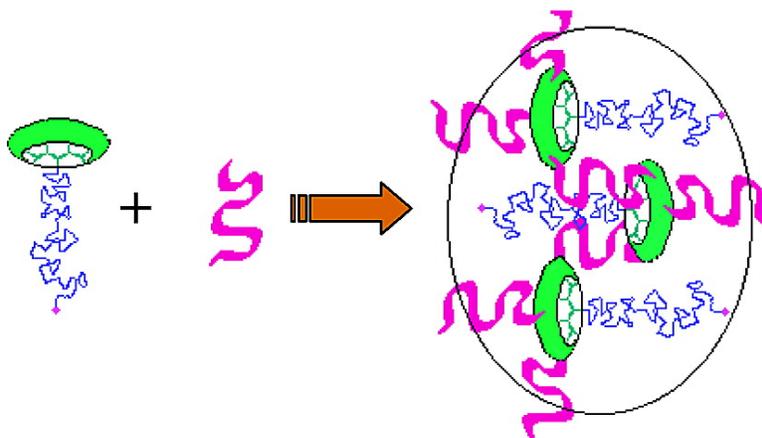


Novel Functionally Grafted Pseudo-Semi-interpenetrating Networks Constructed by Reactive Linear–Dendritic Copolymers

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Novel Functionally Grafted Pseudo-Semi-interpenetrating Networks Constructed by Reactive Linear–Dendritic Copolymers¹

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Abstract: This paper describes the synthesis of amphiphilic pseudo-semi-interpenetrating polymer networks (pseudo-semi-IPNs) containing linear poly(styrene) and poly(ethylene glycol) (PEG) cross-linked through monodendritic fragments. A unique feature of the synthetic strategy is the permanent attachment of the linear segment to the PEG network by a transesterification reaction between the hydroxyl groups at both ends of the PEG and peripheral ethyl ester moieties in the monodendron portion of a linear poly(styrene)–dendritic poly(benzyl ether) AB block copolymer. The proceeding of the reaction is monitored by ¹H NMR and size exclusion chromatography (SEC). The formation of an interlock structure between the linear block and the network matrix in the pseudo-semi-IPN is evidenced by the results from spectroscopic analyses and differential scanning calorimetry measurements. The accessibility of functional centers in the grafted semi-IPN is confirmed by model reactions with fluorescent markers, fluorescence spectroscopy, and NMR techniques and shows the potential of these novel materials as sequestering reagents for resin capture–release applications in parallel synthesis, combinatorial chemistry, and advanced drug design.

Introduction

A typical interpenetrating polymer network (IPN) is composed of two or more independent polymer networks with different chemical compositions. In IPNs, all components have overlapping three-dimensional structures within the same spatial volume and penetrate into each other without chemical bonds between them.² In distinction to normal blends where most components are not compatible with each other and coarse phase separation is usually observed, the interlocked structures (physical cross-links) of IPNs prevent the occurrence of such phase separation to a great extent. Usually, IPNs have randomly dispersed phase domains with a size of few tens of nanometers or no resolvable domain structure at all. That is why these materials often show only a single broad glass transition, which spans over the glass transition of both building components.^{2,3} Thus, IPNs have improved mechanical characteristics, environmental response, and a broad variety of important industrial and biomedical applications (such as artificial implants,⁴ dialysis membranes,⁵ drug-delivery systems,^{6,7} etc.).

Three-dimensional cross-linked structures that contain entangled linear polymers form pseudo-IPNs or semi-IPNs and

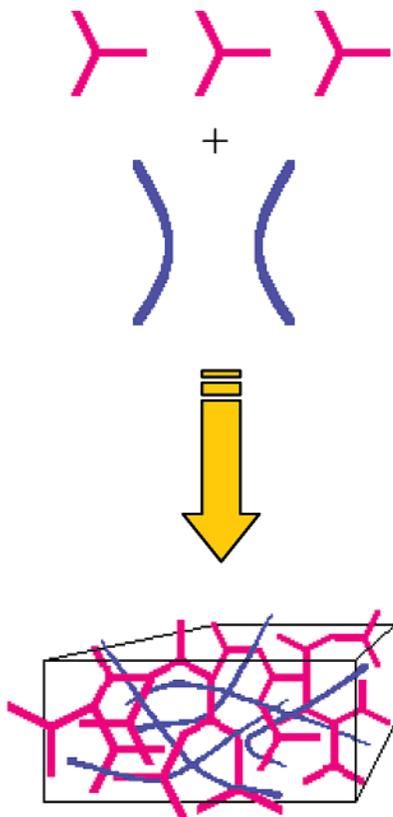
have the potential advantage in offering a better control over the chemical composition and the final properties of the resulting material.^{2,3} Typically, they are produced by reactions of monomers and cross-linking agents or multifunctional polymers in the presence of a preformed linear polymer⁸ (Scheme 1). This method was used to produce semi-IPNs with poly(*N*-isopropylacrylamide),^{6,7} linear PEO,⁹ or poly(vinyl alcohol).¹⁰ Alternatively, semi-IPNs could also be formed by linear polymerization of monofunctional monomers within preformed networks¹¹ (Scheme 2). An intrinsic potential deficiency of all semi-IPNs produced by these methods is the extractability of their linear constituents that might lead to large irregular voids in the network structure, unexpected changes in the chemical balance, and deteriorated performance.

In this paper we explore a novel strategy for the construction of unusual semi-IPNs where the linear polymer is permanently immobilized within the network. A unique feature of this approach is that it employs a cross-linking reaction between a preformed bifunctional linear polymer and a multifunctional dendritic cross-linking moiety located at the end of another linear polymer chain (Scheme 3). The resulting materials are actually

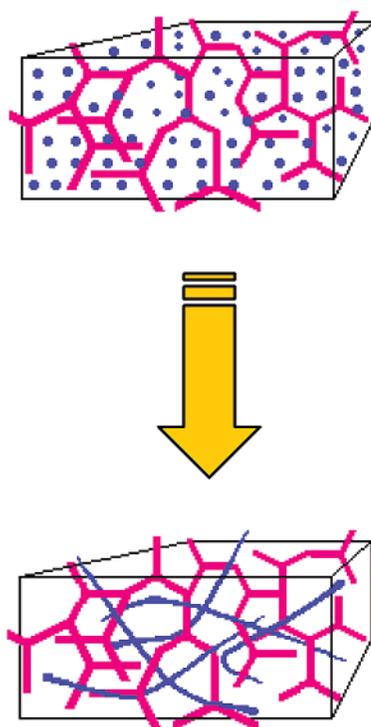
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Scheme 1. Schematic Representation of the Semi-IPN Construction through Polymerization of Multifunctional Monomers or Coupling of Star Polymers in the Presence of a Preformed Linear Polymer

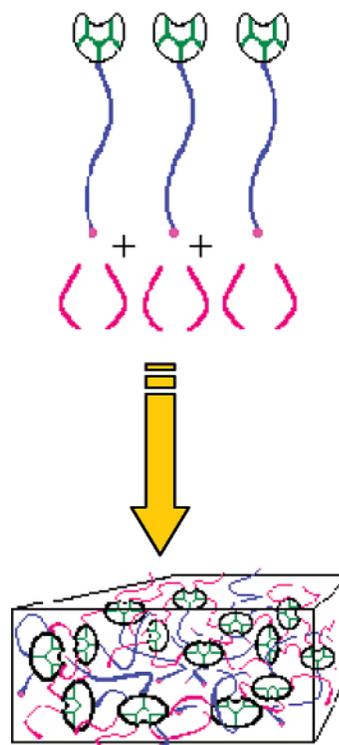


Scheme 2. Schematic Representation of the Semi-IPN Formation by Linear Polymerization of Monofunctional Monomers within Preformed Networks



pseudo-semi-IPNs and could be employed as templates in resin capture–release¹² processes since the dendritic cross-linking junctions could serve as (side) product-harvesting “nano-

Scheme 3. Formation of a Pseudo-Semi-IPN by Cross-Linking Reaction of Bifunctional Linear Polymer with Multifunctional AB Linear–Dendritic Copolymer



pockets” while the end groups of the semi-interpenetrating linear block could be modified to host catalytic- or molecular-recognition functions. As a test of the proposed new concept, we are using the transesterification reaction between poly(ethylene glycol) (PEG) and a linear–dendritic copolymer containing multiple ester groups at the periphery of the dendritic block. The ultimate goal is to produce a functional amphiphilic pseudo-semi-IPN with cross-linked PEG as the hydrophilic three-dimensional lattice and embedded poly(styrene) chains, anchored to the network matrix by monodendritic fragments (Figure 1).

Results and Discussion

The linear–dendritic copolymer used for this study contains poly(styrene) (PSt) as the linear block and surface-modified poly(benzyl ethers) as the dendritic fragment. The copolymer can be conveniently synthesized using the method reported by Fréchet and co-workers.¹³ In this investigation, we employ a modified procedure¹ with an ethyl ester-terminated third-generation monodendritic bromide as the initiator for the metal-mediated radical polymerization¹⁴ (MMRP) of styrene. The polymerization produces an AB copolymer with predictable molecular weight ($M_w = 13\,200$ Da) and relatively narrow molecular weight distribution ($M_w/M_n = 1.04$) calculated by size exclusion chromatography (SEC) analysis with PSt standards.

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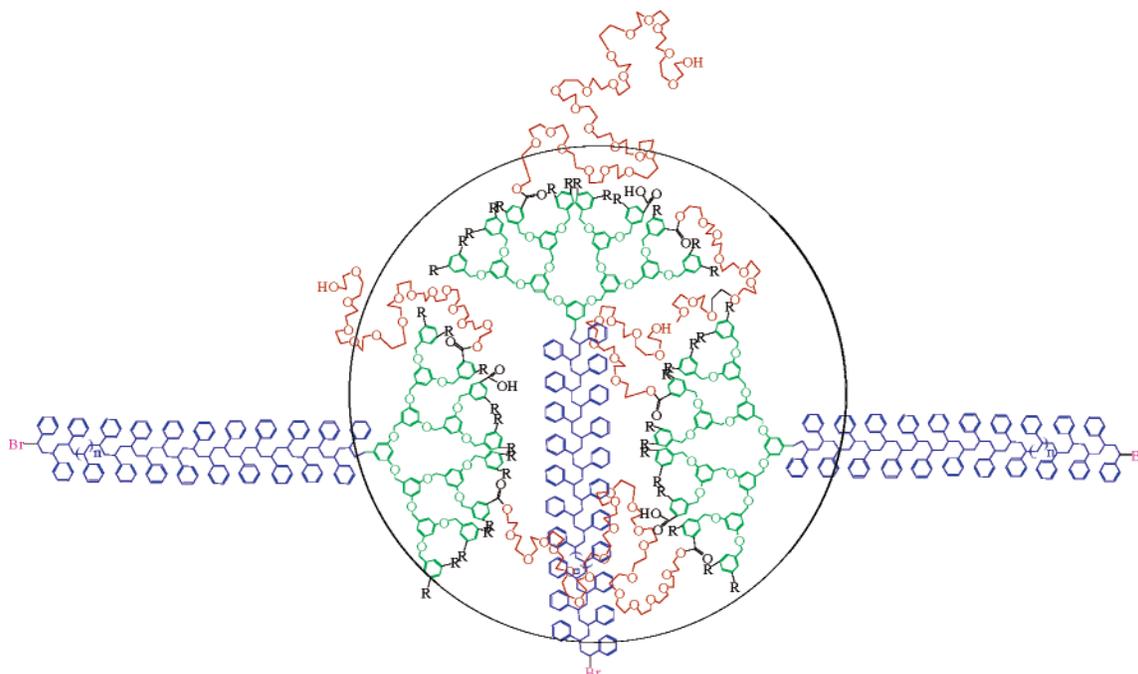


Figure 1. Cross-link junction in a pseudo-semi-interpenetrating network formed by PEG transesterification of linear–dendritic copolymer containing poly(styrene) ($n \approx 100$) and 16 peripheral dendritic ester groups, ($R = -CO_2Et$).

Network Formation. In our study, pseudo-semi-IPNs with different molecular weight PEGs are formed by a transition-metal-catalyzed transesterification reaction^{15–18} between the PEG hydroxyl groups and the dendritic ethyl esters. Initially, a model transesterification experiment was performed in toluene solution, and the progress of the reaction was monitored by ¹H NMR. The ¹H NMR spectrum of the reaction mixture at the initial stages is shown in Figure 2a. The triplet peak at 3.87 ppm is assigned to the methylene protons next to the end hydroxyl groups in the PEG, and the quartet peak at 4.39 ppm is due to methylene protons in the ethyl ester groups at the periphery of dendritic fragments in the linear–dendritic copolymer. As the transesterification proceeds, the triplet and the quartet peaks gradually disappear and could be hardly detected after 9 days (Figure 2d). At the same time, a triplet peak at 4.32 ppm, which is assigned to the methylene protons in ester linkage formed between PEG and dendritic fragments, gradually intensifies with the reaction time (Figure 2, parts b–d). The observed changes in the ¹H NMR spectra could be regarded as direct proof that the ester linkages between the PEG fragments and the linear–dendritic copolymer effectively form during the transesterification reaction. However, the aliquot samples taken from this solution reaction still dissolve in CDCl₃, even after 9 days of reaction. This fact implies that a “grafted” semi-IPN does not form under these conditions despite the observed formation of ester linkages between the two constituents. The reason could be that the achieved reaction conversion is not high enough to form the desired cross-linked structure.

SEC was also used to analyze the products formed during the transesterification reaction in solution. Interestingly, only one new fraction appears to the left of the linear–dendritic copolymer peak (Figure 3). This indicates that this higher

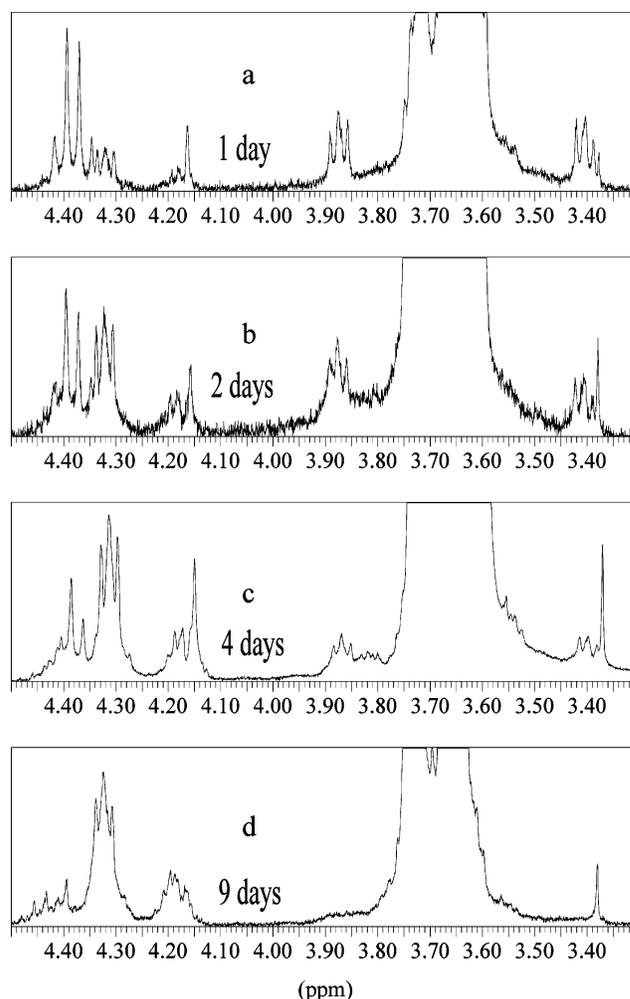


Figure 2. Time evolution of the ¹H NMR spectra of aliquots taken from the model cross-linking reaction in toluene. Room temperature, 300 MHz, CDCl₃. (a) 1 day, (b) 2 days, (c) 4 days, and (d) 9 days.

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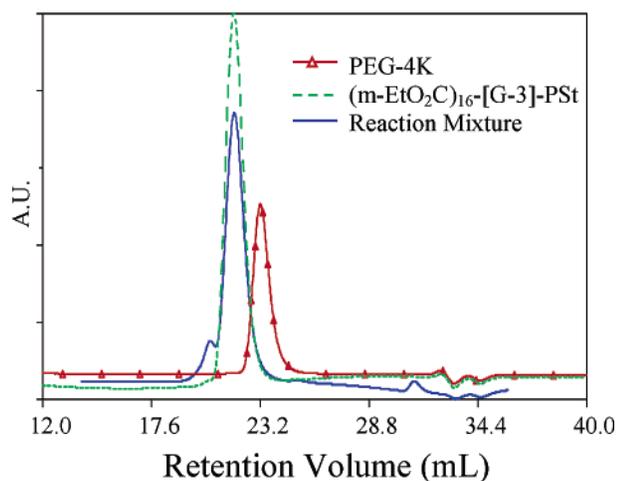


Figure 3. SEC traces of PEG-4K, linear-dendritic copolymer, and sample from the model reaction mixture after 4 days.

molecular weight polymer is most probably the transesterification product formed by the reaction between the linear-dendritic copolymer and PEG. However, the relatively weak signal of this peak suggests that only a small portion of both reagents has reacted. The result also indirectly supports the above assumption that a fully developed network structure could not be obtained in this solution reaction because of the relatively low concentration of the reagents.

It is well-known that bulk reactions usually produce more densely cross-linked structures than the solution reaction between components of the same size and structure.^{16,19} As expected, the same ¹H NMR spectrum as in Figure 2d is observed after only 2 h of reaction. The formation of pseudo-semi-IPNs (i.e., gelation) visibly occurs after 24 h with PEG of medium molecular weight ($M_w = 4000$). The gelation process is slower with higher molecular weight PEGs: 3 days with PEG-11K and 7 days with PEG-15K. This could be explained by the decrease in the mobility of longer PEG chains and the lower probability of collision between the PEGs terminal -OH groups and the peripheral ester functions in the dendritic globules. Interestingly, the cross-linking efficiency is only slightly affected by the size of the PEG fragment. In the three cases investigated, the network yields (in respect to the initial PEG quantity) are rather reproducible: 33.5 and 44% for PEG-4K, 49 and 50% for PEG-11K, and 32% for PEG-15K. The fraction of extractable PEG is then 0.665 and 0.56 for PEG-4K, 0.51 and 0.5 for PEG-11K, and 0.68 for PEG-15K. The data imply that an optimum PEG chain length might exist around 11 000 Da that could achieve the highest link efficiency between two or more monodendritic fragments randomly embedded in the polymer matrix. It is also very important to maintain a continuous dynamic vacuum during the reaction, otherwise the reaction does not proceed at all, even in the bulk state. Obviously the removal of the ethanol formed as a byproduct of the transesterification shifts the reaction equilibrium in favor of the cross-linking ester bond between PEG and the linear-dendritic copolymer.

Solid-State Properties. The resulting pseudo-semi-IPNs contain two amorphous and mutually compatible components:

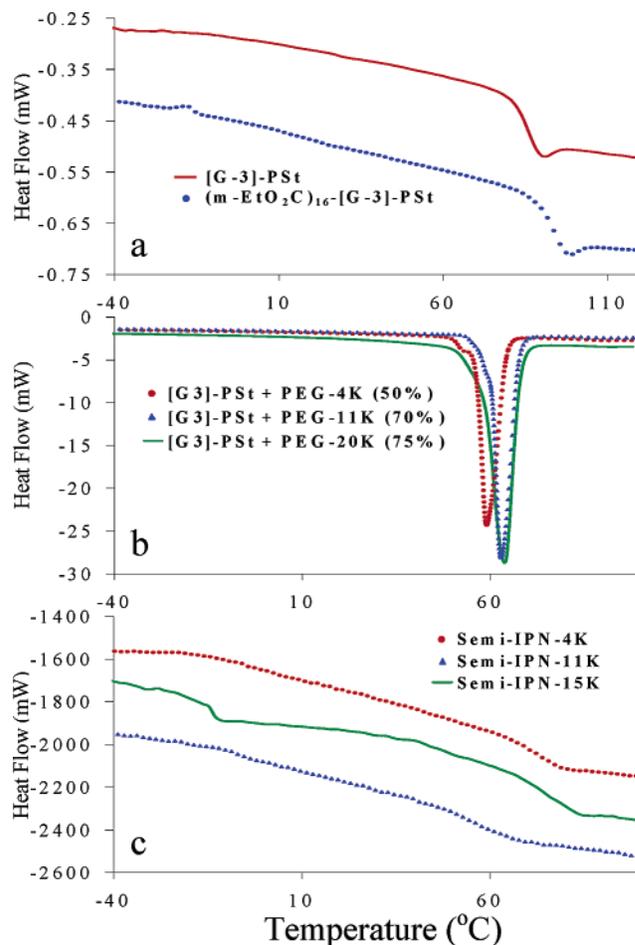


Figure 4. DSC traces of pseudo-semi-IPNs and their precursors and physical blends. (a) Linear-dendritic copolymers containing third-generation poly(benzyl ether) monodendron, [G-3]-, ester-terminated third-generation poly(benzyl ether) monodendron, (m-EtO₂C)₁₆-[G-3]-, and poly(styrene), PSt-. (b) Physical blends of [G-3]-PSt and PEGs with $M_w = 4000$, 11 000, and 20 000 (PEG-4K, PEG-11K, and PEG-20K). (c) Pseudo-semi-IPNs constructed from (m-EtO₂C)₁₆-[G-3]-PSt and PEGs of different molecular weights (4 K, 11 K, and 15 K).

linear PSt and a third-generation ethyl ester monodendron as evidenced by the occurrence of a single glass transition in the DSC trace of the linear-dendritic copolymer²⁰ (Figure 4a). On the other hand, the incorporated crystalline PEG blocks of various molecular weights are intrinsically not miscible with the other two constituents in the network. In our previous studies, we have shown that PEGs are able to crystallize in star-graft copolymers²¹ as well as in network¹⁹ and linear-dendritic²² structures containing poly(benzyl ether) dendrimers and their derivatives as long as the PEG content exceeds 50% (by weight). The same behavior is observed when the physical blends with compositions, identical to the “grafted” semi-IPN, are analyzed by DSC (Figure 4b). All three blends undergo a well-expressed melting transition between 55 and 62 °C because of the phase separation and PEG crystallization. The corresponding pseudo-semi-IPNs (the PEG content is 52, 77, and 75 wt %, respectively), however, do not show any melting

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Table 1. Thermal Characteristics of the Pseudo-Semi-IPNs and Starting Materials

sample	PEG (wt %)	T_g (°C)	T_g^a (°C)	C_p (J/g °C)
[G-3]-PSt	0	93.6		0.31469
(<i>m</i> -EtO ₂ C) ₁₆ -[G-3]-PSt	0	94.1		0.35960
pseudo-semi-IPN-4K ^b	52	-47.8	-13.7	0.27594
	52	72.7		0.07986
pseudo-semi-IPN-11K ^c	77	-46.5	-39.8	0.35394
	77	56.7		0.15052
pseudo-semi-IPN-15K ^d	75	-47.5	-38.8	0.17952
	75	-14.2		0.11465
	75	70.4		0.36348

^a T_g is the theoretical value calculated from the Fox equation.²⁴ ^b Pseudo-semi-IPN synthesized from PEG-4K. ^c Pseudo-semi-IPN synthesized from PEG-11K. ^d Pseudo-semi-IPN synthesized from PEG-15K.

transitions at all (Figure 4c). Previously, Clarson et al. estimated that PEG networks, end-linked with aromatic triisocyanates, would not have a melting transition if the interlink molecular weight (M_c) did not exceed 205 Da because of the fairly high cross-link density and the bulky junction moieties acting as defects in the PEG crystallization.²³ In our study, the M_c values are significantly higher (4, 11, and 15 K, respectively), but the bulkiness of the junction groups (third-generation monodendron vs triisocyanate) and the increased cross-link density (functionality of 16 vs 3) act most probably as compensatory factors. All pseudo-semi-IPN samples exhibit two glass transitions in their DSC traces at temperatures that deviate from the thermal characteristics of the starting linear-dendritic copolymer and PEGs and the values predicted by the Fox equation²⁴ (Figure 4, panels a and c, and Table 1). It is reasonable to believe that at least two phases coexist in each network. One of the domains ($T_g = 56.7$ – 72.7 °C) contains predominantly the linear-dendritic copolymer “contaminated” with some interpenetrating PEG segments. These segments act as plasticizers and depress the domain's T_g . The other phase ($T_g = -47.8$ – 14.2 °C) is rich in PEG that is interlocked with the linear-dendritic component. The latter efficiently constrains the mobility of the PEG chains, which causes the T_g elevation of this phase. Thus, the relatively broad glass transitions, revealed by the DSC measurements, manifest one of the distinctive features of the IPNs: the three-dimensional interlock structure that can suppress the phase separation of the incompatible polymer constituent.

Solution Behavior. Because of their amphiphilic character, all pseudo-semi-IPNs are able to swell both in organic and aqueous liquid media, the equilibration period being rather short (less than 1 h). Despite the relatively high PEG content, however, the weight swelling ratio in CHCl₃ is higher for all three networks than the corresponding value in water (4.1–7.2 to 1.5, respectively). In addition, the materials are fully transparent in organic media and milky-white in H₂O. It is interesting to note that pure PEG networks with similar M_c values (3500 and 15 000) have practically the same equilibrium swelling ratio in chloroform and substantially higher swelling ratio in water (3.9 and 6.9, respectively).²⁵ The observed phenomena suggest that the hydrophobic PSt chains, grafted at the cross-link junctions, collapse in an aqueous environment and substantially hinder the expansion of the hydrophilic PEG

network. In chloroform, all three components of the pseudo-semi-IPNs are fully soluble and the swelling is affected only by the cross-linking density of the gel.

In view of the potential applications of these materials, the investigation of their solution properties is more focused on the mobility of the constituents in various environments. NMR spin-relaxation time (T_1) is a convenient indicator for the extent of polymer-solvent interactions.²⁶ It is known that T_1 is usually expressed by the local motion of the repeating units in the polymer chain, which in turn is mainly affected by the local free volume available (local concentration and viscosity).²⁷ The measurements of the relaxation times are performed in CDCl₃ (good solvent for all components in the semi-IPNs) and in D₂O (good solvent for the PEG cross-linkages) (Table 2). It is seen that the concentration of the sample has notable influence on the T_1 values. The results also show that in CDCl₃ at identical concentrations (14 mg/mL) both the PSt and PEG segments in the semi-IPNs have shorter relaxation times (i.e., restricted mobility) in comparison to the corresponding free chains. Within the network family the lowest mobility (shortest T_1) is observed in the pseudo-semi-IPN constructed with PEG-11K. This is not surprising considering the highest cross-link density (and PEG content) attained in this gel. In D₂O, only the signals of the PEG methylene protons can be observed at 3.65 ppm. In this medium, the linear chains have shorter T_1 because of their excessive solvation by the D₂O molecules. In a clear distinction to the CDCl₃ data the relaxation times of the PEG cross-links in the pseudo-semi-IPN increase with their chain length but are still shorter than the corresponding values in the organic solvent (Table 2). This seemingly surprising result might be explained by the motion restriction imparted through the interlocked hydrophobic PSt blocks that would collapse in the aqueous medium. Besides the steric hindrance, the PSt collapse probably causes also a partial stretching of the network's PEG interlinks. Both factors contribute to the smaller PEG T_1 values observed in D₂O. Since all pseudo-semi-IPNs contain hydrophobic chains of identical size, their effect on the mobility of the PEG cross-linkages would diminish with the chain length increase of the latter. Then the T_1 increase with the interlink molecular weight (M_c) will follow the same pattern reported previously for a normal hydrogel of different type.²⁸

Chemical Modification of Semi-IPNs. In one of the possible scenarios for a resin capture-release application of the novel amphiphilic gels, the dendritic groups would serve as passive harvesting (binding) nanodevices, while the chain ends in the anchored linear fragments would act as mobile catalytic (recognition) centers (Scheme 3). The low content of these end groups (one secondary benzyl bromide moiety per molecule with $M_w = 13\ 200$ Da) necessitates the use of a highly efficient reaction that would not affect the residual ester functions inside the pseudo-semi-IPNs and would attach a detectable tag to the extremities of the linear arms. As a model reaction, we choose the Williamson ether formation with 1-pyrenemethanol. Initially, model reactions between (1-chloroethyl)benzene and 1-pyrenemethanol catalyzed by KOH/18-crown-6, AgNO₃,²⁹ CH₃-

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Table 2. ^1H Spin–Lattice Relaxation Times (T_1) of PEGs, Linear–Dendritic Copolymer, $(m\text{-EtO}_2\text{C})_{16}\text{[G-3]-PSt}$, and Their Pseudo-Semi-IPNs

chemical shift (ppm)	T_1 (s)						$(m\text{-EtO}_2\text{C})_{16}\text{[G-3]-PS}$		
	pseudo-semi- IPN-4K	pseudo-semi- IPN-11K	pseudo-semi- IPN-15K	PEG-4K1	PEG-11K	PEG-15K	140 mg/mL	14 mg/mL	
	Measurements in CDCl_3								
7.2–7.4 ^a	2.949	2.044	3.155				2.606	3.059	
7.1 ^b	1.918	2.044	1.899				1.873	1.965	
6.6 ^b	1.271	1.24	1.230				1.243	1.266	
5.0 ^c							0.714	0.768	
4.9 ^c							0.500	0.543	
4.3 ^d	1.696	1.032	1.728						
3.65 ^e	1.231	0.965	1.172	1.387		1.320			
1.9 ^f	0.893	0.870	0.882				0.788	0.849	
1.3 ^g	0.700	0.757	0.613				0.540	0.678	
	Measurements in D_2O								
3.65 ^e	0.876	0.913	1.087	0.863	0.842				

^a Aromatic protons in dendritic fragments. ^b Aromatic protons in PSt. ^c Ethylene protons in dendritic fragments. ^d Ethylene protons of ester linkage. ^e Ethylene protons in PEG. ^f Methine protons in PSt. ^g Methylene protons in PSt.

COOAg , or CF_3COOAg ³⁰ are performed in THF and CH_2Cl_2 under reflux or at room temperature to establish the optimum reaction conditions. The highest yield (35%) is obtained with the silver trifluoroacetate as catalyst in methylene chloride at room temperature. Then pilot experiments are performed with the real linear–dendritic copolymer and 1-pyrenemethanol under identical conditions. Since the eventual content of the pyrene moiety would be below the detection limit of the ^1H NMR, even at 600 MHz, we are using SEC with a double dRI/UV detection to monitor the reaction progress. The wavelength of the UV detector is set at 343 nm, the characteristic absorption of the pyrene chromophore. As expected, the initial linear–dendritic copolymer does not show an absorption at this wavelength, and its presence is revealed only by the dRI peak in the SEC traces at 22.4 mL (Figure 5a). The 1-pyrenemethanol itself elutes at 32.15 mL with a strong double signal from both detectors. With the reaction advance, the copolymer peak shifts slightly to the left (higher molecular weight) and after 26 h shows well-expressed absorption at 343 nm, indicating a successful pyrene attachment (Figure 5b). From the UV/dRI ratio in the pyrene- and modified copolymer peaks we can *qualitatively* estimate the pyrene incorporation efficiency to be around 45–50%. Finally, the pseudo-semi-IPNs are modified using the same reaction conditions. After 6 days, the excess of 1-pyrenemethanol is removed *quantitatively* by multiple extractions with THF (no pyrene emission recorded in the fluorescence spectra of the final THF extract). The purified solid samples are not transparent and can not be tested by conventional fluorescence spectroscopy in solution. They are subjected to a laser-induced fluorescence (LIF) analysis. The LIF signal intensity visibly increases after the semi-IPNs are introduced in the laser beam path, a clear indication for the presence of the pyrene tags and direct proof for the chemical accessibility of the terminal groups in the mobile PSt arms in the gels.

Conclusions

The results obtained show that unique pseudo-semi-interpenetrating networks could be successfully synthesized by a

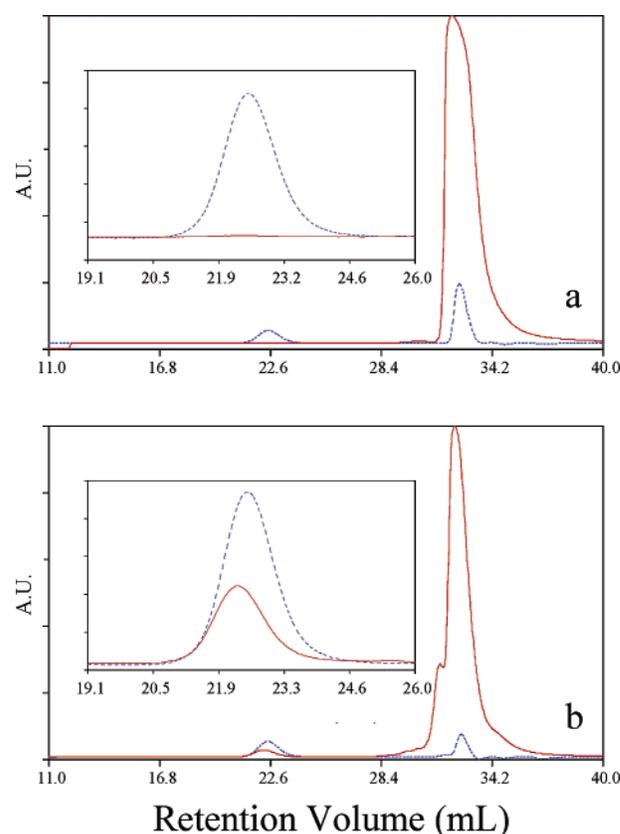


Figure 5. SEC with double detection of the reaction mixture containing 1-pyrenemethanol and [G-3]–PSt before the catalyst addition (a) and 26 h after the catalyst addition (b). UV signal ($\lambda = 343$ nm), solid red line; dRI signal, dotted blue line.

transesterification reaction involving PEGs of different molecular weight and $(m\text{-EtO}_2\text{C})_{16}\text{[G-3]-PSt}$, a linear dendritic AB copolymer containing ethyl ester-terminated third-generation dendritic poly(benzyl ether) and linear poly(styrene) block. The formation of the interlocked semi-IPN structures is convincingly proven by ^1H NMR, SEC, and DSC methods. The accessibility of the terminal functional groups in the linear fragments anchored throughout the semi-IPN is confirmed by several model experiments and fluorescence spectroscopy. The unique structure, solution and solid-state properties, and chemical reactivity of these novel amphiphilic pseudo-semi-IPNs manifest

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their potential suitability for many biomedical-, biotechnological, or combinatorial chemistry applications that require “capture–release” techniques.

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Supporting Information Available: Text providing information about the starting materials, synthetic procedures, and analytical techniques (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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