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3-Chloropropyl Functionalized Dendrigraft Polysiloxanes and Dendritic Polyelectrolytes

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ABSTRACT: Dendrigraft polysiloxanes bearing 3-chloropropyl functional groups pendant to the polymer branches of the last generation were synthesized by the graft on graft method. First, branched polysiloxanes of various topologies, star, comb, and dendritic functionalized with pendant vinyl groups, were prepared. Hydrosilylation by dimethylchlorosilane transformed these groups into silyl chloride functions. Living polysiloxanes obtained by the anionic ring-opening polymerization of 2,4,6-tri-3-chloropropyl-2,4,6-trimethylcyclotrisiloxane were terminated on these silyl chloride groups which resulted in the grafting of the 3-chloropropyl functionalized polysiloxane on the branched polysiloxane core. The 3-chloropropyl groups on the dendrigraft were further used for the quaternization of dimethyloctylamine, 2-hydroxyethyldimethylamine, and triethylamine producing quaternary ammonium salt (QAS) groups. Dendrigrafts having an ionic corona and relatively hydrophobic core were synthesized. Preliminary investigations of the behavior of these polymers in aqueous media indicated their strong tendency toward aggregation and the ability to drive solubilization of organic compounds.

Introduction

Cascade-branched polymers have attracted considerable attention due to their unique solution and surface behavior.[1−4] Among them dendrigraft polymers generated by the graft on graft method have gained prominence.[4−8] An advantage is that they may be synthesized with much better control of structure than hyperbranched polymers. Although the precision in the generation of dendrigrafts is not so good as that of dendrimers, their synthesis is less time-consuming and labor intensive, as high molecular weight may be achieved in a few steps. While the functionalization of dendrimers is usually performed on their periphery, the functional groups in dendrigrafts are most often located completely on the last generation branches which constitute a considerable part of the dendritic polymer.

Since the first contributions of the Tomalia[9] and Gauthier[10] research groups to this field, many dendrigraft polymers have been synthesized;[5,6] however, little effort was devoted to the preparation of dendrigrafts based on a polysiloxane skeleton.[11,12] Polysiloxanes are interesting as building blocks in dendrigrafts because of the unusual static and dynamic flexibility of their chains which may easily adopt many conformations that rapidly interconvert. This structural feature gives polysiloxane unusual properties, such as a very low glass temperature, low-temperature coefficients of rheological properties, high solubility in many solvents, and unusual surface behavior.[13] In previous studies, we worked out the synthesis of vinyl substituted polysiloxane dendrigrafts[11] which were used for the generation of liquid crystal dendritic polysiloxanes,[14] for the preparation of hybrid silica materials,[15] and for the immobilization of transition metal catalysts.[16] Vinyl groups on the dendritic macromolecule may be used for the generation of reactive chlorosilyl groups, thus making possible further building of macromolecular architecture by grafting anionic living polysiloxane.[11] Some time ago we showed that *n*-butyllithium initiated polymerization of cyclotrisiloxane bearing 3-chloropropyl functionality proceeds without cleavage of the 3-chloropropyl group leading to a living polymer with a reactive lithium silanolate group at one chain end,[17] indicating utility as a graft in building dendritic functional polysiloxanes. We have probed this possibility in our present study toward the preparation of polysiloxane dendrigrafts bearing 3-chloropropyl groups, which are versatile precursors for various functional groups.[18] Vinyl functionalized star, comb, and dendrigraft polysiloxanes are used as cores in this synthesis.

The 3-chloropropyl groups are further utilized in this study for the generation of ionic quaternary ammonium salt (QAS) groups yielding amphiphilic water soluble, dendrigraft polysiloxanes. Preliminary investigation into the organic solubilizing nature of these polymers in aqueous media and the association behavior of the dendrigraft amphiphiles has been performed. Some dendrimers and dendrigrafts with a hydrophilic shell and hydrophobic core were reported to serve as nanocontainers in which a variety of hydrophobic small guest molecules were hosted.[19−24] This ability gives the core−shell amphiphilic polymers potential as solubilizers, extractants, drug carriers, microreactors, and catalysts. Furthermore, a number of observations point to the desire of cascade branched polymers toward aggregation in aqueous solutions leading to supramolecular structures.[24−28] They show also a strong affinity to various surfaces.[29,30] These association phenomena are explained not only by electrostatic interaction but also by hydrophobic forces[31] and hydrogen bonding.[32] In this respect, synthesis and study of the aqueous solution behavior of dendrigraft polysiloxane amphiphiles are of great interest.

Experimental Section

Chemicals. Monomers. 2,4,6-Tri(3-chloropropyl)-2,4,6-trimethylcyclotrisiloxane, $\mathbf{P_3}$, was synthesized and purified as described in ref 17.

Catalysts. *N*-Butyllithium, 2.5 M in *n*-hexane (Aldrich), and the Pt(0) Karstedt catalyst, colloidal suspension in xylene containing 11% Pt, kindly offered by General Electric, were used as received.

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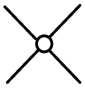
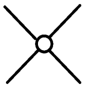
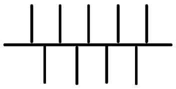
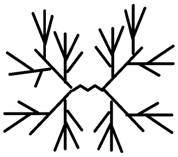
Table 1. The Characteristics of the Vinyl Substituted Cores

Symbol	Topology	Synthesis [a)]		Characteristics				
		Reactive blocks						
		Core	Graft	$M_n \times 10^{-4}$ g·mol^{-1}	M_w/M_n	n_V [b)]	n_B [c)]	$d_V \times 10^3$ [d)] mol·g^{-1}
I		V_4	$Bu(MeViSiO)_mLi$ m=21	0.80 [e)]	1.56 [f)]	86	4	10.7
II		V_4	$Bu[MeViSiO(Me_2SiO)_2]_mLi$ [g)] m=12	1.18 [e)]	1.26 [f)]	47	4	3.98
III		$Bu(ViMeSiO)_{40}SiMe_3$	$Bu(MeViSiO)_mLi$ m=10	3.23 [h)] 3.43 [e)]	1.86 [h)] 1.54 [f)]	300	31	9.3
IV		dendritic polysilox.[a,i)] (on four arms star)	$Bu(MeViSiO)_m(Me_2SiO)_nLi$[j)] m=3.8 n=12.3	35 [h)] 32 [e)]	2.0 [h)] 1.52 [f)]	620	230	1.77

[a] More details in Supporting Information. [b] Average number of vinyl groups in macromolecule. [c] Average number of branches in macromolecule. [d] Density of vinyl groups. [e] From ^1H NMR. [f] From SEC (RI) [size exclusion chromatography (refractive index)] [g] Synthesized by ROP (ring opening polymerization) of VD_2. [h] From MALS (multiangle light scattering). [i] $M_n = 6.9 \times 10^5$, $M_w/M_n = 1.64$, $n_B = 54$, $n_V = 300$, $d_{Vi} = 4.35 \times 10^{-3}$ mol g^{-1}. [j] Gradient copolymer of $D_2V + V_3$ prepared according to ref 32.

Solvents. Toluene (Polskie Odczynniki Chemiczne, POCH) analytical grade was shaken with concentrated H_2SO_4, washed with a $NaHCO_3$ water solution, dried over $MgSO_4$, refluxed with sodium, and distilled under vacuum directly into the reactor. Tetrahydrofuran, THF, (POCH) was refluxed with sodium and distilled from it into an ampule with a Na/K alloy, where the THF was stored and distilled from under vacuum directly into the reactor. Methylene chloride (Chempur) pure p.a., was shaken with concentrated H_2SO_4, washed with a $NaHCO_3$ water solution, dried over $MgSO_4$, and distilled from sodium. Pure butanol (POCH) was used without purification. Pure dimethylformamide, DMF, (POCH) was dried over $MgSO_4$ and distilled under reduced pressure.

Other Reactants. Chlorodimethylsilane, Me_2SiHCl (ABCR), declared purity 96%, was carefully distilled over column and protected from outside moisture in all operations. Dimethyloctylamine, dimethyl-2-hydroxyethylamine, both from Aldrich, and triethylamine (POCH) were purified by distillation.

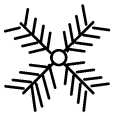
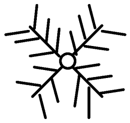
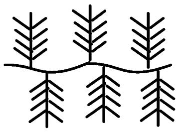
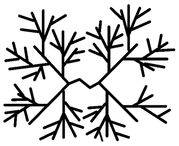
Star-branched, comb-branched, and dendritic-branched vinyl functionalized polymers used here as cores were synthesized by methods similar to those described in ref 11. A description of their preparation is included in Supporting Information.

Synthesis of 3-Chloropropyl Functionalized Dendritic Polysiloxanes. The synthesis was performed in a glass apparatus composed of two reactors A and B connected with each other through a glass pipe with a Rotaflo stopcock. Reactors were equipped with a magnetic stirrer, stopcocks, and a glass joint by which they could be attached to a high vacuum line (hvl). In the synthesis of polymer **1**, the four arms star polysiloxane core **I** containing vinyl groups specified in Table 1 (0.52 g, 5.4×10^{-3} mol of vinyl groups) was placed in reactor A. The reactor was evacuated on a high vacuum line, cooled with liquid N_2, and toluene (8.2 g, 9.5 mL) was distilled into it. Then reactor A was filled with argon, and Karstedt catalyst (3×10^{-6} mol of Pt) was introduced by means of the Hamilton syringe under a positive pressure of argon. The mixture was stirred for 1 h. Then it was cooled in liquid N_2, evacuated on hvl, and Me_2HSiCl (4.9 g, 0.052 mol) was distilled into reactor A. The mixture was stirred at room temperature overnight. The excess of Me_2SiHCl and toluene were removed by distilling them off under high vacuum, and THF (10 mL) was distilled into reactor A by the usual hvl procedure.

In reactor B, 2,4,6-tri(3-chloropropyl)-2,4,6-trimethylcyclotrisiloxane, $\mathbf{P_3}$ (7.0 g, 0.0171 mol) was placed under a positive argon pressure using a Hamilton syringe. The reactor was evacuated on the hvl and, after cooling it in liquid N_2, THF (10 mL) was distilled into the ampule. Then the reactor was filled with argon, and a 2.5 M solution of *n*-BuLi in *n*-hexane (2.18 mL, 5.45×10^{-3} mol) was introduced by means of a precision Hamilton syringe under a positive pressure of argon. The polymerization was carried out at room temperature (23 °C) for 80 min. Then the living polymer solution was transferred under vacuum to reactor A where it was mixed with the solution of the activated core. The mixture was stirred, and the grafting was carried out for 2 h after which a 1.3 M solution of Me_3SiOLi in THF (1 mL) was added to neutralize the remaining SiCl functions. The mixture was stirred for additional 20 min. Then the remaining living polymer and Me_3SiOLi was neutralized by introduction of an excess of Me_3SiCl, and the mixture was stirred for 4 h and left overnight to separate the precipitate. Volatile components were distilled off under vacuum. Then 5 mL of toluene was added, and the mixture was washed several times with a diluted solution of $NaHCO_3$ and water to obtain pH = 7. The polymer solution was dried over $MgSO_4$, and volatile components were distilled off under high vacuum. The polysiloxane was dissolved in dichloromethane and precipitated with a limited amount of methanol. The precipitation procedure was repeated several times. The analysis of the dendrigraft polymer by SEC multi-angle light scattering (MALS) in CH_2Cl_2 gave $M_n = 1.28 \times 10^5$ g mol^{-1}, $M_w/M_n = 1.93$, Rgn = 6.7 nm, dn/dc = 0.051, ^1H NMR gave $M_n = 1.19 \times 10^5$. The analysis by classical SEC (refractive index, RI) standardized on polystyrene gave $M_n = 4.29 \times 10^4$, $M_w/M_n = 1.54$. The ^1H NMR spectrum (Figure 2) showed no vinyl groups. Yield of grafting was estimated to be more than 95%.

All other 3-chloropropyl functionalized dendritic polysiloxanes were synthesized in analogous ways.

Table 2. The Characteristics of the 3-Chloropropyl Substituted Dendritic Polysiloxanes Synthesized by the Grafting of Bu[Cl(CH$_2$)$_3$MeSiO]$_m$Li on the Reactive Siloxane Cores

Symbol	Topology	Number of generations of branches	Synthesis		Characteristics				
			Reactive blocks						
			Core	Graft $^{a)}$ m	M$_n$ x 10$^{-5\ b)}$ g·mol^{-1}	M$_w$/M$_n$$^{b)}$	n$_{Cl}$ x 10$^{-2\ c)}$	n$_B$ $^{d)}$	d$_{Cl}$ x 10$^{3\ e)}$ mol·g^{-1}
1		2	**I**	10	1.28 1.20 $^{f)}$	1.9 1.54 $^{g)}$	8.1	86	6.3
2		2	**II**	12	1.17 0.92 $^{f)}$	2.7	6.8	48	5.8
3		2	**III**	9	3.5 3.3 $^{f)}$	2.0	20	255	5.7
4		4	**IV**	13	15 11 $^{f)}$	2.2	66	740	4.4

[a] Number of [Cl(CH$_2$)$_3$ CH$_3$SiO] units in graft. [b] From MALS (multiangle light scattering). [c] Average number of 3-chloropropyl groups in macromolecule. [d] Average number of branches in macromolecule. [e] Density of 3-chloropropyl groups. [f] From ^{1}H NMR and stoichiometry. [g] From SEC (RI) [size exclusion chromatography (refractive index)]

Table 3. Synthesis of Dendritic QAS−Siloxane Polyelectrolytes

	dendrigraft siloxane polyelectrolyte						
	synthesis				characteristics		
symbol	amine	solvent %	temp (time) °C (h)	yield %	$M_n \times 10^{-5a}$ g/mol	$n_{+-} \times 10^{-3b}$	$d_{+-} \times 10^{3c}$ mol g^{-1}
1a	Me$_2$NCH$_2$CH$_2$OH	DMF	60 (200)	100	2.0	0.81	4.1
1b	Me$_2$N(*n*-Oct)	DMF	60 (200)	87	2.4	0.70	2.9
2a	Me$_2$NCH$_2$CH$_2$OH	DMF	80 (100)	100	1.8	0.68	3.8
2b	Me$_2$N(*n*-Oct)	DMF	80 (100)	89	2.1	0.61	2.9
3a	Me$_2$NCH$_2$CH$_2$OH	*n*-BuOH + DMF^d	80 (60)	100	5.3	2.0	3.8
3b	Me$_2$N(*n*-Oct)	*n*-BuOH + DMF^d	80 (60)	70	5.7	1.4	2.5
3c	Et$_3$N	*n*-BuOH + DMF^d	80 (60)	14	3.8	0.28	0.7
4a	Me$_2$NCH$_2$CH$_2$OH	*n*-BuOH + DMF^d	85 (50)	100	21	6.6	3.1

[a] Calculated from M_n of precursor and yield of the Cl transformation. [b] Number of QAS groups in macromolecule. [c] Density of QAS groups. [d] *n*-BuOH + DMF, 2:1 v/v.

Synthesis of 3(*N*,*N*-dimethyl-*N*-octylammonio)propyl Chloride Substituted Dendritic Polysiloxane, 1b. 3-Chloropropyl substituted polysiloxane **1** (Table 2) (0.40 g, 1.68 × 10^{-3} mol Cl) was dissolved in DMF (1 mL) and dimethyloctylamine (1.50 g, 9.6 × 10^{-3} mol). The mixture was kept with occasional stirring for 200 h at temp 60 °C. Then solvent and excess amine were distilled off under vacuum. A small amount of the amine remained. It was removed by repetitive addition of methylene chloride and distilling off, finally at 60 °C/10^{-3} mm Hg. ^{1}H NMR (Figure 3) showed that the 87% of the 3-chloropropyl groups were transformed into QAS groups.

Synthesis of 3[*N*,*N*-dimethyl-*N*(2-hydroxyethyl)ammonio]propyl Chloride Substituted Dendritic Polysiloxane, 1a. 1 (0.40 g, 1.68 × 10^{-3} mol Cl) was dissolved in DMF (1 mL) and dimethyl-2-hydroxyethylamine (1.0 g, 1.1 × 10^{-2} mol). The mixture was kept for 200 h at temp 60 °C. The excess amine and solvent were removed by distilling them off in vacuum, finally heating the polymer to 60 °C/10^{-3} mm Hg. ^{1}H NMR showed the full transformation of the 3-chloropropyl group into the intended QAS group.

^{1}H NMR (CD$_3$OD) δ in ppm: 0.05−0.3 (br m SiC**H**$_3$), 0.45−0.6 (br m SiC**H**$_2$C**H**$_2$Si), 0.55−0.65 (br s SiC**H**$_2$CH$_2$CH$_2$), 0.9−0.95 (br m C**H**$_3$C), 1.35−1.45 (br m CH$_3$C**H**$_2$C**H**$_2$), 1.80−1.95 (br s SiCH$_2$C**H**$_2$), 3.15−3.25 (br m NC**H**$_3$), 3.40−3.60 (br m C**H**$_2$N), 3.95−4.05 (br s HOC**H**$_2$). Syntheses of other QAS substituted dendrigrafts were performed according to a similar procedure.

Conditions of the syntheses and characteristics of the polymers are presented in Table 3. ^{1}H NMR of the polymer substituted with 3(*N*,*N*,*N*-triethylammonio)propyl chloride, **3c**, (CD$_3$OD) δ in ppm: 0−0.25 (br m SiC**H**$_3$), 0.35−0.5 (br m SiC**H**$_2$C**H**$_2$Si), 0.55−0.7 (br m SiC**H**$_2$CH$_2$CH$_2$), 0.85−0.95 (br m C**H**$_3$CH$_2$CH$_2$), 1.25−1.40 (br m CH$_3$C**H**$_2$C**H**$_2$CH$_2$), 1.35−1.50 (br m C**H**$_3$CH$_2$N$^+$), 1.75−1.90 (br m SiCH$_2$C**H**$_2$CH$_2$N$^+$), 3.40−3.60 (br s C**H**$_2$N$^+$).

Analytical Methods. CAC Determination by Fluorescence Spectroscopy. Dendritic polymer (0.15 g) was dissolved in distilled deionized water in a 10 mL volumetric flask. The solution was then diluted to obtain the required concentrations ranging from 0.001 to 15 g dm^{-3}. A small known amount of pyrene was dissolved in chloroform and added to an empty vessel. Chloroform was allowed to evaporate in a stream of argon before the aqueous solution of

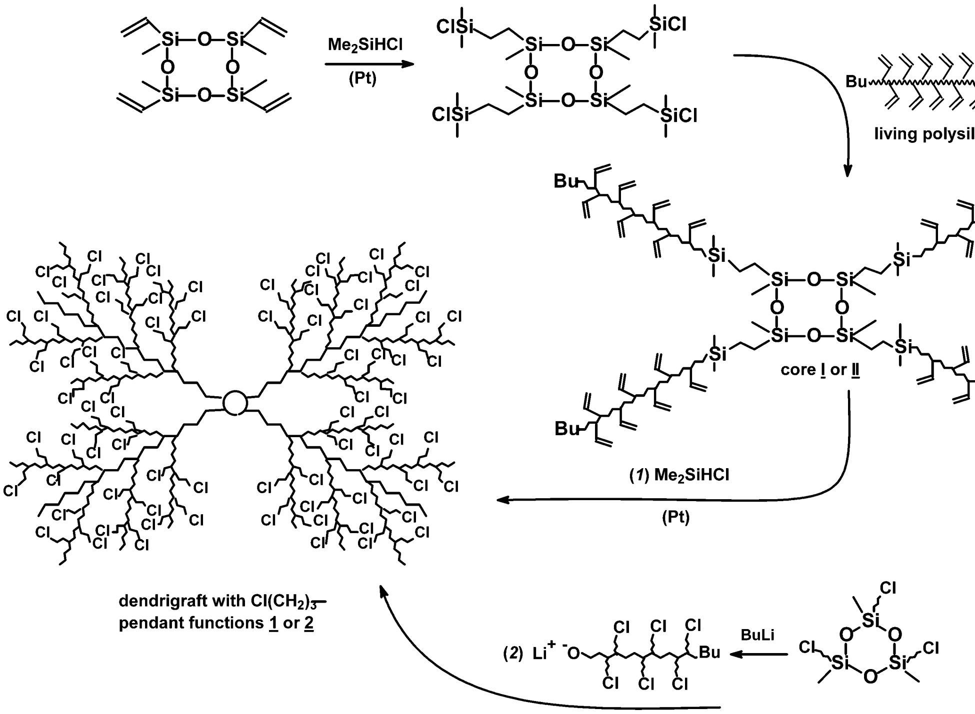


Figure 1. Simplified scheme of the synthesis of 3-chloropropyl functionalized dendrigraft polysiloxanes **1** and **2**. The vinyl functionalized living polysiloxanes were generated by the BuLi initiated ring opening polymerization (ROP) of $(-\text{MeViSiO}-)_3$ or $[-\text{MeViSiO}(\text{Me}_2\text{SiO})_2-]$ for synthesis of core **I** of polymer **1** or core **II** of polymer **2**, respectively (the vinyl functionalized cores **III** and **IV** of polymers **3** and **4**, respectively, were synthesized on similar routes according to the description in ref 11).

polymer was introduced in the quantity suitable to obtain the concentration of pyrene 2×10^{-6} mol dm^{-3}. The mixture was stirred with a magnetic stirrer for 3 h under argon at room temperature. Steady-state fluorescence spectra were recorded on a Perkin-Elmer LS 50 luminescence spectrometer at room temperature. Excitation and emission slit widths were 5 and 3 nm, respectively. For emission spectra, λ_{ex} was 339 nm, and for excitation spectra, λ_{em} was 390 nm. The ratio of intensities in the excitation spectra at 333 and 338.5 nm ($I_{333}/I_{338.5}$) versus the concentration of polymer gives a sigmoidal curve. The maximum of the second derivative of this dependence determines the CAC value in g dm^{-3}.

Determination of Hydrodynamic Diameter. Solutions for photon correlation spectroscopy measurements were prepared by dissolving 0.01 g of polymer in 5 mL of the 0.001 M solution of NaCl in doubly distilled water. All solutions were filtered through 0.45 μm filters prior to analysis. The measurements were performed using a Malvern Zetasizer 3000 HSa spectrometer equipped with a 5 mW helium−neon laser operating at 632 nm. All measurements were carried out at 25 °C at a scattering angle of 90° for the polymer solutions of the concentration of 2 g dm^{-3} for **1b** and **2a** or 1 g dm^{-3} for **3b** and **4a**.

Determination of Pyrene Solubilization. Stock solutions of each polymer containing 15 g of the polymer in 1 dm^3 of distilled water were prepared. An excess of finely powdered pyrene was placed in a round-bottom flask. Then a suitable known amount of the stock polymer solution was added to the flask and completed with distilled water to a volume of 3 mL. The solution was agitated by a magnetic stirrer at 40 °C for 5 h and then allowed to equilibrate at room temperature for 1 day. The solution was then filtered and transferred to an optical cell of a UV instrument with a 10 mm path length. The absorbance at 273 nm was measured with a Hewlett-Packard Kayak XA spectrophotometer.

^{1}H NMR. ^{1}H NMR spectra were taken with Bruker DRX500 (500 MHz) or Bruker AV200 (200 MHz) instruments using CDCl$_3$ as the solvent for 3-chloropropyl substituted dendrigrafts and D$_2$O or D$_3$COD for QAS substituted dendrigrafts (with the exception of the dendrigrafts partially substituted with 3(triethylammonio)propyl groups that were insoluble in water and were studied in CDCl$_3$.

SEC. SEC analysis was performed on a Wyatt Technology Corp. instrument equipped with a LKB 2150 HPLC and Wyatt Optilab REX RI and MALS DAWN EOS laser photometer detectors operating at a wavelength of 632.8 nm. Two TSK columns (7.8 mm × 300 mm G4000HXL with 6 μm bead size, 10^4 Å porosity and 7.8 mm × 300 mm G2000HXL with 5 μm bead size, 250 Å porosity) were used, and CH$_2$Cl$_2$ was the eluent flowing at a rate of 0.8 mL min^{-1}. Dual detector MALS/RI SEC analysis including dn/dc determination was performed using ASTRA version 4.72 software (Wyatt) assuming 100% mass recovery.

Routine analyses were performed using an LDC Analytical refractoMonitor IV instrument working with a constaMetric 3200 RI detector. It was fitted with two columns: SDV 8 mm × 300 mm 5 μm bead size, 10^4 Å porosity and SDV 8 mm × 300 mm 5 μm bead size, 100 Å porosity. Toluene was used as the eluent with a flow rate of 0.7 mL min^{-1}, and linear polystyrene was used as a standard.

Determination of Swelling in Water of the Partially 3-(Triethylammonio)-propyl Chloride Substituted Dendritic Polysiloxane 3c. Dendrigraft polysiloxane **3c** containing 14% of 3-chloropropyl groups converted to 3-[*N*,*N*,*N*-triethylammonio]propyl chloride groups (0.0158 g) was immersed in distilled water for 30 h at 25 °C, occasionally shaking the vessel containing the mixture. The swelled polymer was centrifuged and, after removal of the excess water, was weighed. An amount of 0.4202 g of the swelled polymer was obtained, so the water absorbed made 2560% of the initial polymer weight.

Results and Discussion

Generation of Chloroalkyl Substituted Dendrigraft Polysiloxane. Comb-branched, star-branched, and dendribranched polysiloxanes substituted by vinyl groups were used as the cores for the synthesis of 3-chloropropyl functionalized dendrigraft polysiloxane. The synthetic route for polymers **1** and **2** is illustrated in Figure 1.

Our synthetic methodology for the branched core and the grafting of 3-chloropropyl functionalized branches was strategically chosen to produce dendrigrafts in which all branching units were of the D-type, i.e., $-CH_2MeSiO$, to which branches were connected through the M-type unit, i.e., $-CH_2Me_2SiO_{0.5}$. This strategy permitted us to avoid the T-type units, i.e., $MeSiO_{1.5}$, and Q-type units, i.e., SiO_2, which may be more sensitive to cleavage by a base.[33]

In general, cores were prepared according to a methodology based on the anionic ring opening polymerization of cyclotrisiloxanes and grafting the living polymer on functionalized polysiloxane, as described in our earlier paper.[11] Since some modifications to this synthesis were introduced, its short description is presented as Supporting Information. The characteristics of branched polysiloxanes used as cores are presented in Table 1.

The core **IV** of the synthesis of the largest dendrigraft **4** was a G-3 dendritic copolymer in which the second generation was built of the gradient copolymer of hexamethylcyclotrisiloxane, $\mathbf{D_3}$, and 2,4,4,6,6-pentamethyl-2-vinylcyclotrisiloxane, $\mathbf{D_2V}$,[34] while the gradient copolymer of $\mathbf{D_3}$ with 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, $\mathbf{V_3}$,[11] was the graft in building of the third generation. Using $\mathbf{D_2V}$ and the copolymerization with $\mathbf{D_3}$ resulted in a lower density of the branching points. Moreover, the gradient copolymerization located the vinyl group mostly in the outer part of the cascade branched macromolecules.[11] These features led to a higher yield of grafting of the chloropropyl substituted polysiloxane. The core **III** of dendrigraft **3** was the comb-shaped vinyl functionalized polysiloxane.[11]

The dendritic 3-chloropropyl substituted polysiloxane was generated by the grafting on the activated core of living polysiloxane with pendant 3-chloropropyl groups. The graft was synthesized by the anionic living polymerization of 2,4,6-tri-(3-chloropropyl)-trimethylcyclotrisiloxane described in ref 17 producing polysiloxane with a good control of molecular weight and reasonably low polydispersity with lithium silanolate and unreacted *n*-butyl groups on opposite chain ends. The polymerization was carried out using a low monomer to initiator ratio in order to obtain rather short polymer chains not exceeding on average 10−20 siloxane units. The activation of the core was performed by the quantitative hydrosilylation of vinyl functionality with Me_2SiHCl to produce the reactive silyl chloride groups on which the living polymer was terminated.

The yield of grafts was limited because of the increase in steric hindrance and the decrease in reactive chain diffusion as the grafting reaction progressed. The time of reactive chain end quenching was a compromise between the grafting yield and undesirable chain transfer reactions that increase polydispersity. The grafting was performed for a relatively long time in order to obtain as high a yield of grafting possible, accounting for the relatively broad molecular weight distribution. The unreacted SiCl functions on the core were neutralized with an excess of Me_3SiOLi. The remaining quencher and reactive graft were in turn neutralized with an excess of Me_3SiCl which was removed by evaporation. Since the ungrafted chains were relatively short, they could be separated from the dendritic polymer by a manifold precipitation of the polymer from the methylene chloride/methanol solution.

The 3-chloropropyl functionalized dendrigraft polysiloxanes were characterized by SEC and by ^1H NMR spectroscopy. The characteristics of the polymers are presented in Table 2. The absolute value of the average molecular weight was determined by size exclusion chromatography (SEC) using the Wyatt Technology technique system based on dual detectors, i.e., multiangle light scattering and RI. The M_n and M_w were calculated using refractive index increments (d*n*/d*c*) determined separately for each polymer. It was assumed that the composition of siloxane units in the dendrigraft copolymer are uniformly independent of the size of the macromolecules. The validity of this assumption was confirmed for the vinyl substituted dendrigraft polymer.[11] The average total number of branches n_B in the polymer was calculated from eq 1.

$$n_B = n_B(\text{core}) + \frac{M_n - M_n(\text{core})}{M_n(\text{g}) + M_n(\text{link})} \qquad (1)$$

M_n(g) and M_n(core) are number-average molecular weights of graft and core, respectively, M_n(link) is the molecular weight of the Me_2SiH connecting unit, and n_B(core) is the average number of branches in the core. The yield of grafting is the ratio of $n_B - n_B$(core) to the number of vinyl groups in the core. The value of M_n(g) was estimated from the initial molar monomer to initiator ratio in the synthesis of the graft allowing for the monomer conversion. Important information about the structure of the branched chloropropyl functionalized polysiloxanes may be deduced from the ^1H NMR spectra, an example of which is presented in Figure 2. The spectrum of the chloropropyl functionalized polymer does not show any vinyl groups, which confirms that the Me_2SiHCl addition proceeded as expected from theoretical yields. The three signals of equal integration at 0.6−0.7, 1.8−1.9, and 3.5 ppm belong to the CH_2 protons of the chloropropyl group. The integration of this one $ClCH_2$ proton at 3.5 ppm is used for the quantitative estimation of the functional groups. Since each branch in the macromolecule is terminated by a butyl group, the total number of branches is equal to the number of butyl groups. Thus, the ratio of the integration of the $ClCH_2$ signal, $A_{(C\mathbf{H}_2Cl)}$, to $^2/_3$ of the intensity of Me (butyl) signal at 0.9 ppm, $A_{[C\mathbf{H}_3(CH_2)_3]}$, corresponds to the ratio of the average number of functional groups n_{Cl} to the average total number of branches n_B in the macromolecule (eq 2).

$$\frac{n_{Cl}}{n_B} = \frac{3A_{(C\mathbf{H}_2Cl)}}{2A_{[C\mathbf{H}_3(CH_2)_3]}} \qquad (2)$$

Instead, the ratio of n_{Cl} to $n_B - n_B$(core) gives the average number of functional groups on the grafted branch.

Generation of Ionic Quaternary Ammonium Salt Groups on Dendrigraft Polymers. 3-Chloropropyl groups pendant to branches of dendrigraft polysiloxanes were used to quaternize tertiary amines, dimethyloctylamine, dimethyl-2-hydroxyethylamine, and triethylamine. The amine reagents were selected to introduce to the ammonium cation either a hydrophobic hydrocarbon chain substituent or to generate the cation having a hydrophilic 2-hydroxyalkyl group. The quaternization reaction of these amines by linear polysiloxanes bearing 3-chloropropyl groups have been explored earlier,[35,36] and the synthetic procedure used here was similar. The reaction was performed in dimethylformamide (DMF) or in the mixture of DMF and *n*-butanol at an elevated temperature using a high excess of the amine reagent in relation to the chloroalkyl group. The quaternization of dimethyl-2-hydroxyethylamine occurs more readily than that of dimethyloctylamine. Almost theoretical conversion was obtained using the hydroxyl substituted amine. Dimethyloctylamine showed also a sufficient reactivity to generate a large amount of the QAS groups on dendritic polymer. Instead, we found that triethylamine reacted much less readily and only a small part (<20%) of the chloroalkyl was converted after a long heating of the reaction mixture.

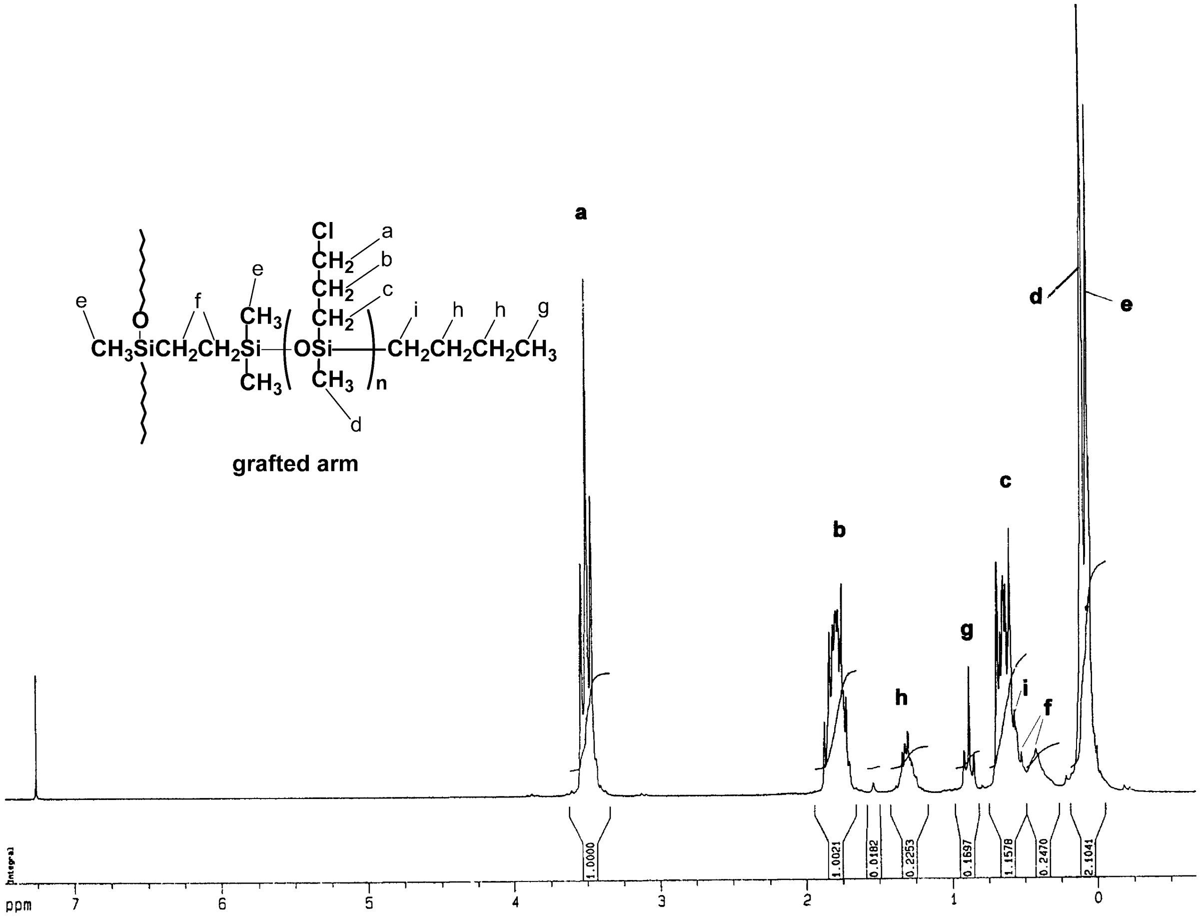


Figure 2. ^{1}H NMR spectrum of 3-chloropropyl functionalized dendrigraft polysiloxane **1**. The spectrum was taken in $CDCl_3$ solution. The chemical shift scale was standardized to tetramethylsilane.

The conditions affording quaternization and characteristics of the QAS substituted dendrigrafts are presented in Table 3. The reaction was followed by ^{1}H NMR spectroscopy. An example of the spectrum of the dendrigraft polyelectrolyte in deuterated water is presented in Figure 3.

The yield of the conversion of 3-$Cl(CH_2)_3$ to QAS was determined from the comparison of the integrations of signals of C$\mathbf{H}_2$−N at 3.3−3.45 ppm, A_{a+c} and C$\mathbf{H}_2$Cl at 3.5−3.6 ppm, $A_{a'}$. The yield was calculated from eq 3.

$$\text{yield} = \frac{0.5A_{a+c}}{0.5A_{a+c} + A_{a'}} \qquad (3)$$

The yield of the transformation of the $Cl(CH_2)_3$ in the reaction with dimethyl-2-hydroxyethylamine was calculated as the ratio of the integration of the HOC$\mathbf{H}_2$ signal to the integration of the $SiCH_2C\mathbf{H}_2$ signal in the ^{1}H NMR spectrum of the postreaction system.

Studies of the Behavior of the QAS Dendrigraft Polysiloxane in Water Solution. All the polycations presented in Table 3, with the exception of one partially substituted with *N*,*N*,*N*-triethylammoniopropyl chloride group, were soluble in water. However, these polymers showed tendencies toward aggregation in aqueous solution. Critical aggregation concentrations (CAC) were determined for some of these cationic dendrigrafts using the well-known pyrene fluorescence probe technique.[37,38] The observed CAC values were in the range of 0.14−0.19 g dm^{-3} (Table 4). The plot of the intensity ratio of the vibronic sub-bands at 338.5 and 333 nm in the pyrene excitation spectrum is shown in Figure 4. The CAC value was determined as the concentration of the polymer corresponding to the maximum of the second derivative of this sub-band intensity ratio. Above CAC, the solubility of the QAS substituted dendritic polysiloxanes was unstable after a long time as the precipitation of the polymer was observed.

The aggregation phenomenon in aqueous solution was also studied by photon correlation spectroscopy. Results are presented in Table 4, and the size distributions of the aggregates are exemplified in Figure 1 of the Supporting Information. An interesting feature in this study was the observation of two populations of aggregates. The smaller size aggregates of dendrigrafts with M_n (2×10^5) to (6×10^5) g mol^{-1} had an average diameter of 40−70 nm while the larger aggregates of these polymers had the size 400−700 nm. The latter are possibly formed by the aggregation of the smaller associates. The aggregation of micelles by ionic forces was observed earlier.[39] The tendency for the formation of the larger aggregates was particularly strong in the case of the polymer with M_n 2×10^6 g mol^{-1} which formed almost exclusively the larger size associates with a high propensity for the precipitation of the polymer from its solution. Both types of dendrigrafts studied here, these having the hydrophilic and hydrogen bond forming 2-hydroxyethyl substituent in the ammonium groups as well as those with hydrophobic *n*-octyl substituent at nitrogen, show a similar inclination to form aggregates. It is likely that electrostatic forces are the most important factors responsible for this association.

The siloxane dendrigraft polyelectrolytes also form aggregates on a surface with a tendency to assemble in a linear fashion. When an aqueous solution of the QAS substituted polysiloxane

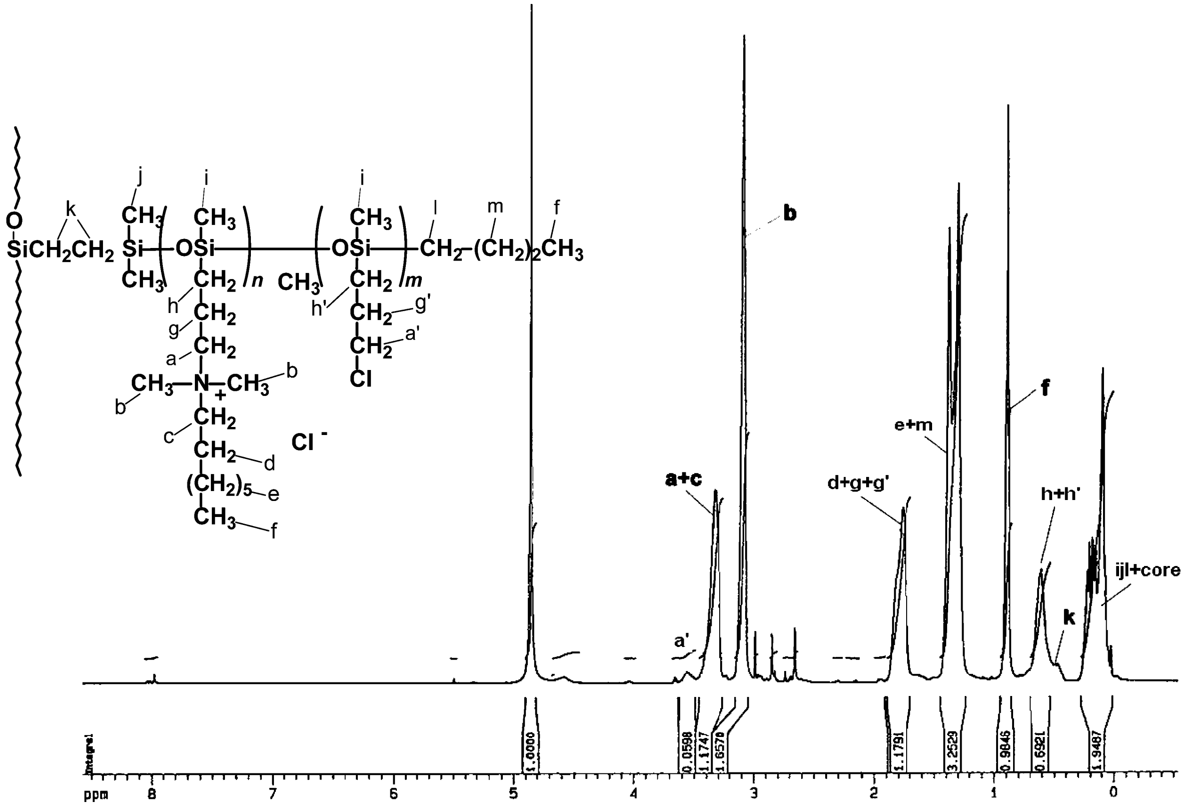


Figure 3. ^{1}H NMR spectrum of 3(*N*,*N*-dimethyl-*N*-*n*-octylammonio)propyl chloride substituted dendrigraft polysiloxane **1a** taken in the D_2O solution. The chemical shift scale is based on Me_4Si as standard.

Table 4. Studies of Water Solutions of Dendritic QAS Substituted Polysiloxanes[a] by Photon Correlation (PCS) and Fluorescence Spectroscopies

symbol	QAS group	$M_n \times 10^{-5}$ g mol^{-1}	$d_{+-} \times 10^{3b}$ mol g^{-1}	small aggregates $D_h{}^c$ nm	large aggregates $D_h{}^c$ nm	% of large aggregates[d] after 24 h	CAC g dm^{-3}
1a	$(HOCH_2CH_2)Me_2N^+-$	2.0	4.2				0.14
1b	*n*-$OctMe_2N^+-$	2.4	2.9	70	500	63	
2a	$(HOCH_2CH_2)Me_2N^+-$	1.8	4.1	50	430	81	
3b	*n*-$OctMe_2N^+-$	5.7	2.5	40	700	40	0.19
				50[e]	540[e]	64[e]	
4a	$(HOCH_2CH_2)Me_2N^+-$	21	3.1	no	520[f]	100[f]	0.15

[a] In PCS studies, concentrations of polymer were 2 g dm^{-3} for **1b** and **2a** and 1 g dm^{-3} for **3b** and **4a**. [b] Density of ionic groups. [c] Average hydrodynamic diameter in nm measured after 24 h since the dissolving of the polymer. [d] Relative to all aggregates. [e] After 5 h (after 24 h partial precipitation occurs). [f] After 1 h when most of the polymer has precipitated.

dendrigraft is allowed to evaporate on a glass slide, the dendritic macromolecules associate forming characteristic crosses on the glass surface which are well seen in an optical microscope (Figure 2 of Supporting Information).

The solubilization of the organic compound in water by the QAS substituted dendrigraft polysiloxane was studied using pyrene as the organic UV-dye. Results are summarized in Figure 5 where concentrations of the saturated pyrene solutions in water are plotted against polymer concentrations for the selected dendrigrafts. A linear increase in the solute concentration with the concentration observed here was similar to earlier results obtained in studies of the solubilization enhancement by ionic dendrimers.[20]

The solubilization effect was not expected to be high as the contribution of the hydrophobic core to the weight of the entire macromolecule is small, ranging from 4% to 17%. The larger part of the dendrigraft is a heavily charged shell. Nevertheless, some polymers exhibit a considerable solubilizing power in water toward pyrene, increasing its concentration by 2−3 orders of magnitude. Particularly effective are polymers having high molecular weights and those bearing the hydrophobic *n*-octyl group in the QAS function. Thus, the *n*-octyl substituted macromolecule with $M_n = 2 \times 10^5$ g mol^{-1} dissolves twice as many pyrene molecules as the macromolecule of comparable size bearing the hydrophilic 2-hydroxyethyl group. However, both of these polymers solubilize much less pyrene than polymers of very high molecular weights. While one molecule of **4a** ($M_n = 2.0 \times 10^6$) dissolves 41 molecules of pyrene, only 0.6 of the pyrene molecule is dissolved by one macromolecule of **1a** ($M_n = 2.0 \times 10^5$). Larger dendritic macromolecules have larger hydrophobic parts able to dissolve nonpolar organic compounds.

The fluorescence spectra of the saturated pyrene solution in water containing 4 g dm^{-3} of dendrigraft **3a** (Supporting Information, Figure 3) determined that pyrene appears almost exclusively as an excimer.

In the reaction of triethylamine with the 3-chloropropyl substituted dendrigraft **3a,** only 14% of the functional groups were transformed to the QAS groups. This polymer is not soluble in water as the density of ionic groups (7.4×10^{-4} mol g^{-1}) is too small. However, a great affinity of dendritic QAS substituted polysiloxane to water is manifested in a great ability

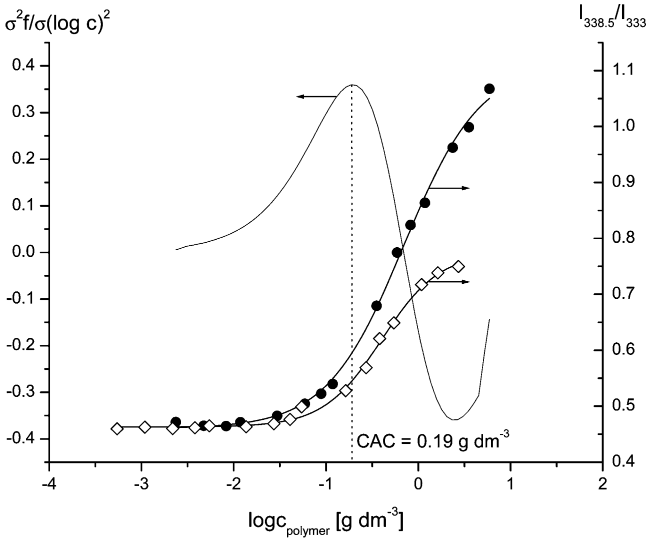


Figure 4. Determination of the critical aggregation concentration (CAC) for 3(*N*,*N*-dimethyl-*N*-octylammonio)propyl chloride substituted polysiloxanes. Intensity ratio of excitation spectra at 338.5 and 333 nm as a function of log concentration for polymers: ●, **3b**; ◊, **4a**. The thin line is the second derivative of the dependence for polymer **3b**.

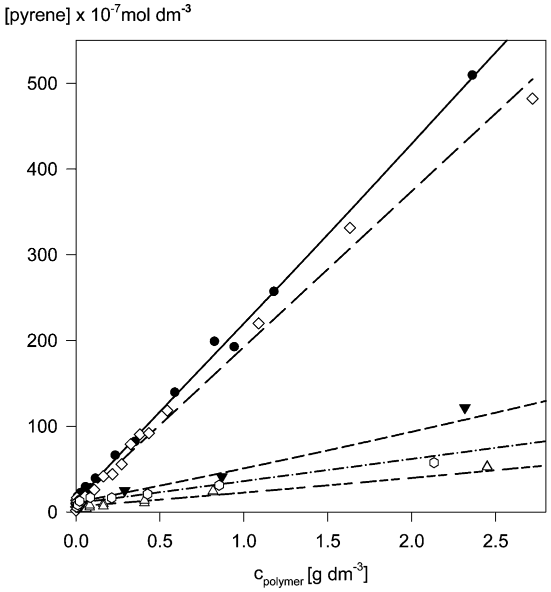


Figure 5. Solubilization of pyrene in the water solution of dendrigraft polysiloxanes substituted by 3(*N*,*N*-dimethyl-*N*-2-hydroxyethylammonio)propyl chloride — - - - — Δ, **1a**; —•—•— ⬡, **2a**; — — — ◊, **4a**; and 3(*N*,*N*-dimethyl-*N*-octylammonio)propyl chloride — — — ▼,**1b**; — ●, **3b**.

of this partially QAS substituted polymer to swelling in water. As our experiment showed, this polysiloxane is able to absorb more than 2500% of the weight of the dry polymer.

Conclusions

Dendritic polysiloxanes containing a great number of 3-chloropropyl functions may be synthesized by a grafting methodology using a branched core polysiloxane of various topologies containing vinyl groups pendant to polymer branches. This method consists of the activation of a star, comb, or dendritic branched polysiloxane core by hydrosilylation of the vinyl group with Me_2SiHCl which generates reactive silyl chloride groups. These groups are used for the termination of the 3-chloropropylmethylsiloxane living polymer or copolymer to attach it to the core. The living polymer graft is generated by the anionic ring opening polymerization of 2,4,6,-tri-(3-chloropropyl)-2,4,6-trimethylcyclotrisiloxane initiated with *n*-butyllithium. This method introduces functional groups into the volume of the dendrigraft.

The presence of 3-chloropropyl groups makes possible the introduction of other functionality by the nucleophilic substitution of chlorine. The reaction with tertiary amines generates ionic quaternary ammonium salt (QAS) groups, producing dendritic polysiloxanes soluble in aqueous media. In aqueous solution they exhibit a considerable susceptibility to aggregation. A solution above the CAC (critical aggregation concentration), which is 0.14−0.19 g dm^{-3}, is unstable and the precipitation of the polymer occurs. Although the polymer contains a great number of ionic groups, it exhibits a considerable solubilization of nonpolar organic compounds in aqueous media, in particular pyrene.

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Supporting Information Available: Synthesis of vinyl-functionalized star-branched polysiloxane, vinyl-functionalized comb-branched polysiloxane III, and vinyl-functionalized dendritic-branched 3G polysiloxane IV, size distribution of aggregates formed in the water solution containing dendrigraft siloxane polyelectrolyte **3b**, SEM of dendrigraft polysiloxane **4a**, fluorescence spectrum of pyrene saturated solution (1.2 × 10^{-5} mol dm^{-3}) in water containing 4 g dm^{-3} (2.2 × 10^{-5} mol dm^{-3}) of dendrigraft polysiloxane **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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