Rheological properties of sulfur-containing hyperbranched polycarbosilanes and related magnetic compositions*

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The rheological properties of hyperbranched polycarbosilanes with butyl and decyl terminal groups and their sulfur-containing analogs were compared. The use of various sulfur-containing precursors made it possible to control both the total sulfur content and the position of sulfur atoms in the molecular structure. The magnetic compositions based on sulfur-containing hyperbranched polycarbosilanes were prepared for the first time, and the influence of the external magnetic field intensity on their rheological properties was studied. The introduction of the sulfur atom improves the stability of the magnetic composition, while their magnetorheological response remains unchanged.

Key words: hyperbranched polycarbosilanes, magnetorheological fluids, rheology.

Magnetorheological fluids (MF) have been known since the middle of the XX century and presently found wide practical use.[1,2] Progress in the area of preparation of new MF is related to both the improvement of processes of preparation and surface treatment of magnetic particles and the use of new disperse media. Hyperbranched polycarbosilanes are considered as a promising basis for the preparation of MF with a wide temperature range of stability and controlled rheological characteristics.[3]

Success in the area of synthesis of sulfur-containing polycarbosilane dendritic systems makes it possible to obtain polymer matrices with different contents and positions of sulfur atoms.[4—9] The introduction of sulfur atoms can substantially enhance the affinity of the polymer matrix to metal and, hence, it seems important to study the influence of the sulfur atoms for specific examples of magnetic compositions based on sulfur-containing hyperbranched polycarbosilanes. It can be expected that the introduction of sulfur atoms would extend possibilities of application of these systems as disperse media, in particular, for the preparation from them of magnetorheological

fluids with high stability and unique properties. In that regard, the study of rheology of these polymers is unambiguously interesting and important from the viewpoint of both basic science and their further practical application.

The purpose of this work is to study the influence of introduction of sulfur atoms on the rheological properties of the polybutanethiol and polydecanethiol derivatives of hyperbranched polyallylcarbosilanes differed by geometric parameters. The presence of sulfur atoms in the composition of the terminal groups can exert a dual effect. On the one hand, the introduction of sulfur atoms inevitably changes intermolecular interactions. On the other hand, it can be expected that the change in the type of the bond (Si—C by S—C) would result in a change in the flexibility and mobility of the terminal groups.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using signals of residual protons of the deuterated solvent (CHCl$_3$, δ 7.25) as an internal standard.

The GLC analysis was carried out on a Khromatek-Analitik-5000 chromatograph (Russia) (katharometer as a detector, helium as a carrier gas, column 2000S3 mm, stationary phase SE-30 (5%) supported on Chromaton-H-AW).

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The GPC analysis was carried out on the chromatographic system consisting of a STAIER high-pressure pump (series 2, Akvilon, Russia), a RIDK 102 refractometer detector (Czechia), and a JETSTREAM 2 PLUS thermostat of columns (KNAUER, Germany). The thermostating temperature was 40 °C. The eluent was THF with a flow rate of 1.0 mL min^{-1}. The column 300S7.8 mm packed with the Phenogel sorbent (Phenomenex, USA) was used. The pore size was 10^4 Å. The passport separation range was 5—500 000.

The intrinsic viscosity of polymers was measured on a Schott Ubbelohde viscosimeter (Germany) with a capillary diameter of 0.53 mm. Measurements were carried out at 25 °C with the accuracy of temperature calibration 0.1 °C.

The samples were studied by the DSC method on a DSC-822e differential scanning calorimeter (Mettler-Toledo) with a heating rate of 10 deg min^{-1}. Thermogravimetric studies were carried out on a Derivatograph-C instrument (MOM, Hungary) at a heating rate of 5 deg min^{-1} in air and in an argon atmosphere for ~10-mg samples.

The rheological characteristics of hyperbranched polycarbosilanes in the temperature range from 10 to 80 °C were measured on an Anton Paar-MCR 302 rheometer in the mode of a constant shear rate with the measuring mode plane—plane with a diameter of 50 mm. The magnetorheological properties of magnetic compositions based on branched polymers were studied with a rheometer using a magnetic cell. The uniform magnetic field perpendicular to the shear plane was formed by an electromagnet, the current in which was controlled in the range from 0 to 5 A. According to the specification of the instrument, the magnetic field in the cell increases linearly with an increase in the current and achieved 1 T at a maximum current of 5 A. In the presence of a sample of magnetic fluid, the magnetic field in the cell changed insignificantly. Further the magnetorheological response of the samples was studied depending on the value of electric current, which was easily controlled.

The complex dynamic modulus of magnetic compositions was measured in the dynamic mode of shear oscillations. The dependences of the storage (G') and loss (G'') moduli on the oscillation frequency and amplitude and on the intensity of the applied external magnetic field were determined.

Prior to use hexane and THF were dried according to standard procedures[10] using prolong reflux and distillation with CaH_2 and kept over molecular sieves 3 Å in an argon atmosphere. Toluene and methanol were distilled on a rotary evaporator. Dimethylchlorosilane was distilled in an argon flow prior to use. The following commercial reagents were used as received: 1-decanethiol (96%, Aldrich Chemical), 1-butanethiol (98%, Acros organics), 1-bromodecane (98%, Acros organics), Mg (99.9%, Acros organics), and benzophenone (99%, Sigma Aldrich). Karstedt´s catalyst (Pt^0 complex with divinyltetramethyldisiloxane, solution in xylene, 2.1—2.4% Pt, ABCR GmbH & Co.) was used for hydrosilylation.

Dimethyldecylsilane. All procedures were carried out in an argon atmosphere. A solution of 1-bromodecane (119.3 g, 1.2500 mol) in anhydrous THF (150 mL) was slowly added dropwise with stirring to a suspension of chipped Mg (16.06 g, 1.5600 mol) pre-heated and activated by a minor amount of I_2 in anhydrous THF (100 mL). At the initial stage, the mixture was heated to boiling to initiate the reaction, and then heating was removed and the process occurred with self-warming. The obtained mix-

ture was cooled down to ~20 °C, and a solution of dimethylchlorosilane (40 g, 0.4228 mol) in anhydrous THF (100 mL) was slowly added with stirring. Then the mixture was refluxed for 4 h with stirring. The residual Grignard reagent (decylmagnesium-bromide) was decomposed. The formed precipitate was dissolved by the slow addition of a 1 *N* aqueous solution of HCl (300 mL) to the mixture with stirring. A biphase system was obtained. Hexane (100 mL) was added to the organic phase and then washed off with water with the salting-out agent (NaCl) to the neutral reaction of washing waters. The organic layer was kept for 1 day over anhydrous Na_2SO_4. The obtained solution was evaporated under atmospheric pressure to the boiling point of hexane, and the residue was distilled *in vacuo* (1 Torr). The target fraction ($T_b = 69$ °C, $p = 1$ Torr) was collected as a colorless transparent liquid. The weight of the fraction was 36.23 g (43%). According to the GLC data, the content of the major substance was 99%.

^{1}H NMR (CDCl$_3$), δ: 0.04, 0.05 (both d, 6 H, SiCH$_3$); 0.50—0.61 (m, 2 H, SiCH$_2$); 0.87 (t, 3 H, CH$_3$, J = 6.5 Hz); 1.20—1.37 (m, 16 H, CH$_2$); 3.76—3.87 (m, 1 H, SiH).

Hyperbranched polyallylcarbosilane (PCS-All) was synthesized using a known procedure[11] with a quantitative yield from methyldiallylsilane (49.22 g, 0.3898 mol) dissolved in dried hexane (70 mL). Karstedt´s catalyst (70 μL) was added to the solution. The reaction course was monitored by the disappearance of proton signals at silicon in the ^{1}H NMR spectrum. Prior to further modification, the polymer was passed through the silica gel layer to purify from catalyst residues (toluene as eluent).

^{1}H NMR (CDCl$_3$), δ: −0.03 (m, 3 H, SiCH$_3$); 0.5 (m, 4 H, SiCH$_2$CH$_2$CH$_2$); 1.30 (m, 2 H, CH$_2$); 1.52 (m, 2 H, SiCH$_2$-CH=CH$_2$); 4.82 (m, 2 H, =CH$_2$); 5.85 (m, 1 H, =CH).

Hyperbranched polycarbosilane with decyl terminal groups (PCS-Si-Dec). All procedures were carried out in argon. A solution of Karstedt´s catalyst (63 μL) was added to a solution of **PCS-All** (5.02 g, 0.0397 mol) and dimethyldecylsilane (8.36 g, 0.0417 mol) in dried hexane (50 mL). The obtained solution was stirred at ~20 °C until the reaction is complete (72 h). The completion of the reaction was monitored by the disappearance of proton signals of the allyl groups in the ^{1}H NMR spectrum. Dried THF (100 mL) was added to the solution), and the obtained mixture was precipitated with methanol (125 mL). The upper layer was separated. Dried THF (70 mL) was added to the residue, and the obtained solution was repeatedly precipitated with methanol (25 mL). The upper layer was separated, and the residue was evaporated from volatile components *in vacuo* (1 Torr). The obtained substance was passed from the silica gel layer to purify from catalyst residues (toluene as eluent). The solution was evaporated from volatile components *in vacuo* (1 Torr). A colorless transparent viscous liquid was obtained in a yield of 11.03 g (84%).

^{1}H NMR (CDCl$_3$), δ: −0.10, −0.07 (both s, 9 H, SiCH$_3$); 0.39—0.63 (m, 10 H, SiCH$_2$); 0.87 (t, 3 H, CH$_3$, J = 6.5 Hz); 1.17—1.38 (m, 20 H, CH$_2$). Found (%): C, 69.62; H, 13.07; Si, 16.91. C$_{19}$H$_{42}$Si$_2$. Calculated (%): C, 69.83; H, 12.98; Si, 17.19.

Hyperbranched sulfur-containing polycarbosilane with decyl terminal groups (PCS-S-Dec) was synthesized using an earlier described procedure[8] from **PCS-All** (7.01 g, 0.0555 mol), 1-decanethiol (12.61 g, 0.0694 mol), benzophenone (0.23 g, 0.0012 mol), and dried THF (140 mL) under UV irradiation for 30 min in an

argon atmosphere with stirring. A transparent yellowish viscous liquid was obtained in a yield of 14.13 g (85%).

^{1}H NMR (CDCl$_3$), δ: −0.15—0.03 (m, 3 H, SiCH$_3$); 0.43—0.68 (m, 6 H, SiCH$_2$); 0.87 (t, 3 H, CH$_3$, *J* = 6.4 Hz); 1.18—1.43 (m, 16 H, CH$_2$); 1.45—1.65 (m, 4 H, SCH$_2$CH$_2$); 2.42—2.55 (m, 4 H, SCH$_2$). 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 sulfur-containing polycarbosilane with butyl terminal groups (PCS-S-Bu) was synthesized similarly to **PCS-S-Dec** from **PCS-All** (7.06 g, 0.0559 mol), 1-butanethiol (6.31 g, 0.0700 mol), benzophenone (0.23 g, 0.0012 mol), and dried THF (60 mL) under UV irradiation for 30 min in an argon atmosphere with stirring. A transparent yellowish viscous liquid was obtained in a yield of 14.913 g (90%).

^{1}H NMR (CDCl$_3$), δ: −0.13—0.02 (m, 3 H, SiCH$_3$); 0.45—0.68 (m, 6 H, SiCH$_2$); 0.90 (t, 3 H, CH$_3$, *J* = 7.1 Hz); 1.17—1.64 (m, 8 H, CH$_2$); 2.49 (t, 4 H, SCH$_2$, *J* = 7.2 Hz). Found (%): C, 60.91; H, 11.35; S, 14.75; Si 12.79. C$_{11}$H$_{24}$SSi. Calculated (%): C, 61.09; H, 11.10; S, 14.82; Si, 12.99.

Hyperbranched hybrid polycarbosilane with (dimethyldecyl)-silyl and decylthiyl terminal groups (PCS-Si/S-Dec). All procedures were carried out in an argon atmosphere. Karstedt´s catalyst (63 μL) was added to a solution of **PCS-All** (5.07 g, 0.0401 mol) and dimethyldecylsilane (4.00 g, 0.0200 mol) in dried hexane (50 mL). The obtained solution was stirred under argon at room temperature until the reaction is complete (48 h), which was monitored by the disappearance of proton signals of the allyl groups in the ^{1}H NMR spectrum. Dried THF (80 mL) was added to the solution, and the obtained mixture was precipitated with methanol (130 mL). The upper layer was separated. Dried THF (70 mL) was added to the solution, and the obtained solution was repeatedly precipitated with methanol (15 mL). The upper layer was separated, and the residue was evaporated from volatile components *in vacuo* (1 Torr). The obtained substance was passed through the silica gel layer to purify from catalyst residues (toluene as eluent). The solution was evaporated from volatile components *in vacuo* (1 Torr). A colorless transparent viscous liquid was obtained in a yield of 8.02 g (88%). Then a solution of the obtained intermediate polymer (8.02 g, 0.0399 mol), 1-decanethiol (3.31 g, 0.0190 mol), and benzophenone (0.10 g, 0.0610 mol) in dried THF (40 mL) was irradiated with a UV lamp (wavelength 365 nm) for 2 h with stirring at ~20 °C. The completion of the reaction was monitored by the disappearance of proton signals of the allyl groups in the ^{1}H NMR spectrum. The obtained solution was precipitated with methanol (100 mL), and the upper layer was separated. Dried THF (15 mL) was added to the residue, the obtained solution was repeatedly precipitated with methanol (30 mL), and this procedure was repeated two times. The upper layer was separated. The residue was evaporated from volatile components *in vacuo* (1 Torr). A yellowish transparent viscous liquid was obtained in a yield of 10.65 g (99% based on intermediate polymer).

^{1}H NMR (CDCl$_3$), δ: −0.12—0.01 (m, 6 H, SiCH$_3$); 0.40—0.65 (m, 8 H, SiCH$_2$); 0.87 (t, 3 H, CH$_3$, *J* = 6.3 Hz); 1.20—1.42 (m, 18 H, CH$_2$); 1.45—1.63 (m, 2 H, SCH$_2$CH$_2$); 2.43—2.54 (m, 2 H, SCH$_2$). Found (%): C, 68.98; H, 12.77; S, 4.15; Si, 13.96. C$_{18}$H$_{39}$S$_{0.5}$Si$_{1.5}$. Calculated (%): C, 68.92; H, 12.54; S, 5.11; Si, 13.43.

Magnetic fluids were prepared by mechanical mixing of the corresponding polymer and carbonyl iron (particle size 3—5 μm) in the polymer : iron weight ratio = 1 : 5.

Results and Discussion

The objects studied are carbosilane hyperbranched polymers similar in chemical composition and structure. They have spacers (1,3-propylidene fragments) of the same lengths between the branching points. The degree of branching of the polymers is the same and equal to 1. The samples differ by the size of terminal groups (butyl and decyl groups). In addition, some polymers contain the sulfur atom in the terminal groups, whose position is varied (Scheme 1).

The polymers studied were obtained from the same initial matrix: hyperbranched polyallylcarbosilane **PCS-All** (see Ref. 11) by polymer-analogous transformations at the allyl groups of the polymer (see Scheme 1).

The polymer-analogous transformations were carried out using hydride addition reactions: hydrosilylation (for the preparation of completely carbosilane hyperbranched polymers) and hydrothiolation (for the introduction of the sulfur heteroatom into the polymer structure). Commercially available mercaptanes, 1-butanethiol and 1-decanethiol, were used as sulfur-containing agents differed by the length of the hydrocarbon radical, and dimethyldecylsilane synthesized by Scheme 2 served as a silicon analog of 1-decanethiol.

Sulfur atoms were introduced by hydrothiolation *via* the radical mechanism with photochemical initiation in a THF medium. A domestic UV lamp (with the radiation maximum at 365 nm) was used as a source of light quanta, and benzophenone (in an amount of 1 mol.% of the stoichiometric amount of the reagents) served as a photosensitizer. The synthesis of sulfur-containing polymer **PCS-S-Dec** by the reaction of polyallylcarboxilane with 1-decanethiol was described in detail.[8] Its butyl analog **PCS-S-Bu** was synthesized similarly using 1-butanethiol. To achieve the complete conversion of the allyl groups, thiols were used in a 25% molar excess relative to the amount of allyl groups.

Polymer **PCS-Si-Dec**, being a silicon analog of sulfur-containing polymer **PCS-S-Dec**, was obtained by the hydrosilylation of the starting polymer **PCS-All** on Karstedt´s catalyst in a hexane medium. Hydridesilane was taken in a 5% molar excess relative to the amount of allyl groups.
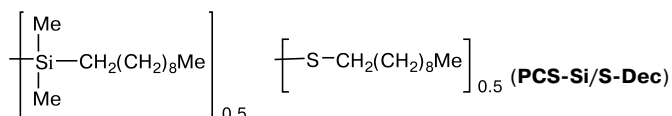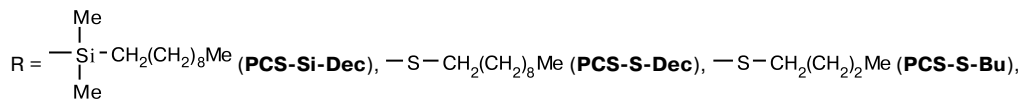
The reactions were carried out at room temperature, and the end of the process was monitored, in all cases, by the disappearance of proton signals of the double bonds of the allyl groups of the starting polyallylcarbosilane at δ 4.82 and 5.85 in the ^{1}H NMR spectrum. The obtained polymers were purified from an excess of the modifying agent by reprecipitation from the reaction mixture with methanol.

Hybrid polymer **PCS-Si/S-Dec** containing both terminal (dimethyldecyl)silyl and decylthiyl groups in the ~50 : 50 ratio was used as an object for comparison. This polymer was synthesized in two stages: hydrosilylation of 50% allyl groups of the initial polyallylcarboxylane by

Scheme 1
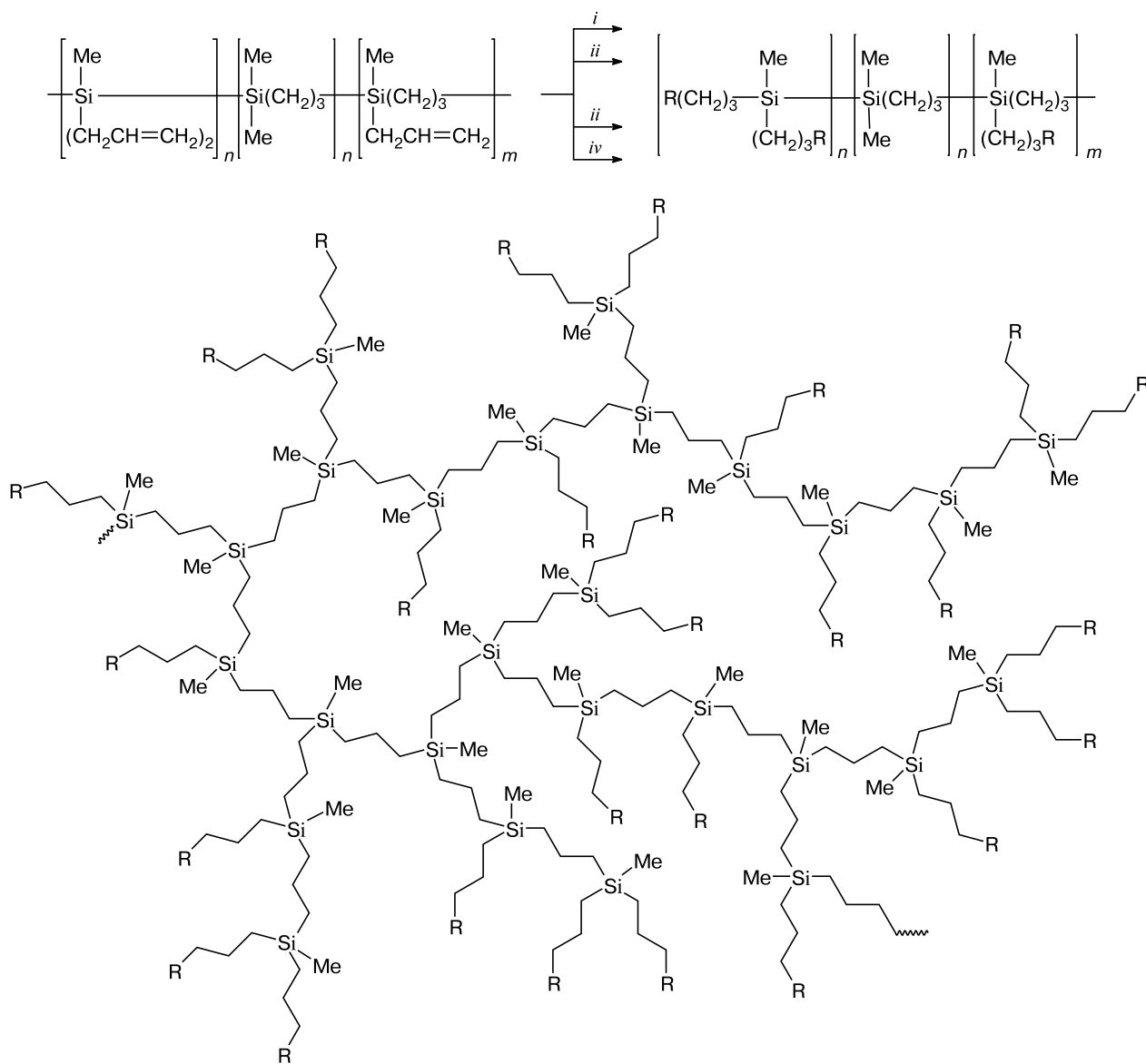
Reagents and conditions: *i*. $(2n + m)\mathrm{HSiMe_2CH_2(CH_2)_8Me}$, $\mathrm{Pt^0}$ catalyst (**PCS-Si-Dec** was obtained); *ii*. $(2n + m)\mathrm{HSCH_2(CH_2)_8Me}$, UV irradiation (**PCS-S-Dec** was obtained); *iii*. $(2n + m)\mathrm{HSCH_2(CH_2)_2Me}$, UV irradiation (**PCS-S-Bu** was obtained); *iv*. (1) $(n + 0.5m)\mathrm{HSiMe_2CH_2(CH_2)_8Me}$, $\mathrm{Pt^0}$ catalyst; (2) $(n + 0.5m)\mathrm{HSCH_2(CH_2)_8Me}$, UV radiation (**PCS-Si/S-Dec** was obtained).

$\mathrm{R} = $ —Si(Me)(Me)–CH$_2$(CH$_2$)$_8$Me (**PCS-Si-Dec**), —S—CH$_2$(CH$_2$)$_8$Me (**PCS-S-Dec**), —S—CH$_2$(CH$_2$)$_2$Me (**PCS-S-Bu**),

$\left[\text{—Si(Me)(Me)—CH}_2\text{(CH}_2\text{)}_8\text{Me}\right]_{0.5}$ $\left[\text{—S—CH}_2\text{(CH}_2\text{)}_8\text{Me}\right]_{0.5}$ (**PCS-Si/S-Dec**)

dimethyldecylsilane followed by the hydrothiolation of the remained allyl groups with 1-decanethiol.

The chemical compositions and structures of the purified compounds were confirmed by ¹H NMR (Fig. 1) and elemental analysis. The ¹H NMR spectra contain signals of protons of all groups that are presented in the synthesized polymers, and the integral intensities of the protons correspond well to their theoretical content in the polymer units.
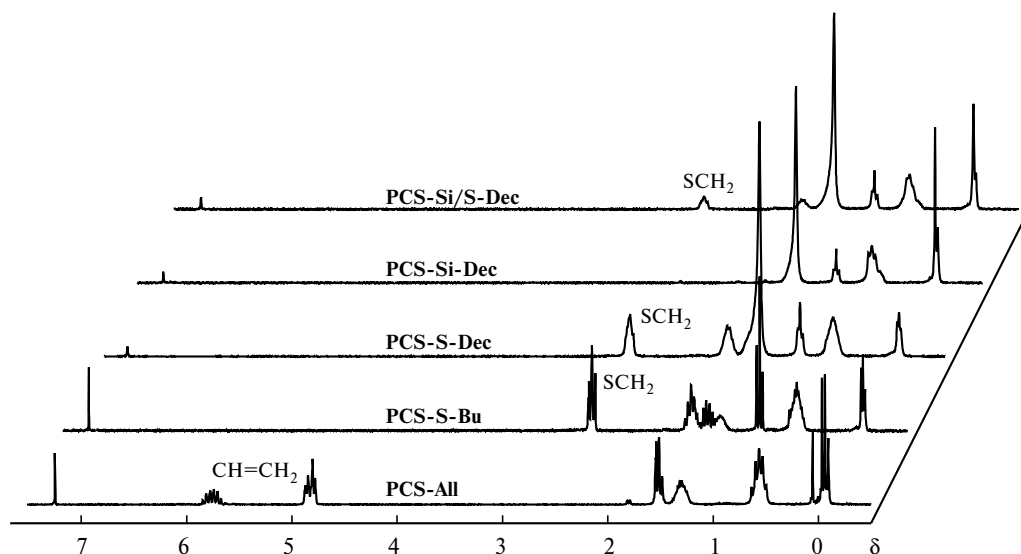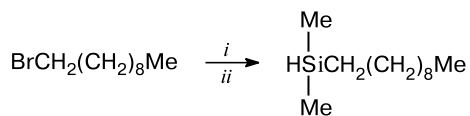
Fig. 1. ^{1}H NMR spectra of synthesized hyperbranched polycarbosilanes.

Scheme 2

$$BrCH_2(CH_2)_8Me \xrightarrow[ii]{i} HSiCH_2(CH_2)_8Me$$

with Me substituents above and below the Si.

Reagents and conditions: *i*. Mg; *ii*. (Me)(Me)HSiCl, –MgClBr.

Sulfur-containing polymers **PCS-S-Dec**, **PCS-S-Bu**, and **PCS-Si/S-Dec** are characterized by signals in a range of δ 2.48 corresponding to the protons of the methylene groups at the thioether bond. The elemental analysis data are well consistent with the theoretical calculations.

An analysis by gel permeation chromatography (GPC) (Fig. 2) showed that the molecular mass characteristics of the modified polymers changed insignificantly relative to the initial polyallylcarbosilane. Each polymer retains the monomodal distribution, indicating the absence of side processes in the course of the reactions. A regular increase in the hydrodynamic radii in the region of highest peaks and molecular weights (relative to the polystyrene standard) of the modified polymers compared to the initial one is observed (Table 1).

The values of intrinsic viscosity [η] of the initial and modified polymers in toluene and THF at 25 °C were determined as one of the main characteristics that makes it possible to evaluate the shape of macromolecules and conformational changes depending on the solvent nature. An analysis of the data in Table 1 indicate that, unlike the initial polymer **PCS-All**, the [η] values of the modified polymers are the same in solvents with different polarities (toluene and THF). At the same time, low values of [η] indicate a compact globular shape of macromolecules of the obtained polymers in the given solvents.

The presence of globular objects along with the values of characteristic viscosity also made it possible to estimate molecular masses of the highest peaks on the chromatogram by the universal calibration method,[12] which are well consistent with the values obtained using the GPC method (see Table 1).

The influence of the heteroatom in the polymer structure on the thermophysical characteristics was evaluated by the TGA and DSC methods. It seems regular that the modified polymers are less thermally stable than the starting polymer **PCS-All** characterized by processes of thermal polymerization of allyl groups and begin to decompose more rapidly in all cases (Fig. 3). As a whole, the introduction of sulfur atoms deteriorates the thermal and thermooxidative stability because of possible oxidation and destruction processes. In a series of the decyl derivatives, the thermal stability decreases in the order
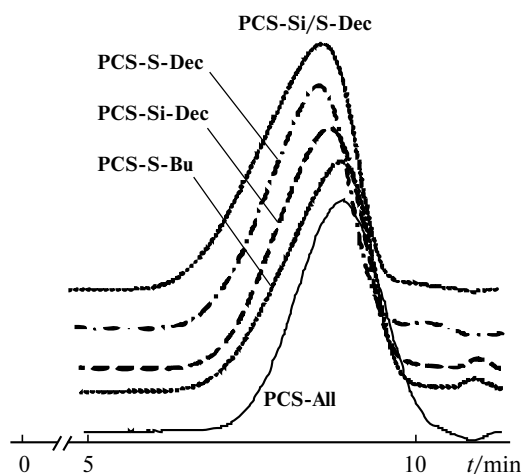

Fig. 2. Chromatograms of synthesized hyperbranched polycarbosilanes (THF as eluent).

**Table 1.** Characteristics of hyperbranched polycarbosilanes

Polymer	$[\eta]$ /dL g^{-1}		R^*/nm	Molecular weight*		T_g	T_m	$T_{10\%}$		η_{20} /Pa s	E_a /kJ mol^{-1}
								°C			
	toluene	TH						air	argon		
PCS-All	0.07	0.08	1.75	5700	4200	−87	—	430	432	0.52	32
PCS-S-Bu	0.07	0.07	1.80	6000	5270	−84	—	315	380	1.86	36
PCS-S-Dec	0.08	0.08	2.11	9000	7440	—	−27	322	345	1.92	37
PCS-Si-Dec	0.07	0.07	1.82	6500	5390	−75	—	325	417	1.45	35
PCS-Si/S-Dec	0.07	0.07	1.97	7000	6920	—	−51	320	380	1.92	36
PCS-Si-Bu	—	—	—	10000	19600**	—	—	—	—	0.60	32

Designations: $[\eta]$ is the characteristic viscosity, R is the hydrodynamic radius, T_g is the glass transition temperature, T_m is the melting point, $T_{10\%}$ is the temperature of 10% mass loss, PSS is the polystyrene standard, UC is the universal calibration method, η_{20} is the viscosity at 20 °C, and E_a is the viscous flow activation energy.
* The value was calculated for the peak in the chromatogram.
** The value was calculated using the dynamic light scattering (DLS) method.

PCS-Si-Dec > > **PCS-Si/S-Dec** > **PCS-S-Dec**. However, all synthesized polymers are fairly thermally stable ($T_{10\%}$ ~ 320 °C).
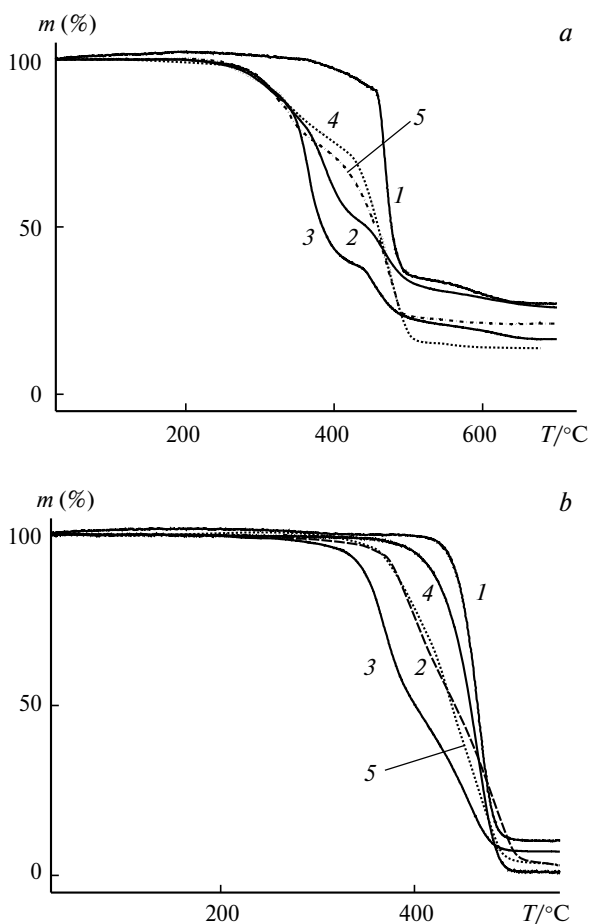
Fig. 3. TGA data for synthesized hyperbranched polycarbosilanes **PCS-All** (*1*), **PCS-S-Bu** (*2*), **PCS-S-Dec** (*3*), **PCS-Si-Dec** (*4*), and **PCS-Si/S-Dec** (*5*) in air (*a*) and in argon (*b*).

At room temperature the initial and modified polymers are transparent viscous liquids. As can be seen from the DSC thermograms (Fig. 4), the presence of long alkyl substituents exerts no decisive effect on crystallization processes characteristic of them. Among the obtained decyl derivatives, sulfur-containing polymers **PCS-S-Dec** and **PCS-Si/S-Dec** are amorphous-crystalline, unlike the completely amorphous polymer **PCS-Si-Dec**. An increased content of sulfur atoms results in a higher thermal effect on melting and a higher melting point ($T_m = -27$ and −51 °C for **PCS-S-Dec** and **PCS-Si/S-Dec**, respectively). In this case, polymer **PCS-Si/S-Dec** occupies an intermediate position between polymers **PCS-S-Dec** and **PCS-Si-Dec**, having the glass transition and crystallization regions in the thermogram (see Fig. 4). Polymer **PCS-S-Bu** is amorphous. The modification of the starting polyallylcarbosilane results in an increase in the glass transition temperature of the final polymer.

Butyl-terminal polymer **PCS-Si-Bu** (see Ref. 13), whose rheological behavior has already been studied earlier,[3] was used as a reference.
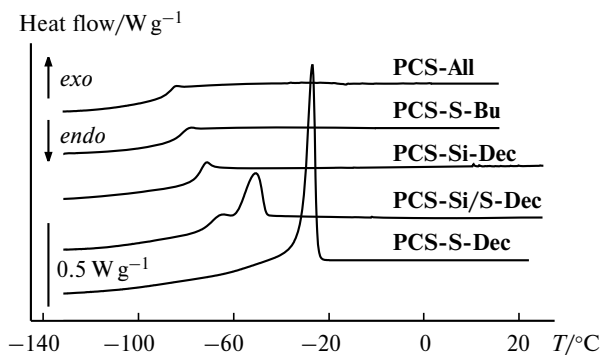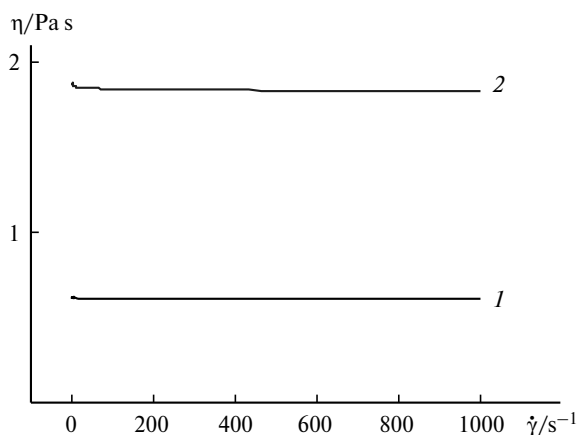

Fig. 4. DSC thermograms of synthesized hyperbranched polycarbosilanes.

Rheology of hyperbranched polymers. The dependences of viscosity of all synthesized polymers on the shear rate in the temperature range from 20 to 80 °C were measured. The flow curves at 20 °C for the polymers with butyl (Fig. 5) and decyl (Fig. 6) terminal groups are presented in Figs 5 and 6. The flow curves for the sulfur-containing sample with butyl terminal groups obtained at different temperatures are exemplified in Fig. 7. It is seen that all polymers studied are Newtonian fluids. The Newtonian behavior of melts of the hyperbranched macromolecules was mentioned[3] and can be explained by a higher density of the molecular structure due to the topology of branchings that impedes entanglement formation.

The activation energy of viscous flow (E_a) was calculated from the temperature dependences of the viscosity of hyperbranched polycarbosilanes (Fig. 8) according to the Arrhenius equation
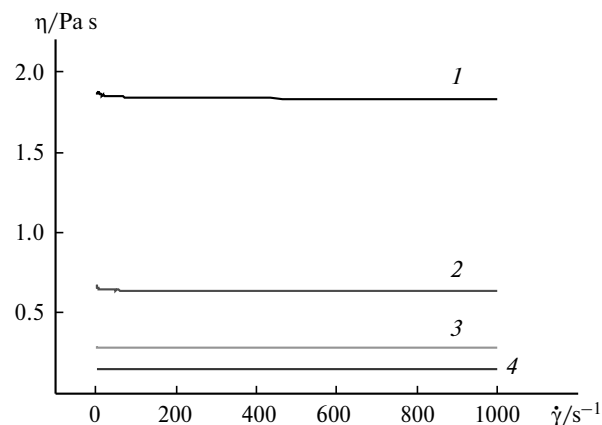
$$\eta = Ae^{E_a/RT},$$

where η is viscosity, R is the universal gas constant, and T is temperature (K). As can be seen from Fig. 8, all depen-

Fig. 7. Flow curves of hyperbranched sulfur-containing polymer **PCS-S-Bu** at 20 (*1*), 40 (*2*), 60 (*3*), and 80 °C (*4*).

dences obtained are straight lines, and the E_a value is determined from the slope ratio.

The characteristics of the objects under study presented in Table 1 make it possible to analyze the influence of introduction of the sulfur heteroatom into the composition of terminal groups and its position and degree of shielding by the terminal chains on the viscoelastic properties of the hyperbranched polymers.

Fig. 5. Flow curves of hyperbranched polycarbosilane with butyl groups **PCS-Bu** (*1*) and its thiol derivative **PCS-S-Bu** (*2*).
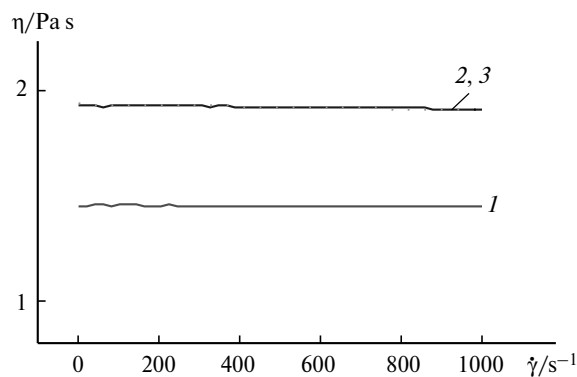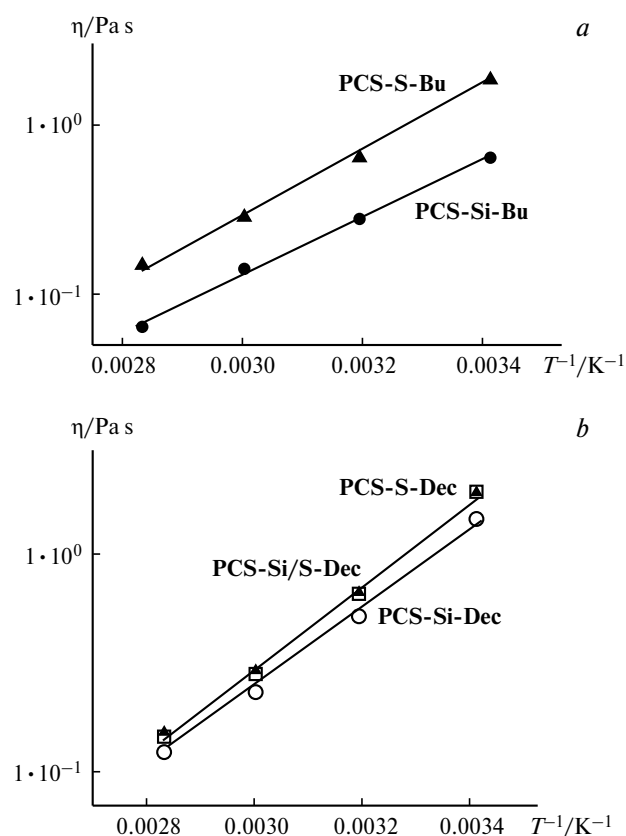

Fig. 6. Flow curves of hyperbranched polycarbosilane with decyl groups **PCS-Si-Dec** (*1*) and its thiol derivatives **PCS-S-Dec** (*2*) and **PCS-Si/S-Dec** (*3*).

Fig. 8. Temperature dependences of the viscosity of hyperbranched polymers with butyl (*a*) and decyl (*b*) terminal groups.

The influence of the length of terminal chains was considered for **PCS-Si-Bu** and **PCS-Si-Dec**. It is seen from the data in Table 1 that the polymer with longer side chains (**PCS-Si-Dec**) is characterized by higher viscosity and activation energy at a similar molecular weight, which is quite expected.[3]

The introduction of sulfur atoms into hyperbranched polycarbosilane with short butyl terminal groups results in a more considerable increase in the values of η and E_a than the elongation of terminal groups does. Indeed, the viscosity at 20 °C and the activation energy of viscous flow of sulfur-containing butyl **PCS-S-Bu** are 1.88 Pa s and 36 kJ mol^{-1}, respectively, whereas these values for sample **PCS-Si-Dec** containing no sulfur atoms are somewhat lower (1.45 Pa s and 35 kJ mol^{-1}).

At the same time, the viscosity and E_a of the sulfur-containing derivatives of hyperbranched polycarbosilanes with decyl terminal groups in which the sulfur atom is less accessible for intermolecular contacts increase insignificantly with the introduction of the heteroatom. The rheological properties of decyl polycarboxilanes are affected more substantially by their structure, in particular, the length of terminal groups, as well as for the samples containing no sulfur. This conclusion is confirmed by a comparison of the activation energy of viscosity flow of sulfur-containing polycarbosilanes with decyl and butyl terminal groups: the η and E_a values are higher for the polymers with longer terminal groups. On the one hand, the sulfur atom is less accessible for intermolecular contacts. On the other hand, the length of the terminal group increases and its flexibility changes due to the sulfur atom: this latter factor exerts a higher effect, increasing η and E_a.

Thus, the introduction of the sulfur atom has a stronger impact on the rheological properties of hyperbranched polymers with short terminal groups. It can be expected that the both types of hyperbranched systems are interesting for further studies of metal-containing compositions. The further enhancement of the intermolecular interaction is possible in the short-chain systems, while in the case of the long-chain systems globules will become denser and the core will become more isolated. The introduction of the sulfur atom will make it possible to control the degree of interaction of metal-containing compositions.

Magnetorheological properties of the magnetic compositions. We also considered the influence of sulfur introduction into terminal groups on the rheological behavior of the magnetic compositions based on hyperbranched polymers.

We obtained the MF based on three samples of polymers: **PCS-S-Dec** containing the sulfur atom in the terminal decyl chains, sulfur-less **PCS-Si-Dec** similar in structure to the former, and the sulfur-containing sample **PCS-S-Bu** with the butyl terminal groups. Carbonyl iron with a particle size of 3—5 μm was chosen as a magnetic filler. The mass content of iron in the obtained compositions was 83%.

The behavior of the compositions in the stationary shear mode was examined first. The flow curves of the MF based on sample **PCS-S-Dec** measured in different magnetic fields are exemplified in Fig. 9, *a*. The rheological behavior of two other samples is similar. It is seen that the introduction of magnetic particles into hyperbranched polymers increases viscosity and also changes the character of the flow. The magnetic compositions demonstrate the non-Newtonian behavior even without magnetic field. This is explained by a high content of the magnetic filler for which the percolation threshold is passed and the particles interact with each other to form three-dimensional structures. For similar magnetic compositions based on decyl polycarbosilanes with different contents of the magnetic filler, the deviation of the flow from the Newtonian character was observed at the content of magnetic particles higher than 72 wt.%.[14]

A significant increase in the viscosity of magnetic fluids is observed in the magnetic field: at low shear rate the
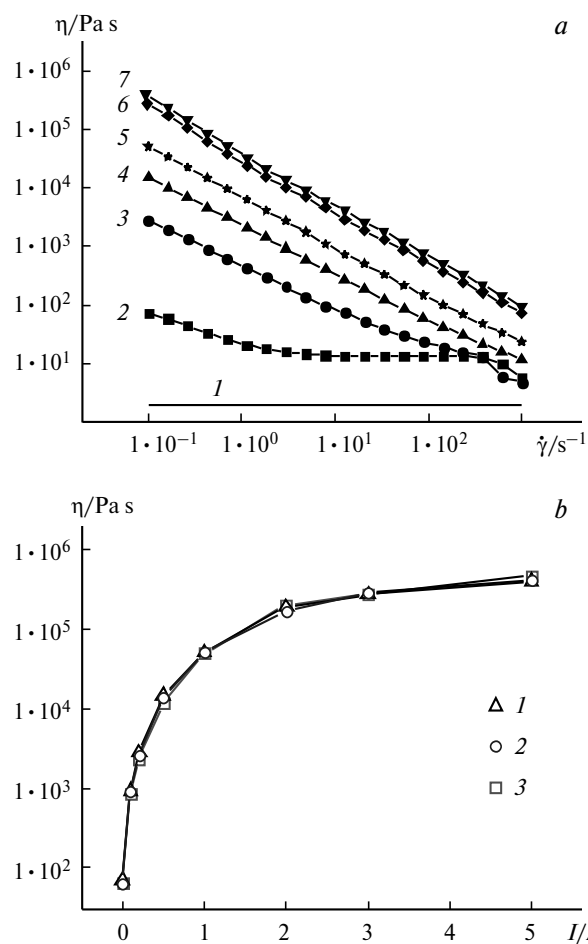
Fig. 9. (*a*) Flow curves for sample **PCS-S-Dec** (*1*) and related MF at different magnetic fields (*I* = 0 (*2*), 0.2 (*3*), 0.5 (*4*), 0.1 (*5*), 3 (*6*), and 5 A (*7*)). (*b*) Dependences of the viscosity of the MF based on **PCS-S-Dec** (*1*), **PCS-Si-Dec** (*2*), and **PCS-S-Bu** (*3*) at a shear rate of 0.1 s^{-1}.
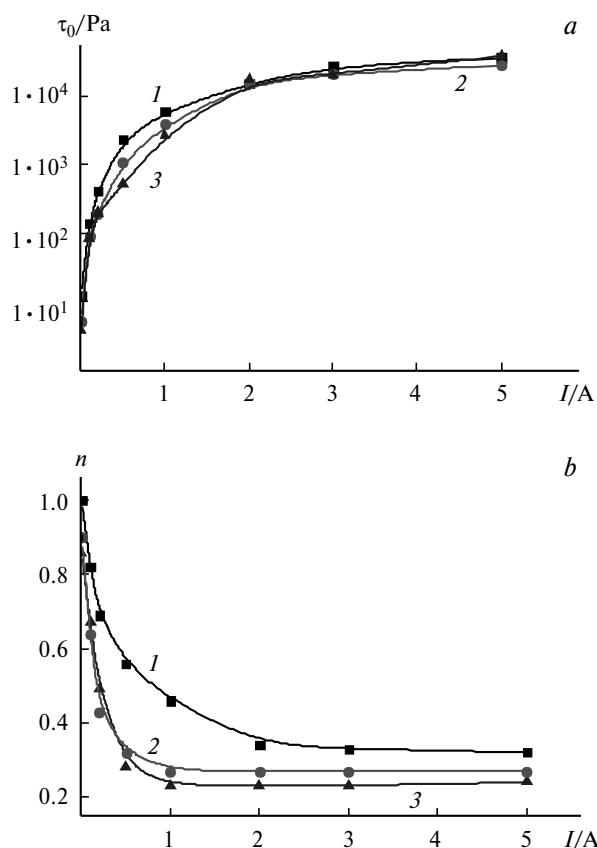
viscosity increases by approximately four orders of magnitude. The dependences of the viscosity of four MF samples on the magnetic field strength at a constant shear rate are shown in Fig. 9, *b*. It is seen that the values of viscosity almost coincide for all MF in the whole range of changing magnetic field.

An increase in the viscosity of the magnetic compositions is accompanied by the appearance of the yield stress. The flow curves are well described by the Herschel—Bulkley equation relating the shear stress (τ) and shear rate ($\dot\gamma$)

$$\tau = \tau_0 + b\dot\gamma^n,$$

where τ_0 is the yield stress, and n is the flow index. The yield stress and flow index for magnetic fluids depending on the magnetic field strength were determined by the experimental data processing (Fig. 10). It is seen that a significant increase in the yield stress is observed already at low magnetic fields (at currents lower than 2 A): the τ_0 value increases by more than three orders of magnitude. The further increase in the magnetic field results in an insignificant increase in the yield stress achieving 30 kPa in the maximum magnetic field, which corresponds to the yield stresses of the commercial magnetic fluids. The
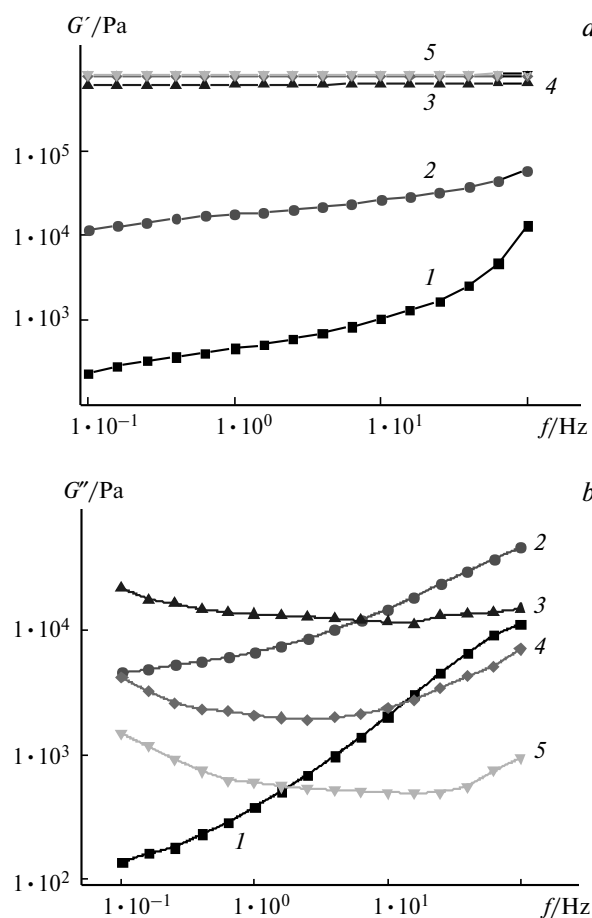
n value is close to unity in the zero magnetic field and rapidly decreases to 0.2—0.3 with an increase in the magnetic field intensity.

The magnetorheological response of MF is caused by the interaction of magnetic particles of the filler in the magnetic field. The magnetic particles minimize the magnetic energy and form ordered structure-chains along the magnetic field lines due to the dipole—dipole interactions thus offering resistance to the shear field. The higher the magnetic field, the stronger the interaction of particles and, hence, the stronger the structures formed by them. As a result, both the viscosity of the compositions and the yield stress increase with an increase in the magnetic field strength. A tendency to saturating η and τ_0 is related to the saturation of magnetization of magnetic particles. For iron particles, the saturation is achieved in the fields about 400 mT, which corresponds to the field values in the magnetic cell of the rheometer at a current of 3—4 A.

The dependences shown in Figs 9 and 10 suggest that the presence of the sulfur atom does not substantially affect

Fig. 10. Dependences of the yield stress (*a*) and flow index (*b*) of the obtained magnetic fluids based on **PCS-Si-Dec** (*1*), **PCS-S-Dec** (*2*), and **PCS-S-Bu** (*3*) on the magnetic field intensity (current).
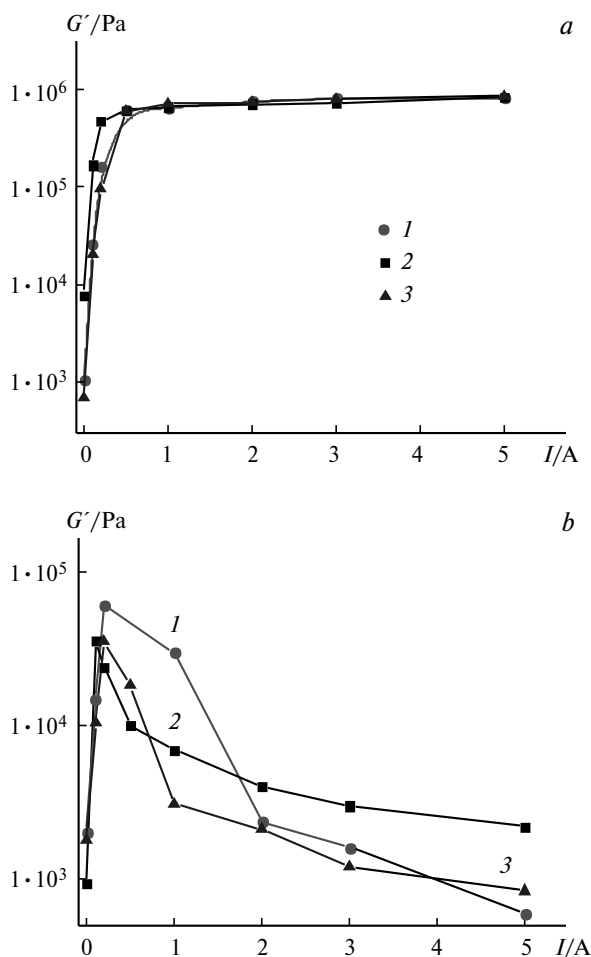

Fig. 11. Frequency dependences of the components of the complex dynamic modulus of the MF based on **PCS-S-Dec** for the storage modulus G' (*a*) and loss modulus G'' (*b*) at $I = 0$ (*1*), 0.1 (*2*), 0.5 (*3*), 2 (*4*), and 5 A (*5*).

the magnetorheological response of the MF. The viscosities of the sulfur-containing and sulfur-less compositions coincide within the measurement error, whereas the yield stress and flow index of the latter are somewhat higher. The distinctions are especially pronounced in the region of weak magnetic fields (at $I = 0.5$—1.5 A). Possibly, a decrease in the yield stress is related to the formation of the polymer layer on the surface of the particles due to the interaction of the sulfur atoms with iron. In the case of **PCS-S-Bu**, the more accessible for interaction sulfur atoms lead to a larger difference in the τ_0 and n values.

Dynamic properties of MF. The rheological properties of MF were examined at the next stage in the dynamic mode of shear oscillations of different amplitudes and frequencies.
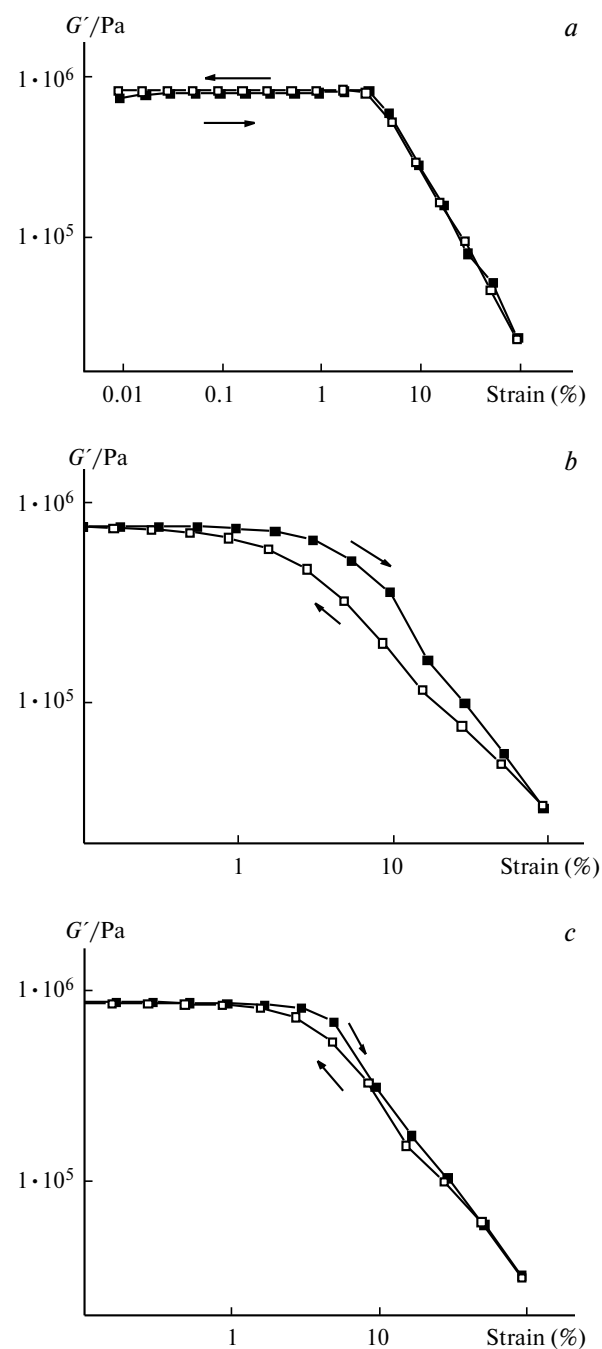
The frequency dependences of the storage modulus G' and loss modulus G'' obtained for sample **PCS-S-Dec** in

different magnetic fields are presented in Fig. 11. The moduli of two other samples behave similarly. The change in the moduli of the samples with an increase in the magnetic field at the constant frequency $f = 1$ Hz is shown in Fig. 12.

In the absence of the field, the MF demonstrates the behavior characteristic of the liquid: the loss modulus is higher than the storage modulus. When the magnetic field is switched on, both moduli begin to increase, but the

Fig. 12. Dependences of the components of the complex dynamic modulus of the obtained MF **PCS-S-Dec** (*1*), MF **PCS-Si-Dec** (*2*), and MF **PCS-S-Bu** (*3*) on the magnetic field strength at a fixed frequency of 10 Hz: *a*, for the storage modulus G' and *b*, for the loss modulus G''.

Fig. 13. Amplitude dependences of the storage modulus of MF **PCS-S-Dec** (*a*), MF **PCS-Si-Dec** (*b*), and MF **PCS-S-Bu** (*c*).

increasing rate of the elastic contribution is higher than that of the dissipative contribution. As a result, already in low fields the $G´$ value becomes higher than $G´´$, indicating the formation of a physical network in the system. This behavior is related to the formation in the magnetic field of chain structures from interacting magnetic particles of the rubber filler playing the role of a strengthening frame-work and causing the dynamic response of the material, which is characteristic of solids.

An increase in the moduli is observed in the range of electric current $I = 0—1$ A. The increase in $G´$ reaches three orders of magnitude. For high values of I, the storage modulus increases insignificantly, whereas the loss modulus begins to decrease. It can be expected that in this range of magnetic fields the strength of magnetic interactions between particles is rather high, and the formed "magnetic couplings" withstand the decomposition of magnetic structures under the action of an external force thus decreasing dissipation in the system. A similar behavior has been observed previously for the MF based on hyperbranched polymers.[14] As can be seen from the data presented in Fig. 11, *b* and earlier obtained results,[14] the value of storage modulus of MF in the maximum field is almost independent of the composition and structure of the branched polymer but is determined by the amount of the magnetic filler.

It should be mentioned that the dynamic modulus of all obtained MF demonstrates the pronounced dependence on the strain amplitude (Fig. 13). This effect is named the Payne effect and is observed for filled elastomers,[15] magnetic elastomers,[16—21] and MF in magnetic fields.[1—2,22]

The dependences presented in Fig. 13 were obtained by a consequent increase and then decrease in the strain amplitude (the direction is indicated by arrows). It is seen that the introduction of sulfur results in an increase in the region of linear viscoelasticity. In addition, the hysteresis observed for a sulfur-less composition is absent for the sulfur-containing MF.

Thus, the introduction of sulfur into the composition of hyperbranched polycarbosilanes affects their rheological properties: the activation energy of viscous flow and block viscosity increase. The effect of sulfur introduction increases with a decrease in the length of terminal groups. The presence of sulfur atoms in hyperbranched polycarbosilanes changes the magnetorheological properties of the MF based on these polycarbosilanes. On the whole, it follows from the results obtained that the introduction of polar groups into the structure of hyperbranched polymers can be an efficient tool for controlling the properties of MF by choosing the type of polar groups or heteroatoms in combination with design of the molecular structure.

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