polymer

Novel synthesis and characterization of hyperbranched polymers

K. Ishizu[*], D. Takahashi, H. Takeda

Department of Polymer Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Abstract

We approached a novel synthesis of hyperbranched polymers via living anionic polymerization. The first-generated star polymer (1G-S) was prepared by copolymerization of poly(4-methylstyrene)-*block*-polystyrene diblock anions with a small amount of divinylbenzene. The peripheral 4-methylstyrene units in the arm were metalated with *s*-butyllithium/tetramethylethylenediamine complex in cyclohexane. The second-generated hyperbranched polymers (2G-H) were prepared by equilibrium polymerization of such 1G-S polyanions with α-methyl-styrene in tetrahydrofuran at $-78°$C, and subsequently the terminal branch ends were capped with a small amount of 4-methylstyrene. The characterization of such hyperbranched polymers was carried out in detail. The ratio values of radius of gyration (R_G) to hydrodynamic radius (R_H) for the 2G-H were in the range of 0.96–1.18. The 2G-H behaved like soft spheres or loose star-structures that were constructed with flexible chains in the inner parts. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched polymers; Star polymer; Anionic polymerization

1. Introduction

Dendrimers are macromolecules with tree-like architectures. The approach developed by Tomalia [1,2] implied that the construction of dendritic molecules started from a functional central core and then proceeded outward. On the other hand, the procedure designed by Frechet [3,4] involved a convergent synthesis, in which the central core was formed at the ultimate step by linking hyperbranched tree-like structures. Such dendrimers that emanate from a central core have begun to receive scientific attention [5,6]. These spherical structures have been proposed as precise nanoscopic building blocks [7]. New architectures have been synthesized, including unimolecular micelles and structures containing dendrimers [8–10] and linear macromolecules [11–13].

In constrast to the above dendrimers, the star-branched or radial polymers have the structure of linked-together linear polymers with a small molecular weight core. Generally, the star polymer has a smaller hydrodynamic dimension than that of a linear polymer with an identical molecular weight. The interest in star polymers arises not only from the fact that they are model branched polymers but also from their enhanced segment densities. Zimm and Stockmayer [14]

were the first to study the conformation of star-shaped polymers. Daoud and Cotton [15] studied the conformation and dimension of star polymers using the scaling theory. Stars with multiarms (the critical number of arms is estimated to be of order 10^2) are expected to form a crystalline array near the overlap threshold (C^*) [16].

More recently, we have studied the spatial organization of polyisoprene (PI) stars (arm number $n = 4$–237) in cyclohexane solution and in bulk [17]. 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 concentration 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 unimolecular micelle formation of dendrimers. It is interesting to study the spatial organization of hyperbranched polymers having a long length of repeating units. Such hyperbranched polymers are expected to exhibit solution properties similar to dendritic polymers.

In this article, we describe a novel synthesis of hyperbranched polymers via living anionic polymerization. This architecture allows us to influence the chain density in spherical particles and to study its effect on the solution properties of the branched polymers.

* Corresponding author. Tel.: +81-3-5734-2634; fax: +81-3-5734-2888.
E-mail address: kishizu@polymer.titech.ac.jp (K. Ishizu).
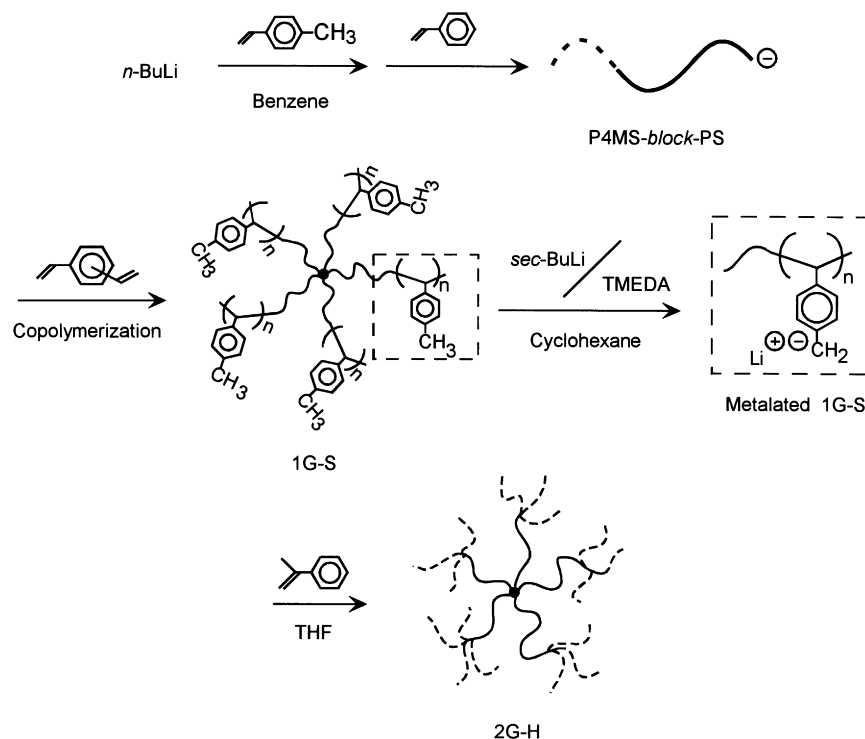
Scheme 1.

2. Experimental

2.1. Synthesis of hyperbranched polymers

The reaction scheme of hyperbranched polymers is shown in Scheme 1. The synthesis of the first-generated polystyrene stars (1G-S) is analogous to the preparation of star polymers [18,19]. First, oligomeric poly(4-methyl-styryl) anions were prepared by the living polymerization technique using the break-seal method in a sealed glass apparatus under a pressure of 10^{-6} mmHg, using *n*-butyl-lithium (*n*-BuLi) as an intiator in benzene. Subsequently, poly(4-methylstyrene)-*block*-polystyrene (P4MS-*block*-PS) diblock anions were prepared by successive addition of the styrene monomer. Details of the synthesis and purification of such diblock anions have been given elsewhere [20,21].

1G-S was prepared by copolymerization of P4MS-*block*-PS diblock anions with a small amount of divinylbenzene (DVB) (DVB: Tokyo Kasei, 65%, m-/p-isomer = 2, 35% ethylstyrene) in benzene. The resulting solution was stirred at 20°C for 48 h. Polymerization was stopped by introducing the viscous solution into an excess of methanol. 1G-S was extensively fractionated in a benzene–methanol mixture to remove the unreacted arm.

The peripheral 4-methylstyrene units of 1G-S were metalated with *s*-BuLi/tetramethylethylenediamine (TMEDA) complex in cyclohexane [22,23]. A yellow lithiated polymer precipitated in the reaction solution. The supertanant was transferred to another vessel by decantation in order to remove the unreacted *s*-BuLi. A crude lithiated polymer was washed with fresh cyclohexane. These procedures were repeated a few times to remove the residual *s*-BuLi. This lithiated polymer was redissolved in tetra-hydrofuran (THF). The unreacted *s*-BuLi was converted to lithium alkoxide by reaction with THF at 25°C. In this treatment, the lithiated benzylic anions were stable in THF solvent [23].

The second-generated hyperbranched polymers (2G-H) were prepared by equilibrium polymerization of the lithiated 1G-S with α-methylstyrene (MS) in THF at −78°C for 36 h. The arm ends were then capped with a small amount of 4-methylstyrene. The resulting solution was poured into an excess of methanol. The resulting polymer was then filtered and was dried under vacuum. In general, it is possible to synthesize up to the *n*th generated hyperbranched polymer (*n*G-H) by repeating above procedures.

2.2. Characterization

The number-average molecular weights ($\bar{M}_n$) of the P4MS-*block*-PS precursors were determined by vapor pressure osmometry (VPO) on a Corona NA 117 vapor pressure osmometer in benzene, or by gel permeation chromatography (GPC) (Tosoh high-speed liquid chromatograph HLC-8020) using universal calibration [24] with THF as the eluent at 38°C, using a TSK gel GMH$_{XL}$ column and a flow rate of 1.0 ml min^{-1}.

The weight-average molecular weights ($\bar{M}_w$), radii of gyration (R_G) and the second virial coefficients (A_2) of

Table 1
Characteristics of poly(4-methylstyrene)-*block*-polystyrene

Code	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$[a]	P4MS block[b] (numbers per molecule)
AB1	0.80[c]	1.06	8.2
AB2	1.81[a]	1.09	16.0

[a] Determined by GPC.
[b] Determined by ^{1}H NMR in CDCl$_3$.
[c] Determined by VPO.

1G-S and 2G-H 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 [25]. The refractive index increment [$(dn/dc)_H$] of hyperbranched polymers was determined by applying the well-known equation:

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

where w_{PS} is the weight fraction of PS, and $(dn/dc)_{PS}$ and $(dn/dc)_{PMS}$ are the refractive indices of PS and PMS, respectively.

The scattering angles were in the range of 30–150°. Sample solutions were filtered through membrane filters
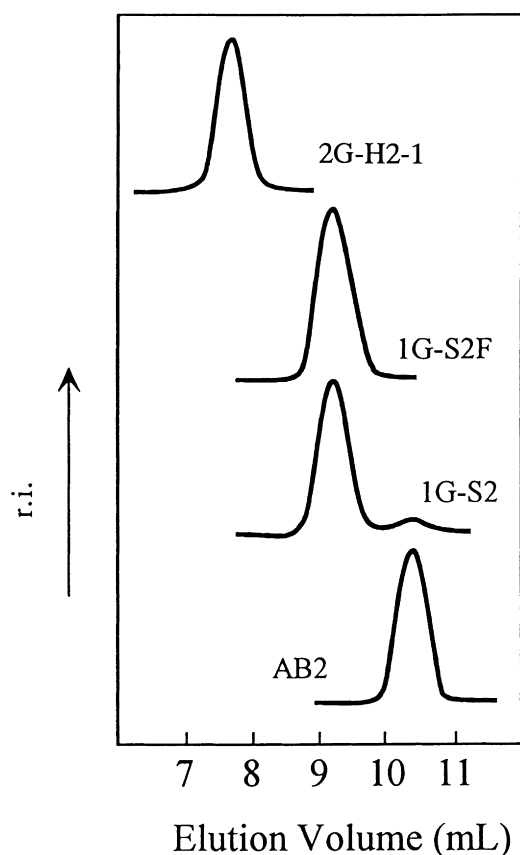

Fig. 1. GPC profiles of diblock copolymer precursor AB2, the first-generated star 1G-S2, star fraction 1G-S2F and the second-generated hyperbranched polymer 2G-H2-1.

with a nominal pore of 0.2 μm just before measurements. Solutions were measured in the concentration range of 2–10 mg ml^{-1}. The values of R_G of the first-generated stars (1G-S) prepared by this work were very small. It was impossible to evaluate R_G from SLS. The R_G was then determined by SAXS. The SAXS intensity distribution $I(\mathbf{q})$ was measured with a rotating-anode X-ray generator (Rigaku Denki Rotaflex RTP 300 RC) operated at 40 kV and 100 mA. The X-ray source was a monochromatized Cu K$_\alpha$ ($\lambda = 1.54$ Å) radiation. In the measurement of a benzene solution (1 wt%) of the sample, we used the cell sandwiched between mica plates as a holder vessel. The background correction was carried out using polyethylene film. The R_G values are estimated by Guinier's method from the following equation [25]

$$\ln I(\mathbf{q}) = \text{const} - (1/3)(R_G^2)\mathbf{q}^2 \qquad (2)$$

where $\mathbf{q}$ is the scattering vector.

The hydrodynamic radii (R_H) of 1G-S and 2G-H were determined using a dynamic light scattering (QELS; scattering angle = 90°, Otsuka Electronics Ltd) in 0.01 wt% benzene ($\eta = 0.654$ cp, $n_D = 1.501$) solution at 25°C. The intrinsic viscosity [η] of 2G-H was determined in benzene at 30°C with an Ubbelohde viscometer.

The content of P4MS in the P4MS-*block*-PS arm was determined by 500 MHz ^{1}H nuclear magnetic resonance (NMR) spectroscopy (JEOL GSX 500) in CDCl$_3$. In order to determine the degree of metalation reaction, the lithiated 1G-S was reacted with 2-(bromomethyl)naphthalene in THF. The resulting polymer was precipitated from methanol. The content of naphthalene groups in the 1G-S was determined by GPC equipped with refractive index (RI) and ultraviolet (UV) (characteristic absorption of naphthalene groups at 311 nm) double detectors (using a calibration constructed from the mixture of PS and naphthalene).

3. Results and discussion

3.1. Synthesis of the first-generated star polymers

Table 1 lists the characteristics of the P4MS-*block*-PS diblock copolymers (AB series). A typical GPC profile of AB2 is shown in Fig. 1. The GPC profile of AB2 has a single and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.09$). The content of P4MS units (16.0 numbers per molecule) was calculated by comparing the two integrated intensities between the aromatic protons ($\delta = 6.4$–7.3 ppm; PS and P4MS units) and the methyl protons ($\delta = 2.35$ ppm; P4MS units).

We prepared 1G-S with varying number of arms by varying the concentration ratio of DVB to P4MS-*block*-PS monoanions ([DVB]/[AB]). Table 2 lists the experimental conditions and the characteristics of the 1G-S stars. A typical GPC profile of the 1G-S2 star is shown in Fig. 1. The GPC distribution is bimodal according to the RI

Table 2
Experimental conditions and characteristics of 1G-S stars (copolymerized in benzene at 20°C for 48 h)

Experiment number	P4MS-*block*-PS		[DVB]/[AB] (mol mol^{-1})	1G-S star			
	Code	[AB] ($\times 10^3$ mol l^{-1})		$\bar{M}_w$[a] ($\times 10^{-5}$)	$\bar{M}_w/\bar{M}_n$[b]	Yield[b] (%)	n_1[c]
1G-S1	AB1	12.9	2.2	1.00	1.06	70	11.8
1G-S2	AB2	6.8	3.4	1.77	1.08	93	8.7

[a] Determined by GPC equipped with a low-angle laser-scattering detector.
[b] Determined by GPC equipped with an RI detector.
[c] Arm numbers per molecule.

monitor. The low molecular weight fraction was in agreement with the elution pattern of the AB2 diblock precursor. Therefore, the copolymerization product is a mixture of the 1G-S star and its precursor. Moreover, macrogelation was not observed in any of the experiments during copolymerization. Polymerization yields are in the range of 70–93%. Each 1G-S star was removed from the corresponding unreacted AB diblock precursor by the precipitation fractionation (benzene–methanol) system. The 1G-S star fraction is denoted as 1G-SF in the following discussion. The GPC profile of 1G-S2F is also shown in Fig. 1. The GPC distribution is unimodal. This star apparently had a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.08$). It should be noticed that the $\bar{M}_w/\bar{M}_n$ determined by GPC is overestimated when compared with the absolute values, because of highly branched structures. The arm numbers of 1G-S1F and 1G-S2F were 12 and 9 per molecule, respectively.

3.2. Synthesis of the second-generated hyperbranched polymers

The peripheral 4-methylstyrene units of 1G-SF were metalated with the *s*-BuLi/TMEDA 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 degree of lithiation was in the range of 56–72 mol% (see

Table 3). The unreacted *s*-BuLi was converted to lithium alkoxide by reaction with THF at 25°C.

2G-H was prepared by anionic equilibrium polymerization of the lithiated 1G-SF with MS in THF at −78°C. Simultaneously with the mixing of the monomer, the yellow color of polybenzylic anions changed to red (characteristic color of PMS anions). Table 3 lists the polymerization conditions and results of 2G-H.

A typical GPC profile of 2G-H2-1 is shown in Fig. 1. In this chart, a single narrow peak appears on the side of the high molecular weight compared to the starting of the 1G-S2F star. It is, therefore, suggested that this product is the hyperbranched polymer. The MS monomers were consumed with 100% conversion within an experimental error. It is also found that the unreacted *s*-BuLi/TMEDA complex was converted to lithium alkoxide by the reaction with THF. The $\bar{M}_w$ (2.57×10^6) was determined by SLS using the Zimm mode. The observed molecular weight distribution was very narrow ($\bar{M}_w/\bar{M}_n = 1.09$). Considering the anionic equilibrium polymerization of MS, the hyperbranched polymer 2G-H is judged to exhibit a monodispersed 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. P4MS units added to the second-generated arm end (2G-H2-1) were 22 (numbers per arm), as a calculated value from the feed amount.

The dilute-solution properties of 1G-SF and 2G-H are listed in Table 4. A typical Zimm plot and QELS data for

Table 3
Polymerization conditions and results of 2G-H (polymerized in THF at −78°C for 48 h)

Expt. No.	1G-SF[a]		MS (mol l^{-1})	4MS ($\times 10^2$ mol l^{-1})	Yield (%)	Hyperbranched polymer			
	Code	Polybenzylic anion ($\times 10^3$ mol l^{-1})				$\bar{M}_w$[b] ($\times 10^{-6}$)	$\bar{M}_w/\bar{M}_n$[c]	n_2[d]	P4MS units[e] (numbers per arm)
2G-H1-1	1G-S1F	4.15	0.293	3.73	100	0.69	1.06	71	9
2G-H1-2	1G-S1F	3.26	0.354	4.19	100	1.01	1.08	71	13
2G-H2-1	1G-S2F	1.13	0.293	2.51	100	2.57	1.09	78	22
2G-H2-2	1G-S2F	1.20	0.454	3.88	100	3.65	1.08	78	32

[a] Degree of metalation: 1G-S1F: 6 numbers per arm; 1G-S2F: 9 numbers per arm.
[b] Determined by SLS using the Zimm mode.
[c] Determined by GPC distribution.
[d] Arm number of the second-generation per molecule.
[e] Calculated value from the amount of feed monomer.

Table 4
Dilute-solution properties of star and hyperbranched polymers

Code	$\bar{M}_w{}^a$ ($\times 10^{-6}$)	$A_2{}^a$ ($\times 10^4$ ml mol g^{-1})	$R_G{}^a$ (nm)	$R_H{}^b$ (nm)	R_G/R_H	$[\eta]^c$ (dl g^{-1})	g'^d
1G-S1F	0.10	3.75	8.2^e	7.0	1.17		
2G-H1-1	0.69	1.89	20.9	21.7	0.96	54.6	0.331
2G-H1-2	1.01	2.03	30.0	29.3	1.01	89.0	0.411
1G-S2F	0.18	4.15	9.1^e	7.5	1.21		
2G-H2-1	2.57	1.54	56.1	47.4	1.18	131	0.309
2G-H2-2	3.65	2.30	57.9	49.1	1.18	148	0.271

[a] Determined by SLS.
[b] Determined by dynamic light scattering.
[c] Intrinsic viscosity in benzene at 30°C.
[d] $g' = [\eta]/[\eta]_i$: ratio of intrinsic viscosity of dendritic PMS to intrinsic viscosity of a linear PMS with the same molecular weight.
[e] Determined by SAXS using Guinier's plot.

2G-H2-1 are shown in Fig. 2a and b, respectively. The values of $\bar{M}_w$, A_2 and R_G of 2G-H2-1 in benzene were derived from Zimm plots (Fig. 2a). In order to discuss the hydrodynamic dimensions and the shape of hyperbranched polymers in solution, we determined the values of R_H (Fig. 2b) and $[\eta]$ in benzene, which are shown in Table 4.

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 second-generated hyperbranched polymers were in the range of 0.96–1.18. It is

Fig. 2. (a) Zimm plot (a); and (b) QELS data for the second-generated hyperbranched polymer 2G-H2-1.

well known that R_G/R_H for linear unperturbed polymers and hard spheres of uniform density is 1.25–1.37 [26] and 0.775 [27,28], respectively. In good solvents, even higher values of R_G/R_H (1.23–1.46) were observed for linear polystyrenes [29]. For regular star polymers, R_G/R_H approached unity at around an arm number of $n = 18$ [30,31]. Upon the introduction of more arms, the segment density increases in the coil and the segment-density distribution becomes uniform [32]. Both effects make star polymers resemble the hard sphere model more closely than the linear polymers. There is a report that R_G/R_H for regular polybutadiene stars ($64 < n < 128$) is in the range of 0.84–0.73 in a good solvent [33].

More recently, we prepared DVB core-crosslinked polyisoprene stars ($40 < n < 237$). The values of R_G/R_H in cyclohexane decreased gradually and approached unity as n became large [19]. As mentioned in Section 1, these stars led to the hierarchical structure transition of cubic lattices during film formation [17]. It is, therefore, reasonable for stars with multiarms to behave as soft spheres, and not as neat hard spheres, that are penetrable near the edge in a good solvent. Hence, it seems that such 2G-H also behave as soft sphere or loose star structures that are constructed with flexible chains in the inner core.

The dependence of the dimension of a hyperbranched polymer on its functionality can be expressed by means of the dimensionless parameter:

$$g' = [\eta]/[\eta]_l \tag{3}$$

where $[\eta]_l$ indicates the intrinsic viscosity of the linear polymer molecule with identical molecular weight. The intrinsic viscosity of linear poly(α(methylstyrene) (PMS) in benzene is given by [34]:

$$[\eta]_i = 1.03 \times 10^{-4} \bar{M}_w^{0.72} \text{ (dl g}^{-1}) \text{ at } 30°C \tag{4}$$

The values of g' are in the range of 0.27–0.41. The hydrodynamic dimension of hyperbranched polymers is smaller than that of linear polymers. The star polymer with arm number $n = 70$ exhibited the characteristics of $R_G/R_H = 1.05$ and $g' = 0.024$ [19]. This reflects chain stretching
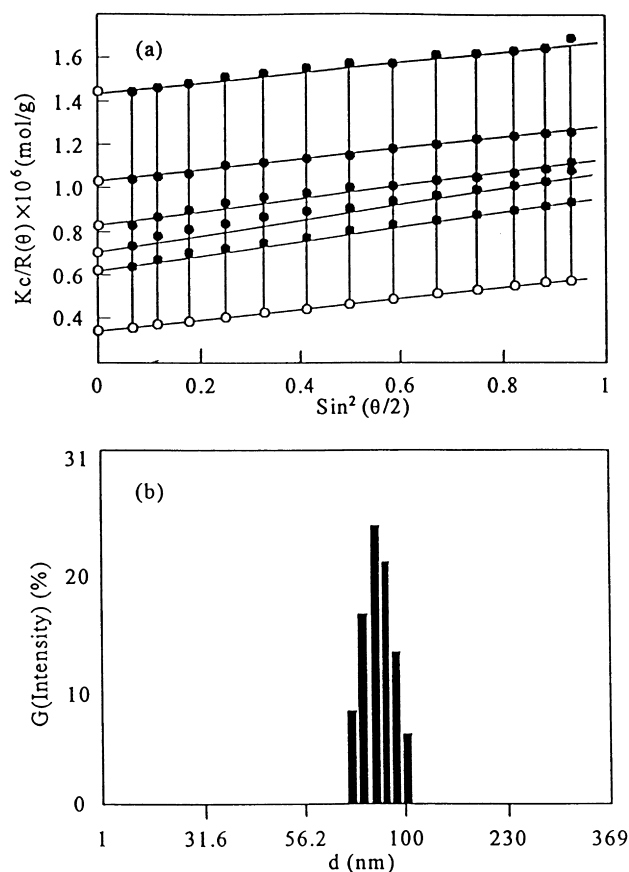
due to steric crowding of the star polymers. Therefore, the viscometric data also support the conclusion that the second-generated hyperbranched polymers assume the conformation of a loose star structure in a dilute solution. In order to increase the dense packing of hyperbranched polymers, the design of a high generation structure (higher than 3rd generation) of hyperbranched polymers seems necessary.

Dense packing is the most important feature of dendritic polymers. It is related to the distance between branching points, the volume of monomer and the branching multiplicities of both the core and building blocks. The void volume of dendritic polymers decreases with generation. Moreover, the density and the porosity are governed by the distance between branching points as well as by the type of molecular spacer employed. It is interesting to study whether the hyperbranched polymers composed of high generation structures show solution properties similar to the dendritic polymers described above. The results obtained will be reported in the near future.

References

[1] Tomalia DA, Baker H, Deward JR, Hall M, Kallos G, Martin S, Roech J, Smith P. Polym J 1985;17:117.
[2] Tomalia DA, Baker H, Deward JR, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P. Macromolecules 1986;19:2466.
[3] Hawker CJ, Frechet JMJ. J Chem Soc Chem Commun 1990:1010.
[4] Wooley KL, Hawker CJ, Frechet JMJ. J Chem Soc Perkin Trans 1 1991:1059.
[5] Tomalia DA, Naylor AM, Goddard WA. Angew Chem 1990;102:119.
[6] Frechet JMJ. Science 1994;263:1710.
[7] Tomalia DA. Adv Mater 1994;6:529.
[8] Newkome GR, Nayak A, Behera RK, Moorefield CN, Baker GR. J Org Chem 1992;57:358.
[9] Hawker CJ, Wooley KL, Frechet JMJ. J Chem Soc Perkin Trans 1 1993:1287.
[10] Percec V, Chu P, Kawasumi M. Macromolecules 1994;27:4441.
[11] Newkome GR, Moorefield CN, Keith J, Baker GR, Escamillo G. Angew Chem 1994;106:701.
[12] Gitsov I, Wooley KL, Frechet JMJ. Angew Chem 1992;104:1282.
[13] Gitsov I, Wooley KL, Hawker CJ, Ivanova P, Frechet JMJ. Macromolecules 1993;26:5621.
[14] Zimm BH, Stockmayer WH. J Chem Phys 1949;17:1301.
[15] Daoud M, Cotton JP. J Phys (Les Ulis Fr) 1982;43:531.
[16] Witten TA, Pincus PA, Cates ME. Europhys Lett 1986;2:137.
[17] Ishizu K, Ono T, Uchida S. J Colloid Interface Sci 1997;192:189.
[18] Ishizu K, Ono T, Uchida S. Polym Plast Technol Eng 1997;36:461.
[19] Ishizu K, Ono T, Uchida S. Macromol Chem Phys 1997;198:3255.
[20] Ishizu K, Uchida S. Polymer 1994;35:4712.
[21] Ishizu K, Uchida S. J Colloid Interface Sci 1995;175:293.
[22] Chung TC, Lu HL, Ding RD. Macromolecules 1997;30:1272.
[23] Ishizu K, Takahashi D, Takeda H. Macromol Chem Phys, in press.
[24] Grubisic Z, Rempp P, Benoit H. J Polym Sci B 1967;5:753.
[25] Katime I, Quintana JR. In: Booth C, Price C, editors. Comprehensive polymer science, 1. Oxford: Pergamon Press, 1989 (chap 5).
[26] Roovers J, Martin JE. J Polym Sci Part B Polym Phys 1989;27:2513.
[27] Yamakawa H. Modern theory of polymer solution, New York: Harper & Row, 1971. p. 321.
[28] Antonietti M, Bremser W, Schmidt M. Macromolecules 1990;23:3796.
[29] Bantel S, Schmidt M, Burchard W. Macromolecules 1982;15:1604.
[30] Solc K. Macromolecules 1973;6:378.
[31] Mattice WI. Macromolecules 1980;13:506.
[32] Stockmayer WH, Fixman M. Ann NY Acad Sci 1953;57:334.
[33] Roovers J, Zhou L-L, Toporowski PM, van der Zwan M, Iatrou H, Hadjichristidis N. Macromolecules 1993;26:4324.
[34] Sakato K, Kurata M. Polym J 1970;1:260.