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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

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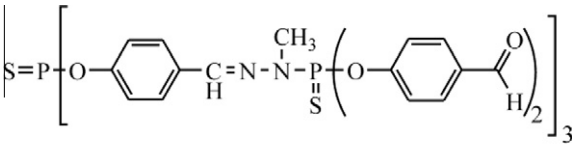
ABSTRACT

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).

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