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Synthesis and solution-properties of two-component hyperbranched copolymers

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Abstract

Two-component hyperbranched copolymers were prepared by the living anionic polymerization technique. The first-generated polystyrene (PS) stars (1G-S) were prepared by copolymerization of poly(4-methylstyrene)-*block*-polystyrene diblock anions with divinylbenzene. The peripheral 4-methylstyrene blocks in the arm were metalated with *s*-butyllithium/tetramethylethylenediamine complex in cyclohexane. The second-generated hyperbranched copolymers (2G-HC) were prepared by anionic copolymerization of such 1G-S polyanions with isoprene in tetrahydrofuran. We studied the solution-properties of such hyperbranched copolymers, 2G-HC, in benzene (good solvent). The 2G-HC behaved like soft spheres or loose star-structures that were constructed with flexible chains in the inner parts. On the other hand, the 2G-HC (PS blocks 31.9 wt%) formed unimolecular micelles even in a high concentration of more than 1 wt% of polymer concentration in a selective solvent such as cyclohexane. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched copolymer; Anionic polymerization; Loose star-structure

1. Introduction

Branched polymers have become a field of considerable scientific and industrial interest. Dendrimers are macromolecules with tree-like architectures [1,2]. These polymers have viscosities lower than linear analogs of similar molecular weight, and the resulting macromolecules can be highly functionalized. On the other hand, the synthesis of hyperbranched polymers has been explored to develop dendritic molecules in a single, one-pot reaction [3–6]. Hyperbranched polymers have some of the qualities of dendrimers but also lack some properties of perfect dendrimers.

In contrast to the above dendrimers and hyperbranched polymers, the star-branched or radial polymers have the structure of linked-together linear polymers with a small molecular core. More recently, we have studied the spatial organization of polyisoprene (PI) stars (arm number $n = 4$–237) in cyclohexane solution and in bulk [7]. It was demonstrated through small-angle X-ray scattering (SAXS) measurements that the solutions were disordered up to the critical overlapping concentration of the stars, C^*, while for concentrations higher than C^*, a cubic phase was noticed. The scattering patterns clearly showed a transition from a body-centered cubic (BCC) to a face-centered cubic (FCC) structure. These phenomena were observed for PI stars with $n > 90$. Such solution behavior of star polymers is very similar to the unimolecule formation on dendrimers. Moreover, the $(AB)_n$ stars composed of asymmetric diblock arms led to similar structural ordering even with a small number of arms ($n > 20$) [8,9]. The arms of these stars were composed of incompatible block segments. Thus, the intramolecular segregation power of the diblock arms for $(AB)_n$ stars is stronger than that for PI stars.

Our interest was focused on the spatial organization of hyperbranched polymers having a long length of repeating units. We have established a novel synthesis of hyperbranched polymers via living anionic polymerization [10]. The first-generated star polymer (1G-S) was prepared by copolymerization of poly(4-methylstyrene)-*block*-polystyrene (PS) diblock anions with a small amount of divinylbenzene (DVB). The peripheral 4-methylstyrene blocks in the arm were metalated with *s*-butyllithium (*s*-BuLi)/tetramethylethylenediamine (TMEDA) complex in cyclohexane. The second-generated hyperbranched polymers (2G-H) were prepared by anionic polymerization of such 1G-S polyanions with α-methylstyrene in tetrahydrofuran (THF). In a dilute solution, the 2G-H behaved like soft spheres or

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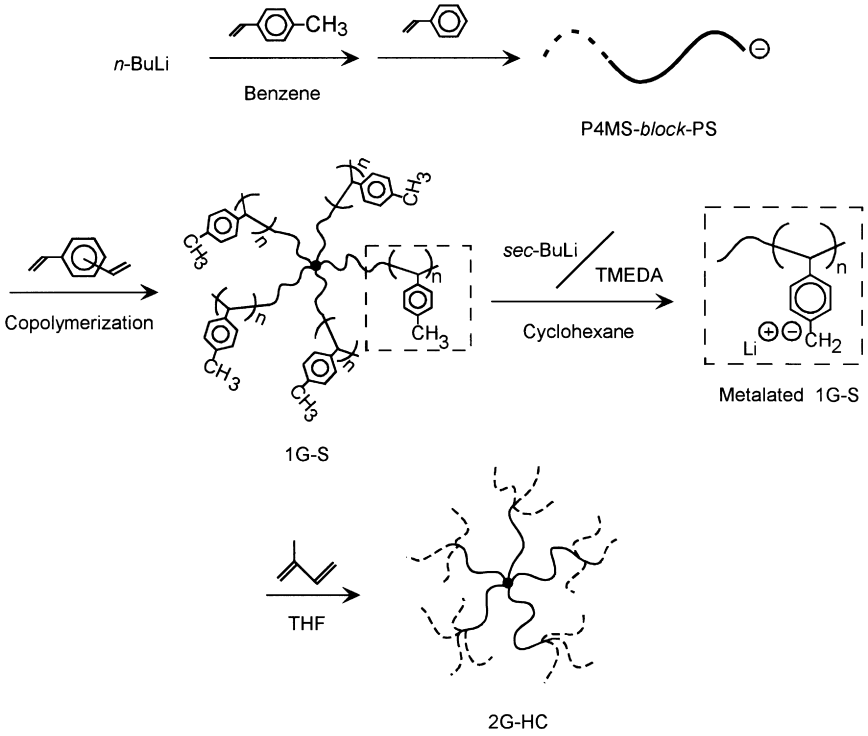

Scheme 1.

loose star-structures that were constructed with flexible chains in the inner parts. It is interesting from such a background to study the solution-properties and microphase separation of two-component hyperbranched copolymers from mutual relation with $(AB)_n$ stars.

In this article, we mention the synthesis and solution-properties of two-component (PS/PI) hyperbranched copolymers. This architecture allows us to study the effect of the chain density on the solution-properties of the branched copolymers.

2. Experimental

2.1. Synthesis of hyperbranched copolymers

The reaction scheme of hyperbranched PS/PI copolymers is shown in Scheme 1, which depicts the synthesis route of hyperbranched copolymers. The synthesis of the 1G-S PS stars is analogous to the preparation of star polymers [7,11]. First, poly(4-methylstyrene)-*block*-polystyrene (P4MS-*block*-PS) diblock anions were prepared by anionic successive addition of the 4-methylstyrene and styrene monomers in benzene using *n*-butyllithium (*n*-BuLi) as an initiator. 1G-S was prepared by copolymerization of P4MS-*block*-PS diblock anions with a small amount of DVB. The 1G-S star polymer was extensively fractionated in a benzene–methanol mixture at 20°C in order to remove the unreacted arm. We determined beforehand the methanol fraction (γ: v/v) at the starting point in turbidity of each P4MS-*block*-PS arm at a wavelength of 500 nm (Hitachi Perkin-Elmer 139 UV-VIS spectrometer).

The peripheral 4-methylstyrene blocks of 1G-S were metalated with *s*-BuLi/TMEDA complex in cyclohexane [12,13]. A yellow lithiated 1G-S star precipitated in the reaction solution. The supernatant was transferred to another vessel by decantation in order to remove the unreacted *s*-BuLi. A crude lithiated star was washed with fresh cyclohexane. These procedures were repeated a few times to remove the residual *s*-BuLi. The lithiated star was redissolved in THF. Details of the syntheses and purifications of such star and lithiated anions have been given elsewhere [10].

The second-generated hyperbranched copolymers (2G-HC) were prepared by anionic polymerization of the lithiated 1G-S with isoprene in THF at −78°C for 36 h, where the lithiated 1G-S was capped with a small amount of α-methylstyrene. The resulting solution was poured into an excess of methanol. The resulting polymer was then filtered and dried under vacuum. In order to isolate the hyperbranched copolymer 2G-HC, we determined also the methanol fraction γ (benzene–methanol system) at the starting point in turbidity of each 1G-S star.

2.2. Characterization

Details of characterization of star and lithiated anions also have been given elsewhere [10]. The molecular weight distribution was determined by gel permeation chromatography (GPC) (Tosoh high-speed liquid chromatograph

Table 1
Solution-properties of the first-generated PS stars

No.	P4MS-*block*-PS arm			1G-S star					
	$10^{-4}\bar{M}_w$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	P4MS[b] (number per molecule)	$10^{-5}\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$ [a]	n_1 [d] (number per molecule)	R_G [c] (nm)	R_H [e] (nm)	R_G/R_H
1G-S1F	2.70	1.10	15.5	4.22	1.11	15.6	12.7	9.9	1.38
1G-S2F	3.28	1.04	26.6	5.26	1.06	16.0	10.4	8.3	1.25
1G-S3F	1.81	1.11	16.0	1.77	1.12	8.7	9.1	7.5	1.21

[a] Determined by GPC.
[b] Determined by ^{1}H NMR in $CDCl_3$.
[c] Determined by SLS in benzene.
[d] Arm number was determined by $\bar{M}_w$s of arm block and 1G-SF star.
[e] Determined by DLS in benzene.

HLC-8020) with THF as the eluent at 38°C, using a TSK gel GMH_{XL} column and a flow rate of $1.0\ \mathrm{ml\ min}^{-1}$. The weight-average molecular weight ($\bar{M}_w$), radius of gyration (R_G) and the second virial coefficient (A_2) of 2G-HC were determined by static light scattering (SLS) in benzene, on a photal TMLS-6000HL (Otsuka Electronics Ltd.) with a He–Ne laser ($\lambda_0 = 632.8$ nm) in the Zimm mode [14]. The refractive index increment [$(dn/dc)_{HC}$] of hyperbranched copolymers was determined by applying the well-known equation:

$$(dn/dc)_{HC} = w_{PS}(dn/dc)_{PS} + (1 - w_{PS})(dn/dc)_{PI} \qquad (1)$$

where w_{PS} is the weight fraction of PS, and $(dn/dc)_{PS}$ and $(dn/dc)_{PI}$ are the refractive indices of PS and PI, respectively. Values of $(dn/dc)_{PS} = 1.06$ and $(dn/dc)_{PI} = 0.014$ ($\mathrm{ml\ g}^{-1}$) were used in benzene at $\lambda_0 = 632.8$ nm wavelength. The scattering angles were in the range of 30–150°. Sample solutions were filtered through membrane filters with a nominal pore of 0.2 μm just before measurement. Solutions were measured in the concentration range of 2–10 mg ml^{-1}.

The hydrodynamic radii (R_H) of 2G-HC were calculated from the diffusion coefficient, which was determined by the extrapolation to zero concentration of dynamic light scattering (DLS; Otsuka Electronics Ltd.) data at 25°C in 0.01–1.0 wt% benzene ($\eta = 0.654$ *cp*, $n_D = 1.501$) or cyclohexane $\eta = 0.898$ *cp*, $n_D = 1.426$) solution using a cumulant analysis. The scattering angle was fixed at 90°C.

The content of PS was determined by ultraviolet (UV; characteristic absorption of PS groups at 254 nm) on a Jasco Ubest-35 UV/VIS spectrometer in chloroform.

3. Results and discussion

3.1. Solution-properties of the first-generated star polymers

We prepared 1G-S with a varying number of arms by varying the concentration ratio of DVB to P4MS-*block*-PS monoanions. All of the GPC distributions for 1G-S series were bimodal. The copolymerization product was a mixture of the 1G-S star and its precursor. Each 1G-S star was removed from the corresponding unreacted diblock precursor by the precipitation fractionation (benzene–methanol system). The 1G-S star fraction is denoted as 1G-SF in the following discussion.

Table 1 lists the solution-properties of the 1G-SF stars in benzene. The ratio R_G/R_H is a sensitive fingerprint of the inner density profile of star molecules and polymer micelles. The values of R_G/R_H for the 1G-SF stars were in the range of 1.21–1.38 (arm number $n_1 = 9$–16). It is well known that R_G/R_H for linear unperturbed polymers and hard spheres of uniform density are 1.25–1.37 [15] and 0.775 [16,17], respectively. In good solvents, even higher values of R_G/R_H (1.23–1.46) were observed for linear PSs [18]. More recently, we prepared DVB core-crosslinked PI stars ($40 < n < 237$). The values of R_G/R_H in cyclohexane decreased gradually and approached unity as n became large [11]. It was concluded that the stars with multiarms behaved as soft spheres, and not as near hard spheres, that were penetrable near the edge in a good solvent. The results obtained in this work showed the same behavior.

3.2. Preparation and solution-properties of the second-generated hyperbranched copolymers

The peripheral 4-methylstyrene blocks of 1G-SF were metalated with *s*-BuLi/TMEDA (1/4: $\mathrm{mol\ mol}^{-1}$) complex in cyclohexane. An aliquot of this lithiated star polymer solution was reacted with 2-(bromomethyl)naphthalene in order to determine the degree of metalation. It was found from GPC analysis, equipped with RI and UV (at 311 nm) that the lithiated 1G-SF anions with various degrees of lithiation (10–70%, see Table 2) were prepared by changing the feed amount ratio of peripheral 4-methylstyrene blocks to *s*-BuLi/TMEDA complex. 2G-HC hyperbranched PS/PI copolymers were prepared by anionic copolymerization between the lithiated 1G-SF end-capped with α-methylstyrene and isoprene in THF. Gradually with the mixing of the monomer, the red color of end-capped α-methylstyryl anions changed to light yellow (characteristic color of PI anions).

Typical anionic copolymerization conditions for the hyperbranched copolymer 2G-HC1-1 are as follows:

[lithiated 1G-S1F anion] $= 4.2 \times 10^{-3}$ mol l^{-1}, [α-methylstyrene] $= 5.1 \times 10^{-3}$mol l^{-1}, [isoprene] $= 0.412$ mol l^{-1} at −78°C for 36 h. GPC profile of 2G-HC1-1 is shown in Fig. 1. In this chart, the GPC distribution is bimodal according to the RI monitor. A narrow peak appears on the side of the high molecular weight compared to the starting 1G-S1F star. Trace of the low molecular weight fraction is observed in the UV monitor at 254 nm. It is, therefore, suggested that this product is a mixture of hyperbranched PS/PI copolymer and PI homopolymer initiated by *s*-BuLi end-capped with α-methylstyrene. It seems that the unreacted *s*-BuLi/TMEDA complex was not quantitatively converted to lithium alkoxide by the reaction with THF in this condition. The hyperbranched PS/PI copolymer (2G-HC1-1F) was separated by the precipitation fractionation (methanol fraction $\gamma = 0.42$ v/v at the starting point in turbidity of 1G-S1F star). GPC profile of the fraction 2G-HC1-1F is also shown in Fig. 1. On the other hand, the low molecular weight fraction was recognized to be a PI homopolymer by ^{1}H NMR. Several samples of PS/PI two-component hyperbranched copolymers 2G-HC-F were prepared by varying the feed concentration ratio of [isoprene] to [lithiated 1G-SF anion]. Characteristics of such hyperbranched copolymers are listed in Table 2. Each observed molecular weight distribution of 2G-HC-F ($\bar{M}_w/\bar{M}_n = 1.07$–$1.13$) is maintained with that of corresponding 1G-SF as the polyanion initiator. Considering the slow propagation rate of polyisoprenyl anions, the hyperbranched copolymers are judged to exhibit a monodisperse arm length. In this work, the arm number of the second-generation is assumed to be identical to the polybenzylic anion number of the 1G-SF star.

The dilute-solution properties of 2G-HC-F in benzene are listed in Table 2. A typical Zimm plot and DLS data for 2G-HC2-2F are shown in Fig. 2(a) and (b), respectively. The values of $\bar{M}_w$, A_2 and R_G in benzene were derived from such a Zimm plot. In order to discuss the hydrodynamic dimensions of hyperbranched copolymers in solution, we determined the values of R_H by DLS in benzene. Fig. 2(b) shows the concentration dependence of the apparent diffusion coefficient D_c. By insertion of the thermodynamic diffusion coefficient D_0 (9.343×10^{-8} cm^2 s^{-1}) in the Stokes–Einstein equation, we calculated a hydrodynamic radius of $R_H = 32.0$ nm for 2G-HC2-2F in benzene. These physical values are also listed in Table 2. The values of R_G/R_H for 2G-HC-F were in the range of 0.76–1.41 and showed lower values than that of corresponding 1G-S as the starting materials except for 2G-HC2-1F. This is due to the crowding effect of segment densities on the second-generated structures. It especially seems that 2G-HC2-3F behaves as a hard sphere even in dilute solution. The inner density of hyperbranched copolymers depends not only on the second-generated PI arm number n_2 but also on the copolymer composition. It can be judged as a general trend that hyperbranched copolymers 2G-HC-F also behave as a soft sphere or a loose star-structure in a good solvent that is constructed with flexible chains in the inner core.

Table 2
Characteristics and solution-properties of the second-generated hyperbranched PS/PI copolymers

No.	1G-SF		2G-HC-F								
	Code	Degree of lithiation[a] (%)	$10^{-6}\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[c]	n_2[d] (number per molecule)	PS block[e] (wt%)	PI block[f] $10^{-4}\bar{M}_w$	$10^{-4}A_2$[b] (mol ml g^{-2})	R_G[b] (nm)	R_H[g] (nm)	R_G/R_H
2G-HC1-1F	1G-S1F	70.0	1.51	1.12	169	27.9	0.64	2.18	23.4	20.6	1.14
2G-HC1-2F	1G-S1F	70.0	1.87	1.13	169	22.6	0.86	1.52	30.3	29.9	1.01
2G-HC2-1F	1G-S2F	10.0	1.14	1.07	43	46.1	1.43	2.04	33.0	23.3	1.41
2G-HC2-2F	1G-S2F	10.0	1.65	1.08	43	31.9	2.61	1.61	35.8	32.0	1.12
2G-HC2-3F	1G-S2F	20.3	1.93	1.08	86	27.2	1.63	0.99	23.9	31.6	0.76

[a] The lithiated 1G-SF was reacted with 2-(bromomethyl)naphthalene. The content of naphthalene groups in the 1G-SF was determined by GPC equipped with RI and UV (at 311 nm) double detectors.
[b] Determined by SLS in benzene.
[c] Determined by GPC.
[d] The second-generated PI arm number.
[e] Determined by UV in $CDCl_3$.
[f] Determined by $\bar{M}_w$ and n_2 of 2G-HC-F.
[g] Determined by DLS in benzene.

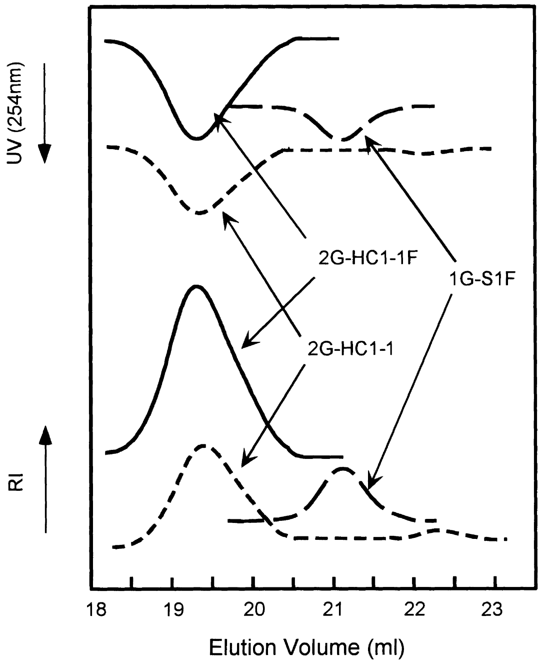

Fig. 1. GPC profiles of 2G-HC1-1, 2G-HC1-1F and 1G-S1F.

In a previous report [19], we indicated that PS-*block*-PI diblock copolymer (PI block 18.2 wt%) formed polymeric micelles, such as PI core–PS corona structure, in *N*,*N*-dimethylformamide (DMF). DMF is a good solvent for PS but a poor one for PI. However, the $(AB)_n$ star composed of the same diblock arm ($n = 14$) showed the constant D_H value in the range of 10^{-4}–10^0 wt% polymer concentration in DMF. It indicated that this $(AB)_n$ star formed unimolecular micelles in such a concentration range. So it is interesting to study the solvent effect of hyperbranched copolymers on the hydrodynamic dimension. The hydrodynamic diameter (D_H) of 2G-HC2-2F was 64.0 nm in benzene (see Table 2). Fig. 3 shows the relationship between D_H and polymer concentration for 2G-HC2-2F (PS blocks 31.9 wt%) in cyclohexane. Cyclohexane is a good solvent for PI but a poor one for PS. D_H shows a constant value (49.3 nm) in the range of 10^{-3}–10^{-1} wt% polymer concentration. As a matter of course, the value of D_H in cyclohexane was smaller than that in benzene. Moreover, D_H decreases suddenly beyond 10^{-1} wt% polymer concentration in cyclohexane. This fact means that the hyperbranched copolymer 2G-HC2-2F forms unimolecular micelles even in high concentration more than 1 wt% of polymer concentration. The inner PS chains of the star polymer are bonded radially with the DVB core, but a strong repulsion force works between the PI and PS chains, due to incompatible segments. So the inner PS parts of stars may behave as a hard core in a selective solvent such as cyclohexane. The second-generated hyperbranched copolymer 2G-HC2-2F led to shrinkage isotropically with an increment of polymer concentration.

It is interesting to make clear the microphase-separated

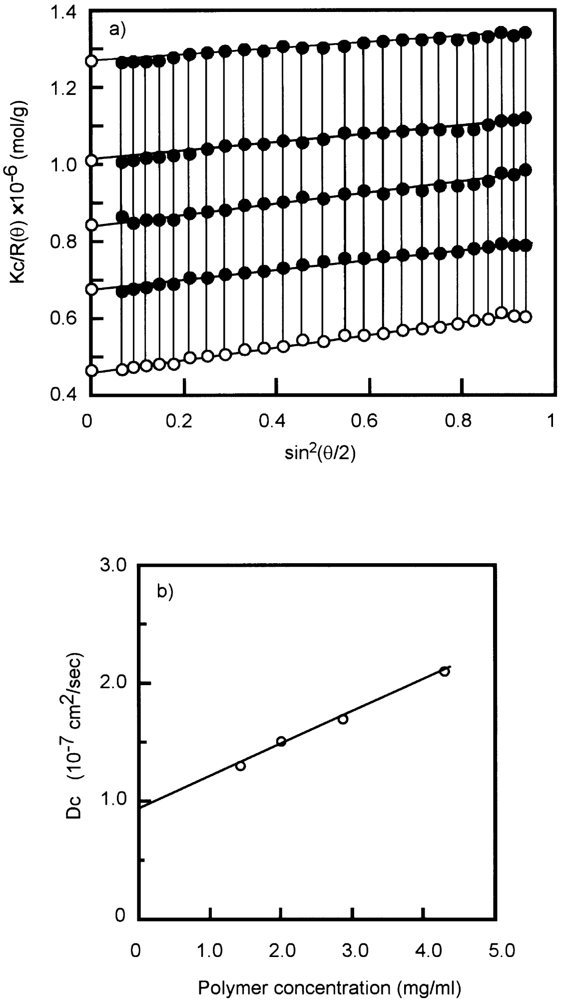

Fig. 2. (a) Zimm plot; and (b) concentration dependence of apparent diffusion coefficient D_c for hyperbranched copolymer 2G-HC2-2F in benzene.

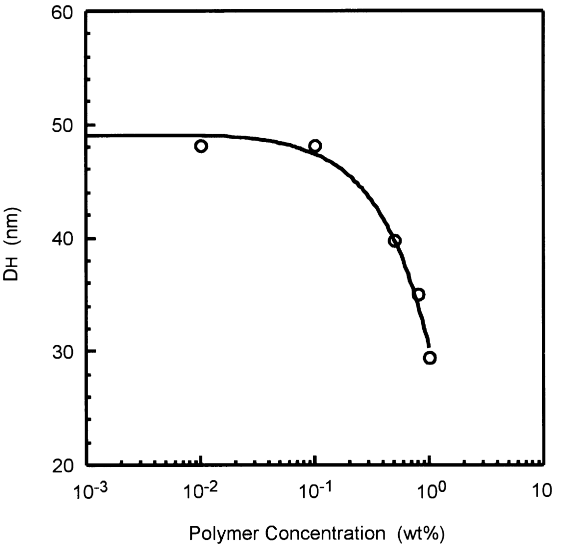

Fig. 3. Relationship between hydrodynamic diameter (D_H) and polymer concentration for 2G-HC2-2F in cyclohexane.

structures of such hyperbranched PS/PI copolymers. The results obtained will be reported in the near future.

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