Rheological properties of nonfunctional derivatives of hyperbranched polycarbosilanes

N. A. Sheremetyeva,[a] V. G. Vasiliev,[b] V. S. Papkov,[b] G. G. Pak,[c] V. D. Myakushev,[a] E. Yu. Kramarenko,[b,d★] and A. M. Muzafarov[a,b]

[a]*N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation
[c]*M. V. Lomonosov Moscow State University of Fine Chemical Technologies,*
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation
[d]*Faculty of Physics, M. V. Lomonosov Moscow State University,*
Building 2, 1 Leninskie Gory, 119991 Moscow, Russian Federation.
E-mail: kram@polly.phys.msu.ru

The rheological properties of melts of nonfunctional hyperbranched polycarbosilane polymers differed in regularity of the structure and chain length between the branch points were studied for the first time. Unlike melts of linear polymers, the studied hyperbranched systems are Newtonian fluids, and the viscosity and activation energy of their viscous flow depend substantially on the molecular parameters and regularity of the molecular structure.

Key words: hyperbranched polycarbosilanes, dendrimers, rheology.

Hyperbranched polymers attracted researchers´ attention due to the whole complex of specific properties, among which are, *e.g.*, high functionality, globular shape, and nonstandard hydrodynamics of their solutions. At the early stages, the main attention was given to the study of the degree of similarity of hyperbranched polymers to their regular analogues: dendrimers.[1—5] One of basic distinctions between hyperbranched polymers and dendrimers is different compositions of units, due to which hyperbranched molecules are more loose than regular analogues. In addition, unlike hyperbranched macromolecules, dendrimers can be used as classical core—shell systems. This fact is more substantial than a difference in the composition of units, since the absence of regularity of the structure affects the hydrodynamic properties even after the chemical modification of hyperbranched polymers that eliminates this composition difference.[6—8] In addition, the structure of these polymers is not transformed into a core—shell system.

Distinctions in the organization of the molecular structure also predetermine different areas of application of dendrimers and hyperbranched systems. Dendrimers have good prospects in the areas where such unique properties as monodispersity, strict regularity, and possibility of controlling the nature of the external layer of the molecular structure are necessary. In particular, they are used in photonics as molecular antennas,[9,10] for the preparation of molecular composites by the synthesis of metal nanoclusters in the internal sphere of dendrimer,[11,12] and for the address delivery of bioactive material.[13] Owing to simplicity of the synthesis, accessibility, and high functionality, hyperbranched polymers found practical use as solidifying agents, modifiers, and cross-linking agents of polymer compositions.[14,15] The use of nonfunctional hyperbranched polymers is known to a significantly less extent. Meanwhile, the specific molecular organization makes it possible to consider them as new disperse media with unique properties for various liquid polymer compositions. Organoelement hyperbranched polymers with a wide temperature range of operability and controlled nature of chemical bonds are especially promising for these purposes. Such systems as polyperfluorophenylgermanes,[16] polycarbosilanes,[17—19] polycarbosilanesiloxanes,[20] and polysiloxanes[21] are known. Other heteroatoms (for example, sulfur) can also be introduced.[22,23]

Hyperbranched polycarbosilanes obtained by the polyaddition reaction are convenient objects for the study of possibilities for application of hyperbranched polymers as disperse media. They do not crystallize, have a broad temperature range of stability, and are chemically inert. The synthesis studied in detail,[8,17,24,25] the existence of a whole series of functional and nonfunctional derivatives,[23,26,27] and a fairly detailed study of the hydrodynamics of solutions[28,29] form a necessary basis for similar investigations.

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The main purpose of the present work is to study the rheological properties of the nonfunctional derivatives of hyperbranched polycarbosilane polymers with different molecular characteristics and to compare them with the properties of the dendrimer, whose molecular weight characteristics are similar to analogous parameters of hyperbranched polycarbosilanes.

Experimental

Organic solvents, *viz.*, hexane and toluene (Acros), were additionally dried by distillation over CaH_2 prior to use; THF was stored over NaOH and distilled over CaH_2. Methyldichlorosilane and dodecyl bromide were distilled prior to use. Carbosilane dendrimer G4($Si_{61}All_{64}$) was used after preliminary chromatographic purification.

Carbosilane dendrimer G5($Si_{125}Bu_{128}$) was synthesized according to a standard procedure[30] by the hydrosilylation of G4($Si_{61}All_{64}$) using methyldichlorosilane and the platinum catalyst PC-072 (Aldrich), being the zero-valent platinum complex with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (solution in xylene) followed by the reaction of BuLi in a hexane solution with G4($Si_{61}Cl_{64}$).

Carbosilane hyperbranched polymer PCS-Bu was synthesized according to an earlier described method,[8] which is a two-stage modification of the starting hyperbranched polymethyldiallylcarbosilane. The first stage was the preparation of the chlorine derivative of the polymer by hydrosilylation with methyldichlorosilane followed by its reaction with butyllithium.

Carbosilane hyperbranched polymer PCS-C11 was prepared by a previously described method[19] based on the reaction of organomagnesium synthesis and polyaddition using the PC-072 catalyst.

Synthesis of methyldidodecylsilane. Dodecyl bromide (5.2 g, 0.02 mmol) and anhydrous tetrahydrofuran (THF) (5 mL) for the initiation of the reaction were added to magnesium (15.56 g, 0.64 mol). Then a solution of dodecyl bromide (139.8 g, 0.56 mol) in anhydrous THF (550 mL) was added dropwise with stirring. The obtained reaction mixture was refluxed with stirring for 2.5 h. On cooling, a solution of methyldichlorosilane (30 g, 0.26 mol) in anhydrous THF (110 mL) was added to the mixture. The mixture was refluxed for 3.5 h. Then the mixture was cooled, and distilled methyl *tert*-butyl ether (400 mL) was added. A precipitate of $MgCl_2$ was dissolved in acidified water, and the layer was separated, washed with water to the neutral pH, and dried over sodium sulfate. The solvent was removed by evacuation on a rotor evaporator. The residue was subjected to vacuum distillation. Methyldidodecylsilane was obtained in a yield of 83.81 g (83.8%), b.p. 210—212 °C (2—3 mm Hg). ^1H NMR ($CDCl_3$), δ: 0.03 (d, 3 H, $SiCH_3$); 0.55 (m, 4 H, $SiCH_2$); 0.88 (m, 6 H, CH_3); 1.4 (m, 40 H, CH_2); 3.7 (m, 1 H, SiH).

Synthesis of PCS-dodec. Methyldidodecylsilane (28.7 g, 0.075 mol) was added dropwise with stirring to a mixture consisting of PCS-C11 (23.9 g, 0.068 mol), anhydrous hexane (120 mL), and Karstedt´s catalyst PC-072 (30 μL). The reaction mixture was stored in argon at 40 °C. The reaction course was monitored using the sampling method and analysis of the ^1H NMR spectra. As the complete conversion of the $CH=CH_2$ groups was achieved, the product was reprecipitated from methyl *tert*-butyl ether to C_2H_5OH. The polymer was obtained in a yield of 50 g (98%), glassy transition point –85 °C, m.p. = –40.8 °C. Found (%): C, 78.55; H, 13.76; Si, 7.65. Calculated (%): C, 78.63; H, 13.63; Si, 7.66. ^1H NMR ($CDCl_3$), δ: –0.9 (s, 6 H, $SiCH_3$); 0.5 (m, 12 H, $SiCH_2$); 0.88 (m, 6 H, CH_3); 1.3 (m, 76 H, CH_2).

Investigation methods. ^1H NMR spectra were recorded on a Bruker WP-250 SY spectrometer using $CDCl_3$ as a solvent. Chemical shifts were determined by the position of the signal from an impurity of nondeuterated $CHCl_3$.

The molecular weight was estimated by gel permeation chromatography (GPC) relative to the polystyrene standards on a chromatographic system consisting of a Staier high-pressure pump series 2 (Akvilon, Russia), a Smartline RI-2300 refractometric detector (KNAUER, Germany), and a Jetstream 2 Plus thermostat of columns (KNAUER, Germany). The temperature was maintained by the thermostat at 40 °C (±0.1 °C), THF was an eluent, the flow rate was 1.0 mL min^{-1}, and columns 300×7.8 mm packed with the Phenogel sorbent (Phenomenex, USA) were used (particle size 5 μm, pore size 10^5 Å). The analysis results were processed using the MultiChrome 1.6 GPC program (Ampersand, Russia) for the calculation of the molecular weight distribution or the UniChrom 4.7 program (Belarus).

Light scattering measurements were carried out on a Shimadzu system equipped with a DGU14U gas separator, an LC-10AD pump, and a CTO-10A thermostat. The column 300×7.8 mm was packed with the Phenogel sorbent (Phenomenex, USA) (pore size 10^3 Å) and equipped with a RID-10A refractometer and a Viscotek 270 double detector (RALS is 90° and LALS is 7°). The Omnisec 4.5 software was used. The system was calibrated using polystyrene standards with $M_w = 10\ 050$, $dn/dc = 0.185$. Using exact concentrations of the samples close to 25.00 mg mL^{-1}, the values of dn/dc were determined from the refractometric data. Then this value was applied in the Omnisec 4.5 software for the calculation of the real M_w from the light scattering data (RALS and LALS).

Fractionation was carried out by adding dropwise ethanol (as a precipitating agent) to a solution of the polymer in methyl *tert*-butyl ether. The third fraction was separated additionally into two fractions using a preparative chromatographic system.

The rheological characteristics of hyperbranched polycarbosilanes and carbosilane dendrimer G5 in the temperature range from 10 to 80 °C were measured on an MCR-302 rheometer (Anton Paar) in the constant shear strain mode (measuring node plane—plane).

Results and Discussion

In this work, we compared for the first time the rheological behavior of the carbosilane hyperbranched systems differed in geometric parameters and of the regular analogue, *viz.*, carbosilane dendrimer, whose molecular weight characteristics are similar to analogous parameters of the hyperbranched systems.

The carbosilane hyperbranched polymers studied in the work are similar in chemical composition and structure and differ only in the length of the spacer between the branch points (three and eleven CH_2 groups, respectively) and in the size of the terminal groups (butyl and dodecyl groups). The degree of branching of the hyperbranched polymers after blocking is the same and equal to 1.

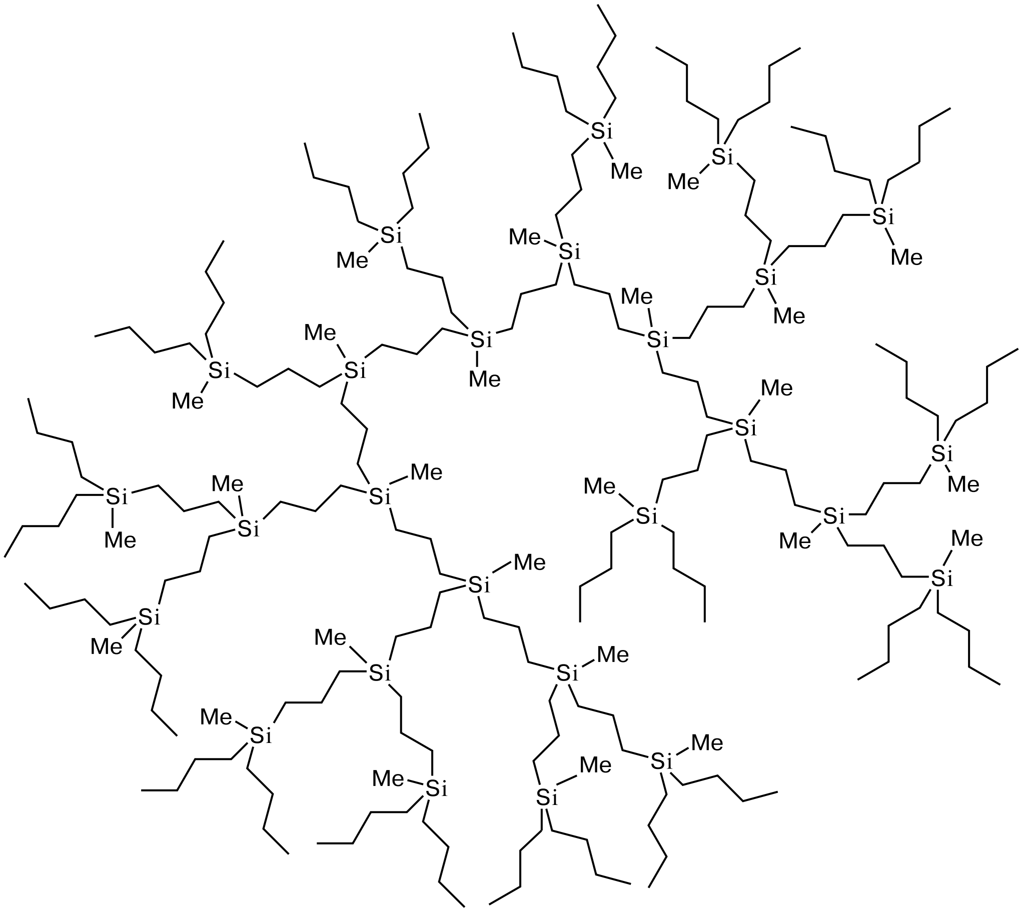


Fig. 1. Fragment of the molecular structure of carbosilane hyperbranched polymer PCS-Bu.

The fragment of the molecular structure of the carbosilane hyperbranched polymer with the spacer length C3 and butyl terminal groups (PCS-Bu) is presented in Fig. 1. The polymer is a full irregular analogue of the carbosilane dendrimer G5($Si_{125}Bu_{128}$) by both the chemical composition and set of units. The synthesis of the polymer was described earlier,[8] and the blocking process completely repeated the cycle of growth of the next layer of the molecular structure of the butyl derivative of the carbosilane dendrimer and consisted of two stages. At the first stage, the dichlorosilyl derivative of the polymer was obtained by hydrosilylation with methyldichlorosilane. At the second stage, the obtained product with chlorosilyl groups interacted with butyllithium.

The GPC curve of the obtained polymer PCS-Bu is presented in Fig. 2 and shows that the sample has a monomodal distribution. This indicates the absence of side interactions between the growing molecules.[17]

Another approach was developed to obtain the nonfunctional derivative of the hyperbranched polymer with undecyl spacers between the branch points (C11 corresponds to eleven CH_2 groups), the fragment of the molecular structure of which is shown in Fig. 3. For this purpose, the modifying agent was preliminarily obtained in high yield by the organomagnesium synthesis in THF similarly to the synthesis of monomers of the AB_2 type (Scheme 1).

The purity and structure of hydridesilane were confirmed by GLC, ^{1}H NMR spectroscopy, and elemental analysis data.

The subsequent modification of the starting hyperbranched polymethyldiundecenylcarbosilane was carried

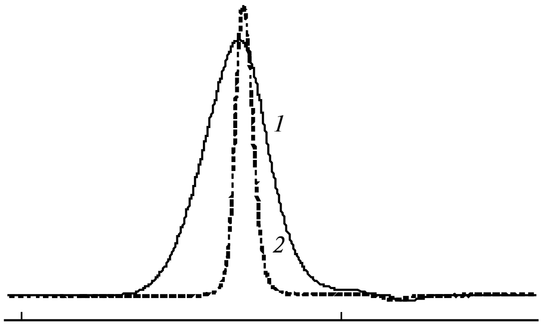


Fig. 2. GPC curves of the samples PCS-Bu (*1*) and G5 ($Si_{125}Bu_{128}$) (*2*).

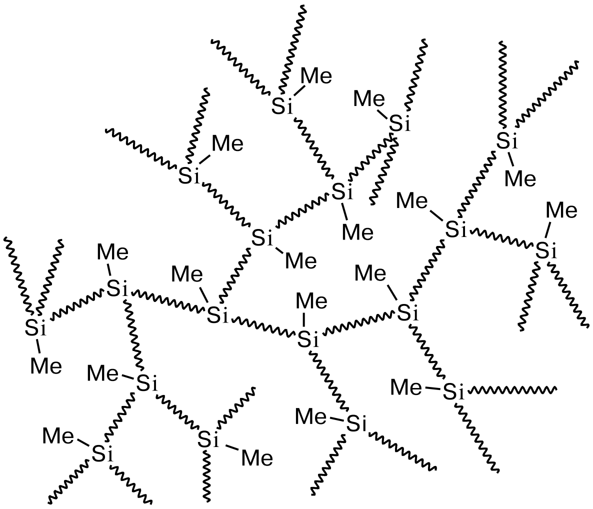
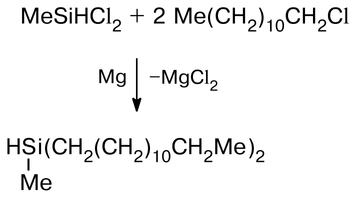


Fig. 3. Fragment of the molecular structure of carbosilane hyperbranched polymer PCS-dodec.

Scheme 1



$$\mathrm{MeSiHCl_2 + 2\ Me(CH_2)_{10}CH_2Cl \xrightarrow[\ ]{Mg,\ -MgCl_2} HSi(Me)(CH_2(CH_2)_{10}CH_2Me)_2}$$

out by the hydrosilylation of double bonds of the polymer with a modifying agent excess in the presence of the platinum catalyst. The obtained polymer was characterized by NMR spectroscopy, GPC, and elemental analysis. The GPC curve of the PCS-dodec sample, which is also monomodal, is presented in Fig. 4.

The hyperbranched objects under study were colorless viscous liquids highly soluble in organic solvents with low viscosity of solutions characteristic of hyperbranched systems. It has previously been shown[8] that their hydrodynamic behavior differs noticeably from that of linear analogues and approaches that of dendrimers. This is caused, to a significant extent, by the fact that hyperbranched molecules are characterized by high density of the molecular structure and the shape does not differ strongly from spherical one.

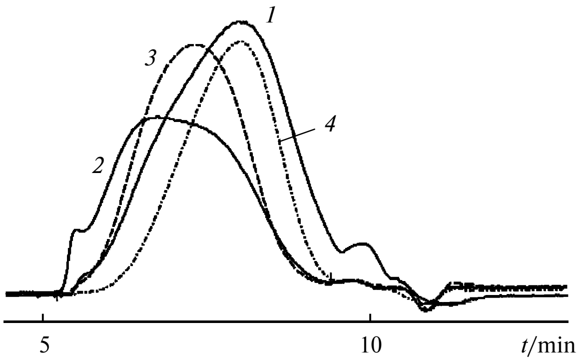


Fig. 4. GPC curves of the nonfractionated sample of PCS-dodec (*1*) and three fractions (*2—4*).

The results of the studies of the hydrodynamic and conformational characteristics of solutions of hyperbranched polymers differed in the chain length between the branch points indicated that the elongation of the spacer was accompanied by an increase in asymmetry of the molecules and resulted in a change in the hydrodynamic characteristics and molecular weight dependence, increasing the distinction of the hyperbranched systems from the dendrimer.[25] The hydrodynamic study of the narrow fractions of the PCS-Bu sample and comparison with the behavior of the dendrimer with a similar molecular weight (MW) revealed an important role of the regularity of branching in the properties exhibited by the hyperbranched macromolecule.[31]

In this work, we continued to study the influence of the structure regularity on the properties of the dendritic systems studying the rheology of these objects in block. To compare the properties of the hyperbranched polymers with dendrimers, we studied the rheological behavior of the carbosilane dendrimer G5($Si_{125}Bu_{128}$) (the calculated MW is 17 903.9). The characteristics of the studied objects are presented in Table 1.

At the first stage, we compared the rheological behavior of PCS-Bu and dendrimer G5($Si_{125}Bu_{128}$). The study of the dependences of the viscosity on the shear rate (Fig. 5) showed that both samples represented Newtonian liquids in the measured temperature range. A similar behavior of the hyperbranched systems was observed earlier, for example, for melts of polyaminoamide dendrimers of various generations.[33] The Newtonian behavior of hyperbranched macromolecules can be explained by a higher density of the molecular structure due to the

Table 1. Molecular weight and rheological characteristics of hyperbranched polycarbosilanes

Polymer	MW		η^b /Pa s	E_a /kJ mol^{-1}
	GPC[a]	DLS		
G5($Si_{125}Bu_{128}$)	—	17903.9[c]	6.5	32
PCS-Bu	10000	19600	0.6	32
PCS-dodec	64000	69900	40	43
PCS-dodec-1	105000	—	80	43
PCS-dodec-2	68000	—	62	43
PCS-dodec-3	34000	—	21	43

[a] As known, GPC gives underestimated values of MW for the dendrimers and hyperbranched systems.[32]

[b] At 20 °C.

[c] Calculation.

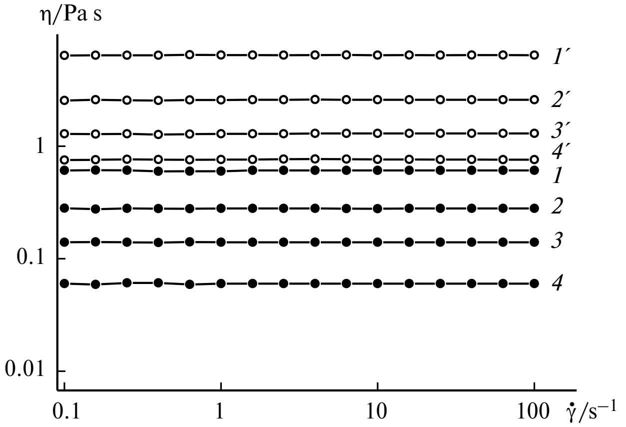


Fig. 5. Flow curves for PCS-Bu (*1—4*) and G5($Si_{125}Bu_{128}$) (*1′—4′*) at different temperatures: 20 (*1, 1′*), 40 (*2, 2′*), 60 (*3, 3′*), and 80 °C (*4, 4′*).

topology of branchings, which impedes the formation of entanglements.

The obtained values of viscosity (η) for the regular and hyperbranched polycarbosilanes at 20 °C are given in Table 1. It is important that at close MW the values of η for the G5($Si_{125}Bu_{128}$) and PCS-Bu systems differ very strongly. An unexpected result was obtained: the viscosity of the dendrimer turned out to be an order of magnitude higher than that of the hyperbranched polymer. When studying their solutions, an opposite dependence[8] was found, which is explained by different conformational behaviors of the regular and irregular systems, in particular, by the fact that hyperbranched macromolecules are swollen more strongly than the dendrimer. In the case of the melt, a high viscosity of G5($Si_{125}Bu_{128}$) can be related to specific features of the intermolecular interactions observed earlier for the dendrimers of high generations.[33,34]

Based on the temperature plots of the viscosity of polycarbosilanes, we calculated the activation energy of viscous flow (E_a) 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). The value of E_a is very sensitive to branchings in chains of linear polymers. The flexibility of the polymer chain exerts the determining effect on E_a and restricts steric hindrances to rotation. The interaction of groups of atoms also significantly affects E_a. The introduction of lateral substituents into the polymer chain increases the sizes of the segment and also induces an increase in E_a that characterizes the strength of the intermolecular interaction.[35]

The temperature plots of the viscosity of PCS-Bu and G5($Si_{125}Bu_{128}$) in the coordinates of the Arrhenius equation are presented in Fig. 6. As can be seen from Fig. 6, the both plots are straight lines, which makes it possible to determine E_a from the slope ratio. Thus, E_a = 32 kJ mol^{-1} for both hyperbranched PCS-Bu and dendrimer. This seems reasonable with allowance for the full identity of both chemical compositions and all elements of molecular structures of compared objects. The regularity of the structure exerts no effect on the activation energy.

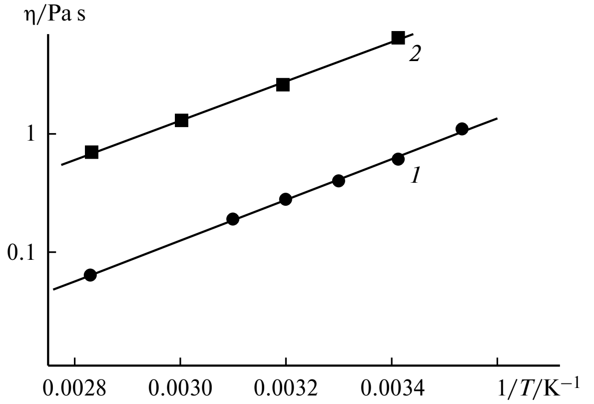


Fig. 6. Temperature plots of the viscosity of hyperbranched polycarbosilanes: PCS-Bu (*1*) and dendrimer G5($Si_{125}Bu_{128}$) (*2*).

At the next stage, the problem about the influence of geometric sizes on E_a was studied. In this case, the rheological characteristics of the hyperbranched polymer with eleven CH_2 groups between the branch points, *viz.*, PCS-dodec, were studied for comparison. It was found that PCS-dodec also behaves as Newtonian liquid (Fig. 7), its viscosity is 40 Pa s, and the activation energy of viscous flow is 43 kJ mol^{-1}. Thus, the elongation of the distance between the branch centers of the hyperbranched polymer increases both the viscosity and E_a. However, the MW of the studied PCS-dodec is significantly higher than that of PCS-Bu.

Three fractions of the PCS-dodec samples with different MW were distinguished for comparison of the studied hyperbranched systems and revealing the dependences of

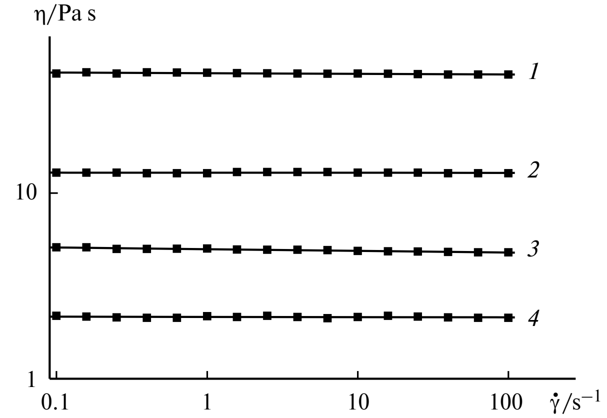


Fig. 7. Flow curves for PCS-dodec at 20 (*1*), 40 (*2*), 60 (*3*), and 80 °C (*4*).

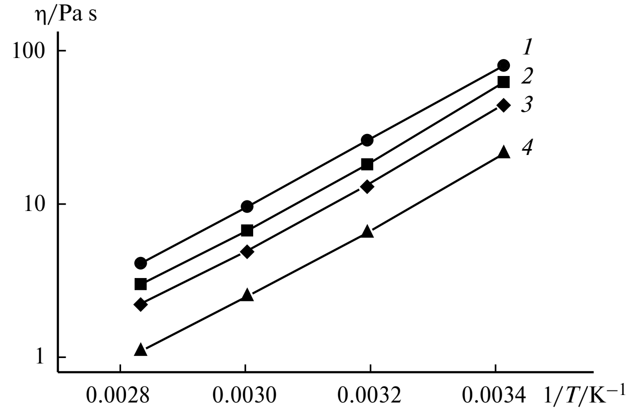


Fig. 8. Temperature dependences of the viscosity of PCS-dodec (*1*) and its fractions with different MW (see Table 1): PCS-dodec-1 (*2*), PCS-dodec-2 (*3*), and PCS-dodec-3 (*4*).

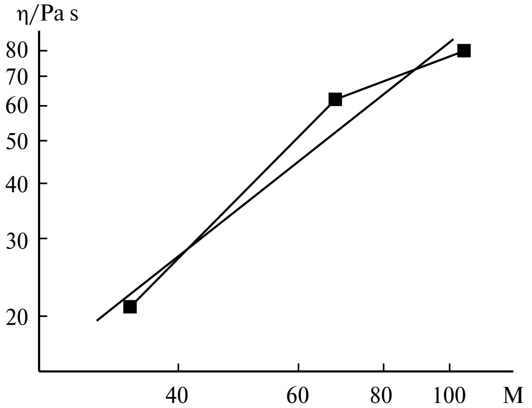


Fig. 9. Viscosity *vs* molecular weight of PCS-dodec (double logarithmic coordinates).

the viscosity and activation energy on the MW of the polymer. The temperature plots of the viscosity of the initial sample and fractions with different MW are shown in Fig. 8. As can be seen from the data presented, the viscosity of the polymers increases with MW and the activation energy of hyperbranched polycarbosilanes remains constant.

The analysis of the obtained data suggests that the spacer length of the hyperbranched polymer exerts a substantial effect on the viscosity of melts. In fact, the viscosity of PCS-dodec-3 with the lowest MW is higher by an order of magnitude than that of PCS-Bu with comparable MW. The strength of intermolecular interactions also increases with the elongation of the spacer, resulting in an increase in E_a.

The data obtained allow one to speak about the pronounced specificity of the behavior of the hyperbranched polymers compared to the classical linear systems. These distinctions are additionally illustrated by the viscosity dependence on the MW obtained from the fractions of the highest-molecular-weight sample PCS-dodec (Fig. 9). It is known that for melts of linear polymers forming cohesions the viscosity dependence of the MW is characterized by the equation $\eta \sim M^{\alpha}$, where α is equal to 3.4. The obtained slope of the straight line in Fig. 9 corresponds to $\alpha = 1.2\pm0.2$, which is significantly lower than the value characteristic of the linear systems. This indicates a deficient of entanglements in the hyperbranched system. A similar value of $\alpha = 1.1$ was obtained[33] for melts of the dendrimers.

Thus, the study showed that the behavior of hyperbranched polycarbosilanes basically differs from the behavior of the classical linear systems and the rheological characteristics of hyperbranched polycarbosilanes can be controlled in wide ranges selecting their molecular parameters. From this point of view, hyperbranched polycarbosilanes can be considered as new promising disperse media with unusual properties for the preparation of filled liquid compositions, such as magnetic liquids, lubrication compositions, and hydraulic liquids of various design.

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