Journal of Colloid and Interface Science 360 (2011) 204–210

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Specific vapor sorption properties of phosphorus-containing dendrimers

Alexander V. Gerasimov [a], Marat A. Ziganshin [a], Alexander E. Vandyukov [b], Valeri I. Kovalenko [b], Valery V. Gorbatchuk [a,*], Anne-Marie Caminade [c,d], Jean-Pierre Majoral [c,d]

[a] Institute of Chemistry, Kazan (Volga Region) Federal University, Kremlevskaya St. 18, Kazan 420008, Russia
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry, KSC RAS, Akad. Arbuzova St. 8, Kazan 420088, Russia
[c] CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, 31077 Toulouse cedex 4, France
[d] Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse, France

ARTICLE INFO

Article history:
Received 20 December 2010
Accepted 8 April 2011
Available online 17 April 2011

Keywords:
Dendrimers
Vapor sorption
Guest exchange
QCM sensor
Thermogravimetry
Differential scanning calorimetry
FTIR microspectroscopy

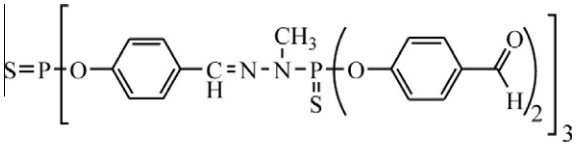
ABSTRACT

Specific combination of guest sorption properties was observed for phosphorus-containing dendrimers, which distinguish them from ordinary polymers and clathrate-forming hosts. The sorption capacity for 30 volatile guests, binding reversibility, guest desorption kinetics and guest exchange, glass transition behavior and ability to be plasticized with guest were studied for phosphorus dendrimers of different generations ($\mathbf{G}_1$–$\mathbf{G}_4$ and $\mathbf{G}_9$) using quartz crystal microbalance sensor, FTIR microspectroscopy, atomic force microscopy, simultaneous thermogravimetry and differential scanning calorimetry combined with mass-spectrometry of evolved vapors. The dendrimers were found to have a different selectivity for different homological series of guests, high glass transition points without plasticization with guest even at high temperatures and saturation levels, moderate guest-binding irreversibility and ability both for effective guest exchange and independent guest sorption. These properties constitute an advantage of the studied dendrimers as receptor materials in various applications.

1. Introduction

Solid dendrimers are good receptors for use in sensors [1] and nanoparticle catalysts [2]. Having tightly packed end groups, dendrimers of higher generations are selective to the size and shape of guest molecules with a preference for the smaller and less branched guests [3,4]. The selectivity of dendrimers may be high because of their ability to sorb different substrates in different binding sites. Being derived from structural considerations [5], the presence of different binding sites in dendrimers was directly proved by ^{1}H NMR [6] and fluorescent [7] titration in solution. For dendrimers in solid state, this feature was concluded from dependence of guest uptake on their generation number [8] and from different adsorption kinetics for different substrates [9]. Only general selectivity of solid dendrimers for guest vapors without differentiation on different binding sites has been studied for polyamidoamine (PAMAM) [10–14], poly(propyleneimine) (PPI) [8,9,14,15] and polyphenylene (PPh) [14,16,17] dendrimers.

The study of such selectivity differentiation was performed in the present work for organophosphorus $\mathbf{G}_n$ dendrimers, of the first ($\mathbf{G}_1$), second ($\mathbf{G}_2$), third ($\mathbf{G}_3$), fourth ($\mathbf{G}_4$) and ninth ($\mathbf{G}_9$) generations with core >P(S)—, spacer unit *p*-(—O—C_6H_4—CH=N—N(CH_3)—), branch unit >P(S)— and terminal group *p*-(—O—C_6H_4—CHO) using quartz crystal microbalance (QCM) technique.



$\mathbf{G}_1$

These dendrimers have an average flexibility of branches compared with the other studied elsewhere: lower than PAMAM, PPI and polyaryl ether (PAE) dendrimers and higher than PPh dendrimers [18]. More flexible dendrimers exhibit a backfolding of their branches, which is believed to give more tightly packed molecular interior and have an impact on the guest encapsulation [19]. For $\mathbf{G}_n$ dendrimers, having longer semi-rigid C_6H_4—CH=N—N(CH_3)—P(S) fragments, backfolding may be of less importance [18], giving space for interpenetration of neighboring molecules in solid phase to reach the tight packing. Both effects may produce a specific binding selectivity of $\mathbf{G}_n$ dendrimers through the absence or presence of guest size exclusion depending on guest ability to come closer to the dendrimer core.

So, in present study, the size exclusion effect by solid $\mathbf{G}_n$ dendrimers was studied for sorption of guests from different homological

* Corresponding author. Fax: +7 843 2927418.
E-mail address: Valery.Gorbatchuk@ksu.ru (V.V. Gorbatchuk).

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.04.017

series. The observed selectivity variation characterizes a molecular recognition ability of the studied receptor when using a suitable standard state [20–22].

The key problem in description of sorption by macromolecular receptor is an ability of sorbate to plasticize the sorbent. If plasticized, a glassy polymer can lose its enhanced selectivity [23,24]. For many dendrimers studied elsewhere, this problem does not occur, as their sorption parameters are determined above their glass transition points [14,16,17]. To characterize this property of the glassy dendrimers $\mathbf{G}_1$–$\mathbf{G}_4$, their glass transition temperatures were determined in the present work. These values were used also to explain an observed specific relationship between an average guest sorption capacity and dendrimer generation number. Glass transition temperatures of polymeric materials usually correlate with their packing efficiency and molecular surface area accessible for solvent molecules [25], and respectively, should correlate with their sorption capacity below the glass transition points. Because of specific dendrimer shape and the above-mentioned possible competition of backfolding and interpenetration, dendrimers may have more complicated relationships of their properties with structural parameters (e.g. generation number). In addition, the ability of $\mathbf{G}_3$ to be plasticized with a sorbed guest was checked in this work.

A related problem for dendrimers is the guest sorption irreversibility. This was observed for receptors of other types with a similar selectivity variation, such as cross-linked poly(acrylamide) derivative [23] and for crystalline clathrate-forming hosts, like calixarenes [26]. In these cases, a strong binding irreversibility was observed [23,26]. This problem was stated [27] or implied [14,16,17] in the vapor sensor studies with the other dendrimers, where rigid conditions of sensor experiments with the temperature of 39–50 °C were used. The irreversible encapsulation of carbon tetrachloride by PAE dendrimer was also shown [28]. Hence, this irreversibility was characterized in the present study for one of the phosphorus dendrimers.

To overcome the vapor sorption irreversibility, the possibility of guest exchange in solid dendrimer phase was studied in the present work. This property helps to compare the studied dendrimers with the other types of receptors, which exhibit a similar guest exchange ability [26,29].

In general, the present study describes a specific position of the organophosphorus dendrimers compared with other types of solid receptor materials by selectivity/reversibility ratio for sorption of volatile guests, by their glass transition behavior and by their ability for guest exchange.

2. Materials and methods

2.1. Materials

Dendrimers were synthesized as described elsewhere: $\mathbf{G}_1$–$\mathbf{G}_4$ [30] and $\mathbf{G}_9$ [31]. The purity of the studied guests dried by standard techniques [32] was tested by GC to be better than 99.5%.

2.2. QCM study of guest sorption

In the present study, the sensor device with 10 MHz QCM crystals of thickness shear mode (TSM) was used [26]. The dendrimer coatings (1.2 μg) prepared by solution drop and drying gives an average decrease of $\Delta F_d \sim 1500$ Hz in the crystal frequency after solvent removal. The corresponding thickness of the dendrimer layer on the gold surface was approximately 90 nm.

In a typical QCM sensor experiment, a liquid guest was sampled with microsyringe to the cell bottom through the dosing hole in the cell cover. The sampled guest amount was 50% larger than necessary to create its saturation vapor in the sealed cell. The guest relative vapor pressure P/P_0 in the sensor cell was kept below saturation level by the vapor leak through dosing hole. This level, in dynamic equilibrium, was equal to $P/P_0 = 0.80 \pm 0.05$. The frequency change of quartz crystal ΔF in this experiment was determined with the reproducibility of 5% for $\Delta F > 100$ Hz. Each dendrimer coating endured at least 2 weeks of everyday sensor experiments without a loss of reproducibility.

To regenerate the dendrimer layers after guest sorption experiment, the coatings were dried by air purge at 45 ± 1 °C until reaching the constant frequency determined at 25 °C. In each case, the guest binding reversibility was examined using also guest exchange with methanol vapor, which has the fastest desorption rate among the guests studied.

The water content in dendrimer coatings dried by hot air purge was checked by the frequency increase for coated crystals equilibrated over P_4O_{10} powder. This increase did not exceed 3 Hz, which is slightly higher than the baseline drift of ±1.5 Hz observed for quartz crystals in empty cell for 2000 s.

The more detailed description of sensor device and experimental technique are given in Supplementary material (SM).

2.3. Atomic force microscopy of dendrimer layers

The roughness of dendrimer layers was determined for $\mathbf{G}_1$–$\mathbf{G}_4$ and $\mathbf{G}_9$ dendrimers using atomic force microscopy as described in SM.

2.4. FTIR microscopy

The reversibility of guest binding and guest exchange in thin layer of dendrimer $\mathbf{G}_3$ on the gold surface of quartz crystal were studied using IR microscope Hyperion 2000 combined with FTIR spectrometer Tensor 27 (Bruker). This dendrimer coating with the average thickness of 300 nm was prepared as written above. Kinetics of propionitrile desorption from this layer and guest exchange for methanol were traced inside the QCM coating on the air by the guest absorbance decrease at $\nu_{CN} = 2245$ cm^{-1}. A visual microscope picture for the layer spot, which IR spectrum was determined, and additional details of FTIR experiment are given in SM.

2.5. TG/DSC/MS experiment

Simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC) analysis of solid dendrimer samples and mass spectrometric (MS) evolved gas analysis were performed using thermoanalyzer STA 449 C Jupiter (Netzsch) coupled with quadrupolar mass-spectrometer QMS 403 C Aeolos as described elsewhere [26]. In each experiment, the temperature rate was 10 K/min, and an argon atmosphere with a total flow rate of 75 ml/min was used. Before the experiment, 7–9 mg samples of dendrimer powders in the aluminum crucibles (40 μl) with lids having three holes, each of 0.5 mm in diameter, were held for 1 h under vacuum of 300 Pa at room temperature on the sample holder inside thermoanalyzer. Detection limit of mass-spectrometer for water is 0.2% w/w for the samples of 9 mg.

The samples of $\mathbf{G}_3$ saturated with methanol and propionitrile were prepared in the same crucibles by equilibration with vapors of these guests ($P/P_0 = 1$) for 72 h at 25 °C in hermetically sealed 15 ml vials. The TG/DSC/MS experiment for these samples began after 20 min of their equilibration at 25 °C in argon flow of 75 ml/min.