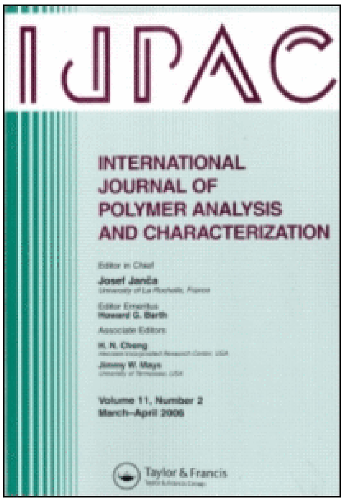

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Model and Hybrid Polystyrenes Containing Trispentafluorophenylgermanium End Groups

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Abstract: The synthesis of the model functionalized polymers of various molecular weight–containing active pentafluorophenylgermanium end groups was performed through chain-transfer reaction to germanium organic compounds-tris(pentafluorophenyl)germane by a free-radical polymerization of styrene. Upon subsequent activated copolycondensation of the obtained polymers with tris(pentafluorophenyl)germane in methyl ethyl ketone environment in the presence of the activator triethylamine hybrid linear-dendritic the block copolymers of polystyrene and perfluorinated poly(phenylenegermane) were obtained. Molar mass and hydrodynamic characteristics of model and hybrid polymers were studied by the methods of size exclusion chromatography, static and dynamic light scattering, and viscometry.

Keywords: Functionalized polymers; Hydrodynamic characteristics; Linear-dendritic block copolymers; SEC; Static and dynamic light scattering; Viscometry

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INTRODUCTION

Intensive development of the chemistry of hyperbranched and hybrid polymers has led to creation of linear-dendritic structures with useful characteristics. Physical and chemical properties of the given polymer class are extremely various and depend on the nature of components and character of interactions between them.[1] There is special interest in investigating the behavior of these polymers in solutions, which differs substantially from the properties of linear macromolecules.

In this connection, recently the attention of researchers has been directed to studying the hydrodynamic properties of hyperbranched polymers modified by linear polymers with various lengths and structures of the chain.[2] The influence of the polarity and thermodynamic quality of the solvent on the ability and character of self-organization of these macromolecules in solutions has been investigated in detail. For example, using the methods of static and dynamic light scattering, self-organization was observed in solutions of triblock terpolymers on the basis of flexible and rigid macromolecules.[3] It was shown that similar ensembles of block-copolymer molecules have a form that is close to cylinders consisting of rigid rings that are enveloped by polymeric macromolecular coils. These structures are similar to the "ring-coil" model. They form due to the hydrogen bonds, which lead to the appearance of the tetramer column systems.

Hybrid macromolecules containing fluorine fragments are important in practice.[4] Inclusion of such groups into macromolecules leads to high selectivity of polymer to solvents and to changes in physical characteristics such as the surface energy, friction coefficient, and glass temperature.[5] Previously, we have synthesized the model polystyrene PS-GeH(C_6F_5)$_2$, whose macromolecules have the bis(pentafluorophenyl)germane groups on the chain ends.[6] Using this PS-GeH(C_6F_5)$_2$, we have obtained the linear-dendritic block copolymers of perfluorinated polyphenylenegermane (PPG(H)) and polystyrene (PPG(H)-PS). The diblock copolymers PS-Ge(C_6F_5)$_2$-PS were synthesized. The properties of PS-GeH(C_6F_5)$_2$, PPG(H)-PS, and PS-Ge(C_6F_5)$_2$-PS in dilute solutions were investigated by size exclusion chromatography (SEC), light scattering, and viscometry methods. It was shown that functionalization of polystyrene chain by the bis(pentafluorophenyl)germane groups leads to supramolecular structure formation in polymer solutions. On other hand, the associative processes were not observed in the PS-Ge(C_6F_5)$_2$-PS solutions because in this case, the fluorine-containing component is surrounded by the long polystyrene chains. Similar self-organization was found in the solution of block copolymers of hyperbranched PPG and linear poly(methyl methacrylate) (PMMA).[7] The PPG-PMMA macromolecules are aggregated in methyl ethyl cetone, ethyl acetate, and dioxane, and elongated micelles are formed. Then the fluorine hyperbranched component content is increased, the association degree increases too, and the micelle shape is changed from rigid rod-like to spherical.

The aim of this work is to investigate the influence of tris(pentafluorophenyl)germane fragments attached to the ends of polystyrene chain on the macromolecular self-organization and to study the structural conformational properties of new dendritic block copolymers of PPG-PS. In order to solve this problem, we have synthesized the model functionalized polymers PS-Ge(C_6F_5)$_3$ and the hybrid linear-dendritic block-copolymers PPG-PS using methods of radical polymerization and following activated polycondensation. The properties of synthesized polymers in dilute solutions were investigated by the methods of molecular hydrodynamics and optics.

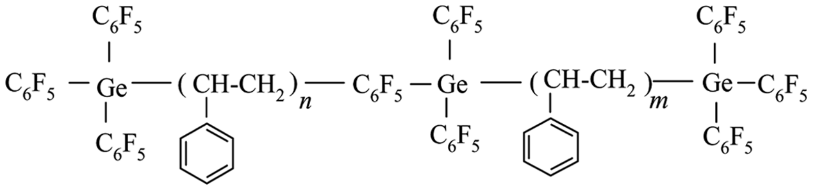
MATERIALS AND METHODS

Synthesis of Model Polymers PS-Ge(C_6F_5)$_3$

Styrene was dried over CaH_2 and distilled under reduced pressure. Solvents and an initiator (azobisisobutyronitrile, AIBN) were purified by standard methods of preparative organic chemistry.[8] Tris(pentafluorophenyl)germane, (C_6F_5)$_3$GeH, was synthesized by a technique described by Zaitsev et al.[9] The synthesis of the model functional polymers PS-Ge(C_6F_5)$_3$-1, PS-Ge(C_6F_5)$_3$-2, and PS-Ge(C_6F_5)$_3$-3 (Table I) was performed through chain-transfer reaction by the free-radical polymerization of styrene in the presence of (C_6F_5)$_3$GeH.[10] Bulk polymerization of monomers in the presence of (C_6F_5)$_3$GeH was carried out in dilatometric ampules at 333 K. The conversion of the monomers was monitored by gravimetry (10%). The polymers were precipitated three times and dried at room temperature to a constant weight in vacuum. Relative constants of chain transfer to (C_6F_5)$_3$GeH in the polymerization of styrene in mass ($T = 333$ K, [AIBN] $= 5 \times 10^{-3}$ mol/L, [styrene] $= 8.7$ mol/L) were determined by the Mayo method in the organogermanium

Table I. Conditions of synthesis and the molar mass characteristics (SEC) of the polymers

Polymers	[(C_6F_5)$_3$ GeH] mol/L	$M_w \times 10^{-4}$ g/mol (functional)	$M_w \times 10^{-4}$ g/mol (hybrid before Soxhlet)	$M_w \times 10^{-4}$ g/mol (block copolymer after Soxhlet)	Fraction of separated PPG, mas.%
PS-Ge(C_6F_5)$_3$-1	5×10^{-3}	7.4	7.6	5.7	8
PS-Ge(C_6F_5)$_3$-2	1×10^{-2}	4.2	3.7	2.6	18
PS-Ge(C_6F_5)$_3$-3	2×10^{-2}	3.5	2.9	1.9	46



Scheme 1. Structures of resulting polymers.

concentration interval from 0 to 2×10^{-2} mol/L. As a result of styrene polymerization, the functional polymers containing the structures shown in Scheme 1 are obtained.

Synthesis of Hybrid PS-PPG on the Basis of Functional PS-Ge(C_6F_5)$_3$

Two solutions were prepared for obtaining a hybrid product.

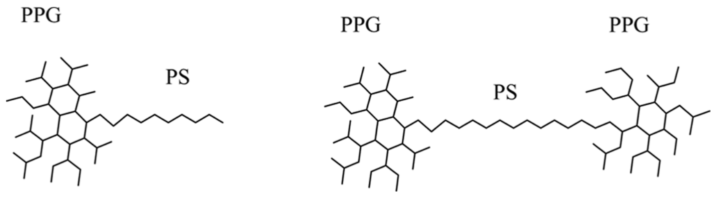
For solution number 1, the functional PS (0.344925 g) was dissolved in 8.6 mL of methyl ethyl ketone. An activator, Et_3N (0.5 mL), was added to this solution (the mole monomer-activator ratio is 1:3).

For solution number 2, monomer $(C_6F_5)_3GeH$ (0.68985 g) was dissolved in methyl ethyl ketone (8.6 mL). The mass ratio of $(C_6F_5)_3GeH$ and PS-Ge(C_6F_5)$_3$ is equal to 2.

Then, solution number 2 was added to solution number 1 (argon atmosphere, room temperature, synthesis duration of 1 h).[11] The obtained polymers were precipitated and dried in vacuum at 313 K to constant weight. The synthesized polymer contains the hybrid linear-dendritic macromolecules with the structures shown in Scheme 2.

Formation of hybrid macromolecules on the basis of the linear and branched polymers was proved by the methods of IR spectroscopy and SEC.

Individual free PPG is also formed during activated polycondensation of model PS-Ge(C_6F_5)$_3$ polymers. This PPG influences the molar mass distribution (MMD) and value of the polydispersity parameter. Consequently, it is necessary to delete the PPG. Hybrid products of



Scheme 2.

polymerization were purified using a method of hot separation (on Soxhlet apparatus) in cyclohexane. As a result, the main polymer was purified. This hybrid linear-dendritic block copolymer PS-PPG was characterized by the methods of SEC, light scattering, and viscometry.

Determination of Molar Mass and Hydrodynamic Characteristics by SEC

The molar mass characteristics of polymers were measured by SEC at 313 K using tetrahydrofurane (THF) as eluent on a Prominence LC-20VP (Shimadzu) instrument with refractive index detector and spectrophotometer ($\lambda = 254\,\text{nm}$) with 10^6 and 10^5 Å columns (TSK-gel). Molar mass (MM) of polymers was calculated using polystyrene (PS) standards.

Technique of Measurement of Hydrodynamic Characteristics

The macromolecular sizes and molar masses of investigated polymers were measured by static and dynamic light scattering methods on a Photocor apparatus (ZAO ANTEK-97, Russia). The optical section of the apparatus used in these measurements was equipped with Photocor goniometer and a Spectra-Physics helium-neon laser with a wavelength of $\lambda = 632.8\,\text{nm}$ and power of 10 mV. The scattering angles θ were varied from 30° to 135°. The correlation function of scattered light intensity was derived with the aid of a Photocor-FG correlator with 288 channels. The data were treated by the cumulant method and the Tikhonov regularization procedure. The values of hydrodynamic radii R_h of polymer molecules were calculated using the Stokes-Einstein equation:

$$R_h = \mathrm{kT}/6\pi\eta_0 D_0 \tag{1}$$

where η_0 is the solvent viscosity, T is the absolute temperature, D_0 is the diffusion coefficient of scattering particles, and k is the Boltzmann constant.

The weight-average molar mass M_w of polymers and the second osmotic virial coefficient A_2 were determined by the standard Debye procedure[11] using the formula

$$\frac{cH}{I_{90}} = \frac{1}{\mathrm{P}(90^\circ)M_w} + 2A_2c \tag{2}$$

where H is the optical constant equal to

$$H = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda_0^4} \tag{3}$$

In Equations (2) and (3), c is the solution concentration, I_{90} is the excessive intensity of light scattered at the angle of 90°, P(90°) is the Debye scattering factor for an angle of 90°, N_A is Avogadro's number, and dn/dc is the refractive index increment.

The dn/dc values were measured on an IRF-23 refractometer (Russia). For both the model and hybrid polymer systems, the refractive index increments coincided within the frames of experimental errors. The incorporation of the hyperbranched PPG block into macromolecules leads to decreasing of the dn/dc values: $dn/dc = 0.160\,\mathrm{cm}^3/\mathrm{g}$ for PS-Ge(C_6F_5)$_3$ and $dn/dc = 0.150\,\mathrm{m}^3/\mathrm{g}$ for PPG-PS.

Figure 1 shows the plots of cH/I_{90} versus concentration c. These plots are typical for dilute polymer solutions. Therefore, the values of weight-average molar mass M_w and second virial coefficient A_2 were calculated from the ratios (2) and (3). The values of M_w are shown in Table II. For all studied polymers, positive and relatively large values of A_2 were obtained. They lie in the interval from 0.3×10^{-3} to $1.6 \times 10^{-3}\,\mathrm{cm}^3\,\mathrm{mol/g}^2$. The A_2 values for hybrid systems are less than those for functional PS-Ge(C_6F_5)$_3$ polymers. This fact verifies the change for the worse (in thermodynamic quality) of the solvent due to the hyperbranched PPG blocks.

Over the studied concentration range, the diffusion coefficients D_0 and the corresponding hydrodynamic radii R_h of macromolecules do not depend on solution concentration c (Figure 2).

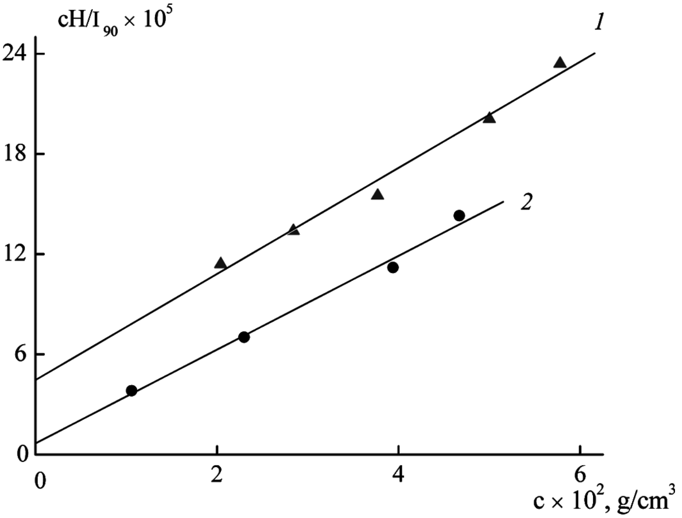


Figure 1. Plot of cH/I_{90} vs. c for the chloroform solution of PS-Ge(C_6F_5)$_3$-3 (curve *1*) and PS-Ge(C_6F_5)$_3$-1 (curve *2*).

Table II. Molar mass and hydrodynamic characteristics of the investigated polymers

Polymers	$M_{w,\mathrm{SEC}}$ $\times 10^{-3}$ g/mol	$M_w \times 10^{-3}$ g/mol	$[\eta]$, cm^3/g	k'	R_h, nm
PS-Ge(C_6F_5)$_3$-1	74	84	42	0.2	3.6
PS-Ge(C_6F_5)$_3$-2	42	39	25	0.3	2.8
PS-Ge(C_6F_5)$_3$-3	35	30	8	0.4	3.0
PS-PPG-1	57	87	27	0.2	5.8
PS-PPG-2	26	38	22	0.3	3.3
PS-PPG-3	19	30	12	0.3	3.1

The intrinsic viscosity $[\eta]$ was measured by an Oswald capillary viscometer. The solvent efflux time was $t_0 = 45.2$ s. For the investigated samples, the values of Huggins constant k' range from 0.2 to 0.4. Such values are typical for linear polymers in a good solvent.

The measurements were carried out in chloroform (density $\rho_0 = 1.486$ g/cm^3, dynamic viscosity $\eta_0 = 0.53$ sP, and refractive index $n_0 = 1.446$) at 21.0°C. All studied solutions were filtered using membrane filters (Millipore, USA) with the pore diameter 0.45 μm.

The obtained molar mass and hydrodynamic characteristics of the model and hybrid polymers are given in Table II.

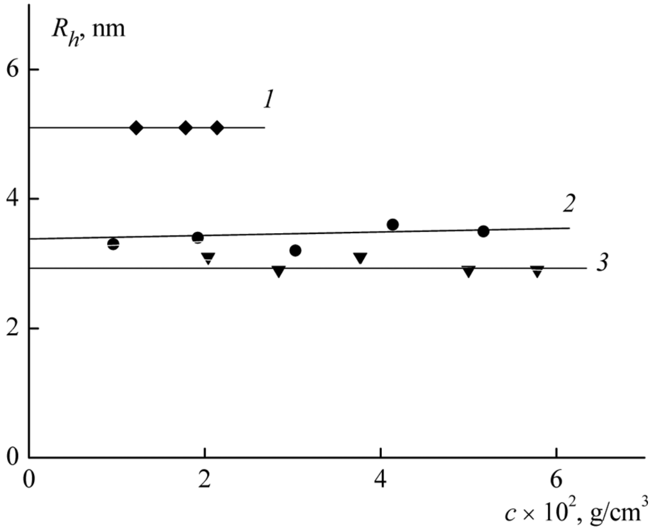


Figure 2. Plot of R_h vs. c for PS-PPG-1 (curve *1*), PS-PPG-3 (curve *2*), and functional polymer PS-Ge(C_6F_5)$_3$-3 (curve *3*).

RESULTS AND DISCUSSION

It can be seen from Tables I and II that in the case of model functionalized PS-Ge$(C_6F_5)_3$ polymers, there is a good agreement between the molar masses estimated by SEC ($M_{w,\mathrm{SEC}}$) and static light scattering (M_w) methods. For hybrid PPG-PS polymers, the values of $M_{w,\mathrm{SEC}}$ and M_w differ substantially. This is due to the incorrect use of the SEC calibration method for the determination of absolute values of molar masses of polymers with hyperbranched blocks. Indeed, the direct use of chromatographic methods involving the employment of linear polymer analogs as standards may yield underestimated molar mass values since the separation process is determined by the hydrodynamic volume of a polymer rather than by its molar mass.[12] As a consequence, SEC provides valuable information about MMD of polymers and gives the estimation of copolymer content when the spectrophotometric detector is used.

The analysis of the data presented in Table I makes it possible to conclude that the molar mass of hybrid polymers considerably decreases after separation of hyperbranched free PPG. Further discussion will explain the reasons for this finding.

The presence of an absorption band at 1520 $\mathrm{cm^{-1}}$ in an IR spectrum of functional PS-Ge$(C_6F_5)_3$ assigned to the vibration of group -C_6F_5 confirms that the given end groups are incorporated in the macromolecules. In the IR spectrum of hybrid PS-PPG, except for bands of absorption of groups -C_6F_5, there are characteristic bands at 980 $\mathrm{cm^{-1}}$, corresponding to the groups -C_6F_4.

From the SEC data presented in Figure 3, it can be seen that the hybrid polymer was obtained from the functional PS-Ge$(C_6F_5)_3$-1 by activated polycondensation. There are two peaks on the MMD (Figure 3, curve 2). One of them corresponds to the hybrid PS-Ge$(C_6F_5)_3$-1 polymer. The second one in the region of low molar mass is related to individual free PPG. In this case, its amount is 8 mas.% of total polymer mass (Table I). One can see from Figure 3 that the refractive index detector does not indicate the hyperbranched macromolecules in low molar mass region ($2.3 < \lg M_w < 4.3$) in contrast to the UV detector. Curve 3 characterizes the MMD of hybrid PS-PPG-1 (the main fraction of a block copolymer after separation). The given curve is displaced to lower molar masses than that of the functional PS-Ge$(C_6F_5)_3$-1 polymer, which is due to the presence of polyphenylengermanium block on the end of the polystyrene chain. This fact confirms the substitution of fluorine atom in para-position pentafluorophenyl rings by the -Ge$(C_6F_5)_3$ groups during activated polycondensation. The MMD curve 4 (Figure 3) for block copolymers PS-PPG-1 was determined by the spectrophotometric detector. The first

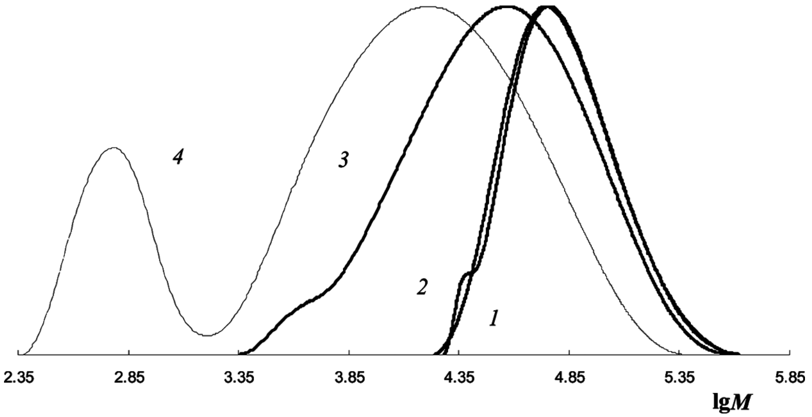


Figure 3. Data from SEC obtained with the refractive index detector for: The functional PS Ge(C_6F_5)$_3$-1 (curve *1*); hybrid product PS and PPG before extraction in Soxhlet extractor (curve *2*); hybrid block copolymers PS-PPG-1 after separation from PPG (curve *3*); and hybrid block copolymers PS-PPG-1 after separation obtained with the spectrophotometric detector ($\lambda = 254$ nm) (curve *4*).

maximum at $\lg M_w = 4.3$ is caused by PPG of the third generation, and the second maximum ($\lg M_w = 2.85$) corresponds to the branched polymer of the second generation.

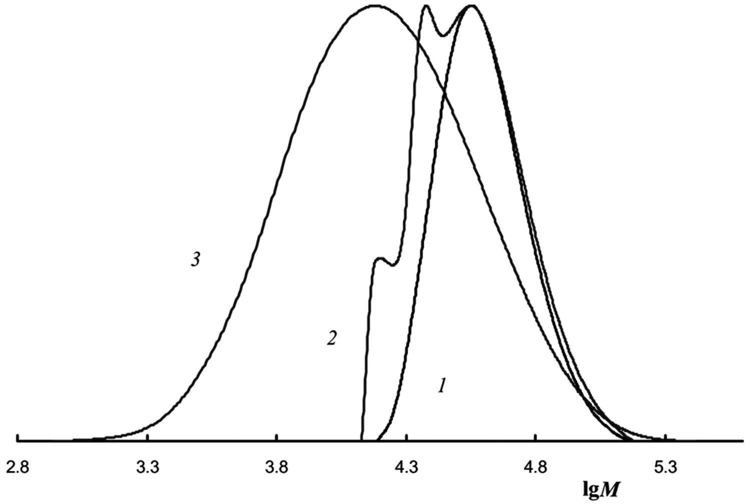


Figure 4. Data from SEC for the functional PS-Ge(C_6F_5)$_3$-2 (curve *1*); hybrid product PS and PPG before extraction (curve *2*); and hybrid block copolymers PS-PPG-2 after separation in Soxhlet extractor (curve *3*) (1, 2, 3—refractive index detector).

Figure 4 shows the chromatographic data for model PS-Ge(C_6F_5)$_3$-2 and hybrid PS-PPG-2 polymers. It is clearly seen that during activated polycondensation, the hybrid product with trimodal MMD is formed. The amount attributed to the individual PPG is 18 mas.%. It is necessary to note that MMD of the cleared block copolymer (after extraction of PPG) is unimodal. These two findings confirm the fact that hybrid PS-PPG with the branched fragment of the third generation is formed during activated polycondensation. The maximum MM corresponding to this polymer is at $\lg M_w = 4.1$. The individual PPG, which is formed independently without participation of functional PS-Ge(C_6F_5)$_3$)-2, is of higher molar mass.

In the case of low molar mass functional PS-Ge(C_6F_5)$_3$-3, the quantity of the separated PPG is equal to 46 mas. %. Therefore, the reaction of activated polycondensation is less effective for a small length of linear polystyrene blocks. MMD curve (Figure 5) of block-copolymer PS-PPG-3 is displaced in the range of low molar masses in comparison with functional polymer. During the synthesis of hybrid macromolecules, the third generation of the hyperbranched blocks on the end of polystyrene chains is formed. Correspondingly, the molar mass of the PPG block is equal to about 10000 g/mol (see Figure 5, curve 2). On other hand, a relatively large amount of individual free PPG (46 mas.%) is observed in the reaction product, and the molar mass of hyperbranched polymers is 15000–20000 g/mol.

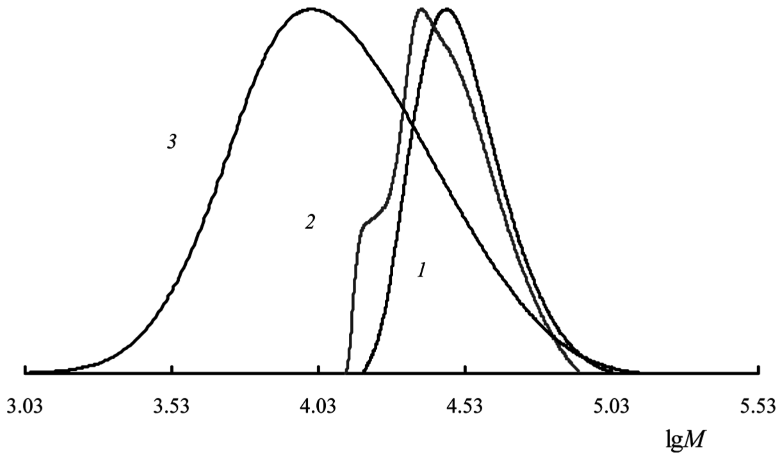


Figure 5. SEC data obtained with the differential refractive index detector for the functional PS-Ge(C_6F_5)$_3$-3 (curve *1*); hybrid product PS and PPG before extraction (curve *2*); and hybrid block copolymers PS-PPG-3 after extraction (curve *3*).

It can be seen from Table I that the fraction of hyperbranched polymer that is not involved in the reactions of formation of hybrid macromolecules considerably increases with the decreasing length of the linear block in the functional polymer. This fact can be explained in the following way. The reaction of the activated polycondensation of functional polystyrene with $(C_6F_5)_3GeH$ in the presence of Et_3N was provided in methyl ethyl ketone, which is a good solvent for both the fluorinated component and linear polystyrene. However, the presence of activator Et_3N in the reaction solution substantially decreases its thermodynamic quality. Accordingly, the growth in molar mass of linear polystyrene is accompanied by growth in the size and density of the macromolecular coils surrounding the active centers. Therefore, the reaction of free PPG formation becomes more preferable with the increase of molar mass.

The hybrid PPG-PS polymers after separation of hyperbranched free PPG were investigated only by light scattering and viscometry.

The molar masses of model functionalized PS-$Ge(C_6F_5)_3$ polymers and the hybrid linear-dendritic block copolymers PPG-PS are close each to other. At first view, this is not understandable. Indeed, the growth of the –$Ge(C_6F_5)_3$ groups to hyperbranched PPG blocks should lead to an increase in molar mass. However, it is necessary to take into account that the molar masses of hyperbranched blocks are not greater than 22000 g/mol since the generation number of PPG is less than three, as mentioned above. Consequently, molar masses of model and hybrid polymers may differ by the same value. Even in the case of low molar mass samples, the difference in the M_w of PS-$Ge(C_6F_5)_3$-3 and PPG-PS-3 does not exceed 30%. Let us recall that the error in molar masses measured by the light scattering method is 15–20% for low molar mass polymers. Therefore, the expected difference in molar masses of PS-$Ge(C_6F_5)_3$ and PPG-PS lies in the range of experimental errors.

The hydrodynamic behavior of the investigated model and hybrid polymers is different. As one can see from Figure 6, the intrinsic viscosities $[\eta]$ of PS-$Ge(C_6F_5)_3$ are close to the values that may be expected for linear polystyrene with the same molar masses. The dependence of $[\eta]$ on molar mass for linear polystyrene in chloroform (Figure 6, dotted line) was plotted using the Kuhn-Mark-Houwink equations $[\eta] \sim M^a$ obtained in the molar mass region, which is close to that for the investigated polymers.[13] It is clear from Figure 6 that the $[\eta]$ values for model functionalized polymers are in agreement with the dependence of $[\eta]$ on molar mass for linear polystyrene. Correspondingly, it is possible to conclude that the conformation of model PS-$Ge(C_6F_5)_3$ macromolecules is practically the same as for chain polystyrene molecules. Hence, the existence of –$Ge(C_6F_5)_3$ on the chain ends does not lead to change in hydrodynamic and conformational properties of polystyrene.

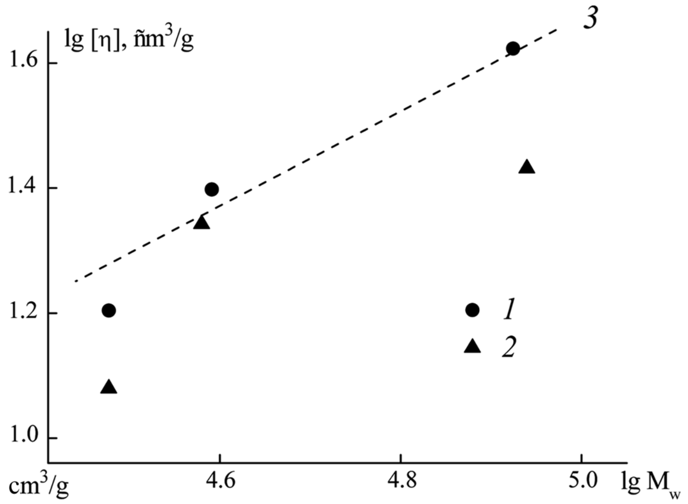


Figure 6. Dependence of the intrinsic viscosity [η] on molar mass for functional (curve *1*), hybrid (curve *2*), and linear PS (curve *3*) in chloroform.

Another situation is for hybrid linear-dendritic PPG-PS block copolymers. At the same molar masses, the intrinsic viscosity of PPG-PS is less than the [η] values of linear polystyrene. This means that the macromolecules of hybrid PPG-PS block copolymers have a more compact and dense structure in solution. It is probably related to the massive rigid block (hyperbranched PPG) presence in hybrid macromolecules. On other hand, it has to be noted that the hydrodynamic radii R_h of PPG-PS macromolecules are close to the R_h values, which may be expected for linear polystyrene chains in chloroform. The estimations analogous to those from work[14] show that the hydrodynamic size of PPG-PS macromolecules differs less than 30% from hydrodynamic radii of polystyrene molecules. Furthermore, the systematic changes in the R_h values are not observed when passing from linear polystyrene to the investigated hybrid (and model) polymers. This contradiction between the data on rotational (intrinsic viscosity) and translational (diffusion coefficient) friction may be explained easily. It is known that in the first approximation, the intrinsic viscosity is proportional to $R_h{}^3$ whereas D_0 is proportional to R_h. Consequently, the intrinsic viscosity is more sensitive to the change in shape and size of polymer molecules than the diffusion coefficient. Correspondingly, we may assume that the difference in conformation of the model PS-Ge(C_6F_5)$_3$ and hybrid PPG-PS macromolecules is rather small and this difference cannot be observed by the light scattering method.

CONCLUSIONS

In contrast to previously investigated systems containing polystyrene linear blocks,[14] supramolecular structures do not exist in solutions of both model functionalized and hybrid polymers. We have observed only isolated macromolecules when using methods of light scattering and viscometry. It may be supposed that such behavior of the polymers investigated in this work is caused by the presence of end tris(pentafluorophenyl)-germane groups in the macromolecules. These groups are more rigid and symmetric than bis(pentafluorophenyl)germane groups. Probably, the coiled polystyrene chains attract the end of fluorine fragments inside macromolecules. The associative processes do not take place due to the absence of fluorine groups on the surface of macromolecular coils.

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