Core−Shell Macromolecules with Rigid Dendritic Polyphenylene Cores and Polymer Shells

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ABSTRACT: The synthesis of core−shell nanoparticles consisting of a shape-persistent polyphenylene dendrimer (**TdG$_2$**) as the core and of different polymers (poly(ethylene oxide), polystyrene and polyisoprene) as *mono-* or *double*-shells is presented. Mono-shell systems are obtained either by a "*grafting-onto*" (arm first) process attaching poly(ethylene oxide) chains to a **TdG$_2$** with an average of 12 chloromethyl functions (**TdG$_2$(CH$_2$Cl)$_{\sim 12}$**) or by a "*grafting-from*" (core first) method using a **TdG$_2$**-dendrimer functionalized with exactly 16 hydroxymethyl groups **TdG$_2$(CH$_2$OH)$_{16}$** as multiinitiator for the living anionic polymerization of ethylene oxide (EO). In both cases, well-defined PEO-functionalized polyphenylene dendrimers with molecular weights between 10^4 and 10^6 Da were obtained. The hydrodynamic radii of the particles were determined by dynamic light scattering to be in the range 5−20 nm, depending on the length of the PEO-chains. Core-*double*-shell systems as examples of a more complex onion-type architecture were synthesized by *"grafting-onto"* of blockcopolymers, respectively poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO) or poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO), on **TdG$_2$**. Because of the use of block-copolymers containing PEO, PI and polystyrene shell structures with regions of different polarity and stiffness in the same nanoparticle were made accessible.

Introduction

Core−shell structures based on latex particles have gained an increasing importance in many industrial applications; typical examples are paints,[1] coatings,[1] diagnostics, drug delivery,[2−4] or supports for catalysts.[5] They principally consist of a stiff core and a flexible shell such as beads prepared from styrene and butyl acrylate.[1] Typically, they are obtained by a two-step emulsion polymerization wherein the polystyrene core is synthesized first and then surrounded with a very flexible poly(butyl acrylate) shell by addition of the acrylate[1] or by emulsion polymerization using block copolymers as the surfactant.[6] Such particles have sizes of 200−500 nm.[7,8] In many cases, the creation of similar structures at least 1 order of magnitude smaller are of interest, not only to increase the ratio of surface to volume but also to improve the particle size distribution. Typical examples are film formation of dispersions,[1] generation of phase separated systems such as SBS-rubbers, and fragmentation processes of polymeric supports[9] for metallocenes applied in olefin polymerizations. For these processes we consider dendrimer based core−shell systems as ideal model systems due to their size and well-defined structures.

Star-shaped core−shell macromolecules based on dendrimer−polymer hybrids have already been synthesized via both "*grafting-onto*" and "*grafting-from*" methods.[10,11] The "*grafting-onto*" approach based on the deactivation of anionic living polymers with a multifunctional dendrimeric electrophile was applied first for the synthesis of polybutadiene starlike structures using carbosilane dendrimers of generation 2.5, 3.5, and 4.5.[12−14] A variant of this method was utilized for the preparation of "miktoarm" star polymers with eight polystyrene and eight polyisoprene arms[15] or diblock copolymers with styrene (30%) and butadiene (70%) as arms.[16] Recently, the "*grafting-onto*" method using poly(propyleneimine)[17] and poly(amidoamine) dendrimers[18−21] has also been reported. The "*grafting-from*" method (core first), in which the polymer chains of the star are grown from an active multifunctional dendrimeric initiator, was applied using ring-opening polymerization of ϵ-caprolactone initiated from benzyl dendritic polyethers and gave polymers possessing hybrid linear−globular architectures.[22] The preparation of dendrimer-like star block copolymers became possible by both anionic and atom transfer radical polymerization of ϵ-caprolactone, methyl methacrylate, and EO.[23] The "*grafting-from*" method was recently extended to the synthesis of star-shaped core−shell macromolecules based on hyperbranched polyglycerols,[24] poly(trimethylene imine) dendrimers,[25] and poly(amidoamine) dendrimers.[26]

While most of the previously examined core−shell structures possess "soft" or "semirigid" dendrimer cores, their rigid analogues are still elusive. We have already synthesized stiff polyphenylene dendrimers[27,28] and developed different methods to functionalize them both statistically and also in a well-defined way with a broad variety of functional groups, e.g., carboxy, amino, chloromethyl, and hydroxymethyl.[29,30] Now we use these unique types of functionalized shape-persistent dendrimers as the core to obtain complex core−shell structures with layers of different polarity and flexibilty.

Two approaches will be presented for the formation of such flexible-shell stiff-core particles: (*i*) a "*grafting-onto*" reaction of PEO chains to a polyphenylene dendrimer with statistically functionalized chloromethyl units; (*ii*) a "*grafting-from*" reaction using a well-defined hydroxymethyl functionalized polyphenylene dendrimer as multifunctional initiator in an EO polymerization. In addition, the "*grafting-onto*" approach is applied for the preparation of *double*-shell-core nanoparticles by grafting PI-*b*-PEO and PS-*b*-PEO block copolymers on the dendrimer surface.

Even if dendrimers are by far more difficult to obtain than latexes, rigid and shape-persistent polyphenylene

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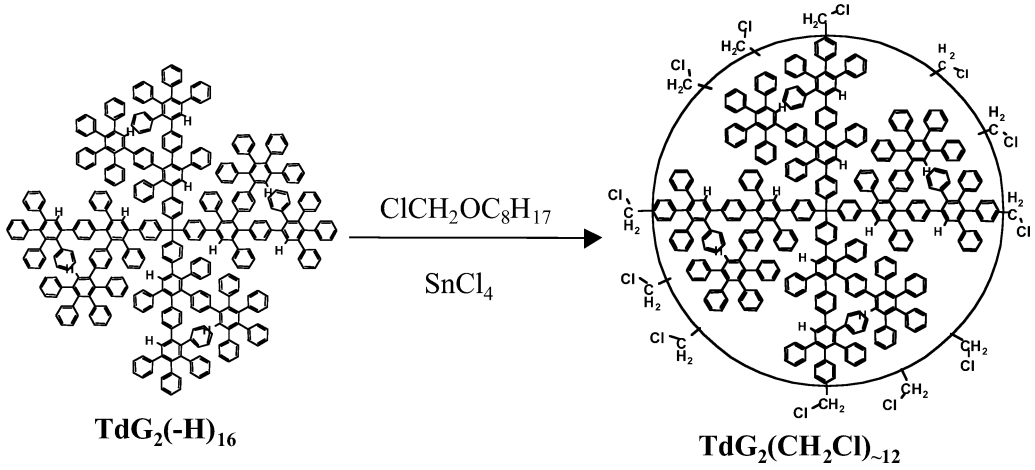
Scheme 1. Chloromethylation of $TdG_2(-H)_{16}$



dendrimers decorated with PEO chains can serve as ideal test examples for stiff-core flexible-shell latex particles as part of the above-mentioned applications.

Results and Discussion

To synthesize core−shell nanoparticles with defined size and surface polarity, one has to consider that the number of arms is not really decisive. Since it has already been shown that even one single hydrophilic chain is able to surround and stabilize a hydrophobic chain by forming a so-called unimolecular micelle,[31] in a first approach, we have avoided the very complicated synthesis required to achieve a perfectly functionalized dendrimer with an exactly defined number of attached PEO arms. Instead, we looked into a one-step statistical functionalization of a **TdG_2** to obtain a chloromethylated dendrimer for the subsequent *"grafting-onto"* reaction with PEO monoanions. Within the "*grafting-from*" approach, we synthesized a structurally well-defined second-generation hexadecahydroxymethyl functionalized polyphenylene dendrimer with a tetrahedral core (**$TdG_2(CH_2OH)_{16}$**)[29] to serve as a multifunctional initiator for the polymerization of EO.

Synthesis of Core-*mono*-Shell Dendrimers. (a) Synthesis of Core-*mono*-Shell Nanoparticles Using the "*Grafting-onto*" Method. Synthesis of Chloromethyl Functionalized Polyphenylene Dendrimer $TdG_2(CH_2Cl)_{\sim 12}$. For the grafting of living PEO-chains onto functionalized polyphenylene dendrimers, we investigated the chloromethylation reaction of nonfunctionalized dendrimer (**$TdG_2(—H)_{16}$**) by using 80 equiv of chloromethyloctyl ether in the presence of $SnCl_4$. A statistically chloromethylated **TdG_2** containing an average of 12 chloromethyl groups **$TdG_2(CH_2Cl)_{\sim 12}$** was obtained (Scheme 1). The number of CH_2Cl groups was determined by MALDI−ToF mass spectrometry and ^1H NMR spectroscopy.

In the MALDI−ToF mass-spectra of **$TdG_2(CH_2Cl)_{\sim 12}$** two broad peaks were observed; the main peak corresponds to chloromethylated products with molecular weights ranging from 5300 to 5760 Da, indicating 8−17 chloromethyl groups. A second peak at 4000−4300 Da corresponds to $^3/_4$ of the molecular weight of the **$TdG_2(CH_2Cl)_{\sim 12}$**, due to the cleavage of one branch from the dendrimer during the mass-spectrometric measurement. This phenomenon has previously been observed and discussed in the literature.[32]

The average number of chloromethyl groups can also be calculated from their ^1H NMR spectra using the relative intensity of the aromatic protons at 7.6−6.2 ppm and the chloromethyl protons at 4.7−4.0 ppm. The analysis of the spectra indicates the presence of 12 CH_2-Cl groups, which is in a good agreement with the MALDI−ToF data. The broad signal at 4.7−4.0 ppm results from the different isomeric CH_2Cl groups on the dendrimer due to the statistical chloromethylation reaction, which causes an ortho-, meta- and para-substitution in the different aromatic rings.

The preparation of core-*mono*-shell nanoparticles using this chloromethylated dendrimer involved a two-step synthesis. First, EO was polymerized by living anionic polymerization to produce PEO with well-defined chain lengths. In a second step, these living PEO-chains were grafted onto the surface of **$TdG_2(CH_2Cl)_{\sim 12}$** by a nucleophilic substitution reaction (Williamson reaction) between the living anionic ends of the PEO-chains and the chloromethyl groups of the dendrimer (Scheme 2).

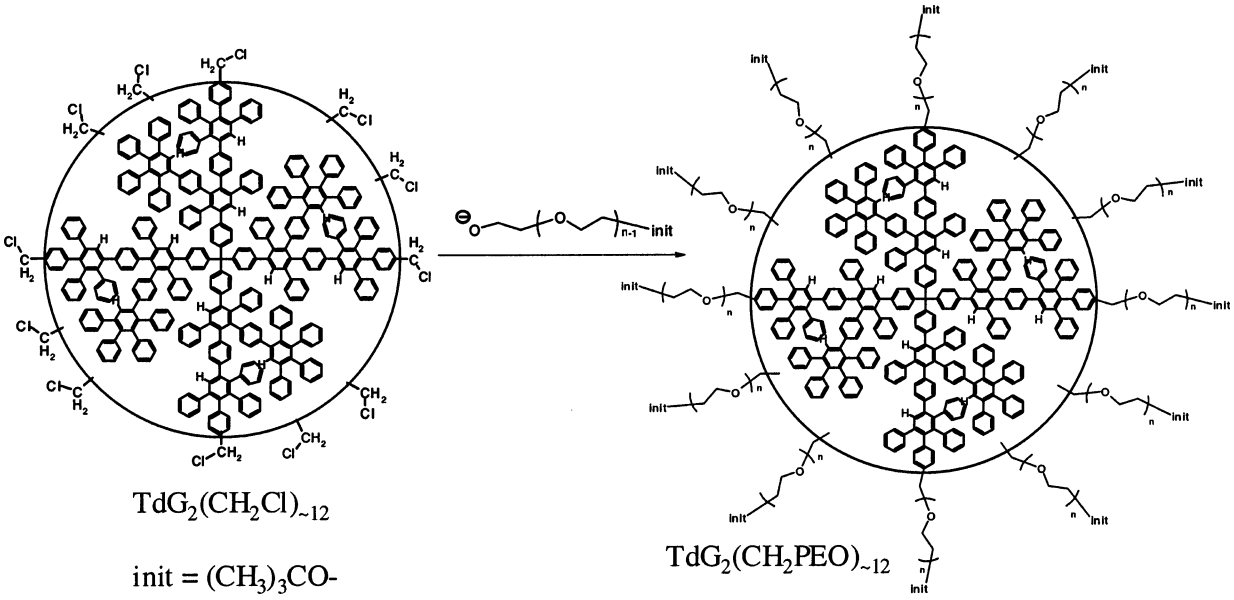
A 10-fold molar excess of PEO chains in respect to a chloromethyl group was used. The crude product was purified from unreacted single PEO chains using a stirred ultrafiltration cell equipped with a polyether sulfone membrane. After purification, the GPC elugrams (Figure 1) showed monodisperse products with a low polydispersity index.

The molecular weight of a single PEO chain was calculated theoretically and calculated from the ^1H NMR spectra by comparing the relative signal intensities of the *tert*-butyl (from the initiator of the EO polymerization) and the PEO protons (Table 1). The GPC data were obtained from aliquots taken from the reaction mixture before addition of the **$TdG_2(CH_2Cl)_{\sim 12}$**. A relatively high polydispersity index was obtained for low molecular weight PEO (Table 1, **1**), and nearly monodisperse PEO was obtained for a higher molecular weight (Table 1, **2** and **3**).

The molecular weights of the core−shell nanoparticles prepared by the "*grafting-onto*" process were determined by GPC and ^1H NMR spectroscopy (Table 1). M_n was calculated from the relative signal intensities of the protons of the dendrimer scaffold and of the PEO-chains. Since ^1H NMR spectroscopy does not use any standards or approximations, especially for **3** (Table 1), the results were considered as more reliable than the values obtained from GPC measurements.

From the molecular weights of the core-*mono*-shell nanoparticles and the single PEO chains we were able to determine the average number of the PEO-arms

Scheme 2. PEO Grafting onto the Surface of $TdG_2(CH_2Cl)_{\sim 12}$



attached to the dendrimer core (Table 1). ^{1}H NMR spectroscopy revealed that with increasing PEO-chain length, the degree of PEO-functionalization decreases. Only in the case of the very short PEO chains (440 Da, **1**, Table 1) was nearly complete conversion observed. In the other cases, the conversion was limited probably due to a steric hindrance caused by the already attached longer polymer chains which shield the reactive sites on the dendrimer surface. This aspect is supported by the results of a previous work describing the grafting reaction of polystyrene and polyisoprene monoanions on a polyetherketone chain. It has been shown that upon increasing the number of reactive sites, the conversion in the grafting reaction is limited by steric factors.[33]

One important characteristic of the core-*mono*-shell systems is the size of the particles, usually defined as the hydrodynamic radius (R_h) in a particular solvent.

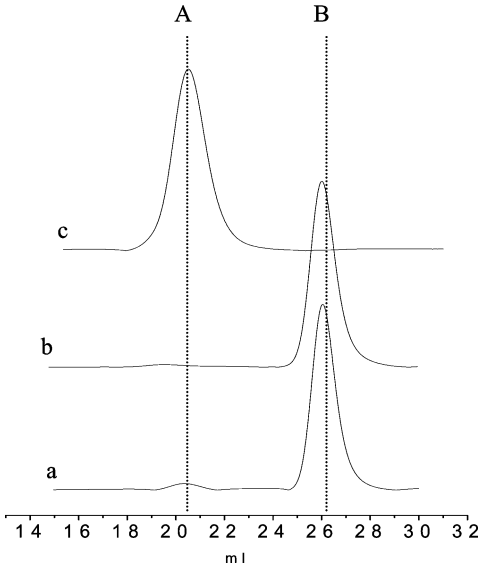


Figure 1. Purification of the product (**1** in Table 1) by ultrafiltration−GPC−elugrams (standard, PEO; eluent, DMF): (a) crude mixture before purification; (b) single PEO chains removed by ultrafiltration; (c) core−shell particles after purification from the single PEO-chains. (A) Appearance of the core-*mono*-shell particles. (B) Appearance of the single PEO-chains.

Table 1. Molecular Weight of the Single PEO Chains and the Obtained Core-*mono*-Shell Nanoparticles by ^{1}H NMR Spectroscopy (250 MHz, Room Temperature, CD_2Cl_2) and GPC (Standard, PEO; Eluent, DMF), Number of PEO-Arms per Dendrimer Molecule and Hydrodynamic Radius (R_h) by Dynamic Light Scattering (DLS) i THF

	PEO arms			core−shell nanoparticles				
	^{1}H NMR	GPC		^{1}H NMR		GPC			DLS R_h
expt no.	M_n	M_n	PDI	M_n	NA[a]	M_n	PDI	NA[a]	(nm)
1	440	340	1.33	10500	11.4	9400	1.69	8.9	4.0
2	9000	7300	1.06	91500	9.6	110000	1.08	11.6	10.4
3	14000	13700	1.09	130000	8.9	200000	1.34	13.9	12.0

[a] NA: number of PEO arms calculated using M_n obtained by ^{1}H NMR spectroscopy.

The R_h of the prepared core-*mono*-shell nanoparticles was measured by dynamic light scattering (DLS) in THF (Table 1). The radius increases from 4 to 12 nm with the extension of the PEO chains grafted onto the dendrimer surface (in comparison, the size of **TdG_2** was reported to be 3 nm).[28,34]

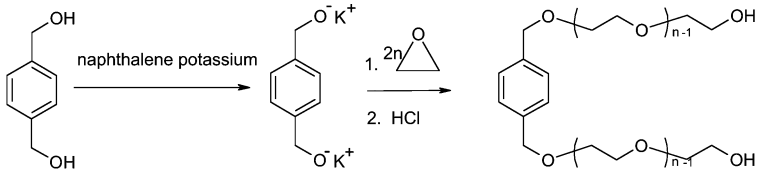
(b) Synthesis of Core-*mono*-Shell Nanoparticles Using the "*Grafting-from*" Method. In the "*grafting-from*" procedure, we applied a hydroxyfunctionalized dendrimer, which after deprotonation can serve as multifunctional initiator for an EO polymerization. While the number of attached chains is defined by the number of initiator sites on the dendrimer surface, the chain lengths of the attached PEO molecules cannot be determined because there is no possibility of cleaving them from the core and measuring them separately.

Grafting of EO from 1,4-Dihydroxymethylbenzene. Model Reaction. To check the feasibility of the reaction chosen, some model experiments for the polymerization of EO on 1,4-dihydroxymethylbenzene were performed (Scheme 3).

The molecular weights, theoretically calculated and determined from ^{1}H NMR spectroscopy and GPC measurements, are presented in Table 2.

The ^{1}H NMR spectra show that the methylene signal of 1,4-dihydroxymethylbenzene is shifted considerably from that in the PEO functionalized 1,4-dihydroxymethylbenzene. The absence of methylene signals of 1,4-dihydroxymethylbenzene in the spectrum of the final

Scheme 3. Polymerization of EO on 1,4-Dihydroxymethylbenzene



1,4-dihydroxymethyl benzene PEO-functionalized 1,4-dihydroxymethyl benzene

Table 2. Molecular Weights of the Products Prepared by Polymerization of EO from 1,4-Dihydroxymethylbenzene (^{1}H NMR Spectroscopy, 250 MHz, CD_2Cl_2, Room Temperature; GPC, Standard = PEO, Eluent = DMF)

expt no.	M_n		GPC	
	theoretical[a]	^{1}H NMR	M_n	PDI
4	1000	1200	1100	1.13
5	6000	6200	4800	1.27
6	20000	18700	19000	1.07

*gram EO/mol initiator.

product suggests that polymerization of EO proceeds from both available hydroxymethyl groups.

Grafting of Poly(ethylene oxide) from a Hydroxymethyl Functionalized Polyphenylene Dendrimer. Next we used a second-generation polyphenylene dendrimer with 16 hydroxymethyl groups on its surface, **$TdG_2(CH_2OH)_{16}$**, the synthesis of which has been reported elsewhere.[29] The target was a well-defined core-*mono*-shell nanoparticle comprising of a stiff polyphenylene core and flexible PEO-shell made by the polymerization of EO from the dendrimer surface.

Dendrimer **$TdG_2(CH_2OH)_{16}$** was first converted to a macromolecular anionic initiator **$TdG_2(CH_2O^-)_{16}$** by deprotonation with naphthalene potassium.[22] Anionic polymerizations of EO using multifunctional macroinitiators have previously been investigated.[35,36] It was found that the rate of polymerization ($R_p = k_p[O^-][M]$) was much lower than the rate of the proton exchange between protonated and deprotonated OH groups ($R_{exch} > R_p$, $R_{exch} = k_{exch}[O^-][OH]$). Therefore, the polymerization started from each functional group even when only 30% of hydroxyl groups were deprotonated. This suggests that all 16 hydroxymethyl groups on the dendrimer can act as efficient initiators (Scheme 4).

The obtained core-*mono*-shell molecules were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, GPC, DSC, and DLS. Molecular weights (Table 3), calculated from ^{1}H NMR spectra, were much higher than the M_n values obtained by GPC. Such "underestimation" of the molecular weights determined by GPC has already been reported for calixarene star polymers[37] and poly(methyl methacrylate) star polymers[38] and is attributed to the difference in shape between the stars and the linear PEO standards used in the GPC measurements. Monomodal distributions were observed in all cases.

To measure the hydrodynamic radius (R_h) of the prepared core-*mono*-shell nanoparticles, we performed DLS measurements in THF and water. The results showed that an increase in size accompanies the increase in molecular weight as well as the increase in the PEO chain length. An exception is **10** (in water) as here the R_h is smaller than the R_h of **9**. It should be pointed out that the R_h values in water are approximately twice as large as those in THF. This fact can be explained by a more stretched conformation of PEO in water than in THF.[39] DLS of **7** resulted in particles with R_h up to 200 nm indicating an aggregation. Because of the shorter PEO chains, the separation of the hydrophobic cores is decreased which thus facilitates aggregation. However, as even a very small number of larger aggregates results in a much more intense signal in comparison to the single dendrimers, a quantification is impossible. In this case GPC measurements are more reliable, and as they fail to reveal aggregates, it can be assumed that they are present only in a negligible amount.

Synthesis of Core-*double*-Shell Dendrimers. A more demanding approach is the synthesis of core-*double*-shell systems containing layers with different polarity and flexibility. In this approach we can only apply the "*grafting-onto*" method using amphiphilic diblock copolymers as in a "*grafting-from*" process with alcoholates generated on the periphery of the dendrimers other monomers than EO or propylene oxide cannot be initiated. Therefore, the combination of monomers becomes very limited. As it was shown above, the drawback of the "*grafting-onto*" method is that in the case of longer polymer chains the shielding effect of the already connected polymer chains limits the number of attachable arms. To minimize this effect, relatively short copolymer chains were synthesized (Table 4) and their attachments to a **TdG_2** with fewer functionalities (**$TdG_2(CH_2Cl)_{\sim 8}$**) investigated.

PI-*b*-PEO and PS-*b*-PEO blockcopolymers were chosen as copolymers in the "*grafting-onto*" process to obtain core-*double*-shell structures with layers of different polarity. They were synthesized by the polymerization of EO using PI−O^-K^+ or PS−O^-K^+ as polymeric initiators.[40] Nearly monodisperse homo and diblock copolymers were obtained and characterized by GPC, ^{1}H NMR spectroscopy and MALDI−ToF mass-spectrometry (Table 4).

The composition of PS−OH and PS-*b*-PEO as well as the microstructure of the polyisoprene block (1,4-, 10%; 1,2-, 30% or 3,4-, 60%) were determined by ^{1}H NMR spectroscopy. In the case of PS−OH and PS-*b*-PEO, we calculated the molecular weight of the polymers using the relative intensity of the aromatic protons of polystyrene at $\delta = 7.3-6.3$ ppm and those of the initiator at $\delta = 0.9-0.6$ ppm. However, this method was not applicable in the case of PI−OH and PI-*b*-PEO due to overlapping signals of the initiator and the PI protons. The measurement of the molecular weight was restricted to GPC and MALDI−ToF spectrometry.

For the *grafting-onto* reaction (Scheme 5) we used two second-generation polyphenylene dendrimers with an average number of 8 (**$TdG_2(CH_2Cl)_{\sim 8}$**) and 12 (**$TdG_2(CH_2Cl)_{\sim 12}$**) chloromethyl groups on their surface (see Experimental Part). The synthesis is essentially the same as that in Scheme 2.

To involve all chloromethyl groups in the etherification reaction (Williamson reaction), a 5-fold molar excess of block copolymer chains in respect to the chloromethyl groups was used. The crude products (elugram no. 3, Figure 2) were purified from the block copolymers by

Scheme 4. Poly(ethylene oxide) "*Grafting-from*" the Surface of $TdG_2(CH_2OH)_{16}$

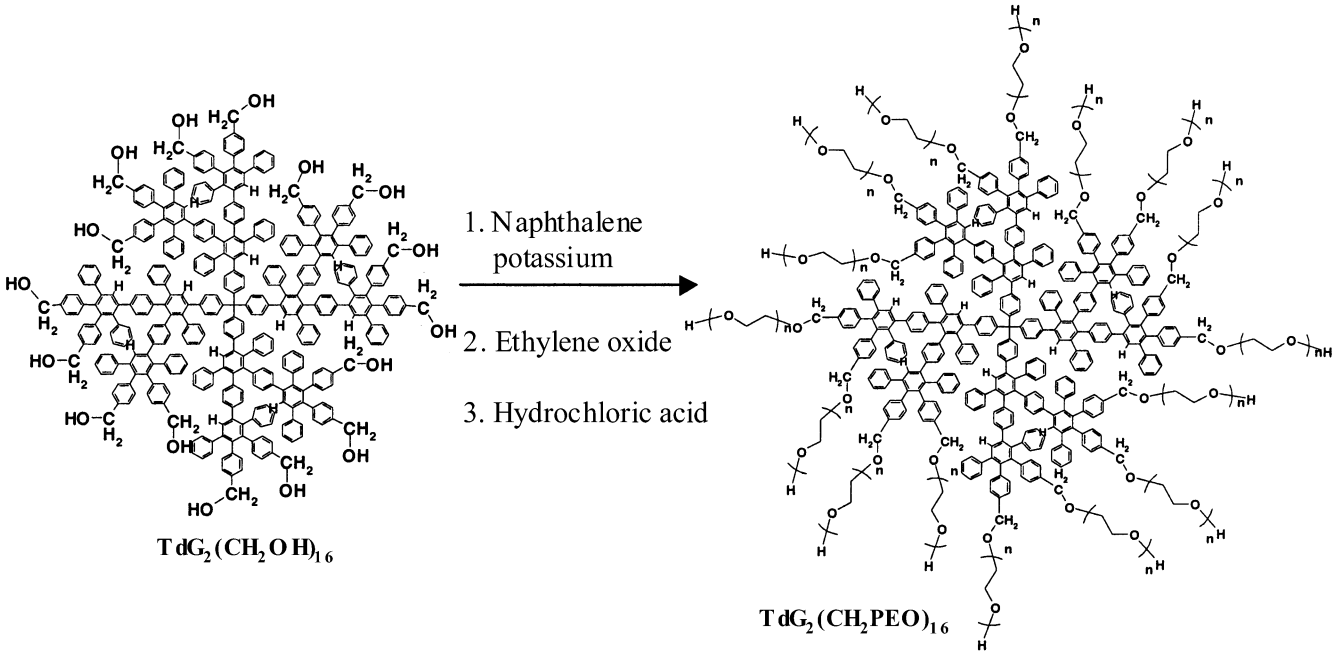


Table 3. Molecular Weights of the Core-*mono*-Shell Particles Prepared by Grafting of EO from $TdG_2(CH_2OH)_{16}$ (^{1}H NMR, 250 MHz, CD_2Cl_2, Room Temperature; GPC, Standard = PEO, Eluent = DMF; DLS in THF and Water)

expt no.	^{1}H NMR M_n	GPC		DLS, R_h (nm)	
		M_n	PDI	THF	water
7	8700	4100	2.17	aggregates	aggregates
8	50200	17000	1.24	*a*	5.5
9	353000	75700	1.34	8.6	15.8
10	1040 000	120000	1.58	28.8	10.0

[a] Out of the range of the instrument.

Table 4. Molecular Weight and Polydispersity Index of the Obtained Homopolymers and Block Polymers (^{1}H NMR, 250 MHz, CD_2Cl_2, Room Temperature; GPC, Standards = PS or PI, Eluent = THF; MALDI−ToF−MS, Dithranol Matrix, Ag^+(PI−OH), without Salt (PI-*b*-PEO), Li^+(PS−OH), K^+(PS-*b*-PEO))

	GPC		^{1}H NMR	MALDI−ToF−MS	
product name	M_n	PDI	M_n	M_n	PDI
PI−OH	700	1.11		890	1.09
PI-*b*-PEO	1400	1.12		1400	1.15
PS−OH	2200	1.08	2200	2400	1.08
PS-*b*-PEO	6000	1.07	5400	5700	1.03

preparative GPC (elugram no. 4, Figure 2) resulting in the products **D(PEO—PS)12** and **D(PEO—PI)12** with a low polydispersity index (1.05−1.13).

The molecular weights of the prepared core−shell nanoparticles were determined using GPC and ^{1}H NMR spectroscopy (see Table 5). Molecular weights calculations using ^{1}H NMR spectroscopy were based on the relative intensity of the aromatic protons of the dendrimer at δ = 7.5−6.3 ppm and the PI protons at δ = 5.2−4.5 ppm in the spectra of **D(PEO—PI)8** and **D(PEO—PI)12**. However, in the case of PS-*b*-PEO substituted dendrimers the signals of the aromatic protons of polystyrene overlapped with those of the dendrimer. In these examples we used the relative intensity of the methylene protons (dendrimer-CH_2−Cl) and aromatic protons of the dendrimer in the spectra of $\mathbf{TdG_2(CH_2Cl)_{\sim 8}}$ or $\mathbf{TdG_2(CH_2Cl)_{\sim 12}}$ and applied that ratio to the spectra of **D(PEO—PS)8** and **D(PEO—PS)-12** in order to calculate the integral part of aromatic protons of the dendrimer and those of the polystyrene.

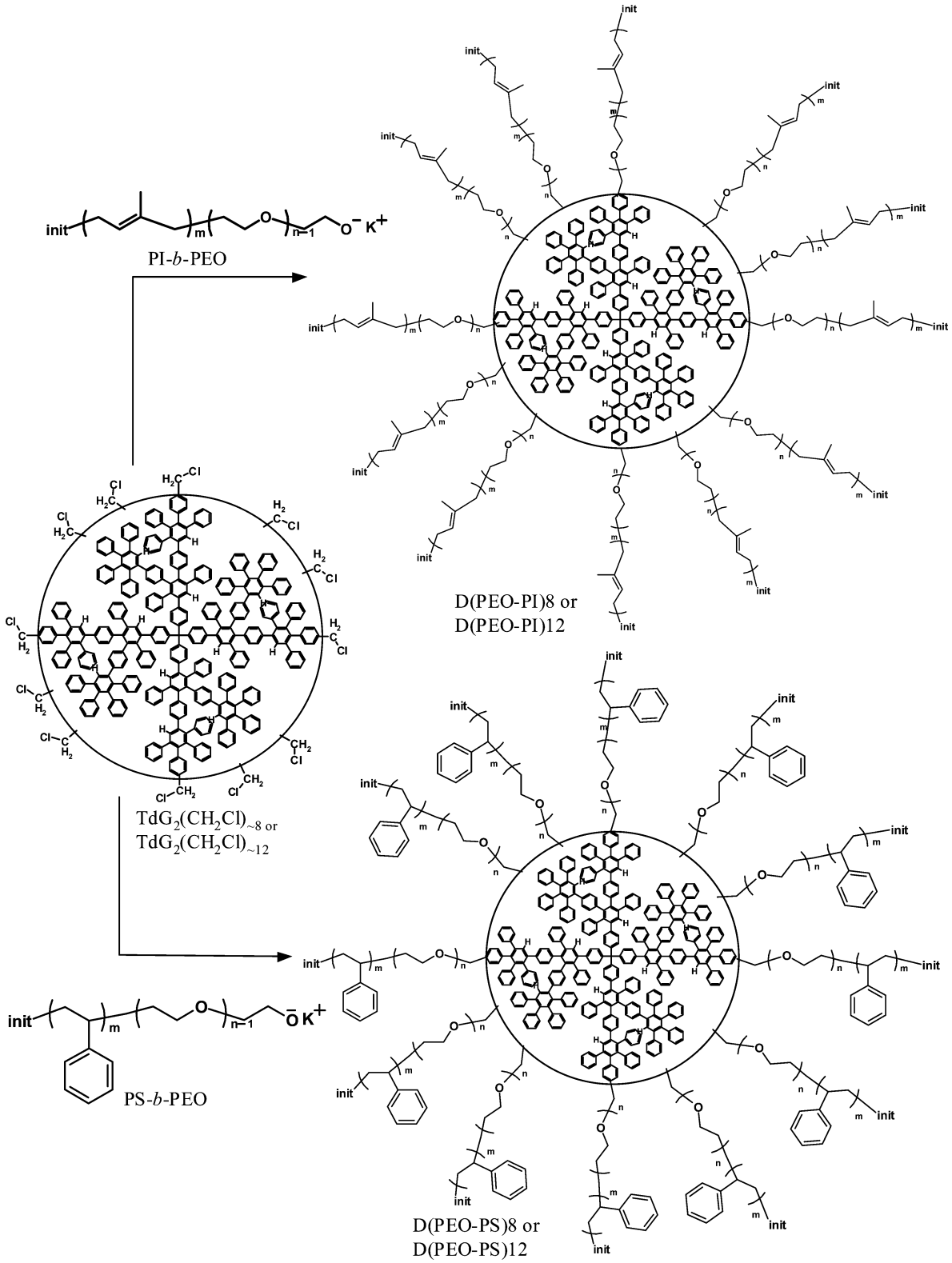
Similar to the grafting reactions mentioned above, complete substitution reactions were observed only in the case of a lower degree of functionalization (∼8) and shorter block copolymer chains (number of arms 8.4 for **D(PEO—PI)8**). Increasing the number of the functional groups (∼12) was accompanied by a decreasing the number of attached arms (10.0 in the case of **D(PEO—PI)12**). Longer copolymer chains resulted in an incomplete substitution reaction as well. Only 5.8 arms were detected for **D(PEO—PS)8** and 8.9 for **D(PEO—PS)12**.

To obtain the molecular weights of the prepared core−shell macromolecules, MALDI−ToF mass-spectrometry was applied. Unfortunately, only a mass spectrum of the system **D(PEO—PI)8** with the lowest molecular weight was successfully obtained (Figure 3) proving a similar molecular weight as calculated by NMR spectroscopy. The possible reasons for the failure of this method are the higher molecular weights combined with the complexity of the structure. It is known that with increasing molecular weight, the signal-to-noise ratio in MALDI−ToF−MS deteriorates and therefore, spectra of block copolymers with a mixed composition are difficult to measure.[41]

One important characteristic of the core-*double*-shell systems is the hydrodynamic radius (R_h) in a particular solvent. The R_h of the prepared core-*double*-shell nanoparticles was measured by DLS in THF solutions (Figure 4). It is noteworthy that the R_h of the core was reported to be 3 nm[28,34] and this radius increases with the increasing length of the diblock chains and the number of the arms grafted onto the dendrimer surface to 7.3 nm. The results once again show that an increase in molecular weight is accompanied by an increase in size (Figure 4).

The measurements at low angles (60 and 90°) deviated substantially from the linear fit in the cases of **D(PEO—PI)12** and **D(PEO—PI)8**. This error had to be attributed to the technical limit of the used particle

Scheme 5. Synthesis of the PI-*b*-PEO and PS-*b*-PEO Substituted Polyphenylene Dendrimers D(PEO-PS)12(8) and D(PEO-PI)12(8)



sizer (ALV 5000 Correlator (Malvern Instruments)) being 5 nm.

It is expected that such onion-type dendrimers with hydrophilic and hydrophobic shells can adjust their surface polarity to the polarity of the solvent by rearranging their different blocks in such a way that always the layer with the same polarity as the solvent forms the outer shell.

This was studied for thin layers of **D(PEO—PS)12** by contact angle measurements. Several solutions of **D(PEO—PS)12** in solvents of different polarity: THF/water and THF/hexane were prepared and spin-coated on a silicon-wafer substrates. Thickness of the layer was adjusted by varying the concentration of **D(PEO—PS)12** in THF (1.0, 0.1, and 0.01 g/L) (rotation of the spin-coater: 3000 rpm). Surface morphologies of

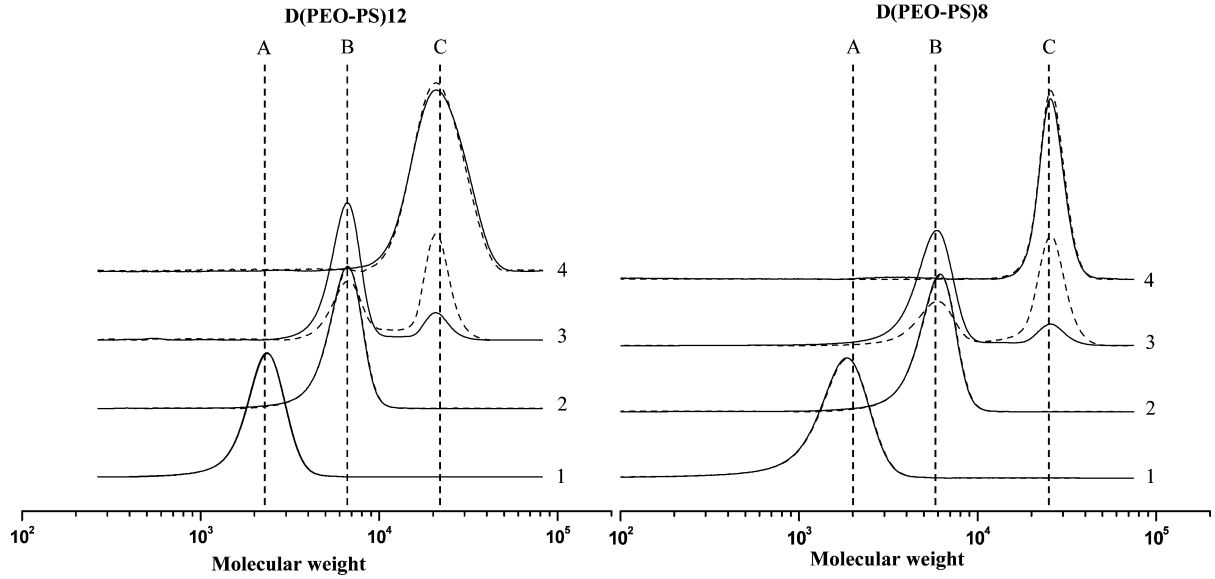


Figure 2. GPC curves (PI and PS standards, THF eluent; RI detector, solid line; UV-detector (255 nm), dashed line): Left: **D(PEO—PS)12** (1, PS−OH; 2, PS-*b*-PEO; 3, **D(PEO—PS)12** crude; 4, **D(PEO—PS)12** purified). Right: **D(PEO—PI)12** (1, PI−OH; 2, PI-*b*-PEO; 3, **D(PEO—PI)12(8)** crude; 4, **D(PEO—PI)12** purified).

Table 5. Number of Arms and Molecular Weight of Obtained Core−Shell Macromolecules (^{1}H NMR, 500 MHz, $C_2D_2Cl_4$, 373 K; GPC, Standards PS or PI; Eluent, THF)

sample	parameter	^{1}H NMR spectroscopy	GPC[a]
D(PEO—PI)8	M_n	**17100**	12600
	no. of arms	**8.4**	5.2
D(PEO—PS)8	M_n	**38300**	28500
	no. of arms	**5.8**	4.1
D(PEO—PI)12	M_n	**19500**	17100
	no. of arms	**10.0**	8.3
D(PEO—PS)12	M_n	**56000**	26000
	no. of arms	**8.9**	3.6

[a] PDI: **D(PEO−PI)8**, 1.13; **D(PEO−PS)8**, 1.05; **D(PEO−PI)12**, 1.07; **D(PEO−PS)12**, 1.05.

D(PEO—PS)12 layers were examined by AFM shown in Figure 5.

Even single dendrimers could be visualized and the diameter determined as ∼15 nm, which is in perfect agreement with R_h = 7.3 nm found by DLS (Figure 4). The root-mean-square roughness values for the **D(PEO—PS)12** films from 0.01, 0.1, and 1.0 g/L solutions are 0.327, 0.198, and 0.180 nm, respectively, indicating that a higher **D(PEO—PS)12** concentration is more favorable for the formation of uniform surface morphologies. Complete coverage of the substrates' surface was reached at 1.0 g/L (Figure 5 B) and this concentration was used for preparation of four solutions of **D(PEO—PS)12** in THF with 5 and 1%v/v water as well as 5 and 30% v/v hexane. Thickness of the layers prepared out of these solutions was determined by ellipsometry (null-type ellipsometer).

To study the influence of the polarity of the solvent used in the spin-coating process on the surface polarity of the dendrimer contact angle measurements were used. The results are summarized in Table 6.

The contact angle measurements indicated that an increase of the polarity of the media (Table 6. nos. 1 and 2) is accompanied by a decrease of the contact angle and vice versa, (Table 6. nos. 4 and 5). The obtained results confirmed that an amphiphilic core-*double*-shell macromolecules can rearrange its structure depending on the polarity of the surrounding media. Nonpolar solvents will provoke a less polar surface (PS), while polar solvents will induce a more polar outer layer (PEO). This effect is not very pronounced, but nevertheless significant. The week effect can be explained by the relatively short PEO chains in comparison to the PS-block. This limits the possibility of the PEO blocks directly attached to the core and fully cover the hydrophobic polystyrene chains.

Conclusions

"*Grafting-onto*" and "*grafting-from*" methods were used for the synthesis of core−shell nanoparticles. In the "*grafting-onto*" process a statistically functionalized dendrimer GPC and light scattering confirm that the resulting core-*mono*-shell nanoparticles exhibit low polydispersities. The "*grafting-onto*" method allows for a full characterization of the products obtained in terms of number and length of the PEO-arms. The drawback of this method is a shielding effect of already connected polymer chains limiting the number of attachable arms. The "*grafting-from*" method avoids this limitation allowing the growth of the chains from all initiating sites on the dendrimer. However, the products obtained by this method could not be fully characterized since the length of a single polymer chain attached to the dendrimer cannot be determined.

These new stiff-core flexible-shell nanoparticles are more than one magnitude smaller than comparable core−shell latex particles. We suggest that such particles will serve as model compounds for all applications of organic nanoparticles where size of the particle plays an important role for the properties. Thus, they are currently investigated as supports for metallocenes catalyzing the olefin polymerization. It is expected that the obtained results can improve the understanding of the role of the established organic supports[9] in the heterogenized olefin polymerization. In earlier experiments a drastic influence of the supports size on the polymerization behavior was observed as indicated by an increase in the activity and productivity of the catalysts.[42]

Furthermore, such core−shell structures have a high tendency toward a well-controlled self-assembly on

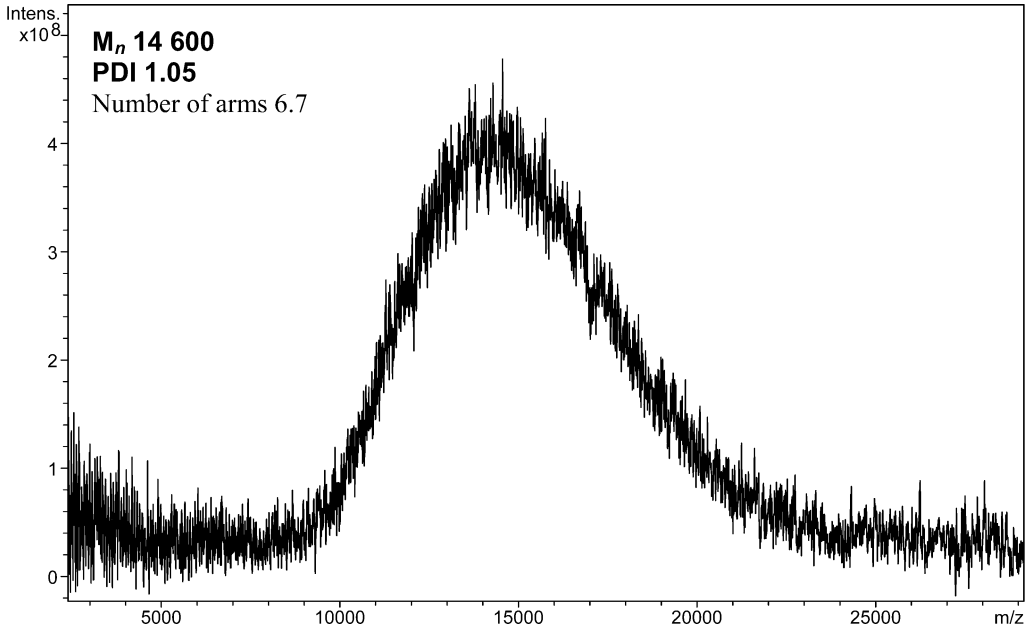


Figure 3. MALDI−ToF mass-spectrum of **D(PEO—PI)8** (dithranol matrix, Na^+).

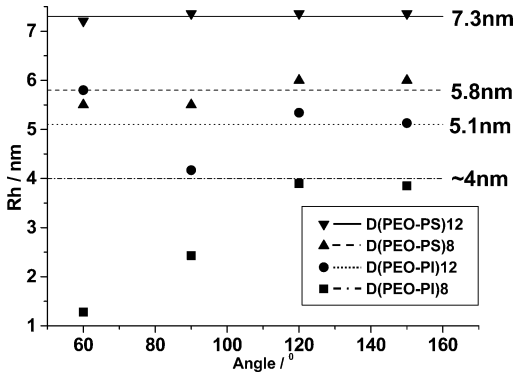


Figure 4. DLS (R_h in THF) of the obtained core-*double*-shell nanoparticles.

surfaces, demonstrated in some first AFM experiments.

The incorporation of such particles as model compounds for impact modifiers in polymers is currently performed and should allow for an investigation of the influence of the nanoparticle size on the material (mechanical) properties (e.g., impact strength).

Finally, the herein-described "*grafting-onto*" approach was extended to more complex onion-type architectures such as *double*-shell structures by using block copolymers (PI-*b*-PEO, PS-*b*-PEO) instead of homopolymers. Remarkably, a "*sandwich*" structure with a polar (hydrophilic) layer between two hydrophobic layers was obtained. Such materials may serve as nanocontainer allowing for a selective loading of polar compounds in the hydrophilic PEO shell. Of particular interest is the behavior of these structures in solvents of different polarity. One can expect that these systems behave like so-called Janus micelles,[43] adjusting their surface polarity to the solvent, in nonpolar media, the polyisoprene or polystyrene at the surface and in polar media the PEO blocks. This was already confirmed as first contact angle measurements of **D(PEO—PS)12** layers on a SiO_2-surface proved that an increase in media polarity provoked conformational changes getting the PEO-blocks on the surface of the particles, while the PS blocks form the outer layer in less polar media.

Comparing our dendrimers to other structures it should be emphasized that polyphenylene dendrimers are rigid and shape persistent. The functionalities are locally fixed on the surface of the dendrimer and cannot disappear in the core by conformational movements. The globular structure cannot be changed by a solvent or by swelling. As a major advantage it can be considered that due to the stiffness of the core all changes of size, conformation or surface polarity can be exclusively attributed to the shell. Furthermore, they are due to the absence of amide bonds or ester linkage extremely hydrophobic, which maximizes the differences in polarity between the core and a hydrophilic shell. This should facilitate the systematic investigation of solvent effects on the conformation but also of the incorporation of different compounds as drugs or dyes into the core−shell architecture.

Experimental Part

Materials. All materials for the synthesis of dendrimers were commercial products (Aldrich, Fluka, Fischer, Strem, and Acros) and were used as obtained. All solvents were HPLC grade and were purified according to procedures published elsewhere.[44] *sec*-Butyllithium (1.3 M) solution (Fluka) and *n*-butyllithium (1.6 M) solution (Acros) were used as received. Isoprene and styrene (Fluka) were distilled over *n*-butyllithium and fluorenyllithium, respectively, in a Schlenk-tube prior to use. Ethylene oxide (Fluka) was stored over CaH_2 and distilled over *n*-butyllithium in a Schlenk-tube prior to use. Naphthalene potassium was synthesized according to a procedure described elsewhere.[45] Potassium *tert*-butoxide solution (1 M in THF, Fluka) was used as received.

Instruments. Gel permeation chromatography (GPC) analyses were performed in (*i*) water with a Waters pump model 590, detectors RI ERC-7510 and UV−vis Soma S-3702 (255 nm), temperature = 25 °C, standard = PEO, concentration = 1.000 g/L, flow rate = 0.8 mL/min, columns "TSK−Gel" G3000PW_{XL} 500, 10^4, and 10^6 Å, and particle size 13 μm, (*ii*) DMF with a Waters pump model 590, detectors RI ERC-7512 and UV−vis Soma S-3702 (255 nm), temperature = 60 °C, standards = PEO or PS, concentration = 1.000 g/L, flow rate = 1.0 mL/min, columns "MZ-Gel" SDplus 500, 10^4, and 10^6 Å, and particle size = 10 μm, and (*iii*) THF with a Waters pump model 515, detectors RI 101 ERC and UV−vis S-3702 Soma (255 nm), temperature = 30 °C, standards = PS or PI,

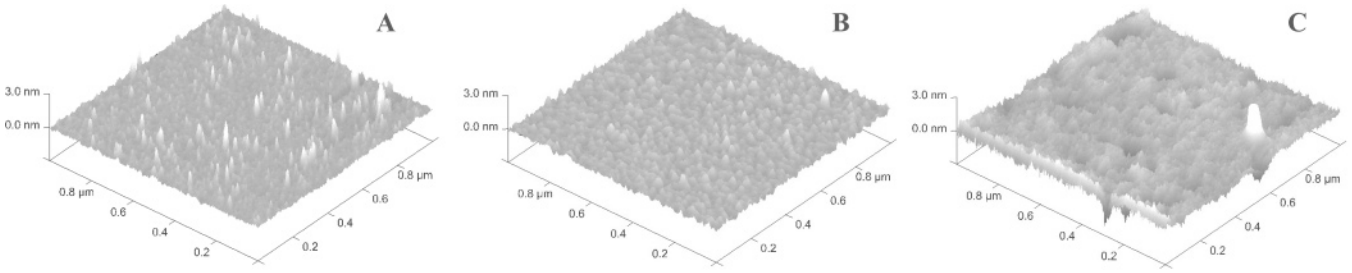


Figure 5. Surface topographs of **D(PEO—PS)12** layers deposited by spin-coating technique at 3000 rpm on a SiO_2 surface (from THF with the following concentrations: (A) 0.01, (B) 0.1, and (C) 1.0 g/L).

Table 6. Composition of the Solvent, Thickness, and Contact Angle of the D(PEO-ps)12 Layers Prepared by Spin-Coating

no.	solvent	ratio [v/v (%)]	thickness (nm)[a]	contact angle θ_{water} (grad)[b]
1	THF/water	95/5	38	63.1
2	THF/water	99/1	36	63.7
3	THF	100	35	64.9
4	THF/hexane	95/5	36	66.0
5	THF/hexane	70/30	38	66.9

[a] Standard deviations less than ±3 nm. [b] Standard deviations less than ±1°.

concentration = 1.000 g/L, flow rate = 1.0 mL/min, columns "MZ-Gel" SDplus 500, 10^4, and 10^6 Å, and particle size = 10 µm.

^{1}H NMR spectra were recorded on a "Bruker-Spectrospin" (250 MHz) at room temperature.

^{13}C NMR spectroscopy was performed on a "Bruker AMX 300" spectrometer at room temperature.

DLS measurements were performed on an ALV 5000 Correlator (Malvern Instruments), ALV-SP81 goniometer, Avalanche photodiode laser krypton-ion-laser 647.1 nm, Spectra Physics model Kr 2025.

MALDI—ToF mass spectrometry measurements were performed on VG ZAB2-SE-FPD Spectrofield, Bruker Reflex I (MALDI−ToF) and Bruker Reflex II (MALDI−ToF) mass spectrometers.

DSC. Mettler Digital Scanning calorimeter 300, with a heating rate of 10 K/min.

TGA. Mettler 300 Thermogravimetric analyzer.

AFM Measurements. The samples were scanned with a Dimension 3100 model (Veeco, Santa Barbara, CA) at room temperature under ambient conditions. Single beam silicon cantilevers (Olympus OMCL-AC160TS-W2 tapping mode) with spring constants of ~45 N/m and resonant frequencies of ~300 kHz were used. All topographs were recorded in tapping mode. The resulting images have been flattened and plane fitted, some have been median and low-pass filtered.

Ellipsometry was performed on a null-ellipsometer with external reflection mode. The laser for ellipsometry measurements had a wavelength of 632.8 nm (Uniphase, 5 mW).

Contact angle goniometry was carried out on DSA10-MK2 model (Krüss GmbH, Hamburg, Germany) contact angle measuring system with full computer control and automated image analysis system. Drops of liquid of known volume (1 µL) were applied from a microsyringe to the surface of the test material. The reported values are the average of at least 8 drops placed and measured on different parts of the sample surface. The precision of measurements was below ±1°.

Preparation of the Thin Films. D(PEO—PS)12 was dissolved in 1% and 5% v/v water/THF and 5% and 30% v/v hexane/THF solutions with concentration 1 g/L. The solutions were ultrasonicated for 10 min, filtered through syringe filters (Millex, Millipore Corp., Bedford, MA) with a pore size of 5 µm, and ultrasonicated for another 5 min. Thin **D(PEO—PS)-12** films were prepared by spin-coating the solutions onto cleaned,[46] hydrophilic silicon wafer substrates. Spin-coating was typically performed at a spinning speed of 3000 rpm. Freshly prepared layers were dried under dynamic vacuum for a period of 10 h. Ellipsometry measurements revealed film thickness of around 40 nm.

Synthesis. All reactions were carried out under an inert atmosphere of argon unless stated otherwise.

1. **Chloromethylation of TdG_2(—H)$_{16}$.** In a Schlenk tube (250 mL) equipped with a magnetic stirrer and a reflux condenser was dissolved **TdG_2(—H)$_{16}$** (2.00 g, 0.42 mmol) in dry dichloromethane (140 mL). Chloromethyloctyl ether (32.6 mmol (80 equiv) or 16.3 mmol (40 equiv) per dendrimer molecule) and $SnCl_4$ (8.16 or 4.8 mmol) (20 equiv, 1/4 equiv per equiv of chloromethyloctyl ether) were added. The color of the reaction mixture turned brownish-red. The reaction mixture was stirred at 40 °C for 7 h, followed by addition of dichloromethane (80 mL) and concentrated hydrochloric acid (6 mL). After being washed with water (6 × 300 mL), the organic layer was dried over magnesium sulfate, filtered, concentrated to 40 mL, and precipitated in 600 mL of diethyl ether. The white precipitate was filtered and dried at 60 °C. The product was extracted with ethanol in a Soxhlet apparatus for 24 h. Yield: 1.91 g (83%).

^{1}H NMR (250 MHz, $C_2D_2Cl_4$, room temperature), δ, ppm: 7.6−6.2 (overlapping broad peak, H $_{arom}$), 4.8−4.0 (m, CH_2Cl).

MALDI—ToF (matrix dithranol, sodium triflate) *m/z*: **TdG_2-(CH_2Cl)$_{\sim 12}$** broad peak 5300−5800 (100%, M^+), broad peak 4000−4350 (3/4 of the dendrimer, M^+ − one dendron); **TdG_2-(CH_2Cl)$_{\sim 8}$** broad peak 5100−5400 (100%, M^+), broad peak 3800−4050 (3/4 of the dendrimer, M^+ − one dendron).

2. PEO Grafting onto $TdG_2(CH_2Cl)_{\sim 12}$. Variable amounts (Table 7) of EO were added to a THF solution of potassium *tert*-butoxide (100 mL). The polymerization (high-vacuum Schlenk technique) was carried out in THF at 40 °C for 6, 16, or 69 h respectively (**1**, **2**, **3**). Aliquots (50 mL) were taken from each reaction mixture for determination of MW of the single PEO chains prior to addition of **$TdG_2(CH_2Cl)_{\sim 12}$**. Then **TdG_2-(CH_2Cl)$_{\sim 12}$** was added and the reaction was continued at 40 °C for 48, 69, or 96 h respectively (**1**, **2**, **3**). The reaction mixtures and the samples taken were precipitated from a 15-fold excess of hexane. The excess PEO-chains were removed by filtration in a stirred ultrafiltration cell "Millipore" model 8050 equipped with a poly(ether sulfone) membrane cutoff 50 000 in the first case and 100 000 in the last two cases. The compounds were freeze-dried overnight and then dried for 2 days under vacuum.

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ_H, ppm: 7.6−6.4 (overlapping broad peak, H $_{arom}$), 4.6−4.1 (m, CH_2Cl), 3.8−3.2 (s, −CH_2CH_2O−), 1.2−1.0 (s, (CH_3)CO−).

^{13}C NMR (75 MHz, $CDCl_3$, room temperature), δ_C, ppm: 137.5, 135.1, 130.0, 127.7, 113.0, 109.5, 72.8, 72.3, 70.4, 69.9, 69.2, 61.3, 40.5.

GPC (standard, PEO; eluent, DMF):

expt no.	M_n	PDI
1	9400	1.69
2	110000	1.08
3	200000	1.34

DLS R_h [nm]: 4.0 (**1**), 10.4 (**2**), and 12.0 (**3**).

TGA/DSC. Decomposition starts at 150 °C with maximum rate of degradation at 380 °C and ended at 550 °C. T_g (**1**) = 46.5 °C, T_g (**2**) = 54.8 °C, and T_g (**3**) = 57.6 °C

Table 7. Amounts of the Reagents and Yields of the Core-*mono*-Shell Nanoparticles Obtained by the "*Grafting-onto*" Method

expt no.	*t*-BuOK (mol × 10^{-3})	ethylene oxide (mol × 10^{-2})	$TdG_2(CH_2Cl)_{\sim 12}$ (mol × 10^{-6})	Ph−CH_2−Cl (mol × 10^{-5})	yield (g; %)
1	2.2	5	9.1	10.9	1.9; 84
2	1.3	29	5.5	6.5	12.6; 99
3	1.3	44	5.5	6.5	17.8; 92

Table 8. Amounts of the Reagents and Yields of the Products Obtained by Polymerization of EO on 1,4-Dihydroxymethylbenzene (Model Reaction)

expt no.	1,4-dihydroxymethylbenzene (mol × 10^{-4})	Ph−CH_2−OH (mol × 10^{-4})	ethylene oxide (mol × 10^{-3}	yield (g; %)
4	8.50	17.0	19.3	1.07; 99
5	5.85	11.7	80.1	3.62; 98
6	1.75	3.5	80.1	3.43; 96

Table 9. Amounts of the Reagents and Yields of the Products Obtained by the "*Grafting-from*" Procedure

expt no.	$TdG_2(CH_2OH)_{16}$ (mol × 10^{-6})	Ph−CH_2−OH (mol × 10^{-5})	ethylene oxide (mol × 10^{-2})	yield (g; %)
7	9.3	15	0.34	0.12; 60
8	9.3	15	1.7	0.64; 80
9	4.7	7.5	3.4	1.28; 84
10	4.7	7.5	8.5	2.83; 75

3. Polymerization of EO on 1,4-Dihydroxymethylbenzene (Model Reaction). A high-vacuum Schlenk technique for anionic polymerization was used for this synthesis. A variable amount of 1,4-dihydroxymethylbenzene (Table 8) was titrated with a THF solution of naphthalene potassium for 2 h at 22 °C. The calculated amount of EO was added and the temperature was increased to 40 °C for 20, 24, and 64 h, respectively (**4**, **5**, and **6**). The reaction was quenched with an excess of degassed acetic acid. The product was precipitated in hexane, collected by filtration, and dried under vacuum for 2 days.

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ, ppm: 7.31 (s, H_{arom}), 4.52 (s, PhCH_2O), 3.8−3.3 (s, −CH_2CH_2O−) [for comparison ^{1}H NMR of 1,4-dihydroxymethylbenzene, δ 7.34 (s, H_{arom}), 4.65 (s, PhCH_2OH)].

GPC (standard, PEO; eluent, DMF):

expt no.	M_n	PDI
4	1100	1.13
5	4800	1.27
6	19000	1.07

4. PEO Grafting from $TdG_2(CH_2OH)_{16}$. The high-vacuum Schlenk technique for anionic polymerization was used. Naphthalene potassium was obtained by addition of a solution of naphthalene (0.096 g, 0.75 mmol) to a potassium mirror (0.147 g, 3.8 mmol) in THF (50 mL). The reaction was performed at 22 °C for 2 h. The reaction mixture turned dark green. After filtration the solution was used for titration of $TdG_2(CH_2OH)_{16}$ (Table 9) in THF (100 mL). The titration was carried out at 22 °C until the green color slowly disappeared (approximately 10 min). When the titration was complete, the reaction mixture was cooled to 5 °C and calculated amounts of EO were added. The temperature was slowly increased to 40 °C, and the polymerization was carried out at this temperature for 48 h. The reaction was quenched with an excess of degassed hydrochloric acid. The obtained products were precipitated in hexane, collected by filtration, and dried in vacuo for 2 days.

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ_H, ppm: 7.6−6.2 (overlapping broad peak, H_{arom}), 4.8−4.0 (m, CH_2Cl), 3.8−3.2 (s, −CH_2CH_2O−).

^{13}C NMR (390 MHz, $CDCl_3$, room temperature), δ_C, ppm: 137.8, 134.6, 126.4, 123.6, 121.5, 120.9, 110.6, 109.2, 108.0, 73.6, 72.8, 70.5.

GPC (standard, PEO; eluent, DMF):

expt no.	M_n	PDI
7	4100	2.17
8	17000	1.24
9	75700	1.34
10	120000	1.58

DLS R_h [nm]:

expt no.	THF	water
7	aggregates	aggregates
8	*a*	5.5
9	8.6	15.8
10	28.8	10.0

[a] Out of the range of the instrument

TGA/DSC. Decomposition starts at 200 °C with maximum rate of degradation at 400 °C and ended at 500 °C. T_g = 61 °C.

5. Synthesis of Diblock Copolymers. All reactions were carried out under high vacuum using a high-vacuum Schlenk technique for anionic polymerization. The synthesis of PI-*b*-PEO and PS-*b*-PEO was done by an established synthetic strategy,[40] detailed procedures of which are given below.

5.1. Synthesis of End-Hydroxy-Functionalized Polyisoprene (PI—OH). Isoprene (10.0 mL, 100 mmol) and THF (100 mL) were consecutively cryodistilled into a reactor. *sec*-Butyllithium (10.5 mL, 6.8 mmol) was added, and polymerization was performed for 3 h at −77 °C. The color of the reaction mixture turned to yellow. Ethylene oxide (4.5 mL, 91 mmol) was distilled into the reactor and the mixture was warmed to 50 °C for 30 min. An excess of hydrochloric acid was added in order to terminate the reaction. The product was precipitated in water and extracted with diethyl ether. The organic layers were collected and dried over magnesium sulfate and filtered. The solvent was evaporated and the residue was dried at 40 °C under dynamic vacuum for 48 h. Yield: 6.23 g (91%).

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ, ppm: 5.9−5.6 (q, −C*H*=CH_2), 5.2−4.8 (q, −CH=CH_2), 4.8−4.5 (d, −C(CH_3)=CH_2), 3.7−3.4 (t, CH_2CH_2OH), 2.3−1.8 (m, −C*H*(C(CH_3)=CH_2)−), 1.7−1.5 (s, −C(CH_3)=CH_2), 1.5−1.1 (m, −CH_2− 3,4-microstructure), 0.9−1.1 (m, −CH_2− 1,2-microstructure), 0.8 (m, initiator $CH_3CH_2(CH_3)CH$−), 0.7 (m, initiator $CH_3CH_2(CH_3)$CH−).

MALDI—ToF—MS (matrix dithranol, THF, Ag^+): homologous series with repetitions m/z_{calcd} = 68, m/z_{found} = 68 ± 2, and maximum at m/z = 687 with M_n 894 and PDI 1.09.

GPC (standard, PI; eluent, THF): M_n 700 and PDI 1.11.

5.2. Synthesis of Poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO). PI−OH (2.1 g, 2.8 mmol) was introduced into a reactor and dried at 40 °C overnight. THF (60 mL) was cryodistilled and the solution was titrated by a THF-solution of naphthalene potassium (~0.5 M) at 0 °C until the slight green color persisted for more than 2 min. After 30 min, EO (4.0 mL, 80 mmol) was distilled into the reactor and the mixture was kept at 22 °C for 3 h. The reaction mixture was

Table 10. Amounts of the Diblock Copolymers and Dendrimers

	diblock copolymers		dendrimers	
product name	PI-*b*-PEO (g; mmol)	PS-*b*-PEO (g; mmol)	**$TdG_2(CH_2Cl)_{\sim 12}$** (g, mmol, mmol $-CH_2Cl$ groups)	**$TdG_2(CH_2Cl)_{\sim 8}$** (g, mmol, mmol $-CH_2Cl$ groups)
D(PEO—PI)12	0.605, 0.43		0.036, 6.4×10^{-3}, 7.7×10^{-2}	
D(PEO—PS)12		2.549, 0.43	0.04, 7.2×10^{-3}, 8.6×10^{-2}	
D(PEO—PI)8	0.403, 0.29			0.032, 6.0×10^{-3}, 4.8×10^{-2}
D(PEO—PS)8		1.77, 0.30		0.029, 5.5×10^{-3}, 4.4×10^{-2}

heated at 50 °C for 4 days. An excess of hydrochloric acid was added in order to terminate the reaction. The product was precipitated in hexane at −30 °C, filtered, and dried under dynamic vacuum for 48 h. Yield: 5.0 g (90%).

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ, ppm: 5.9−5.6 (q, $-CH=CH_2$), 5.2−4.8 (q, $-CH=CH_2$), 4.8−4.5 (d, $-C(CH_3)=CH_2$), 3.7−3.4 (s, $-(CH_2CH_2O)_n-$), 2.3−1.8 (m, $-CH(C(CH_3)=CH_2)-$), 1.7−1.5 (s, $-C(CH_3)=CH_2$), 1.5−1.1 (m, $-CH_2-$ 3,4-microstructure), 0.9−1.1 (m, $-CH_2-$ 1,2-microstructure), 0.8 (m, initiator $CH_3CH_2(CH_3)CH-$), 0.7 (m, initiator $CH_3CH_2(CH_3)CH-$).

MALDI—ToF—MS (matrix dithranol, without salt): maximum at m/z = 1362 with M_n 1395 and PDI 1.15.

GPC (standard, PI; eluent, THF): M_n 1400 and PDI 1.12.

5.3. Synthesis of End-Hydroxy-Functionalized Polystyrene (PS—OH). Styrene (10.0 mL, 87.3 mmol) and cyclohexane (100 mL) were consecutively cryodistilled into a reactor. *sec*-Butyllithium (3.5 mL, 4.5 mmol) was added, and polymerization was performed for 3 h at −77 °C. The color of the reaction mixture turned to orange-red. Ethylene oxide (4.5 mL, 91 mmol) was distilled into the reactor and the mixture was heated at 50 °C for 1 h. An excess of hydrochloric acid was added in order to terminate the reaction. The product was precipitated in methanol, filtered, and dried at 40 °C under dynamic vacuum for 48 h. Yield: 8.8 g (95%).

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ, ppm: 7.3−6.3 (overlapping broad peak, H_{PS}^{arom}), 3.6 (t, $-CH_2CH_2$-OH), 2.1−1.7 (m, $-CH-_{PS}$), 1.7−1.2 (m, $-CH_2-_{PS}$), 0.8 (m, initiator $CH_3CH_2(CH_3)CH$), 0.7 (m, initiator $CH_3CH_2(CH_3)$-CH−).

MALDI—ToF (matrix dithranol, THF, Li^+): homologous series with repetitions m/z_{calcd} = 104, m/z_{found} = 104 ± 2, and maximum at m/z = 2312 with M_n 2434 and PDI 1.08.

GPC (standard, PS; eluent, THF): M_n 2200 and PDI 1.08.

5.4. Synthesis of Poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO). PS−OH (3.0 g, 1.4 mmol) was introduced into the reactor and dried at 40 °C overnight. THF (100 mL) was cryodistilled and the solution was titrated by a THF solution of naphthalene potassium (∼0.5 M) at 0 °C until the slight green color persisted for more than 2 min. After 30 min, EO (4.0 mL, 80 mmol) was distilled into the reactor and the mixture was kept at 22 °C for 3 h. The reaction mixture was heated at 50 °C for 6 days. An excess of hydrochloric acid was added in order to terminate the reaction. The product was precipitated in diethyl ether at −30 °C, filtered, and dried under dynamic vacuum for 48 h. Yield: 5.1 g (78%).

^{1}H NMR (250 MHz, CD_2Cl_2, room temperature), δ, ppm: 7.3−6.3 (overlapping broad peak, H_{PS}^{arom}), 3.6 (m, $-(CH_2CH_2O)_n-$), 2.1−1.7 (m, $-CH-_{PS}$), 1.7−1.2 (m, $-CH_2-_{PS}$), 0.8 (m, initiator $CH_3CH_2(CH_3)CH-$), 0.7 (m, initiator $CH_3CH_2(CH_3)$-CH−).

MALDI—ToF (matrix dithranol, K^+): homologous series with maximum at m/z = 5817 with M_n 5684 and PDI 1.03.

GPC (standard, PS; eluent, THF): M_n 6000 and PDI 1.07.

6. Synthesis of Core—Shell Macromolecules. Calculated amounts of diblock copolymers (Table 10) were introduced into the reactor and dried at 40 °C overnight. THF (100 mL) was cryodistilled, and the solution was titrated by a THF solution of naphthalene potassium (∼0.5 M) at 0 °C until the slight green color persisted for more than 2 min. After 30 min a THF solution (30 mL) of the appropriate dendrimer (**$TdG_2(CH_2Cl)_{\sim 12}$** or **$TdG_2(CH_2Cl)_{\sim 8}$**) (Table 10) was added into the reactor and the mixture was heated at 50 °C for 7 days. An excess of hydrochloric acid was added in order to deactivate the living diblock chains. The products were precipitated in hexane at −77 °C, filtered, and dried under dynamic vacuum for 48 h. Part of the crude products was purified from the single diblock chains by preparative GPC (Figure 2).

Characterizations of D(PEO—PI)12 and D(PEO—PI)8.

^{1}H NMR spectroscopy (500 MHz, $C_2D_2Cl_4$, 373 K), δ, ppm: 7.5−6.3 (obp, H_{Dendr}^{arom}), 5.2 (s, $CH_2=CH-$ 1,2-structure), 4.9−4.6 (obp, $CH_2=CH-$ 1,2-structure, $CH_2=C(CH_3)-$ 3,4-structure) 4.3−4.0 (m, Dendr-CH_2O-PEO−PI), 3.6 (s, $-CH_2CH_2O-$), 2.3−1.8 (m, $-CH-$ backbone 3,4-structure), 1.6 (s, $CH_2=C(CH_3)-$ 3,4-structure), 1.5−1.1 (m, $-CH_2-$ backbone 3,4-structure), 1.1−0.9 (m, $-CH_2-$ backbone 3,4-structure and CH_3-backbone of 1,2-structure), 0.8 (m, $CH_3CH_2(CH_3)CH-$), 0.7 (m, $CH_3CH_2(CH_3)CH-$).

GPC (standard, PI; eluent, THF):

name	M_n	PDI
D(PEO−PI)12	17100	1.07
D(PEO−PI)8	12600	1.13

MALDI—ToF—MS (matrix dithranol, Na^+) of **D(PEO—PI)-8**: maximum at m/z = 14 807 with M_n 14 680 and PDI 1.05.

DLS (solvent: THF). $R_h^{D(PEO—PI)12}$ = 5.1 nm, $R_h^{D(PEO—PI)8}$ = ∼4 nm.

Characterizations of D(PEO—PS)12 and D(PEO—PS)8.

^{1}H NMR spectroscopy (500 MHz, $C_2D_2Cl_4$, 373 K), δ, ppm: 7.5−6.3 (obp, $H_{PS+dendr}^{Arom}$), 4.3−4.0 (q, Dendr-CH_2O-PEO−PS), 3.6 (s, $-CH_2CH_2O-$), 2.1−1.7 (m, CH_{PS}^{aliph}), 1.7−1.2 (m, $CH_{2\ PS}^{aliph}$), 0.8 (m, $CH_3CH_2(CH_3)CH-$), 0.7 (m, $CH_3CH_2(CH_3)$-CH−).

GPC (standard, PS; eluent, THF):

name	M_n	PDI
D(PEO−PS)12	26000	1.05
D(PEO−PS)8	28500	1.05

DLS (solvent, THF): $R_h^{D(PEO—PS)12}$ = 7.3 nm, $R_h^{D(PEO—PS)8}$ = 5.8 nm.

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