Novel Nanoscopic Architectures. Linear–Globular ABA Copolymers with Polyether Dendrimers as A Blocks and Polystyrene as B Block

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ABSTRACT: The synthesis of novel linear–dendritic triblock copolymers was achieved *via* anionic polymerization of styrene (St) initiated by potassium naphthylide, subsequent modification of the "living" poly-St with 1,1-diphenylethylene, and final quenching with reactive dendrimers. The effectiveness of the coupling was high as confirmed by size-exclusion chromatography (SEC) with photodiode array detection. The ABA block copolymers were characterized by SEC with coupled viscometry and multiangle laser light scattering, NMR, and thermal analysis. It was found that, in solution, these hybrid materials have radii of gyration between 2.5 and 15 nm. They undergo a shape transition from an extended globular form to a statistical coil as the molecular weight of their linear (poly-St) block increases. All ABA copolymers seem to experience substantial entanglements in the solid state, but they have a single T_g with values ranging from 313 to 367 K, indicating that the linear and dendritic blocks are miscible on the molecular level unlike physical mixtures of their two individual components.

Introduction

Polymers and copolymers with complex and well-defined structures (stars, rings, dendrimers, ladders, etc.) are drawing increasing attention in the search for materials with unconventional or improved properties.[1] Hybrid copolymers consisting of flexible and rigid segments are particularly interesting because of the breadth and variety of their potential applications from drug delivery systems to compatibilizing agents, thickeners, etc. Recently, we were able to develop methods for the synthesis of novel hybrid copolymers with linear–globular architecture. Using preformed poly(ethylene glycol)s and poly(ethylene oxide)s as the linear component and aromatic dendritic polyethers as the globular component, we obtained for the first time amphiphilic hybrid block copolymers containing both flexible and semirigid blocks.[2] These materials exhibit interesting solution- and solid-state properties.[3]

This article describes the synthesis and some properties of hybrid copolymers of linear–globular type that consist of aralkyl fragments only. In contrast to the materials reported previously, these novel block copolymers were designed to be completely amorphous. Polystyrene (PSt) was chosen for the linear and flexible block because it can be easily prepared in a variety of molecular weights by "living" anionic polymerization and its properties are well known. The aromatic dendritic polyethers based on the 3,5-dihydroxybenzyl repeating unit[4] were used as the semirigid globular segments. In a preliminary report[5] we have shown that ABA copolymers containing PSt as the B block and dendritic polyethers as the A blocks also possess unusual solution behavior.

Experimental Section

The purification of all materials, their transfer, storage, and dispensing, and the polymerization and coupling reactions were carried out under high vacuum (10^{-5} mmHg) in all-glass devices equipped with break seals.

Materials. The solvent, tetrahydrofuran (THF; Aldrich), was dried by several consecutive distillations over sodium/potassium alloys until the blue color that developed remained. The initiator, naphthalene-K, was formed by the reaction of naphthalene with a potassium mirror in THF at room temperature. The monomer, styrene (St; Aldrich), was dried by double distillation over CaH_2; it was then stored in break seals at −15 °C.

1,1-Diphenylethylene (1,1-DPE; Aldrich) was purified by several consecutive distillations over potassium mirror until no red color was observed; it was also stored in break seals at −15 °C.

The dendritic block, [G-4]-Br, was synthesized as described earlier,[4] dried on the vacuum line for 12 h, and dissolved in dry THF. Then the solvent was distilled several times on a potassium mirror to remove any impurities such as H_2O or CH_2Cl_2 that might have remained trapped in the solid dendritic bromide. Finally, the solution was stored at −15 °C prior to use.

Polymerization. The polymerization of St and the coupling reactions were carried out under high vacuum (10^{-5} mmHg) in the all-glass reaction vessel shown in Figure 1. A typical polymerization procedure is described as follows: A potassium mirror was formed on the walls of part **A** by distillation, the appendix containing the remaining K (Figure 1, **1**) was sealed, and, after high vacuum was reached, the whole system was sealed off. THF (40 mL) was added and its ampule was sealed off. After the system was rinsed several times with dry THF, the break seal with naphthalene (0.011 g, 8.62×10^{-5} M) was crushed (Figure 1, **2**) and the initiator was formed under intensive shaking. After 1 h the equipment was turned upside down and the dark green initiator solution was transferred quantitatively through a glass filter directly into the polymerization vessel **B**. Part **A** was sealed off, and the polymerization vessel was cooled to −70 °C for 30 min. Then the break seal containing the monomer (2 mL, 1.812 g, 1.74×10^{-2} M) was crushed (Figure 1, **St**) and styrene was distilled slowly (within 2 h) into the vigorously stirred solution. After the addition of St was completed, the polymerization mixture was stirred for 30 min at the same temperature and 1,1-DPE (0.21 mL, 0.214 g, 1.2×10^{-3} M) from another break seal was added (Figure 1, **1,1-DPE**). The reaction mixture was stirred for 30 min, while the break seal containing the solution of dry [G-4]-Br in THF (0.076 g, 2.28×10^{-5} M in 7 mL of THF) in one of the attached appendixes (Figure 1, **C**) was cooled to −70 °C. Then the break seal was crushed and the dendritic bromide solution was quantitatively titrated by the "living" PSt. The completion of the reaction was easily

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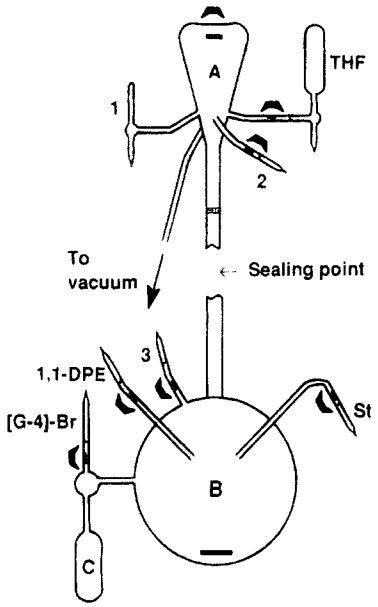


Figure 1. Schematic presentation of the all-glass apparatus used in the synthesis of linear–dendritic ABA copolymers in vacuum: A, reaction flask for the preparation of (naphthalene)-potassium (1, appendix with potassium; 2, breaking seal containing sublimed naphthalene; THF, ampule with dry THF); B, polymerization vessel (St, breaking seal containing dry St; 1,1-DPE, breaking seal containing dry 1,1-diphenylethylene for the modification of the "living" PSt; 3, breaking seal with degassed methanol); C, ampule for the coupling of "living" PSt with fourth-generation dendritic bromide ([G-4]-Br).

followed by the disappearance of the red color of the "living" polymer. The remaining "living" polymer was quenched with degassed methanol (Figure 1, **3**), and both the copolymer and PSt were isolated by precipitation from THF in diethyl ether. Traces of unreacted [G-4]-Br were removed from the copolymer by fourfold precipitation from THF into a 2-propanol/acetone mixture (3:2 v/v). PSt: M_n(calcd) = 42000, M_n(found) = 42500. ^{1}H-NMR ($CDCl_3$): δ 1.44 (br s, PhCHCH_2), 1.87 (br s, PhCH (rr)), 2.07 (br s, PhCH ($mr + rr$)), 2.18 (br s, PhCH (mm)), 6.58 (br s, PhH (o)), 7.1 (br s, PhH ($m + p$)). Copolymer: M_n(calcd) = 48500, M_n(found) = 56000. ^{1}H-NMR ($CDCl_3$): δ 1.44 (br s, PhCHCH_2 of PSt), 1.87 (br s, PhCH (rr) of PSt), 2.07 (br s, PhCH ($mr + rr$) of PSt), 2.18 (br s, PhCH (mm) of PSt), 4.91, 4.97 (each s, Ar and PhCH_2O of dendrimer), 6.52–6.65 (m, PhH of St and dendritic monomer units), 7.1 (br s, PhH ($m + p$) of PSt), 7.28–7.35 (m, PhH of dendritic monomer units). ^{13}C-NMR ($CDCl_3$): δ 40.25, 40.48, 41.67, 42.59, 43.38, 43.74, 44.05, 44.94, 45.90, 46.32, 48.37 ($CHCH_2$ of PSt), 69.36, 69.87, 69.95 (CH_2O of dendrimer), 101.17, 101.47 (ArC), 106.27, 106.33, 106.46 (ArC), 127.26, 127.38, 127.51, 127.93, 128.00, 128.22, 128.52 ($C_2 + C_3$ of dendrimer and PSt), 136.48, 136.59, 136.67, 136.75, 137.10 (ArC + PhC of dendrimer), 139.11, 139.17, 139.45, 139.49, 139.80 (ArC + PhC of dendrimer), 145.03, 145.23, 145.30, 145.62, 146.02 (C_1 of PSt), 159.84, 159.97, 160.05 (ArC + PhC of dendrimer).

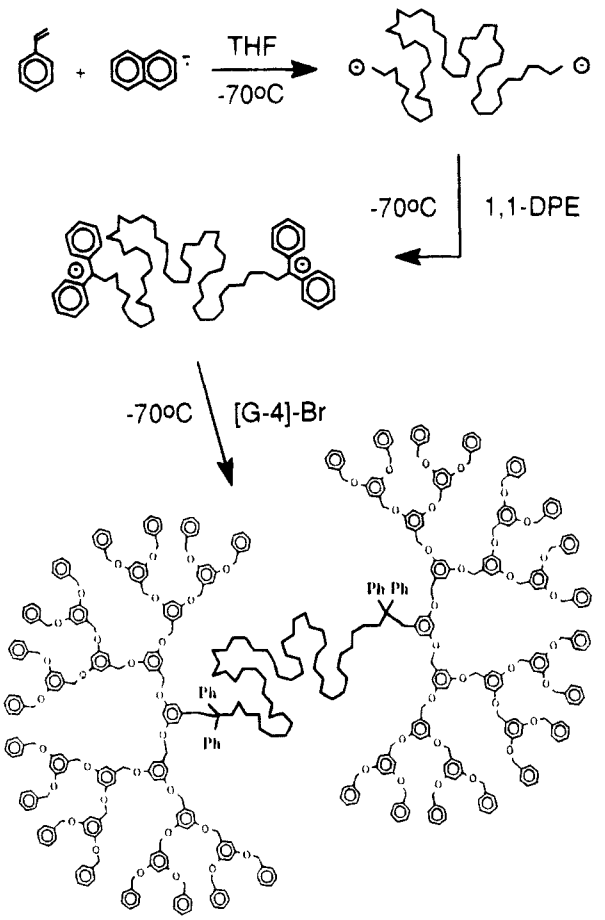
Methods. ^{1}H-NMR spectroscopy and ^{13}C-NMR spectroscopy were performed on a Bruker WM 300 (300 MHz) and Varian WXR 400 (400 MHz) spectrometers at room temperature. Solutions in $CDCl_3$ were made, and the solvent proton and carbon signals were used as internal standards.

Size-exclusion chromatography (SEC) with double detection was performed at 45 °C on a chromatography line consisting of an M510 pump, a U6K universal injector, three 7-μm ultraStyragel columns with pore sizes 100 Å, 500 Å, and Linear, a differential refractive index (DRI) detector M410, and a photodiode array (PDA) detector M991 (all Millipore Co., Waters Chromatography Division). THF was used as eluent at a nominal flow rate of 1 mL/min.

The solution behavior of PSt and its hybrid copolymers was investigated at 40 °C by SEC with coupled viscometric detection (SEC/VISC) and multiangle laser light scattering (SEC/MALLS). The mobile phase was THF eluting at a nominal rate of 1 mL/min. The SEC/VISC chromatograph incorporated the same solvent delivery system and injector as described above and two detectors connected in parallel: a Viscotek Model 110 differential viscometer and a refractoMonitor (Milton Roy) DRI detector. The column set contained four 5-μm PL Gel columns (Polymer Laboratories) with pore sizes 100 Å, 500 Å, 1000 Å, and Mixed C. The molecular weight characteristics of the polymers were calculated by a "universal calibration" curve constructed with 23 monodisperse PSt standards. The SEC/MALLS system included a Waters M590 pump, a Hewlett-Packard 1050 automatic injector, three 10-μm PL Gel "mixed" columns (Hewlett-Packard), and a DAWN-F laser photometer (Wyatt Technology Co.) connected in series with a Waters 410 differential refractometer. The dn/dc values of the initial building fragments and the resulting block copolymers were determined in THF on a Wyatt/Optilab 903 interferometric refractometer using DNDC measurement program Version 2.02 (Wyatt Technology Co.). The molecular weight characteristics and the sizes of the materials investigated were obtained using Astra 2.02 software (Wyatt Technology Co.).

The thermal characteristics of the materials obtained were investigated on a differential scanning calorimetry (DSC) module from Seiko Instruments, Inc. The analysis conditions were as follows: heating rate, 10 °C/min; purging gas, nitrogen at 50 mL/min; sample containers, crimped aluminum pans. The calculations were carried out on an SSC 5200H thermal analysis station (Seiko Instruments) using Seiko thermal analysis software Version 3.

Scheme 1



Results and Discussion

I. Synthesis. The reaction sequence for the synthesis of PSt with dendritic end groups (hybrid ABA block copolymers) is shown in Scheme 1. In this scheme the polystyrene dianion is represented in an abbreviated and highly schematic form emphasizing only the presence of the two "living" anionic ends separated by a linear polymer chain. We discovered that, despite its

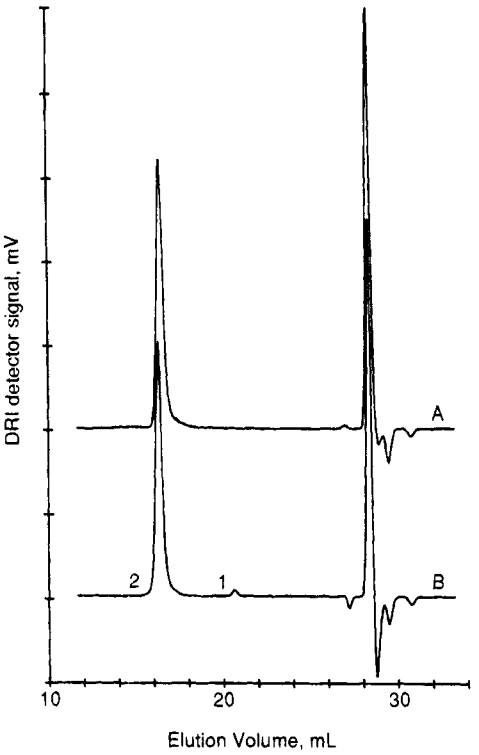


Figure 2. SEC traces of the initial PSt block obtained after the quenching of "living" PSt with methanol (A) and the reaction mixture after the quenching of the same "living" polymer with [G-4]-Br (run 5, Table 2) (B). Columns, PL Gel 100 Å, 500 Å, 1000 Å, and Mixed C; eluent, THF; nominal flow rate, 1.0 mL/min; temperature, 40 °C.

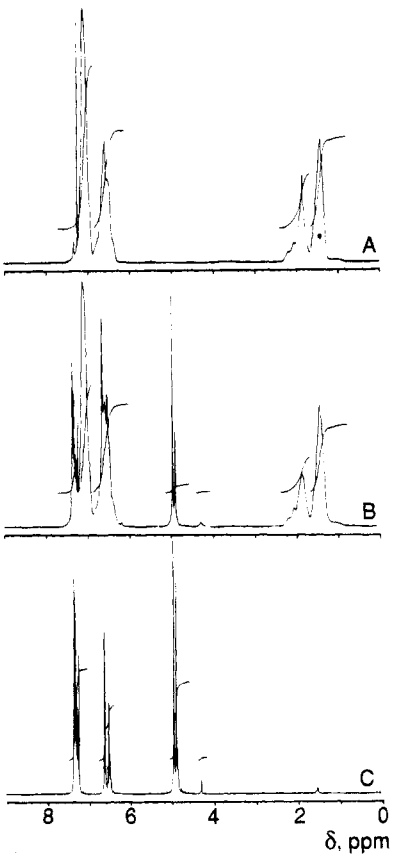


Figure 3. ^{1}H-NMR spectra of the initial PSt block obtained after the quenching of "living" PSt with methanol (A) and the reaction mixture after the quenching of the same "living" polymer with [G-4]-Br (B) and [G-4]-Br (C). Solvent $CDCl_3$, 400 MHz, 22 °C.

bulkiness and even at −70 °C, the fourth-generation dendritic bromide ([G-4]-Br) still undergoes the side reactions that have been previously documented for the reactions involving "living" PSt and benzylic halomethyl groups.[6–8] Therefore the nucleophilicity of the PSt dianions was decreased by addition of 1,1-DPE prior to reaction with [G-4]-Br. In addition, the "living" polymer was always added to the dendrimer solution (excess of [G-4]-Br) to further decrease the likelihood of any side reactions. Therefore, there is a possibility that a small amount of unreacted dendrimer might remain in the mixture after completion of the reaction. The effectiveness of the coupling is difficult to monitor by SEC with conventional double DRI/UV detection because both the dendrimer and PSt absorb light at 254 nm, and if the PSt block is sufficiently long, the differences in the elution volumes of the isolated products before and after the coupling reaction are very close. A typical example is shown in Figure 2. It is seen that the initial PSt (Figure 2A) and the block copolymer (Figure 2B, peak 2) elute at almost the same time. In addition, the reaction product is slightly contaminated with a small amount (approximately 3%) of unreacted [G-4]-Br (Figure 2B, peak 1). The ^{1}H-NMR spectrum of the same reaction mixture also confirms the presence of unreacted [G-4]-Br (PhCH_2Br: δ = 4.32 ppm, Figure 3B) and therefore cannot be used to provide quantitative information on the chemical composition of the copolymer. SEC with coupled PDA detection proves to be particularly useful in the separation and identification of all compounds of this reaction mixture. A two-dimensional plot of the sample confirms the presence of two components with different spectral characteristics (Figure 4, 1 and 2). The UV spectra of components 1 and 2 are taken in the range 190–350 nm and compared with the UV spectrum of the PSt precursor (Figure 5, 1–3). Component 1 and pure [G-4]-Br have identical absorption maxima at 238 and 277 nm; PSt (Figure 5, 3) also has two distinguished absorption bands at 223 and 259 nm. It is obvious that the UV spectrum of peak 2

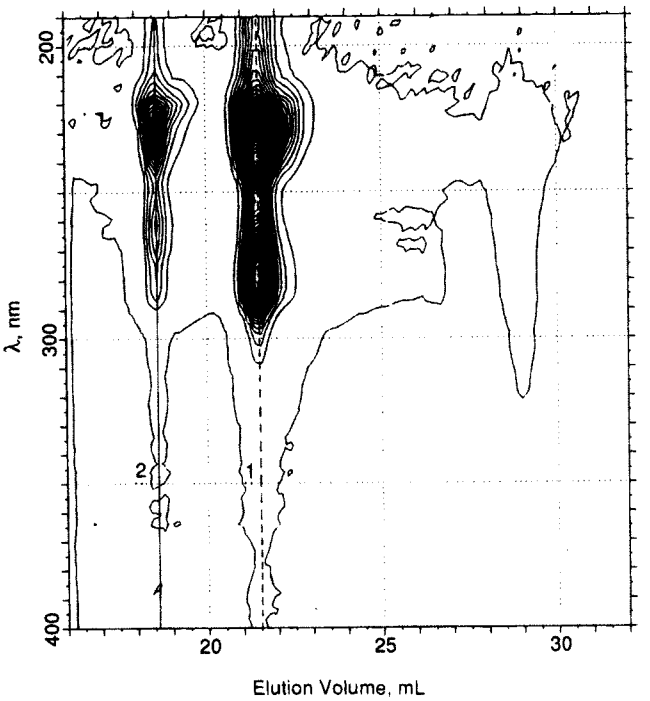


Figure 4. Two-dimensional chromatogram obtained by SEC with PDA detection of the reaction mixture after the quenching of "living" PSt with [G-4]-Br (see also Figures 2 and 3): 1, component 1 of Figure 2; 2, component 2 of Figure 2. Columns, ultraStyragel 100 Å, 500 Å, and Linear; eluent, THF; nominal flow rate, 1.0 mL/min; temperature, 45 °C.

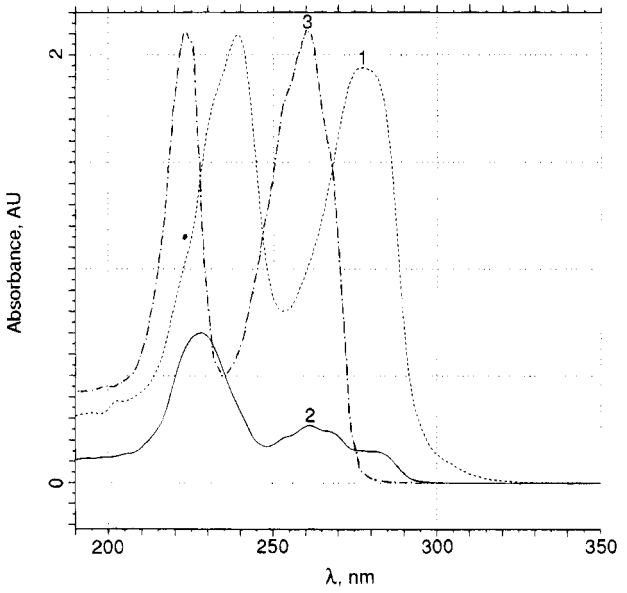


Figure 5. Ultraviolet spectra of the components of the reaction mixture after the quenching of "living" PSt with [G-4]-Br (see also Figures 2–4) obtained by SEC with PDA detection: 1, component 1 of Figures 2 and 4, identical to the spectrum of pure [G-4]-Br; 2, component 2 of Figures 2 and 4; 3, initial PSt block obtained after the quenching of "living" PSt with methanol (Figure 2A).

comprises a combination of the UV spectra of PSt and [G-4]-Br (Figure 5, 2; λ_{max} = 229, 262, and 283 nm). The intensity of the absorption band at 283 nm shows a dendritic content corresponding to two [G-4] groups as confirmed by the concentration calibration made with pure dendrimer.

The molecular weight characteristics of the initial PSt blocks and the resulting ABA hybrid copolymers are listed in Table 1. It should be emphasized that all copolymers contain two dendritic units as confirmed by the spectroscopic and chromatographic analyses. The molecular weights calculated by the universal calibration method (SEC/VISC) for copolymers containing PSt blocks with molecular weights below 12000 and fourth-generation dendrimers are lower than the calculated values (Table 1, runs 1, 2a, and 3). On the other hand, the attachment of dendritic fragments of lower generation, [G-2] and [G-3], to PSt affords products with apparent molecular weights that match the predicted values (Table 1, runs 2b and 2c). These facts can be explained with the smaller hydrodynamic volume of the [G-4] copolymers caused by the increased content of more compact and dense dendritic moieties. Surprisingly, starting with run 4 (PSt blocks with molecular weights higher than 40000), the molecular weights of the [G-4] copolymers determined by SEC/VISC and the "universal calibration" method are increasingly higher than the calculated values. Comparative measurements of the same products performed by SEC/MALLS show excellent agreement with the calculated values (Table 1, runs 5–8). Obviously, the universal calibration is not able to provide accurate information for the molecular weight characteristics of these hybrid copolymers. For this reason the solution properties of the ABA triblock copolymers and their building blocks were investigated in detail.

II. Solution Properties. It is well known that the concentration of the polymer in a specific solvent affects its SEC elution volume, *i.e.*, the molecular weight determined in that solvent.[9] It was shown that the elution volume of several polymers, including PSt, in a good solvent increases as the concentration of the polymer solution increases.[9] This "concentration effect" was attributed to the decrease in the hydrodynamic volumes of the solvated polymers with increasing concentration[10,11] and to redistribution phenomena caused by the increased viscosity of the polymer samples introduced into the SEC system.[12] The existence of a concentration dependence of the elution volumes of the initial PSt blocks and the dendritic fragments (*i.e.*, their molecular weights calculated through the "universal" calibration) was investigated with the SEC/VISC line used in this study. For the dendritic fragment no influence of the concentration on the elution volume was detected over the concentration range 0.2–3.0 mg/mL typically used in our SEC experiments (Figure 6). Plotted on the same figure is the behavior of a PSt standard that has a molecular weight close to that of the dendrimer (M_p = 3250 for PSt and 3354 for [G-4]-Br, respectively, where M_p is the molecular weight at the top of the polymer peak in the SEC traces). This plot shows a slight increase in the elution volume with increasing concentration, but this increase levels off at concentrations above 1.5 mg/mL. The PSt samples with molecular weights 8560, 12700, and 42500 (Table 1, runs 2–4) used elsewhere to prepare ABA triblock structures were investigated in the same concentration range and behave similarly. Hence, the "concentration effect" can be excluded as a reason for the lower apparent molecular weights observed in runs 2–4. All further investigations of the solution behavior of the hybrid linear–dendritic block copolymers were performed at concentrations between 2 and 4 mg/mL—a range in which the elution volumes do not depend on concentration.

The intrinsic viscosities ($[\eta]$) of the ABA hybrid copolymers with narrow molecular weight distributions (M_w/M_n < 1.05) and their precursors were measured in THF at 40 °C by SEC/VISC (Table 2). It should be mentioned that each sample was injected at least six times and that the value reported is that obtained by averaging all measurements. The radii of gyration (R_g) of the same samples were calculated from $[\eta]$ and Unical 4.04 software (Viscotek) by combining the Flory–Fox (eq 1) and Ptitsyn–Eizner equations (eq 2):[13]

$$R_g = (1/\sqrt{6})(M[\eta]/F)^{1/3} \quad (1)$$

$$F = 2.86 \times 10^{21}(1 - 2.63\epsilon + 2.86\epsilon^2) \quad (2)$$

The values for $M[\eta]$ were determined from the universal calibration curve, and ϵ in eq 2 was calculated from the formula $\epsilon = (2\alpha - 1)/3$, where α is the Mark–Howink–Sakurada (MHS) exponent constant that was also obtained from the universal calibration. For the first samples of the series, the viscosity of the ABA triblock hybrids is higher than that of the starting PSt precursors (Table 2, runs 2a and 3). Remarkably, the values of $[\eta]$ for the ABA copolymers are increasingly lower than those of the PSt B blocks when the molecular weights of the latter exceed 40000. At the same time, all radii of gyration of the copolymers are higher than those of their PSt precursors. This is an indication that in THF solution the molecules of the hybrid block copolymers are undergoing a shape transition as the molecular weight of their linear central blocks increases. Indeed, the MHS plot for PSt standards, the PSt precursors, and their ABA dendritic copolymers reveals that such transition takes place (Figure 7). PSt with molecular weights up to 17000 form statistical coils in THF (MHS α = 0.514, ref 3) and more extended

Table 1. Molecular Weight Characteristics of PSt and Their Hybrid Linear–Dendritic Block Copolymers

	initial PSt block			ABA hybrid copolymer				
run	M_n (calc)	M_p[a] (SEC)	M_w/M_n (SEC)	M_n[b] (calc)	M_p[c] (SEC)	M_w/M_n (SEC)	M_w[d]	dendritic fragment
1	474[e]	440	1.01	7024	3000	1.02	6900	[G-4]
2a	8000	8560	1.03	15110	13800	1.02	12800	[G-4]
2b				11714	10500	1.03		[G-3]
2c				10014	9950	1.02		[G-2]
3	12000	12700	1.05	19350	18100	1.05	17500	[G-4]
4	42000	42500	1.02	49050	56000	1.02		[G-4]
5	54000	54000	1.05	60550	65400	1.05	60000	[G-4]
6	67000	65500	1.05	72050	79000	1.05	71300	[G-4]
7	97000	97000	1.04	103550	114000	1.04	104000	[G-4]
8	170000	170000	1.03	176550	190000	1.03	176000	[G-4]
9	800000	802000	1.18	808550	1364000	1.15		[G-4]

[a] Molecular weight at the top of the polymer peak in the SEC traces calculated by universal calibration; the M_w values obtained by SEC/MALLS deviate on average by 5%. [b] Molecular weight calculated by adding the molecular weights of two dendrimer fragments to M_p of the initial PSt block. [c] Molecular weight at the top of the polymer peak in the SEC traces calculated by universal calibration. [d] Weight-average molecular weight obtained by SEC/MALLS. [e] Molecular weight of the α-methylstyrene tetramer obtained by naphthalene-K at room temperature. The hybrid ABA was obtained by direct quenching of the tetramer dianion with [G-4]-Br without using 1,1-DPE.

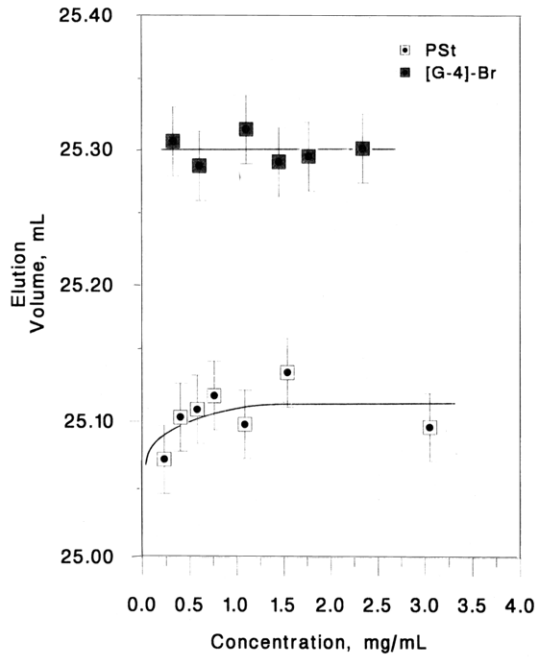


Figure 6. Concentration dependence of the elution volumes of PSt standard with molecular weight 3250 and [G-4]-Br, molecular weight 3354. Injection volume, 100 μL. Analysis conditions: as in Figure 2.

structures when the molecular weight increases above that value (MHS α = 0.747, ref 3). It is seen that the first three ABA copolymers with molecular weights up to 50000 have structures resembling that of an unfolded coil with MHS α close to 0.747, and at molecular weights higher than 50000 their molecules start folding back to a more globular shape (MHS α = 0.538). It is obvious that after the attachment of the semirigid and compact dendritic fragments to the flexible PSt coils the resulting hybrid macromolecules will have a density distribution that is not uniform throughout their hydrodynamic volume. This is supported by the finding that their radii of gyration increase while the viscosities decrease. It should be emphasized that most theoretical models for the universal calibration predict that it will be valid for linear or branched macromolecules with different chemical compositions *only* if the polymers have uniform density and rigidity.[14,15] Probably, this is the reason for the overestimated values of the molecular weights of the hybrid ABA copolymers calculated by the universal calibration. As was the case for dendrimers,[16] these new nanoscopic architectures demonstrate the serious limitations that underlay the concept of universal calibration.

The calculations of molecular weights determined by SEC/MALLS are based on the following generalized formula:[17]

$$R_\theta = K^* M_w c P(\theta) [1 - 2A_2 M_w P(\theta) c] \quad (3)$$

where R_θ is the excess Rayleigh ratio of the light scattered from the polymer solution at 15 discrete angles in the flow cell of the DAWN-F laser photometer; K^* is a constant for vertically polarized light given by the equation $K^* = 4\pi n_0 (dn/dc)^2 \lambda_0^{-4} N_A^{-1}$ (n_0 is the refractive index of the solvent, dn/dc is the differential refractive index increment with the polymer concentration, λ_0 is the wavelength of the incident light in vacuum, and N_A is Avogadro's number), M_w is the weight-average molecular weight, c is the concentration of polymer molecules in the solvent, $P(\theta)$ is a theoretical form factor of the scattered light intensity as a function of scattering angle, and A_2 is the second virial coefficient. Since the detection occurs at multiple angles, the value of θ can be extrapolated to 0 where $P(\theta) = 1$ and eq 3 becomes

$$R_\theta = K^* M_w c [1 - 2A_2 M_w c] \quad (4)$$

For polymer molecules with sizes well below λ_0 (632.8 nm) the scattering will be isotropic and will not depend on the density distribution of the macromolecules but mostly on their dn/dc values. The PSt dn/dc value (0.184 mL/g) can be used also for the ABA hybrid copolymers if the PSt blocks are sufficiently long (M_w > 50000). This approximation yields accurate molecular weights for the copolymers shown in Table 1, runs 5–8. When the content of dendritic groups is nearly equivalent to that of the linear block, the use of the PSt dn/dc value leads to underestimation of the molecular weight measured by SEC/MALLS (Table 1, runs 2a and 3). The ABA copolymer containing α-methylstyrene tetramer as the linear B block (Table 1, run 1) was available in a quantity sufficient to enable the separate measurement of its dn/dc value. The dn/dc value of this copolymer (0.206 mL/g) is between those published for a [G-4] monodendron (0.211 mL/g) and a [G-4] tridendron (0.204 mL/g),[16] suggesting that it should be regarded more as a dendritic didendron than as a linear–dendritic copolymer. Using this dn/dc value, measured in THF at 25 °C, the light scattering measurement provides a fairly accurate estimate of the molecular weight of this ABA hybrid copolymer with a very short B block.

Table 2. Solution Behavior of Dendrimers, PSt, and Their Hybrid Copolymers in THF at 40 °C

run	building block	$[\eta]$ (dL/g)	R_g (nm)	ABA copolymer	$[\eta]$ (dL/g)	R_g (nm)
	[G-1]-OH	0.023[a]	0.56[a]			
	[G-2]-OH	0.028[a]	0.84[a]			
	[G-3]-OH	0.035[a]	1.10[a]			
	[G-4]-OH	0.039[a]	1.41[a]			
2a	PSt8600	0.067	2.00	[G-4]-PSt8600-[G-4]	0.091	2.50
3	PSt12700	0.076	2.45	[G-4]-PSt12700-[G-4]	0.100	2.84
4	PSt42500	0.200	6.08	[G-4]-PSt42500-[G-4]	0.195	6.55
5	PSt54000	0.266	6.80	[G-4]-PSt54000-[G-4]	0.252	7.52
6	PSt65500	0.275	7.62	[G-4]-PSt65500-[G-4]	0.259	8.19
7	PSt97000	0.423	7.82	[G-4]-PSt97000-[G-4]	0.340	9.14
8	PSt170000	0.546	12.91	[G-4]-PSt170000-[G-4]	0.435	14.97

[a] Data from ref 3.

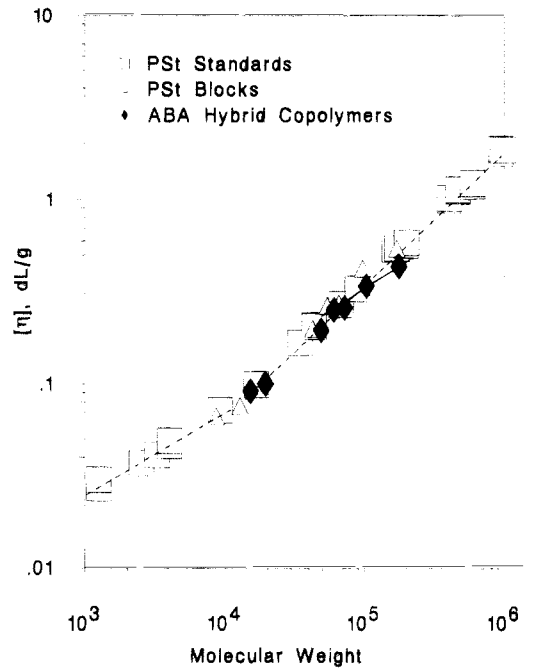


Figure 7. Mark–Houwink–Sakurada plot for PSt standards, the initial PSt blocks obtained in this study, and the hybrid linear–dendritic copolymers. Analysis conditions: as in Figure 2.

III. Solid-State Properties. The PSt and the fourth-generation dendrimer used to build the ABA hybrid block copolymers are amorphous materials characterized by a well-defined glass-transition temperature (T_g). Several factors, including the molecular weight[18,19] and the occurrence and degree of entanglement,[20] have been found to influence the value of T_g for PSt. In contrast, dendrimers should not experience the sort of entanglement that is typical of conventional linear polymers because of their dense hyperbranched architecture. Therefore, their T_g values depend mostly on the molecular weight and the number and composition of their chain ends.[21] As a result, it was interesting to study the changes in the thermal characteristics of PSt after the incorporation of dendritic poly(benzyl ethers). All T_g values were determined by oscillating and conventional DSC measurements that monitor the onset of the transition. It is assumed that this procedure is more precise than the half-height method that uses the midpoint of the inflection tangent.[22] It was found earlier[21] that the value of T_g is only slightly dependent on the molecular weight for the series of didendron dendrimers [G-x]-C-[G-x], (from $x = 2$ to $x = 5$), confirming the lack of entanglement in these macromolecules (Table 3). On the contrary, the T_g value for PSt increases significantly as the polymer molecular weight exceeds 30000, a phenomenon that was attributed to the increased occurrence of entanglements[20] (Table 3). It is worth mentioning that, in all of the cases we investigated, each hybrid ABA copolymer has a single T_g while physical mixtures of dendrimer and PSt (therefore having the same gross composition) exhibit two glass transitions corresponding to the T_gs of the individual compounds. For example, the copolymer [G-4]-PSt12700-[G-4] shows a single glass transition at 349.5 K while the PSt precursor with a molecular weight of 12700 mixed with 34 wt % of [G-4]-Br has two distinct glass transitions at 314 K (dendrimer) and 362 K (PSt).

Table 3. Glass Transition Temperatures of PSt, Dendritic Poly(benzyl ethers), and Their Hybrid Copolymers

run	compd	mol wt	T_g (K)	$T_{g(calc)}$ (K)[a]
	[G-4]-Br	3354	314	
	[G-2]-C-[G-2][b]	1656	306[c]	
	[G-3]-C-[G-3][b]	3354	311[c]	
	[G-4]-C-[G-4][b]	6750	311[c]	
	[G-5]-C-[G-5][b]	13542	312[c]	
	PSt	2850	343[d]	
	PSt	4000	353[d]	
2	PSt	8600[e]	363	
3	PSt	12700[e]	368	
	PSt	17500	369[d]	
	PSt	37000	378[d]	
5	PSt	54000[e]	372	
7	PSt	97000[e]	375	
8	PSt	170000[e]	377	
	PSt	275000	379[d]	
	PSt	600000	380.5[d]	
	PSt	2000000	381[d]	
1	[G-4]-PSt440-[G-4]	6900[e]	313	
2a	[G-4]-PSt8600-[G-4]	12800[e]	341	340.9
3	[G-4]-PSt12700-[G-4]	17500[e]	349.5	348.8
5	[G-4]-PSt54000-[G-4]	60000[e]	365	365.3
7	[G-4]-PSt97000-[G-4]	104000[e]	366	370.8
8	[G-4]-PSt170000-[G-4]	176000[e]	367	374.5

[a] T_g calculated according to the formula $\ln T_g = m_1 \ln T_{g1} + m_2 \ln T_{g2}$.[23] [b] Obtained from the corresponding dendritic bromide [G-x]-Br, $x = 2-5$, and a bifunctional core, 4,4′-biphenol.[21] [c] Data from ref 21. [d] Data from ref 19. [e] M_w obtained by SEC/MALLS.

Within the molecular weight range of 10000–60000, the T_g values of the hybrid block copolymers are very close to those obtained by the formula[23]

$$\ln T_g = m_1 \ln T_{g1} + m_2 \ln T_{g2}$$

where m is the content of each block in weight percent and T_g, T_{g1}, and T_{g2} are the glass transition temperatures for the copolymer and its building blocks, respectively. These facts indicate that, as a result of the chemical links connecting the dendritic and the linear fragments, the ABA copolymers are intimate mixtures without phase separation of their blocks (*i.e.*, the mixing occurs on a molecular level).

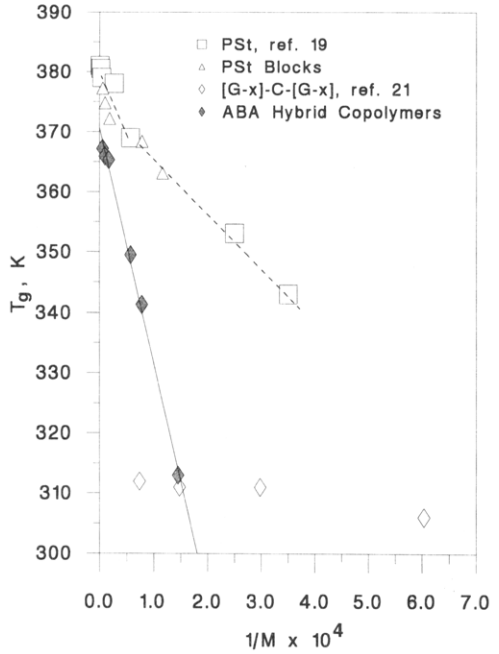


Figure 8. Molecular weight dependence of the glass transition temperature (T_g) for PSt,[19] the initial PSt blocks obtained in this study, [G-x]-C-[G-x] didendron dendrimers obtained after coupling of dendritic bromides [G-x]-Br (x = 2–5) with 4,4′-biphenol,[21] and the hybrid linear–dendritic copolymers.

The "free volume–chain end" theory[24,25] suggests a linear relationship between the T_g of the polymer and the reciprocal of its molecular weight according to the formula

$$T_g = T_{g\infty} - K/M$$

where $T_{g\infty}$ is the glass transition temperature at infinite molecular weight M and K is a constant taking into account the contributions of end groups to the free volume of the system. All ABA copolymers in this study could be tested by this theory since they have a constant number of end groups with the same chemical composition ([G-4]). The plot of T_g *vs* $1/M$ reveals the distinct thermal behavior of the hybrid copolymers in comparison to their building blocks (Figure 8). The molecular weight dependence of the T_g values for PSt is characterized by two straight lines with slopes $K_1 = 9.7 \times 10^4$ (correlation coefficient 0.966) for $M < 37000$ and $K_2 = 19.2 \times 10^4$ (correlation coefficient 0.921) for $M > 37000$, respectively. These values are close to those already published for this polymer.[20] Interestingly, all data points for the ABA copolymers fit on a single line with a correlation coefficient of 0.997 and $T_{g\infty}$ and K values of 370.7 K and 39.1×10^4, respectively (Figure 8). Obviously, the hybrid copolymers constructed form PSt and dendrimers are experiencing a certain form of entanglement throughout the whole molecular weight range. The data for the dependence of the T_g on $1/M$ for didendron dendrimers [G-x]-C-[G-x][21] are shown in Figure 8 for comparison purposes only. It was previously stated[21] that this relationship is not valid for macromolecules with increasing number of chain ends. Interestingly, [G-4]-C-[G-4] could be regarded as the first member of the family of the ABA copolymers since its T_g value fits on the same straight line.

Conclusion

The coupling of a "living" polystyrene with reactive dendrimers proved to be an effective method for the formation of novel nanoscopic architectures containing both linear and dendritic blocks that have an entirely amorphous character. Thus, materials containing fourth-generation dendritic end groups at each extremity of linear polystyrene blocks with varying chain lengths could be obtained. These hybrid copolymers exhibit interesting solution and solid-state properties. SEC/VISC studies show that the ABA copolymers are not entangled and undergo a transition from an extended globular form to a statistical coil when the molecular weight of their linear central block exceeds 50000. Conversely, in the solid state the same materials seemed to form more entangled structures, in which both blocks show miscibility on a molecular level.

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