

Preparation and Properties of Novel Hyperbranched Poly(dimethylsiloxane)s

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ABSTRACT: Hyperbranched poly(dimethylsiloxane)s (HPDMSs) were synthesized by the self polycondensation of an AB₂ monomer, [bis(diethylaminodimethylsiloxy)methylsiloxy]dimethylsilanol that was generated *in situ* from a precursor compound, [bis(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol, with bromine and diethylamine. The polymerization was carried out at 80°C without any catalysts. The molecular weight (M_w) of HPDMSs increased with elapsing of the reaction time from 5700 to 11500, where HPDMSs turned from liquid to solid with increasing M_w . HPDMSs with lower M_w showed good solubility from nonpolar solvents to methanol, while higher M_w ones dissolved in ethyl ether and tetrahydrofuran. Dimethylphenylsilyl group was introduced as an end group by adding dimethylphenylsilanol at the end of the polymerization. As the end silane-phenyl bond is cleaved with irradiation of UV light, the properties of HPDMSs with phenylsilyl end group such as viscosity, solubility and T_g were changed after UV irradiation.

KEY WORDS Poly(dimethylsiloxane) (PDMS) / Hyperbranched Poly(dimethylsiloxane) (HPDMS) /

Linear poly(dimethylsiloxane)s (PDMSs) are widely used in commercial applications^{1–3} such as adhesion, coating, dielectric fluids, antifoams, medical, and pharmaceutical applications, because of their outstanding properties.^{3,4,18} Recently, the interest of hyperbranched polymers has been increasing at an amazing rate because they^{5–7} are the nearest analogs of dendrimers having specific rheological properties coming from their globular shape and high functionalities caused by a number of terminals. Although dendrimers are usually synthesized by complicated multi-step reactions,¹⁰ the preparation of hyperbranched polymers consists of a simpler one-step self polycondensation of AB_x type monomers.^{7–9} The study of siloxy-type hyperbranched polymers must be an especially appealing target, if one considers the wide-spread applications of linear poly(siloxane)s^{3,11} as mentioned above. According to the literatures, hyperbranched polysiloxanes, such as poly(siloxysilane)s^{12–14} poly(alkoxysilane)s¹⁵ and poly(carbosiloxane)s¹⁶ obtained by continuous hydrosilylation reaction starting from monomers containing silylhydride and alkene functionalities,¹⁷ have been reported. In these cases, the repeating units are always composed of silane-carbon moiety as well as silane-oxygen one. Although we reported stepwise synthesis of poly(dimethylsiloxane) dendrimers¹⁸ consisted of only silane-oxygen main frame, hyperbranched poly(dimethylsiloxane)s (HPDMSs) prepared by one step synthesis have not been reported so far. HPDMSs, which is supposed to have features useful in various areas such as catalysts, adhesives, and surface

active materials,¹⁹ would be readily modified and modulated by the introduction of the tunable end groups.

In this work, we report the synthesis of novel HPDMSs by continuous formation of siloxane bond starting from an AB₂ monomer.

EXPERIMENTAL

Measurements

¹H, ¹³C NMR, and ²⁹Si NMR measurements were carried out by a JEOL JNM-AL 300 MHz spectrometer in CDCl₃ without TMS. Infrared (IR) spectra were obtained using a Shimadzu FT-IR 8100 Fourier transform infrared spectrophotometer. Gel permeation chromatography (GPC) measurements were performed with tetrahydrofuran (THF) as an eluent using a JASCO HPLC 880PU with a Shodex KF-802.5 column. Vapor pressure osmometry (VPO) measurements were performed in benzene using a Corona Electric VPO at 40°C. Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a Seiko TGA 6200 and a Seiko DSC 6200 with a heating rate 10°C min⁻¹ under N₂. Inherent viscosities (η_{inh} s) were measured by use of an Ostwald-type capillary viscometer in THF at 30°C at a concentration of 0.05 g dL⁻¹.

Materials

N,N-diethylamine and bromobenzene were purified by distillation. Dichlorodimethylsilane and trichloromethylsilane were purchased from Aldrich chemical company and used without further purification. The

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solvents such as THF, diethyl ether, and hexane were dried by distillation over sodium benzophenone ketyl. Carbon tetrachloride was distilled over CaCl₂.

Preparation of AB₂ Monomer. [Bis(phenyldimethylsiloxy)methylsiloxy]dimethylsilanol(6) was prepared by method as precviously reported.¹⁸

Preparation of Hyperbranched Poly(dimethylsiloxane) (HPDMS); P4. To a solution of 14.9 g (0.034 mol) of 6 in 500 mL of carbon tetrachloride, bromine solution of 28.3 mL (3 mol L⁻¹ carbon tetrachloride) was added. The solution was stirred at room temperature for 60 min. Excess of bromine was quenched by flowing the reaction vessel with ethylene gas. To the obtained colorless solution, 9.96 g (0.14 mol) of diethylamine was dropped at room temperature. After the mixture was refluxed for 24 h, 15.5 g (0.102 mol) of dimethylphenylsilanol was added, and refluxed for additional 24 h. The mixture was diluted with 200 mL of ether and washed with 200 mL of water. The organic layer was dried over anhydrous magnesium sulfate, and HPDMS was obtained by precipitation from THF with hexane. Yield 69%, $M_w/M_n = 1.70$. ¹H NMR (CDCl₃, δ ppm); 7.54 (m), 7.32 (m), 0.33 (s), 0.14 (t), 0.06 (d). ¹³C NMR (CDCl₃, δ ppm); 133.01, 129.16, 127.61, 0.70 (m), -2.3, -2.7. ²⁹Si NMR (CDCl₃, δ ppm); -1.76, -7.44, -16.66, -21.26, -57.37, -65.67. IR (KBr, cm⁻¹); 3074, 2905, 1427, 1259, 1118, 1026, 831, 790, 700. Elemental Anal. Calcd for C₁₅H₃₂O₅Si₅: C, 41.23; H, 7.58. Found: C, 41.13; H, 7.46

Preparation of Model Compound (9). Bis(phenyldimethylsiloxy)methyl(diethylamino)silane (5-NEt₂). The diethylamine 29.3 g (0.4 mol) in 100 mL of ether was slowly dropped to the solution of 76.2 g (0.2 mol) of 5 in 600 mL of ether at room temperature. After the mixture was stirred for 1 h, and filtered the diethylaminehydrochloride under N₂. The solution was evaporated and distilled *in vacuo* to afford the pure [Bis(phenyldimethylsiloxy)methyl(diethylamino)silane. Yield 83%, bp 132°C (0.5 mmHg) ¹H NMR (CDCl₃, δ ppm); 7.42 (m,10H), 2.94 (q,4H), 0.98 (t,6H), 0.35 (s,12H), 0.25 (s,3H).

Bis(phenyldimethylsiloxy)methylsilanol (5-OH). To 150 mL of 3.1 g (0.17 mol) of water was added 71.0g (0.17 mol) of 5-NEt₂ at 0°C, and after the solution was stirred for 30 min vigorously, separated the organic layer. The extract was dried over anhydrous magnesium sulfate, evaporated and distilled *in vacuo* under N₂. The pure [Bis(phenyldimethylsiloxy)methylsilanol was obtained as colorless liquid. Yield 67%, bp 135°C (0.5 mmHg) ¹H NMR (CDCl₃, δ ppm); 7.35 (m, 10H), 0.43 (s,12H), 0.33 (s,3H).

[Bis(diethylaminodimethylsiloxy)methylsiloxy]dimethylchlorosilane (8-Cl). The 91.7 mL (3 M) of Br₂ was added to solution of 40.3 g (0.11 mol) of 5-OH in 150 mL of carbon tetrachloride. After the mixture was stirred for 1 h at room temperature, the excess Br₂ was quenched by ethylene gas. To the solution, 32.9 g (0.45 mol) of diethylamine was dropped at room temperature and the mixture was stirred for 30 min.

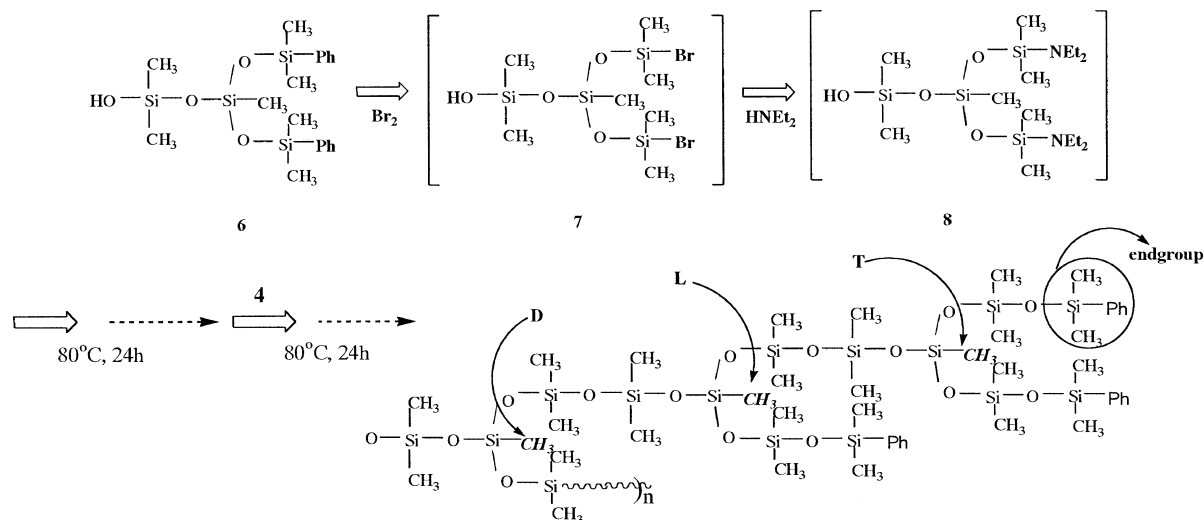
The amino-substituted 5 solution was filtered under N₂, and added to 14.2 g (0.11 mol) of dichlorodimethylsilane and 11.1 g (0.11 mol) of TEA in 200 mL of ether. The mixture was stirred for 2 h at 20°C and filtered the triethylaminehydrochloride. After evaporation of the solvent, pure [Bis(diethylaminodimethylsiloxy)methylsiloxy]dimethylchlorosilane was obtained by distillation *in vacuo*. Yield 48%, bp 152°C (0.5 mmHg). ¹H NMR (CDCl₃, δ ppm); 2.94 (q,4H), 0.97 (t,6H), 0.43 (s,12H), 0.21 (s,6H), 0.14 (s,3H).

Bis[Bis(phenyldimethylsiloxy)methylsiloxy]-di-dimethylsiloxy methylsiloxydimethylsilanol (9). The solution which have 22.7 g (0.05 mol) of 8-Cl and 46.1 g (0.11 mol) of 6 in 350 mL of carbon tetrachloride was stirred for 8 h at 80°C. After the solution was cooled at room temperature, added 1.3 g (0.07 mol) of water and was stirred for 30 min. The organic layer was separated and the extract was dried over anhydrous magnesium sulfate. The pure compound 9 was obtained by evaporation of solvent and distillation *in vacuo*. Yield 54%, bp 195°(0.01 mmHg).¹H NMR (CDCl₃, δ ppm); 7.47(m, 20H), 0.14(s, 30H), 0.43 (s, 24H), 0.06(s, 6H)

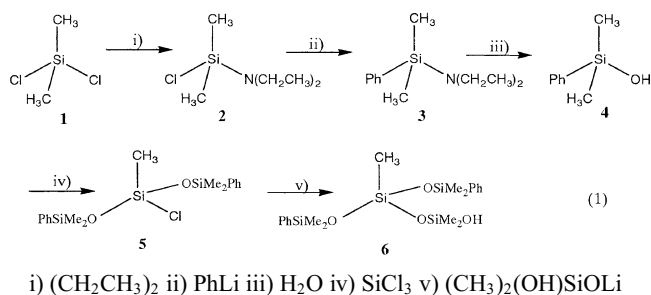
RESULTS AND DISCUSSION

Monomer Synthesis

The AB₂ monomer was designed to have one nucleophilic silanol and two electrophilic silane atom (Si⁺ species), that was diethylaminosilane unit. In the previous paper¹⁸ for the preparation of dimethylsiloxane dendrimers, we showed that diethylaminosilane groups generated from phenylsilane were highly reactive forward silanol units to form siloxane bonds. Due to the high reactivity, the diethylaminosilane groups were prepared *in situ* by the addition of diethylamine to the corresponding silylbromide solution which was also prepared from the corresponding phenylsilanes and bromine without isolation. This unique synthetic method was employed as a propagation reaction for the synthesis of HPDMSs in the present study. Thus, the AB₂ monomer possessing diethylaminosilanes as the Si⁺ species was obtained by *in situ* operation starting from the precursor compound having phenylsilane. Preparation of the precursor,



[bis(dimethylphenylsiloxy)methylsiloxy]dimethylsilanol **6**, is shown in eq 1.



Dimethylphenylsilanol **4** was prepared by hydrolysis of compound **3** that was prepared from dichlorodimethylsilane *via* diethylamination and the following reaction with phenyllithium. The precursor **6** was synthesized by the reaction between **4** and methyltrichlorosilane, then the subsequent addition of dimethylsilanediol. As shown in Scheme 1, AB_2 monomer **8** that was not isolated because of instability against moisture was prepared by the treatment of precursor **6** in carbon tetrachloride with bromine to produce silylbromide **7**, and then with diethyl amine.

Polymerization

Polymerization of AB_2 monomer **8** that was generated from the precursor **6** *in situ* was proceeded through the formation of siloxane bond. The obtained HPDMSs had the diethylaminosilyl terminal group. When the polymerization was carried out at room temperature for 24 h, a clear liquid was isolated. GC-mass measurement of the liquid only showed the unreacted AB_2 monomer which was substituted trimethylsilyl group. Therefore, the reaction was increased to 80°C . The results of the polymerization are summarized in Table I.

Table I. Results of polymerizaion

Entry	Time ^c h	State	M_n^d $\times 10^3$	M_w/M_n^e	T_g K	Yield %
P1 ^a	8	liq.	3.2	1.83	—	48
P2 ^a	16	liq.	6.3	1.46	—	74
P3 ^a	24	sol.	9.8	1.69	168	53
P4 ^b	48	sol.	10.2	1.42	181	69

^a(P1–P3) polymers before the endcapping. ^bA polymer having dimethylphenylsilyl terminal. ^cPolymerization was proceeded underdry N_2 in CCl_4 at 80°C . ^dDetermined by VPO in benzene and calculated based on polystyrene standard. ^eDetermined by GPC with THF as eluent.

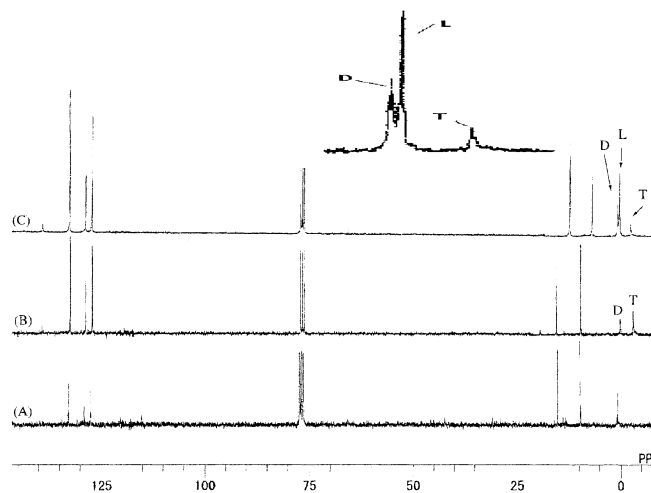
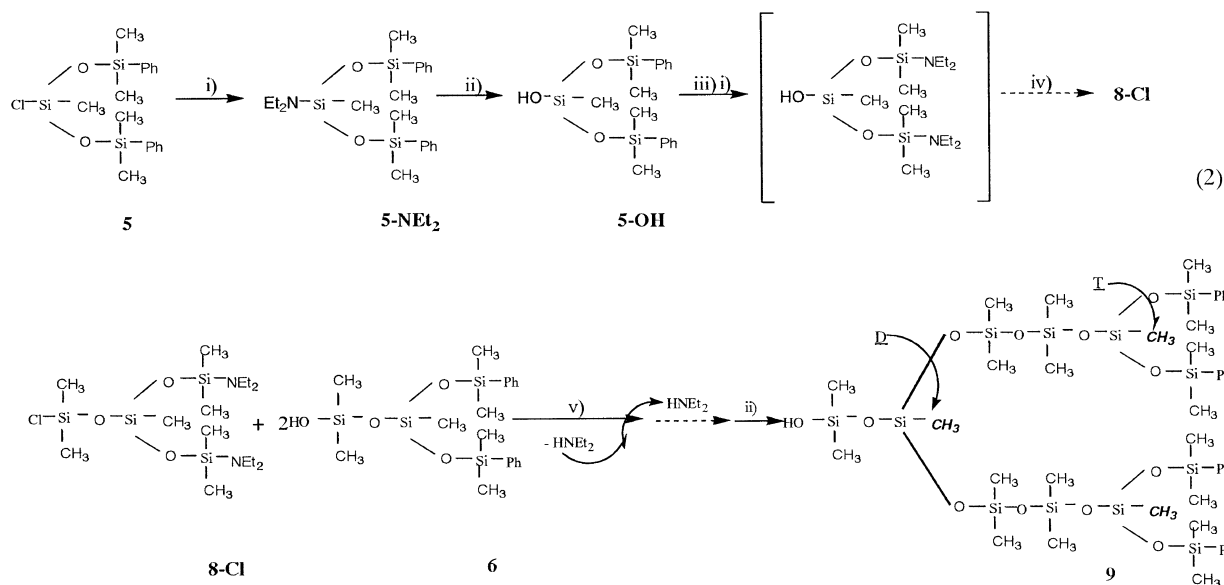


Figure 1. ^{13}C NMR spectra of monomer, precursor **6** (A), model compound **9** (B), and polymer (C).

The molecular weights increased gradually with increasing reaction time, where polymers **P1** and **P2** were obtained as colorless liquid while **P3** with 24 h reaction time and **P4** endcapped with dimethylphenylsilyl group were solid.

The degree of branching of HPDMSs was determined by ^{13}C NMR spectroscopy (Figure 1). Methyl



i) $(\text{CH}_2\text{CH}_3)_2\text{NH}$ ii) H_2O iii) $\text{Br}_2, \text{CH}_2=\text{CH}_2$. iv) $\text{Me}_2\text{SiCl}_2, \text{TEA}$ v) 80°C 8 h

groups at the branching silicon atom ($\text{Si}(\text{CH}_3)$) in the polymers must exist in one of three possible local environments as illustrated in scheme I. The model compound **9** was prepared as shown in eq 2. From these spectral data, the ratio of D:L:T in **P4** is calculated as 1:2.02:0.93. Using the equations derived by Frey and co-workers,²⁰ we obtained the degree of branching (DB) was calculated to be 0.49. However, if considering unusually high integration of the D compared with other units (L,T), **P4** is regarded that might contain the cyclic dimethylsiloxane structures.

Physical Properties of HPDMSs. Table I shows glass transition temperature (T_g) of HPDMSs. The polymer having diethyl amine terminal groups, **P3** exhibited relatively higher T_g of 168 K compared with 146 K of linear PDMS that reflects the curvature structure of the HPDMS. The fact that **P4** possessed a 13 K higher T_g compared with that of **P3** suggested that introduction of the bulky terminal group, **4** increased the T_g of HPDMSs.

As shown in Table II, solubility of HPDMSs depended on their molecular weight. **P1** and **P2** were soluble in variety of solvents including the less polar organic solvents and methanol. The solubility of **P3** was restricted in comparison with those of **P1** and **P2**. Polymer **P4**, which has dimethylphenylsilyl terminal group, was soluble in benzene and methanol as well as ether type solvents. That is, the solubility of HPDMSs was much better than that of linear PDMSs that are only soluble in less polar solvent such as toluene. The wide range of solubility of HPDMSs is caused by highly branched chemical structure.

Figure 2 presents the change of the UV-visible absorption spectra of the **P4** film before and after the irra-

Table II. Solubility of Hyperbranched poly(dimethylsiloxane)

Polymer ^a	CCl_4	Hexane	Benzene	Et_2O	THF	MeOH
P1	⊙	⊙	⊙	⊙	⊙	⊙
P2	⊙	⊙	⊙	⊙	⊙	⊙
P3	●	●	●	⊙	⊙	○
P4	●	●	○	⊙	⊙	○

^aPolymer (● insoluble ○ partially soluble ⊙ soluble).

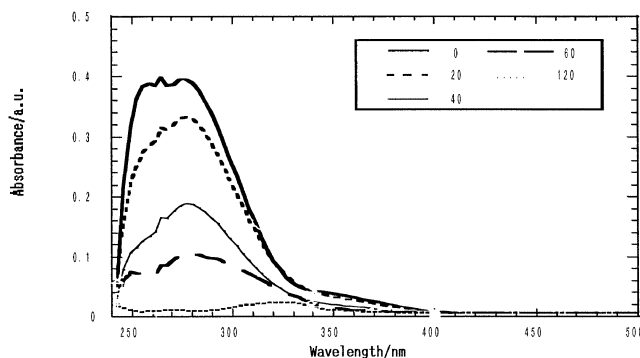


Figure 2. UV-Vis. absorption spectra of HPDMS(**P4**) with irradiation of UV light.

diation of UV light. Due to the unique terminal group, **P4** showed a medium strength of absorption caused by the $\pi-\pi^*$ transition of phenyl group in the phenyl-silane. With elapsing of the UV irradiation time, the absorption decreased, which was caused by the cleavage of silane-phenyl bond. As shown in Table III, change of some properties such as the increase of T_g and viscosities, and the decrease of solubility in solvents was observed after UV irradiation to **P4**. As it³ is known that phenyl-silane bond can be cleaved by UV irradiation to afford silyl and phenyl radicals, the crosslinking reaction between terminal silyl radicals might produced

Table III. Changes of properties of HPDMSs after UV irradiation

	M_w/M_n	η_{inh}	T_g	Solubility		
	$\times 10^4$	$dL g^{-1}$	K	Et ₂ O	THF	MeOH
P4	1.05/0.74	0.045	181	○	⊙	○
P4a	2.45/1.76	0.133	197	●	○	●

P4; before irradiation of UV light. P4a; after irradiation of UV light.

higher molecular weight of HPDMSs.

CONCLUSION

HPDMSs were prepared by the self polycondensation of a new AB₂ monomer containing one silanol and two diethylaminosilyl groups. These hyperbranched polymers exhibited high solubility and low viscosities, and showed slightly higher T_g s than those of the linear PDMSs. The T_g s depended on the terminal chemical structure. In the case of **P4** possessing phenyl-silane terminal group, crosslinking reaction was observed by UV irradiation. The UV induced crosslinking might be used for interesting applications, such as photoresist introducing block copolymer system.

REFERENCES

1. a) L. S. Miller, A. L. Rhoden, N. Byrne, J. Heptinstall, and D. J. Walton, "Materials Science and Engineering", 1995, p187.
b) C. Todd and T. Byers, *Cosmet. Toil*, **91**, 29 (1996).
2. R. Kobayashi, S. Yobe, and T. Nomura, *Polym. Adv. Technol.*, **8**, 351 (1997).
3. a) S. J. Clarson, J. A. Semlyen, "Siloxane Polymers", 1993.
b) P. R. Dvornic, R. W. Lenz, "High Temperature Siloxane Elastomers", Hüthig & Wepf Publishers, Neugasse, 1990 Base1.
c) J. M. Zeigler and F. W. Gordon Fearon, Ed., "Silicon-Based Polymer Science: A Comprehensive Resource", Advanced in Chemistry Series No. 224, American Chemical Society, Washington, D.C., 1989, chapt. 1.
4. J. E. Mark, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **38(1)**, 437 (1999).
5. a) S. R. Turner and B. I. Voit, *Polymer news.*, **22**, 197 (1997).
b) J. M. J. Fréchet and C. J. Hawker, *React. Funct. Polym.*, **26**, 127 (1995).
c) B. I. Voit, *Acta Polym.*, **46**, 87 (1995).
6. E. Malmström and A. Hult, *Macromol. Chem. Phys.*, **197**, 3199 (1996).
7. a) Y. H. Kim, O. W. Webster, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **29(2)**, 310 (1988).
b) Y. H. Kim, O. W. Webster, *J. Am. Chem. Soc.*, **112**, 4592 (1990).
8. Y. H. Kim, U. S. Patent 4 857 630 (Aug. 15, 1989).
9. Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, **112**, 4592 (1990).
10. a) J. M. J. Fréchet, *Science*, **263**, 1710 (1994).
b) D. A. Tomalia, A. M. Naylor, and W. Goddad, *Angew. Chem.*, **102**, 119 (1990).
c) G. R. J. Newkome, *Adv. Heterocycl. Chem.*, **33**, 1445 (1996).
11. a) J. Li, Z. Li, C. Zhan, J. Qin, and Y. Li, *Synth. Met.*, **101**, 127 (1999).
b) H. Jiang and A. K. Kakkar, *Macromolecules*, **31**, 4170 (1998).
12. F. J. Miravet and J. M. J. Fréchet, *Macromolecules*, **31**, 3461 (1998).
13. a) L. J. Mathias and T. W. Carothers, *J. Am. Chem. Soc.*, **113**, 4043 (1991).
b) C. Gong, J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 2970 (2000).
14. S. J. Rubinsztajn, *J. Inorg. Organomet. Polym.*, **4**, 61 (1994).
15. V. V. Kazakova, V. D. Myakushev, T. V. Strelkova, and A. M. Muzafarov, *Polym. Sci. Ser. A*, **41**, 283 (1999).
16. C. Lach, P. Müller, H. Frey, R. Mulhaupt, *Macromol. Rapid Commun.*, **18**, 253 (1997).
17. a) A. M. Muzafarov, M. Golly, and M. Möller, *Macromolecules*, **28**, 8444 (1995).
b) L. J. Mathias, T. W. Carothers, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **32(3)**, 633 (1991).
18. A. Morikawa, M. Kakimoto, and Y. Imai, *Macromolecules*, **24**, 3469 (1991).
19. a) J. Michl, *Chem. Rev.*, **95**, 1135 (1995).
b) M. G. Steinmetz, *Chem. Rev.*, **95**, 1527 (1995).
c) H. N. Waltenburg and J. T. Yates, Jr., *Chem. Rev.*, **95**, 1589, (1995).
20. D. Hölter and H. Frey, *Acta Polym.*, **48**, 298 (1997).