Arborescent Graft Copolymers: Highly Branched Macromolecules with a Core-Shell Morphology

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ABSTRACT: Macromolecules incorporating a highly branched polystyrene core and a poly(ethylene oxide) shell were synthesized. A comb-branched (generation $G = 0$) polystyrene was prepared by initiating the polymerization of styrene with *sec*-butyllithium, capping with 1,1-diphenylethylene, and titrating the living anions with a solution of chloromethylated linear polystyrene. A twice-grafted ($G = 1$) core with protected hydroxyl end groups was obtained using (6-lithiohexyl)acetaldehyde acetal to initiate the polymerization of styrene, followed by capping and grafting on the chloromethylated comb polymer. The acetal functionalities were hydrolyzed, and the core was titrated in solution with potassium naphthalide, before adding ethylene oxide. To maintain a narrow apparent molecular weight distribution, it was necessary to eliminate residual chloromethyl sites by a metal−halogen exchange reaction, prior to shell growth. Core-shell polymers based on a $G = 1$ core with $\bar{M}_w = 7 \times 10^5$ g·mol^{-1} containing 19% and 66% poly(ethylene oxide) by weight were prepared, with apparent polydispersities $\bar{M}_w/\bar{M}_n \approx 1.1-1.2$. Another sample incorporating a $G = 4$ core with $\bar{M}_w$ of $\sim 10^8$ g·mol^{-1} containing 36% poly(ethylene oxide) by weight was also synthesized. The hydrodynamic radii of the core and core-shell polymers were determined by dynamic light scattering. Based on the $\bar{M}_w$ estimated for the poly(ethylene oxide) chains, the hydrophilic chains exist in a randomly coiled conformation. The solubility behavior of the macromolecules is consistent with a core-shell morphology: the amphiphilic copolymers are easily desolvated from tetrahydrofuran solutions, giving transparent dispersions in water or methanol.

Introduction

Branched polymers have physical properties distinct from their linear counterparts both in solution and in the solid state. A particularly challenging aspect of branched polymer synthesis concerns the development of techniques for the preparation of polymers with a well-defined structure. Dendritic polymers[1,2] are a good example of well-defined branched molecules for which extensive control is gained over size, shape, and branching as well as the chemical functionality of the chain ends. Recently, analogous structures based on polyethylenimine (combburst polymers)[3,4] and polystyrene (arborescent graft polymers)[5] were also described. One important advantage of these branched polymeric structures is that very high molecular weights are attained in a few reaction steps.

Block copolymers, and particularly those combining hydrophilic and lipophilic segments, have interesting solution properties related to their ability to form micellelike structures. While polymeric micelles can be more stable than surfactant molecule aggregates, they are still prone to rearrangement when solvency conditions are changed, or when subjected to flow, potentially leading to solution instability. One way to alleviate this problem is to modify the structure of the amphiphilic polymer such that its ability to rearrange is limited. Star-branched amphiphilic block copolymer structures[7] should lead to more stable micellar morphologies, although the branching functionality attained in these systems is generally low.

A highly stable micellelike structure should result from molecules incorporating a core with an even higher branching functionality than the star-branched block copolymers. Arborescent graft polymers are highly branched styrene polymers which can be prepared with branching functionalities in the thousands and molecular weights well over 10^6-10^7 g·mol^{-1}.[8] These molecules will now be used as building blocks to prepare micellelike core-shell structures with a hydrophilic poly(ethylene oxide) shell. The synthesis of systems with different core sizes and shell thicknesses will be described in this paper.

Synthetic Strategy. The synthesis of arborescent graft polymers, serving as core material, has been briefly described previously.[6] The reaction steps involved in the preparation of the core-shell molecules are detailed in Scheme 1. Polystyryl anions are prepared using *sec*-butyllithium to initiate the polymerization and capped with 1,1-diphenylethylene, to produce the anionic species **1**. A low-polydispersity, randomly chloromethylated linear polymer reacts almost quantitatively with anions **1** in a grafting reaction at −30 °C, in the presence of tetrahydrofuran. Ungrafted chains can be removed easily from the comb (generation $G = 0$) polymer **2** by fractionation. Further cycles of chloromethylation and grafting reactions can, if desired, lead to increasingly branched structures, identified as generations $G = 1$, $G = 2$, and so on.

The addition of a poly(ethylene oxide) shell on the molecule requires a modification of the basic grafting technique. For illustrative purposes, the preparation of a core-shell molecule with a $G = 1$ core can be described. A chloromethylated comb ($G = 0$) polymer **3** is used as a substrate in a grafting reaction, as in the preparation of a styrene $G = 1$ polymer. In this case, however, a bifunctional initiator such as (6-lithiohexyl)acetaldehyde acetal containing a protected hydroxyl functionality is used to initiate the polymerization of styrene. The living anions **4**, capped with 1,1-diphenylethylene and reacted with the chloromethylated $G = 0$ polymer, yield a $G = 1$ branched polymer with protected hydroxyl end groups. After fractionation and deprotection of the $G = 1$ core polymer under mildly acidic conditions, potassium naphthalide is used to titrate the hydroxyl groups of polymer **5** in solution. The alcoholate

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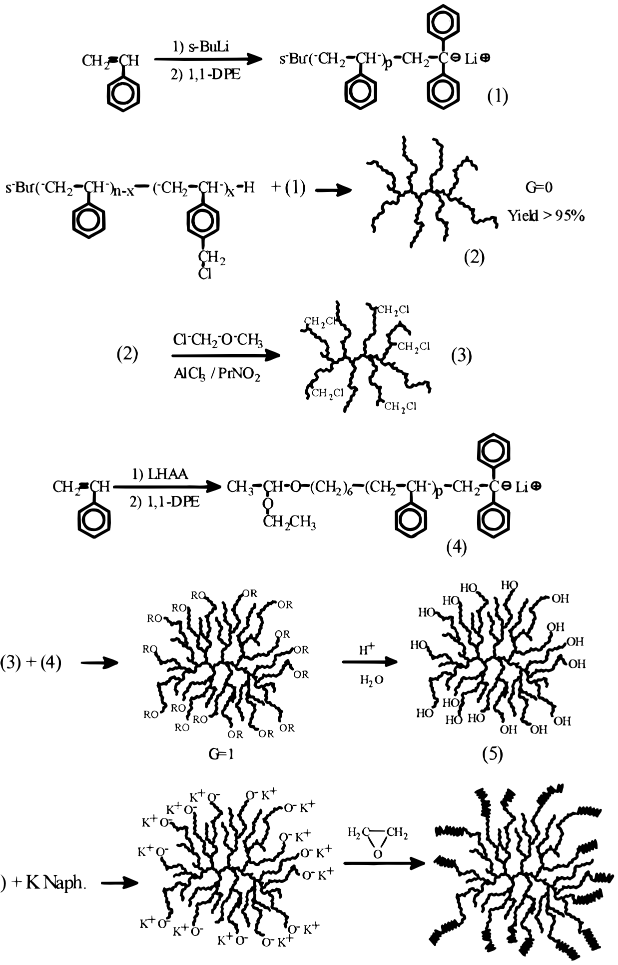
Scheme 1. Reaction Steps Used To Synthesize an Arborescent Copolymer with a $G = 1$ Polystyrene Core and a Poly(ethylene oxide) Shell



anions thus generated can initiate the polymerization of ethylene oxide. The “thickness” of the hydrophilic layer can be controlled by varying the amount of ethylene oxide added in the shell growth step.

Experimental Procedures

The main features of arborescent graft polymer synthesis were described elsewhere.[6] Therefore, only the procedures that have been improved significantly will be described.[9] Purification of the monomers and other reagents used a high-vacuum line connected to a nitrogen purification system and reusable glass ampules. The ampules were equipped with Young high-vacuum PTFE stopcocks and ground glass joints, so they could be mounted directly on the polymerization reactor.

Solvent Purification and Reagents. Tetrahydrofuran (THF; Caledon, reagent) and diethyl ether (BDH, reagent) were purified by distillation over sodium–benzophenone ketyl. Toluene (BDH, OmniSolv) was distilled from oligomeric styryl anions. Carbon tetrachloride (Anachemia, reagent), used in the chloromethylation, was dried by distillation over phosphorus pentoxide. All solvents were purified in stills under a slight overpressure of dry nitrogen and were transferred directly to the reactor or ampule preparation setups through PTFE tubing.

A solution of *sec*-butyllithium (1.3 M in cyclohexane) was obtained from Aldrich. Two bifunctional initiators, (3-lithiopropyl)acetaldehyde acetal and (6-lithiohexyl)acetaldehyde acetal, were synthesized in a few reaction steps, according to a published procedure.[10] The activity of all organolithium initiator solutions was determined by the Gilman double-titration method.[11] A potassium naphthalide solution was prepared from potassium metal (Aldrich; 1.17 g, 30 mmol) and naphthalene (Aldrich, scintillation grade; 5.77 g, 45 mmol) in dry THF (200 mL) obtained from the distillation still. The concentration of the solution was determined using the following titration method: Dry THF (50 mL) was transferred to an oven-dried Erlenmeyer flask purged with nitrogen. Solvent impurities were titrated with the potassium naphthalide solution, contained in a syringe, to a faint green coloration. A 100-mg portion (0.454 mmol) of 2,6-di-*tert*-butyl-4-methylphenol (Aldrich, 99%), previously dried under vacuum, was then quickly added to the solvent, which was again titrated to a faint green coloration. The concentration of sodium naphthalide was determined from the volume of solution consumed in the titration.

Styrene (Aldrich, 99%) was purified by stirring and distilling over CaH_2 at reduced pressure. It was stored under nitrogen at −20 °C until further use. Ethylene oxide (Eastman Kodak) was stirred over CaH_2 (Aldrich) overnight, followed by vacuum distillation into a thick-wall ampule, and stored at room temperature. Both monomers were subjected to a last purification step immediately before polymerization. The capping agent 1,1-diphenylethylene (Aldrich, 97%) was purified by adding enough *n*-butyllithium solution (Aldrich, 2.5 M in hexanes) to get the deep red 1,1-diphenylhexyllithium coloration, followed by reduced pressure distillation.

Chloromethyl methyl ether was prepared from dimethoxymethane and thionyl chloride using a variation of a procedure published in the literature.[12] **Warning:** Chloromethyl methyl ether, and particularly bis(chloromethyl) ether, often present as an impurity, are potent carcinogens. All the procedures described should only be carried out in an efficient fume hood with extreme precaution. Crude chloromethyl methyl ether with a boiling point of 55–58 °C was purified by distillation over anhydrous $AlCl_3$ (Aldrich, 98%). The purity of the product, and in particular the absence of dimethoxymethane, was confirmed by ^{1}H-NMR analysis prior to its use in the chloromethylation reaction. Commercially available (technical grade) chloromethyl methyl ether (Aldrich) was also used in the chloromethylation, but was first purified with $AlCl_3$.

Core-Shell Polymers Based on a $G = 1$ Core. Grafting Reaction ($G = 0$ Polymer). Styrene (22 mL, 0.192 mol) was further purified immediately before polymerization with phenylmagnesium chloride (Aldrich, 2.0 M solution in THF, 5 mL) using high-vacuum purification techniques.

A 2-L glass polymerization reactor equipped with a vacuum-tight mechanical stirrer was used to polymerize styrene and to prepare the graft polymers. The reactor was first evacuated and flamed and then filled with nitrogen. Toluene (300 mL) was added, followed by the *sec*-butyllithium initiator solution (4.0 mmol, for a calculated $\bar{M}_n = 5 \times 10^3$ g·mol^{-1}) and styrene. After a 5-min waiting period, the reactor was cooled to −78 °C, and dry THF (150 mL) was added slowly to increase the rate of polymerization. After 15 min, the reaction was terminated with degassed methanol. The polymer was recovered by precipitation in methanol, filtration, and drying under vacuum.

Grafting sites were introduced into the linear polymer by a chloromethylation reaction. A substitution level of 25 mol % was normally used, to give ~12 grafting sites per chain on average. Polystyrene (3.5 g, 33.6 mmol), previously dried under vacuum overnight, was dissolved in 350 mL of dry carbon tetrachloride. A catalyst solution was prepared by dissolving 2.6 g (19.5 mmol) of anhydrous $AlCl_3$ (Aldrich, 99.99%) in 65 mL of 1-nitropropane (Aldrich, 98%), and diluting with 130 mL of dry CCl_4. Purified chloromethyl methyl ether (35 mL, 0.46 mol) was then added to the polymer solution, followed by 140 mL of the catalyst solution. The mixture was left to react for 30 min at room temperature. Workup of the product first involved stopping the reaction by adding 10 mL of glacial acetic acid. The volatile components were then removed using a vacuum pump connected to two liquid nitrogen traps in series, to minimize the risk of exposure to chloromethyl methyl ether. The polymer, redissolved in $CHCl_3$ (20 mL), was extracted with three 50-mL portions of acetic acid/water (1:1) to remove catalyst residues. The product was finally precipitated in methanol, recovered by filtration, and dried under vacuum. The exact substitution level was determined by ^{1}H-NMR analysis.

Residual water was removed from the chloromethylated polymer (3.0 g, 6.45 mequiv of CH_2Cl) prior to the grafting reaction, using azeotropic distillation with dry THF. An ampule containing 1,1-diphenylethylene (1.2 mL, 6.82 mmol), previously purified, was prepared by the same procedure.

For the preparation of the comb ($G = 0$) polymer, ampules containing styrene monomer, 1,1-diphenylethylene, and the chloromethylated linear polymer were mounted on the reactor. The polymerization conditions used to generate the polystyryl anions were identical to those used in the preparation of the linear polymer. After the 15-min waiting period following the addition of tetrahydrofuran, the capping agent was added, resulting in a color change from deep orange to deep red. After increasing the temperature of the reactor to −30 °C (benzyl alcohol/1-butanol/dry ice bath), a sample was removed with a syringe and terminated with degassed methanol, for the characterization of the branches. The solution was then slowly titrated with the chloromethylated polymer to a fading pink color over a 1-h period. After a 0.5-h wait, residual living ends were destroyed with degassed methanol. The polymer was recovered by precipitation in methanol, filtration, and drying under vacuum. Ungrafted chains were removed from the crude product by precipitation fractionation.

Model Reactions Using the Bifunctional Initiators. The bifunctional initiators (3-lithiopropyl)acetaldehyde acetal and (6-lithiohexyl)acetaldehyde acetal were used in test reactions to determine the conditions necessary to achieve a narrow molecular weight distribution in the polymerization of styrene. In all cases, monomer ampules containing 10 mL (87 mmol) of styrene, prepared as described above, were used for the test reactions. The amount of initiator used (1.82 mmol) was for a target $\bar{M}_n$ of 5×10^3 g·mol^{-1}.

In a first test, the 3-lithiopropyl compound was added to a solution of the monomer in 200 mL of toluene at −30 °C. Since no change in color was detected, the reactor was cooled to −78 °C and THF (150 mL) was slowly added, again with no visible change in color. The reactor was warmed to room temperature, and the orange coloration of polystyryl anions slowly appeared over a 5−10-min period. After stirring for 1 h, the reaction was terminated with methanol.

A second attempt used a technique reported in the literature,[13] in which an unreactive initiator is allowed to equilibrate with α-methylstyrene in diethyl ether prior to the initiation reaction. The 3-lithiopropyl compound (1.82 mmol) was mixed with a 5-fold excess of α-methylstyrene (1.18 mL, 9.1 mmol) in diethyl ether (20 mL). Since no visible change occurred after 1 h, THF (5 mL) was added to the ampule, resulting in the slow development of a deep red color. The mixture was used to initiate the polymerization of styrene in toluene (200 mL) at −30 °C, to give a yellow solution. After 15 min, the reactor was cooled to −78 °C and THF (100 mL) was slowly added. The reaction was terminated after 10 min.

The initiator (6-lithiohexyl)acetaldehyde acetal was used in the last two test reactions. In one case, the polymerization was initiated in THF (200 mL) at −78 °C. In the last case, the reaction was initiated in toluene (100 mL) at room temperature, before cooling to −78 °C and adding THF (100 mL). In both cases, the orange coloration of polystyryl anions appeared quickly upon addition of the initiator.

Preparation of $G = 1$ Hydroxyl-Functionalized Core. The $G = 0$ comb polymer was chloromethylated (14 mol% degree of substitution), and ampules containing styrene (10 mL, 87 mmol), 1,1-diphenylethylene (0.49 mL, 2.72 mmol), and the chloromethylated polymer (2.18 g, 2.72 mequiv of CH_2Cl) were prepared as described previously. The polymerization of styrene was initiated with (6-lithiohexyl)acetaldehyde acetal (1.81 mmol) in toluene (200 mL) at room temperature. After cooling the reactor to −78 °C, THF (100 mL) was slowly added. Fifteen minutes later, the polystyryl anions were capped with 1,1-diphenylethylene and slowly titrated with the chloromethylated $G = 0$ polymer. Fractionation of ungrafted material and hydrolysis of the acetal functionalities were accomplished in a single step by adding a small amount (0.1% v/v) of concentrated hydrochloric acid (11 M) to the fractionation. Hydrolysis was confirmed by monitoring the disappearance of the weak infrared acetal absorption band at ∼1120 cm^{-1}.[14]

Addition of Poly(ethylene oxide) Shell on $G = 1$ Core. Two core-shell polymers based on a $G = 1$ core, containing around 30% and 70% poly(ethylene oxide) by weight, respectively, were synthesized by varying the amount of ethylene oxide used in the shell growth. An ethylene oxide ampule was prepared from the previously purified monomer, which was further purified with phenylmagnesium chloride under vacuum. The exact amount of monomer transferred (1.10 g), for a target poly(ethylene oxide) content ∼30 wt % in the core-shell polymer, could be determined by weighing the ampule.

The hydroxyl-functionalized core polymer (2.75 g) was loaded into a thick-wall ampule with a small stirring bar and dried by the THF azeotrope technique used for the chloromethylated polymer. The polymer was then dissolved in 300 mL of dry THF and titrated, using a potassium naphthalide solution, to a faint green coloration. After freezing the solution in liquid nitrogen, ethylene oxide was recondensed to the ampule, which was then filled with a partial pressure of nitrogen. The ampule was warmed to 60 °C for 2 days to polymerize the ethylene oxide. The product was characterized by ^{1}H-NMR and FT-IR spectroscopy, and by size exclusion chromatograpy (SEC).

SEC analysis of the core-shell polymer revealed the occurrence of cross-linking reactions leading to a broadened distribution. Side reactions were attributed to the presence of residual chloromethyl sites in the core polymer. Thus it was necessary to deactivate these sites with a metal−halogen exchange reaction prior to shell growth. The exchange was carried out by dissolving the hydroxyl-functionalized polymer (1 g) in 150 mL of dry THF, followed by addition to 10 mL of *n*-butyllithium (2.5 *M*) solution at −78 °C. After 1 h, water (10 mL) was added to the mixture. Lithium hydroxide residues were eliminated by removing the solvent, redissolving the polymer in $CHCl_3$ (25 mL), and extracting three times with 25-mL portions of 2.5 M HCl. The exchanged polymer, when used in the shell growth process, led to a product with a narrow apparent molecular weight distribution. The other core-shell polymer based on a $G = 1$ core and containing ∼70% poly(ethylene oxide) by weight was prepared by the same technique, using a larger amount of ethylene oxide monomer.

Core-Shell Polymers Based on a $G = 4$ Core. A $G = 3$ arborescent graft polymer was prepared by repeating chloromethylation−grafting−fractionation cycles four times (using *sec*-butyllithium as an initiator in all cases), as described in the preparation of the comb polymer. The hydroxyl-functionalized $G = 4$ graft polymer was derived from a chloromethylated $G = 3$ graft polymer and the (6-lithiohexyl)acetaldehyde acetal initiator. The molecular weight of the branches was ∼5×10^3 g·mol^{-1} for each generation. The core polymer, after fractionation and hydrolysis, was used to prepare a core-shell polymer containing ∼30% poly(ethylene oxide) by weight. A first attempt, without metal−halogen exchange, led to an insoluble product. When the core was subjected to a metal−halogen exchange reaction prior to shell growth as previously described, however, the product was completely soluble in common organic solvents. The composition of the polymer was determined by ^{1}H-NMR and FT-IR analysis.

Characterization. Light scattering measurements were used to obtain absolute molecular weights and hydrodynamic radii for the polymers prepared. The measurements were made on a Brookhaven BI-200SM light scattering goniometer equipped with a Lexel 2-W argon ion laser operating at 514 nm and a Brookhaven BI-2030AT 201-channel correlator. Static light scattering measurements, used to determine the molecular weights, were carried out in toluene, at concentrations of 1% (w/v) or less, depending on the generation. The weight-average molecular weight $\bar{M}_w$ of the core polymers was determined by extrapolation to zero angle and zero concentration according to the usual Zimm technique. The dynamic measurements, yielding average hydrodynamic radii of some of the polymers, were carried out at 90° in dilute THF solutions (<0.2% w/v) containing 4% acetic acid by volume. The correlator was operated in the exponential sampling mode, the

Table 1. Absolute Molecular Weight and Branching Functionality of the Core Polymers Used To Prepare Core-Shell Polymers[a]

	branches		graft polymer	
generation	$\bar{M}_n/10^3$ g·mol^{-1}	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$(ls)/g·mol^{-1}	f_W
	First Series ($G = 1$ Core)			
core	4.4	1.08		
0	4.5	1.07	7.3×10^4	14
1	13.5	1.05	7.0×10^5	44
	Second Series ($G = 4$ Core)			
0	4.3	1.03	6.7×10^4	14
1	4.6	1.03	8.7×10^5	170
2	4.2	1.04	1.3×10^7	2800
3	4.4	1.05	9×10^7	16000
4	4.9	1.08	2×10^8	27000

[a] The branch molecular weights were determined from SEC analysis, and $\bar{M}_w$(ls) from light scattering.

Table 2. Molecular Weights of the Core Polymers Determined by Gel Permeation Chromatography

	DRI detector		viscometer
generation	$\bar{M}_n$/g·mol^{-1}	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$(ov)/g·mol^{-1}
	First Series ($G = 1$ Core)		
0	3.4×10^4	1.08	6.5×10^4
1	1.7×10^5	1.09	5.3×10^5
	Second series ($G = 4$ core)		
0	4.0×10^4	1.07	8.5×10^4
1	1.3×10^5	1.07	6.2×10^5
2	3.0×10^5	1.20	3.1×10^6
3	4.4×10^5	1.15	1.6×10^7

last four data acquisition channels being used for baseline measurements. The translational diffusion coefficients used in the radius calculations were determined from second-order cumulant analysis of the normalized electric field correlation function $|g^{(1)}(\tau)|$, to better account for polydispersity effects.

All precursor samples (branches) and graft polymers were characterized by size exclusion chromatography, with the exception of the $G = 4$ core polymer and the resulting core-shell structure, which were retained in the columns. Some measurements were obtained on a Waters 150-C high-temperature SEC system equipped with a differential refractometer (DRI) detector and a Viscotek on-line viscometer. A Jordi DVB linear mixed-bed column was used for the analysis, 1,2,4-trichlorobenzene serving as the mobile phase in this case. The core-shell polymers based on a $G = 1$ core were also characterized on a Waters SEC system equipped with a Jordi DVB mixed-bed column and a DRI detector. Either pure tetrahydrofuran, a 96:4 (v/v) mixture of tetrahydrofuran and acetic acid, or pure *N*,*N*-dimethylformamide served as the mobile phase.

The composition of the core-shell polymers was determined using FT-IR and ^{1}H-NMR analysis. Infrared analysis was performed on a Bomem MB series instrument, using 0.5% solutions of the polymers in chloroform. A calibration curve was established for poly(ethylene oxide) content analysis with chloroform solutions of polystyrene and poly(ethylene oxide), both with a molecular weight of ~5000, mixed in different proportions. The ratio of the sum of absorbance intensities for peaks at 2922, 1601, and 1452 cm^{-1} for polystyrene, and 2890, 1350, and 1106 cm^{-1} for poly(ethylene oxide) was used in the calibration. The composition of the core-shell polymers and of a block copolymer sample was also determined, for comparison, by ^{1}H-NMR analysis on a Bruker 250 MHz instrument, in deuterated choroform. The ratio of integrated peak intensities at 6.3−7.4 and 3.6 ppm, corresponding to polystyrene and poly(ethylene oxide), respectively, were used in the calculations. Analysis of the same polymers by infrared spectroscopy, and the good agreement between the results obtained by both techniques, confirmed the validity of the FT-IR calibration curve.

Spectroscopic techniques provided composition information for the core-shell polymers. A series of solubility tests were also carried out to provide evidence for a core-shell morphology. The core-shell polymers prepared, when dispersed in methanol or water from the solid state using sonication, yielded turbid dispersions. Tetrahydrofuran solutions, 1−3% (w/v), of the polymers based on a $G = 1$ core, added dropwise to methanol or water, resulted in clear solutions. The $G = 4$ core-shell polymer under the same conditions led to a slightly opalescent solution.

Results and Discussion

Core Polymers. The absolute weight-average molecular weights ($\bar{M}_w$) of the branched styrene polymers used for the two series of core-shell polymers prepared are given in Table 1. The values reported for the branches were obtained from SEC analysis of samples removed from the reactor prior to the grafting reaction. The molecular weights of the branched polymers were determined from the static light scattering measurements. Since each grafting cycle used branches with a molecular weight of ~5000, a geometric growth in the molecular weight of the polymers is expected for successive generations. This is more or less the case for the lower generations ($G = 0-2$), but the growth rate is somewhat lower than expected for the upper generations. This effect was previously rationalized[6] in terms of overcrowding effects limiting the accessibility of chloromethyl grafting sites buried inside the highly branched polymer structure. The quantity f_w, also reported in Table 1, is the average branching functionality of generation i. It is defined as

$$f_w = \frac{\bar{M}_w(i) - \bar{M}_w(i-1)}{\bar{M}_w(\text{br})}$$

where $\bar{M}_w(i)$ and $\bar{M}_w(i-1)$ are the absolute weight-average molecular weights of generation i and of the previous generation, respectively, and $\bar{M}_w$(br) is the molecular weight of the branches of generation i. The increases in branching functionality reported in Table 1 follow the same trends as the absolute molecular weights.

Size exclusion chromatography results for the core polymers using the DRI detector and a linear polystyrene standards calibration curve are given in Table 2. The apparent polydispersity ($\bar{M}_w/\bar{M}_n$) of the graft polymers is ~1.1−1.2 in all cases. While the polydispersity data for the graft polymers are apparent rather than absolute, they should be indicative of a relatively narrow molecular weight distribution. This is remarkable, given that the absolute molecular weights reported in Table 1 reach ~10^8. Comparison of Table 2 with Table 1 also confirms that the apparent molecular weights determined from the linear polystyrene standards calibration curve are strongly underestimated. This is reasonable, given the compact structure the graft polymers are expected to have.

The number-average molecular weights, $\bar{M}_n$(ov), determined from the on-line viscometer data, are also reported in Table 2. The data analysis algorithm used[15] should allow calculation of an absolute number-average molecular weight based uniquely on the viscometer data. The method uses the so-called *viscosity distribution*, consisting of $w_i[\eta_i]$ as a function of $M_i[\eta_i]$, where w_i, $[\eta_i]$, and M_i represent the weight fraction, intrinsic viscosity, and molecular weight, respectively, of the polymer in each slice analyzed. The product $w_i[\eta_i]$ is obtained directly from the on-line viscometer, and $M_i[\eta_i]$ is derived from the elution volume with the help of a universal calibration curve obtained for linear polystyrene standards. The number-average molecular weight of the sample is then calculated as the reciprocal of the −1 moment of the viscosity distribution:[15]

$$\bar{M}_n = (\mu^{-1})^{-1} = \left(\sum \frac{w_i}{M_i}\right)^{-1}$$

Comparison of $\bar{M}_n$(ov) values in Table 2 and $\bar{M}_w$(ls) values determined from static light scattering (Table 1) reveals discrepancies between both sets of results, the magnitude of the discrepancies increasing for the higher generations. For the comb ($G = 0$) polymers, the ratio $\bar{M}_w(\text{ls})/\bar{M}_n(\text{ov})$ for both core sample series is consistent, within error limits, with a relatively low polydispersity. The ratio observed for the $G = 3$ sample, $\bar{M}_w(\text{ls})/\bar{M}_n(\text{ov}) = 5.6$, on the other hand, seems unrealistically high, considering that the apparent polydispersity determined for the same sample from SEC analysis using only the DRI detector is $\bar{M}_w/\bar{M}_n = 1.15$ (Table 2). The discrepancies between the two techniques could be due to the inability of the viscometric method to describe the behavior of highly branched polymers. Similar effects were observed in analyzing polymers with a high density of long branches using a universal calibration curve.[16] While the universal calibration method is not directly involved in the algorithm used, it is still implicitly assumed that the elution volume is directly related to the product $M_i[\eta_i]$, representing the hydrodynamic volume of the polymer molecules eluted. Molecular weights determined for the whole samples, using static light scattering (Table 1) are, consequently, probably more reliable for the branched polymers.

Model Reactions with Bifunctional Initiators. Two bifunctional initiators containing protected hydroxyl functionalities, (3-lithiopropyl)acetaldehyde acetal and (6-lithiohexyl)acetaldehyde acetal, were tested for their ability to produce polymers with a narrow molecular weight distribution. The SEC diagrams corresponding to four different test reactions are shown in Figure 1.

Initiation of styrene polymerization with (3-lithiopropyl)acetaldehyde acetal proved to be very slow. No reaction was observed in toluene or in a mixture of toluene and THF at low temperature. Even at room temperature, the orange polystyryl anions coloration appeared very slowly. Considering that polymerization is very fast in the presence of THF, a slow initiation reaction should lead to a broad molecular weight distribution. This is confirmed in the SEC diagram of Figure 1a, for which the product had a $\bar{M}_w = 4.8 \times 10^3$ g·mol^{-1} and a polydispersity $\bar{M}_w/\bar{M}_n = 1.96$. Equilibration of the 3-lithiopropyl initiator with α-methylstyrene prior to the initiation reaction led to the appearance of a sharp peak in the diagram of Figure 1b, as well as a very long tail extending in the low molecular weight region. The long tail is presumably due to incomplete equilibration of the initiator with α-methylstyrene prior to the initiation reaction. The very long equilibration time needed (a few hours) at room temperature likely resulted in the destruction of a portion of the active centers during the equilibration process. Organolithium compound solutions in THF are known to have a short half-life at room temperature due to a ring cleavage reaction.[17] Incomplete equilibration and the side reaction would also explain the high molecular weight ($\bar{M}_w \approx 8 \times 10^4$ g·mol^{-1}) obtained for the sharp peak, since the molecular weight is inversely proportional to the amount of initiator used in anionic polymerization.

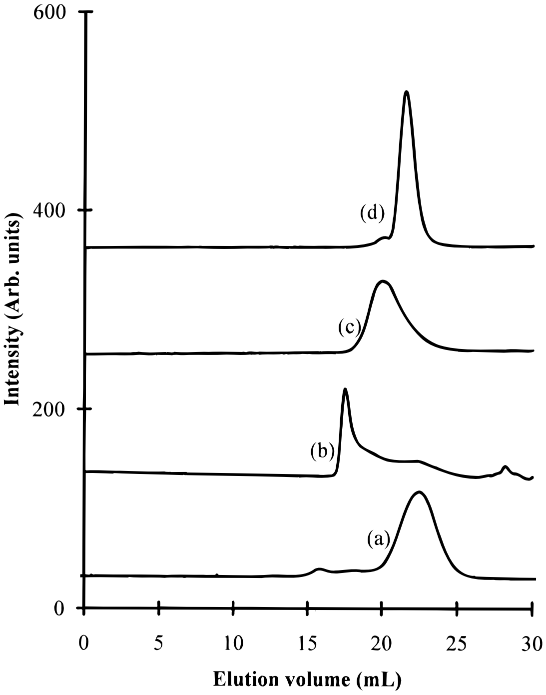


Figure 1. SEC diagrams of polymers prepared from bifunctional initiators: (a) (3-lithiopropyl)acetaldehyde acetal in toluene/THF, (b) same compound, using preequilibration with α-methylstyrene, (c) (6-lithiohexyl)acetaldehyde acetal in THF, and (d) same compound in toluene.

The 6-lithiohexyl compound, used as initiator for the polymerization in THF at −78 °C, resulted in a significant improvement in the polydispersity of the products, as shown in the diagram of Figure 1c. The molecular weight distribution was unimodal, with $\bar{M}_w = 1.7 \times 10^4$ g·mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.52$. The rapid appearance of the polystyryl anion coloration indicates a fast initiation reaction, though still somewhat slow compared to propagation, as demonstrated by the high polydispersity of the polymer. Toluene was selected as polymerization solvent in the last test reaction, in the hope of further decreasing the polydispersity of the products. Figure 1d shows that initiation in toluene led to a very narrow peak, with $\bar{M}_w = 7.7 \times 10^3$ g·mol^{-1} and $\bar{M}_w/\bar{M}_n = 1.09$. Tetrahydrofuran was added to the reaction, after initiation was complete, as indicated by a stable coloration of the solution. The purpose of adding THF was only to increase the rate of the propagation reaction, leading to a complete reaction after 10−15 min. Given the low polydispersity obtained, the fourth procedure was selected for the preparation of the living polymer used in the preparation of the functional cores.

Hydroxyl-Functionalized Cores. The presence of a weak acetal absorption band[14] at 1120 cm^{-1} in the FT-IR spectra of the $G = 1$ and $G = 4$ core polymers confirmed the introduction of the protected hydroxyl functionalities in the core. Hydrolysis of the acetal groups of the $G = 4$ core in a toluene/water mixture was attempted according to a published procedure[14] but resulted in an insoluble product. Fractionation of the functional core in a toluene/methanol mixture, used to remove ungrafted chains from the crude product, also led to a significant decrease in the acetal band intensity. Partial hydrolysis during fractionation could be explained by the presence of water and acid impurities in the solvents, combined with the relatively high temperature (60 °C) used initially in the fractionation process. To further enhance the hydrolysis reaction, a small

Table 3. Composition Analysis of Styrene−Ethylene Oxide Copolymers by FT-IR and ^{1}H-NMR

sample	wt % poly(ethylene oxide) FT-IR	wt % poly(ethylene oxide) NMR
$G = 1$, ∼30% PEO	19	22
$G = 1$, ∼70% PEO	66	62
$G = 4$, ∼30% PEO	36	21
PS−PEO block copolymer	26	28

amount of a mineral acid solution (HCl) was added in the fractionation flask. The resulting product showed almost complete disappearance of the acetal band. The hydrolysis reaction of the $G = 1$ core polymer left the molecular weight distribution unaffected, as demonstrated by comparing SEC diagrams before and after fractionation. The hydrolyzed $G = 4$ core could not, like its acetal precursor, be characterized by SEC, since it was retained on the column.

Core-Shell Polymers. Composition Analysis. The composition of the three core-shell polymers prepared was determined by FT-IR and ^{1}H-NMR analysis. The FT-IR calibration curve, prepared from mixtures of the homopolymers in dilute solution, used peak absorbance intensities for multiple peaks associated with polystyrene and poly(ethylene oxide). This method was preferred over correlations involving individual peak ratios to achieve a better correlation of the calibration data. The validity of the calibration curve was verified by comparing the poly(ethylene oxide) contents determined by this technique to ^{1}H-NMR analysis results for the different polymers as well as for a linear polystyrene−poly(ethylene oxide) block copolymer sample. The analysis results for the different samples are summarized in Table 3. There is good agreement between all results obtained by the two techniques, except for the system based on a $G = 4$ core, where the NMR result (21 mol %) is clearly lower than that obtained from FT-IR analysis (36%). A similar problem was encountered in the NMR analysis of the chloromethylation level of upper generation polymers ($G = 2$ and above), for which NMR results were invariably lower than expected. Peak broadening and baseline shift are obvious in the NMR spectrum of the $G = 4$ core-shell polymer. The difference observed in the analysis by the two techniques is, therefore, likely due to a decreased mobility of the polymer chains leading to inaccurate peak areas in the NMR spectrum. The FT-IR composition analysis result should thus be more reliable for the $G = 4$ core-shell polymer.

SEC Analysis. A first shell growth attempt involved titration of the $G = 1$ hydroxyl-functionalized core in solution with potassium naphthalide, followed by addition of ethylene oxide and polymerization. While the product was eluted sooner than the core polymer, the reaction also resulted in major SEC peak broadening, with an increase in the apparent polydispersity from 1.08 (hydroxyl-functionalized core polymer) to 3.90 when pure THF served as eluent (Figure 2a). Analysis of the core polymer by NMR revealed the presence of a very small amount (<1−2 mol %) of residual chloromethyl groups, resulting from incomplete grafting reactions. When exposed to potassium naphthalide, the chloromethyl functionalities likely underwent a metal−halogen exchange reaction with potassium, leading to very reactive benzylpotassium species (Scheme 2). The organopotassium compound is subject to Wurtz−Fittig coupling. Intramolecular cross-linking of the chains would have no effect on the molecular weight distribution. Intermolecular reactions, however, could lead to multimer formation, and considerable broadening of the molecular weight distribution, as indicated in Scheme 2. To verify that residual chloromethyl groups were the source of the problem, they were deactivated prior to addition of the shell. This was achieved by exchange with *n*-butyllithium, present in a large excess, to minimize the occurrence of Wurtz−Fittig coupling of the benzyllithium species. Addition of water to the reaction mixture converted the lithium derivative to methyl

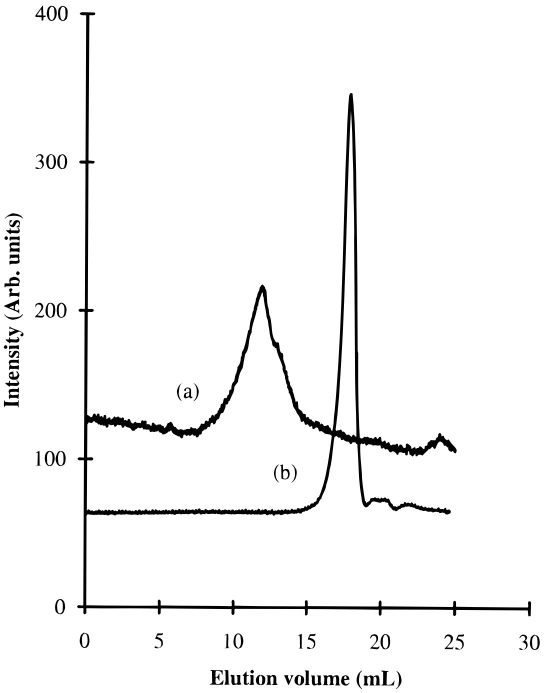
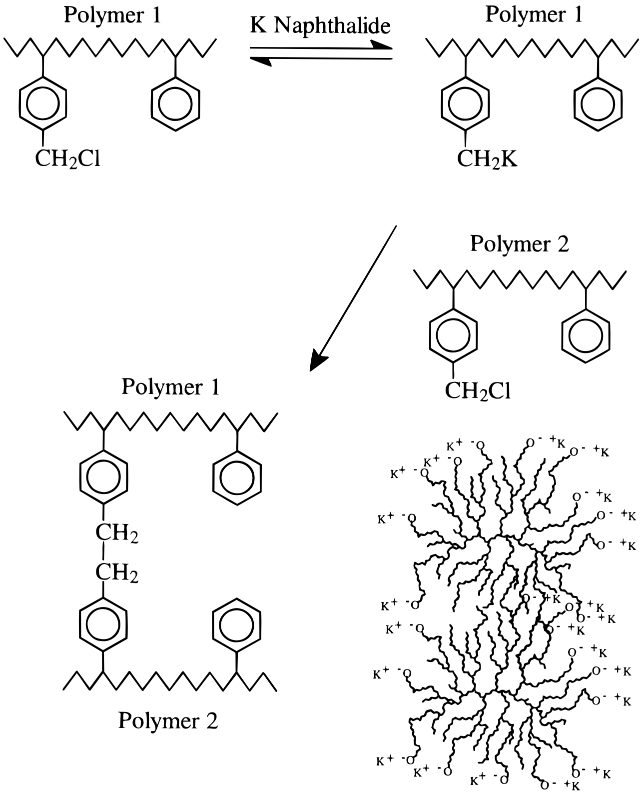


Figure 2. SEC diagrams (in THF) of core-shell polymers prepared from $G = 1$ core (a) without deactivation of residual chloromethyl groups and (b) after deactivation.

Scheme 2. Cross-Linking Reaction of Residual Chloromethyl Groups



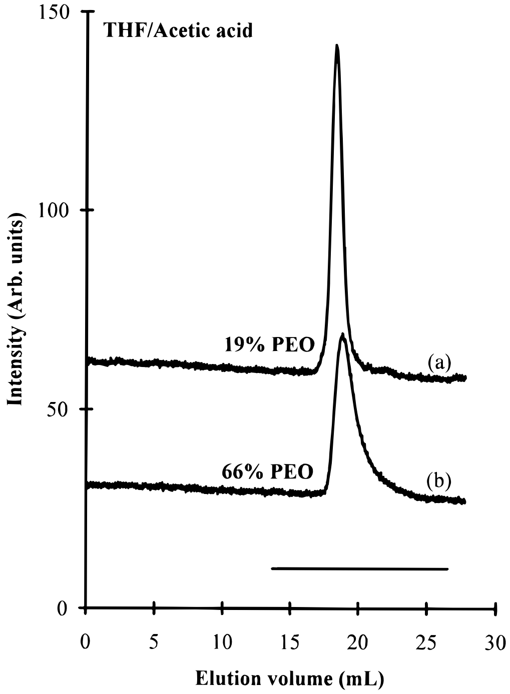


Figure 3. SEC diagrams of core-shell polymers with $G = 1$ core in 96:4 THF/acetic acid: (a) 19% and (b) 66% poly(ethylene oxide) by weight, based on FT-IR analysis.

groups. The resulting polymer, used in the shell growth process, led to a much narrower SEC peak (Figure 2b), with an apparent $\bar{M}_w = 1.4_5 \times 10^5$ g·mol^{-1} and an apparent polydispersity in pure THF $\bar{M}_w/\bar{M}_n = 1.20$. The poly(ethylene oxide) content of the sample determined by FT-IR analysis was 19% by weight. The asymmetry the SEC peak (Figure 2b) on the low-elution-volume side could be explained by a small amount of residual cross-linking reactions or else by aggregation of the molecules in solution. To identify the cause of the problem, the polarity of the mobile phase was increased slightly by adding 4% glacial acetic acid to the THF eluent. Analysis under these conditions led to a symmetrical peak (Figure 3a) and a lower apparent polydispersity value ($\bar{M}_w/\bar{M}_n = 1.11$), confirming that peak broadening was in fact due to association, rather than cross-linking.

A second core-shell sample, prepared from the same "deactivated" core polymer, containing 66% poly(ethylene oxide) by weight, was prepared by adding more ethylene oxide to the titrated core. Analysis of the second sample by SEC using the THF/acetic acid mixture yielded a higher polydispersity, $\bar{M}_w/\bar{M}_n = 1.76$, with considerable tailing at higher elution volumes (Figure 3b). The purpose of adding acetic acid to the mobile phase was to increase the polarity of the solvent and thus minimize association of the molecules in solution. The tailing observed for the polymer with a high poly(ethylene oxide) content suggests that adsorption of the polymer on the column packing material (styrene–divinylbenzene copolymer beads) is taking place. Replacement of the THF/acetic acid mixture with *N*,*N*-dimethylformamide, a more powerful solvent, eliminated tailing problems in the more hydrophilic core-shell polymers (Figure 4b). The sample with only 19% poly(ethylene oxide) content (Figure 4a), on the other hand, displays signs of association as a shoulder on the high molecular weight (low elution volume) side. This seems reasonable, given that DMF is a poor solvent for polystyrene, and the molecular weight of the core portion of the molecule is high ($\bar{M}_w = 7.0 \times 10^5$ g·mol^{-1}).

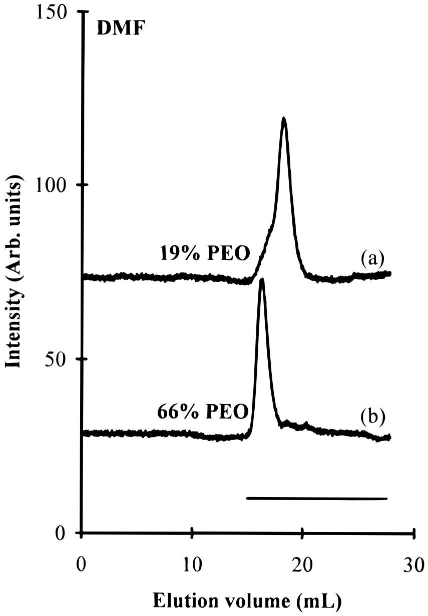


Figure 4. SEC diagrams of core-shell polymers with $G = 1$ core in DMF: (a) 19% and (b) 66% poly(ethylene oxide) by weight, based on FT-IR analysis.

Table 4. Comparison of the Apparent Molecular Weights Determined by SEC Analysis of the Core-Shell Polymers Based on a $G = 1$ Core in Two Different Solvents

PEO content (wt %)	THF/acetic acid		*N*,*N*-dimethylformamide	
	$\bar{M}_n$/g·mol^{-1}	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$/g·mol^{-1}	$\bar{M}_w/\bar{M}_n$
19	1.3×10^5	1.11	4.4×10^5	1.21
66	4.9×10^4	1.76	1.1×10^6	1.07

The analysis results of the SEC measurements obtained for the core-shell polymers using THF/acetic acid and DMF as the mobile phase are summarized in Table 4. Comparison of the results for each core-shell polymer illustrates the importance of mobile phase composition in the chromatographic analysis of amphiphilic polymers. Much lower apparent polydispersities are obtained when the composition of the mobile phase is selected such that polymer adsorption or aggregation is prevented. One question that must be addressed in the SEC analysis of copolymers is the relative sensitivity of the detector to each component of the copolymer. For a homopolymer, a DRI detector has a response proportional to the concentration of the polymer and its difference in refractive index relative to the mobile phase. The analysis of a core-shell polymer using a solvent with a refractive index identical with or very close to that of the shell material would, consequently, not reflect the polydispersity of the shell reliably. To verify the effect of mobile phase composition on SEC analysis, the relative response of the DRI detector to polystyrene and to poly(ethylene oxide) in different solvents was determined. This was done by comparing the peak areas obtained when pure polystyrene and pure poly(ethylene oxide) samples were injected separately at the same concentration. In the worst case observed, when DMF served as the mobile phase, the response due to polystyrene was about twice as large as that of poly(ethylene oxide). This implies that, in the sample containing 66% poly(ethylene oxide), the DRI responses associated with the polystyrene core and with the poly(ethylene oxide) shell portions of the molecule are approximately equal. Consequently, the apparent polydispersity values reported in Table 4 must reflect trends properly, i.e., likely no significant increase in the "absolute" polydispersity took place during addition of the shell.

Another legitimate concern is that, given the large size of the core-shell molecules, the exclusion limit of the column used in the analysis may have been exceeded. Once the hydrodynamic volume of the molecules exceeds the size of the largest pores accessible in the column support, separation becomes ineffective. This gives rise to the familiar upturn in the calibration curve in the low-elution-volume limit. If part of the molecular weight distribution of the polymer overlaps with that portion of the curve, the distribution may be distorted, leading to biased apparent molecular weight values. To verify that this effect was not a problem in the core-shell polymers analyzed, a horizontal line was included in Figures 3 and 4, corresponding to the *linear* portion of the calibration curve in each case. It can be seen that the whole peak areas fall within the linear portion of the curve, and miscalculations due to distortion of the apparent molecular weight distribution are, therefore, unlikely.

Optimization of the reaction conditions used to prepare core-shell polymers based on a $G = 1$ core was convenient, because of the versatility of size exclusion chromatography to monitor the occurrence of side reactions. This was, however, not the case for the core-shell polymer based on a $G = 4$ core, because even the bare core was too large to be eluted from the column.

Growth of a shell on a $G = 4$ core polymer without deactivation of residual chloromethyl groups led to precipitation of the polymer in the titration step. Addition of ethylene oxide yielded a copolymer containing ~25% ethylene oxide by weight and insoluble in the usual solvents for polystyrene and poly(ethylene oxide). The effect of cross-linking reactions is clearly more extreme in the case of the $G = 4$ polymer than the $G = 1$ core, for which the apparent molecular weight distribution was simply broadened. This is easy to understand, since the $G = 4$ polymer ($\bar{M}_w \approx 2 \times 10^8$ g·mol^{-1}) is ~300 times larger than the $G = 1$ core ($\bar{M}_w = 7.0 \times 10^5$ g·mol^{-1}), making it correspondingly more sensitive to the occurrence of cross-linking reactions. A second try, involving deactivation of residual chloromethyl groups as described, led to a soluble product containing 36% poly(ethylene oxide) by weight. The fact that no cross-linking took place in this system is also confirmed by comparing the hydrodynamic radii determined by dynamic light scattering measurements before and after shell growth, as discussed below.

Table 5. Hydrodynamic Radii of Core-Shell Polymers Determined from Dynamic Light Scattering and Molecular Parameters Calculated for the Shell Materials[a]

sample	R_h/nm	δ/nm	PEO chain $\bar{M}_w$/g·mol^{-1}	extended PEO chain length/nm	D_h PEO chain/nm
$G = 1$ core	12.9				
$G = 1$, 19% PEO	16.8	3.9	3.7×10^3	30	2.1
$G = 1$, 66% PEO	23.3	10.4	3.1×10^4	250	6.1
$G = 4$ core	63.7				
$G = 4$, 36% PEO	66.0	2.3	4.8×10^3	39	2.4

[a] The poly(ethylene oxide) (PEO) contents used in the calculations are based on the FT-IR analysis.

Dynamic Light Scattering. To demonstrate the addition of a poly(ethylene oxide) shell on the polystyrene core, dynamic light scattering was used to compare the hydrodynamic radii of the polymers before and after shell growth. Hydrodynamic radii were calculated from the z-average diffusion coefficients (D_z) obtained from second-order cumulant analysis of the normalized correlation function, to better account for polydispersity effects, according to the Stokes–Einstein equation,

$$R_h = kT/6\pi\eta_o D_z$$

where k is Boltzmann's constant, T is the temperature in kelvin, and η_o is the solvent viscosity. The average hydrodynamic radii derived for the different polymers are summarized in Table 5. All values determined by this method are expected to be accurate within 1%. The corresponding values of the hydrodynamic thickness of the poly(ethylene oxide) layer, $\delta = R_h(\text{core-shell}) - R_h(\text{core})$, are reported in the third column. Clearly, a significant increase in the radius of the $G = 1$ core takes place as the poly(ethylene oxide) shell is added. The addition of a larger amount of ethylene oxide monomer leads to a larger increase in the dimensions of the molecules. The molecular weight of the poly(ethylene oxide) chains contained in the shell can be calculated, using the FT-IR composition analysis reported in Table 3. It must be assumed that the polydispersity of the polymers remains constant in the shell growth process and that all chain ends introduced in the last grafting reaction acted as initiating sites for ethylene oxide. For example, the $G = 1$ sample containing 19% PEO (or 81% polystyrene) by weight has a core molecular weight $\bar{M}_w = 7.0 \times 10^5$ g·mol^{-1}. This corresponds to a total molecular weight $\bar{M}_w(\text{tot}) = (7.0 \times 10^5 / 0.81)$ g·mol^{-1} = 8.6×10^5 g·mol^{-1}, or a "shell molecular weight" $\bar{M}_w(\text{shell}) = 1.6 \times 10^5$ g·mol^{-1}. The corresponding molecular weight of the individual poly(ethylene oxide) chains, reported in the fourth column of Table 5, was obtained by dividing $\bar{M}_w(\text{shell})$ by the branching functionality of the last core generation reported in Table 1 (i.e., $f_w = 44$ for the $G = 1$ core). The last two columns of Table 5 give the fully extended chain length and the hydrodynamic diameter calculated for poly(ethylene oxide) chains with the molecular weights specified. The parameters used in the extended chain length calculations were as follows: C–C bond length, 1.54 Å; C–O bond length, 1.43 Å; C–C–O bond angle, 109.5°; C–O–C bond angle, 105°. The hydrodynamic diameters were calculated from the equation

$$D_h = (3M[\eta]/5\pi N_A)^{1/3}$$

where N_A is Avogadro's number and M is molecular weight and using the equation $[\eta]/\text{mL·g}^{-1} = 0.130M^{0.5}$ for the intrinsic viscosity of poly(ethylene oxide) under θ conditions.[18] Calculation parameters corresponding to θ conditions rather than good solvency conditions were preferred. This is to account for the presumably high concentration of poly(ethylene oxide) chains in the outer portion of the molecules and the ensuing contraction of the coils. Comparison of the hydrodynamic poly(ethylene oxide) layer thickness δ with the two limiting cases reported in Table 5 provides information on the conformation of the chains. If the chains were randomly coiled, δ should have a value comparable to the hydrodynamic diameter calculated for the coiled chains. If, on steric grounds, the hydrophilic chains were forced into a partly extended chain conformation, δ should tend toward the fully extended chain length. Comparison of the values in Table 5 reveals that, in spite of the highly crowded structure of arborescent polymers, the poly(ethylene oxide) chains clearly exist in a coiled conformation.

Solubility Behavior. Evidence for a core-shell morphology can be found in an examination of the solubility characteristics of the copolymers prepared. All core-shell polymers can be dispersed in water or methanol from the solid state with the help of sonication. Some turbidity would be expected for dispersions of the $G = 4$ core-shell, given its large size. The smaller $G = 1$ core-shell polymers, on the other hand, should give clear solutions if molecular dispersion is achieved. Dispersions obtained uniquely by sonication of the samples were very turbid in all cases, indicating extensive aggregation of the molecules. This implies that enough interpenetration of the molecules is taking place in the solid state to cause intermolecular bridging by hydrophobic segments of the molecules. The second approach used to disperse the polymers involved the preparation of 1−3% solutions in THF and dropwise addition of the solution to water or methanol. Both $G = 1$ samples gave limpid solutions, and the $G = 4$ solution was slightly opalescent under these conditions. Solubilization of the molecules in polar solvents like water or methanol is only possible if a significant amount of hydrophilic material, such as the poly(ethylene oxide), is in the outer portion of the molecules, acting as steric stabilizer for the hydrophobic core portion. The extreme stability of the core-shell structures obtained is also highlighted by the simplicity of the desolubilization process used. This contrasts with the conditions necessary to obtain micellar structures from amphiphilic block copolymers, requiring very gradual changes in the solvent quality of the dispersion medium. Even under carefully controlled conditions, larger aggregates are also obtained.[19] The greater colloidal stability attained in the arborescent core-shell polymers is presumably a direct consequence of their highly branched structure, leading to a limited ability to rearrange in solution.

Conclusions

The results obtained demonstrated the preparation of single molecules with a core-shell morphology, using the procedures outlined. The analysis of the core-shell polymers by size exclusion chromatography requires careful selection of the mobile phase composition to avoid artifacts such as association or adsorption of the molecules on the column support. Strong evidence for core-shell morphology is found in the solubility behavior of the polymers in polar solvents. An important remaining question concerns the detailed morphology of the molecules and, in particular, the character of the core-shell interface and of the surface of the molecules. Some mixing of the polystyrene and the poly(ethylene oxide) phases would be expected, because of the diffuse layer growth mechanism suggested for arborescent polymers. The presence of polystyrene chains at the surface of the molecules could also have important implications in terms of dispersion stability and the occurrence of flocculation through bridging. For this reason, detailed morphological investigations of arborescent core-shell polymers using neutron scattering are currently under way to determine the radial segmental density profiles of the polystyrene and the poly(ethylene oxide) phases in the molecules.

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Supporting Information Available: Detailed reagent purification and polymerization procedures, including drawings of high-vacuum glassware attachments (9 pages). Ordering information is given on any current masthead page.

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