Polystyrene–Poly(propylene imine) Dendrimers: Synthesis, Characterization, and Association Behavior of a New Class of Amphiphiles

J. C. M. van Hest, D. A. P. Delnoye, M. W. P. L. Baars, C. Elissen-Román, M. H. P. van Genderen, and E. W. Meijer*

Abstract: A new class of amphiphilic macromolecules has successfully been synthesized by creating well-defined diblock copolymers of polystyrene (PS, $M_n = 3.2 \times 10^3$, $M_w/M_n = 1.04$) with poly(propylene imine) dendrimers. A polystyrene core molecule with a primary amine end-group was prepared by a quantitative three-step modification procedure of acid-functionalized polystyrene. On this core molecule, five different generations from PS-*dendr*-NH_2 up to PS-*dendr*-$(NH_2)_{32}$ were constructed in high yields. The molecular structure of the block copolymers was analyzed in detail with NMR and IR spectroscopy and electrospray mass spectrometry. With conductivity measurements and monolayer pressure–area isotherm determinations, we observed generation-dependent amphiphilic behavior. Dynamic light scattering and transmission electron microscopy showed that amphiphile geometry had a distinct effect on aggregation behavior; this is in qualitative agreement with Israelachvili's theory. Critical association concentrations determined with the pyrene probe luminescence technique were as low as 5×10^{-7} M. The amphiphiles presented here, therefore, show a resemblance to traditional block copolymers with regard to size and stability, and are similar to surfactants with respect to tuning of the shape.

Keywords
amphiphiles · block copolymers · dendrimers · micelles · surfactants

Introduction

The physical behavior of amphiphilic block copolymers is an area which is still not well understood, though extensively investigated.[1] This is partly due to the large number of parameters that influence aggregation. Another problem, which makes research in this field even more difficult, is the fact that polymer systems are not as well-defined as traditional surfactants.[2] To be able to investigate the applicability of theoretical models based on the behavior of low molecular weight surfactants[3] to polymeric systems, it is necessary to synthesize new, better-defined amphiphilic structures.[4] Dendrimers are a type of molecules that can make a positive contribution to a better understanding of the structure–property relationship in amphiphiles. These well-defined, highly branched macromolecules have acquired a growing scientific interest as building blocks in new molecular architectures.[5] They have been applied, for example, in unimolecular micelles and structures containing dendrimers and linear macromolecules.[6] Chapman's hydraamphiphiles[7] and the amphiphilic polymers described by Zhong and Eisenberg,[8] which can be regarded as the first approach toward polystyrene–dendrimer structures with variable polar head-group size, already show the versatility of the introduction of dendrimers into amphiphilic molecules. Recently, we have reported hybrid polystyrene–dendrimer block copolymers that fill the gap between the low molecular weight surfactants and amphiphilic polymers.[9] These structures show generation-dependent aggregation behavior, which is consistent with Israelachvili's theory of the effect of amphiphile geometry on type of aggregation. In this paper we report the procedures for the preparation of the core molecule, the dendrimer synthesis, and the characterization of the molecular structure in great detail. Furthermore, amphiphilic behavior of these molecules at both an air/water and a water/toluene interface is investigated and their generation-dependent aggregation behavior is described. The dendritic architectures presented here can be regarded as a new type of amphiphiles in between traditional organic surfactants and amphiphilic block copolymers. Finally, they are important structures in the emerging field of self-assembled dendrimers.[10]

Results and Discussion

Synthesis of the core molecule: In order to grow poly(propylene imine) dendrimers on polystyrene by the divergent method, well-defined primary-amine-functionalized polystyrene had to be prepared as the core molecule. The anionic polymerization technique was chosen for the preparation of polystyrene (PS) because of the control over molecular weight and end-group functionalization. In a first approach, direct amination was

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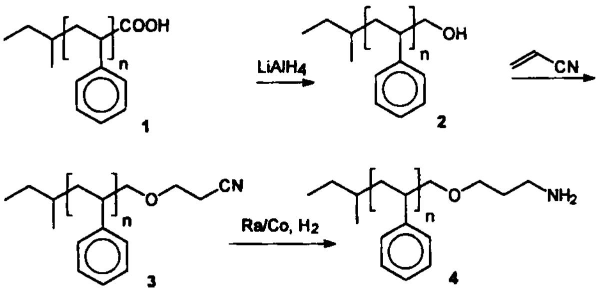
investigated with *N*-trimethylsilylbenzaldiimine as end-cap reagent.[11] However, no quantitative modification was obtained. Furthermore, a model study with α-methyl benzylamine, which resembles the PS chain-end after functionalization, showed that a double Michael addition onto the primary amine function suffered from severe steric hindrance. Therefore, an indirect amination procedure was developed, as is depicted in Scheme 1. In this procedure a standard quantitative end-cap reaction with CO_2 was used and a spacer was created between polystyrene and the primary amine function. Anionic polymerization was performed on the 100 g scale under a 2.5 bar N_2 atmosphere, with *sec*-BuLi as initiator and cyclohexane as solvent. Quantitative introduction of the acid function was possible with a slightly modified literature procedure:[12] addition of THF and CO_2 to the reaction mixture resulted in the formation of 5% polystyrene dimer from reaction of two polystyryl anions with the same CO_2 molecule. Therefore, the living polymer solution was siphoned into a THF solution saturated with CO_2, and complete modification was achieved. The polystyrene-COOH (PS-COOH, **1**, Scheme 1) obtained, with M_n of $3-8 \times 10^3$ g mol^{-1} and M_w/M_n values around 1.05, could be quantitatively reduced to the corresponding alcohol (PS-CH_2OH, **2**) with $LiAlH_4$. PS-CH_2OH was cyanoethylated with acrylonitrile, followed by hydrogenation of the nitrile to a primary amine. The cyanoethylation step in this reaction scheme is a modification of the method developed by Percec for the preparation of nitrile-functionalized poly(isobutylene).[13]



Scheme 1. Modification of polystyrene for the introduction of a primary amine function.

Cyanoethylation reactions to obtain PS-$CH_2OCH_2CH_2CN$ (**3**) were performed in a two-phase system of toluene/$NaOH_{(aq)}$, to which a phase-transfer catalyst was added. Toluene was necessary to solubilize PS-CH_2OH, and the combination of NaOH and phase-transfer catalyst made it possible to introduce a base in the organic phase that was strong enough to catalyze the Michael addition of acrylonitrile onto the alcohol function. Cyanoethylation reactions were quantitative in 30 min for all of the molecular weights tested. Of key importance in this reaction was the use of the combination of NaOH and the phase-transfer catalyst trioctylmethylammonium chloride (TOMA). Experiments with other base systems such as the organic base 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), which made a homogeneous reaction system possible, Lewatite resin, which was very successful in catalyzing the cyanoethylation of alcohol-functionalized poly(ethylene oxide), or the phase-transfer catalyst tetrabutylammonium hydroxide (TBAH) reacted very slowly and not quantitatively (Table 1). The method based on TOMA was rather robust: the excess of acrylonitrile or the amounts of TOMA and NaOH could be varied over a broad range without changing the reactivity or yield of the reaction. Only when more than 40 equiv of NaOH were added did dicyanoethyl ether become a significant by-product and the yield drop to 80%.

Table 1. Cyanoethylation experiments of PS-CH_2OH (3.2×10^3 g mol^{-1}).

Base system	(mol equiv)	acrylonitrile (mol equiv)	T (°C)	Reaction time	Yield (%)
Lewatite resin	0.6 g equiv	350	45	2 d	–
DBU	1.1	180	25	8 d	40
DBU	4	20	45	8 d	40
TBAH	1	20	25	1 d	80–90
TOMA/NaOH	1/4	25	25	10 min	100
TOMA/NaOH	1/2.7	4.5	25	10 min	95
TOMA/NaOH	1/4	4.5	45	10 min	90
TOMA/NaOH	0.4/3	24	25	10 min	95
TOMA/NaOH	0.5/1.2	4.5	25	60 min	>95
TOMA/NaOH	10/40	4.5	25	10 min	80

A problem occurred during the workup of the reaction mixture containing the higher molecular weight polystyrene. When the mixture was concentrated before precipitation, PS-CH_2-OCH_2CH_2CN with $M_n = 8 \times 10^3$ g mol^{-1} showed considerable retro-Michael reaction. By adjusting the procedure and precipitating the mixture directly into methanol, no traces of retro-Michael reaction could be detected. Moreover, at this point separation of PS, PS-CH_2OH, and PS-$CH_2OCH_2CH_2CN$ was, if necessary, readily performed by flash chromatography. The extent of reaction could easily be followed with TLC, while IR, ^{1}H NMR, and ^{13}C NMR spectra provided unambiguous evidence of the formation of PS-$CH_2OCH_2CH_2CN$, even for the higher molecular weight polystyrenes.

The hydrogenation of the nitrile function to a primary amine was a modification of the method described for poly(propylene imine) dendrimer synthesis.[9a] Modifications that had to be made were a change of solvent to toluene/CH_3OH 3/1 v/v to dissolve PS-$CH_2OCH_2CH_2CN$ and the application of longer reaction times. The use of NH_3 was of great importance for a successful hydrogenation. Without NH_3, yields after workup did not exceed 50%, whereas with NH_3 yields >90% could be obtained. NH_3 also had a positive effect on the reaction rate. The disappearance of the CN signal (at 2252 cm^{-1}) observed with IR spectroscopy was a suitable method for following the hydrogenation reaction. The primary amine stretching vibration was somewhat obscured by the H_2O absorption band, but was clearly visible for PS-$CH_2OCH_2CH_2CH_2NH_2$ of $M_n = 3.2 \times 10^3$ g mol^{-1} (**4**). TLC proved to be another method with which the reaction could be followed. ^{1}H NMR and ^{13}C NMR spectroscopy excluded side reactions, and the combination of these techniques made it possible to identify the reaction product as PS-$CH_2OCH_2CH_2CH_2NH_2$. No purification procedure was necessary. The only loss of material resulted from some adsorption of polymer onto the catalyst. Yields of the hydrogenation reaction therefore amounted to 90%.

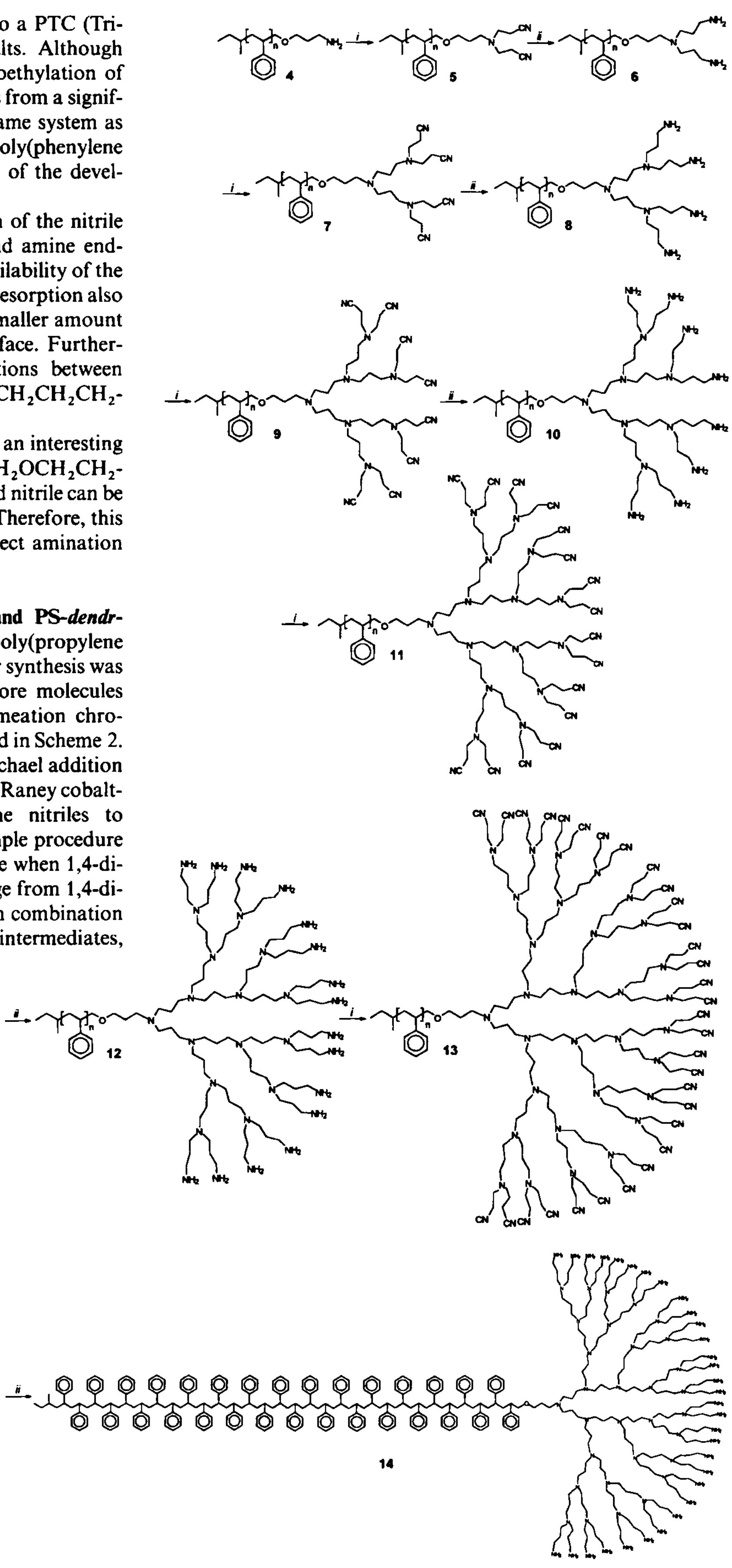
The choice of the base system for the cyanoethylation reaction is not straightforward. The difference in reactivity of polyethylene oxide and polystyrene toward acrylonitrile in the presence of Lewatite resin can be explained by a large difference in polarity between the polymers: the alcohol functionality of PS-CH_2OH is shielded too much by the polystyrene chain. The organic base used, DBU, on the other hand, is not strong enough to deprotonate the alcohol. TOMA, as a phase-transfer catalyst, is able to introduce sufficient OH^- into the chemical environment of the hydroxyl function of polystyrene to obtain the alkoxide form, and makes the Michael reaction possible. The choice of phase-transfer catalyst (PTC) is also critical, as can be shown from the lower modification results with TBAH. An explanation could be the lower availability of OH^- in this case. Cyanoethylation of a polymeric alcohol has already been described for polyisobutylene.[13] In this case too a PTC (Triton B) was necessary to give quantitative results. Although longer reaction times are reported for the cyanoethylation of polyisobutylene, it is not clear whether this results from a significant difference in reactivity. In our group the same system as that described in this paper has been used for poly(phenylene ether) (PPE),[14] thereby showing the versatility of the developed method.

NH_3 plays a crucial role in the hydrogenation of the nitrile function. It causes a fast exchange of nitrile and amine endgroups on the catalyst, thereby increasing the availability of the active sites and enhancing the reaction rate. This desorption also results in higher yields after workup, because a smaller amount of polymer remains attached to the catalyst surface. Furthermore, NH_3 prevents undesired coupling reactions between intermediate secondary amines and $PS-CH_2OCH_2CH_2CH_2-NH_2$.

After optimization of this four-step procedure, an interesting indirect route has been developed toward $PS-CH_2OCH_2CH_2-CH_2NH_2$. Also the intermediate acid, alcohol, and nitrile can be used for a variety of reactions onto polystyrene. Therefore, this method can be seen as a good alternative to direct amination procedures.

Synthesis of PS-*dendr*-$(NH_2)_n$ with $n = 1-32$ and PS-*dendr*-$(CN)_n$ with $n = 2-32$: To obtain polystyrene-poly(propylene imine) block copolymers, the divergent dendrimer synthesis was performed onto $PS-CH_2OCH_2CH_2CH_2NH_2$ core molecules with $M_n = 3.2 \times 10^3\,g\,mol^{-1}$ (based on gel permeation chromatography (GPC) of $PS-CH_2OH$), as is depicted in Scheme 2. The reaction sequence, consisting of a double Michael addition of acrylonitrile onto primary amines, followed by Raney cobalt-catalyzed heterogeneous hydrogenation of the nitriles to amines, has proven to be a very efficient and simple procedure for the preparation of dendrimers on a large scale when 1,4-diaminobutane is used as core molecule. The change from 1,4-diaminobutane to $PS-CH_2OCH_2CH_2CH_2NH_2$, in combination with the developing amphiphilic character of the intermediates, required adjustment and optimization of both cyanoethylation and hydrogenation steps of the dendrimer reaction sequence compared with the 1,4-diaminobutane route. For the cyanoethylation, the choice of solvent combination was of considerable importance. The first reaction step toward PS-*dendr*-$(CN)_2$ (**5**) was possible in acrylonitrile as reactive solvent; the other reactions had to be performed in a heterogeneous system of toluene/water. Acetic acid was used as catalyst in all cases. To obtain stable emulsions, the water-to-toluene ratio had to be adjusted for each cyanoethylation step.

Hydrogenations were performed under conditions that were similar to the poly(propylene imine) dendrimer synthesis with 1,4-diaminobutane as core molecule, under 80 bar H_2 pressure and with Raney cobalt as catalyst. However, also in this case the solvent had to be changed to a toluene/MeOH 3/1 v/v mixture in order to dissolve the products. Furthermore, as was also noticed for the hydrogenation of $PS-CH_2OCH_2CH_2CN$, the addition of NH_3 was of utmost importance. Without NH_3 it was impossible to hydrogenate fully even PS-*dendr*-$(CN)_4$ (**7**).



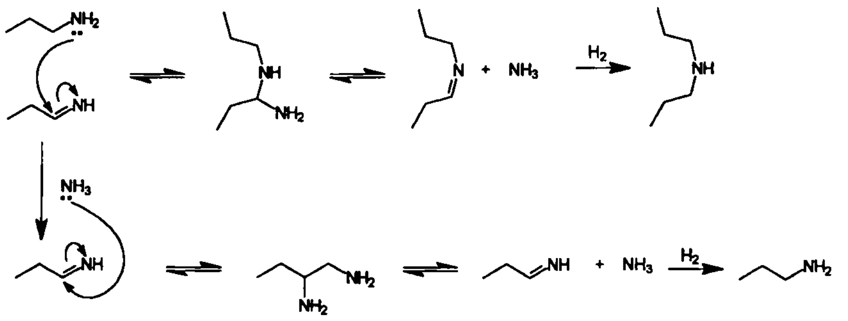
Scheme 2. Synthetic route toward PS-dendr-$(NH_2)_{32}$: i) Cyanoethylation with acrylonitrile in water/toluene, catalyzed by acetic acid; ii) hydrogenation at 80 bar H_2 pressure with Raney cobalt as catalyst.

Side reactions occurred as intramolecular bridging between a primary amine and an imine function took place, and the yields after workup were drastically decreased when no NH_3 was used. NH_3 made it possible to circumvent these problems. When hydrogenations were performed on a small scale (< 1 g), serious cobalt contamination and carbamate formation were observed. Performing the workup under N_2 atmosphere prevented the latter problem. When the reactions were performed on a larger scale (> 5 g) neither problem occurred. All nitrile and amine products, with the exception of PS-*dendr*-$(NH_2)_{32}$ (**14**), could be purified by precipitation techniques. The polarity of the medium that was used for precipitation had to be increased as the number of generations increased, from MeOH to ammonia. PS-*dendr*-$(NH_2)_{32}$ was too polar to be precipitated even in ammonia. Column-chromatographic purification of the nitrile intermediates was possible up to PS-*dendr*-$(CN)_{16}$ (**11**). With this technique, side products such as poly(acrylonitrile) and acetylated PS–$CH_2OCH_2CH_2CH_2NH_2$ could easily be removed. All of the products were obtained in good yields after workup.

The cyanoethylation experiments demonstrate the development of amphiphilicity of the molecules. Because the Michael addition is performed at the interface of the water/toluene mixture, stability of the emulsion is important. The increasing polarity of the dendrimer with increasing generation made it necessary to add more water to the system. During reaction, it was difficult to follow the cyanoethylation, either with TLC or with spectroscopic techniques. This is a result of the formation of protonated dendritic structures owing to the presence of HOAc. Optimization of the reaction time was therefore difficult. Column chromatography made it possible to separate a number of side products from the desired dendritic structures. The difference in polarity between amine- and nitrile-functionalized dendrimers is large, and incompletely cyanoethylated structures could therefore be removed. However, it was not possible to remove side products in which, for example, one of the 16 amine functions had not reacted. After optimization, the cyanoethylation reactions could be performed quantitatively, and column chromatographic purifications were therefore not necessary most of the time.

The role of NH_3 during hydrogenation, as earlier observed for the preparation of PS–$CH_2OCH_2CH_2CH_2NH_2$, is a crucial but also a fairly well-known one.[15] One of the major side reactions that can occur during dendrimer synthesis is the intramolecular bridging reaction between an imine and a primary amine function, with the release of NH_3 (Scheme 3). NH_3 is thought to compete with the primary amines in attack on the intermediate imine. The attack of NH_3 leads to the formation of the desired amine.

Especially in the case of the hydrogenations, the scale of reaction was important. Precipitation and filtration techniques could be performed more effectively at larger scales, with the result that cobalt was removed and carbamate formation could be prevented. The hydrogenation step was the most difficult to control in the reaction sequence and could give rise to by-products. These by-products could not be separated from the desired product with column chromatography because of the high polarity of both materials. In the multistep divergent dendrimer synthesis it was therefore almost impossible to completely prevent formation of side products or to isolate the pure product. The divergent synthesis can in this respect be regarded as the polymeric approach toward dendrimers. On the other hand, to obtain the end product a 13-step synthesis had to be performed onto a polymer in a well-defined manner. This makes this procedure an unprecedented effort in the area of polymer modification reactions.



Scheme 3. The mechanism of intramolecular bridging and the role of NH_3.

Characterization of PS-*dendr*-$(NH_2)_n$ with $n = 1–32$ and PS-*dendr*-$(CN)_n$ with $n = 2–32$: The process of hydrogenation could be followed very well by means of IR spectroscopy. The disappearance of the CN stretching vibration around 2245 cm^{-1} was used as an indicator for the end of the reaction. Only in the case of the preparation of PS-*dendr*-$(NH_2)_{32}$, even after several hydrogenation attempts, did the CN signal not disappear completely; this signal was estimated to be less than 3% of the original stretching vibration. Besides IR spectroscopy, all products were characterized with ^1H NMR and ^{13}C NMR spectroscopy. With both techniques, positive structural identification was achieved. With ^{13}C NMR spectroscopy, it was possible to analyze the structures in great detail, as is shown in Figure 1 for PS-*dendr*-$(CN)_{16}$. All of the signals present in the spectrum could be assigned. It was possible to discern between the different dendritic layers of the molecules, as

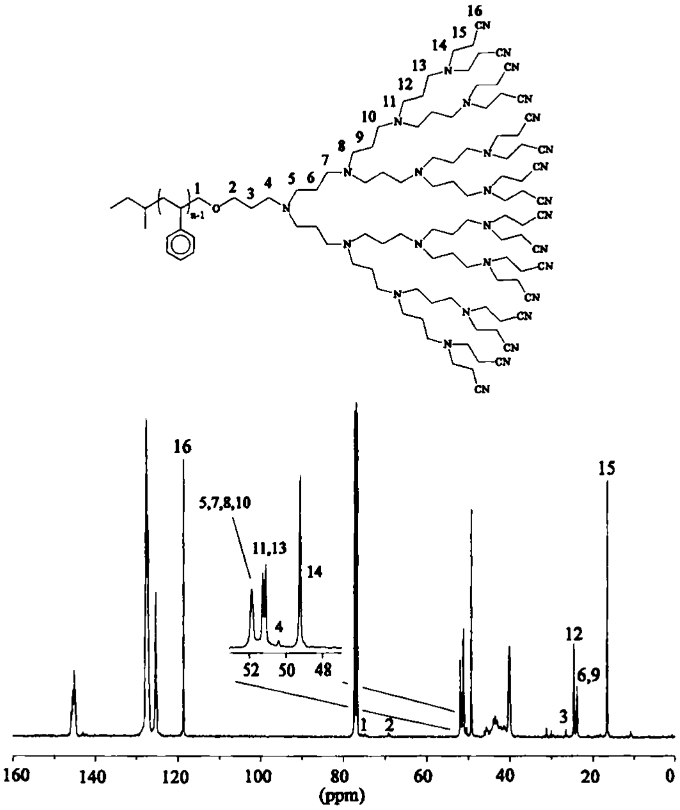


Fig. 1. ^{13}C NMR spectrum of PS-*dendr*-$(CN)_{16}$ in $CDCl_3$.

was clearly noticed for the resonances of the carbons next to the tertiary amines (around $\delta = 50$) and the carbons in between the tertiary amines (around $\delta = 25$). Even single carbons were visible (C^3 and C^4). The signals of the carbon atoms next to the ether function (C^1 and C^2) were much broader, owing to the effect of tacticity of the polymer backbone. The signals that are not numbered in the ^{13}C NMR spectrum originate from the *sec*-butyl group. All of the other ^{13}C NMR spectra could be assigned likewise; solubility problems occurred only in the case of PS-*dendr*-$(NH_2)_{32}$, and characterization with NMR spectroscopy became very difficult. In this case, only the PS chains were visible in $CDCl_3$. After storage of the PS-*dendr*-$(NH_2)_{32}$ foam for 2 months, the product had become insoluble, even in DMSO. After an extraction process with water and toluene a product was obtained that was soluble in organic phases. Again, however, characterization with $CDCl_3$ only showed polystyrene, and other solvents used gave ambiguous results. In the case of PS-*dendr*-$(NH_2)_8$ (**10**) ^{13}C NMR spectroscopy revealed a few very small additional peaks (< 5%), which could possibly be related to a side product. Electrospray mass spectrometry was performed on PS-*dendr*-$(NH_2)_8$ (Fig. 2), and the spectrum shows the peaks for m/z with $z = 4$. The analysis shows at least 17 individual peaks that are all related to the polydispersity of the polystyrene unit ($M_w/M_n = 1.04$ based on GPC of PS-CH_2OH). The calculated $M_n = 4020$ of PS-*dendr*-$(NH_2)_8$, based on the GPC of PS-CH_2OH ($M_n = 3200$), is very close to the M_n on top (3965) as determined with electrospray mass spectrometry. From the latter, we determined $M_w/M_n = 1.02$, which is again in good agreement with that estimated from GPC. The "dispersity" of the dendrimer block is, however, of a totally different order than the dispersity of the well-defined polystyrene chain; only a small imperfection of the dendrimer head-group (peaks at $m/z = 953.1$ and 979.3, $z = 4$) is seen.

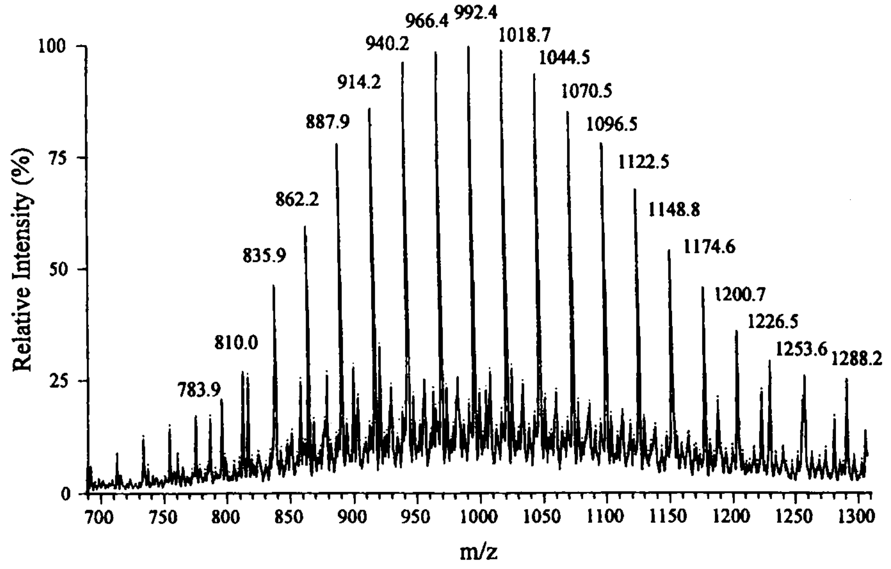


Fig. 2. Electrospray mass spectrum of PS-*dendr*-$(NH_2)_8$. The correct mass can be calculated by multiplication of the values by 4 and subtraction of 4.

Although electrospray mass spectrometry is a very powerful technique for analysis of synthesized products, it is also a quite complex characterization method, still under development. Sample preparation and interface techniques especially need meticulous optimization in order to measure samples satisfactorily. Furthermore, the polydispersity of "normal" polymers hampers detailed analysis of the small defects in the dendrimer part. Characterization with NMR spectroscopy therefore remains the most frequently used technique for our block copolymers. With this analysis method no imperfections can be detected for the nitrile intermediates and the stratified structure of the dendrimers becomes perfectly clear. An approximation of the resolution of ^{13}C NMR spectroscopy is demonstrated by the fact that $OCH_2CH_2\mathit{C}H_2N$ is visible; the limit of detection is below 5%. One very important aspect of NMR characterization is that every intermediate has to be fully characterized. The very small amounts of impurities or side products that were noticed for PS-*dendr*-$(NH_2)_8$ are no longer visible for the higher generations. Because of the symmetry of the dendrimers, these imperfections are camouflaged, because the chemical environments of the imperfections and the correct structure become almost identical. The preparation of PS-*dendr*-$(NH_2)_{32}$ proves to be a reaction at the limits of the synthetic possibilities. From IR spectroscopy it can be concluded that approximately one out of 32 nitrile functions has not been hydrogenated. The NMR characterization difficulties are partly a result of the amphiphilic character; the dendrimer head-groups are aggregated in and shielded from deuterated solvents such as $CDCl_3$. Storage of PS-*dendr*-$(NH_2)_{32}$ as a solid gives rise to an intermolecular bridging process that results in an insoluble material. Although this process is not observed for the other generations, it is sometimes noticed for the poly(propylene imine) dendrimers.[16] However, samples that were freshly prepared from PS-*dendr*-$(NH_2)_{32}$ for aggregation and amphiphile behavior were not affected by intermolecular bridging and their properties were hardly influenced by the probably incompletely hydrogenated structures. From the characterization results it can be concluded that our aim, obtaining a well-defined series of polystyrene-poly(propylene imine) dendrimer diblock copolymers, has been accomplished quite successfully, and has brought us to the limits of the present synthetic and characterization possibilities.

Amphiphilic behavior of PS-*dendr*-$(NH_2)_n$: The development of amphiphilic and aggregation behavior as a function of dendrimer generation of PS-*dendr*-$(NH_2)_n$ was studied with five different techniques: the amphiphilic character at a toluene/water interface was investigated with conductivity measurements, and at a water/air interface with monolayer experiments. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to examine the aggregates formed by the different generations in aqueous solutions, while the critical association concentrations were determined with the pyrene probe luminescence technique.

Conductivity measurements: To a stirred 3×10^{-4} M dispersion of PS-*dendr*-$(NH_2)_n$ in a 0.01 M KCl solution, a 3×10^{-4} M amphiphile solution in toluene was added dropwise. By measuring the conductivity of the system as a function of the toluene/water ratio, it could be estimated whether toluene or water was the continuous phase. At the point where the conductivity dropped to zero, the phase inversion point was reached and toluene became the dispersing phase. The effect of dendrimer generation on the position of this inversion point was investigated with PS-*dendr*-$(NH_2)_n$ for $n = 2-16$. PS-*dendr*-$(NH_2)_{32}$ could not be measured in the same manner, because it proved to be insoluble in toluene. The conductivity measurements show a distinct difference between PS-*dendr*-$(NH_2)_{16}$ and the lower generations. For PS-*dendr*-$(NH_2)_n$ with $n = 2-8$ there is a strong tendency to stabilize toluene as the continuous phase. PS-*dendr*-$(NH_2)_2$ (**6**) even showed a remarkable phase inversion at 2 vol% of toluene. This can be explained by the fact that polystyrene is the dominant part in the amphiphilic structure and, according to the empirical rules of Bancroft,[17] the organic phase as continuous phase is preferred. PS-*dendr*-$(NH_2)_{16}$ (**12**) is a much more balanced amphiphile and is therefore equally capable of stabilizing toluene or water as dispersing phase.

Monolayer experiments: Amphiphilic behavior at an air/water interface was studied by means of monolayer experiments. Surface pressure–area isotherms were recorded for PS-*dendr*-$(NH_2)_n$ with $n = 1-16$. The monolayers formed were also investigated with a Brewster angle microscope (BAM),[18] which made it possible to investigate the type of structures that are formed in the monolayer. The results are shown in Figure 3.

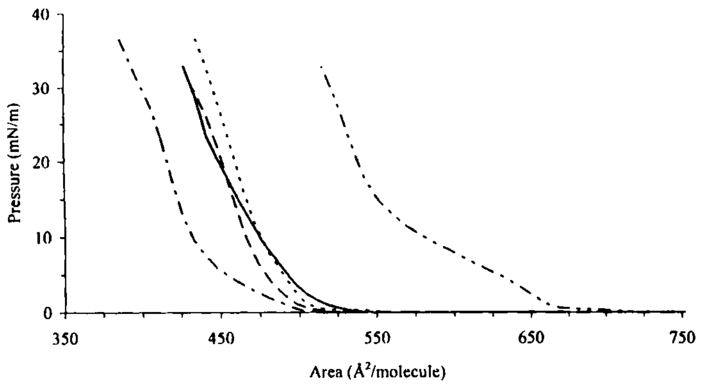


Fig. 3. Pressure–area isotherms; — PS-$OCH_2CH_2CH_2NH_2$; -- PS-*dendr*-$(NH_2)_2$; ··· PS-*dendr*-$(NH_2)_4$; -·- PS-*dendr*-$(NH_2)_8$; -·-·- PS-*dendr*-$(NH_2)_{16}$.

The development of amphiphilic character is also clear from the monolayer experiments. Only for PS-*dendr*-$(NH_2)_n$ with $n = 8$ and 16, a normal pressure–area isotherm is obtained, which shows a transition from the gaseous through the liquid to the solid state. For these two generations an estimation of head-group dimensions is possible (PS-*dendr*-$(NH_2)_8$: head-group area = 440 Å², head-group diameter = 23.7 Å; PS-*dendr*-$(NH_2)_{16}$: head-group area = 570 Å², head-group diameter = 26.9 Å). The lower generations all show the same type of curves and go directly to solid-state behavior. In these cases solid polystyrene films are formed, which, at the point of increase of surface pressure, collide and cover the total area between the barriers. With BAM these colliding plateaus were also observed. These films are formed because of the dominance of the polystyrene-chain interactions over the dendrimer head-group interactions. The areas per molecule that can be estimated are determined more by polystyrene than by the dendrimer head-group. This explains why for PS-*dendr*-$(NH_2)_8$ a lower value is found for the pressure–area isotherm. This is the first generation for which the influence of the head-group on the behavior at the air/water interface has to be taken into account.

Critical association concentrations: Many techniques can be used for the determination of critical association concentrations (cac's); however, not all of them are sensitive enough to detect the onset of aggregation if this occurs at very low concentrations. Since the cac's of block copolymers are usually much lower than those of low molecular mass surfactants,[19] we used pyrene as a fluorescent probe and calculated the effective cac's from the changes in the spectral characteristics of pyrene as a function of surfactant concentration.[20] If we represent the intensity of the emission spectra as a function of the block copolymer concentration, we obtain cac_1 directly.[21] From the excitation spectra we obtain cac_2 by representing the ratio I_{340}/I_{335} vs $\log C$. The experimental results for PS-*dendr*-$(NH_2)_n$ with $n = 8$ and 16 obtained from excitation spectra are shown in Figure 4, with cac's of 4 and 5×10^{-7} M. The cac values obtained from excitation data are always lower than those found by emission spectra. No cac's could be measured for the lower generations because these products are insoluble in water (only the higher generations are soluble in water, while small dendritic head-groups are not able to compensate for the low solubility of the polystyrene chain in water). No significant differences were found between the cac's for different generations[22] as the length of the hydrophobic chain remains the same for all the block copolymers. It has been pointed out before[21, 23] that the onset of micelle formation in amphiphilic block copolymers is mainly determined by the nature and the length of the hydrophobic block. Also for most low molecular mass surfactants in aqueous solutions, the free energy of micelle formation is proportional to the length of the alkyl chain.[24, 25, 26]

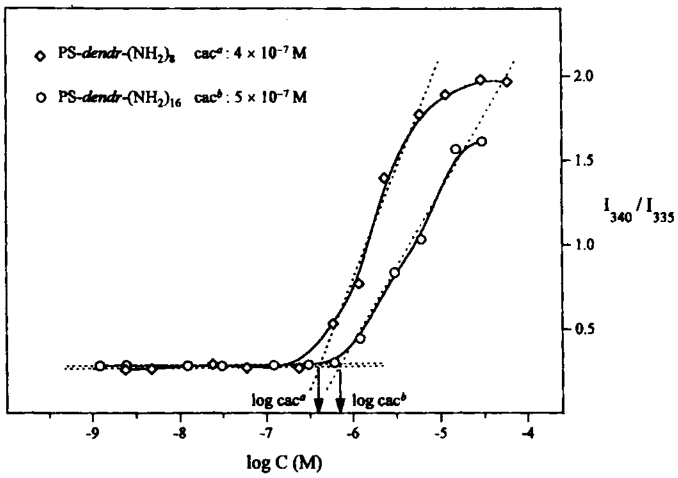


Fig. 4. Plots of fluorescence intensity ratio I_{340}/I_{335} from excitation spectra of pyrene in aqueous solutions in the presence of ◇ PS-*dendr*-$(NH_2)_8$ and ○ PS-*dendr*-$(NH_2)_{16}$.

Dynamic Light Scattering: DLS measurements were performed for PS-*dendr*-$(NH_2)_4$ (**8**) in toluene and for PS-*dendr*-$(NH_2)_n$ ($n = 8$ to 32) in water. Concentrations of all of the aggregates were 3×10^{-4} mol L^{-1}. For the aqueous aggregates, turbid systems were obtained, except for PS-*dendr*-$(NH_2)_{32}$. PS-*dendr*-$(NH_2)_4$ showed single-particle behavior in toluene. A hydrodynamic radius of 3.4 nm could therefore be estimated. The aqueous aggregates were much more difficult to interpret. For PS-*dendr*-$(NH_2)_{16}$ complicated structures were observed that could be identified as large threadlike structures with a hydrodynamic radius of 120 nm. This type of aggregation remained unchanged even after extreme dilution. The other structures, however, showed so much clustering of the aggregates that no particle dimensions could be estimated. Dilution of the samples did not improve the results.

Clustering occurs when dendritic head-groups are directed toward the periphery of the aggregates, where they are able to form electrostatic interactions. These interactions are also noticed for the normal poly(propylene imine) dendrimers.[27] The fact that even after extreme dilution the aggregates and clusters remain intact means that these intermolecular interactions are very strong. They can only be reduced by modification of the dendrimers or by inverted micellar behavior. This is the case for PS-*dendr*-$(NH_2)_4$ in toluene. Single-particle behavior points in the direction of inverted micellar structures, in which case the head-groups are shielded from the environment by the polystyrene chains.

Transmission electron microscopy studies: Aqueous aggregates of PS-*dendr*-$(NH_2)_n$ with $n = 8$, 16 and 32 (3×10^{-4} mol L^{-1}) were studied with three different TEM techniques: negative staining with uranyl acetate, Pt shadowing, and freeze fracture. All three techniques gave consistent results (Fig. 5): in the case of PS-*dendr*-$(NH_2)_8$ flexible bilayers were formed,[28] PS-*dendr*-$(NH_2)_{16}$ showed rodlike micelles with a diameter of 12 nm, and PS-*dendr*-$(NH_2)_{32}$ gave spherical micelles with diameters between 10–20 nm. For this last sample no freeze-fracture results could be obtained. Acidification of PS-*dendr*-$(NH_2)_8$ from pH = 7 to pH = 1 did not influence the aggregation type. Furthermore, after 4 weeks the same aggregates were still observed for PS-*dendr*-$(NH_2)_8$.

The observed diameters of rodlike and spherical micelles are of the same order of magnitude as would be expected for a bilayer of the diblock copolymers. With respect to clustering and stability of aggregates, TEM is consistent with the DLS measurements. The stability of the aggregates formed is remarkable: spherical micelles can be made visible with the TEM techniques used.[29] The well-known transition behavior for simple amphiphiles[2a] from micellar cylinders to micelles upon dilution is not observed in this case. The aggregates formed of PS-*dendr*-$(NH_2)_8$ are shown to be stable over time for at least a month. This structure also shows pH-independent behavior. This can be explained by the fact that at pH = 7 the primary amines are already partly protonated, so that a change to lower pH does not have a drastic effect on head-group charge and size.

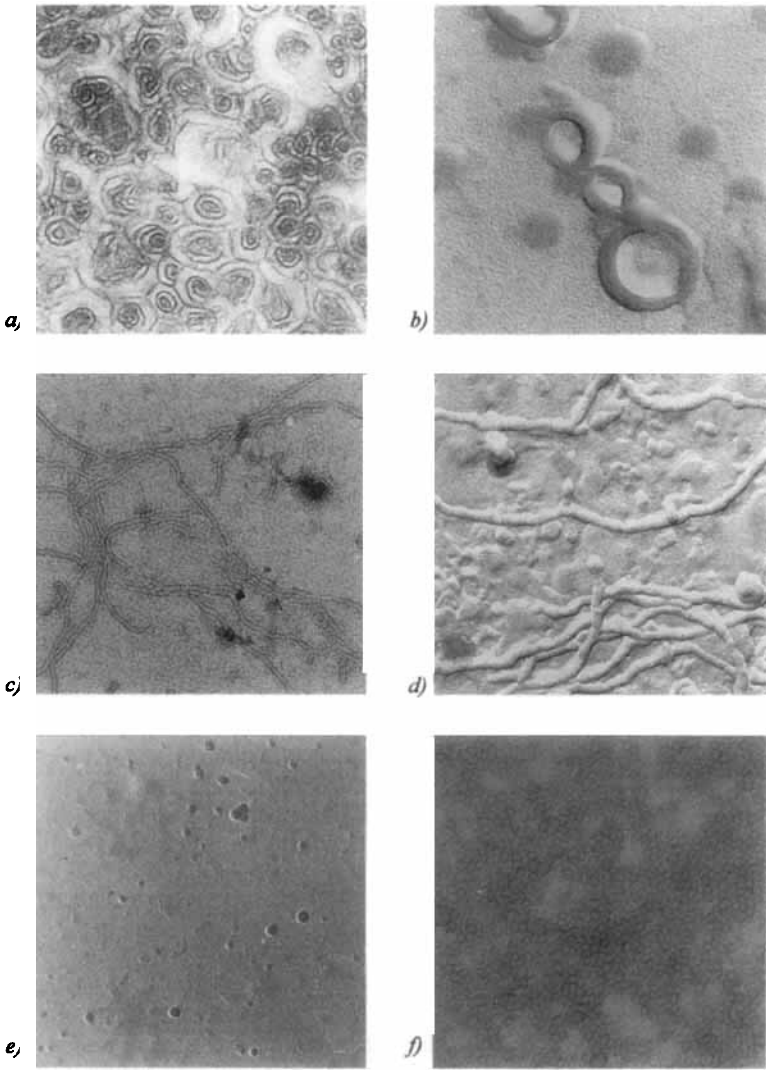


Fig. 5. a) PS-*dendr*-$(NH_2)_8$, negative staining, × 107000; b) PS-*dendr*-$(NH_2)_8$, Pt shadowing, vesicular structures, × 84000; c) PS-*dendr*-$(NH_2)_{16}$, negative staining, × 84000; d) PS-*dendr*-$(NH_2)_{16}$, freeze-fracture, micellar rods, × 84000; e) PS-*dendr*-$(NH_2)_{32}$, Pt shadowing, × 24400; f) PS-*dendr*-$(NH_2)_{32}$, negative staining, spherical micelles, × 135000.

Discussion

The results obtained with both TEM and DLS are in perfect qualitative agreement with Israelachvili's theory on surfactant assembly.[3, 30] He postulates that the geometry of the amphiphile determines what kind of aggregates are formed, using the packing parameter $P = V/(a_0 \times l_0)$, in which V = apolar chain volume, a_0 = head-group area and l_0 = chain length. Starting with a small head-group compared with the chain, inverted micelles are to be expected.

With increasing head-group size, aggregates change from planar bilayers through vesicles and rodlike micelles to spherical micelles. This process is exactly what is observed going from PS-*dendr*-$(NH_2)_4$ to PS-*dendr*-$(NH_2)_{32}$. Changing head-group size and not the chemical nature of the amphiphilic structures is only possible with dendrimers and results in proof for Israelachvili's theory of shape-dependent aggregation behavior. A model for traditional surfactants is now qualitatively applicable for this special kind of amphiphilic block copolymers.

For a quantitative comparison with Israelachvili's theory, knowledge of dendrimer head-group size, chain length and volume are necessary. The head-group areas, determined with monolayer techniques, are known for PS-*dendr*-$(NH_2)_n$ with $n = 8$, 16. The volume of the chain can be estimated from the Van der Waals volume of a styrene unit (63 cm^3 mol^{-1}).[31] For 30 units this results in a volume of 1897.5 cm^3 mol^{-1}. From these values the packing parameter P can be calculated, with 6 nm as chain length (estimated from the TEM pictures). From preset values of P the corresponding l_0 can be calculated (Table 2).

Both methods show a large discrepancy between what is calculated and what is expected based on theory. An explanation may be that for block copolymers this theory is oversimplified and corrections have to be made for the strongly differing entropic factors when polymers are compared with small organic molecules. Furthermore, although a random coil conformation can be expected for atactic polystyrene, phase separation can give rise to extended chain conformations and therefore it is very difficult to estimate the exact chain dimensions. The fact that a perfect qualitative agreement is found, however, proves that the basic theoretical ideas of Israelachvili's model are correct and universally applicable.

Table 2. Quantitative validation of Israelachvili's theory.

Product	P_{lit}	l_0 calcd [a] (Å)	P calcd [b]
PS-*dendr*-$(NH_2)_8$	0.50–1.00	7.2–14	0.12
PS-*dendr*-$(NH_2)_{16}$	0.33–0.50	11.1–17	0.09

[a] Calculated with $V = 1897.5\,cm^3 mol^{-1}$. [b] Calculated with l_0 = 6 nm.

By comparing the polystyrene–poly(propylene imine) dendrimer amphiphiles with low molecular weight surfactants and traditional amphiphilic block copolymers, it becomes clear that our structures combine properties of both. A feature shared with surfactants is the ability to change the type of aggregation by adjusting amphiphile geometry. For surfactants this is a well-known phenomenon, and forms the basis of Israelachvili's theory.[30] Changes in aggregation type can also be induced by solubilization,[32] varying the concentration,[33] or changing the ratio in mixed systems.[34] For amphiphilic block copolymers the possibilities are much more restricted. The main aggregation form is the spherical micelle, whereas some anomalous behavior is reported that leads to metastable wormlike micelles[35] or ellipsoidal structures.[36] For polystyrene–poly(ethylene oxide)–polystyrene triblock copolymers a change from spherical to rodlike micelles on increasing the temperature is reported.[37] By means of polymerizable surfactants or polymers with amphiphilic side chains, it is possible to obtain a broader variety of aggregation types.[38] However, this is a different class of amphiphiles, for which the aggregate consists mostly of one polymer, and of which the composition is less well-defined. Variation of aggregation within a series of block copolymers is observed for two-dimensional self-assembly of a polystyrene–peralkylated poly(vinyl pyridine) block copolymer.[39] On addition of polystyrene homopolymer different structures, varying from rings to sphercial micelles, were observed. Varying the ratio of block lengths of a polystyrene–polyisoprene diblock copolymer resulted in different aggregation types in the solid phase, from lamellar structures to the so-called ordered bicontinuous double diamond morphology.[40] An increase in head-group size of the polystyrene–poly(propylene imine) dendrimer amphiphiles induced phase separation in the bulk, which could be seen in the fourth and fifth generation. The solid-phase morphology of these molecules is still unknown. Changing three-dimensional solvated aggregates by tuning the geometry as observed for our structures, however, is a new feature for block copolymers.

An advantage that our systems share with block copolymers is the stability of the aggregates formed. The strong interactions between the polymers in the core of the structure[41] makes it possible to observe micelles with TEM[39] and GPC.[42] The very low deaggregation rate was also observed by Riess et al. for block copolymers used in emulsion polymerization.[43] For our structures, stability is also proven by the techniques mentioned above and by the fact that on dilution no change occurs in aggregation type. This also points in the direction of low critical association concentration (cac) values. The cac values found are comparable to those of traditional block copolymer systems. Our systems therefore offer very interesting possibilities of use as stabilizers for vesicle and emulsion polymerization.

Polystyrene–poly(propylene imine) dendrimers can furthermore contribute to a better understanding of aggregation behavior of amphiphilic block copolymers, because the polar part of our molecules is as well-defined as a polymer can be, and heterogeneity of the structures, which can sometimes affect amphiphilic behavior,[44] is very much diminished.

Conclusions

It is possible to prepare a new series of amphiphilic diblock copolymers by a divergent poly(propylene imine) dendrimer synthesis onto a primary amine functionalized polystyrene core molecule. Every intermediate of this 10-step reaction procedure can be characterized in great detail. Study of the behavior of these amphiphiles at toluene/water and air/water interfaces clearly demonstrates the development of amphiphilicity with increasing generation. The change of aggregation type from inverted micellar structures for PS-*dendr*-$(NH_2)_4$ through vesicles and rodlike micelles to spherical micelles for PS-*dendr*-$(NH_2)_{32}$ is in qualitative agreement with the theory of Israelachvili concerning surfactant assembly. The amphiphiles described in this paper are similar in shape but different in size compared with traditional surfactants, while similar in size but different in shape compared with traditional block copolymers. This new class of amphiphiles can therefore contribute to a better understanding of the relation between molecular structure and amphiphilic properties.

Experimental Procedure

General procedures: ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer at 400.13 and 100.62 MHz, respectively. All δ values are given relative to tetramethylsilane. Infrared samples were prepared according the KBr technique and were measured on a Perkin–Elmer 1605 FT. GPC analyses were performed on a Waters 590 GPC, with a PL-GEL 352 column and THF as eluent, and with a Spectra physics GPC, with Viscotek H 502 and Shodex RI 71 detectors, equipped with two PL-GEL mixed-C 30 cm columns, and with $CHCl_3$ as eluent. TLC was performed with Merck 60 F_{254} silica gel plates, and compounds were visualized with I_2 vapor or under UV light (λ = 254 nm). Column chromatography was performed with Merck silica gel 60, 70–230 mesh ASTM. Flash chromatography was performed with Merck silica gel 60, 230–400 mesh ASTM.

Glassware was kept in a stove at 150 °C before use. THF p.a. was distilled from Na/benzophenone; DMF was distilled and stored on molecular sieves (3 Å). All other solvents (p.a. quality) and reagents were used without further purification, except for CH_2Cl_2 (chemical purity), *n*-hexane (distilled before use) and methanol used for precipitations (technical grade).

Anionic polymerization: A 1.5 L BEP 280 Büchi glass reactor was used for the large-scale anionic polymerization. The reactor was evacuated at 60 °C and purged with nitrogen prior to use. Reactions were carried out under 2.5 bar N_2 pressure. Nitrogen was purified over a column filled with activated BTS catalyst to remove O_2, followed by a column of molecular sieves (3 Å) to remove traces of H_2O. Styrene was purified at −18 °C over a column filled with Al_2O_3 granulates, and stored in a storage vessel under nitrogen pressure at 4 °C. Cyclohexane was purified over a column of molecular sieves (3 Å) and stored under nitrogen. *sec*-Butyllithium (1.3 M solution in cyclohexane/*n*-hexane 92/8 v/v) and CO_2 were used as purchased.

Dendrimer synthesis: A Parr reactor, type 4561 (300 mL), equipped with 4642 controller was used for the hydrogenation reactions. Raney cobalt (Grace) was kindly provided by DSM.

DSC measurements were performed on a Perkin–Elmer TAC 7/DX, with a heating rate of 40 °C min^{-1}.

Monolayer experiments were performed in a home-built trough maintained at room temperature (140 × 210 mm). The surface pressure was measured by means of Wilhelmy plates mounted on a Trans-Tek transducer (Connecticut, USA). The surface of compressed monolayers was studied with a Brewster angle microscope (NFT BAM-1), equipped with a 10 mW He–Ne laser with a beam diameter of 0.68 mm, operating at 632.8 nm. Reflections were detected with a CCD camera. On the subphase (Milli-Q water) 50–150 µL of a solution of the amphiphiles in $CHCl_3$ was spread and allowed to evaporate. The rate of compression was 7.0 cm^2 min^{-1}.

Conductivity measurements were performed in a heterogeneous toluene/water system, with a CDM 83 conductivity meter and a Philips conductivity cell PW 9550. The cell constant was 0.872 cm^{-1}; calibrations used 0.1 M and 0.01 M KCl solutions. Measurements were performed at room temperature. A 0.01 M KCl solution (20 mL) in which 3.3×10^{-4} M amphiphile was dispersed was starting point of the measurements. To this mixture a 3.3×10^{-4} M amphiphile solution in toluene was added dropwise. The conductivity was measured continuously.

Critical association concentrations: Steady-state fluorescence spectra were run in a Perkin–Elmer luminescence spectrometer LS 50 B in right-angle geometry (90° collecting optics) with slit openings of 5 nm for emission and 2.5 nm for excitation. 1 cm square quartz cells were filled with ≈ 3 mL solution with [Py] = 4.8×10^{-7} M.

For fluorescence emission spectra λ_{ex} was 339 nm, for excitation spectra λ_{em} was 390 nm. The block copolymer was dissolved in an emulsion of tetrahydrofuran and water while being shaken. After removal of the organic solvent in a rotatory evaporator at 35 °C, a stock solution of the polymer in water was obtained. All samples were prepared by adding a known amount of pyrene in acetone to a series of empty 10 mL volumetric flasks; after evaporation of the acetone, known amounts of the stock solution of amphiphile were added and diluted with distilled water in order to obtain final polymer concentrations between 10^{-4} and 10^{-9} M. The flasks were sealed and stirred for ≈20 h at room temperature to allow the pyrene and the aggregates to equilibrate.

TEM samples were prepared by the following procedure: the amphiphiles were dissolved in toluene or tetrahydrofuran (2 mL). After addition of water (25 mL), the organic solvents were evaporated and stable aggregates of 3×10^{-4} M were formed. A droplet of the sample was placed on a Cu grid, covered with formvar, and allowed to dry for 1 min, after which the droplet was removed. Negative staining was performed by addition of a droplet of a 2 wt % uranyl acetate solution over 15 s. Pt-shadowed samples were prepared by covering the dried sample with Pt with a Balzers Sputter unit. Freeze-fractured samples were prepared by addition of a droplet of the amphiphile dispersion onto a gold microscope grid (150 mesh), placing this between two copper plates and fixed in supercooled liquid pentane. Sample holders were placed in a Balzers freeze-etching system BAF 400 D at 10^{-7} Torr and heated to −105 °C. After fracturing, the samples were etched for 1 min (ΔT = 20 °C), shadowed with Pt (layer thickness 2 nm) and covered with carbon (layer thickness 20 nm). Replicas were allowed to warm to room temperature and left in 20% chromic acid for 16 h. After rinsing with water they were allowed to dry. All samples were studied with a Philips TEM 201 (60 kV).

Dynamic light scattering was performed at DSM Research, Geleen, with an ALV/SP-86 goniometer equipped with a Spectra Physics 2000 Ar$^+$ laser (514.5 nm, 300 mW). A Glan–Thompson prism was used for detection of the vertically polarized scattered light. The intensity–auto correlation functions were determined with an ALV-5000 multibit correlator. Aqueous aggregates were prepared according to the method described for the TEM samples.

Electrospray mass spectra were recorded on an API 300 MS/MS Perkin–Elmer sciex mass spectrometer, with a mass range of 3000. Compounds were dissolved at concentrations of 150 ppm in 50% MeOH/50% THF, and 0.1% HCOOH was added. The sample solution was delivered directly to the ES-MS by a Harvard syringe pump at a flow rate of 5 μL min^{-1}. The mass spectrometer was used in positive ion mode by applying a voltage of 5.5 kV to the capillary, while the orifice was set at 35 V. Mass spectra were collected in full scan mode, scanning over $30 < m/z < 2500$ in 25 s. Dry air was used as nebulizer gas at a flow rate of 1.04 L min^{-1}. Nitrogen was used as drying bath gas at a flow rate of 0.63 L min^{-1}. Electrospray data were deconvoluted by the Bio-reconstruct program.

PS–COOH (1): Cyclohexane was siphoned from the storage vessel into the reactor by application of N$_2$ pressure. The reactor was cooled to 10 °C. A weighed amount of styrene was siphoned in likewise. The solution was stirred at 800 rpm. Next the appropiate amount of *sec*-butyllithium was added through a syringe. After addition, the temperature was raised to 60 °C and the reaction allowed to continue for 2 hours. A 5-neck 2 L round-bottomed flask equipped with magnetic stirrer, argon inlet and outlet, CO$_2$ inlet, THF inlet, and a sealed reactor connection tube was dried according to general procedures. THF (500 mL) was distilled into the flask. After the flask had been cooled in an ice bath, the THF was saturated with CO$_2$, disconnected from the argon system and THF distillation apparatus and connected by the tube to the polymerization reactor. Under nitrogen pressure the contents of the polymerization vessel were siphoned into the THF. The solution was neutralized with acidified methanol, concentrated, and precipitated in a tenfold excess of methanol. Yields obtained after decanting and drying in vacuo at 60 °C were >90%, COOH functionalization yields >95%. ^{1}H NMR (CDCl$_3$): δ = 0.54–0.78 (br, 6H, C*H*$_3$CH$_2$CH(C*H*$_3$)(CH$_2$CHPh)$_n$), 0.78–2.44 (CH$_3$C*H*$_2$CH(CH$_3$)(C*H*$_2$C*H*Ph)$_{n-1}$C*H*$_2$CHPhCOOH), 3.00–3.30 (br, 1H, (CH$_2$CHPh)$_{n-1}$CH$_2$C*H*PhCOOH), 6.25–7.32 (CH$_2$CH*Ph*); ^{13}C NMR (CDCl$_3$): δ = 11.0–11.4 (m, *C*H$_3$CH$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 18.5–19.8 (m, CH$_3$CH$_2$CH(*C*H$_3$)(CH$_2$CHPh)$_n$), 28.7–30.4 (m, CH$_3$*C*H$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 31.5 (CH$_3$CH$_2$*C*H(CH$_3$)(CH$_2$CHPh)$_n$), 40.8 (CH$_3$CH$_2$CH(CH$_3$)(CH$_2$*C*HPh)$_{n-1}$), 40.3–46.7 (br, CH$_3$CH$_2$CH(CH$_3$)(*C*H$_2$CHPh)$_n$), 49.5 (CH$_3$CH$_2$CH(CH$_3$)(CH$_2$CHPh)$_{n-1}$CH$_2$*C*HPhCOOH), 124.1–127.0 (br, CH$_2$CH*Ph*$_{para}$), 127.0–129.5 (br, CH$_2$CH*Ph*$_{ortho+meta}$), 145.1–146.5 (br, CH$_2$CH*Ph*$_{ipso}$), 178.8–179.8 (br, (CH$_2$CHPh)$_{n-1}$CH$_2$CHPh*C*OOH); IR: $\tilde{\nu}_{C=O}$ = 1706 cm^{-1}.

PS–CH$_2$OH (2): To a solution of **1** (70 g, calculated $M_n = 3.2\times10^3$ g mol^{-1}) in THF (400 mL) approximately 1.7 g LiAlH$_4$ (2 mol/mol acid) was added. After 0.5 h of reaction no acid could be detected on TLC. To remove excess LiAlH$_4$ a 1 M sodium hydroxide solution (10 mL) was added to the solution. After extraction of the polymer with a toluene/saturated NaCl solution the alcohol **2** was precipitated in CH$_3$OH and dried in vacuo (60 °C), yielding 69.5 g (99%). Several molecular weights were prepared, but the PS-dendr-(NH$_2$)$_n$ series were prepared from the samples with GPC $M_n = 3.2\times10^3$ g mol^{-1} and $M_w/M_n = 1.04$. ^{1}H NMR (CDCl$_3$): δ = 0.54–0.78 (br, 6H, C*H*$_3$CH$_2$CH(C*H*$_3$)(CH$_2$CHPh)$_n$), 0.78–2.44 (CH$_3$C*H*$_2$CH(CH$_3$)(C*H*$_2$C*H*Ph)$_{n-1}$), 2.44–2.68 (br, 1H, CH$_2$C*H*PhCH$_2$OH), 3.38–3.65 (br, 2H, CH$_2$CHPhC*H*$_2$OH), 6.28–7.25 ((CH$_2$CH*Ph*)$_n$); ^{13}C NMR (CDCl$_3$): δ = 11.0–11.4 (br, *C*H$_3$CH$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 18.0 (NCH$_2$*C*H$_2$CN), 18.5–19.8 (br, CH$_3$CH$_2$CH(*C*H$_3$)(CH$_2$CHPh)$_n$), 27.0 ((CH$_2$CHPh)$_n$*C*H$_2$), 28.7–30.4 (br, CH$_3$*C*H$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 31.5 (CH$_3$CH$_2$*C*H(CH$_3$)(CH$_2$CHPh)$_n$), 40.3 (br, (CH$_2$*C*HPh)$_n$), 40.0–46.5 (br, (*C*H$_2$CHPh)$_n$), 66.6–68.2 (br, (CH$_2$CHPh)$_n$*C*H$_2$OH), 124.1–127.0 (br, CH$_2$CH*Ph*$_{para}$), 127.0–129.5 (br, CH$_2$CH*Ph*$_{ortho+meta}$), 145.1–146.5 (br, CH$_2$CH*Ph*$_{ipso}$); IR: $\tilde{\nu}_{O-H}$ = 3583 cm^{-1}.

PS–CH$_2$OCH$_2$CH$_2$CN (3): 66.0 g of **2** ($M_n = 3.2\times10^3$ g mol^{-1}, $M_w/M_n = 1.04$ as determined with GPC) was dissolved in toluene (350 mL) in a 500 mL 2-neck round-bottomed flask equipped with condenser and thermometer. A solution of NaOH (25 wt%, 11.2 mL, ≈4 mol NaOH/mol **2**) and trioctylmethylammonium chloride (TOMA, 9.3 g, 1 mol/mol **2**) were added. This two-phase system was stirred and heated for 30 min at 80 °C, then cooled to room temperature, after which 30.33 g acrylonitrile (≈25 mol/mol **2**) was added dropwise. After 15 min of reaction TLC showed only a very small amount of **2**, after one hour no further change could be detected. The reaction mixture was then precipitated in methanol and filtered off. Compound **3** was purified by flash chromatography (eluent *n*-hexane/diethyl ether/CH$_2$Cl$_2$ 14/3/3 v/v/v). Yield: 54.91 g **3** (83%). Purity was confirmed by TLC, ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (CDCl$_3$): δ = 0.54–0.78 (br, 6H, C*H*$_3$CH$_2$CH(C*H*$_3$)(CH$_2$CHPh)$_n$), 0.78–2.44 (CH$_3$C*H*$_2$C*H*(CH$_3$)(C*H*$_2$C*H*Ph)$_{n-1}$), 2.34–2.45 (2H, CH$_2$C*H*$_2$CN), 2.99–3.20 (2H, C*H*$_2$OCH$_2$CH$_2$CN), 3.32–3.44 (2H, CH$_2$OC*H*$_2$CH$_2$CN), 6.28–7.25 ((CH$_2$CH*Ph*)$_n$); ^{13}C NMR (CDCl$_3$): δ = 11.0–11.4 (br, *C*H$_3$CH$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 18.0 (NCH$_2$*C*H$_2$CN), 18.5–19.8 (br, CH$_3$CH$_2$CH(*C*H$_3$)(CH$_2$CHPh)$_n$), 18.7 (CH$_2$*C*H$_2$CN), 27.0 ((CH$_2$CHPh)$_n$*C*H$_2$), 28.7–30.4 (br, CH$_3$*C*H$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 31.5 (CH$_3$CH$_2$*C*H(CH$_3$)(CH$_2$CHPh)$_n$), 40.3 (br, (CH$_2$*C*HPh)$_n$), 40.0–46.5 (br, (*C*H$_2$CHPh)$_n$), 65.0 (*C*H$_2$OCH$_2$CH$_2$CN), 69.2 (CH$_2$O*C*H$_2$CH$_2$CN), 117.8 (CH$_2$OCH$_2$CH$_2$*C*N), 124.1–127.0 (br, CH$_2$CH*Ph*$_{para}$), 127.0–129.5 (br, CH$_2$CH*Ph*$_{ortho+meta}$), 145.1–146.5 (br, CH$_2$CH*Ph*$_{ipso}$); IR: 2251.6 cm^{-1} CN stretch.

PS–CH$_2$OCH$_2$CH$_2$CH$_2$NH$_2$ (4): 28.48 g **3** (calculated $M_n = 3.26\times10^3$ g mol^{-1}) was dissolved in a mixture of toluene/methanol 3/1 v/v and transferred into the Parr reactor vessel. Raney cobalt catalyst (14 g) suspended in water was decanted, rinsed with methanol (3 times) and toluene (once) and added to the substrate in the toluene/methanol 3/1 v/v mixture. Next the total volume was brought to 225 mL. After closing the reactor the solution was purged 3 times with H$_2$. NH$_3$ (27 g) was added to the system. The reaction mixture was mechanically stirred for 7 h at 50 °C and 80 bar H$_2$ pressure. The hydrogenation could be followed well by the decrease of the CN stretching vibration in the IR spectrum. After the reaction mixture had been cooled and the pressure released, the catalyst was filtered off on a glass filter over a layer of diatomaceous earth. After evaporation of the solvent the product was taken up in THF and precipitated in a tenfold excess of methanol. After filtration and drying in vacuo at 60 °C, 26.49 g of product was obtained (93%). The purity was confirmed by TLC, IR, ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (CDCl$_3$): δ = 0.73–1.22 (9H, *Bu*(CH$_2$CHPh)$_n$), 1.22–1.71 ((C*H*$_2$CHPh)$_n$), 1.71–2.35 ((CH$_2$C*H*Ph)$_n$), 2.58–2.74 (2H, CH$_2$OCH$_2$CH$_2$C*H*$_2$NH$_2$), 2.91–3.13 (2H, C*H*$_2$OCH$_2$CH$_2$CH$_2$NH$_2$), 3.15–3.32 (2H, CH$_2$OC*H*$_2$CH$_2$CH$_2$NH$_2$), 6.28–7.25 ((CH$_2$CH*Ph*)$_n$); ^{13}C NMR (CDCl$_3$): δ = 14.0 (*C*H$_3$CH$_2$CH$_2$CH$_2$(CH$_2$CHPh)$_n$), 22.5 (CH$_3$*C*H$_2$CH$_2$CH$_2$(CH$_2$CHPh)$_n$), 26.9 (CH$_3$CH$_2$*C*H$_2$CH$_2$(CH$_2$CHPh)$_n$), 27.0 ((CH$_2$CHPh)$_n$*C*H$_2$), 30.9 (CH$_2$OCH$_2$*C*H$_2$CH$_2$N), 31.8 (CH$_3$CH$_2$CH$_2$*C*H$_2$(CH$_2$CHPh)$_n$), 33.4 (CH$_2$OCH$_2$*C*H$_2$CH$_2$NH$_2$), 39.6 (CH$_2$OCH$_2$CH$_2$*C*H$_2$NH$_2$), 40.3 (br, (CH$_2$*C*HPh)$_n$), 40.0–46.5 (br, (*C*H$_2$CHPh)$_n$), 68.8 (*C*H$_2$OCH$_2$CH$_2$CH$_2$NH$_2$), 68.9 (CH$_2$O*C*H$_2$CH$_2$CH$_2$NH$_2$), 124.1–127.0 (br, CH$_2$CH*Ph*$_{para}$), 127.0–129.5 (br, CH$_2$CH*Ph*$_{ortho+meta}$), 145.1–146.5 (br, CH$_2$CH*Ph*$_{ipso}$).

PS-*dendr*-(CN)$_2$ (5): To a solution of 49.28 g of **4** (two batches) in toluene (100 mL), HOAc (10.95 g, 11 molequiv), water (50 mL) and acrylonitrile (100 mL) were added. The mixture was heated under reflux over 24 h and the solution was evaporated in vacuo. The crude solid was dissolved in CH$_2$Cl$_2$ and the solution was again evaporated in vacuo to remove residual HOAc. The product was taken up in THF and precipitated in a tenfold excess of a mixture of methanol and a few drops of ammonia. After filtration and drying in vacuo (60 °C) 49.33 g (97%) of dinitrile **5** was obtained. DSC: T_g = 79.3 °C; ^{1}H NMR (CDCl$_3$): δ = 0.54–0.78 (br, 6H, C*H*$_3$CH$_2$CH(C*H*$_3$)(CH$_2$CHPh)$_n$), 0.78–2.44 (CH$_3$C*H*$_2$CH(CH$_3$)(C*H*$_2$C*H*Ph)$_{n-1}$C*H*$_2$CHPhCH$_2$OCH$_2$C*H*$_2$CH$_2$N), 2.16 (4H, NCH$_2$C*H*$_2$CN), 2.30 (2H, OCH$_2$CH$_2$C*H*$_2$N), 2.66 (4H, NC*H*$_2$CH$_2$CN), 3.10–3.48 (br, 4H, CH$_2$CHPhC*H*$_2$OC*H*$_2$CH$_2$CH$_2$N), 6.25–7.32 ((CH$_2$CH*Ph*)$_n$); ^{13}C NMR (CDCl$_3$): δ = 11.0–11.4 (br, *C*H$_3$CH$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 18.0 (NCH$_2$*C*H$_2$CN), 18.5–19.8 (br, CH$_3$CH$_2$CH(*C*H$_3$)(CH$_2$CHPh)$_n$), 27.5 (NCH$_2$*C*H$_2$CH$_2$N), 28.7–30.4 (br, CH$_3$*C*H$_2$CH(CH$_3$)(CH$_2$CHPh)$_n$), 31.5 (CH$_3$CH$_2$*C*H(CH$_3$)(CH$_2$CHPh)$_n$), 40.3 (CH$_3$CH$_2$CH(CH$_3$)(CH$_2$*C*HPh)$_n$), 40.0–46.5 (br, CH$_3$CH$_2$CH(CH$_3$)(*C*H$_2$CHPh)$_n$), 49.5 (OCH$_2$CH$_2$*C*H$_2$N), 49.9 (N*C*H$_2$CH$_2$CN), 67.0–67.6 (br, (CH$_2$CHPh)$_n$CH$_2$O*C*H$_2$CH$_2$CH$_2$N), 75.0–76.5 (br, (CH$_2$CHPh)$_n$*C*H$_2$OCH$_2$CH$_2$CH$_2$N), 118.7 (2C, *C*N), 124.1–127.0 (br, CH$_2$CH*Ph*$_{para}$), 127.0–129.5 (br, CH$_2$CH*Ph*$_{ortho+meta}$), 145.1–146.5 (br, CH$_2$CH*Ph*$_{ipso}$); IR: $\tilde{\nu}_{CN}$ = 2246 cm^{-1}; 3025, 2923.7, 1943.3, 1872.1, 1803.7, 1744.2, 1664.9, 1601.0, 1492.9, 1451.9, 1372.8, 1116.3, 1028.4, 906.5, 756.7, 699.1, 539.4 cm^{-1}.

PS-*dendr*-(NH$_2$)$_2$ (6): Dinitrile **5** (25.00 g, calculated $M_n = 3.35\times10^3$ g mol^{-1}) was hydrogenated for 24 h according to the procedure described for the synthesis of **4**. 9 g catalyst and 35 g NH$_3$ were used. Diamine **6** (22.45 g, 89%) was obtained after the crude solid was taken up in THF and precipitated in H$_2$O. The purity was confirmed by TLC, IR, ^{1}H NMR and ^{13}C NMR. DSC: T_g = 77.9 °C. ^{1}H NMR

(CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.44 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_{n-1}C\mathit{H}_2CHPhCH_2OCH_2C\mathit{H}_2CH_2N + NCH_2C\mathit{H}_2CH_2N}$), 2.32–2.50 (6H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NC\mathit{H}_2CH_2CH_2NH_2}$), 2.67 (4H, $\mathrm{NCH_2CH_2C\mathit{H}_2NH_2}$), 3.10–3.48 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 18.4–19.9 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 25.6 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 29.9 ($\mathrm{NCH_2CH_2CH_2NH_2}$), 28.7–30.4 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 30.9 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH_2}$), 31.4 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.4 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.7 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH_2}$), 40.0–46.4 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 50.5 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.8 ($\mathrm{N\mathit{C}H_2CH_2CH_2NH_2}$), 68.6–69.0 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.0–76.4 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 124.1–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.0–129.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{NH} = 3436.3$, 3382.2 cm^{-1}.

PS-*dendr*-(CN)$_4$ (7): To a solution of diamine **6** (28.80 g, calculated $M_n = 3.36 \times 10^3$ g mol^{-1}) in toluene (200 mL) 6.0 g HOAc (11 molequiv), water (100 mL) and acrylonitrile (100 mL) were added. The mixture was heated under reflux for 65 h. After workup an impurity was detected on TLC and ^{1}H NMR. The product was purified by flash chromatography. By elution with CH$_2$Cl$_2$ all impurities were removed. Elution with 3% MeOH in CH$_2$Cl$_2$ gave the desired pure tetranitrile 7 (22.89 g, 80%). DSC: $T_g = 74.9$ °C. ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.74 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_nCH_2OCH_2CH_2CH_2N}$), 1.55–1.62 (br, 6H, $\mathrm{OCH_2C\mathit{H}_2CH_2N + NCH_2C\mathit{H}_2CH_2N}$), 2.35–2.42 (br, 6H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NCH_2CH_2C\mathit{H}_2N}$), 2.41 (t, $J = 6.6$ Hz, 8H, $\mathrm{NCH_2C\mathit{H}_2CN}$), 2.53 (t, $J = 6.7$ Hz, 4H, $\mathrm{NC\mathit{H}_2CH_2CH_2N}$), 2.75–2.85 (br, 8H, $\mathrm{NC\mathit{H}_2CH_2CN}$), 3.11–3.45 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 16.9 ($\mathrm{NCH_2\mathit{C}H_2CN}$), 18.5–19.8 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 24.9 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 26.9 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.7–30.4 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 31.5 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.3 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.0–46.5 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 49.5 ($\mathrm{N\mathit{C}H_2CH_2CN}$), 50.3 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.3/51.5 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 67.9–68.7 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.0–76.5 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 118.7 ($\mathrm{\mathit{C}N}$), 124.1–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.0–129.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{CN} = 2245$ cm^{-1}.

PS-*dendr*-(NH$_2$)$_4$ (**8**): Tetranitrile 7 (19.80 g, calculated $M_n = 3.57 \times 10^3$ g mol^{-1}) was hydrogenated over 24 h according to the procedure described for the synthesis of **4**. 12 g catalyst and 30 g NH$_3$ were used. Tetraamine **8** (17.75 g, 90%) was obtained after the crude solid was taken up in THF and precipitated in H$_2$O. DSC: $T_g = 72.7$ °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.44 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_{n-1}C\mathit{H}_2CHPhCH_2O}$), 1.60–1.70 (br, 14H, $\mathrm{OCH_2C\mathit{H}_2CH_2N + NCH_2C\mathit{H}_2CH_2N}$), 2.25–2.38 (br, 10H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NC\mathit{H}_2CH_2C\mathit{H}_2N}$), 2.42 (t, $J = 6.7$ Hz, 8H, $\mathrm{NC\mathit{H}_2CH_2CH_2NH_2}$), 2.70 (t, $J = 6.7$ Hz, 8H, $\mathrm{NCH_2CH_2C\mathit{H}_2NH_2}$), 3.10–3.48 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 18.4–19.9 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 24.5 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 27.0 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.7–30.4 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 30.9 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH_2}$), 31.4 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.4 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.7 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH_2}$), 40.0–46.4 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 50.9 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.8 ($\mathrm{N\mathit{C}H_2CH_2CH_2NH_2}$), 52.2 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 69.0–69.4 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.0–76.4 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 124.1–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.0–129.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{NH} = 3436.3$, 3378.7 cm^{-1}.

PS-*dendr*-(CN)$_8$ (**9**): To a solution of tetraamine **8** (17.00 g, calculated $M_n = 3.60 \times 10^3$ g mol^{-1}) in toluene (170 mL) HOAc (2.0 g, 11 molequiv), water (85 mL), and acrylonitrile (60 mL) were added. The mixture was heated under reflux for 48 h. The solution was evaporated in vacuo. The crude solid was dissolved in CH$_2$Cl$_2$ and the solution was again evaporated in vacuo to remove residual HOAc. The product was taken up in THF and precipitated in a tenfold excess of a mixture of methanol and ammonia (9/1 v/v). After filtration and drying in vacuo (60 °C), 14.0 g (75%) of octanitrile **9** was obtained. DSC: $T_g = 61.7$ °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.74 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_nCH_2OCH_2CH_2CH_2N}$), 1.60 (s, 12H, $\mathrm{NCH_2C\mathit{H}_2CH_2N}$) 2.37 (br, 14H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NCH_2CH_2C\mathit{H}_2N}$), 2.43 (t, $J = 6.6$ Hz, 16H, $\mathrm{NCH_2C\mathit{H}_2CN}$), 2.53 (t, $J = 6.7$ Hz, 12H, $\mathrm{NC\mathit{H}_2CH_2CH_2N}$), 2.80 (t, $J = 6.6$ Hz, 16H, $\mathrm{NC\mathit{H}_2CH_2CN}$), 3.13–3.45 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 17.0 ($\mathrm{NCH_2\mathit{C}H_2CN}$), 18.8–20.0 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 24.6 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 25.1 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 27.2 ($\mathrm{CH_2\mathit{C}H_2CH_2N}$), 28.3–30.6 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 31.6 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.4 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.2–47.0 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 49.6 ($\mathrm{N\mathit{C}H_2CH_2CN}$), 50.9 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.5/51.7 ($\mathrm{NCH_2CH_2\mathit{C}H_2N}$), 52.2/52.4 ($\mathrm{N\mathit{C}H_2CH_2CH_2N}$), 69.6–69.2 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.2–76.2 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 119.1 (8C, $\mathrm{\mathit{C}N}$), 125.2–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.1–130.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.6 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{CN} = 2247$ cm^{-1}.

PS-*dendr*-(NH$_2$)$_8$ (**10**): Octanitrile **9** (12.50 g, calculated $M_n = 4.00 \times 10^3$ g mol^{-1}) was hydrogenated over 26 h according to the procedure described for the synthesis of **4**, with 160 mL solvent, 7.9 g catalyst, and 15.6 g NH$_3$. Octaamine **10** (11.94 g, 95%) was obtained after the crude solid was taken up in THF and precipitated in ammonia. The product was free of carbamate. DSC: $T_g = 73.6$ °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.44 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_{n-1}C\mathit{H}_2CHPhCH_2O}$), 1.55–1.65 (br, 30H, $\mathrm{OCH_2C\mathit{H}_2CH_2N + NCH_2C\mathit{H}_2CH_2N}$), 2.25–2.41 (br, 26H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NC\mathit{H}_2CH_2C\mathit{H}_2N}$), 2.45 (t, $J = 6.7$ Hz, 16H, $\mathrm{NC\mathit{H}_2CH_2CH_2NH_2}$), 2.72 (t, $J = 6.7$ Hz, 16H, $\mathrm{NCH_2CH_2C\mathit{H}_2NH_2}$), 3.10–3.48 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 18.4–19.9 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 24.4 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 28.1 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.7–30.4 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 30.5 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH_2}$), 31.4 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.4 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.5 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH_2}$), 40.0–46.4 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 50.7 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.8 ($\mathrm{N\mathit{C}H_2CH_2CH_2NH_2}$), 52.2 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 69.0–69.4 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.0–76.4 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 124.1–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.0–129.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{N-H} = 3375/3289$ cm^{-1}; electrospray mass: 3236, 3340, 3444, 2444, 2548, 3653, 3756, 3861, 3965 (M_n on top), 4071, 4174, 4278, 4382, 4486, 4591, 4694, 4799, 4902 and 5010; experimental $M_w/M_n = 1.02$.

PS-*dendr*-(CN)$_{16}$ (**11**): To a solution of octaamine **10** (11.25 g, calculated $M_n = 4.02 \times 10^3$ g mol^{-1}) in toluene (100 mL), HOAc (1.8 g, 11 molequiv), water (100 mL), and acrylonitrile (60 mL) were added to obtain a stable emulsion. The mixture was heated under reflux over 30 h. The solution was evaporated in vacuo. The crude solid was dissolved in CH$_2$Cl$_2$, and the solution was again evaporated to remove residual HOAc. The product was taken up in THF and precipitated in a tenfold excess of H$_2$O. After filtration and drying in vacuo (60 °C), 12.75 g (93%) of hexadecanitrile **11** was obtained. DSC: $T_g = -26.3$ and 65.5 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.74 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_nCH_2OCH_2CH_2CH_2N}$), 1.52–1.62 (br, 26H, $\mathrm{NCH_2C\mathit{H}_2CH_2N}$), 2.25–2.41 (br, 30H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NCH_2CH_2C\mathit{H}_2N}$), 2.45 (t, $J = 6.6$ Hz, 32H, $\mathrm{NCH_2C\mathit{H}_2CN}$), 2.54 (t, $J = 6.7$ Hz, 28H, $\mathrm{NC\mathit{H}_2CH_2CH_2N}$), 2.82 (t, $J = 6.6$ Hz, 32H, $\mathrm{NC\mathit{H}_2CH_2CN}$), 3.13–3.45 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 16.6 ($\mathrm{NCH_2\mathit{C}H_2CN}$), 18.8–20.0 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 23.9 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 24.6 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 26.6 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.1–30.2 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 31.3 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.1 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 39.8–46.6 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 49.2 ($\mathrm{N\mathit{C}H_2CH_2CN}$), 50.4 ($\mathrm{OCH_2CH_2\mathit{C}H_2N}$), 51.1/51.3 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 51.9 ($\mathrm{N\mathit{C}H_2CH_2CH_2N}$), 69.2–69.6 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.2–76.2 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 118.7 (16C, $\mathrm{\mathit{C}N}$), 125.2–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.1–130.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.6 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{CN} = 2246$ cm^{-1}; 1657.9, 1640.5 cm^{-1}.

PS-*dendr*-(NH$_2$)$_{16}$ (**12**): Hexadecanitrile **11** (10.75 g, calculated $M_n = 4.9 \times 10^3$ g mol^{-1}) was hydrogenated over 50 h according to the procedure described for the synthesis of **4**, with toluene/MeOH = 2/1 v/v (160 mL) as solvent, 10.9 g catalyst and 25 g NH$_3$. Hexadecaamine **12** (10.00 g, 93%) was obtained after the crude solid had been taken up in THF and precipitated in ammonia. DSC: $T_g = -10.2$ and 77.6 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.44 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_{n-1}C\mathit{H}_2CHPhCH_2O}$), 1.52–1.62 (br, 62H, $\mathrm{OCH_2C\mathit{H}_2CH_2N + NCH_2C\mathit{H}_2CH_2N}$), 2.30–2.41 (br, 58H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NC\mathit{H}_2CH_2C\mathit{H}_2N}$), 2.45 (t, $J = 6.7$ Hz, 32H, $\mathrm{NC\mathit{H}_2CH_2CH_2NH_2}$), 2.72 (t, $J = 6.7$ Hz, 32H, $\mathrm{NCH_2CH_2C\mathit{H}_2NH_2}$), 3.10–3.48 (br, 4H, $\mathrm{CH_2CHPhC\mathit{H}_2OC\mathit{H}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0$–11.4 (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 18.4–19.9 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 24.4 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 28.1 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.7–30.4 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 30.8 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH_2}$), 31.4 ($\mathrm{CH_3CH_2\mathit{C}H(CH_3)(CH_2CHPh)_n}$), 40.4 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 40.5 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH_2}$), 40.0–46.4 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 51.5 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH_2}$), 50.0–53.0 (br, $\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 68.0–69.0 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.0–76.4 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 124.1–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.0–129.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.5 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{N-H} = 3362/3286$ cm^{-1}.

PS-*dendr*-(CN)$_{32}$ (**13**): To a solution of hexadecaamine **12** (9.50 g, calculated $M_n = 5.0 \times 10^3$ g mol^{-1}) in toluene (200 mL), HOAc (1.3 g, 11 molequiv), water 200 mL), and acrylonitrile (100 mL) were added to obtain a stable emulsion. The mixture was heated under reflux over 64 h. The solution was evaporated in vacuo. The crude solid was dissolved in CH$_2$Cl$_2$ and the solution was again evaporated in vacuo to remove residual HOAc. The product was taken up in THF and precipitated in a tenfold excess of ammonia. After filtration and drying in vacuo (60 °C), 9.22 g (80%) of 32-nitrile **13** was obtained. DSC: $T_g = -23.8$ and 59.9 °C. ^{1}H NMR (CDCl$_3$): $\delta = 0.54$–0.78 (br, 6H, $\mathrm{C\mathit{H}_3CH_2CH(C\mathit{H}_3)(CH_2CHPh)_n}$), 0.78–2.74 ($\mathrm{CH_3C\mathit{H}_2CH(CH_3)(C\mathit{H}_2C\mathit{H}Ph)_nCH_2OCH_2CH_2CH_2N}$), 1.52–1.68 (br, 60H, $\mathrm{NCH_2C\mathit{H}_2CH_2N}$), 2.30–2.62 (br, 122H, $\mathrm{OCH_2CH_2C\mathit{H}_2N + NCH_2CH_2C\mathit{H}_2N}$), (2.45 (t, $J = 6.6$ Hz, 64 H, $\mathrm{NCH_2\mathit{CH}_2CN}$), 2.82 (t, $J = 6.6$ Hz, 64 H, $\mathrm{N\mathit{CH}_2CH_2CN}$), 3.13–3.45 (br, 4 H, $\mathrm{CH_2CHPh\mathit{CH}_2O\mathit{CH}_2CH_2CH_2N}$), 6.25–7.32 ($\mathrm{(CH_2CH\mathit{Ph})_n}$); ^{13}C NMR (CDCl$_3$): $\delta = 11.0–11.4$ (br, $\mathrm{\mathit{C}H_3CH_2CH(CH_3)(CH_2CHPh)_n}$), 16.8 ($\mathrm{NCH_2\mathit{C}H_2CN}$), 18.8–20.0 (br, $\mathrm{CH_3CH_2CH(\mathit{C}H_3)(CH_2CHPh)_n}$), 23.7 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 24.6 ($\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 26.5 ($\mathrm{OCH_2\mathit{C}H_2CH_2N}$), 28.1–30.2 (br, $\mathrm{CH_3\mathit{C}H_2CH(CH_3)(CH_2CHPh)_n}$), 31.3 ($\mathrm{CH_3CH_2\mathit{CH}(CH_3)(CH_2CHPh)_n}$), 40.1 ($\mathrm{CH_3CH_2CH(CH_3)(CH_2\mathit{C}HPh)_n}$), 39.8–46.6 (br, $\mathrm{CH_3CH_2CH(CH_3)(\mathit{C}H_2CHPh)_n}$), 49.0 ($\mathrm{N\mathit{C}H_2CH_2CN}$), 52.0–50.4 (br, $\mathrm{OCH_2CH_2\mathit{C}H_2N}$, $\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 69.6–69.2 (br, $\mathrm{(CH_2CHPh)_nCH_2O\mathit{C}H_2CH_2CH_2N}$), 75.2–76.2 (br, $\mathrm{(CH_2CHPh)_n\mathit{C}H_2OCH_2CH_2CH_2N}$), 118.7 ($\mathrm{\mathit{C}N}$), 125.2–127.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{para}}}$), 127.1–130.0 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ortho+meta}}}$), 145.1–146.6 (br, $\mathrm{CH_2CH\mathit{Ph}_{\mathit{ipso}}}$); IR: $\tilde{\nu}_{\mathrm{CN}} = 2246$ cm^{-1}; 1667.9 cm^{-1}.

PS-*dendr*-(NH$_2$)$_{32}$ (14): Dotriacontanitrile **13** (7.72 g, calculated $M_n = 6.50 \times 10^3$ g mol^{-1}) was hydrogenated according to the procedure described for the synthesis of **4**, with 8.0 g catalyst and 19.8 g NH$_3$. Reaction was performed over 72 h in 160 mL solvent (toluene/MeOH = 1/1 v/v). After this time no further decrease of the CN stretching vibration ($\tilde{\nu}_{\mathrm{C \equiv N}}$) in the IR spectrum could be detected. After workup, reaction was prolonged under identical circumstances (i.e., addition of the same quantities of solvents and reactants) for 72 h. After this time again no further decrease of the CN stretching vibration could be detected. After workup reaction was again prolonged under identical circumstances for another 26 h. After evaporation, 5.05 g (64%) of 32-amine **14** was obtained. Precipitation in ammonia was not possible owing to the amphiphilic character of **14**. Direct structural evidence from ^{1}H NMR and ^{13}C NMR was not possible because of carbamate formation. IR: $\tilde{\nu}_{\mathrm{N-H}} = 3362/3281$ cm^{-1}.

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