8892 *Macromolecules* **2006,** *39,* 8892−8894

Synthesis and Characterization of Crystalline Hyperbranched Polysiloxysilane with POSS Groups at the Terminal Position

Makoto Seino, Teruaki Hayakawa, Yoshihito Ishida, and Masa-aki Kakimoto*

Department of Organic and Polymeric Materials,
Tokyo Institute of Technology, O-okayama, Meguro-ku,
Tokyo 152-8550, Japan

Received August 2, 2006
Revised Manuscript Received November 10, 2006

Introduction. Hyperbranched polymers have attracted much attention because of their special physical and chemical properties caused by the branching structure.[1] As compared to their linear analogues, hyperbranched polymers possess considerably higher solubility in organic solvents, lower viscosity, and decreased interchain entanglement. Hyperbranched polymers are typically prepared by growth polymerization of AB_n-type monomers, and the resulting macromolecules have a large number of terminal functional groups. The properties of hyperbranched polymers are extremely dependent on the terminal functional groups and can be tailored by chemical modification.

Dendritic polymers such as dendrimer and hyperbranched polymer are usually unable to crystallize due to their highly branched topology.[2] However, crystallization can be induced by the attachment of long alkyl chains as molecular scaffold.[3−7] For hyperbranched polymers, to date crystallization has only been studied to a very limited extent. Hult et al. have observed crystallization for aliphatic hyperbranched polyesters bearing alkyl chains with more than 12 carbons as terminal groups.[4] Frey et al. have systematically studied the thermal properties of crystalline esterified aliphatic hyperbranched polyether polyols.[5] In these cases, flexible long alkyl chains crystallize expelling the hyperbranched backbone, and the crystallinity depends on the length and substituent degree of the alkyl chains.

Recently, there has been considerable interest in organic−inorganic hybrid materials. In particular, polyhedral oligomeric silsesquioxane (POSS), which has a molecular sized silica-like cage structure and can be functionalized with a wide variety of organic groups, is an interesting class of inorganic components.[8] The incorporation of POSS into some polymers has led to enhancements in thermal and mechanical properties.[8a,b,f,j] POSS groups are dispersed as isolated aggregates and can form crystalline domains throughout polymer matrix.[9] The enhancement of properties is attributed to both dispersion and aggregation of POSS groups.

Among reported hyperbranched polymers so far, silicon-containing hyperbranched polymers are beginning to attract interest as new organic−inorganic hybrid materials.[10] Hyperbranched polysiloxysilane (HBPS) is an especially attractive material because of remarkable properties of the siloxane bond such as flexibility, thermal stability, and dielectric constant.[11] In addition, the terminal vinyl or hydrosilane (SiH) groups of HBPS can be modified easily by hydrosilylation reaction.[11a] In this study, we prepared HBPS with POSS groups at the terminal position to develop novel crystalline hyperbranched polymers.

Scheme 1

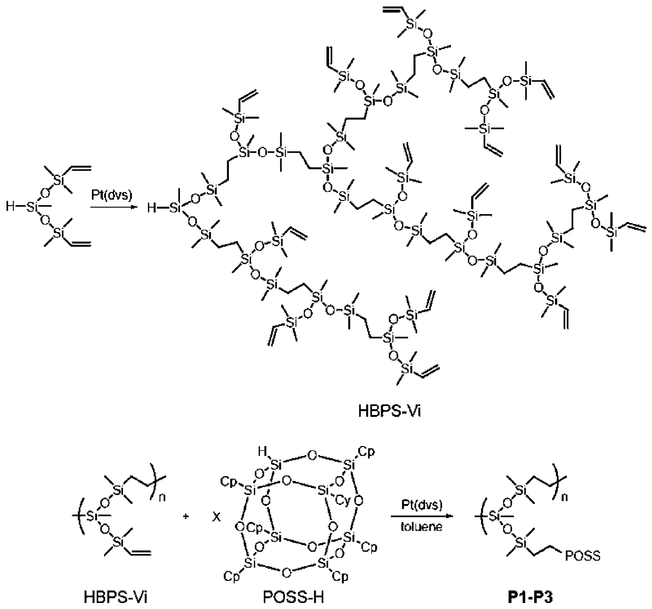

Table 1. Hydrosilylation Reaction of HBPS-Vi with POSS-H

polymer	POSS-H feed (X)[a]	POSS (%)[b]	M_w[c]	M_w/M_n[c]	T_g[d]	T_m[d]
P1	2.7[e]	100	24 300	1.4	18	233
P2	0.5	57	19 800	1.7	16	211
P3	0.2	21	15 600	1.7	18	167

[a] Equivalent with respect to HBPS-Vi. [b] Estimated from ^1H NMR spectra. [c] Determined by GPC against PS standard curve. [d] DSC: 10 °C/min from −50 to 270 °C under N_2 two cycles. Second heating was used for all calculations. [e] Done in two steps of 1.33 equiv.

Results and Discussion. HBPS having terminal vinyl groups (HBPS-Vi) was synthesized by the literature method.[12] The molecular weight of HBPS-Vi was $M_w = 9300$ and $M_w/M_n = 2.0$. HBPS with terminal POSS groups in varying amounts (**P1**−**P3**) were prepared by hydrosilylation reaction of HBPS-Vi with hydro-heptacyclopentyl-substituted POSS (POSS-H) (Scheme 1). **P1**−**P3** were isolated by preparative GPC, and unreacted POSS-H was removed completely. The molecular weights, substituent degrees of POSS groups, and thermal properties are summarized in Table 1. Although HBPS-Vi was a viscous liquid polymer, **P1**−**P3** were white solid materials. The molecular weight of polymers increased in proportion to the feed amount of POSS-H. The chemical structures of **P1**−**P3** were characterized by NMR and IR spectra.[13] There is no vinyl signal in the ^1H NMR spectrum of **P1**, indicating that all vinyl groups were hydrosilylated with POSS groups. The ^1H NMR spectra of **P2** and **P3** showed residual vinyl signals. The substituent degrees of POSS groups of **P2** and **P3** were calculated to 57% and 21%, respectively, from the relative integral ratio of remained vinyl groups. The values correspond to the feed amounts of POSS-H.

Thermal behavior of **P1**−**P3** was investigated by differential scanning calorimetry (DSC). **P1**−**P3** display both a glass transition temperature (T_g) and a melting point (T_m). For **P1**−**P3**, the T_g is increased compared to the T_g of HBPS-Vi, and a T_m is now observed, which is assumed to be due to POSS regions as HBPS-Vi is amorphous. It should be emphasized that POSS-H decomposes before a T_m is observed. The increase of

---

* Corresponding author: e-mail mkakimot@o.cc.titech.ac.jp; Tel +81-3-5734-2433; Fax +81-3-5734-2875.

10.1021/ma061748q CCC: $33.50

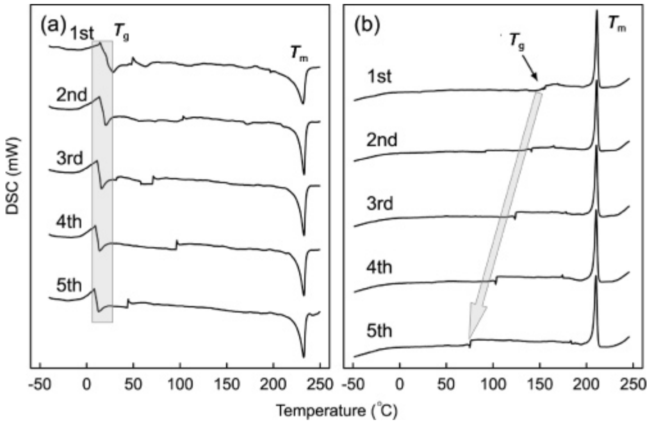

Figure 1. DSC diagrams of **P1**: heating (a) and cooling (b).

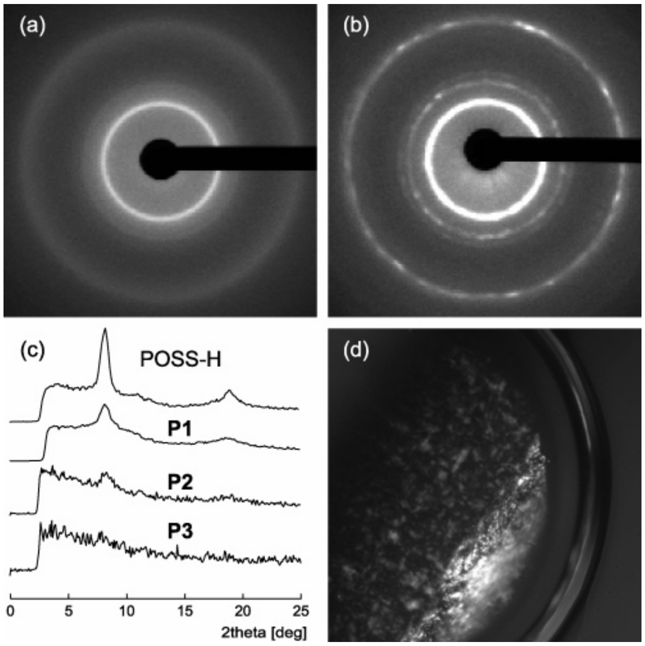

Figure 2. Wide-angle X-ray scattering patterns of **P1** (a) and POSS-H (b). Optical density of scattering angle 2θ of the patterns of POSS-H, **P1**, **P2**, and **P3** (c). Micrograph of **P1** under cross polarizer (d).

T_g can be explained by the steric effect and interaction of POSS groups, which restrict polymer motion.[7b] The decrease of T_m is considered because the hyperbranched polysiloxysilane backbone interferes with crystallization of POSS groups and makes the crystal domain size smaller. As seen in Table 1, the T_m decrease with decreasing content of POSS groups, indicating that the crystallinity is dependent on the content of POSS groups, since the higher content of POSS groups should make aggregates and crystalline domains more easily. In order to investigate the crystallization behavior of **P1**−**P3**, DSC curves were measured for five heating/cooling cycles. Figure 1 shows DSC curves of **P1** for five heating/cooling cycles. Interestingly, the T_g decreased gradually with increasing cycles. (For **P2** and **P3**, the T_g peaks during cooling were unobservable.) These findings suggest that POSS phase separates gradually into aggregates from hyperbranched siloxysilane segments by repetition of melt and recrystallization. The T_g and decreasing change in cooling are higher than those in heating. These are considered because POSS crystal domains formed in cooling retard polymer motion, and the POSS obstacle is decreased with phase separating.

The crystallinity of **P1**−**P3** was characterized by X-ray diffraction. The wide-angle X-ray scattering (WAXS) patterns of **P1** and POSS-H are shown in Figure 2a,b. In the pattern of **P1**, the two typical crystalline peaks of POSS molecules were observed at 8.22° and 18.82° (*d*-spacings 10.76 and 4.72).[9] **P1** showed a very similar diffraction pattern to POSS-H, suggesting that the crystal structure of **P1** is the same as that of POSS-H, which has a hexagonally packed structure.[14] The terminal POSS groups seem to aggregate and form crystal domains, leaving the hyperbranched polysiloxysilane backbone unaffected. The optical densities of scattering angle 2θ of the patterns of **P1**−**P3** and POSS-H (Figure 2c) reveal that the degree of crystallinity is proportional to the content of POSS groups as mentioned above.

To investigate the growth of crystallites, **P1**−**P3** were heated to the melt and cooled slowly below the melting point. The micrograph of **P1** clearly demonstrates that **P1** forms crystallites (Figure 2d). This indicates that crystallinity can be induced by the attachment of POSS groups to chain end of HBPS as molecular scaffold. In the cases of **P2** and **P3**, crystallites were not observed.

In summary, we have synthesized HBPS with POSS groups at the terminal position with controllable extent of substitution. The POSS groups crystallize, and the degree of crystallinity was proportional to the content of POSS groups. The use of POSS as assembling block is possible to create new crystalline hyperbranched polymers.

Acknowledgment. The authors thank Prof. Junji Watanabe, Prof. Masatoshi Tokita, and Dr. Stephen J. Grunzinger of Tokyo Institute of Technology for helpful discussions. This work was supported by a Giant-in Aid for Scientific Research from the Ministry of Education, Culture Science, Sports and Technology, Japan, No. 16350030.

Supporting Information Available: Experimental procedures and characterization data for HBPS-Vi, **P1**, **P2**, and **P3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gan, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183.

(2) Kim, Y. H. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 1685.

(3) Schenning, A. P. H. J.; Elissen-Román, C.; Weener, J.; Baars, M. W. P. L.; van der Gaast, S. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 8199.

(4) Malmström, E.; Johansson, M.; Hult, A. *Macromol. Chem. Phys.* **1996**, *197*, 3199.

(5) Sunder, A.; Bauer, T.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 1330.

(6) Wei, H.; Shi, W.; Shen, X.; Nie, K. *Eur. Polym. J.* **2002**, *38*, 1899.

(7) Ornatska, M.; Peleshanko, S.; Genson, K. L.; Rybak, B.; Bergman, K. N.; Tsukruk, V. V. *J. Am. Chem. Soc.* **2004,** *126*, 9675.

(8) For examples, see: (a) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435. (b) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302. (c) Harrison, P. G.; Kanneng-iesser, R. *Chem. Commun.* **1996**, 415. (d) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380. (e) Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1999**, *32*, 1194. (f) Fu, B. X.; Zhang, W. H.; Hsiano, B. S.; Rafailovich, M.; Sokolov, J.; Sauer, B. B.; Phillips, S.; Blanski, R. *High Perform. Polym.* **2000**, *12*, 565. (g) Choi, J.; Harcup, J.; Yee, A. F.; Zhu, Q.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 11420. (h) Zheng, L.; Farris, J.; Coughlin, E. B. *Macromolecules* **2001**, *34*, 8034. (i) Devaux, E.; Rochery, M.; Bourbigot, S. *Fire Mater.* **2002**, *26*, 149. (j) Xu, H.; Kuo, S.; Lee, J.; Chang, F. *Macromolecules* **2002**, *35*, 8788.

(9) (a) Romo-Uribe, A.; Mather, R. T.; Haddad, T. S.; Lichtenhan, J. D. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1857. (b) Fu, B. X.; Hsiao, B. S.; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. T.; Jeon, H. G.; Phillips, S.; Lichtenhan, J.; Schwab, J. *Polymer* **2001**, *42*, 599. (c) Zeng, L.; Waddon, A. J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375. (d)

Waddon, A. J.; Zehng, L.; Farris, R. J.; Coughlin, E. B. *Nano Lett.* **2002**, *2*, 1149.

(10) Jones, R. G., Ando, W., Chojnowski, J., Eds. *Silicon-Containg Polymers*; Netherlands, 2000.

(11) (a) Miravet, J. F.; Fréchet, J. M. J. *Macromolecules* **1998**, *31*, 3461. (b) Rubinsztajn, S. *J. Inorg. Organomet. Polym.* **1994**, *4*, 61. (c) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(12) Seino, M.; Yokomachi, K.; Hayakawa, T.; Kikuchi, R.; Kakimoto, M.; Horiuchi, S. *Polymer* **2006**, *47*, 1946.

(13) For detailed synthetic procedures and characterization, see the Supporting Information.

(14) (a) Waddon, A. J.; Coughlin, E. B. *Chem. Mater.* **2003**, *15*, 4555. (b) Barry, A. J.; Daudt, W. H.; Domicone, J. J.; Gilkey, J. W. *J. Am. Chem. Soc.* **1955**, *77*, 4248.

MA061748Q