Synthesis of thioether derivatives of hyperbranched carbosilane polymer*

*A. N. Tarasenkov,[a] E. V. Getmanova,[a] M. I. Buzin,[b] N. M. Surin,[a] and A. M. Muzafarov[a]**

[a]*N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, 70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation, Fax: +7 (495) 335 9000. E-mail: antarr@bk.ru*
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5085*

Novel hyperbranched functional and non-functional carbosilane polymers bearing the thioether groups were synthesized. Thioether derivatives were prepared by the UV initiated hydrothiolation of the hyperbranched poly(allyl)carbosilane polymer with 1-decanethiol and 3-mercaptopropyl(methyl)dimethoxysilane.

Key words: hyperbranched polycarbosilane, hydrothiolation, 1-decanethiol, 3-mercaptopropyl(methyl)dimethoxysilane.

Elaboration of new methodologies for the synthesis and modification of dendric macromolecules is an ongoing challenge for the continued success in this field of polymer chemistry. Highly selective reactions producing little or no byproducts and working well under desired conditions,[1,2] so called "click reactions", are valuable synthetic tool. Efficiency of this approach for the synthesis of dendric macromolecules was demonstrated[3,4] by the preparation of the fourth—sixth generation dendrimers bearing ester groups on the base of thriazine. For organosilicon dendrimers and especially for carbosilane systems, extensively used hydrosilylation reaction is of particular value. The only limitation of this unique reaction is the need for the platinum catalyst. From this point of view, hydrothiolation of the multiple bonds is of great interest as it is initiated by UV irradiation, characterized by quantitative conversion of the functional groups, and, therefore, easily scalable.

The urgency of the subject is confirmed by the recently published works[5,6] devoted to the synthesis of various polyfunctional compounds and carbosilane dendrimers. Synthesis of thiol derivatives of carbosilane dendrimers was realized earlier,[7,8] however, the authors used nucleophilic substitution, which resulted in the precipitate formation and required its additional separation step. The radical reactions are free from these drawbacks allowing significant simplification of the protocol.

In addition to more simple and efficient protocol, introduction of the thiol groups in carbosilane dendrimer structure opens prospects for complexation with transition metal salts and design of novel materials and molecular devices.[9] Hydrothiolation should be considered as a process expanding the molecular design capabilities in this field rather than an alternative to hydrosilylation.

Introduction of new elements in a molecular structure of hyperbranched polymers is also of great importance. Among carbosilane dendrimers, hyperbranched poly(allyl)carbosilanes are often used as convenient and affordable model for evaluating the efficiency of different synthetic strategies.[10,11] Until recently, no data on the synthesis of thioether derivatives of hyperbranched polycarbosilanes has been reported. Therefore, evaluation of the efficiency of this approach towards this group of compounds is important. Besides the interest in the extension of addition of thiols to the double bonds (thiol—ene reactions) on hyperbranched poly(allyl)carbosilanes, incorporation of the thiol bridges into their molecular structure and simultaneous transformation of the polymer into nonfunctional state can lead to novel polymer systems with practically useful properties. Thus, it is known that incorporation of sulfur into organosilicon oligomers led to a substantial increase in their lubricity.[12] For dendrimers, application as base-material for lubricating compositions is of low value, while for hyperbranched analogs this practical application is quite promising.

The aim of the present work is the synthesis of thioether derivatives of both functional and non-functional polycarbosilane hyperbranched polymers.

Results and discussion

Hyperbranched poly(allyl)carbosilane polymer **1** synthesized by polyaddition of methyldiallylsilane in the pres-

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2495—2500, December, 2011.
1066-5285/11/6012-2544

ence of the Karstedt catalyst[13,14] (Scheme 1) was used as the starting compound.

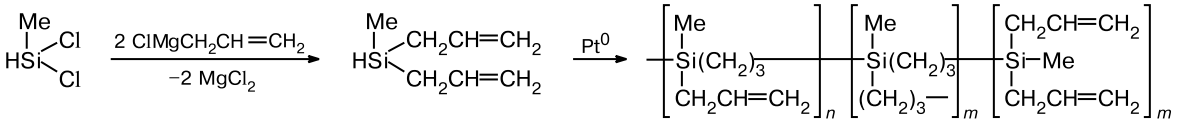
Thiolation of hyperbranched carbosilane polymer **1** yielded non-functional (**2**) and functional (**3**) thioether derivatives (Scheme 2).

Addition of thiols (1-decanthiol and 3-mercaptopropyl(methyl)dimethoxysilane) to the double bonds of polymer **1** was carried out under UV irradiation. Benzophenone (1 mol.% of the stoichiometric amounts of the reactants) was used for initiation of the radical reaction. A Camelion LH26-3U lamp (λ_{max} = 365 nm, 26 W) was used as a source of a UV light. To achieve complete conversion of the allyl groups, 25% excess of thiols was used. The reaction was carried out at ambient temperature until the lack of the signals of the double bonds at δ 4.82 and 5.85 in the ^{1}H NMR spectrum (Fig. 1). Under these conditions, the addition of the thiols to the allyl groups was completed within 30 min, which was confirmed by ^{1}H NMR spectroscopy. The resulting sulfur-containing polycarbosilanes **2** and **3** were separated from the thiol excess by precipitation with methanol. The structure of the polymer **2** was unambiguously assigned by the presence in the ^{1}H NMR spectrum (see Fig. 1, spectra *2*) of the signals for the decyl groups at δ 0.86 and 1.25 and the signals for the methylene group at the sulfur atom at δ 2.50.

In the case of decylthio derivative **2**, addition of thiol to the allyl groups of polymer **1** led to both incorporation of sulfur into the molecular structure of the polymer and the blocking of the functional groups. In the case of polymer **3**, the pattern is completely different. The feature of polymer **3** is the ability to further modification involving reactive methoxysilyl groups in the silyl-substituted moieties. Thus, polymer **3** forms gel in the presence of moisture in the air. The possibility to transform the functional groups of polymer **3** was shown by the replacement of the methoxy groups with the butyl groups by the treatment with butyllithuim (Scheme 3).

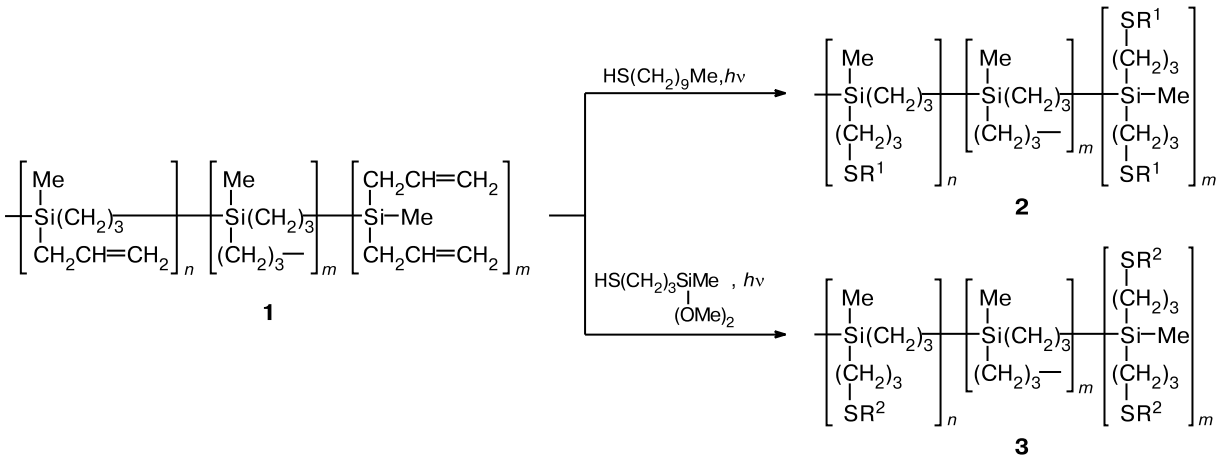
The ^{1}H NMR spectrum of polymer **3** exhibits signals of the methoxy group protons at δ 3.47 and 3.49 and signals of the protons of the methylene groups at the sulfur atom at δ 2.50. The ^{1}H NMR spectra of polymers **4** and **2** are similar with the corresponding difference in the integral intensities for the signals of the butyl and decyl groups. The position of the signals and the integral intensities of the signals are in complete agreement with the structures of the polymers synthesized.

Scheme 1



1

Scheme 2



1 **2** **3**

$R^1 = (CH_2)_9Me$, $R^2 = (CH_2)_3Si(Me)(OMe)_2$; $h\nu$ is UV radiation.

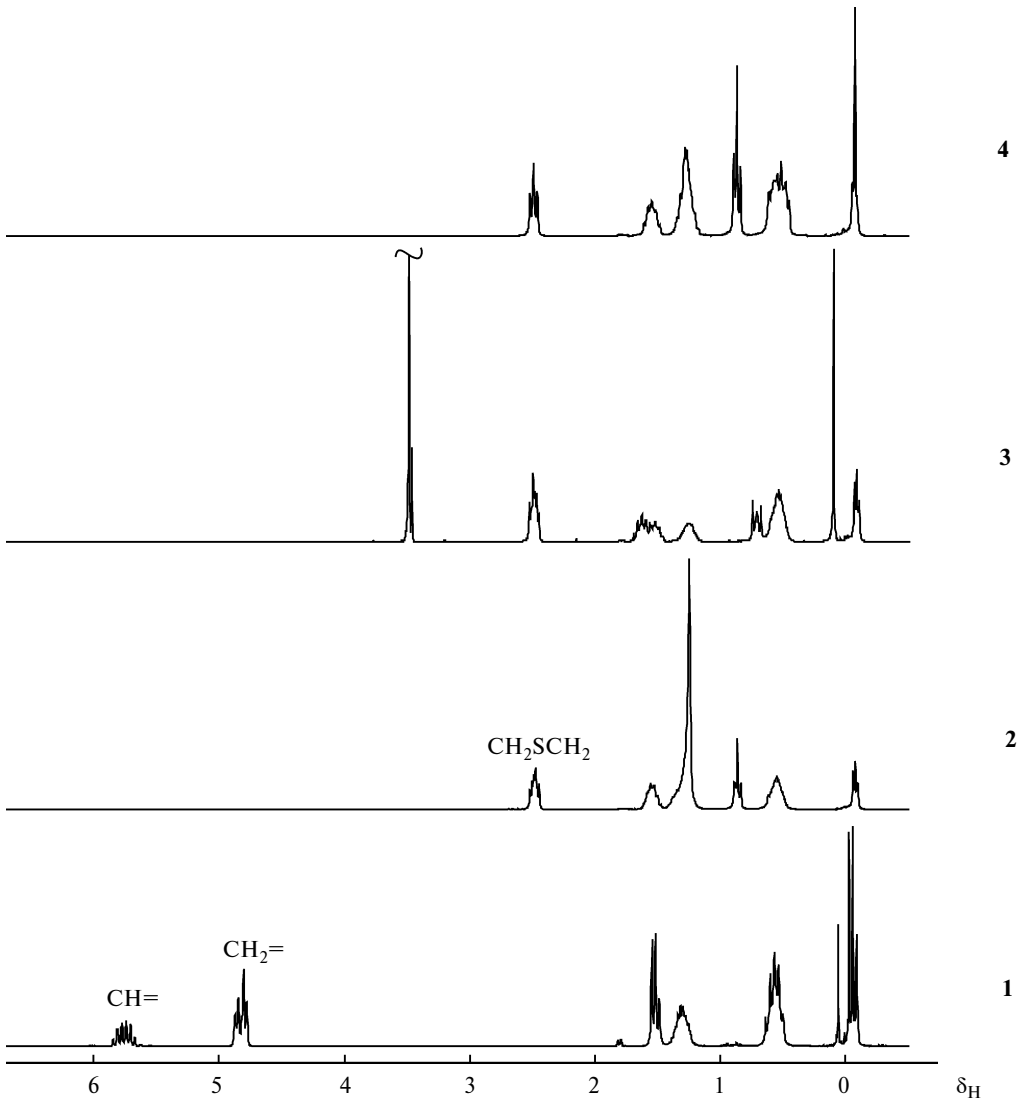
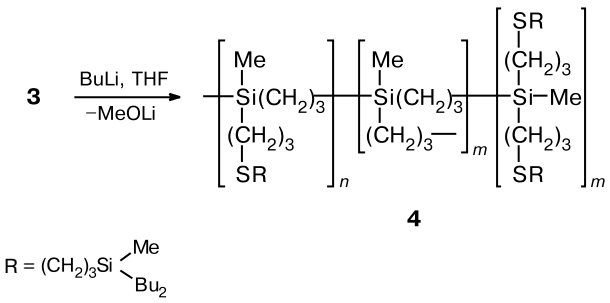


Fig. 1. ^{1}H NMR spectra (in $CDCl_3$) of polymer **1** and its thioether derivatives **2**, **3**, and **4**.

Scheme 3



Gel permeation chromatography (GPS) curves of the starting and modified polymers are compared on Fig. 2. It is obvious that all curves are similar, however in the case of polymers **2**—**4** curves are shifted in the higher mass range as compared with the curve for the starting poly(allyl)carbosilane **1**. This fact is in good agreement with some increase in hydrodynamic radius upon hydrothiolation.

In the case of polymer **3**, prolonged irradiation of the reaction mixture (>1 h) resulted in the appearance of the higher molecular weight fractions detected by GPS (Fig. 3). These peaks could be explained by the chain transfer to the methoxysilyl groups known for the radical reactions of the alkoxy-substituted organosilicon compounds. For example, this process was documented for the radical polymerization of vinylmethyldi(alkoxy)silanes.[15]

From Fig. 3, one can made two important conclusions. At first, the radical hydrothiolation can be complicated by side reaction of the chain transfer to the alkoxy group. And, at second, this undesirable process can be avoided by optimization of the irradiation time of the reaction mixture.

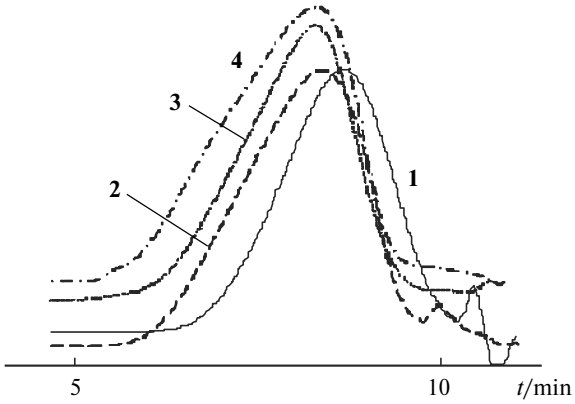


Fig. 2. GPC curves of polymer **1** and its thioether derivatives **2**, **3**, and **4**.

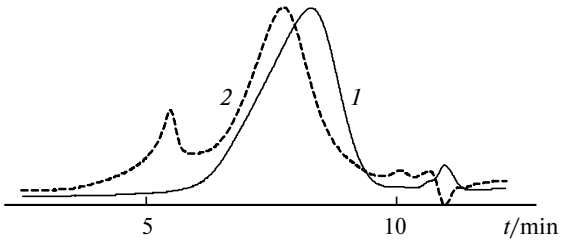


Fig. 3. GPC curves of polymer **3** after UV irradiation for 30 min (*1*) and 1 h (*2*).

Some characteristics of the synthesized non-functional polymers **2** and **4** in comparison with that for the starting poly(allyl)carbosilane **1** are given in Table 1.

Low values of intrinsic viscosity indicated the compact form of all polymers studied. Intrinsic viscosity values are practically independent from solvent used and increased slightly with an increase in the size of the substituent in the carbosilane polymer. Thus, polymer **4** with the most bulky substituent has the highest intrinsic viscosity value.

According to the DSC data (Fig. 4, Table 1), the increase in the size of the substituent resulted in some increase in glass transition temperature for polymer **4** as compared with the starting polymer **1**. In contrast to fully amorphous polymers **1** and **4**, polymer **2** bearing long aliphatic substituents is amorph-crystalline polymer. Thermal gravimetric analysis (TGA) (Fig. 5) of the modified compounds **2** and **4** revealed decrease in both thermal and thermal oxidative stability. The observed decrease in thermal and thermal oxidative stability can

Table 1. Selected physicochemical properties of polymers **1**, **2**, and **4**

Polymer	[η]/dL g^{-1}		T_g/°C	n^{24}_D	θ/deg
	Toluene	THF			
1	0.07	0.07	−86	1.5005	85 (89)
2	0.08	0.08	−27*	1.4989	77 (73)
4	0.09	0.10	−79	1.4985	84 (86)

Note. [η] is intrinsic viscosity; T_g is glass transition temperature; θ is contact angle on polypropylene or copper plate (given in parenthesis).
* Melting point.

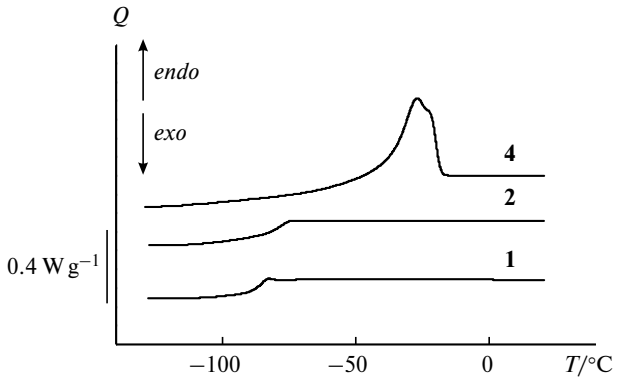


Fig. 4. DSC curves of polymers **1**, **2**, and **4**; Q is the heat flow.

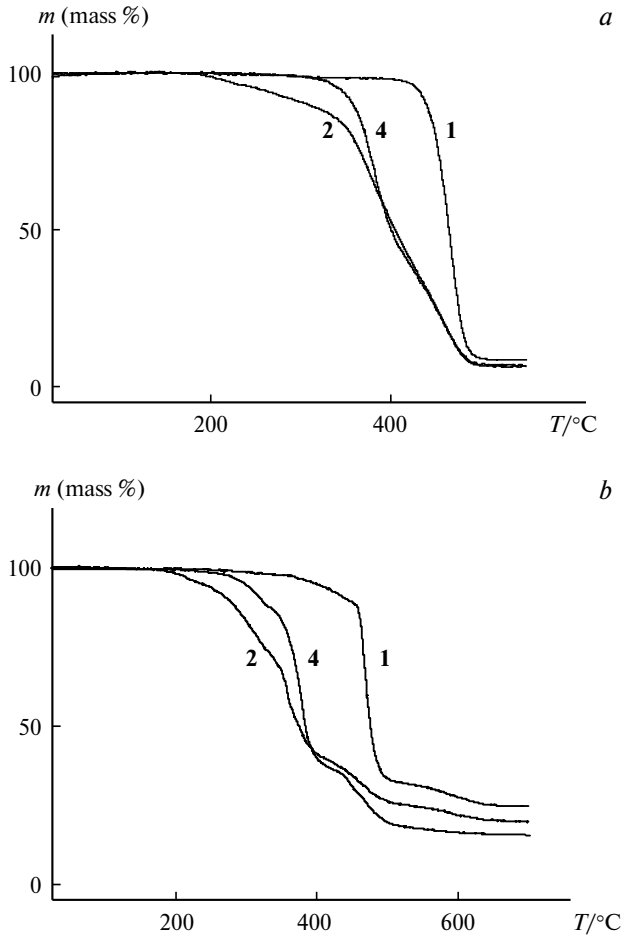


Fig. 5. TG curves for polymers **1**, **2**, and **4** obtained under argon (*a*) and in air (*b*); *m* is weight of the residue.

apparently be explained by the formation of a dense framework upon degradation of the polyfunctional starting sample, while non-functional thioether derivatives inferior the functional analogs. This difference in the behavior of functional and non-functional hyperbranched polycarbosilanes was noted previously.[16] Contact angle on the hydrophobic surfaces for polymer **2** is significantly different from those values for polymers **1** and **4**. This fact indirectly evidenced that the long alkyl substituents prevent contact of the sulfur-containing fragments with the surface.

In summary, applying simple and versatile thiolation reaction we synthesized sulfur-containing hyperbranched functional and non-functional carbosilane polymers. These polymers are of interest for the studying complexation with the transition metal salts and for the synthesis of the molecular composites with unusual or useful properties.

Experimental

^{1}H NMR spectra were run on a Bruker WP-250 SY instrument (working frequency is 250.13 MHz) in $CDCl_3$ with Me_4Si as internal standard.

Gel permeation chromatography was performed on a Laboratorni pristroje liquid chromatograph (Chechoslovakia), detection with RIDK-102 refractometer, Phenogel 500 kD column, elution with THF.

Intrinsic viscosity was measured on a Ubbelohde viscometer with capillary diameter of 0.53 mm at 20 °C, accuracy of the temperature calibration was 0.1 °C.

Contact angles were measured on a KRÜSS Easy Drop Standard instrument with DSA v. 1.90.0.14 software. The volume of the drops was 1.5 μL. Contact angles were calculated by the Young—Laplace equation. In the glove box, the polymers were applied on the support as a thin layer and kept at 35 °C for 1 h for the uniform distribution over the surface. The supports were copper and polypropylene plates.

The DSC measurements were performed on a DSC-822 differential scanning calorimeter (Mettler-Toledo) at heating rate of 10 degree min^{-1}. Glass transition temperature was determined on the middle of the DSC curve slope.

Thermogravimetric analysis was performed in air and under argon on a Derivatograph-C instrument (MOM, Hungary), the rate of temperature increase was 5 degree min^{-1}, the weight of the samples was ~10 mg.

All solvents were dried prior to use by standard procedures[17] by prolonged reflux and distillation over CaH_2 and were kept over molecular sieves 3 Å. 1-Decanthiol, 3-mercaptopropyl(methyl)dimethoxysilane, *n*-butyllithium (Aldrich Chemical Co.) were used as purchased. Benzophenone was recrystallized prior to use from MeOH. The Karstedt catalyst (divinyltetramethyldisiloxane platinum(0)), solution in xylene, 2.1—2.4% Pt, was purchased from Aldrich Chemical Co.

Hyperbranched poly(allyl)carbosilane polymer (1) was synthesized according to the known procedure[13] in quantitative yield. ^{1}H NMR ($CDCl_3$), δ: –0.03 (m, 3 H, $SiCH_3$); 0.5 (m, 4 H, $SiC\underline{H}_2CH_2C\underline{H}_2$); 1.30 (m, 2 H, CH_2); 1.52 (m, 2 H, $SiC\underline{H}_2CH{=}CH_2$); 4.82 (m, 2 H, $CH_2{=}$); 5.85 (m, 1 H, CH=).

Hyperbranched (decylthio)carbosilane polymer (2). A stirred mixture of compound **1** (0.344 g, 0.0027 mol), 1-decanethiol (0.593 g, 0.0034 mol), benzophenone (0.011 g, 0.061 mmol), and anhydrous THF (5 mL) was irradiated with a UV lamp for 30 min under argon. The completion of the reaction was monitored by the ^{1}H NMR spectroscopy by the disappearance of the allyl group signals. Polymer **2** was precipitated by addition of MeOH (20 mL) to the reaction mixture. The transparent viscous precipitate was washed with MeOH (2×5 mL) and dried *in vacuo* (1 Torr) until constant weight to give polymer **2** in a yield of 0.809 g (99%), highly viscous transparent oil. ^{1}H NMR ($CDCl_3$), δ: –0.08 (m, 3 H, Si—CH_3); 0.55 (m, 6 H, Si—CH_2); 0.86 (t, 3 H, CH_3, J = 6.7 Hz); 1.25 (m, 16 H, CH_2); 1.56, 1.75 (both m, 4 H, $C\underline{H}_2$—CH_2—S); 2.50 (m, 4 H, CH_2—S—CH_2). Found (%): C, 67.99; H, 12.18; S, 10.79; Si, 9.16. $C_{17}H_{36}SSi$. Calculated (%): C, 67.92; H, 12.07; S, 10.67; Si, 9.34.

Hyperbranched [di(methoxy)(methyl)silyl]propylthiocarbosilane polymer (3) was synthesized analogously to compound **2** from polymer **1** (0.290 g, 0.0023 mmol), 3-mercaptopropyl(methyl)dimethoxysilane (0.523 g, 0.0029 mmol), benzophenone (0.001 g, 0.052 mmol), and THF (4 mL). Compound **3** was obtained in a yield of 0.479 g (68%), highly viscous transparent oil. ^{1}H NMR ($CDCl_3$), δ: –0.08 (m, 3 H, Si—CH_3); 0.10 (s, 3 H, Si—CH_3); 0.54 (m, 6 H, Si—CH_2); 0.71 (m, 2 H, CH_2—Si); 1.26 (m, 2 H, CH_2); 1.53 (m, 2 H, $C\underline{H}_2$—CH_2—S); 1.63 (m, 2 H, S—CH_2—$C\underline{H}_2$); 2.50 (m, 4 H, CH_2—S—CH_2); 3.47, 3.49 (both s, 6 H, OCH_3). Found (%): C, 51.15; H, 9.73; S, 10.26; Si, 18.11. $C_{13}H_{30}O_2SSi_2$. Calculated (%): C, 50.93; H, 9.86; S, 10.46; Si, 18.32.

Hyperbranched [di(butyl)(methyl)silyl]propylthiocarbosilane polymer (4). A stirred mixture of polymer **1** (0.975 g, 0.0077 mmol), 3-mercaptopropyl(methyl)dimethoxysilane (1.737 g, 0.0096 mmol), benzophenone (0.032 g, 0.173 mmol), and anhydrous THF (13 mL) was irradiated with a UV lamp for 30 min under argon. The completion of the reaction was monitored by the ^{1}H NMR spectroscopy by the disappearance of the allyl group signals. The resulting reaction mixture was added dropwise to a magnetically stirred solution of Bu^nLi (15 mL, 2.5 *M* solution in hexane) in THF (40 mL) at 0 °C, the mixture was stirred at 0 °C for 9 h, and kept at ambient temperature for 12 h. Excess of Bu^nLi was decomposed by the addition of MeOH (5 mL), the mixture was washed with water until neutral, and dried with Na_2SO_4. The volatiles were removed *in vacuo* (1 Torr), the oily residue (2.086 g) was dissolved in hexane (30 mL), and the polymer was precipitated by the addition of EtOH (60 mL). The precipitate was washed with EtOH (2×5 mL) and dried *in vacuo* (1 Torr) until constant weight. Polymer **4** was obtained in a yield of 1.821 g (66%), highly viscous transparent oil. ^{1}H NMR ($CDCl_3$), δ: –0.07 (s, 6 H, Si—CH_3); 0.53 (m, 12 H, Si—CH_2); 0.87 (t, 6 H, CH_3, J = 7.0 Hz); 1.28 (m, 10 H, CH_2); 1.55 (m, 4 H, $C\underline{H}_2$—CH_2—S); 2.49 (t, 4 H, CH_2—S—CH_2, J = 7.3 Hz). Found (%): C, 63.72; H, 11.72; S, 9.17; Si, 15.37. $C_{19}H_{42}SSi_2$. Calculated (%): C, 63.61; H, 11.80; S, 8.94; Si, 15.65.

This work was financially supported by the Ministry of Education and Science of the Russian Federation (Federal Target Program "Scientific and Scientific-Pedagogical Personnel of Innovative Russia on 2009—2013", State Contract No. 02.740.11.0259) and the Council for Grants at the President of the Russian Federation (the Program

for the State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-4342.2010.3).

References

1. L. M. Campos, K. L. Killops, R. Sakai, J. M. J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore, C. J. Hawker, *Macromolecules*, 2008, **41**, 7063.
2. N. B. Cramer, T. Davies, A. K. O´Brien, Ch. N. Bowman, *Macromolecules*, 2003, **36**, 4631.
3. K. L. Killops, L. M. Campos, Craig J. Hawker, *J. Am. Chem. Soc.*, 2008, **130**, 5062.
4. P. Antoni, M. J. Robb, L. Campos, M. Montanez, A. Hult, E. Malmström, M. Malkoch, C. J. Hawker, *Macromolecules*, 2010, **43**, 6625.
5. Ch. Rissing, D. Y. Son, *Organometallics*, 2008, **27**, 5394.
6. Ch. Rissing, D. Y. Son, *Organometallics*, 2009, **28**, 3167.
7. Sh. W. Krska, D. Seyferth, *J. Am. Chem. Soc.*, 1998, **120**, 3604.
8. B. A. Omotowa, J. M. Shreeve, *Macromolecules*, 2003, **36**, 8336.
9. R. M. Crooks, M. Zhao, Li Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181.
10. N. A. Sheremetyeva, N. V. Voronina, A. V. Bystrova, V. D. Miakushev, M. I. Buzin, A. M. Muzafarov, *Advances in Silicones and Silicone-Modified Materials, ACS Symposium Series*, Eds S. J. Clarson, M. J. Owen, S. D. Smith, M. E. Van Dyke, ACS Publ., Washigton, Vol. **1051**, 2010, p. 111.
11. N. A. Belov, N. A. Sheremet´eva, Yu. P. Yampol´skii, A. M. Muzafarov, *Vysokomol. Soedin., Ser. A*, 2009, **51**, 775 [*Polym. Sci., Ser. A* (*Engl. Transl.*), 2009, **51**, 518].
12. M. V. Sobolevskii, I. I. Skorokhodov, K. P. Grinevich, *Oligoorganosiloksany. Svoistva, poluchenie, primenenie* [*Oligo-(organo)siloxanes. Properties, synthesis, application*], Khimiya, Moscow, 1985, p. 216 (in Russian).
13. A. M. Muzafarov, O. B. Gorbatsevich, E. A. Rebrov, G. M. Ignat´eva, T. B. Chenskaya, V. D. Myakushev, A. F. Bulkin, V. S. Papkov, *Vysokomol. Soedin., Ser. A*, 1993, **11**, 1867 [*Polym. Sci., Ser. A* (*Engl. Transl.*), 1993, **11**, 1575].
14. C. Drohmann, M. Moeller, O. B. Gorbatsevich, A. M. Muzafarov, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 741.
15. B. D. Lavrukhin, T. V. Strelkova, N. A. Chernyavskaya, A. A. Zhdanov, *Vysokomol. Soedin., Ser. A*, 1987, **29**, 272 [*Polym. Sci. USSR, Ser. A* (*Engl. Transl.*), 1987, **29**].
16. O. B. Gorbatsevich, PhD Thesis (chem.), Institute of Synthetic Polymer Materials, Moscow, 1996, p. 120. (in Russian).
17. W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth Heinemann, Oxford, 2002, p. 530.

Received July 27, 2011;
in revised form October 6, 2011