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

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 (G_1–G_4 and 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 G_n dendrimers, of the first (G_1), second (G_2), third (G_3), fourth (G_4) and ninth (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.
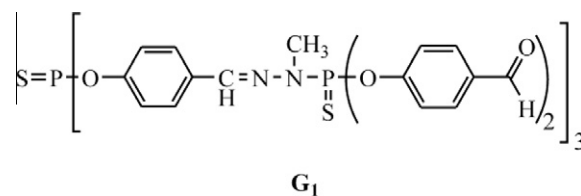
G_1

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 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 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 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).

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 G_1–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 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: G_1–G_4 [30] and 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 G_1–G_4 and 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 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 $v_{CN} = 2245$ 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 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.

2.6. Limiting activity coefficients

Limiting activity coefficients γ_t^∞ of guests in toluene solution were determined at 25 °C using static method of gas chromatographic headspace analysis with an error of ±10% as described elsewhere [21].

3. Results and discussion

3.1. Guest binding selectivity by dendrimers in sensor coatings

The sorption capacity and selectivity of G_1–G_4 dendrimers were characterized by QCM method for vapors of 29 organic guests and water with relative vapor pressure of $P/P_0 = 0.80$ at 25 °C. The determined QCM sensor responses ΔF are given in Table 1. Besides, for several vapors, ΔF values were determined with G_9 coating. Typical sensor responses for guest vapors are given on Fig. 1.

The analysis of the data in Table 1 indicates a similar non-monotonous influence of dendrimer generation on ΔF values for the guests from the same homological series (alkanes, aliphatic alcohols and nitriles, alkylbenzenes). In most cases, this effect is stronger for initial members of these series with polar functional groups and weaker for guests with larger alkyls. A non-monotonous generation effect on sensor responses was observed also for PAMAM dendrimers [10].

No simple relationships are obvious between the observed sensor responses ΔF and structural parameters of guests. To rationalize such relationships, a proper choice of a standard thermodynamic state for the observed guest sorption parameters is necessary [20]. The guest standard state for determination of sensor responses ΔF at the fixed guest activity, or relative vapor pressure P/P_0, Table 1, is its pure liquid state. Such an approach was used also in sensor studies for PAMAM [10,11] and PPI [15] dendrimers. This standard state is better for characterization of receptor selectivity than the guest vapor with fixed concentration or partial vapor pressure, P. In the latter case, the properties of guest vapor are more relevant for observed selectivity than those of receptor [20].

A less ambiguous analysis of molecular recognition can be made using standard state of infinitely dilute guest solution in a model solvent, which has approximately the same molecular group composition as the neighboring dendrimer groups for bound guest [22]. This standard state excludes the effect of generally different molecular interactions in pure liquids of different guests. A suitable model solvent for the studied dendrimers may be toluene. Hence, the coefficients K may be calculated for a guest partition between the infinitely dilute solution in toluene and solid dendrimer phase[1]:

$$K = \frac{\Delta F \gamma_t^\infty MW_d}{\Delta F_d MW} \tag{1}$$

where ΔF_d is a quartz crystal frequency change caused by dendrimer coating, MW_d and MW are formula weights of dendrimer and guest, respectively, γ_t^∞ is limiting activity coefficient of guest in toluene, Table 1. Eq. (1) is an extension of one offered [20] for vapor/receptor partition coefficient. The details of corresponding formalism for this equation and calculated partition coefficients K are given in SM.

A rather regular picture of dendrimer selectivity for guest vapors may be seen in the correlation between ln K values and guest molar refraction, $MR_D = (MW/\rho)(n_D^2 - 1)/(n_D^2 + 2)$, given in Fig. 2 and SM. Here, ρ and n_D are the guest density and refraction index, respectively. Molar refraction is a good molecular size parameter [22,36,37]. There is a general decrease of partition coefficient ln K with the increase of guest size, which indicates a size exclusion effect for guest molecules. Still, the size exclusion effect is not the same for different homological series of guests. Each of the studied series has almost a linear relationship ln K vs. MR_D but with a different slope. The selectivity of G_1–G_4, Fig. 2, SM, decreases in the order: aliphatic alcohols > nitriles > arenes > alkanes, being high for aliphatic alcohols, while practically absent for n-alkanes.

A strong and various size exclusion effect observed for G_1–G_4 may be the cause of their higher selectivity for organic vapors than that observed elsewhere for many other dendrimers, where sensor responses ΔF are determined at the fixed or approximately the fixed relative vapor pressure P/P_0 of guests. The ratio of such ΔF values for the different guests (excluding water) does not exceed 5 for PPh [16], PAMAM [10,11,13] and PPI [9,15] dendrimers, if salts are not formed by the host–guest interaction. Dendrimers G_1–G_4 are more selective in 1.6–16 times for the same sets of organic guests, which include at least one bad guest with three methylene groups in a molecule.

The observed dependence of the size exclusion effect on the guest functional group for the studied dendrimers may be caused by the sorption of guests from different homological series in different sets of binding sites. According, to the relationships shown on Fig. 3, the utmost difference of these sets may be expected for

Table 1

Sensor responses of dendrimers for organic guest vapors with relative vapor pressure $P/P_0 = 0.80$ at 25 °C.[a] Sensor responses ΔF are normalized to the coating mass with corresponding frequency decrease of $\Delta F_d = 1500$ Hz.

No.	Sorbate	MR_D (cm³ mol⁻¹)	γ_t^∞	ΔF (Hz)			
				G_1	G_2	G_3	G_4
1	H₂O	3.7	344[b]	23	26	30	35
2	MeOH	8.2	21.8[c]	280	48	261	225
3	EtOH	13.0	17.4[c]	205	46	168	142
4	n-PrOH	17.5	15.9[c]	75	27	72	53
5	i-PrOH	17.6	12.9[f]	67	29	74	40
6	n-BuOH	22.1	11.6	62	30	42	34
7	MeCN	11.1	4.33[c]	262	177	530	810
8	EtCN	16.0	2.92[c]	292	256	424	898
9	n-PrCN	20.4	1.87[d]	418	402	490	961
10	n-BuCN	25.2	1.73	364	355	543	1104
11	n-Pentane	25.3	1.25	39	14	72	20
12	c-Hexane	27.7	1.36[c]	41	17	68	14
13	n-Hexane	29.9	1.50[c]	35	15	53	16
14	n-Heptane	34.5	1.68[c]	30	13	50	13
15	n-Octane	39.2	1.69[c]	31	14	60	13
16	Isooctane	39.2	1.74	32	14	61	13
17	n-Nonane	43.8	1.90[c]	29	14	48	12
18	CH₂Cl₂	16.4	0.98[e]	624	843	819	1711
19	CHCl₃	21.3	0.80[d]	873	1098	1229	714
20	CCl₄	26.4	1.15[d]	488	35	156	53
21	1,2-C₂H₄Cl₂	20.9	1.21	782	824	849	1526
22	C₂HCl₃	25.3	0.99	539	533	530	1106
23	C₂Cl₄	30.3	1.61	341	172	483	236
24	1-C₃H₇Cl	20.8	0.99	338	241	299	464
25	Benzene	26.3	0.97[c]	588	462	375	1364
26	Toluene	31.0	1.00	489	397	285	1288
27	Ethylbenzene	35.7	1.01	468	436	241	1069
28	Acetone	16.2	1.82[d]	486	449	491	507
29	1,4-Dioxane	21.7	1.15[d]	642	966	693	1784
30	Pyridine	24.2	1.28[d]	659	784	805	1549

[a] G_9 layers have ΔF values of 28, 191, 118, 62, 46, 43, 16, and 15 Hz for H₂O, MeOH, EtOH, benzene, toluene, ethylbenzene, CCl₄ and C₂Cl₄, respectively.
[b] Data from Ref. [33].
[c] Data from Ref. [34].
[d] Data from Ref. [21].
[e] Data from Ref. [22].
[f] Data from Ref. [35].

---

[1] Partition coefficient K is meaningful, if guest does not saturate host, and, respectively, does not give a stable guest–host inclusion compound, or clathrate, with a specific stoichiometry, which may have very complicated relationship to guest structure [21]. No saturation was observed for G_3 on the sorption isotherm of typical guest propionitrile, SM.
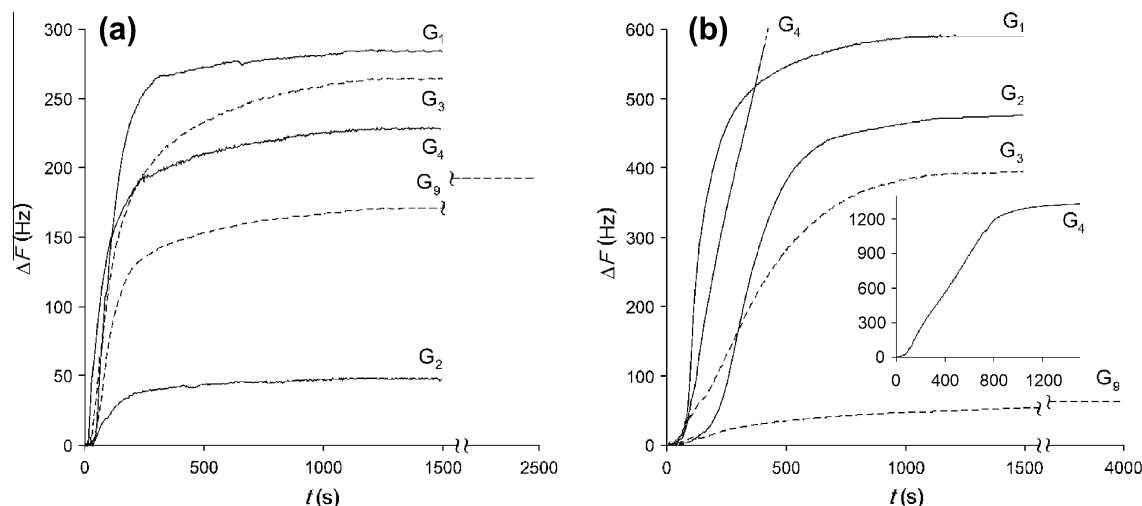
Fig. 1. (a–b) Responses of QCM sensor coated with dendrimers G_1, G_2, G_3, G_4 and G_9 to methanol (a) and benzene (b) vapors with the relative vapor pressure of $P/P_0 = 0.80$ at 25 °C. Sensor responses ΔF are normalized to the coating mass corresponding to 1500 Hz of frequency decrease.
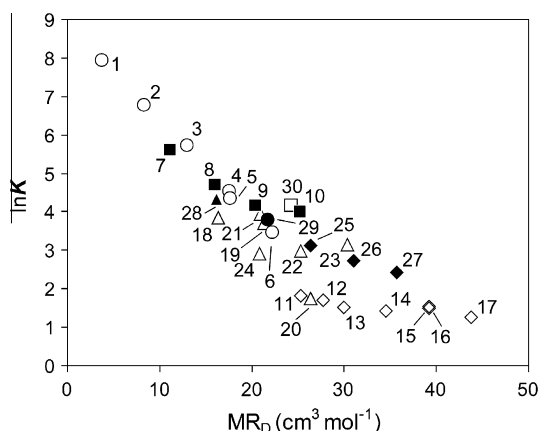
Fig. 2. Correlation of guest partition coefficients $\ln K$ and molar refraction MR_D for dendrimer G_3. Point numbers correspond to entry numbers in Table 1.

water and alkanes, which occupy the ultimate positions on the plots of $\ln K$ vs. MR_D for each dendrimer.

This ability was checked for G_3 by subsequent sampling of liquid water and n-heptane in a large excess to the QCM sensor cell without intermediate regeneration of sensor coating, Fig. 3. In this experiment, sampling of water gives $\Delta F = 30$ Hz. The resulting hydrated G_3 gives a response to n-heptane vapor of $\Delta F = 50$ Hz, Fig. 3a, which is the same as for the coating regenerated by hot air purge at 45 °C, Fig. 3b. Such air purge removes more than 90% of bound water according to the experiment with drying of dendrimer coatings by P_4O_{10}. So, the sorption of water and n-heptane by G_3 is independent, which is possible if they are bound in different sites.

Solvent vapors can be also sorbed independently, if they plasticize polymer [23]. But in this case, an initially glassy polymer loses its size exclusion effect [23]. For the studied dendrimers, water and alkanes are bad guests according to ΔF data from Table 1. Better guests, like alcohols, nitriles and aromatic hydrocarbons, Table 1, still have a size exclusion effect as can be seen in Fig. 2. So, the independent sorption of water and n-heptane is not caused by dendrimer plasticization.

The independent sorption of these guests and the high size exclusion effect means the sorption in the bulk of dendrimer phase. This conclusion is confirmed also by the low roughness of surface observed for the studied dendrimers, which is equal to 1.2 (G_1),

0.8 (G_2), 0.9 (G_3), 1.1 (G_4), and 0.3 nm (G_9). So, these dendrimers do not have intricate surface for significant adsorption on the solid–air interface.

The observed correlations of $\ln K$ vs. MR_D reveal the limits of G_1–G_4 selectivity. Being various for different homological series of guests, this structure–property relationship is still much more regular than for clathrate-forming receptors, like calixarenes, where such relationships may be practically unpredictable in the case of binding both inside host molecular cavities and internal space [38]. In this respect, the studied dendrimers constitute a specific type of receptors with rather regular size exclusion effect as for cross-linked polymers [23] and dried protein [24], but without apparent plasticization consequences for selectivity as for calixarenes.

### 3.2. Glass transition behavior

To characterize the polymer-like properties of dendrimers G_1–G_4, their glass transition behavior was studied. Glass transition temperatures T_g were determined for G_1–G_4 samples by simultaneous TG/DSC method. The DSC curves and a typical TG curve for these samples in the first run of thermal analysis are shown in Fig. 4. Corresponding T_g values, points of DSC peak T_m and enthalpies of glass transition ΔH are given in Table 2. The dendrimer samples aged in the first TG/DSC run from 30 to 200 °C have the glass transition points increased on 8–13 °C in the second run, SM. Respectively, the enthalpies ΔH of the aged samples are reduced to less than half of their values in the first run. A significant thermal decomposition of the studied dendrimers begins above 270 °C [39], SM. The DSC parameters obtained for aged G_1 and G_3 samples correspond to those observed elsewhere for the same dendrimers [40].

The observed glass transition points T_g of G_1–G_4 are in the range of 74–115 °C, which is well above the temperature of QCM sensor experiment, 25 °C. This may be a cause of their higher selectivity compared with the PAMAM and PPI dendrimers, which T_g points are below room temperature [41,42]. Respectively, the glassy state should impose a stronger size restriction on the guest sorption than a rubbery (mobile) one. A loss of vapor sorption selectivity above the glass transition point was observed, for example, for cross-linked derivative of polyacrylamide [23].

The glass transition temperatures determined for the studied dendrimers help to explain the observed dependence of their average sorption capacity and selectivity on generation number. The
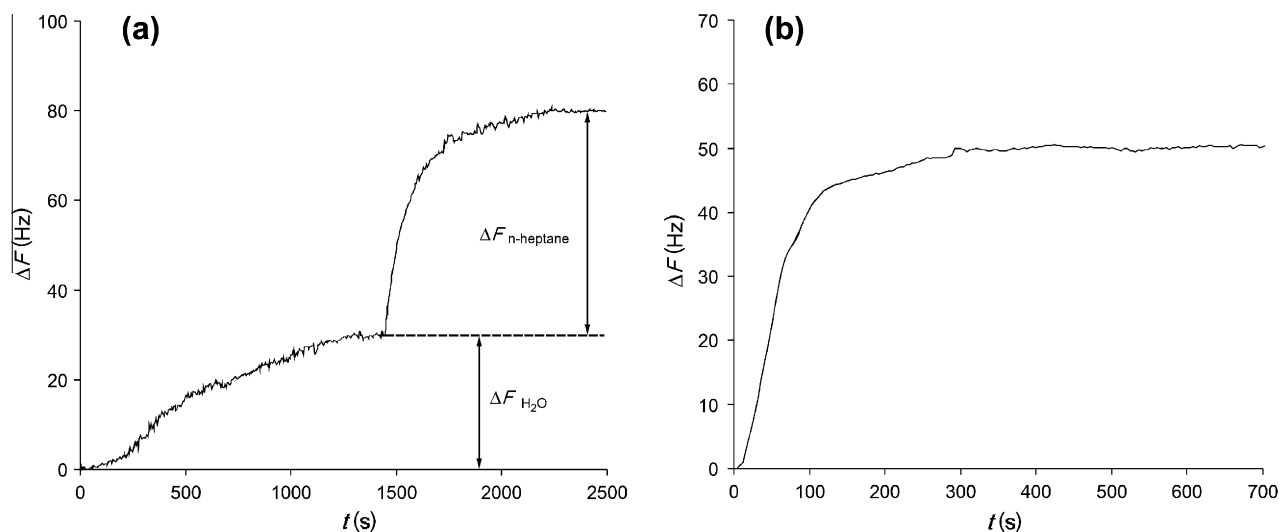
Fig. 3. (a–b) Responses of QCM sensor coated with G_3 to (a) water and n-heptane vapors (b) to n-heptane vapor with the relative vapor pressure of $P/P_0 = 0.8$ at 25 °C. Sensor responses ΔF are normalized to the coating mass corresponding to 1500 Hz of frequency decrease.
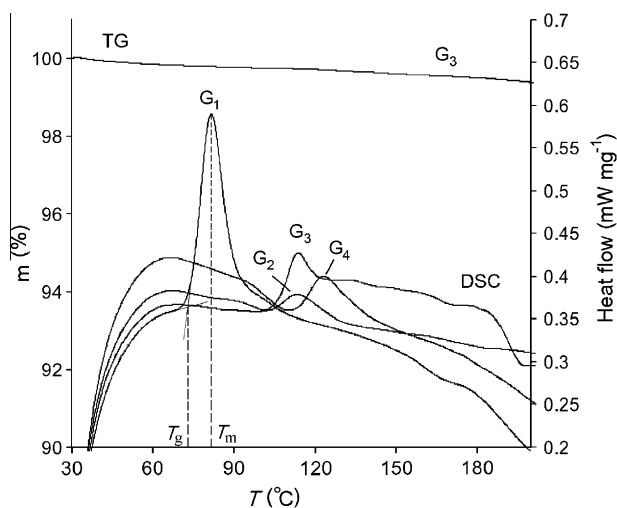
Fig. 4. The curves of simultaneous TG/DSC for G_1, G_2, G_3 and G_4 dendrimers. Complete TG/DSC data are given in SM.


Fig. 5. The data of simultaneous TG/DSC/MS study for G_3 saturated with propionitrile vapor ($P/P_0 = 1$, $T = 25$ °C) for 72 h, and equilibrated in argon flow for 20 min at 25 °C. Heating rate is 10 K/min.

Table 2
Parameters of DSC curves of dendrimer powders in TG/DSC experiment.

Dendrimer	T_g^a (°C)	T_m^b (°C)	ΔH^c (J g^{-1})
G_1	74.2	81.6	13
G_2	104.4	113.1	3.3
G_3	105.7	113.9	2.8
G_4	114.6	123.3	4.3

[a] Onset temperature of endothermic transition.
[b] Temperature of DSC peak.
[c] Error of ΔH determination is 1 J g^{-1}.

values of T_g and DSC peak point T_m increase in the order $G_1 < G_2 \approx G_3 < G_4$. The points T_g and T_m of G_2 are higher on 15–16 °C than calculated from the linear dependence of these temperatures on N for G_1, G_3 and G_4. So, G_2 may be more tightly packed in solid phase than the other dendrimers, and, respectively, may have lower sorption capacity at least for bad guests. Such drop in sensor responses ΔF of G_2 is observed for alcohols, alkanes, tetrachloroethylene, CCl$_4$, and 1-C$_3$H$_7$Cl, Table 1.

A related correlation with glass transition temperatures is observed for vapor sorption selectivity of dendrimers estimated by the standard deviation from the mean of ΔF values for the studied set of guests, which is equal to 259, 328, 309 and 614 Hz for G_1, G_2, G_3 and G_4, respectively. So, dendrimer G_2 has a higher selectivity than that expected from its monotonous change with increase of generation number.

The absence of dendrimer plasticization with guest was observed in TG/DSC/MS study of G_3 saturated with propionitrile, which is an average guest by its sorption capacity ΔF, Table 1. The data obtained are given in Fig. 5. The inflection point of DSC curve at 111.7 °C may correspond to glass transition point T_g. At $T_m = 137.7$ °C, G_3 melts giving peaks on DSC curve and on the ion thermogram for propionitrile molecular ions ($m/z = 54$). This shape of DSC curve is in line with the properties of polymers saturated with solvents and heated through glass transition point [43]. Specific feature of G_3 saturated with propionitrile is its essentially higher T_g and T_m points than for pure G_3, Table 2, while the enthalpy ΔH of the peak at T_m is nearly the same for both samples. So, propionitrile, being inside dendrimer phase at T_g point, according to the ion thermogram on Fig. 5, performs rather antiplasticization of G_3. This may be explained by reduction of branches mobility
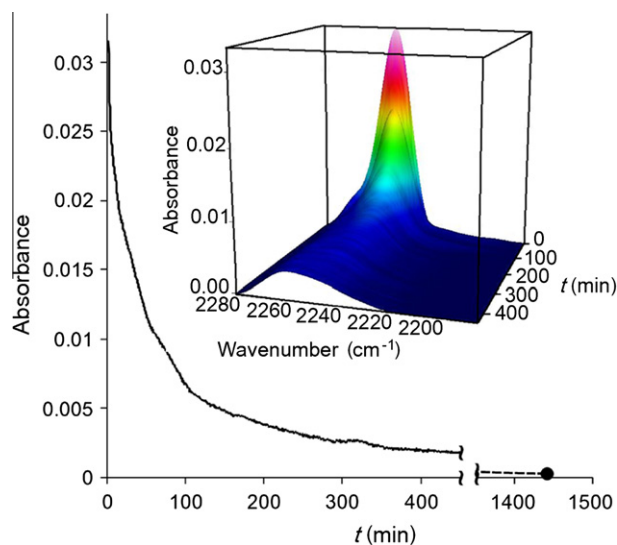
Fig. 6. Kinetics of propionitrile desorption from G_3 dendrimer on the air at 20 °C by absorbance of CN-group at $\nu_{CN} = 2245$ cm^{-1} from FTIR microspectroscopy data.

when guest is inside dendrimer voids. This glass transition behavior is quite opposite to that observed for glassy polymers in absence of strong guest-polymer H-bonding or coordination [44]. The observed absence of plasticization of G_3 with propionitrile is in agreement with the strong size exclusion effect observed for G_1–G_4 saturated with various guests, Fig. 2, SM.

3.3. Binding irreversibility and guest exchange

The guest-binding irreversibility was studied for G_3. For this, a sample of G_3 layer with a thickness of 300 nm saturated with pro-pionitrile vapor at room temperature (20 °C) was exposed to the open air, and its IR spectra were determined every minute for the first $t = 7.5$ h, and then one spectrum was determined at $t = 24$ h, Fig. 6. In the last spectrum, the dendrimer sample had not any noticeable absorbance of CN-group at $\nu_{CN} = 2245$ cm^{-1}.

The observed desorption rate is slower nearly in two orders of magnitude than the guest adsorption rate in QCM experiment, where 20 min is enough to reach 99% of G_1–G_4 sorption capacity in most cases, including the systems with propionitrile vapor, Figs.

1 and 3, SM. Slower sorption kinetics was observed for low volatile guest ethylbenzene and for all studied guests with G_9.

The high ratio of guest adsorption/desorption rates shows the irreversibility extent in the system of G_3 with EtCN. A high binding irreversibility was observed also for ethylbenzene, n-BuCN, pyridine, chloroalkenes and chloroalkanes, except 1-chloropropane and CCl_4, which cannot be removed completely from G_1–G_4 coatings by air purge at 45 °C in a reasonable time. The same was observed for n-BuOH, 1,4-dioxane and 1-chloropropane with G_2–G_4, and for aromatic hydrocarbons, CCl_4 and C_2Cl_4 with G_9. Water, methanol and ethanol are completely eliminated from the studied dendrimers by this procedure. So, dendrimers G_1–G_4 bind most of the studied guests irreversibly, which is normal both for glassy polymer [23] and crystalline clathrate-forming receptors [26,45].

To compare the studied dendrimers with receptors of these two types and to elaborate the host regeneration technique from the irreversibly bound guests, the guest exchange was studied for G_3 saturated with propionitrile. Methanol was used as the guest replacing agent, because it is a good leaving guest for hydrophobic clathrate-forming receptors [26]. In TG/DSC experiment, the most of the bound methanol desorbs from G_3 powder during 20 min of pre-heating equilibration at room temperature. Thereafter, a sample of G_3 initially saturated with methanol loses only 0.9% of its mass below 200 °C, SM, which is a small portion of the methanol/host mass ratio (17%), in the saturated G_3 coating, Table 1.

The guest exchange for methanol was studied using FTIR microspectroscopy for two samples of dendrimer G_3 coating with the average thickness of 300 nm saturated with propionitrile vapor at $P/P_0 = 0.8$ and 20 °C. Both samples were simultaneously exposed to the open air at this temperature, and their IR spectra were recorded using FTIR microscope, Fig. 7. Full IR spectrum of G_3 coating is given in SM. For one of the samples, this exposure was interrupted by saturation with methanol vapor ($P/P_0 \approx 0.8$) for 13 min. This saturation takes away the absorption band of guest CN-group at 2245 cm^{-1} as can be seen in Fig. 7b. For the sample exposed only to the air, this band persists staying at much later time, Fig. 7a. So, methanol effectively replaces propionitrile in solid dendrimer phase. This technique was used in the present work for dendrimer regeneration in sensor experiments in all mentioned cases, where significant guest-binding irreversibility was observed.

The observed guest exchange is in agreement with the observed high glass transition point of G_3, the absence of its plasticization with sorbed guest and the size exclusion effect. Such exchange is not possible for cross-linked glassy polymer that is plasticized with
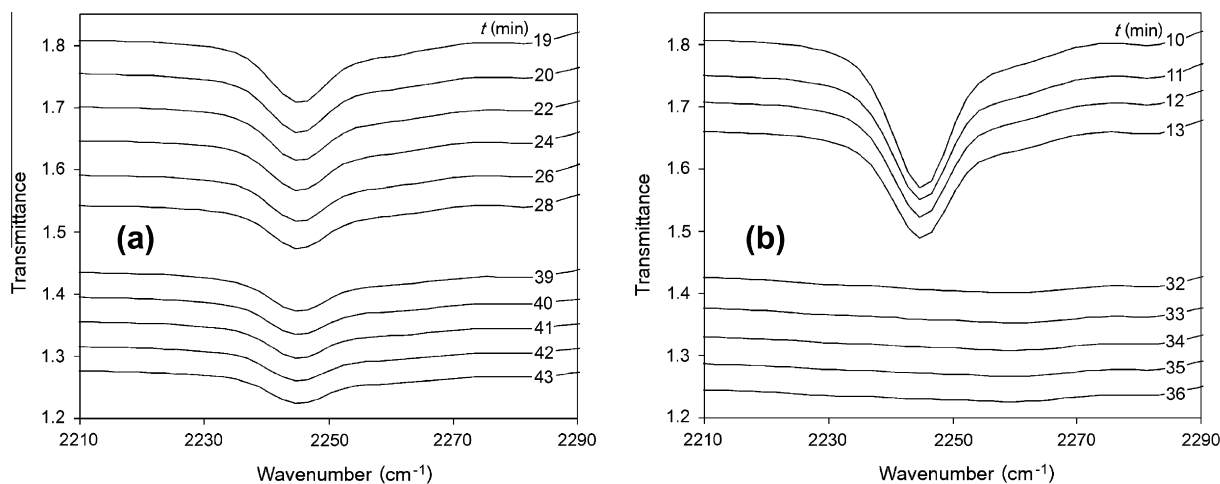
Fig. 7. (a–b) FTIR microspectroscopy study of guest exchange in G_3. The ν_{CN} region of IR spectra of two G_3 coatings initially saturated with propionitrile vapor $P/P_0 = 0.8$ at room temperature 20 °C (RT): (a) for the sample exposed to the air, RT; (b) for the sample, which exposure to the air was interrupted by saturation with methanol vapor ($P/P_0 \approx 0.8$, RT) for 13 min after $t = 13$ min. The time t since the sample exposure to the open air is indicated for each spectrum.

the sorbed solvent [23]. This property puts the studied dendrimer in line with clathrate-forming receptors, for which guest exchange in solid phase also takes place [26,29,46].

4. Conclusions

The observed combination of guest sorption properties of organophosphorus dendrimers helps to find their position in the range of the other receptor materials. Each separate property described has an analogy in the features of other types of receptors. But taken together, they give quite a new picture.

So, the different selectivity of dendrimers for different homological series of guests, general size exclusion effect and guest-binding irreversibility resemble the same properties of a cross-linked glassy polymer. But one cannot expect that a soluble glassy polymer would not be plasticized with good solvent. The guest exchange and absence of plasticization observed for G_3 is an intrinsic feature of crystalline clathrate-forming receptors, like calixarenes, but these hosts do not have a glass transition behavior contrarily to dendrimers.

Being glassy, the studied dendrimers have a higher guest selectivity than isotropic polymers. So, in some extent, it may be called a molecular recognition. Still, this selectivity is lower than that of calixarenes, which may recognize a guest even in a mixture with its close homologue [47]. The cause may be the absence of pseudo-polymorphic transitions in dendrimer phase observed for G_3 at the guest sorption/desorption. No significant cooperativity of this process is observed, which restricts the selectivity.

In general, the study reveals the presence and limits of molecular recognition of volatile compounds in sorption by phosphorus-containing dendrimers, linking it with their other properties. As a result, dendrimers studied were found to have several combined features both of cross-linked glassy polymer and calixarenes.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2011.04.017.

References

[1] J.M.J. Frëchet, S. Hecht, Angew. Chem. Int. Ed. 40 (2001) 74.
[2] L.J. Twyman, A.S.H. King, I.K. Martin, Chem. Soc. Rev. 31 (2002) 69.
[3] Y. Niu, R.M. Crooks, C.R. Chim. 6 (2003) 1049.
[4] S.V. Aathimanikandan, B.S. Sandanaraj, C.G. Arges, C.J. Bardeen, S. Thayumanavan, Org. Lett. 7 (2005) 2809.
[5] U. Boas, J.B. Christensen, P.M.H. Heegaard, J. Mater. Chem. 16 (2006) 3785.
[6] G.R. Newkome, B.D. Woosley, E. He, C.N. Moorefield, R. Guther, G.R. Baker, G.H. Escamilla, J. Merrill, H. Luftmann, Chem. Commun. 24 (1996) 2737.
[7] B. Klajnert, A. Pastucha, D. Shcharbin, M. Bryszewska, J. Appl. Polym. Sci. 103 (2007) 2036.
[8] N. Krasteva, B. Guse, I. Besnard, A. Yasuda, T. Vossmeyer, Sens. Actuators B 92 (2003) 137.
[9] Y. Joseph, N. Krasteva, I. Besnard, B. Guse, M. Rosenberger, U. Wild, A. Knop-Gericke, R. Schlögl, R. Krustev, A. Yasuda, T. Vossmeyer, Faraday Discuss. 125 (2004) 77.
[10] M. Wells, R.M. Crooks, J. Am. Chem. Soc. 118 (1996) 3988.
[11] L.L. Miller, Y. Kunugi, A. Canavasi, S. Rigaut, C.N. Moorefield, G.R. Newkome, Chem. Mater. 10 (1998) 1751.
[12] T. Gao, E.S. Tillman, N.S. Lewis, Chem. Mater. 17 (2005) 2904.
[13] L.L. Miller, J.S. Bankers, A.J. Schmidt, D.C. Boyd, J. Phys. Org. Chem. 13 (2000) 808.
[14] N. Krasteva, I. Besnard, .B. Guse, .R.E. Bauer, K. Müllen, A. Yasuda, T. Vossmeyer, Nano Lett. 2 (2002) 551.
[15] H. Tokuhisa, R.M. Crooks, Langmuir 13 (1997) 5608.
[16] M. Schlupp, T. Weil, A.J. Berresheim, U.M. Wiesler, J. Bargon, K. Müllen, Angew. Chem. Int. Ed. 40 (2001) 4011.
[17] N. Krasteva, Y. Fogel, R.E. Bauer, K. Müllen, Y. Joseph, N. Matsuzawa, A. Yasuda, T. Vossmeyer, Adv. Funct. Mater. 17 (2007) 881.
[18] G. Magro, P. Marchand, R.-M. Sebastian, .C. Guyard-Duhayon, A.-M. Caminade, J.-P. Majoral, Eur. J. Org. Chem. 2005 (2005) 1340.
[19] A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665.
[20] J.W. Grate, S.J. Patrash, M.H. Abraham, C.M. Du, Anal. Chem. 68 (1996) 913.
[21] V.V. Gorbatchuk, A.G. Tsifarkin, I.S. Antipin, B.N. Solomonov, A.I. Konovalov, J. Seidel, F. Baitalov, J. Chem. Soc. Perkin Trans. 2 (11) (2000) 2287.
[22] V.V. Gorbatchuk, A.G. Tsifarkin, I.S. Antipin, B.N. Solomonov, A.I. Konovalov, P. Lhotak, I. Stibor, J. Phys. Chem. B 106 (2002) 5845.
[23] V.V. Gorbatchuk, N.A. Mironov, B.N. Solomonov, W.D. Habicher, Biomacromolecules 5 (2004) 1615.
[24] V.V. Gorbatchuk, M.A. Ziganshin, B.N. Solomonov, M.D. Borisover, J. Phys. Org. Chem. 10 (1997) 901.
[25] A.R. Katritzky, M. Kuanar, S. Slavov, C.D. Hall, Chem. Rev. 110 (2010) 5714.
[26] L.S. Yakimova, M.A. Ziganshin, V.A. Sidorov, V.V. Kovalev, E.A. Shokova, V.A. Tafeenko, V.V. Gorbatchuk, J. Phys. Chem. B 112 (2008) 15569.
[27] T. Vossmeyer, B. Guse, I. Besnard, R.E. Bauer, K. Müllen, A. Yasuda, Adv. Mater. 14 (2002) 238.
[28] D. Seebach, J.-M. Lapierre, K. Skobridis, G. Greiveldinger, Angew. Chem. Int. Ed. Engl. 33 (1994) 440.
[29] M.A. Ziganshin, L.S. Yakimova, K.R. Khayarov, V.V. Gorbatchuk, M.O. Vysotsky, V. Böhmer, Chem. Commun. (2006) 3897.
[30] N. Launay, A.M. Caminade, R. Lahana, J.P. Majoral, Angew. Chem. Int. Ed. Engl. 33 (1994) 1589.
[31] M. Slany, M. Bardaji, M.J. Casanove, A.M. Caminade, J.P. Majoral, B. Chaudret, J. Am. Chem. Soc. 117 (1995) 9764.
[32] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, Butterworth, 2000.
[33] J.H. McMinn, M.J. Sowa, S.B. Charnick, M.E. Paulaitis, Biopolymers 33 (1993) 1213.
[34] V.V. Gorbatchuk, A.G. Tsifarkin, I.S. Antipin, B.N. Solomonov, A.I. Konovalov, J. Inclusion Phenom. Macrocyclic Chem. 35 (1999) 389.
[35] V.V. Gorbatchuk, M.A. Ziganshin, N.A. Mironov, B.N. Solomonov, Biochim. Biophys. Acta 1545 (2001) 326.
[36] B.N. Solomonov, A.I. Konovalov, Russ. Chem. Rev. 60 (1991) 25.
[37] V.V. Gorbatchuk, A.G. Tsifarkin, I.S. Antipin, B.N. Solomonov, A.I. Konovalov, Mendeleev Commun. 9 (1999) 11.
[38] M.A. Ziganshin, A.V. Yakimov, G.D. Safina, S.E. Solovieva, I.S. Antipin, V.V. Gorbatchuk, Org. Biomol. Chem. 5 (2007) 1472.
[39] C.O. Turrin, V. Maraval, J. Leclaire, E. Dantras, C. Lacabanne, A.M. Caminade, J.P. Majoral, Tetrahedron 59 (2003) 3965.
[40] E. Dantras, J. Dandurand, C. Lacabanne, A.M. Caminade, J.P. Majoral, Macromolecules 35 (2002) 2090.
[41] E.M.M. de Brabander-van den Berg, E.W. Meijer, Angew. Chem. Int. Ed. Engl. 32 (1993) 1308.
[42] D.A. Tomalia, P.R. Dvornic, in: Polymeric Materials Encyclopedia, CRC Press, 1996.
[43] D.M. Price, D.J. Hourston, F. Dumont, Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., 2000.
[44] G. Dlubek, F. Redmann, R. Krause-Rehberg, J. Appl. Polym. Sci. 84 (2002) 244.
[45] T. Dewa, K. Endo, Y. Aoyama, J. Am. Chem. Soc. 120 (1998) 8933.
[46] G.S. Ananchenko, K.A. Udachin, A. Dubes, J.A. Ripmeester, T. Perrier, A.W. Coleman, Angew. Chem. Int. Ed. 45 (2006) 1585.
[47] G.D. Safina, L.R. Validova, M.A. Ziganshin, I.I. Stoikov, I.S. Antipin, V.V. Gorbatchuk, Sens. Actuators B 148 (2010) 264.