Online journal “Fluorine notes” ISSN 2071-4807, Vol. 4(137), 2021; DOI: 10.17677/fn20714807.2021.04.03

ARTICLE INFO
Received 02 July 2021
Accepted 10 July 2021
Available online August 2021

PRORERTIES OF HYPERBRANCED PERFLUORINATED POLYPHENYLENEGERMANE MOLECULES

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Abstract: The simplest structure of perfluorinated polymer of hyperbranched polyphenylenegermane (HBP PPG) is considered. For this structure, the characteristic sizes and molecular weights of polymers of first - third generations were calculated. Experiments on small-angle X-ray scattering (SAXS) and X-ray diffraction of HBP PPG have been carried out. Using the experimental data as the base, the individual characteristic sizes of amorphous polymer macromolecules were determined.

Keywords: perfluorinated hyperbranched polyphenylgermane, characteristic molecule dimensions.

Introduction

Nowadays, the polymers are a principal materials used in a wide variety of industries. In most cases, these polymers are consisted of linear macromolecules, which are in the form of individual long chains. In this case, each individual macromolecule in the process of polymerization has one growth point, in which the monomers are sequentially connected with each other by covalent bonds.

Polymerization of bis-, tris- and poly- functional compounds leads to formation branched polymers, for which the number of growth points in the macromolecule increases during polymerization. The parameters characterizing various polymers have a multilevel structure (chemical, topological, supramolecular). This also applies to hyperbranched polymers (HBPs) studied in this paper. The synthesis and description of main properties of HBPs are considered in [1].

HBPs are polymers with complex architecture, distinguished in topology of macromolecules, a high volume concentration of chain links within macromolecules, and the presence of a large number of functional groups on their periphery. One of the main advantages of HBPs synthesis used in [1] (in comparison with traditional polymerization processes) is high rate of one-stage polymerization processes.

Among organic polymers, fluorine-containing polymers are of considerable interest. Perfluorinated polymers (i. e. polymers, containing as high as possible percentage of fluorine F) have a low dielectric absorption (up to the low-frequency part of THz range), a relatively low value of refractive index, have mechanical strength and high heat&chemical resistance [2]. Surface properties of such polymers are actual, whereas it has a low surface energy (which externally manifests itself as a small coefficient of mechanical friction μ with polymer surface). Note that polymerization of some of these polymers (and copolymers) requires ultrahigh pressures, which complicates their synthesis.

Formulation of the problem and methods of its solution

In this paper, we investigated the molecules of amorphous perfluorinated hyperbranched polyphenylenegermane (HBP PPG). The first purposeful synthesis of such polymer by one-step method was carried out by team members of Academician G.A. Razuvaev scholar school, when epy germanium derivatives $(C_6F_5)_3GeX$ were used as Flory monomers of AB_3 type (note, that X = H [3] was usually used). During polymerization of compound studied in this paper, the initial “monomer” was tris-(pentafluorophenylene) germane, that reacted within an hour (at room temperature) with triethylamine $(H_3C\text{-}CH_2)_3N$. Description of HBP PPG polymerization reaction in this case, see in [1].

Theoretical computational studies of polymer molecules were carried out on the assumption that all molecules have a certain definite regular structure (such as in Fig. 1). For such structure of HBP PPG quantum-chemical calculations for molecules were carried out using the ORCA program [4]. In this computations we used HF-3c procedure [5], based on Hartree-Fock method with three corrections (for dispersion, for incompleteness of used basis and for basic superposition error). The HF-3c procedure is a complete procedure included in ORCA program.

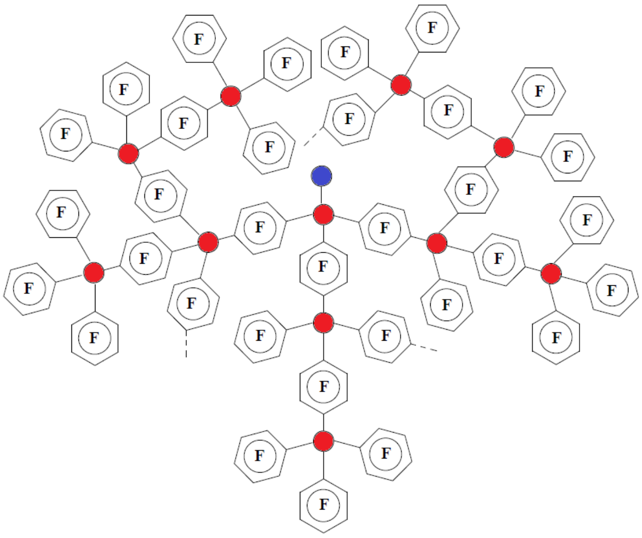


Figure 1. *Model of simplified structure of HBP PPG polymer (see [1], p. 34)*

In this figure, the germanium (Ge) atoms are highlighted in red and hydrogen atom (H) in the center of structure – in blue.

X-ray measurements of scattering and diffraction were carried out per HBP PPG samples in the form of a fine powder. In these experiments, the powder of HBP PPG of third generation was used.

Measurements of small-angle X-ray scattering (SAXS) intensity were carried out via diffractometers AMUR-K and HECUS SYSTEM-3 equipped with Kratki collimation systems and single-coordinate position-sensitive detectors OD3M, at a fixed radiation wavelength l = 1.542 Å (CuKα line for sharp focus tube with copper anode, monochromator was made of pyrolytic graphite). X-ray beam cross section was 0.2 × 8 mm, the scattering angle range corresponded to the range of values of scattering vector modulus $0.01 < s < 1.15$ Å^{-1} (where $s = (4\pi.\sin\theta)/\lambda$, 2q is scattering angle). The samples were placed in a glass cuvette. X-ray diffraction pattern of these samples was measured in Bragg-Brentano geometry [6] (“in reflection mode”) via Rigaku MiniFlex 600 diffractometer (CuKα line, λ = 1.5418Å, 40kV, 15mA, Ni-K$_\beta$-filter) in angular range 2θ = 4 - 45°with a scanning step of 0.02° and at speed of 0.8°/min. The beam size incident on the samples was set using horizontal and vertical slits (10 mm and 0.625°, respectively), that made from lavsan film with a thickness of 10 microns. The measurement time for one sample was 20 min. The experimental data were normalized to incident beam intensity, after which a correction for collimation distortions was introduced into them. The scattering data from empty cell was subtracted from scattering data by the samples.

For studies by X-ray diffraction, HBP PPG powder was applied to a glass cuvette. X-ray diffractogram of samples was measured in Bragg-Brentano geometry [6] (“in reflection mode”) via

Rigaku MiniFlex 600 diffractometer (CuKα line, λ = 1.5418Å, 40kV, 15mA, Ni-K_β filter) in angular range 2θ = 4 - 45°, with a scanning step of 0.02° and at speed of 0.8° / min. The beam size incident on the samples was set by horizontal and vertical slits (10 mm and 0.625°, respectively).

Sizes of HBP PPG molecules

The starting monomer was tri(pentafluorophenyl)germane molecule shown in Fig. 2.

***Figure 2**. Monomer molecule tri(pentafluorophenyl)germane ($F_{15}C_{18}$)GeH.*

At monomer center there is a Ge atom, covalently bonded to hydrogen atom H. The polymer is formed by attaching the monomers through F atoms in the para-positions of all phenyl groups. In case of an infinite large polymer, any Ge atom can be considered as a center, and all such atoms (except only 1) have four attached phenyl groups. Next, we considered molecules obtained by adding monomers to tetra(pentafluorophenyl)germane (i.e. molecules of the next (second) stage). For it, the geometry was optimized and the vibrational frequencies were calculated: it are started from 5 cm^{-1}, and molecule diameter is about 16 Å.

In the next third step, there are twelve attachment positions, resulting in a molecule of 573 atoms. The geometry is also optimized for it and the vibrational frequencies can be calculated. Within the framework of the simplified polymer structure (see Fig. 1), further attachment of monomers to all available positions is impossible for steric reasons.

Table 1 shows the results of calculations molecular weight of HBP PPG macromolecule (depending on the "generation" number), as well as their characteristic sizes. For second generation the shape of HBP PPG molecule is close to spherical (with diameter d), for third generation - is close to elliptical.

Table 1. *Results of calculations molecular weight of HBP PPG macromolecule.*

No generation of HBP PPG	Macromolecule mass MW, u	Characteristic dimensions of molecule, Å
1	575	
2	2239	d»16
3	7232	» 30 x 30 x 19

The calculated molecular weight M_W for third generation of HBP PPG (with 7232 u) corresponds to the interval in which the mass of low molecular weight fraction was measured for these polymers (see [3], p. 49). The authors also explain the limitation of M_W by steric difficulties arising during polymerization of HBP PPG. It was shown that M_W is actually limited to 22,000 u for any models of third generation of HBP PPG (see [3], p.49). Compared with the data in Table 1, there is a threefold difference, which, in our opinion, is due to scarcity of computational model.

Small-angle scattering of X-rays (SAXS) and neutrons is one of the most effective non-destructive methods for studying the supra-atomic structure of disordered and partially ordered materials at a resolution of 1–100 nm (at so-called “nanoscale region”). The main advantage of small-angle scattering method is its generality: it can be used upon study of disordered objects, and does not require special sample preparation. The experimental SAXS results obtained for SB PPG samples are shown in Fig. 3.

The SAXS data recorded at s near 0.9 $(Å)^{-1}$ show a very weakly pronounced maximum corresponding to characteristic size 2π/0.9 » 7 Å. This maximum, according to [8, p. 78], reflects the internal structure of HBP PPG molecule with a resolution of about 1 nm. Theoretical calculations carried out for second generation of PFHs give very close data, d » 6.6 Å is the distance between different Ge atoms located on opposite sides of the same fluorophenyl ring.

The shape of SAXS intensity curve confirms the HBP PPG data – it is an amorphous substance, since there are no pronounced diffraction maxima at the scattering curve.

Using the Guinier approximation [9], from initial section of scattering curve, one can estimate the radius of gyration of the particles R_g:

$$\ln I_{\exp}(s) » \ln I_{\exp}(0) - \frac{s^2 R_g^2}{3} \qquad (1)$$

This approximation is based on a model that assumes that substance is composed of identical particles. Nevertheless, in the case of polydisperse samples, the analysis of intensity graph shape of SAXS makes it possible to estimate the distribution of molecular particles and their aggregates along the radii of gyration using the tangent method [10], which are carried out in different sections of scattering curve plotted in Guinier coordinates.

This method, which is often used by many researchers, is approximate, but it allows to rough estimate of size of scattering inhomogeneities distribution [10]. Note that Guinier approximation is used within narrow range of scattering vector modulus, and also - that the tangents to Guinier plot reflect dimensional parameters within narrow range of scattering vector modulus. For SAXS measurements, instead of tangents, we used a linear approximation of Guinier data at intervals within about 5% of full range, i.e. carried out the statistical averaging of results over the nearest neighborhood. It should be noted that formfactor parameter of molecule is not used in Guinier approximation.

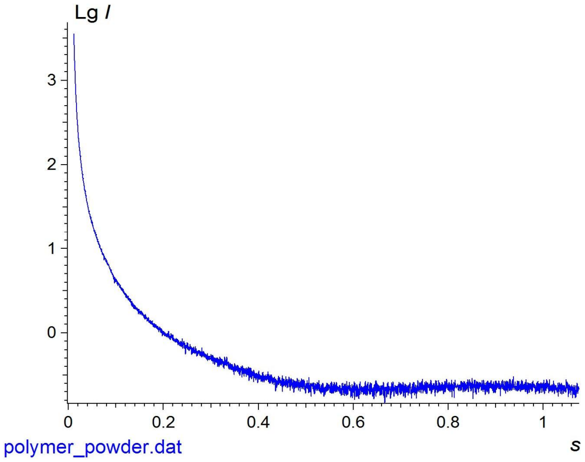
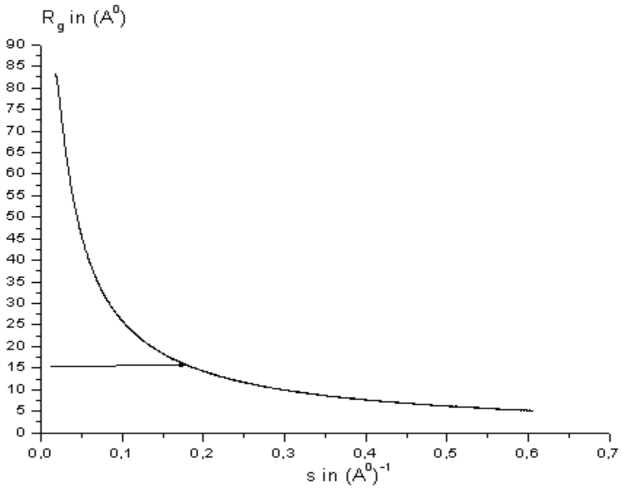


***Figure 3**. Experimental small-angle scattering intensity **I** from sample of HBP PPG powder.*

The main result (relating to concentration of molecules) falls at s> 0.2 (Å)$^{-1}$. Fig. 4 it follows that the boundary between two sections at SAXS curve corresponds to a point with a minimum radius of curvature r. According to [12], the radius of curvature of a plane curve y = y (x) is calculated according to a formula:

$$(1/r) = y'' / [1+(y')^2]^{3/2} \qquad (2)$$

where y' = dy/dx is the first derivative; y" = d^2y/dx^2 is the second derivative of function y = y (x). The horizontal line in Figure 4 shows the approximate position of the point with minimum radius of curvature. The small-angle section corresponds to scattering by chaotic fluctuations of molecular aggregates density; at large angles, the main contribution to the scattering gives the shape of molecules and, with angle increase, gives their internal structure.



Fiure 4*. Dependence of gyration radius R_g on scattering vector modulus.*

The results of X-ray diffraction measurements for HBP PPG powder are shown in Fig. 5.

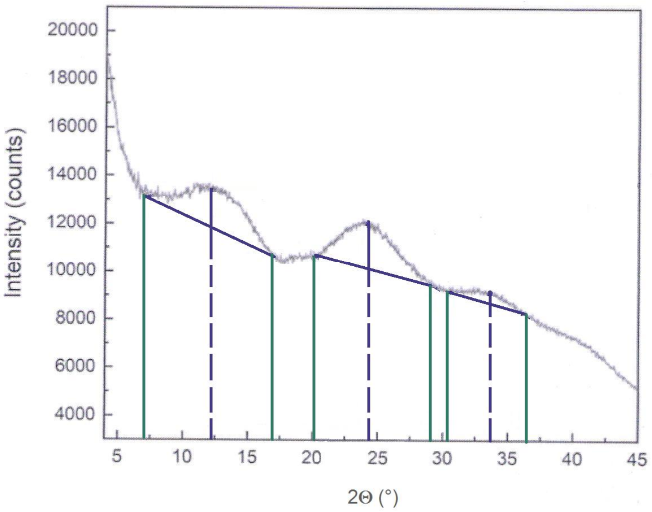


Figure 5. *Experimental results, obtained by using HBP PPG diffractogram.*

General character of curve showed in Fig. 5 confirms that PPG is an amorphous substance that has 3 characteristic sizes. The angles corresponding to the maximums of 2q are equal 12°, 24° and 33.3°. In [13] is provided so-called “Scherer's formula”, which was used to calculate the characteristic dimensions of inhomogeneity L.

The characteristic size of inhomogeneities is calculated according to a formula:

$$L = l \,/\, (b \cdot \cos q) \qquad (3)$$

where b is the maximum half-width (in radians). The value of a characterizes the ratio of maxima at the diffractogram to the total signal level for a given angle. The larger the value a, the more noticeable is signal against the general background.

Table 2. *The characteristic size of the HBP PPG molecules.*

No	2q, max, Deg.	Cos q	D(2q), Deg.	Dq, Deg.	b, Rad.	L, **A**^{0}	a
1	12	0,995	9,67	4,84	0,084	18,5	0,18
2	24	0,978	8,33	4,16	0,073	21,6	0,23
2	33,3	0,958	5,0	2,50	0,044	36,6	0,12

Use of HBP PPG molecules

The peculiarities of HBP PPG molecules are related with the fact that these molecules are easily soluble in most solvents, and these molecules themselves are non-toxic [1]. For "inflation" of polymer (i. e. obtaining a large volume of externally accessible pores in the polymer), it is possible to use in the process of pore formation the supercritical CO_2 [14]. This may allow hereafter to use SB PPG as a matrix for introduction of necessary drugs.

Like most perfluorinated polymers, SB PPG can be used as a material (or its component) in microelectronics.

Acknowledgments

This study was supported by the Ministry of Science and Higher Education RF. X-ray diffraction analysis was carried out using scientific equipment of the Center for Shared Use of the Federal Research Center RAS "Crystallography and Photonics". The authors are grateful to A.P. Sviridov and V.I.Sokolov for useful discussions.

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