Solution and Solid-State Properties of Hybrid Linear–Dendritic Block Copolymers

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ABSTRACT: The solution and solid-state properties of hybrid linear–dendritic polyether copolymers are investigated by size-exclusion chromatography with coupled viscometric detection, polarized light microscopy, and X-ray analysis. The results obtained show that the block copolymers are able to form mono- and multimolecular micelles depending on the dendrimer generation and the concentration in methanol/water (good solvent for the linear blocks). Only monomolecular micelles are observed in THF (good solvent for the dendritic blocks). The linear blocks are able to crystallize in spherulites, axialites, or unique dendritic structures depending on the overall composition of the copolymers and the solvent used.

Introduction

Large macromolecular assemblies and agglomerates play an important role in living matter and its artificial reproduction, and the study of the mechanism of molecular recognition and the properties of the resulting products are of crucial interest. AB and ABA block copolymers are convenient tools used for modeling of these processes. Usually in a specific solvent/nonsolvent system, ABA triblocks form micelles with a core consisting of insoluble B blocks and a surrounding shell of A blocks that extend into the solvent phase. Reports on ABA triblock copolymers that are able to form micelle cores through their A blocks are very rare,[1,2] due in part to the lack of suitable materials. Theoretical studies predict that these systems are entropically unfavorable.[3]

In spite of some interesting recent publications reporting the existence of the above-discussed systems,[4,5] there is still a certain controversy concerning the possibility for micelle formation by self-assembly of the end blocks in ABA block copolymers. The difficulties encountered with such materials are usually caused by the lack of a sufficient number of samples with narrow polydispersity having a monotonous change in chemical composition. In addition, the existing systems have flexible A and B blocks, which leads to the formation of ill-defined micelles whose constitution depends on concentration, temperature, and solvent. Therefore it is desirable to prepare new ABA block copolymers that are able to form micelles having constant compositions not influenced by the concentration or the temperature, but only but the specific solvent. The study of such copolymers will contribute to the understanding of the mechanism of macromolecular recognition and self-assembly. A recent report suggests that multimolecular micelles built by self-assembly of dendritic moieties are more stable than the conventional ones obtained from linear blocks.[6] However, a drawback of these rigid macromolecules is their insufficient flexibility that limits the shape and the geometry of the possible assemblies.

We were recently able to develop convenient methods for the synthesis of a new type of hybrid block copolymers containing both flexible (linear) and more rigid (dendritic) blocks.[7,8] By changing the size of the dendrimers and the length of the linear block as well as its chemical nature, products with a broad variety of desirable and useful properties might be obtained.

The scope of the present article is the investigation of the properties of AB and ABA copolymers consisting of semirigid hydrophobic amorphous A blocks (dendritic aromatic polyethers) and flexible hydrophilic and crystalline B blocks (linear aliphatic polyethers). In theory, these materials should be able to crystallize or remain glossy in the solid state or to dissolve, micellize (self-assemble), or swell in different solvents, depending on their chemical composition and architecture. Indeed, in a preliminary investigation of these ABA systems we observed certain tendencies of the hybrid copolymers to form the rarely reported micelles containing A blocks in their cores.[8]

Experimental Section

Materials. Poly(ethylene glycol)s (PEGs) with nominal molecular weights between 1000 and 20000 and narrow molecular weight distributions were commercially available products of Scientific Polymer Products, Inc. Poly(ethylene oxide)s (PEO)s with molecular weights 4000 and 7500 were synthesized by living anionic polymerization of ethylene oxide using (diphenylmethyl)potassium as initiator.[9] The other PEOs were purchased from Millipore Corp. (Waters Chromatography Division). The molecular weight characteristics of the polymers used are summarized in Table I. All PEGs and PEOs were dried by azeotropic distillation of benzene before use.

The dendritic polyether blocks used in this study were formed according to well-known procedures described in detail earlier.[10] To simplify schematic representations of the hybrid block copolymers, the abbreviated structures shown in Scheme I will be used.

The hybrid linear–dendritic AB and ABA block copolymers were obtained by reaction of PEGs and PEOs with dendritic bromides of different generations under an inert atmosphere using a method already described.[8] Their purity was checked by size-exclusion chromatography (SEC) and ^{1}H NMR.

Tetrahydrofuran (THF), methanol, and water (HPLC grade, Fisher Scientific) were used as received.

Solutions of the block copolymers were prepared by heating a determined amount of the polymer with the solvent chosen in a volumetric flask at 60 °C for 30 min and allowing the solution to cool and equilibrate for 24 h. It was established that this procedure yields the most reproducible results.

Methods. SEC analysis was performed on a liquid chromatograph consisting of a Waters 510 pump, a U6K injector (Waters), a Viscotek 110 differential viscometer, and a differential refractometer (refractoMonitor (Milton Roy)), the detectors being connected in parallel. THF at 40 °C and methanol–water (1:1 v/v, with 0.1 M NaN_3) at 30 °C with nominal flow rates of 1 mL/min were used as the mobile phases. The separations were achieved across banks of four 5-μm PL Gel columns (Polymer Laboratories) with porosities 100 Å, 500 Å, 1000 Å, and Mixed

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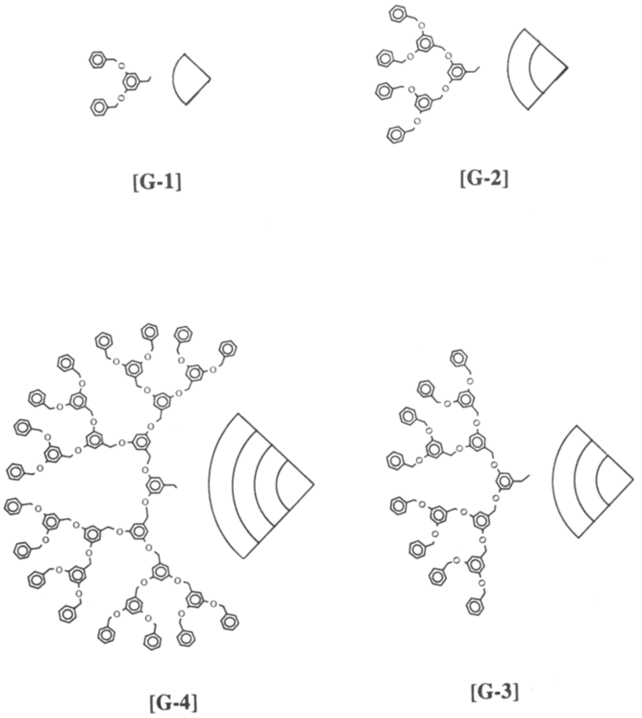
Table I. Molecular Weight Characteristics of PEG and PEO Used in the Synthesis of Hybrid AB and ABA Block Copolymers

designation	$M_w{}^a$	$M_w/M_n{}^a$	$M_w{}^b$	$M_w/M_n{}^b$
PEG1000	1060	1.01	1050	1.03
PEG2000	2064	1.05	2400	1.03
PEG4000	3660	1.10	3900	1.02
PEG5000	5000	1.05	5300	1.01
PEG11000	10900	1.19	10700	1.04
PEG20000	19700	1.34	19700	1.11
PEO4000			3900	1.04
PEO7500			7520	1.03
PEO26000	26000	1.20	21400	1.01
PEO46000	46000	1.10	38300	1.01

[a] Value supplied by the vendor. [b] Value determined by aqueous SEC with PEG and PEO standards.

Scheme I



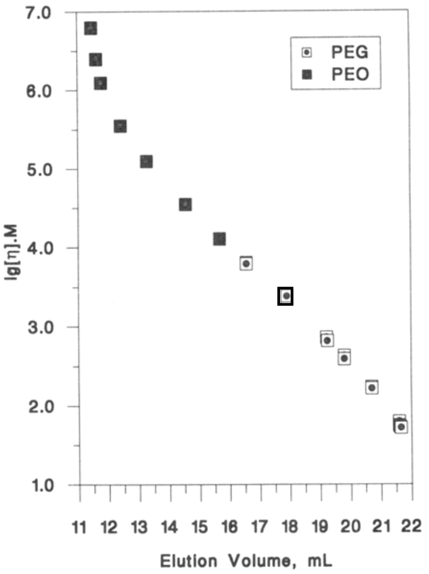


Figure 1. Universal calibration curve for linear polyether standards (PEG and PEO). Columns, Shodex PROTEIN KW 802.5 and 804; eluent, methanol–water (1:1 v/v, with 0.1 M NaN_3); nominal flow rate, 1.0 mL/min; temperature, 30 °C.

C in THF or two Waters/Shodex PROTEIN KW 802.5 and 804 columns for the aqueous SEC measurements. The system was calibrated with 16 monodisperse polystyrene (PSt) or 14 PEO and PEG standards. The molecular weight characteristics were calculated using universal calibration. The radius of gyration (R_g) was calculated from the intrinsic viscosity ([η]) and Unical 4.04 software (Viscotek) by combined Flory–Fox (eq 1) and Ptitsyn–Eizner equations (eq 2):[11]

$$R_g = (1/6^{1/2})(M[\eta]/\Phi)^{1/3} \tag{1}$$

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

where $M[\eta]$ was determined directly from the universal calibration curve and $\epsilon = (2a-1)/3$, a being the Mark–Houwink–Sakurada exponent constant which was also obtained from the universal calibration. Each sample was injected at least two times at each concentration, and the average value of two measurements was taken.

The morphology of films of hybrid block copolymers was observed by optical microscopy using an Olympus BH-2 optical microscope fitted with crossed polarizers. Samples were prepared by casting a copolymer solution on glass substrates and evaporating the solvents slowly in a closed chamber for 24 h unless otherwise specified.

X-ray diffraction measurements were conducted at 2°-2θ/min in a Scintag PAD-X diffractometer operating at 45 kV and 25 mA with Ni-filtered Cu Kα radiation. The samples were analyzed as plaques of pressed powder or thin films cast on glass substrates.

Results and Discussion

I. Solution Behavior. The solution behavior of the hybrid AB and ABA copolymers was investigated by SEC with a coupled differential viscometer in two different solvent systems: water–methanol (1:1) and THF. Our preliminary studies indicated that these are selective solvents for the linear B block and for the dendritic A block, respectively.[8]

I.1. Solution Properties in Methanol–Water. The PROTEIN KW columns chosen for the aqueous studies contain porous silica gel with chemically bonded hydroxyl groups enabling the use of both water and polar organic solvents. The universal calibration curve constructed by PEO and PEG samples is shown in Figure 1. All standards fall on a single curve with very small deviations from the best third-order fit. It is obvious that the separation mechanism in this particular system is based on the hydrodynamic volume of the polymers with no visible distortion from hydrophobic interactions or ion exclusion. The Mark–Houwink–Sakurada (MHS) plot shows two distinct lines for PEG and PEO with correlation coefficients 0.994 and 0.999, respectively (Figure 2). This peculiar feature of both families of standards has also been reported for other polymers[12] and is caused not by differences in their chemical composition but most probably by uncoiling of the polymer chains with increasing molecular weight. The calculated values for the MHS constant a are 0.583 for PEG ($K = 9.616 \times 10^{-4}$) and 0.766 for PEO ($K = 2.042 \times 10^{-4}$). They are in close agreement with the data reported for the same polymers in other aqueous mixtures.[13] The dendritic bromides used in the synthesis of the hybrid block copolymers and their hydroxyl analogs are not soluble in the eluent chosen (methanol–water (1:1)). Therefore, their solution behavior can only be estimated after their attachment to PEO or PEG.

The data for AB hybrid block copolymers are presented in Table II. It is obvious that even the attachment of a water-soluble block cannot drive the dendrimer into solution unless the linear chains are sufficiently long. The

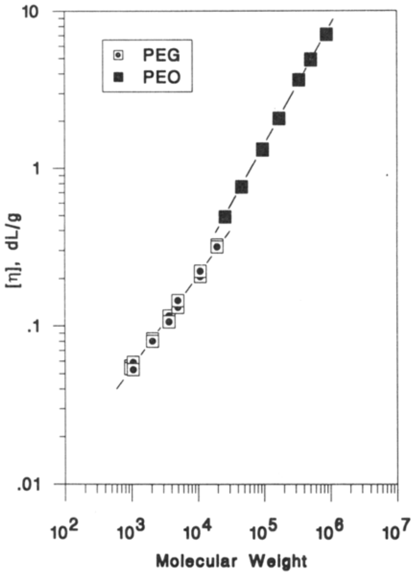


Figure 2. Mark–Houwink–Sakurada plot for linear polyether standards (PEG and PEO). Analysis conditions: as in Figure 1.

Table II. Solution Behavior of Poly(ethylene oxide)s and Their Dendritic AB Block Copolymers in CH_3OH/H_2O at 30 °C

initial linear block	[η], dL/g	R_g, nm	dendritic copolymer	[η], dL/g	R_g, nm
PEO4000	0.131	2.69	PEO4000-[G-4]	insoluble[a]	
PEO7500	0.160	4.09	PEO7500-[G-4]	insoluble[a]	
PEO26000	0.491	7.21	PEO26000-[G-4]	0.138	6.97
PEO46000	0.760	10.22	PEO46000-[G-4]	0.172	9.14
PEO7500	0.160	4.09	PEO7500-[G-1]	0.186	3.80
PEO7500	0.160	4.09	PEO7500-[G-2]	0.144	2.91[b]
PEO7500	0.160	4.09	PEO7500-[G-3]	insoluble[a]	
PEO7500	0.160	4.09	PEO7500-[G-4]	insoluble[a]	

[a] Transparent droplets. [b] These values are concentration dependent; see Figure 3 and text for further explanations.

significant decrease in the intrinsic viscosity ([η]) of the copolymer solutions and the parallel decrease in the radius of gyration (R_g) of the hydrid structures containing [G-4] blocks indicate that the block copolymers are undergoing an intramolecular micellization. Unimolecular micelles consisting of a small, dense, dendritic core tightly surrounded by a PEO corona are formed. The influence of the size of the dendritic block was investigated with PEO7500, a linear polymer that is long enough to allow its dissolution in aqueous media, but not so large as to suppress the specific influence of the dendritic part. It should be mentioned that the solution of the diblock copolymer of PEO7500 and the first-generation dendrimer [G-1], PEO7500-[G-1], has a higher viscosity than the solution of the linear precursor alone, while the calculated radius of gyration of this block copolymer is lower than that of PEO7500 under the same conditions. Assuming that the micelles formed adopt a radial geometry, this fact is not surprising and reflects only the low density compactness of the [G-1] core[14,15] (eq 3[15]).

$$[\eta] = 2.5/\rho \qquad (3)$$

where ρ is the density of the monomolecular micelle. Indeed, increasing the size of the dendritic block attached to the PEO7500 from [G-1] to [G-2] yields a copolymer and solutions that have much lower R_g values and viscosities than measured for the linear precursor under the same analysis conditions (Table II). Increasing the concentration of the solutions of the same sample of PEO7500-[G-2] only causes slight changes in [η] and R_g values, but a second peak with a higher apparent molecular weight appears in the SEC traces (Figure 3). The hydrodynamic radius of this peak is above 8 nm, and its intrinsic viscosity is only 0.056 dL/g, indicating that it consists of multimolecular micelles with extremely dense dendritic cores (eq 3). From the apparent molecular weight of the peak (71000) one can estimate that these micelles might contain approximately 7 or 8 molecules of the AB copolymer.

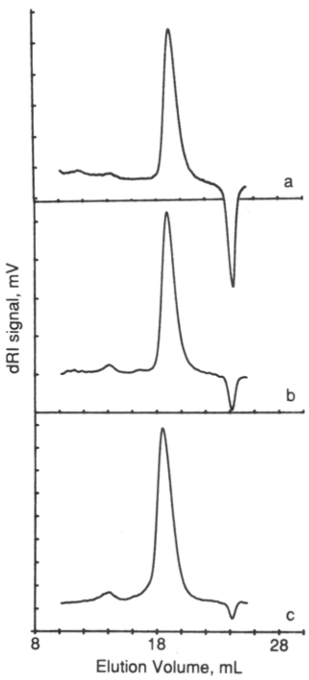


Figure 3. SEC traces of PEO7500-[G-2] obtained at different concentrations: (a) 1.45×10^{-3} g/mL; (b) 4.28×10^{-3} g/mL; (c) 7.26×10^{-3} g/mL. Analysis conditions: as in Figure 1.

The solution behavior of ABA hybrid copolymers is documented in Table III. In general, materials containing more than 30 wt % of dendritic blocks are not soluble in methanol–water. However, it should be emphasized that the solubility of the copolymers is also strongly influenced by size of the dendritic block. For example, [G-1]-PEG4000-[G-1] and [G-3]-PEG20000-[G-3] contain 13.43 and 13.80 wt % dendrimer, but only the first copolymer is soluble in the SEC eluent. The same phenomenon is observed with [G-2]-PEG2000-[G-2] (37.73 wt %), [G-3]-PEG5000-[G-3] (37.31 wt %), and [G-4]-PEG11000-[G-4] (37.97 wt %) where only the first copolymer is completely soluble and the others form swollen gels (Table III). Obviously, an optimal balance between the size of the dendrimer and the length of the linear block is required to enable the dissolution of the copolymer in CH_3OH/H_2O.

As evidenced by SEC analysis, soluble ABA block copolymers containing [G-1] moieties have lower hydrodynamic volumes (longer elution times) but again yield solutions with higher viscosities than their linear precursors (Table III, runs 5, 9, and 12; Figures 4b and 5b). All these facts can be explained in terms of the above-discussed monomolecular micelles.

Attachment of [G-2] blocks to the same linear chain yields copolymers that are able to exist in two different forms in solution, one form having a significantly larger hydrodynamic volume than the other. This is demonstrated by the SEC traces for runs 6, 10, and 14 (Table III). For example, at concentrations below 5×10^{-3} g/mL

Table III. Solution Behavior of Poly(ethylene glycol)s and Their Dendritic ABA Block Copolymers in CH_3OH/H_2O at 30 °C

run	linear block	[η], dL/g	R_g, nm	copolymer	[η], dL/g	R_g, nm
1	PEG1000	0.054	1.25	[G-1]-PEG1000-[G-1]	insoluble[a]	
2	PEG1000	0.054	1.25	[G-2]-PEG1000-[G-2]	insoluble[a]	
3	PEG1000	0.054	1.25	[G-3]-PEG1000-[G-3]	insoluble[a]	
4	PEG1000	0.054	1.25	[G-4]-PEG1000-[G-4]	insoluble[a]	
5	PEG2000	0.083	1.86	[G-1]-PEG2000-[G-1]	0.142	0.48
6	PEG2000	0.083	1.86	[G-2]-PEG2000-[G-2]	0.062	1.07[b]
7	PEG2000	0.083	1.86	[G-3]-PEG2000-[G-3]	insoluble[a]	
8	PEG2000	0.083	1.86	[G-4]-PEG2000-[G-4]	insoluble[a]	
9	PEG5000	0.139	3.04	[G-1]-PEG5000-[G-1]	0.221	2.31
10	PEG5000	0.139	3.04	[G-2]-PEG5000-[G-2]	0.128	1.14[c]
11	PEG5000	0.139	3.04	[G-3]-PEG5000-[G-3]	swollen gel	
12	PEG5000	0.139	3.04	[G-4]-PEG5000-[G-4]	swollen gel	
13	PEG11000	0.235	4.29	[G-1]-PEG11000-[G-1]	0.290	3.86
14	PEG11000	0.235	4.29	[G-2]-PEG11000-[G-2]	0.107	2.30[d]
15	PEG11000	0.235	4.29	[G-3]-PEG11000-[G-3]	0.189	27.79
16	PEG11000	0.235	4.29	[G-4]-PEG11000-[G-4]	swollen gel	

[a] Transparent droplets. [b] These values are concentration dependent; see text for further explanations. [c] These values are concentration dependent; see Figure 4c and text for further explanations. [d] These values are concentration dependent; see Figures 5c and 6 and text for further explanations.

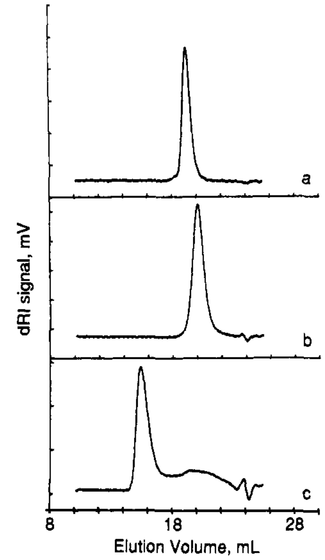


Figure 4. SEC profiles of PEG5000 (a), [G-1]-PEG5000-[G-1] (b), and [G-2]-PEG5000-[G-2] (c). Analysis conditions: as in Figure 1.

(1.3×10^{-3} mol/L) [G-2]-PEG2000-[G-2] has a structure with the hydrodynamic characteristics given in Table III (run 6). Increasing the concentration to 8×10^{-3} g/mL (2.1×10^{-3} mol/L) causes the appearance of a second peak with R_g = 3.6 nm and [η] = 0.426 dL/g, but the same low molecular weight component is still present in the SEC trace. The same phenomenon is observed with [G-2]-PEG5000-[G-2]. Increasing the solution concentration from 1.3×10^{-3} g/mL (1.9×10^{4} mol/L) (Table III, run 10) to 2.3×10^{-3} g/mL (3.4×10^{-4} mol/L) increases the size of the peak corresponding to the moiety with higher hydrodynamic characteristics (R_g = 4.98 nm and [η] = 0.181 dL/g). A further increase in concentration to 3.3×10^{-3} g/mL (Figure 4c) with or without heating of the solutions for several hours at 60 °C has no marked effect on the [η] and R_g values.

The transition from a smaller to a larger structure is easily seen in run 14 with block [G-2]-PEG11000-[G-2] (Figures 5c and 6). At 1×10^{-3} g/mL (8.2×10^{-5} mol/L) only the species with a low hydrodynamic volume exist (Table III, run 14 and Figure 6a). A twofold increase in concentration causes the appearance of a larger hydrodynamic volume species which has a transient size (Figure 6b). When the concentration reaches 6×10^{-3} g/mL (4.9×10^{-4} mol/L) or at higher values, an equilibrium size is reached with well-defined hydrodynamic characteristics (R_g = 8.45 nm and [η] = 0.18 dL/g) as shown in Figures 5c and 6c.

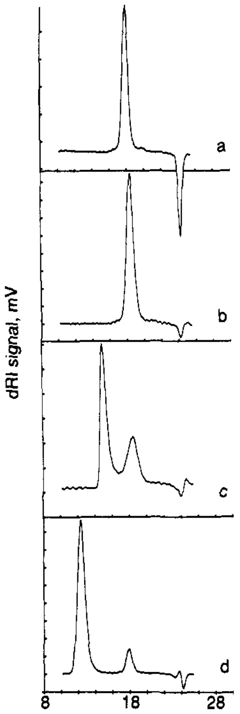


Figure 5. SEC eluograms of PEG11000 (a), [G-1]-PEG11000-[G-1] (b), [G-2]-PEG11000-[G-2] (c), and [G-3]-PEG11000-[G-3] (d). Analysis conditions: as in Figure 1.

In aqueous solutions the larger hydrodynamic volume species of triblock copolymer [G-3]-PEG11000-[G-3] prevails at concentrations between 1.5×10^{-3} and 5×10^{-3} g/mL ((1.08–3.61) $\times 10^{-4}$ mol/L) even after heating the solution at 60 °C for several hours (Table III, run 15, and Figure 5d).

The existence of two types of species with different sizes observed with the solutions of the hybrid ABA copolymers cannot be attributed to impurities of linear precursors or incompletely functionalized PEGs. The SEC traces of the same materials in THF show single sharp peaks free of starting materials (Figures 7 and 8). The ABA composition of the block copolymers is confirmed also by ^1H NMR. Thus, we believe that the appearance of two

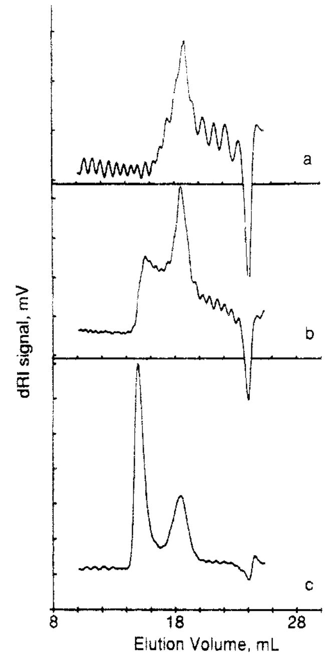


Figure 6. Influence of the concentration of [G-2]-PEG11000-[G-2] on SEC profiles: (a) 1 × 10^{-3} g/mL; (b) 2 × 10^{-3} g/mL; (c) 6 × 10^{-3} g/mL. Analysis conditions: as in Figure 1.

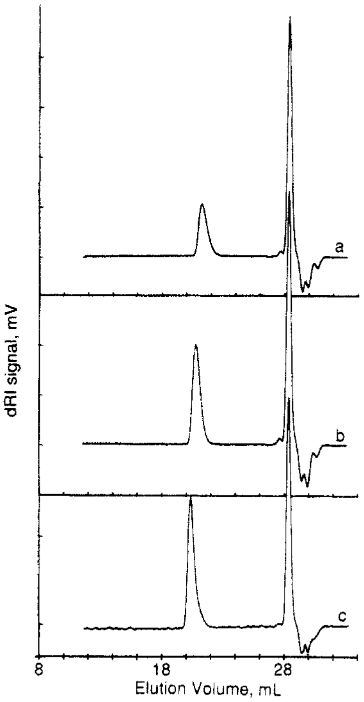


Figure 7. SEC traces of PEG2000 (a), [G-1]-PEG2000-[G-1] (b), and [G-2]-PEG2000-[G-2] (c). Columns, PL Gel 100 Å, PL Gel 500 Å, PL Gel 1000 Å, and Mixed C; eluent, THF; nominal flow rate, 1.0 mL/min; temperature, 40 °C.

peaks in the aqueous SEC traces of these materials is caused by the existence of two or more populations of structures with different sizes and shapes. There are increasing numbers of studies reporting both experimental data and theoretical models for the association behavior of triblock copolymers in solvents selective for the middle block. These also provide experimental proof for the existence of two species with different sizes in the solvents studied.[4,16] To our knowledge, the hybrid linear–dendritic block copolymers reported in this study are the only polymer systems able to form multimolecular micelles that are not destroyed by dilution or prolonged heating of their solutions. For example, [G-3]-PEG11000-[G-3] is able to form aqueous solutions whose composition remains constant for more than 144 h over a broad range of concentrations and temperatures. This unique behavior might be explained partially by the slow establishment of an entanglement–disentanglement equilibrium in the dendritic cores of the micelles due to the highly branched structure of the end blocks. The possible assemblies are presented in Scheme II. The experimental data suggest that copolymers containing [G-1] blocks exclusively form monomolecular micelles (type A) with loose cores, rela-

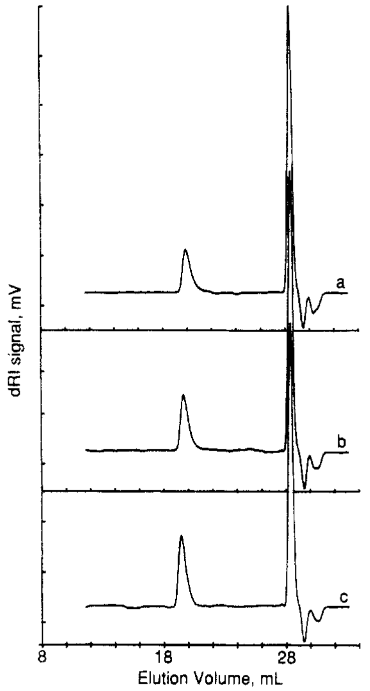
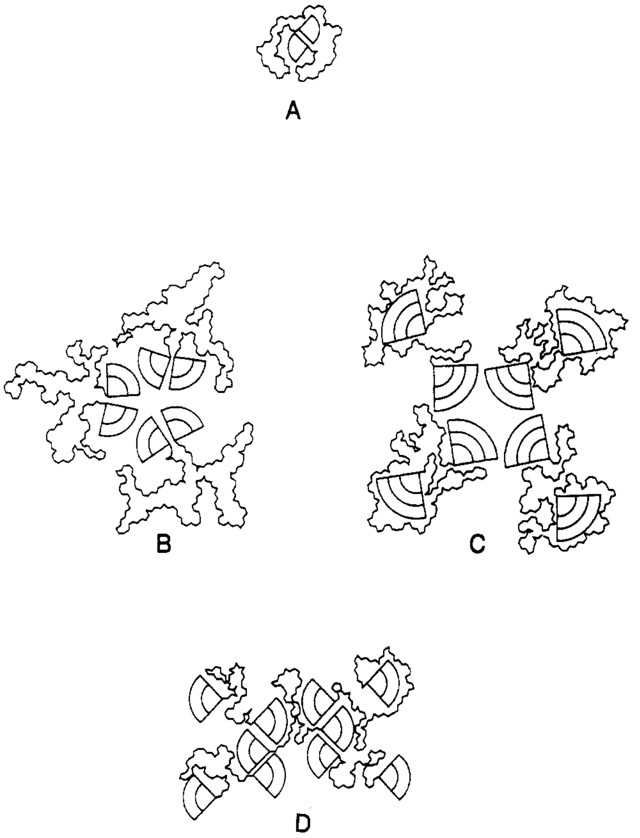


Figure 8. SEC traces of PEG 5000 (a), [G-1]-PEG5000-[G-1] (b), and [G-2]-PEG5000-[G-2] (c). Analysis conditions: as in Figure 7.

Scheme II



tively smaller sizes than their linear precursors, and arc- or ring-like shapes depending on the length of the PEG block. Their hydrodynamic characteristics are not affected by changes in concentration and temperature. Incorporation of dendritic blocks of higher generation enables the resulting copolymers to form other micellar complexes. The monomolecular micelles of type A are still present, but the existence of multimolecular micelles of types B and C (Scheme II) might be also justified due to the increased possibility for hydrophobic–hydrophobic and π–π interactions of the end blocks in these systems. Unfortunately, due to solubility problems, an insufficient number of samples is available to allow the quantitative prediction of the most probable form among the two types of multimolecular micelles for the copolymers containing [G-2] and [G-3] blocks.

In some cases (Table III, runs 11, 12, and 16) the weight ratio of the soluble to the insoluble parts and the spatial arrangement of the dendritic blocks are not favorable for the dissolution of the corresponding copolymer in CH_3OH/H_2O. Obviously, this affects all block copolymers containing the larger [G-4] dendritic blocks. However, the materials show a strong tendency to swell in methanol–water, suggesting the formation of highly branched structures (Scheme IID) or even physical networks. Despite the lack of experimental evidence, structures of this type have been envisioned by Tirrell and co-workers[4] and Maechling-Strasser et al.[5] The strong swelling of the insoluble copolymers and the presence of broad peaks and shoulders between the two finite structures in the SEC traces of the soluble materials could be considered as evidence that such intermediate structures might exist.

I.2. Solution Properties in THF. To understand fully the behavior of the hybrid block copolymers in THF, the properties of their building blocks are compared to those of polystyrene (PSt) standards in the same medium. THF is shown to be a good solvent for aromatic polyether dendrimers regardless of size, but an increasingly poor solvent for PEG[8] as molecular weight increases. It is also known that in this solvent, dendrimers with generation numbers higher than 4 deviate strongly from the universal calibration curve.[17] In this study, however, the investigation is limited to dendrimers within generations 1–4 where this deviation is much less profound. The analysis of MHS plots for conventional PSt standards, PEG, and dendritic alcohols shows that they interact in a different manner with the SEC eluent (Figure 9). PSt uncoils in THF as its molecular weight increases (MHS $a = 0.514$ for $M < 10^4$; $a = 0.747$ for $M > 2 \times 10^4$), while PEG shrinks with increasing molecular weight (MHS $a = 0.858$ for $M < 2 \times 10^3$; $a = 0.499$ for $M > 3 \times 10^3$). Dendritic alcohols behave uniformly as compact spheres for generation numbers 1–4 (MHS $a = 0.229$). It should be pointed out that the linear correlation coefficients for all three relationships are better than 0.994.

The hydrodynamic characteristics of dendritic alcohols, linear PEO, and their hybrid AB block copolymers are listed in Table IV. It should be mentioned that all copolymers investigated appear as single peaks in the SEC traces over a broad concentration range: $(2–7) \times 10^{-3}$ g/mL. For AB copolymers containing [G-4] moieties, the R_g values increase with the length of the linear block. The intrinsic viscosity of the AB blocks PEO4000-[G-4] and PEO7500-[G-4] is slightly higher than that of the parent PEOs but for larger PEO blocks it becomes much lower than $[\eta]$ of the linear precursors (Figure 10). The observed phenomenon resembles the solution behavior of pure dendrimers where the viscosity also goes through a maximum as molecular weight increases.[17,18]

Attachment of the small [G-1] moiety to PEO7500 notably decreases the intrinsic viscosity and the radius of gyration, but dendritic generations higher than 2 have no

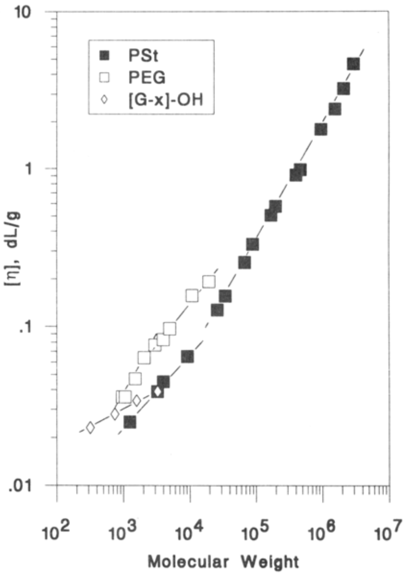


Figure 9. Mark–Houwink–Sakurada plots for PSt, PEG, and [G-x]-OH (x = 1–4). Analysis conditions: as in Figure 7.

Table IV. Solution Behavior of Poly(ethylene oxide)s and Their Dendritic AB Block Copolymers in THF at 40 °C

initial block	$[\eta]$, dL/g	R_g, nm	dendritic copolymer	$[\eta]$, dL/g	R_g, nm
[G-1]-OH	0.023	0.56			
[G-2]-OH	0.028	0.84			
[G-3]-OH	0.035	1.10			
[G-4]-OH	0.039	1.41			
PEO4000	0.082	2.08	PEO4000-[G-4]	0.096	2.12
PEO7500	0.145	2.75	PEO7500-[G-4]	0.161	2.62
PEO26000	0.273	3.73	PEO26000-[G-4]	0.236	3.91
PEO46000	0.487	3.82	PEO46000-[G-4]	0.210	4.19
PEO7500	0.145	2.75	PEO7500-[G-1]	0.116	2.26
PEO7500	0.145	2.75	PEO7500-[G-2]	0.168	2.51
PEO7500	0.145	2.75	PEO7500-[G-3]	0.165	2.54
PEO7500	0.145	2.75	PEO7500-[G-4]	0.161	2.62

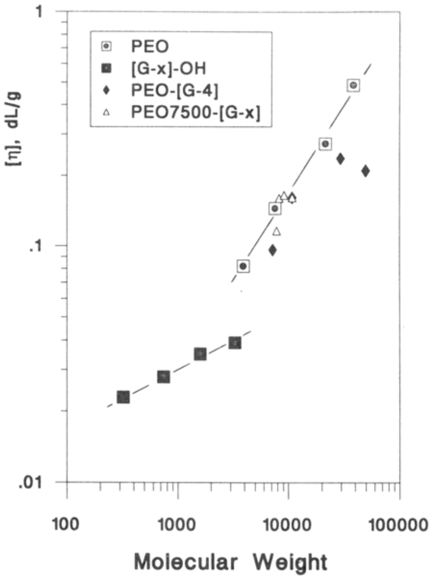


Figure 10. Mark–Houwink–Sakurada plots for PEO, [G-x]-OH (x = 1–4), PEO-[G-4], and PEO7500-[G-x] (x = 1–4). Analysis conditions: as in Figure 7.

Table V. Solution Behavior of Poly(ethylene glycol)s and Their Dendritic ABA Block Copolymers in THF at 40 °C

run	building block	[η], dL/g	R_g, nm	copolymer	[η], dL/g	R_g, nm
1	PEG1000	0.035	1.04	[G-1]-PEG1000-[G-1]	0.048	0.91
2	PEG1000	0.035	1.04	[G-2]-PEG1000-[G-2]	0.053	0.88
3	PEG1000	0.035	1.04	[G-3]-PEG1000-[G-3]	0.056	1.51
4	PEG1000	0.035	1.04	[G-4]-PEG1000-[G-4]	0.059	1.45
5	PEG2000	0.055	1.27	[G-1]-PEG2000-[G-1]	0.063	1.08
6	PEG2000	0.055	1.27	[G-2]-PEG2000-[G-2]	0.059	1.07
7	PEG2000	0.055	1.27	[G-3]-PEG2000-[G-3]	0.062	1.28
8	PEG2000	0.055	1.27	[G-4]-PEG2000-[G-4]	0.062	2.01
9	PEG5000	0.093	1.62	[G-1]-PEG5000-[G-1]	0.092	1.61
10	PEG5000	0.093	1.62	[G-2]-PEG5000-[G-2]	0.094	1.62
11	PEG5000	0.093	1.62	[G-3]-PEG5000-[G-3]	0.092	1.72
12	PEG5000	0.093	1.62	[G-4]-PEG5000-[G-4]	0.098	1.90
13	PEG11000	0.125	2.83	[G-1]-PEG11000-[G-1]	0.057	2.33
14	PEG11000	0.125	2.83	[G-2]-PEG11000-[G-2]	0.077	2.25
15	PEG11000	0.125	2.83	[G-3]-PEG11000-[G-3]	0.110	2.53
16	PEG11000	0.125	2.83	[G-4]-PEG11000-[G-4]	0.143	2.67

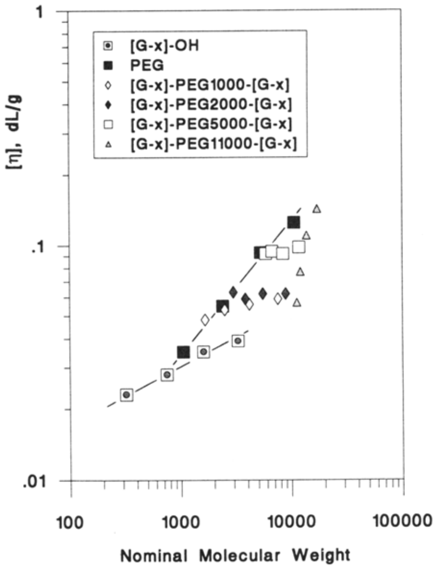


Figure 11. Mark–Houwink–Sakurada plots for PEG, [G-x]-OH (x = 1–4), and their ABA block copolymers. Analysis conditions: as in Figure 7.

profound effect on the viscosity and R_g of the resulting copolymers (Table IV, Figure 10).

It is interesting to note that in the ABA copolymer series dendrimer sizes affect only marginally the hydrodynamic characteristics of the hybrid macromolecules for PEG with molecular weights between 1000 and 5000 (Table V). For this molecular weight range difference in the intrinsic viscosities of the block copolymers and their linear precursors decreases with the molecular weight of the PEG and changes only slightly with dendrimer generation (Figure 11). It seems that these ABA copolymers interact to notably lesser extent with the solvent than their building blocks.

The sharp decrease in [η] and R_g values with attachment of [G-1] is observed again for the PEG11000 series. This strange behavior may be due in part to the collapse of the copolymer molecules in THF as observed previously for PEO7500-[G-1]. A partial association (or interaction) of the end blocks is also possible in both macromolecules—*i.e.*, [G-1]/diphenylmethane for the AB, and [G-1]/[G-1] for the ABA copolymers. The combination of both processes was proposed to explain the lower apparent molecular weights and the ^{1}H NMR data in our previous study on the same materials.[8] However, we cannot fully explain why the linear polymers should shrink after incorporation of [G-1] blocks but then uncoil with attachment of the more dense dendritic blocks of the higher generations (Figures 10 and 11).

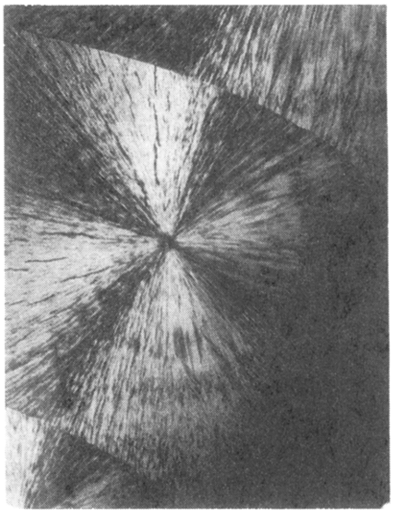


Figure 12. Polarized optical micrograph of PEG20000 film cast from CH_3OH/H_2O (1:1). Magnification: 80×. [N.B.: The micrograph has been reduced to 70% of its original size for printing purposes.]

II. Solid-State Behavior. Block copolymers containing immiscible crystalline and amorphous blocks are of theoretical and practical importance and have been the subject of numerous investigations. A peculiar feature of these copolymers is that their crystallization from solvents selective for the crystalline block proceeds simultaneously with their micellization. That is why many factors will influence the solid-state properties of these materials. It has been shown, for example, that the casting solvent and the conditions of thermal treatment have a strong effect on the morphology of AB and ABA copolymers containing polystyrene (amorphous) and PEO (crystalline) blocks.[19,20] It should be emphasized that all previous studies were performed on systems constructed from flexible linear blocks. It would be interesting to evaluate the influence of an amorphous, but semirigid component on the crystallization behavior of the same crystalline block (PEO or PEG).

We have used polarized light microscopy to investigate the phase behavior of the various copolymers. All results presented below refer to Figures 12–16, shown with the same magnification (80×), allowing comparisons of sizes and textures. Pure PEG crystallizes from THF, $CHCl_3$, and CH_3OH/H_2O solutions and forms spherulite structures. The dimensions of the individual spherulites

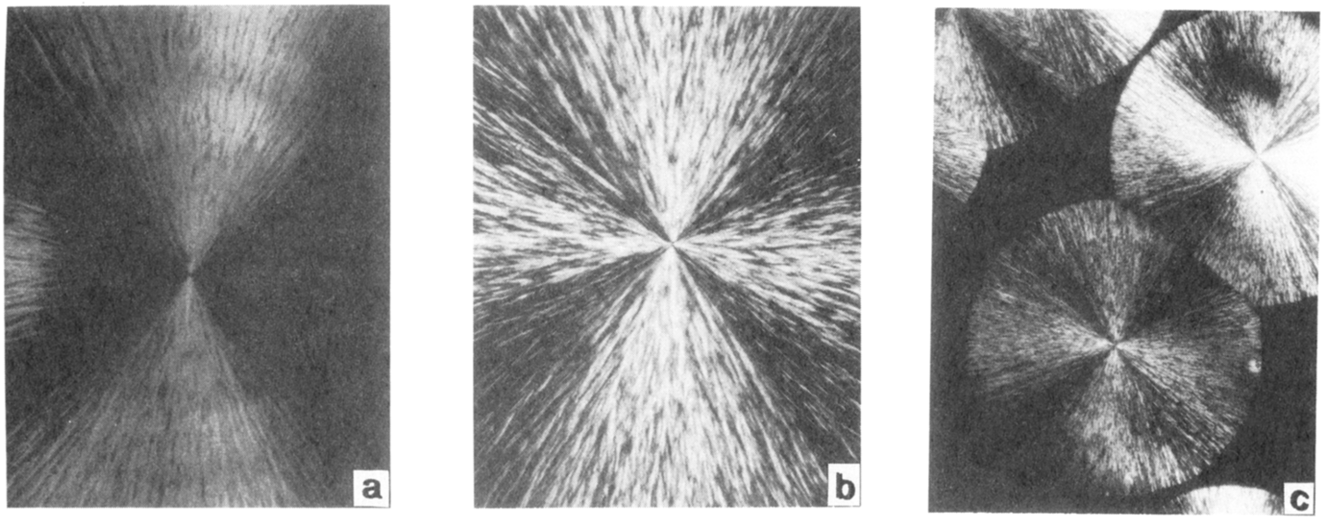


Figure 13. Polarized optical micrographs of [G-1]-PEG5000-[G-1] (a), [G-2]-PEG5000-[G-2] (b), and [G-3]-PEG5000-[G-3] (c). Films cast from $CHCl_3$. Magnification: 80×. [N.B.: The micrographs have been reduced to 70% of their original sizes for printing purposes.]

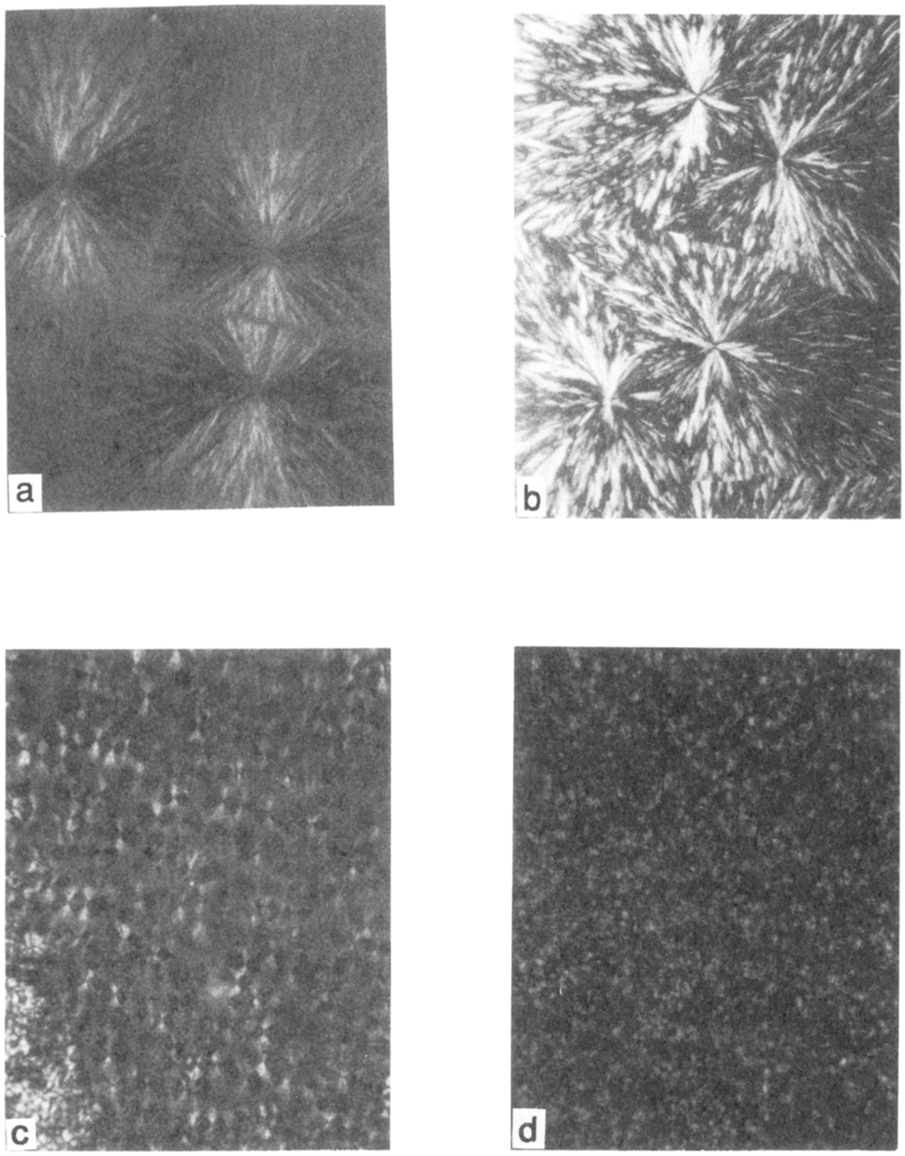


Figure 14. Polarized optical micrographs of [G-1]-PEG5000-[G-1] (a), [G-2]-PEG5000-[G-2] (b), [G-3]-PEG5000-[G-3] (c), and [G-4]-PEG5000-[G-4] (d). Films cast from THF. Magnification: 80×. [N.B.: The micrographs have been reduced to 70% of their original sizes for printing purposes.]

depend on the nature of the solvent and decrease in the order $CHCl_3 \approx CH_3OH/H_2O > THF$. Independently of the solvent used, all observed structures have circular cross-sections and show a typical Maltese-cross pattern between

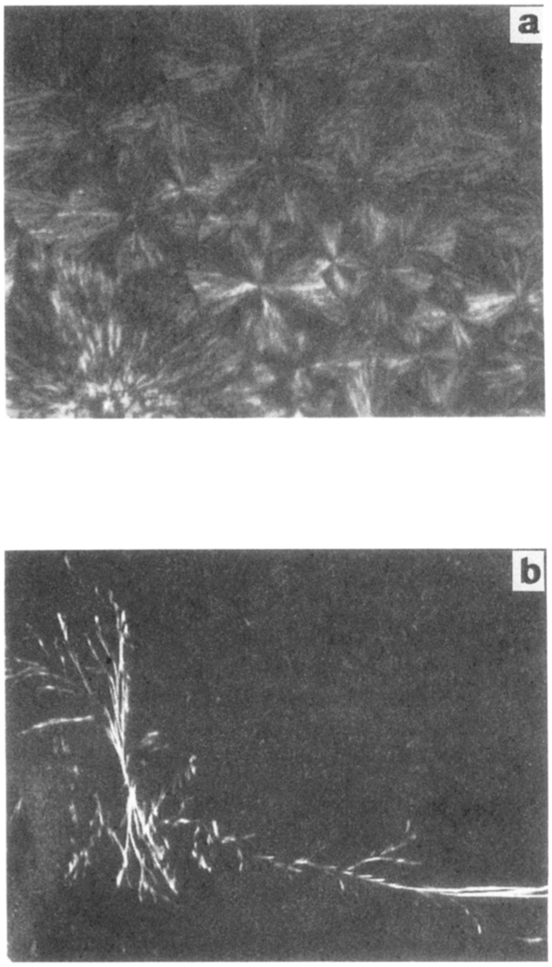


Figure 15. Polarized optical micrographs of [G-3]-PEG20000-[G-3]. Films cast from THF (a) and CH_3OH/H_2O (b). Magnification: 80×. [N.B.: The micrographs have been reduced to 70% of their original sizes for printing purposes.]

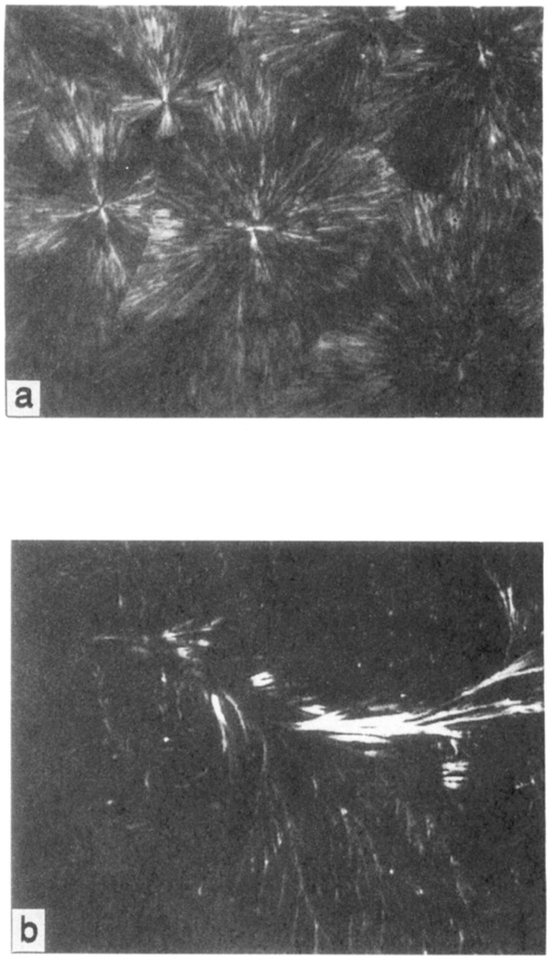


Figure 16. Polarized optical micrographs of [G-4]-PEG20000-[G-4]. Films cast from $CHCl_3$ (a) and CH_3OH/H_2O (b). Magnification: 80×. [N.B.: The micrographs have been reduced to 70% of their original sizes for printing purposes.]

crossed polarizers (Figure 12). Although the first two members of the dendrimer family used in this investigation are crystalline,[10] their films cast from THF or chloroform do not exhibit the same behavior. The influence of the dendrimer size and the casting solvent was investigated with [G-x]-PEG5000-[G-x], where x varies from 1 to 4. All analyses were performed under the same experimental conditions ([copolymer] = 2×10^{-3} g/mL; time, 5 h; 25 °C). Figure 13 shows micrographs of copolymer films obtained in $CHCl_3$, which is a good solvent for both blocks. It is seen that in this solvent [G-1]-PEG5000-[G-1] crystallizes in spherulites with the same texture (Figure 13a) as observed for the pure PEG. Incorporation of second-generation dendrimer affects only the morphology but not the size of the spherulites formed. They still exhibit the Maltese cross, but the texture is rougher, indicating that the dendritic blocks interfere with the PEG during crystallization. Spherulitic growth is slower in films prepared from [G-3]-PEG5000-[G-3], yielding formations with much smaller sizes (Figure 13c). However, their texture remains almost unchanged in comparison to the previous block copolymer. Attachment of [G-4] to PEG5000 produces materials that are completely amorphous.

The change from $CHCl_3$ to THF, which is a better solvent for the semirigid dendritic blocks than for the PEG blocks, significantly affects the morphology of the copolymer films. As evidenced by Figure 14, full crystallization of PEG is prevented, and only axialites are formed with dimensions and textures that depend on the dendrimer size in analogy to observations made with chloroform as the solvent.

A twofold decrease in the molecular weight of the linear block (PEG2000 and lower) prevents its crystallization even at lower generations ([G-2]). With a fourfold increase in chain length (PEG20000), it is able to accommodate the semirigid blocks of third and fourth generation. THF and $CHCl_3$ solutions yield smaller or larger spherulites, respectively (Figures 15a and 16a), with the typical fibrilar texture observed previously with PEG5000 ABA triblocks. More interesting is the examination of solutions of these materials in methanol–water (1:1). With one exception, [G-3] and [G-4] copolymers with lower PEG content are completely insoluble in this mixture. However, [G-3]-PEG20000-[G-3] and [G-4]-PEG20000-[G-4] form fine dispersions of swollen gel-like particles. These dispersions were cast carefully onto glass substrates and the solvents were evaporated within 5 days in a closed chamber with a controlled temperature (30 ● 0.1 °C). Surprisingly, the resulting films have an entirely different morphology (Figures 15b and 16b). Irregular dendritic formations which cannot be attributed to cracks in the films are observed. To a certain extent they resemble the structures reported by Newkome and co-workers for dumbbell-shaped polyamidoarborols,[7] but they are much larger. It might be speculated that these unusual formations are derived from the structures outlined in Scheme IID. X-ray analysis shows that these films remain crystalline (Figure 17b). It should be pointed out that the increase in the dendrimer content above 30 wt % results in copolymers

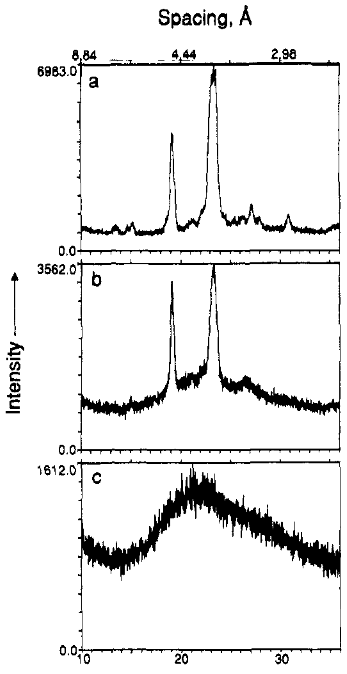


Figure 17. X-ray diffraction patterns of PEG20000 (a), [G-4]-PEG20000-[G-4] (b), and [G-4]-OH (c).

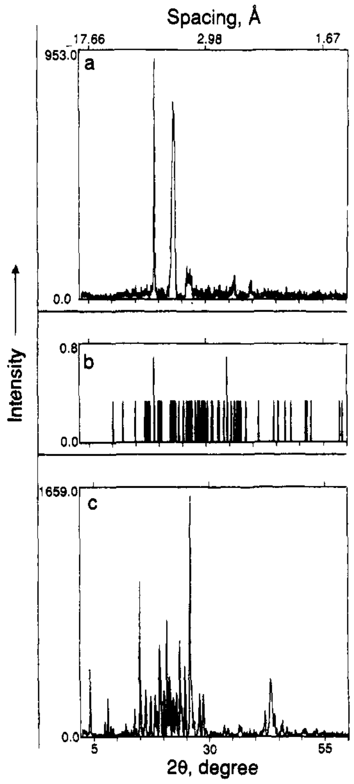


Figure 18. X-ray diffraction patterns of PEG2000 (a), [G-2]-PEG2000-[G-2] (b), and [G-2]-OH (c).

which are not only insoluble in methanol–water but are also entirely amorphous. In spite of the fact that both building blocks of [G-2]-PEG2000-[G-2] (dendrimer content 37.73%) are crystalline, no crystalline reflections are detected in the X-ray pattern of the copolymer (Figure 18). The same is observed with [G-1]-PEG1000-[G-1] (dendrimer content 36.55%), but not with [G-2]-PEG5000-[G-2] (dendrimer content 21.53%) and [G-1]-PEG2000-[G-1] (dendrimer content 20.13%). It is interesting to note that in the last two products the dendrimer content is rather high, but only the crystalline reflections of the corresponding PEG are detected (Figure 19), indicating that the linear crystalline block is sufficiently long and flexible to accommodate the semirigid dendritic structures in the PEG lamellae.

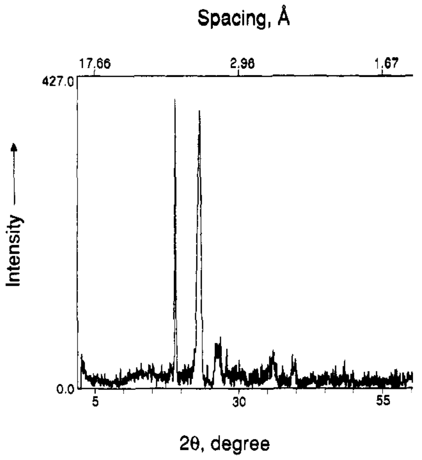


Figure 19. X-ray diffraction pattern of [G-2]-PEG5000-[G-2].

Conclusions

The results obtained show that the novel linear–dendritic polyether copolymers containing both flexible and semirigid structures form a broad variety of assemblies with different sizes and some unconventional shapes.

This is the first study reporting that the geometry and the constitution of the micelles formed from a block copolymer having the specific composition [G-3]-PEG-11000-[G-3] are affected only by the nature of the solvent used. In aqueous medium several other AB and ABA linear–dendritic copolymers are able to form unique mono- or multimolecular micelles with dendritic cores depending on their composition and the concentration of the solution. The "entanglement" caused by the association of the highly branched end blocks stabilizes the multimolecular assemblies and prevents their destruction by increased temperatures. Screening of the linear part of the block copolymer by the dendritic blocks and their partial association prevent the formation of multimolecular micelles in THF.

The interactions of the hybrid dendritic–linear AB and ABA block copolymers with the solvent are also reflected in the morphology obtained for the films cast from that solvent.

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