Synthesis and Characterization of Linear, Hyperbranched, and Dendrimer-Like Polymers Constituted of the Same Repeating Unit

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Abstract: The synthesis of a linear polymer that includes both P=N and P=S double bonds, and P−O and P−C single bonds is reported by using two different paths that involve deprotection reactions and the Staudinger reaction. The preparation of hyperbranched polymers made up of $OC_6H_4P(Ph)_2$=N−P=S repeating units is also described. Five generations of dendrimers originating from the same building blocks were prepared. The characterisation of all these phosphorus-based macromolecular architectures (solution behaviour, size exclusion chromatography, intrinsic viscosity, thermal behaviour) revealed marked differences in their respective behaviour.

Keywords: degree of branching · dendrimers · hyperbranched polymers · phosphorus · polymers

Introduction

It is well documented that regular dendrimers and also hyperbranched polymers exhibit very unique properties compared with those of their linear analogues.[1] Dendritic macromolecules are uniformly branched three-dimensional structures assembled through a regular succession of monomer and branching units. Other features of dendritic polymers include their inability to induce any chain entanglement in their structure, their uniformity in size and their number of terminal functional groups that increases with the number of generations. On the other hand, dendritic structures can mostly only be produced with a poor final yield, and their synthetic step-by-step methodologies—either the divergent approach[2] or the convergent method[3]—are generally not well suited to the production of large quantities of these polymers. In contrast, hyperbranched polymers[4–6] can be prepared at low cost and on a large scale by using a trifunctional AB_2 monomer in a one-pot synthesis, in which A and B are antagonistic functional groups.

The synthesis of hyperbranched polymers was attempted long after Flory speculated that AB_x monomers should undergo self-condensation and afford soluble and highly branched materials with a three-dimensional globular shape for a sufficiently high degree of polymerization.[7] No real example could be proposed to illustrate Flory's prediction until the 90's when all of a sudden, a noticeable number of studies reported the step-growth polymerisation of AB_2 type monomers and the synthesis of hyperbranched polymers based on polyphenylenes, aliphatic and aromatic polyesters, polyethers and polyether-ketones, polyamides and polyamines, polyurethanes and polyureas, polysilanes and polysiloxanes, polyimides and polyetherimides, vinyl polymers and so forth. Excellent review articles that highlight the essential features of hyperbranched polymers are now available.[1b, c, 4, 5]

In contrast to regular dendrimers, hyperbranched macromolecules obtained by the polycondensation of AB_2-type monomers are irregular structures that are not flawless, with, in particular, numerous unreacted B sites carried by linear units that coexist with dendritic and terminal units. Even though their characteristic properties mainly depend on their "degree of branching" (also named the "branching factor"), it is established that these properties resemble those found for regular dendrimers:[1, 4, 5] high solubility, low viscosity, absence of chain entanglement and thermal stability.

Besides the "conventional approach" that involves the polycondensation of AB_2-type monomers, recent progress has been made towards better control of both the branching pattern and the molar mass distribution in hyperbranched polymers.[5] These new developments include the "core dilution/slow monomer addition" technique, proton transfer polymerisation, as well as the ring opening multi-branching polymerisation (ROMBP) or the self-condensing vinyl polymerisation (SCVP) of latent AB_2-type monomers.[5]

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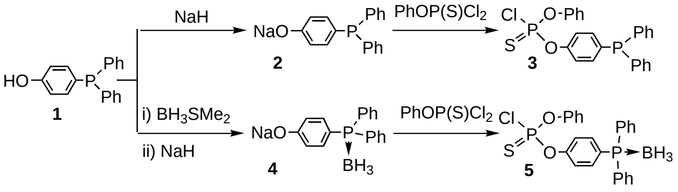
On the other hand, a comparative study of the properties exhibited by dendrimers, hyperbranched polymers and linear macromolecules of same repeating unit can provide an acute insight into how their molecular features (topology of their building block, polydispersity) affect the structure–property relationship. A few reports have addressed this issue, but they mainly focused on organic polymers.[8–12] No similar studies have been undertaken on phosphorus-containing polymers in spite of the enormous variety of reactions that can be performed starting from phosphorus and the well-known properties of some useful phosphorus-based polymers.[13, 14] Indeed, polyphosphazenes have properties seldom found in organic polymers (flexibility, flame resistance, hydrolytic and chemical stability, etc.) and therefore serve in many applications in different domains of science and technology.[14] Furthermore, synthetic methods leading to phosphorus-containing dendrimers have been described in the literature,[13] and specific applications for this class of macromolecules are now envisaged.[15–18] In contrast, no attempt has yet been made to prepare phosphorus-containing hyperbranched homologues so that their properties could be compared with those exhibited by dendrimers of the same building block.

We report here our first efforts in this direction, that is, the synthesis and the characterisation of some physical properties of a new series of linear, hyperbranched and dendritic polymers, all of which are developed from the same starting phosphorus reagent and made up exclusively of $OC_6H_4P(Ph)_2{=}N{-}P(S)$ units.

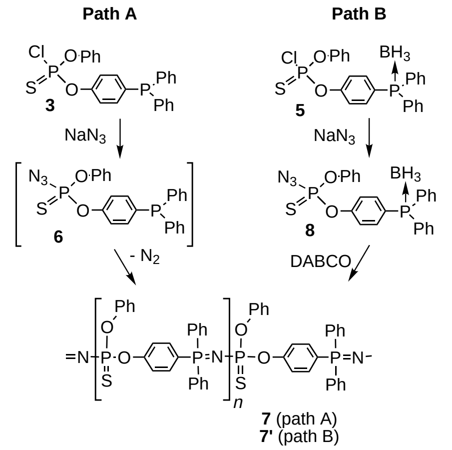
Results and discussion

Synthesis

Synthesis of the linear polymers **7** *and* **7′**: The key reagent chosen for the synthesis of linear polymers **7** and **7′**, which include both P=N and P=S double bonds, as well as P–O and P–C single bonds regularly distributed along the polymer backbone, was phenoxy-(4-diphenylphosphino)phenoxychlorophosphane sulfide (**3**) or its corresponding boron adduct **5**, prepared as shown in Scheme 1. Compound **3** was obtained in 80 % yield after work up from reaction of the sodium salt of the 4-hydroxyphenyldiphenyl phosphane (**2**)[19] (1 equiv) with phenoxydichlorophosphane sulfide (1 equiv) in THF at −95 °C. Compound **3** exhibits characteristic signals in ^{31}P NMR spectroscopy [$\delta = -6.2$ (s, PPh_2), 58.4 (s, P–Cl)]. An analogous reaction conducted with **4** affords the phosphane complex **5** in 85 % yield [^{31}P: $\delta = 20.5$ (br s, $Ph_3P \rightarrow BH_3$), 57.7 (s, P–Cl)] Two strategies can be followed for the preparation of linear polymers. The first strategy (path A, Scheme 2) involves the treatment of **3** with sodium azide leading to the transient intermediate **6**, which undergoes an intermolecular Staudinger reaction with elimination of nitrogen and formation of polymer **7**. The second strategy (path B, Scheme 2) consists of the reaction of **5** with sodium azide leading to the formation of azide **8**, the last step being the phosphane decomplexation by means of a base such as 1,4-diazabicyclo[2.2.2]octane (DABCO) which affords the transient species **6**, then the polymer **7′**.



Scheme 1.



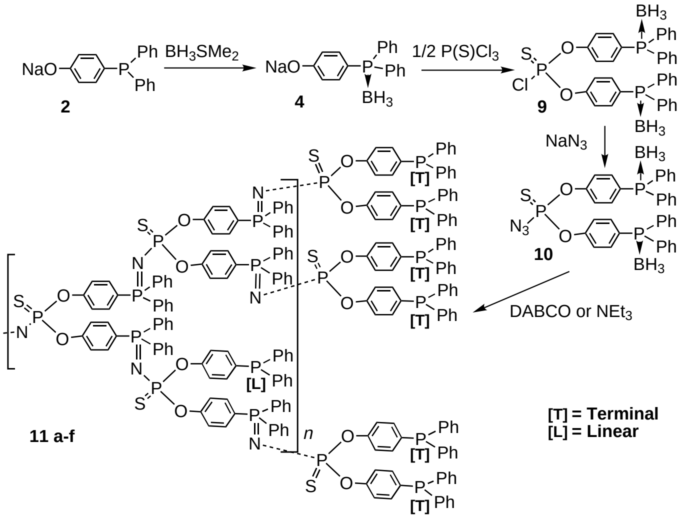
Scheme 2.

All these transformations can be monitored by ^{31}P NMR spectroscopy. As an example, the substitution reaction allowing the preparation of **8** from **5** is characterised in ^{31}P NMR spectroscopy by a slight variation of the chemical shift which can be attributed to the XP(S) unit (**5** X = Cl, $\delta = 57.7$; **8** X = N_3, $\delta = 58.2$). Moreover, the intermolecular Staudinger reaction initiated by adding DABCO to **8** can also be monitored by ^{31}P NMR spectroscopy: The signal at $\delta = 58.2$ disappears in favour of two doublets at $\delta = 13.2$ (P=N) and 50.6 (P=S) with $^2J(P,P) = 29.1$ Hz, corresponding to the formation of the P=N–P=S linkages.

Although the polycondensates **7** and **7′** formed from this AB monomer contain the same repeating units as those present in the hyperbranched (**11**) and dendritic (**13**) polymers described in the next section, they cannot be viewed as true analogues of **11** and **13**, because unlike these last two they do not carry more than one free B function. Since these unreacted B functions are known to dramatically influence the physical properties of the resulting materials, several authors have prepared linear polycondensates from AB_2 monomers,[9, 10] for instance, after protecting one of the two B functions.[9] They could then prepare linear, hyperbranched and/or dendritic polymers that carry approximately the same number of reacted and unreacted B functions. With the synthesis of **7** and **7′**, our purpose was not to obtain true analogues of **11** and **13**, but rather to optimise the Staudinger reaction.

Synthesis of hyperbranched polymers **11**: These polymers were synthesised by the one-pot condensation reactions of a newly designed AB_2 monomer that is synthesised as follows. Treatment of the sodium salt of the phosphane boron adduct **4**

(1 equiv) with P(S)Cl$_3$ (0.5 equiv) affords the compound **9**. Then addition of sodium azide to **9** in acetone leads to the targeted AB$_2$-type monomer **10** in 70% yield. Deprotection of the two phosphane units of **10** is carried out by using a tertiary amine, a process that readily triggers condensation reactions in many directions, leading to the formation of hyperbranched polymers **11** (Scheme 3, Table 1).



Scheme 3.

In order to vary the molecular features of this series of polymers **11**, the nature of the amine used to deprotect the phosphane units (either DABCO or triethylamine was employed) and the nature of the solvent (THF or toluene) were varied. The temperature, the initial concentration of monomer **10** to be polymerised and the reaction time were three parameters that were also investigated with a view of varying both the molar masses (see section solution behaviour) and the degree of branching (DB, see later discussion).

Here also ^{31}P NMR serves as a tool to monitor the course of the polymerisation. Indeed, the disappearance of both singlets corresponding to the starting reagent **10** in conjunction with the appearance of doublets of doublets due to the formation of P=N–P=S linkages and of singlets due to the linear (L) and terminal (T) phosphane groups is observed.

*Synthesis of dendrimers **13-[G$_1$]** to **13-[G$_5$]***: The synthetic strategy for the dendrimers **13-[G$_1$]** to **13-[G$_5$]** and **13-[G'$_1$]** to **13-[G'$_4$]** involves the reiteration of a sequence of two reactions: i) a Staudinger type reaction between species that have free phosphane groups and the azide **10**, the latter bearing complexed phosphane groups and ii) the deprotection of the resulting phosphane-boron adducts with a base like DABCO. Such a methodology was applied to the preparation of dendrimers up to the fifth generation (Scheme 4).

The starting reagent is the trisphosphane **12** which can be easily prepared by treating **2** (1 equiv) with P(S)Cl$_3$ (1/3 equiv); then compound **12** is treated with **10** giving rise to the first-generation dendrimer **13-[G$_1$]**, with evolution of nitrogen. As in the case of the synthesis of linear and hyperbranched polymers, formation of P=N–P=S units can be readily detected by ^{31}P NMR spectroscopy (two doublets at $\delta = 13.7$ (P=N) and 50.3 (P=S) with ^2J(P,P) = 30 Hz). The next sequence of two reactions that gives rise to the second-generation dendrimers **13-[G$_2$]**, through the decomplexation of terminal C$_6$H$_4$–PPh$_2$(BH$_3$) groups to afford **13-[G'$_1$]** and the addition of the azide **10** (6 equiv) to the six free phosphane groups of **13-[G'$_1$]** can be also rigorously followed by ^{31}P NMR spectroscopy (see Table 2). Several washings with a degassed mixture of toluene and diethyl ether (1:5) are necessary in order to eliminate traces of the [DABCO, BH$_3$] complex. The repetition of this sequence of reactions successively affords the third, fourth and fifth generations. ^{31}P NMR data of all the generations are given in Table 2.

Characterisation of dendrimers, and hyperbranched and linear polymers based on [OC$_6$H$_4$ P(Ph)$_2$=N–P(S)] units

Solution behaviour: Phosphorus-based hyperbranched and dendritic samples could be easily distinguished from the linear polymers upon dissolving them in common organic solvents (THF, acetone and dichloromethane). The branched architectures were found to be readily soluble in these media, whereas polymers of linear structure hardly gave homogenous solutions in similar conditions of temperature and concentration. This significantly different solubility behaviour of branched systems compared with that of linear polymers mirrors the topological constraints imposed by the multiple

Table 1. Synthesis[a] and solution properties of phosphorus-based hyperbranched polymers **11**.

	Polymerisation conditions				Characterisation in solution of polymers **11**			
	DABCO[b] [equiv]	T [°C]	time [h]	M_w[c] [g mol^{-1}]	M_w[d] [g mol^{-1}]	PDI[d]	[η][e] [dL g^{-1}]	DB[f]
11a	2.0	80	24	1100[g]	10700	1.16	0.041	0.83
11b	2.0	25	24	850	3600	1.19	0.032	0.84
11c	2.2	25	24	1100	36700	8.1	0.036	0.85
11d	2.2	70	12	1200	8600	2.02	0.041	0.84
11e	3.4	25	24	900	13600	2.51	0.030	0.84
11f	21.2	25	240	1800[h]	42400	1.5	0.053	0.83

[a] The solvent used was toluene except for the synthesis of **11f**, for which THF was employed. [b] Number of equivalents of amine used to deprotect the phosphane units, relative to the molar amount of monomer **10**. Et$_3$N was employed to synthesise **11f**. [c] Determined by standard SEC in THF (calibration with polystyrene standards). [d] Determined by MALLS/SEC in THF (see text); (dn/dc) = 0.253; PDI = M_w/M_n. [e] Intrinsic viscosity measured in CH$_2$Cl$_2$. [f] Degree of branching determined by ^{31}P NMR spectroscopy (see text). [g] $M_w = 1800$ g mol^{-1} by standard SEC in CHCl$_3$ (calibration with PS standards). [h] $M_w = 2600$ g mol^{-1} by standard SEC in CHCl$_3$ (calibration with PS standards).

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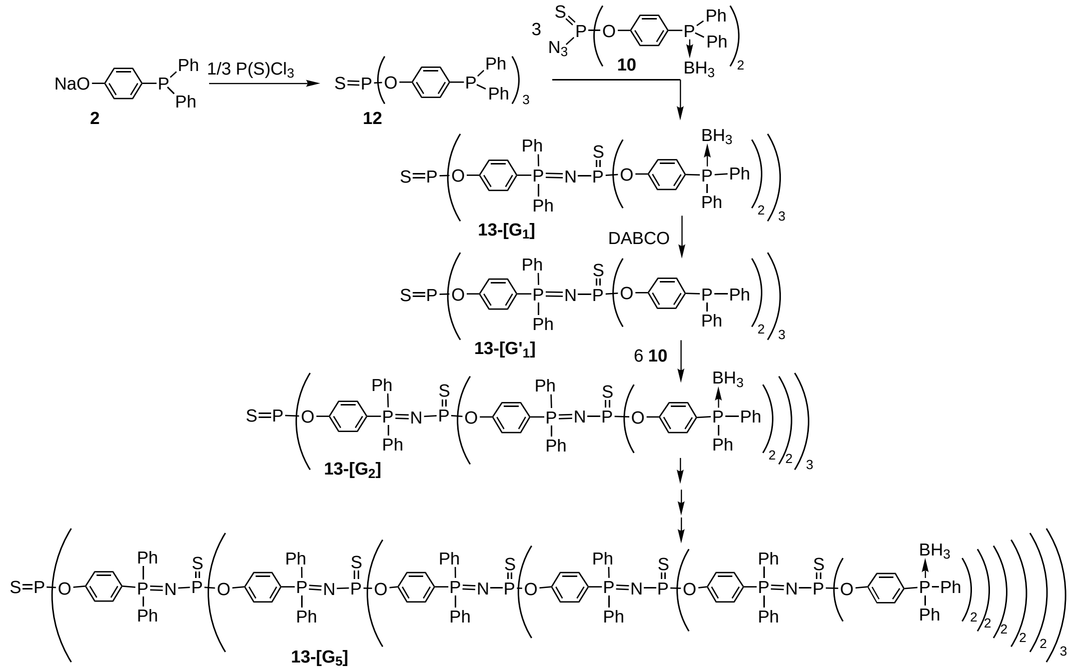


Scheme 4.

Table 2. ^{31}P NMR chemical shifts of dendrimers **13-[G$_1$]** to **13-[G$_5$]** and **13-[G′$_1$]** to **13-[G′$_4$]**.

	δ^{31}P in CDCl$_3$ (^2J(P,P) [Hz])											
	P$_0$	P$_1$	P$_2$	P$_3$	P$_4$	P$_5$	P$_6$	P$_7$	P$_8$	P$_9$	P$_{10}$	P$_{11}$
13-[G$_1$]	49.6	13.7 (30.0)	50.3 (30.0)	20.0								
13-[G′$_1$]	49.6	12.8 (31.4)	51.0 (31.4)	− 6.4								
13-[G$_2$]	49.5	14.2 (30.0)	49.9 (30.0)	14.0 (29.2)	50.0 (29.2)	19.9						
13-[G′$_2$]	49.5	14.1 (30.1)	50.0 (30.1)	13.2 (29.6)	50.8 (29.6)	− 6.3						
13-[G$_3$]	49.4	14.1 (30.1)	49.8 (30.1)	14.4 (29.2)	49.7 (29.2)	14.0 (29.2)	50.0 (29.2)	19.9				
13-[G′$_3$]	49.5	14.0 (30.5)	49.8 (30.5)	14.4 (29.2)	49.7 (29.2)	13.2 (29.5)	50.8 (29.5)	− 6.4				
13-[G$_4$]	49.5	14.5 (30.0)	49.7 (30.0)	14.5 (30.0)	49.7 (30.0)	14.5 (30.0)	49.7 (30.0)	14.1 (30.1)	50.0 (30.1)	19.7		
13-[G′$_4$]	49.5	14.4 (30.0)	49.6 (30.0)	14.4 (28.0)	49.6 (28.0)	14.4 (28.0)	49.6 (30.0)	13.2 (29.5)	50.7 (29.5)	− 6.5		
13-[G$_5$]	49.5	14.4 (31.0)	49.7 (31.0)	14.4 (31.0)	49.7 (31.0)	14.4 (31.0)	49.7 (31.0)	14.4 (31.0)	49.7 (31.0)	14.0 (29.0)	50.0 (29.0)	19.8

branching points in branched structures.[1, 4] When such systems are put in contact with a solvent, the solvent can easily provide the energy necessary to disrupt the interactions existing between molecules and make such structures soluble; this is not the case for linear chains.

Molar masses and molar masses distribution: After the branched materials were checked on their higher solubility in THF in comparison with the linear materials, they were characterised by size exclusion chromatography (SEC) by using apparatus equipped with a multi-angle laser-light-scattering (MALLS) detector, after the increment of their refractometric index (dn/dc) was first measured. By this means, one can not only get access to the molar mass distribution of each sample, but also determine their true molar mass. For comparison purposes, samples were also analysed by using a "standard" SEC equipped with both refractometric and UV detectors, though this characterisation was not done systematically.

The solution properties pertaining to all the compounds, linear, dendritic and hyperbranched, are summarised in Tables 3, 4 and 1, respectively.

As shown in Table 4, the experimental values of M_w determined for dendrimers agree with the expected values,

Table 3. Solution properties of phosphorus-based linear polymers **7**.

	M_w[a] [g mol^{-1}]	dn/dc [mL g^{-1}]	M_w[b] [g mol^{-1}]	PDI[b]	$[n]$ [dL g^{-1}]
7	790	0.213	6730	1.21	0.043
7′	850	0.213	14 800	1.32	0.046

[a] Determined by standard SEC in THF (calibration with polystyrene standards). [b] Determined by MALLS/SEC in THF (see text); PDI = M_w/M_n.

Table 4. Solution properties of phosphorus-based dendrimers.

	dn/dc [mL g^{-1}]	M_w[a] [g mol^{-1}]	PDI[a]	$[\eta]$ [dL g^{-1}]
13-[G$_1$]	0.228	3200	1.015	0.06
13-[G$_2$]	0.234	6900	1.008	0.12
13-[G$_3$]	0.222	15 100	1.008	0.13
13-[G$_4$]	0.234	29 900	1.012	0.04
13-[G$_5$]	0.251	60 200	1.029	0.03
13-[G′$_1$]	0.216	2850	1.086	0.02
13-[G′$_2$]	0.242	7000	1.036	0.11
13-[G′$_3$]	0.235	13 000	1.017	0.12
13-[G′$_4$]	0.235	22 000	1.014	0.04

[a] Determined by MALLS/SEC in THF (see text); PDI = M_w/M_n.

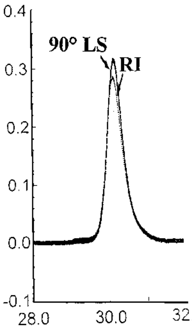


Figure 1. MALLS/SEC trace (refractometric = RI detector and light scattering = LS detector) of **13-[G$_3$]**.

confirming that the Staudinger condensation of phosphanes with azides is clean and free of any side reaction. The MALLS/SEC traces of these samples were found to be monomodal, symmetrical and free of any contaminant, mirroring a narrow distribution of molar masses (Figure 1).

In contrast, the MALLS/SEC traces of the hyperbranched polymers were typical of those exhibited by samples with a broad distribution of molar masses (Figure 2). The two signals arising from the light scattering (LS) and the refractometric detectors were indeed dissymmetrical, whereas the LS signal emphasised the presence of high molar mass species, the other revealed the existence of oligomers.

On the other hand, Table 1 shows that the choice of experimental conditions has a dramatic effect on both the molar mass and the polydispersity index of the hyperbranched materials obtained.

It is worth pointing out that the M_w values of the hyperbranched polymers, as given by MALLS/SEC, drastically differ from those obtained by standard SEC. The absolute molar masses of hyperbranched polymers are, indeed, significantly higher than the apparent values derived from standard SEC whose columns are calibrated with linear polystyrene standards. This difference is explained by the densely branched structures of polymers **11** so that their hydrodynamic volume is lower than that of a linear homologue of same molar mass. Another indication that standard SEC is not suitable for the determination of molar masses of branched polymers such as **11** was the fact that the change of the mobile phase (THF in place of chloroform) provided a wide variation in the values obtained. Thus, the elution profile is found to be sensitive to the nature of the mobile phase; this is likely to be due to a difference in the hydrodynamic volume of the polymers in the two solvents tried.

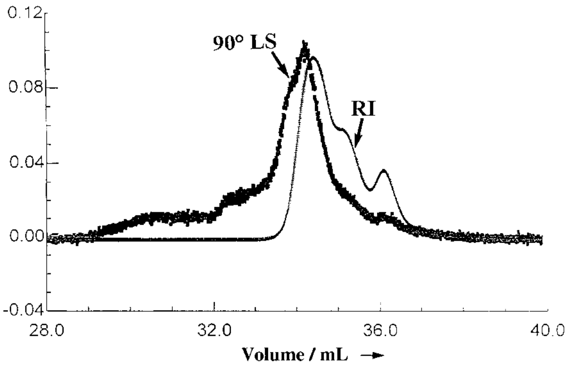


Figure 2. MALLS/SEC trace (refractometric = RI detector and light scattering = LS detector) of hyperbranched phosphorus-based polymer **11**.

It should be noted that the high polydispersity index obtained for polymer **11c** (PDI = 8.1, as determined by MALLS/SEC) is presumably due to the presence of low molar mass oligomers that were not removed after the recovery of this compound.

Intrinsic viscosity: The dependence of the intrinsic viscosity $[\eta]$ is generally described by the empirical Kuhn–Mark–Houwink–Sakurada (KMHS) equation: $[\eta] = KM^{\alpha}$, in which the constants K and α are specific to the system investigated. For instance, α depends on the shape of the macromolecules and on its segment distribution; for macromolecules with a sphere shape, $\alpha = 0$, whereas for coiling chains $\alpha = ½$ or $\alpha = 0.754$ whether these chains are in a θ (θ conditions correspond to an equal affinity of monomer repeating units for solvent and other repeating units) or in a good solvent. Being expressed in mL g^{-1}, $[\eta]$ cannot be viewed as a measure of the viscosity of a macromolecule, but is rather used as an indicator of its hydrodynamic volume. By using the Einstein approach, the viscosity can also be expressed as $[\eta] = \phi(s^3/M)$, in which s and ϕ are the radius of gyration and the so-called Flory–Fox constant, respectively. This equation can also be written in a more simple way as the ratio of the hydrodynamic volume (V_h) to the molar mass (M) of the macromolecules.

In the case of dendrimers,[1] their molar masses are expected to increase exponentially with the number of generations (g+1) upon following a ($2^{g+1} - 1$) progression, whereas their hydrodynamic volumes are supposed to expand in $(g+1)^3$. The function $(g+1)^3/(2^{g+1} - 1)$ and, accordingly, $[\eta]$ should pass through a maximum between the third and fourth generations. The bell-shaped curve experimentally exhibited by $[\eta]$ in the case of dendrimers was first observed by Fréchet et al.[20] and exactly the same behaviour was observed with our phosphorus-based dendrimers (Figure 3). As for hyperbranched polymers, their $[\eta]$ values are expected to increase very moderately with the molar mass; this is known to be the case when the exponent α taking very low values in the KMHS equation. This behaviour is consistent with the fact

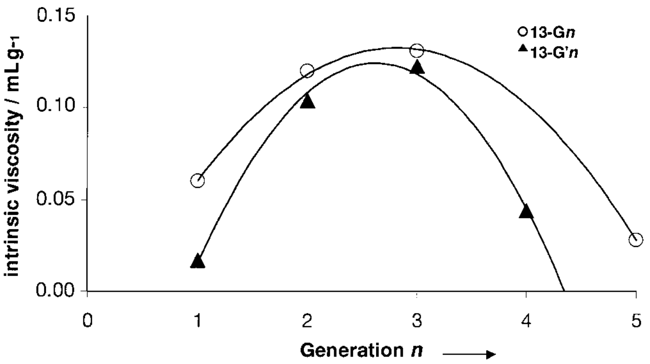


Figure 3. Intrinsic viscosity of phosphorus-based dendrimers.

that hyperbranched polymers are densely packed macromolecules that behave like moderately solvated spheres.[1d, 21]

As the series of hyperbranched polymers exhibit significantly different molar mass distribution, it was not attempted to plot the variation of their $[\eta]$ as a function of their mass average molar mass. However, the comparison of the intrinsic viscosity of dendrimers and hyperbranched polymers of approximately the same molar mass shows that the hydrodynamic volume of the latter is lower than that of their dendritic homologues, in agreement with Fréchet's findings.[1d, 20] In addition, $[\eta]$ remains almost constant for hyperbranched polymers, which is likely related to their rather low molar masses (Table 1).

*Degree of branching of hyperbranched polymers **11***: Apart from their broad molar mass distribution as compared with that exhibited by regular dendrimers, the degree of branching (DB) is another characteristic feature of hyperbranched polymers derived from the polycondensation of AB_2-type monomers.[4] To determine the DB of compounds **11**, we used the definition proposed by Fréchet and Hawker [Eq. (1)]:[22]

$$\mathrm{DB} = \frac{[\mathrm{D}] + [\mathrm{T}]}{[\mathrm{D}] + [\mathrm{L}] + [\mathrm{T}]} \tag{1}$$

in which [D], [L] and [T] are the concentrations of dendritic, linear and terminal units, respectively. Since the number of dendritic units is very close to that of terminal units, the above formula can be rewritten[22] as Equation (2).

$$\mathrm{DB} = \frac{2[\mathrm{T}]}{2[\mathrm{T}] + [\mathrm{L}]} \tag{2}$$

It has been predicted[6] that DB should reach a theoretical value of 0.5 for the "conventional" step-growth polymerization of AB_2-type monomers provided the reaction occurs randomly, in absence of any side event (like intramolecular cyclisation), and if the reactivity of the functional B groups is independent of molar mass and conversion.

However, several teams have proposed novel methods to obtain branched macromolecules with a limited number of linear units with a view to generating hyperbranched systems whose behaviour would resemble that exhibited by regular dendrimers. For instance, some authors "manipulated" AB_n ($n = 2$, 3, 4 and 6) monomers,[22, 23] whereas Hobson and Feast suggested a way to activate the second B group after the first one had reacted.[24] Another strategy consists in further converting the linear units into dendritic units by post-chemical modification.[25] More recently, Maier et al. described an elegant approach to hyperbranched polymers with a DB of 100% (without any linear unit) from an AB_2 monomer, A being a maleimide group and B an azine function.[26] When an A group reacts with one B group, an unstable intermediate is reversibly formed that favours the subsequent reaction of the second B group, irreversibly. In other words, either both B groups of a repeating unit react successively or neither B group reacts at all.

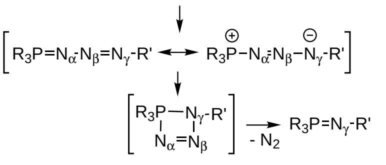
On the other hand, the calculation of DB generally requires the use of model compounds that possess similar structures to that of linear (L), dendritic (D) and terminal (T) units present in the corresponding hyperbranched polymer.[4, 22–26] Upon characterisation by NMR spectroscopy, the chemical shifts due to D, L and T units of these model compounds can be identified and their intensity evaluated. In our case, the regular dendrimers described above were used to assign the peaks that were detected in the ^{31}P NMR spectra of polymers **11**, particularly those corresponding to terminal units. The DB of polymers **11** could be determined by comparison of the intensities of the peaks assigned to the terminal units at $\delta = -3.1$ and to the linear units at $\delta = -2.9$. DB was derived from Equation (3) since measurements were done on part B of the AB_2 system with the intensity of the signal of a terminal unit B being twice the intensity of the signal of a linear unit B (see Scheme 3).

$$\mathrm{DB} = \frac{I_{[\mathrm{T}]}}{I_{[\mathrm{T}]} + I_{[\mathrm{L}]}} \tag{3}$$

It should be stressed that the spectroscopic data of all the hyperbranched polymers synthesised were essentially the same irrespective of the nature of the amine tried and the temperature of the reaction. Therefore, the results obtained show that DB is almost the same (0.83–0.85), irrespective of the experimental conditions employed (Table 1). Of particular interest is the fact that these values are higher than those generally reported in the literature (DB = 0.5–0.6). Our results compare well with those obtained by others[24–26] who determine DB values in the range of 0.8–0.9.

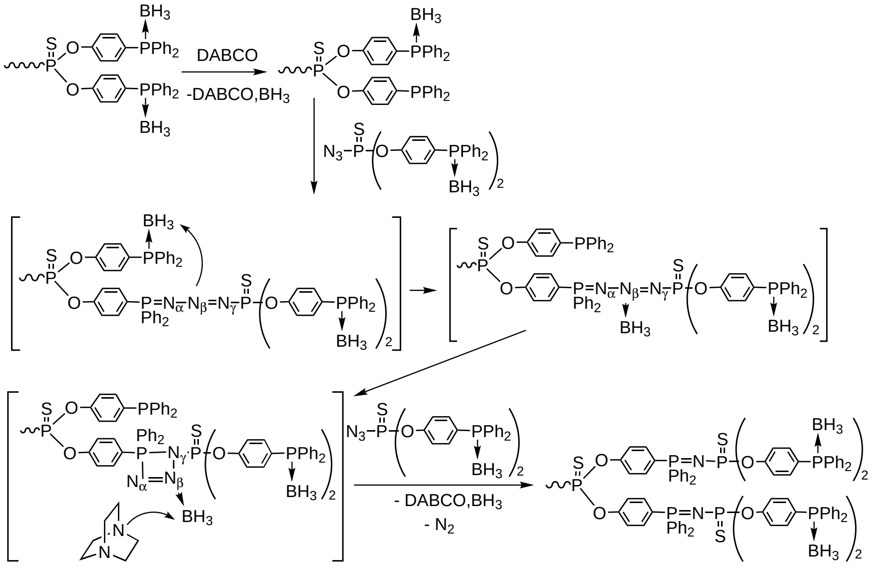
To account for the enhanced values obtained in our case, one can assume that the formation of a first P=N linkage in an AB_2 unit can intramolecularly activate the second B group and favour its reaction.

Indeed, such a reaction leading to a P=N double bond proceeds by nucleophilic attack of the phosphane on the terminal α-nitrogen atom of the azide to afford a linear, unstable phosphazide, which then dissociates to the iminophosphorane form with elimination of dinitrogen (Scheme 5).



Scheme 5.

A few phosphazide complexes were characterised, with complexation taking place through α-, β- or γ-nitrogen atoms.[27] One can assume that an intramolecular complexation with BH_3 of one of the three nitrogen atoms of the phosphazide unit, probably the less hindered nitrogen atom N_b, takes place with decomplexation and therefore activation of the neighbouring phosphino group (Scheme 6).



Scheme 6.

Thermal behaviour: Owing to their globular shape and their highly branched structures, dendrimers and hyperbranched polymers are expected to be amorphous, although some exceptions are reported such as the hyperbranched polyethers of Percec which exhibit liquid crystalline properties.[28]

In analogy with their solution properties, the thermal properties of dendrimers and hyperbranched structures and, namely, their glass transition temperatures (T_g's) also depend on the nature of their end groups, as well as factors that are specific to the inner part such as the backbone rigidity, the degree of branching, etc. Insofar as the terminal end groups do not exhibit peculiar features (polarity), Stutz suggested, in his study of the parameters influencing T_g in dendritic polymers,[29] that the T_g should be essentially governed by the chemical structure of the repeating units more than any other factors. Therefore, only little differences could be observed between linear and highly branched structures.

Differential scanning calorimetry (DSC) was used to determine the T_g's of our phosphorus-based polymers. The results obtained confirmed that these materials are all amorphous. As expected, significant differences were observed between dendrimers of the same generation depending upon the nature of their terminal groups (Table 5). A higher T_g was observed for the series of dendrimers fitted with BH_3 end groups (ranging from 120 to 150 °C) relative to that of their homologues carrying phosphane functionalities (T_g ranged from 69 to 87 °C). Steric crowding of the external layer may be the reason for the higher T_g in the case of dendrimers complexed with BH_3. T_g's were also found to slightly increase with the generation number; this is certainly due to the increase in the molar mass of the object considered. As for the hyperbranched homologues, they exhibited T_g values between 109 and 114 °C. The slight differences in T_g's between regular dendrimers and hyperbranched polymers can be ascribed to the presence of very low molar mass compounds in hyperbranched polymers (plasticiser effect), the latter exhibiting broad molar mass distribution (see Table 1).

As for the case of linear compounds described above, their T_g values are reported for indicative purpose. Considering that these polymers are not the true linear analogues of the dendrimers **13** and hyperbranched polymers **11**, there is no reason for them to exhibit the same T_g as that measured for the phosphorous-based branched compounds.

Therefore, as expected, the T_g behaviour of these phosphorus-containing polymers is independent of their overall structure and shape, but rather depends on the chemical nature of their repeating units and end groups.

The thermal stability of all these phosphorus-containing polymers was also investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (Table 5). After a loss of 2–7% due to the evolution of residual volatiles at 150–200 °C (solvents), both kinds of dendrimers were found to be thermally stable up to 400 °C, irrespective of the generation considered. On the other hand, only minor differences were

Table 5. Glass transition temperature (T_g), and TGA data of phosphorus-based polymers.

	M_w[a] [g mol^{-1}]	PDI[a]	T_g[b] [°C]	T_{dec}[c] [°C]
13-[G$_1$]	3200	1.015	119.7	444
13-[G$_2$]	6900	1.008	138.8	458
13-[G$_3$]	15100	1.008	144.4	470
13-[G$_4$]	29900	1.012	146.3	463
13-[G$_5$]	60200	1.029	148.2	438
13-[G'$_1$]	2850	1.086	69.2	422
13-[G'$_2$]	7000	1.036	77.8	465
13-[G'$_3$]	13000	1.017	83.5	472
13-[G'$_4$]	22000	1.014	87.4	476
7	6730	1.21	109	419
7'	14800	1.32	101	355
11a	42500	1.47	114	427
11d	8600	2.02	110	453
11f	38000	1.38	109	476

[a] Determined by MALLS/SEC in THF (see text); (dn/dc) = 0.253. [b] Glass transition temperature determined by DSC. [c] Temperature of decomposition determined by TGA from the point of intersection between the initial base line and the slopping portion at the beginning of the weight loss of the polymer.

observed between the two series of dendrimers, those complexed with BH_3 and those incorporating free terminal phosphane units. Likewise, hyperbranched polymers exhibited similar stabilities to those of their dendritic homologues.

These results on the thermal behaviour of phosphorus-containing materials are fully consistent with the outcome of previous investigations.[4, 29]

Conclusion

A series of polymers constituted of $[OC_6H_4P(Ph)_2{=}N{-}P(S)]$ repeating units have been covalently assembled in dendritic, hyperbranched, and linear structures. By using AB-type monomers for the preparation of linear chains, AB_2-type reagents for hyperbranched polymers, and appropriate building blocks in reiterated reactions for dendrimers, samples of different topology could be obtained through the Staudinger reaction of phosphane groups with azido functions. In the case of the hyperbranched structures, a higher degree of branching (DB = 0.8–0.9) than that expected for AB_2 repeating units (DB = 0.5–0.6) could be obtained, presumably due to the activation of the second B group during the reaction of the first one.

The characterisation of these phosphorus-based macromolecular structures in solution revealed marked differences in their respective behaviour. A bell-shaped curve could be established for the $[\eta]$ behaviour of the dendrimers, whereas the $[\eta]$ of hyperbranched polymers was found to vary moderately with the molar mass. They were shown to depend on both the chemical nature of the repeating units and the terminal functions, as well as the T_g's of these branched structures.

Experimental Section

General: All manipulations were carried out with standard high vacuum and dry-argon techniques. ^1H, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AC200, AC250, DPX300 or AMX400 spectrometers. References for NMR chemical shifts are $SiMe_4$ for ^1H and ^{13}C NMR and 85% H_3PO_4 for ^{31}P NMR. The numbering used for NMR assignments is depicted in Figure 4. Compound **1** was prepared according to the literature.[19]

Measurements: Thermogravimetric analyses were carried out by using a Perkin–Elmer TGA7 thermogravimetric analyser. Glass transition temperatures were determined by differential scanning calorimetry with a Perkin–Elmer DSC7 apparatus. For both TGA and DSC analyses, heating rates were 10 K min^{-1}. The T_g was taken as the midpoint of the inflection tangent, on the second or subsequent heating scan after the sample was quickly (50 K min^{-1}) quenched below its T_g following the first heating. Apparent molar masses were determined with size exclusion chromatography apparatus equipped with a Varian refractive index detector and a JASCO 875 UV/VIS absorption detector fitted with three TSK columns (G4000HXL, G3000HXL, G2000HXL). Calibration in the case of RI detection was performed by using linear polystyrene standards. The actual molar masses were calculated from the response of a multi-angle laser-light-scattering detector (Wyatt Technology) Astra software version 4.20, which was connected to the size exclusion chromatography (MALLS/SEC) line. The d*n*/d*c* values for all these samples were measured in THF, at 25 °C, with a laser source operating at 633 nm. Capillary viscosity measurements were made in CH_2Cl_2 at 25 °C with viscometers from semaTECH.

Synthesis of 3: A solution of the sodium salt **2** (3.38 g, 11.25 mmol) in degassed THF (35 mL) was added dropwise to a solution of phenoxy dichlorophosphane sulfide (2.55 g, 11.25 mmol) maintained between −100 and −85 °C. After stirring for 12 h at room temperature, the reaction mixture was centrifuged, the solvent was evaporated and the residue was extracted with THF/pentane (1:3) to give **3** as a colourless oil. Yield: 80%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.015): $\delta = -6.2$ (s, P_1), 58.4 (s, P_0); ^1H NMR ($CDCl_3$, 200.132): $\delta = 7.26$–7.43 (m, 19H; C_6H_5, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.896): $\delta = 121.07$ (d, $^3J(C,P_0) = 4.59$ Hz, C_2), 121.3 ("t", $^3J(C,P_0) = {}^3J(C,P_1) = 6.04$ Hz, C_0^2), 126.53 (s, C_4), 128.66 (d, $^3J(C,P_1) = 7.92$ Hz, C_1^3), 129.00 (s, C_1^4), 129.89 (s, C_3), 133.73 (d, $^2J(C,P_1) = 19.7$ Hz, C_1^2), 135.21 (d, $^2J(C,P_1) = 20.5$ Hz, C_0^3), 135.7 (d, $^1J(C,P_1) = 10.3$ Hz, C_0^4), 136.64 (d, $^1J(C,P_1) = 11$ Hz, C_1^1), 150.18 (d, $^2J(C,P_0) = 9.69$ Hz, C_1), 150.6 (d, $^2J(C,P_0) = 9.94$ Hz, C_0^1); elemental analysis calcd (%) for $C_{24}H_{19}ClO_2P_2S$ (468.9): C 68.48, H 4.05, N 4.08; found C 68.39, H 3.98, N 3.97.

Synthesis of 4: A solution of BH_3, SMe_2 in THF (2 M, 85 mL, 17 mmol) was added to a solution of **1**[19] (3.78 g, 13 mmol) in degassed THF (20 mL) at 0 °C. After stirring overnight at room temperature, the solvent was evaporated and the resulting powder was purified on column chromatography on silica (eluent CH_2Cl_2). The boron complex was isolated in 90% yield. A solution of this complex (2.46 g, 8.43 mmol) in THF (15 mL) was added dropwise to a heterogenous solution of NaH (0.246 g, 10.28 mmol) at room temperature. After stirring for 4 h at room temperature,the mixture was centrifuged and filtered to afford **4** as a pale yellow powder. Yield: 98%; $^{31}P\{^1H\}$ NMR ([D_8]THF, 81.015): $\delta = 21.5$ (br s); ^1H NMR ([D_8]THF, 250.133): $\delta = 0.34$ (br s, 3H; BH_3), 6.31 (dd, $^3J(H,H) = 8.7$ Hz, $^4J(H,P) = 2.2$ Hz, 2H; H_0^2), 7.07–7.39 (m, 12H; C_6H_5, H_0^3); $^{13}C\{^1H\}$ NMR ([D_8]THF, 50.323): $\delta = 107.38$ (d, $^1J(C,P) = 69.0$ Hz, C_0^4), 120.98 (d, $^3J(C,P) = 11.7$ Hz, C_0^2), 129.42 (d, $^3J(C,P) = 9.9$ Hz, C_1^3), 131.44 (s, C_1^4), 134.27 (d, $^1J(C,P) = 56.66$ Hz, C_1^1), 134.15 (d, $^2J(C,P) = 9.8$ Hz, C_1^2), 136.6 (d, $^2J(C,P) = 11.3$ Hz, C_0^3), 175.21 (s, C_0^1); elemental analysis calcd (%) for $C_{18}H_{17}BNaOP$ (314.1): C 68.83, H 5.46; found C 68.78, H 5.37.

Synthesis of 5: A solution of the sodium salt **4** (2.30 g, 7.33 mmol) in degassed THF (20 mL) was added dropwise to a solution of phenoxy dichlorophosphane sulfide (1.66 g, 7.33 mmol) maintained between −100 and −85 °C. After stirring for 12 h at room temperature, the reaction mixture was centrifuged, the solvent was evaporated and the residue was washed with pentane (10 mL) to give **5** as a colourless oil. Yield: 95%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.015): $\delta = 20.5$ (br s, P_1), 57.7 (s, P_0); ^1H NMR ($CDCl_3$, 250.133): $\delta = 1.24$ (br s, 3H; BH_3), 7.28–7.66 (m, 19H; C_6H_5, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.323): $\delta = 121.04$ (d, $^3J(C,P_0) = 4.73$ Hz, C_2), 121.53 (dd, $^3J(C,P_0) = 5.66$ Hz, $^3J(C,P_1) = 10.79$ Hz, C_0^2), 126.4 (br s, C_4), 127.44 (d, $^1J(C,P_1) = 56.8$ Hz, C_0^4), 128.43 (d, $^1J(C,P_1) = 57.92$ Hz, C_1^1), 128.76 (d, $^3J(C,P_1) = 9.81$ Hz, C_1^3), 129.78 (s, C_3), 131.36 (s, C_1^4), 132.97 (d, ^2J $(C,P_1) = 9.36$ Hz, C_1^2), 134.88 (d, $^2J(C,P_1) = 10.56$ Hz, C_0^3), 149.9 (d, $^2J(C,P_0) = 10.7$ Hz, C_1), 152.15 (dd, $^2J(C,P_0) = 8$ Hz, $^4J(C,P_1) = 2.76$ Hz, C_0^1); elemental analysis calcd (%) for $C_{24}H_{22}BClO_2P_2S$ (482.7): C 59.72, H 4.59; found C 59.56, H 4.49.

Synthesis of the linear polymer 7: A solution of **3** (6.35 g, 13.5 mmol) in CH_3CN (20 mL)was added dropwise to a solution of sodium azide (0.9 g, 13.5 mmol) in CH_3CN (20 mL). The resulting mixture was stirred for two

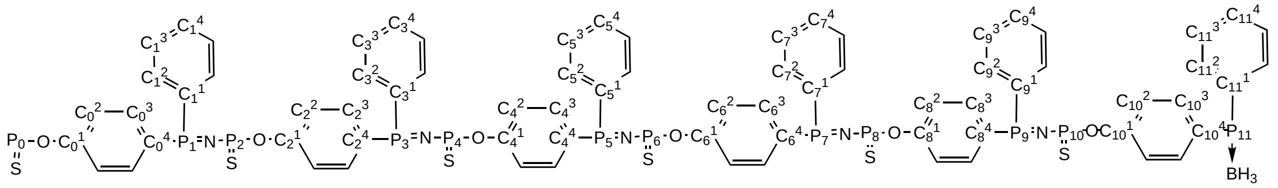


Figure 4. Numbering scheme used for NMR spectroscopic assignments.

days at room temperature and the precipitate filtered. Extraction with CH_2Cl_2 gave a powder; this was washed with CH_3CN (2 × 20 mL) to give the polymer **7** (5 g) as a white powder. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.015): δ = 13.2 (d, ^2J(P,P) = 29.1 Hz, P=N), 50.6 (d, ^2J(P,P) = 29.1 Hz, P=S); ^{1}H and ^{13}C NMR could not be rigorously interpreted (overlapping of signals).

Synthesis of the linear polymer 7′: 1,4-Diazabicyclo[2.2.2]octane (DABCO, 0.208 g, 1.84 mmol) was added to a solution of **8** (0.9 g, 1.84 mmol) in toluene/CH_2Cl_2 (3:5, 160 mL). The resulting mixture was stirred for 4 h and then the solvents were removed to give a powder; this was washed twice with CH_3CN (20 mL) to give **7′** (0.4 g) as a white powder. ^{31}P{^{1}H} NMR ($CDCl_3$, 81.015): δ = 13.2 (d, ^2J(P,P) = 29.1 Hz, P=N), 50.6 (d, ^2J(P,P) = 29.1 Hz, P=S); ^{1}H and ^{13}C NMR could not be rigorously interpreted (overlapping of signals).

Synthesis of 8: Sodium azide (0.47 g, 7.17 mmol) was added to a solution of **5** (3.37 g, 6.98 mmol) in acetone (30 mL). The resulting mixture was stirred for 12 h at room temperature and then the solvent removed. THF (30 mL) was added and the resulting mixture was filtered off to eliminate the sodium salts. Evaporation of THF afforded a powder purified by column chromatography (eluent pentane/toluene 1/1). Compound **8** was obtained as a white powder. Yield: 70%; m.p. 93 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 32.438): δ = 20.8 (br s, P_1), 58.2 (s, P_0); ^{1}H NMR ($CDCl_3$, 200.132): δ = 1.58 (br s, 3H; BH_3), 7.22–7.67 (m, 19H; C_6H_5, C_6H_4); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.323): δ = 120.98 (d, ^3J(C,P_0) = 4.6 Hz, C_2), 121.48 (dd, ^3J(C,P_0) = 4.63 Hz, ^3J(C,P_1) = 10.72 Hz, C_0^2), 126.21 (d, ^5J(C,P_0) = 2.11 Hz, C_4), 127.05 (d, ^1J(C,P_1) = 57.8 Hz, C_0^4), 128.5 (d, ^1J(C,P_1) = 58.5 Hz, C_1^1), 128.8 (d, ^3J(C,P_1) = 10.4 Hz, C_1^3), 129.8 (s, C_3), 131.36 (d, ^4J(C,P_1) = 2.21 Hz, C_1^4), 132.98 (d, ^2J(C,P_1) = 9.76 Hz, C_1^2), 134.91 (d, ^2J(C,P_1) = 10.67 Hz, C_0^3), 149.7 (d, ^2J(C,P_0) = 9.1 Hz, C_1), 152.2 (dd, ^2J(C,P_0) = 7.4 Hz, ^4J(C,P_1) = 2.9 Hz, C_0^1); I.R. (KBr): $\tilde{\nu}$ = 2162 cm^{-1} (N_3); elemental analysis calcd (%) for $C_{24}H_{22}BN_3O_2P_2S$ (489.3): C 58.91, H 4.53, N 8.59; found C 58.85, H 4.48, N 8.51.

Synthesis of 9: A solution of **4** (5 g, 15.9 mmol) in THF (50 mL) was added dropwise to a solution of $SPCl_3$ (0.8 mL, 7.85 mmol) maintained between −100 and −95 °C. After stirring for 12 h at room temperature, the reaction mixture was centrifuged and filtered, and the solvent was evaporated to give **9** as a white powder. Yield: 93%; m.p. 98 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 81.015): δ = 20.8 (br s, P_1), 56.5 (s, P_0); ^{1}H NMR ($CDCl_3$, 200.132): δ = 1.5 (br s, 6H; BH_3), 7.3–7.7 (m, 28H; C_6H_5, C_6H_4); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.896): δ = 121.6 (dd, ^3J(C,P_0) = 5.5 Hz, ^3J(C,P_1) = 11.4 Hz, C_0^2), 127.93 (d, ^1J(C,P_1) = 60.2 Hz, C_0^4), 128.5 (d, ^1J(C,P_1) = 57.9 Hz, C_1^1), 128.9 (d, ^3J(C,P_1) = 10.9 Hz, C_1^3), 131.6 (s, C_1^4), 133.1 (d, ^2J(C,P_1) = 9.7 Hz, C_1^2), 135.11 (d, ^2J(C,P_1) = 10.3 Hz, C_0^3), 152.1 (d, ^2J(C,P_0) = 10 Hz, C_0^1); elemental analysis calcd (%) for $C_{36}H_{34}B_2ClO_2P_3S$ (680.7): C 63.52, H 5.03; found C 63.38, H 4.89.

Synthesis of 10: Sodium azide (0.56 g, 8.6 mmol) was added to a solution of **9** (5.5 g, 8.36 mmol) in acetone (30 mL). The resulting mixture was stirred for 12 h and then the solvent was evaporated. Addition of THF (30 mL) to the resulting powder followed by centrifugation, filtration, then evaporation of the solvent, gave a powder; this was purified by column chromatography on silica gel (eluent toluene/pentane 3/2) to give **10** as a white powder. Yield: 70%; m.p. 149 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 81.015): δ = 20.9 (br s, P_1), 57.7 (s, P_0); ^{1}H NMR ($CDCl_3$, 200.13): δ = 1.5 (br s, 6H; BH_3), 7.29 (dt, ^4J(H,P_0) = ^4J(H,P_1) = 1.7 Hz, ^3J(H,H) = 8.7 Hz, 4H; H_0^2), 7.43–7.61 (m, 24H; C_6H_5, H_0^3); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.323): δ = 121.37 (dd, ^3J(C,P_0) = 5 Hz, ^3J(C,P_1) = 10.9 Hz, C_0^2), 127.3 (d, ^1J(C,P_1) = 57.7 Hz, C_0^4), 128.4 (d, ^1J(C,P) = 58.07 Hz, C_1^1), 128.76 (d, ^3J(C,P_1) = 10.56 Hz, C_1^3), 131.34 (s, C_1^4), 132.96 (d, ^2J(C,P_1) = 9.96 Hz, C_1^2), 134.93 (d, ^2J(C,P_1) = 10.77 Hz, C_0^3), 151.8 (dd, ^2J(C,P_0) = 8.6 Hz, ^4J(C,P_1) = 2.9 Hz, C_0^1); IR (KBr): $\tilde{\nu}$ = 2168 cm^{-1} (N_3); elemental analysis calcd (%) for $C_{36}H_{34}B_2N_3O_2P_3S$ (687.3): C 62.91, H 4.99, N 6.11; found C 62.82, H 4.86, N 5.99.

Synthesis of 11 a–e: DABCO (**a**,**b**: 0.21 g, 1.93 mmol; **c**,**d**: 0.23 g, 2.12 mmol; **e**: 0.36 g, 3.28 mmol) was added to a solution of the azide **10** (0.6 g, 0.87 mmol) in degassed toluene (**a**: 12 mL, **b**–**d**: 15 mL, **e**: 68 mL). The resulting mixture was stirred for 24 h (**a**: 80 °C; **b**, **c**, **e**: room temperature; **d**: 70 °C), then the solvent was evaporated to give a powder; this was purified by washing with a degassed mixture of toluene/diethyl ether (1:10). Hyperbranched polymers **11 a–e** were obtained as a white powders (0.4 g).

Synthesis of 11 f: A large excess of triethylamine (14 mL, 100 mmol) to a solution of the azide **10** (3.22 g, 4.7 mmol) in degassed THF (12 mL) at room temperature. The resulting mixture was stirred for 10 days and then the solvent was evaporated to give a powder; this was purified by washing with degassed mixture of THF/diethyl ether (1:10). Hyperbranched polymer **11 f** was obtained as a white powder (2.5 g).

NMR data for 11 a–f: ^{31}P{^{1}H} NMR ($CDCl_3$, 101.256): δ = −6.3 (m, PPh_2), 14.2 (m, P=N), 50.0 (m, P=S); ^{1}H and ^{13}C NMR could not be rigorously interpreted (overlapping of signals).

Synthesis of 12: $SPCl_3$ (0.21 mL, 2.22 mmol) was added to a solution of the sodium salt **2** (2 g, 6.66 mmol) in degassed THF (20 mL). After stirring for 12 h at room temperature, the reaction mixture was centrifuged and filtered, the solvent was evaporated and the residue purified by column chromatography on silica gel with a pentane/toluene 3/2 solution as eluent. Compound **12** was obtained as a white powder. Yield: 80%; m.p. 61 °C; ^{31}P{^{1}H} NMR ($CDCl_3$, 81.015): δ = −6.3 (s, P_1), 52.1 (s, P_0); ^{1}H NMR ($CDCl_3$, 250.133): δ = 7.2 (d, ^3J(H,H) = 8.6 Hz, 6H; H_0^2), 7.25–7.36 (m, 36H; C_6H_5, H_0^3); ^{13}C{^{1}H} NMR ($CDCl_3$, 50.323): δ = 121.01 ("t", ^3J(C,P_0) = ^3J(C,P_1) = 6.1 Hz, C_0^2), 128.45 (d, ^3J(C,P_1) = 6.8 Hz, C_1^3), 128.76 (s, C_1^4), 132.97 (d, ^1J(C,P_1) = 9.56 Hz, C_0^4), 133.53 (d, ^2J(C,P_1) = 19.62 Hz, C_1^2), 135.03 (d, ^2J(C,P_1) = 20.5 Hz, C_0^3), 136.6 (d, ^1J(C,P_1) = 10.62 Hz, C_1^1), 150.8 (d, ^2J(C,P_0) = 7.85 Hz, C_0^1); elemental analysis calcd (%) for $C_{54}H_{42}O_3P_4S$ (894.9): C 72.48, H 4.73, N 6.11; found C 72.2, H 4.67, N 6.01.

Dendrimer 13-[G$_1$]: A solution of azide **10** (2.76 g, 4.02 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **12** (1.2 g, 1.34 mmol) in CH_2Cl_2 (5 mL) at room temperature. The resulting mixture was stirred for 3 h, then the solvent was evaporated to give a residue, which was washed with THF/pentane (1:10, 2 × 20 mL). Dendrimer **13-[G$_1$]** was isolated as a white powder. Yield: 95%; ^{1}H NMR ($CDCl_3$, 250.133): δ = 1.25 (br s, 18H; BH_3), 7.19 (dt, ^3J(H,H) = 8.5 Hz, ^4J(H,P_2) = ^4J(H,P_3) = 1.4 Hz, 12H; H_2^2), 7.33–7.66 (m, 114H; C_6H_5, C_6H_4); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.896): δ = 121.41 (dd, ^3J(C,P_0) = 4.7 Hz, ^3J(C,P_1) = 13.9 Hz, C_0^2), 121.9 (dd, ^3J(C,P_2) = 5.2 Hz, ^3J(C,P_3) = 10.4 Hz, C_2^2), 124.26 (d, ^1J(C,P_3) = 60.13 Hz, C_2^4), 126.20 (dd, ^1J(C,P_1) = 110 Hz, ^3J(C,P_2) = 3 Hz, C_0^4), 127.88 (dd, ^1J(C,P_1) = 105 Hz, ^3J(C,P_2) = 4 Hz, C_1^1), 128.79 (d, ^3J(C,P_3) = 10.5 Hz, C_3^3), 128.86 (d, ^3J(C,P_1) = 13.2 Hz, C_1^3), 129.3 (d, ^1J(C,P_3) = 54 Hz, C_3^1), 131.28 (s, C_3^4), 132.67 (d, ^2J(C,P_1) = 11.32 Hz, C_1^2), 132.99 (s, C_1^4), 133.07 (d, ^2J(C,P_3) = 9.5 Hz, C_3^2), 134.50 (d, ^2J(C,P_3) = 10.56 Hz, C_2^3), 134.98 (d, ^2J(C,P_3) = 9.5 Hz, C_0^3), 153.42 (dd, ^2J(C,P_2) = 8.01 Hz, ^4J(C,P_3) = 3.8 Hz, C_0^1), 154.47 (br d, ^2J(C,P_0) = 7.23 Hz, C_2^1); elemental analysis calcd (%) for $C_{162}H_{144}B_6N_3O_9P_{13}S_4$ (2873): C 67.73, H 5.05, N 1.46; found C 67.52, H 4.98, N 1.32.

Dendrimer 13-[G′$_1$]: DABCO (0.703 g, 6.272 mmol) was added to a solution of the boron complex **13-[G$_1$]** (3 g, 1.045 mmol) in degassed toluene (100 mL). After stirring for 12 h at room temperature, the solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2/pentane 10:1) to give **13-[G′$_1$]** as a white powder. Yield: 80%; ^{1}H NMR ($CDCl_3$, 250.133): δ = 7.09–7.67 (m, 126H; C_6H_5, C_6H_4); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.896), 121.24 (dd, ^3J(C,P_0) = 5.13 Hz, ^3J(C,P_1) = 13.81 Hz, C_0^2), 121.69 ("t", ^3J(C,P_2) = ^3J(C,P_3) = 6.4 Hz, C_2^2), 126.61 (br d, ^1J(C,P_1) = 108 Hz, C_0^4), 128.18 (dd, ^1J(C,P_1) = 108.35 Hz, ^3J(C,P_2) = 3.5 Hz, C_1^1), 128.47 (d, ^3J(C,P_3) = 6.5 Hz, C_3^3), 128.67 (s, C_3^4), 128.76 (d, ^3J(C,P_1) = 11.68 Hz, C_1^3), 132.14 (d, ^1J(C,P_3) = 9.87 Hz, C_2^4), 132.67 (s, C_1^4), 132.69 (d, ^2J(C,P_1) = 10.69 Hz, C_1^2), 133.56 (d, ^2J(C,P_3) = 19.18 Hz, C_3^2), 134.85 (d, ^2J(C,P_3) = 20.94 Hz, C_2^3), 135.02 (d, ^2J(C,P_1) = 12.31 Hz, C_0^3), 137.27 (d, ^1J(C,P_3) = 10.82 Hz, C_3^1), 152.73 (d, ^2J(C,P_2) = 8.61 Hz, C_2^1), 153.27 (dd, ^2J(C,P_0) = 7.95 Hz, ^4J(C,P_1) = 3.86 Hz, C_0^1); elemental analysis calcd (%) for $C_{162}H_{126}N_3O_9P_{13}S_4$(2790): C 69.75, H 4.55, N 1.51; found C 69.54, H 4.42, N 1.37.

General procedure for the synthesis of dendrimers 13-[G$_2$], 13-[G$_3$], 13-[G$_4$] and 13-[G$_5$]: The same procedure used for the preparation of **13-[G$_1$]** was applied for the synthesis of dendrimers **13-[G$_2$]**, **13-[G$_3$]**, **13-[G$_4$]** and **13-[G$_5$]** from **13-[G′$_1$]**, **13-[G′$_2$]**, **13-[G′$_3$]** and **13-[G′$_4$]**, respectively, and the azide **10**.

Dendrimer 13-[G$_2$]: White powder, 90% yield; ^{1}H NMR ($CDCl_3$, 250.133): δ = 1.27 (br s, 36H; BH_3), 7.15–7.56 (m, 294H; C_6H_5, C_6H_4); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.896): δ = 121.47 (dd, ^3J(C,P_0) = 5.8 Hz, ^3J(C,P_1) = 13.9 Hz, C_0^2), 121.67 (dd, ^3J(C,P_2) = 5.5 Hz, ^3J(C,P_3) = 11.6 Hz, C_2^2), 121.84 (dd, ^3J(C,P_4) = 5.6 Hz, ^3J(C,P_5) = 9.87 Hz, C_4^2), 123.36 (dd, ^1J(C,P_3) = 110.43 Hz, ^3J(C,P_4) = 3.6 Hz, C_2^4), 124.09 (d, ^1J(C,P_5) = 59.81 Hz, C_4^4), 126.1 (dd, ^1J(C,P_1) = 110 H; ^3J(C,P_2) = 4 Hz, C_0^4), 127.68 (dd, ^1J(C,P_1) = 108.2 Hz, ^3J(C,P_2) = 4.1 Hz, C_1^1), 128.31 (dd, ^1J(C,P_3) = 106.2 Hz,

^{3}J(C,P$_{4}$) = 3.6 Hz, C$_{3}^{1}$), 128.73 (d, ^{3}J(C,P$_{3}$) = 12.6 Hz, C$_{3}^{3}$), 128.8 (d, ^{3}J(C,P$_{5}$) = 10 Hz, C$_{5}^{3}$), 128.9 (d, ^{3}J(C,P$_{1}$) = 12 Hz, C$_{1}^{3}$), 129.1 (d, ^{1}J(C,P$_{5}$) = 52 Hz, C$_{5}^{1}$), 131.28 (br s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$), 132.64 (d, ^{2}J(C,P) = 11.76 Hz, C$_{1}^{2}$, C$_{3}^{2}$), 133.06 (d, ^{2}J(C,P$_{5}$) = 9.75 Hz, C$_{5}^{2}$), 134.33 (d, ^{2}J(C,P$_{3}$) = 11.95 Hz, C$_{2}^{3}$), 134.5 (d, ^{2}J(C,P$_{5}$) = 10.19 Hz, C$_{4}^{3}$), 135.01 (d, ^{2}J(C,P$_{1}$) = 12.2 Hz, C$_{0}^{3}$), 153.42 (br d, ^{2}J(C,P$_{0}$) = 8 Hz, C$_{0}^{1}$), 154.52 (d, ^{2}J(C,P$_{4}$) = 10.82 Hz, C$_{4}^{1}$), 155.49 (dd, ^{4}J(C,P$_{3}$) = 3.69 Hz, ^{2}J(C,P$_{2}$) = 7.63 Hz, C$_{2}^{1}$); elemental analysis calcd (%) for $C_{378}H_{330}B_{12}N_{9}O_{21}P_{31}S_{10}$ (6745.5): C 67.31, H 4.93, N 1.87; found C 67.11, H 4.81, N 1.81.

Dendrimer 13-[G$_{3}$]: White powder, 90 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 1.1 (br s, 72 H; BH$_{3}$,), 7.14 – 7.57 (m, 630 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.4 (m, C$_{0}^{2}$), 121.7 (m, C$_{2}^{2}$, C$_{4}^{2}$), 121.8 (dd, ^{3}J(C,P$_{7}$) = 5.8 Hz, ^{3}J(C,P$_{7}$) = 11 Hz, C$_{6}^{2}$), 123.1 (br d, ^{1}J(C,P$_{3}$) = 111 Hz, C$_{2}^{4}$), 123.3 (br d, ^{1}J(C,P$_{5}$) = 110.7 Hz, C$_{4}^{4}$), 124.1 (d, ^{1}J(C,P$_{7}$) = 60.1 Hz, C$_{6}^{4}$), 125.9 (br d, ^{1}J(C,P$_{1}$) = 110 Hz, C$_{0}^{4}$), 127.6 (dd, ^{1}J(C,P$_{1}$) = 105 Hz, ^{3}J(C,P$_{2}$) = 4 Hz, C$_{1}^{1}$), 128.1 (dd, ^{1}J(C,P$_{3}$) = 108 Hz, ^{3}J(C,P$_{4}$) = 4 Hz, C$_{3}^{1}$), 128.3 (br d, ^{1}J(C,P$_{5}$) = 105.3 Hz, C$_{5}^{1}$), 128.7 (br d, ^{3}J(C,P) = 15.1 Hz, C$_{1}^{3}$, C$_{3}^{3}$, C$_{5}^{3}$), 128.8 (d, ^{3}J(C,P$_{7}$) = 9.9 Hz, C$_{7}^{3}$), 129.2 (d, ^{1}J(C,P$_{7}$) = 50 Hz, C$_{7}^{1}$), 131.3 (br s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$, C$_{7}^{4}$), 132.6 (d, ^{2}J(C,P) = 11 Hz, C$_{1}^{2}$, C$_{3}^{2}$, C$_{5}^{2}$), 133.03 (d, ^{2}J(C,P$_{7}$) = 9.8 Hz, C$_{7}^{2}$), 134.3 (d, ^{2}J(C,P) = 12.6 Hz, C$_{2}^{3}$, C$_{4}^{3}$), 134.5 (d, ^{2}J(C,P$_{7}$) = 11.1 Hz, C$_{6}^{3}$), 135.0 (d, ^{2}J(C,P$_{1}$) = 11.9 Hz, C$_{0}^{3}$), 153.4 (br d, ^{2}J(C,P$_{0}$) = 8 Hz, C$_{0}^{1}$), 154.5 (d, ^{2}J(C,P$_{7}$) = 8.9 Hz, C$_{6}^{1}$), 155.6 (dd, ^{2}J(C,P) = 8.5 Hz, ^{4}J(C,P) = 3.5 Hz, C$_{2}^{1}$, C$_{4}^{1}$); elemental analysis calcd (%) for $C_{810}H_{702}B_{24}N_{21}O_{45}P_{67}S_{22}$ (14491): C 67.14, H 4.88, N 2.03; found C 66.97, H 4.77, N 1.98.

Dendrimer 13-[G$_{4}$]: White powder, 88 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 1.3 (br s, 144 H; BH$_{3}$), 7.2 – 7.5 (m, 1302 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.6 (m, C$_{0}^{2}$, C$_{2}^{2}$, C$_{4}^{2}$, C$_{6}^{2}$), 121.85 (dd, ^{3}J(C,P$_{8}$) = 4.5 Hz, ^{3}J(C,P$_{9}$) = 10.2 Hz, C$_{8}^{2}$), 123.1 (br d, ^{1}J(C,P) = 110 Hz, C$_{2}^{4}$, C$_{4}^{4}$), 123.3 (br d, ^{1}J(C,P) = 111 Hz, C$_{6}^{4}$), 124.1 (d, ^{1}J(C,P$_{9}$) = 60.0 Hz, C$_{8}^{4}$), 127.9 (br d, ^{1}J(C,P) = 108 Hz, C$_{1}^{1}$), 128.1 (dd, ^{1}J(C,P) = 105 Hz, ^{3}J(C,P) = 3.4 Hz, C$_{3}^{1}$, C$_{5}^{1}$), 128.3 (dd, ^{1}J(C,P$_{7}$) = 106.3 Hz, ^{3}J(C,P$_{8}$) = 3.5 Hz, C$_{7}^{1}$), 128.76 (br d, ^{3}J(C,P) = 15.3 Hz, C$_{1}^{3}$, C$_{3}^{3}$, C$_{5}^{3}$, C$_{7}^{3}$), 128.8 (d, ^{3}J(C,P$_{9}$) = 9.8 Hz, C$_{9}^{3}$), 129.2 (d, ^{1}J(C,P$_{9}$) = 48 Hz, C$_{9}^{1}$), 131.3 (br s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$, C$_{7}^{4}$, C$_{9}^{4}$), 132.6 (br d, ^{2}J(C,P) = 10.9 Hz, C$_{1}^{2}$, C$_{3}^{2}$, C$_{5}^{2}$, C$_{7}^{2}$), 133.03 (d, ^{2}J(C,P$_{9}$) = 9.8 Hz, C$_{9}^{2}$), 134.3 (br d, ^{2}J(C,P) = 13.3 Hz, C$_{2}^{3}$, C$_{4}^{3}$, C$_{6}^{3}$), 134.5 (d, ^{2}J(C,P$_{9}$) = 10.4 Hz, C$_{8}^{3}$), 134.8 (d, ^{2}J(C,P$_{1}$) = 11.9 Hz, C$_{0}^{3}$), 153.4 (br m, C$_{0}^{1}$), 154.5 (dd, ^{2}J(C,P$_{8}$) = 8.3 Hz, ^{4}J(C,P$_{9}$) = 3.1 Hz, C$_{8}^{1}$), 155.6 (dd, ^{2}J(C,P) = 6.9 Hz, ^{4}J(C,P) = 3.6 Hz, C$_{2}^{1}$, C$_{4}^{1}$, C$_{6}^{1}$), (C$_{0}^{4}$ not detected); elemental analysis calcd (%) for $C_{1674}H_{1446}B_{48}N_{45}O_{93}P_{139}S_{46}$ (29982): C 67.06, H 4.86, N 2.10; found C 66.87, H 4.80, N 2.01.

Dendrimer 13-[G$_{5}$]: White powder, 80 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 1.26 (br s, 288 H; BH$_{3}$), 7.15 – 7.46 (m, 2646 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.7 (m, C$_{0}^{2}$, C$_{2}^{2}$, C$_{4}^{2}$, C$_{6}^{2}$, C$_{8}^{2}$), 121.8 (dd, ^{3}J(C,P$_{10}$) = 4.6 Hz, ^{3}J(C,P$_{11}$) = 9.8 Hz, C$_{10}^{2}$), 123.3 (br d, ^{1}J(C,P) = 112.2 Hz, C$_{0}^{4}$, C$_{2}^{4}$, C$_{4}^{4}$, C$_{6}^{4}$, C$_{8}^{4}$), 124.11 (d, ^{1}J(C,P$_{11}$) = 60.1 Hz, C$_{10}^{4}$), 128.1 (br d, ^{1}J(C,P) = 98.3 Hz, C$_{1}^{1}$, C$_{3}^{1}$, C$_{5}^{1}$, C$_{7}^{1}$), 128.32 (br d, ^{1}J(C,P$_{9}$) = 109.5 Hz, C$_{9}^{1}$), 128.76 (br d, ^{3}J(C,P) = 15.6 Hz, C$_{1}^{3}$, C$_{3}^{3}$, C$_{5}^{3}$, C$_{7}^{3}$, C$_{9}^{3}$), 128.8 (br d, ^{3}J(C,P$_{11}$) = 10.1 Hz, C$_{11}^{3}$), 129.24 (d, ^{1}J(C,P$_{11}$) = 44.8 Hz, C$_{11}^{1}$), 131.31 (br s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$, C$_{7}^{4}$, C$_{9}^{4}$, C$_{11}^{4}$), 132.6 (br d, ^{2}J(C,P) = 10.8 Hz, C$_{1}^{2}$, C$_{3}^{2}$, C$_{5}^{2}$, C$_{7}^{2}$, C$_{9}^{2}$), 133.02 (d, ^{2}J(C,P$_{11}$) = 9.62 Hz, C$_{11}^{2}$), 134.3 (br d, ^{2}J(C,P) = 12.9 Hz, C$_{2}^{3}$, C$_{4}^{3}$, C$_{6}^{3}$, C$_{8}^{3}$), 134.5 (br d, ^{2}J(C,P$_{11}$) = 10.7 Hz, C$_{10}^{3}$, C$_{0}^{3}$), 154.54 (br d, ^{2}J(C,P$_{10}$) = 8.6 Hz, C$_{10}^{1}$), 155.57 (br d, ^{2}J(C,P) = 6.7 Hz, C$_{2}^{1}$, C$_{4}^{1}$, C$_{6}^{1}$, C$_{8}^{1}$), (C$_{0}^{1}$, C$_{0}^{4}$ not detected); elemental analysis calcd (%) for $C_{3402}H_{2934}B_{96}N_{93}O_{189}P_{283}S_{94}$ (60964): C 67.02, H 4.85, N 2.14; found C 66.85, H 4.72, N 2.06.

General procedure for the synthesis of dendrimers 13-[G′$_{2}$], 13-[G′$_{3}$] and 13-[G′$_{4}$]: The same procedure used for the preparation of **13-[G′$_{1}$]** was applied for the synthesis of dendrimers **13-[G′$_{2}$]**, **13-[G′$_{3}$]** and **13-[G′$_{4}$]** from **13-[G$_{2}$]**, **13-[G$_{3}$]** and **13-[G$_{4}$]**, respectively, and DABCO, except concerning the purification. In these cases, the residue was purified by washing with a degassed mixture of toluene/diethyl ether (1:10).

Dendrimer 13-[G′$_{2}$]: White powder, 87 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 7.1 – 7.6 (m, 294 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.6 (m, C$_{0}^{2}$, C$_{2}^{2}$), 121.7 (“t”, ^{3}J(C,P$_{4}$) = ^{3}J(C,P$_{5}$) = 6.1 Hz, C$_{4}^{2}$), 123.73 (br d, ^{1}J(C,P$_{3}$) = 111.07 Hz, C$_{2}^{4}$), 126.2 (br d, ^{1}J(C,P$_{1}$) = 108 Hz, C$_{0}^{4}$), 127.8 (br d, ^{1}J(C,P$_{1}$) = 110 Hz, C$_{1}^{1}$), 128.48 (d, ^{3}J(C,P$_{5}$) = 6.54 Hz, C$_{5}^{3}$), 128.67 (s, C$_{5}^{4}$), 128.71 (dd, ^{1}J(C,P$_{3}$) = 108.3 Hz, ^{3}J(C,P$_{4}$) = 3.5 Hz, C$_{3}^{1}$), 128.76 (d, ^{3}J(C,P) = 11.1 Hz, C$_{1}^{3}$, C$_{3}^{3}$), 132.06 (d, ^{1}J(C,P$_{5}$) = 10.25 Hz, C$_{4}^{4}$), 132.61 (d, ^{2}J(C,P$_{1}$) = 8 Hz, C$_{1}^{2}$), 132.62 (s, C$_{1}^{4}$, C$_{3}^{4}$), 132.71 (d, ^{2}J(C,P$_{3}$) = 10.8 Hz, C$_{3}^{2}$), 133.57 (d, ^{2}J(C,P$_{5}$) = 19.4 Hz, C$_{5}^{2}$), 134.38 (d, ^{2}J(C,P$_{3}$) = 12.39 Hz, C$_{2}^{3}$), 134.8 (d, ^{2}J(C,P$_{1}$) = 14.8 Hz, C$_{0}^{3}$), 134.85 (d, ^{2}J(C,P$_{5}$) = 20.9 Hz, C$_{4}^{3}$), 137.34 (d, ^{1}J(C,P$_{5}$) = 10.82 Hz, C$_{5}^{1}$), 152.83 (d, ^{2}J(C,P$_{4}$) = 8.8 Hz, C$_{4}^{1}$), 153.42 (dd, ^{2}J(C,P$_{0}$) = 7.87 Hz, ^{4}J(C,P$_{1}$) = 3.94 Hz, C$_{0}^{1}$), 155.41 (dd, ^{2}J(C,P$_{2}$) = 10.13 Hz, ^{4}J(C,P$_{3}$) = 3.65 Hz, C$_{2}^{1}$); elemental analysis calcd (%) for $C_{378}H_{294}N_{9}O_{21}P_{31}S_{10}$ (6579.5): C 69.00, H 4.50, N 1.92; found C 68.31, H 4.37, N 1.77.

Dendrimer 13-[G′$_{3}$]: White powder, 90 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 7.2 – 7.6 (m, 630 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.6 (m, C$_{0}^{2}$, C$_{2}^{2}$, C$_{4}^{2}$), 121.7 (“t”, ^{3}J(C,P$_{7}$) = ^{3}J(C,P$_{7}$) = 6.3 Hz, C$_{6}^{2}$), 123.3 (dd, ^{1}J(C,P$_{3}$) = 110.6 Hz, ^{3}J(C,P$_{4}$) = 4 Hz, C$_{2}^{4}$), 123.7 (dd, ^{1}J(C,P$_{5}$) = 110.6 Hz, ^{3}J(C,P$_{7}$) = 3.4 Hz, C$_{4}^{4}$), 126.2 (br d, ^{1}J(C,P$_{1}$) = 108 Hz, C$_{0}^{4}$), 127.7 (dd, ^{1}J(C,P$_{1}$) = 110 Hz, ^{3}J(C,P$_{2}$) = 4 Hz, C$_{1}^{1}$), 128.3 (dd, ^{1}J(C,P$_{3}$) = 108.2 Hz, ^{3}J(C,P$_{4}$) = 3.3 Hz, C$_{3}^{1}$), 128.55 (d, ^{3}J(C,P$_{7}$) = 6.3 Hz, C$_{7}^{3}$), 128.7 (dd, ^{1}J(C,P$_{5}$) = 108.1 Hz, ^{3}J(C,P$_{7}$) = 3.5 Hz, C$_{5}^{1}$), 128.76 (s, C$_{7}^{4}$), 128.9 (d, ^{3}J(C,P) = 13.3 Hz, C$_{1}^{3}$, C$_{3}^{3}$, C$_{5}^{3}$), 132.12 (d, ^{1}J(C,P$_{7}$) = 10.1 Hz, C$_{6}^{4}$), 132.76 (s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$), 132.76 (d, ^{2}J(C,P) = 11.5 Hz, C$_{1}^{2}$, C$_{3}^{2}$, C$_{5}^{2}$), 133.6 (d, ^{2}J(C,P$_{7}$) = 19.5 Hz, C$_{7}^{2}$), 134.42 (d, ^{2}J(C,P) = 12.7 Hz, C$_{2}^{3}$, C$_{4}^{3}$), 134.9 (br d, J(C,P) = 20 Hz, C$_{0}^{3}$, C$_{6}^{3}$), 137.4 (d, ^{1}J(C,P$_{7}$) = 11.2 Hz, C$_{7}^{1}$), 152.9 (d, ^{2}J(C,P$_{7}$) = 9.8 Hz, C$_{6}^{1}$), 153.5 (dd, ^{2}J(C,P$_{0}$) = 7.9 Hz, ^{4}J(C,P$_{1}$) = 3.9 Hz, C$_{0}^{1}$), 155.5 (dd, ^{2}J(C,P) = 7.9 Hz, ^{4}J(C,P) = 3.7 Hz, C$_{2}^{1}$, C$_{4}^{1}$); elemental analysis calcd (%) for $C_{810}H_{630}N_{21}O_{45}P_{67}S_{22}$ (14159): C 68.71, H 4.48, N 2.08; found C 68.41, H 4.25, N 1.97.

Dendrimer 13-[G′$_{4}$]: White powder, 78 % yield; ^{1}H NMR (CDCl$_{3}$, 250.133): δ = 7.1 – 7.5 (m, 1302 H; C$_{6}$H$_{5}$, C$_{6}$H$_{4}$); ^{13}C{^{1}H} NMR (CDCl$_{3}$, 62.896): δ = 121.5 – 121.8 (m, C$_{0}^{2}$, C$_{2}^{2}$, C$_{4}^{2}$, C$_{6}^{2}$, C$_{8}^{2}$), 123.2 (br d, ^{1}J(C,P) = 111 Hz, C$_{2}^{4}$, C$_{4}^{4}$), 123.7 (br d, ^{1}J(C,P$_{7}$) = 109.7 Hz, C$_{6}^{4}$), 127.7 (br d, ^{1}J(C,P$_{1}$) = 106 Hz, C$_{1}^{1}$), 128.2 (br d, ^{1}J(C,P) = 106 Hz, C$_{3}^{1}$, C$_{5}^{1}$), 128.5 (d, ^{3}J(C,P$_{9}$) = 6.9 Hz, C$_{9}^{3}$), 128.7 (br d, ^{1}J(C,P$_{7}$) = 105.7 Hz, C$_{7}^{1}$), 128.7 (s, C$_{9}^{4}$), 128.8 (d, ^{3}J(C,P) = 13.6 Hz, C$_{1}^{3}$, C$_{3}^{3}$, C$_{5}^{3}$, C$_{7}^{3}$), 132.1 (d, ^{1}J(C,P$_{9}$) = 10.1 Hz, C$_{8}^{4}$), 132.6 (s, C$_{1}^{4}$, C$_{3}^{4}$, C$_{5}^{4}$, C$_{7}^{4}$), 132.7 (d, ^{2}J(C,P) = 11.2 Hz, C$_{1}^{2}$, C$_{3}^{2}$, C$_{5}^{2}$, C$_{7}^{2}$), 133.6 (d, ^{2}J(C,P$_{9}$) = 19.5 Hz, C$_{9}^{2}$), 134.4 (d, ^{2}J(C,P) = 12.1 Hz, C$_{2}^{3}$, C$_{4}^{3}$, C$_{6}^{3}$), 134.9 (br d, ^{2}J(C,P) = 21.0 Hz, C$_{0}^{3}$, C$_{8}^{3}$), 137.3 (d, ^{1}J(C,P$_{9}$) = 10.5 Hz, C$_{9}^{1}$), 152.9 (d, ^{2}J(C,P$_{8}$) = 8.9 Hz, C$_{8}^{1}$), 153.4 (br m, C$_{0}^{1}$), 155.4 – 155.6 (m, C$_{2}^{1}$, C$_{4}^{1}$, C$_{6}^{1}$) (C$_{0}^{4}$ not detected); elemental analysis calcd (%) for $C_{1674}H_{1302}N_{45}O_{93}P_{139}S_{46}$ (29318): C 68.58, H 4.48, N 2.15; found C 68.21, H 4.32, N 2.07.

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