>Si<sub>3</sub>: C, 70.45 (70.46); H, 9.36 (9.47); Si, 11.46 (11.54).

**3,5-Bis{3-(triallylsilyl)propyloxy}benzaldehyde (2a)**. The benzyl alcohol derivative **1a** (19 g, 36.2 mmol) was oxidized by MnO<sub>2</sub> (71 g, 816 mmol) in 200 mL of CH<sub>2</sub>Cl<sub>2</sub>. After 24 h stirring at room temperature, MgSO<sub>4</sub> (71 g) was added, and the mixture was passed through a celite plug, dried over MgSO<sub>4</sub>, and evaporated to dryness. The residue was then purified by column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>–hexane: 1–2) to give 16.7 g (88%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.90 (1H, s, CHO), 6.99 (2H, d, *J* = 2.2 Hz, ArH), 6.69 (1H, t, *J* = 2.2 Hz, ArH), 5.80 (6H, m, CH=), 4.90 (12H, m, =CH<sub>2</sub>), 3.95 (4H, t, CH<sub>2</sub>O), 1.83 (4H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.64 (12H, m, SiCH<sub>2</sub>CH=), 0.72 (4H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 191.9 (CHO), 160.5 (C<sub>3</sub>Ar), 138.3 (C<sub>1</sub>Ar), 134.0 (CH=), 113.8 (=CH<sub>2</sub>), 107.9 (C<sub>4</sub>Ar), 107.5 (C<sub>2</sub>Ar), 70.7 (CH<sub>2</sub>O), 23.2 (CH<sub>2</sub>CH<sub>2</sub>O), 9.4 and 7.4 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>31</sub>H<sub>46</sub>O<sub>3</sub>Si<sub>2</sub>: C, 71.22 (70.53); H, 8.88 (8.88); Si, 10.71 (10.78).

**3,4,5-Tris{3-(triallylsilyl)propyloxy}benzaldehyde (2b)** was prepared by using the same procedure as for **2a**. Starting from 4.8 g of **1b** (6.5 mmol) and 26 g of MnO<sub>2</sub> (300 mmol) in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> gave after purification 4.2 g (88%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.84 (1H, s, CHO), 7.08 (2H, s, ArH), 5.75 (9H, m, CH=), 4.90 (18H, m, =CH<sub>2</sub>), 4.04 and 4.00 (6H, 2t, CH<sub>2</sub>O), 1.85 (6H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.63 (18H, m, SiCH<sub>2</sub>CH=), 0.70 (6H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 191.1 (CHO), 153.2 (C<sub>3</sub>Ar), 143.5 (C<sub>4</sub>Ar), 134.0 (CH=), 131.4 (C<sub>1</sub>Ar), 113.8 (=CH<sub>2</sub>), 107.9 (C<sub>2</sub>Ar), 75.9 and 71.6 (CH<sub>2</sub>O), 24.3 (CH<sub>2</sub>CH<sub>2</sub>O), 19.4 and 7.4 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>43</sub>H<sub>66</sub>O<sub>4</sub>Si<sub>3</sub>: C, 70.64 (70.64); H, 9.11 (9.19); Si, 11.49 (11.59).

**3,5-Bis{3-(triallylsilyl)propyloxy}styrene (G1-bis)**. To an ice-cooled dry THF solution (150 mL) of potassium *tert*-butoxide (1.9 g, 16.9 mmol) and methyltriphenylphosphonium bromide (6.0 g, 16.9 mmol) was added a solution of the benzaldehyde **2a** (8 g, 15.3 mmol) in 20 mL of THF. The resulting mixture was stirred at room temperature overnight. Water (2 mL) was added to quench the residual potassium *tert*-butoxide. The solvent was evaporated to dryness, and CH<sub>2</sub>Cl<sub>2</sub> was added to the residue. Drying (MgSO<sub>4</sub>), evaporation in vacuo, and chromatography on silica gel (eluent Et<sub>2</sub>O–hexane: 1–30) afforded 6.6 g (83%) of a colorless oil which was stored at –30 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.63 (1H, dd, <sup>3</sup>*J*<sub>trans</sub> = 17.5 Hz and <sup>3</sup>*J*<sub>cis</sub> = 11.0 Hz, ArCH=), 6.55 (2H, d, *J* = 2.2 Hz, ArH), 6.36 (1H, t, *J* = 2.2 Hz, ArH), 5.85 (6H, m, CH<sub>2</sub>CH=), 5.70 (1H, dd, <sup>3</sup>*J*<sub>trans</sub> = 17.5 Hz and <sup>2</sup>*J*<sub>gem</sub> = 0.6 Hz, ArCH=CH<sub>2</sub>), 5.24 (1H, dd, <sup>3</sup>*J*<sub>cis</sub> = 11.0 Hz and <sup>2</sup>*J*<sub>gem</sub> = 0.6 Hz, ArCH=CH<sub>2</sub>), 4.95 (12H, m, CH=CH<sub>2</sub>), 3.90 (4H, t, CH<sub>2</sub>O), 1.83 (4H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.64 (12H, m, SiCH<sub>2</sub>CH=), 0.72 (4H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 160.2 (C<sub>3</sub>Ar), 139.4 (C<sub>1</sub>Ar), 136.8 (ArCH=CH<sub>2</sub>), 134.1 (CH<sub>2</sub>CH=CH<sub>2</sub>), 114.1 (ArCH=CH<sub>2</sub>), 113.8 (CH<sub>2</sub>CH=CH<sub>2</sub>), 104.8 (C<sub>2</sub>Ar), 100.9 (C<sub>4</sub>Ar), 70.4 (CH<sub>2</sub>O), 23.3 (CH<sub>2</sub>CH<sub>2</sub>O), 19.5 and 7.5 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>32</sub>H<sub>48</sub>O<sub>2</sub>Si<sub>2</sub>: C, 73.80 (74.06); H, 9.30 (9.72); Si, 10.75 (10.74). MS (FAB+): *m/z* (%) = 521.6 (20) [M + H]<sup>+</sup>, 479.6 (100) [M – allyl]<sup>+</sup>, 311.3 (100) [M – 1 dendron]<sup>+</sup>. MS (FAB Na<sup>+</sup>): *m/z* = 543.6 (15) [M + Na]<sup>+</sup>, 311.3 (100).

**3,4,5-Tris{3-(triallylsilyl)propyloxy}styrene (G1-tris)** was prepared by using the same procedure as for compound **G1-bis**. The treatment of 4.1 g of the benzaldehyde derivative **2b** (5.6 mmol) with 0.7 g of potassium *tert*-butoxide (6.3 mmol) and 2.27 g of

methyltriphenylphosphonium bromide (6.35 mmol) in THF solution afforded 3.3 g (80%) of a colorless oil which was stored at –30 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.61 (1H, dd, <sup>3</sup>*J*<sub>trans</sub> = 17.5 Hz and <sup>3</sup>*J*<sub>cis</sub> = 11.0 Hz, ArCH=), 6.60 (2H, s, ArH), 5.80 (9H, m, CH<sub>2</sub>CH=), 5.65 (1H, dd, <sup>3</sup>*J*<sub>trans</sub> = 17.5 Hz and <sup>2</sup>*J*<sub>gem</sub> = 0.6 Hz, ArCH=CH<sub>2</sub>), 5.20 (1H, dd, <sup>3</sup>*J*<sub>cis</sub> = 11.0 Hz and <sup>2</sup>*J*<sub>gem</sub> = 0.6 Hz, ArCH=CH<sub>2</sub>), 4.90 (18H, m, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.95 and 3.93 (6H, 2t, CH<sub>2</sub>O), 1.83 (6H, m, CH<sub>2</sub>CH<sub>2</sub>O), 1.63 (18H, m, SiCH<sub>2</sub>CH=), 0.72 (4H, m, SiCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.9 (C<sub>3</sub>Ar), 138.1 (C<sub>1</sub>Ar), 136.8 (ArCH=CH<sub>2</sub>), 134.2 and 134.1 (CH<sub>2</sub>CH=CH<sub>2</sub>), 132.9 (C<sub>4</sub>Ar), 113.7 (CH<sub>2</sub>CH=CH<sub>2</sub>), 112.8 (ArCH=CH<sub>2</sub>), 105.0 (C<sub>2</sub>Ar), 75.9 and 71.6 (CH<sub>2</sub>O), 24.2 and 23.5 (CH<sub>2</sub>CH<sub>2</sub>O), 19.5 and 7.5 (CH<sub>2</sub>Si). Anal. Calcd (found) for C<sub>44</sub>H<sub>68</sub>O<sub>3</sub>Si<sub>3</sub>: C, 72.48 (72.17); H, 9.41 (9.47); Si, 11.52 (11.54). MS (FAB Na<sup>+</sup>): *m/z* = 750.2 (15) [M – H + Na]<sup>+</sup>, 686.2 (30) [M – allyl]<sup>+</sup>, 368.2 (100).

**Anionic Polymerization Procedure.** The polymerizations were carried out into a flame-dried reactor under an argon atmosphere. The desired charge of monomer in THF or benzene solution (2 mL) was added to the solution of initiator in appropriate solvent under vigorous shaking. The final monomer concentration was *c* = 0.20 mol L<sup>–1</sup> for **G1-bis** and *c* = 0.15 mol L<sup>–1</sup> for **G1-tris**. The polymerization was run at controlled temperature and reaction time and then terminated by addition of a few drops of degassed methanol. After concentration, the crude polymerization mixture was passed through a column filled with SEC gel (SX1 Bio-Beads gel; eluent: THF) under gravity flow to separate the polymer from the possible unreacted monomer. The polymer fraction was concentrated and dried under vacuum at 60 °C to offer the polymer as a transparent viscous oil. The block copolymerization was performed in a classical way. The first-stage polymerization of **G1-bis** was initiated with *sec*-BuLi in THF at –78 °C. After an appropriate reaction time, a small portion of the living **poly(G1-bis)** solution was taken up for analysis. Immediately after, styrene was added with vigorous stirring, and the mixture was stirred for an additional 30 min time under the same conditions. After quenching with MeOH, the copolymer was recovered by two precipitations in MeOH from THF solution and then dried under vacuum for 2 days at 60 °C.

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