

Trapping Dendrimers in Inorganic Matrices: DAB-Am-*n*/Zinc Arsenate Composites

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Received April 3, 2001. Revised Manuscript Received June 26, 2001

Layered dendrimer-loaded zinc arsenates (ZnAs) were synthesized under hydrothermal conditions. The so-called DAB-Am-*n* family of dendrimers is used to produce ZnAs solids with variable interlayer distances. Analysis of the *00k* X-ray diffraction reflections reveals that the higher-generation DAB-Am-*n* dendrimers are “squeezed” between the ZnAs layers, judging from the observation of interlayer spacings that increase more slowly with dendrimer generation than the actual average diameters of the free dendrimers. Transmission electron microscopy shows that, under the synthetic conditions adopted here, the ZnAs sheets are subject to some level of bending and defects. The temperature-programmed oxidation patterns and elemental analysis of these materials are also discussed.

Introduction

Mono- and polyamines, just as mono- and polyalcohols, have strong tendency to form layered structures with phosphates of titanium and zirconium.^{1–6} Recently, we described the use of a family of dendritic polyamines as templates, namely, DAB-Am-*n*, to produce spheroidal, mesoscopic cavities in amorphous silicas.^{7,8} With polyamidoamines (PAMAMs), such synthetic route has also been exploited.^{9,10} All DAB-Am-*n* polyamines have a 1,4-diaminobutane (DAB, or putrescine, NH₂(CH₂)₄NH₂) core. Two -(CH₂)₃NH₂ groups can then be attached¹¹ to each of the core molecule's terminal N atoms, to form the so-called “generation 1” tetradentate dendrimer, or DAB-Am-4. Further growth toward higher “generations” readily suggests itself, as each of the four primary amine groups in DAB-Am-4 can also be subjected to further -(CH₂)₃NH₂ branching.

The use of a single molecule, rather than the popular approach with amine micelles,¹² to make a mesosized

cavity is undoubtedly interesting from a fundamental standpoint. However, exploiting such large templates as macrochelators instead offers an even more attractive possibility: Their polyamine nature makes them particularly suitable chemical traps for a number of transition metal ions. In other words, a host–guest chemistry that has recently been proven in solution,^{13,14} can be extended to make well-defined metal and metal oxide clusters embedded in solid matrices.¹⁵ Earlier, we had used Cu²⁺ to “stain” a DAB-Am-6/silica composite for better transmission electron microscopy imaging.⁷ Virtually at the same time, Ruckenstein and Yin¹⁶ reported on a similar strategy to incorporate copper in silica/PAMAM composites. The Ruckenstein and Yin materials are related to ours on the same matrix/dendrimer pair,¹⁰ and to the work of Chujo et al.⁹ The dendrimer/silica systems reported thus far lack long-range order.

The technological importance of well-defined, 2- and 3-D ordered metal oxide nanoparticles and semiconductor clusters has already been discussed.¹⁷ In brief, certain collective, desirable magnetic, and electronic effects arise from 2- and 3-D ordering of nanosized metal oxide clusters.^{17a, b} Furthermore, the synthesis of supported metal and metal oxide clusters with controlled sizes has historically been a key issue in the field of heterogeneous catalysis.^{17c} Thus, the importance of starting to search for ways to immobilize DAB-Am-*n*

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Table 1. Summary of Materials Preparation Conditions

sample	dendrimer generation	dendrimer (mmols)	As ₂ O ₅ (mmols)	Zn(NO ₃) ₂ ·6H ₂ O (mmols)	aging temp (°C)	aging time (days)	pH _i -pH _f ^a
ZAsO/G5	5	0.0375	1.2	2.4	70	5	10.24–10.52
ZAsO/G4	4	0.0750	1.2	2.4	70	5	10.28–10.44
ZAsO/G3	3	0.1500	1.2	2.4	70	5	10.32–10.40
ZAsO/G2	2	0.3000	1.2	2.4	70	5	10.11–10.23
ZAsO/G1 ^b	1	0.6000	1.2	2.4	80	5	9.8–9.7

^a pH_i was set using 50% CsOH. ^b Note that a different aging temperature was adopted for ZAsO/G1.

metal ion hosts inside a sufficiently porous (to allow postsynthesis incorporation of metal ion guests) solid matrix while achieving a high level of structural ordering becomes apparent. The main objective of this contribution is to report on the use of DAB-Am-*n* dendrimers to make lamellar solids from zinc arsenate solutions via hydrothermal methods. This chemistry can readily be extended to other systems, such as Zn, Ti, and Zr phosphates. Interlayer spacing is controlled by dendrimer size. To the best of our knowledge, the closest relative to the present work is that of Kijima et al.,⁶ who intercalated an hexadentate PAMAM in preformed γ -, and α -Zr phosphates. We opted for the DAB-Am-*n* family instead of PAMAM, because the former only has C–C, C–H, N–H, and C–N bonds, which we expect a priori to be significantly more stable at pH values departing from neutrality than the multitude of amide bonds present in PAMAMs.

Experimental Section

Synthesis Protocol. A rather large number of experiments were conducted in order to optimize the synthesis conditions. These experiments primarily involved screening of reagent ratios, aging temperature, aging time, pH, and the use of different precursors. For instance, potassium arsenic acid (KH₂AsO₄) did not yield ordered materials. Our primary objective was to attempt finding a region in the variables hyperspace that fit all dendrimer generations. The general procedure described below was especially suitable for the larger members of the DAB-Am-*n* family.

The following synthesis protocol was successfully adopted for preparation of all materials, with the exception of those based on the smallest DAB-Am-*n* members, DAB-Am-4 and DAB-Am-8. Nevertheless, for the two smallest dendrimers it was still possible to obtain layered ZnAs phases that were clearly detectable by X-ray diffraction (XRD). From one preparation to another, it is only the amount of DAB-Am-*n* dendrimer (and obviously, its generation suffix) that is changed. However, the different molar ratios used were based on the idea that it is the number of –NH₂ terminal group equivalents that needs to be preserved. Thus, the following ratios remained constant, 1:1:0.5:691 for (terminal NH₂):ZnO:As₂O₅:H₂O, respectively. Table 1 summarizes conditions and amounts employed in each sample preparation. In the pH range adopted in this work, the state of dissolved As₂O₅ prior to oligomerization/condensation can be understood in terms of the three dissociation constants, *K*₁, *K*₂, and *K*₃, of AsO₄H₃. These are 5 × 10^{–3}, 4 × 10^{–5}, and 6 × 10^{–10}, respectively.¹⁸ The second and third dissociation constants of AsO₄H₃ are more than 2 orders of magnitude larger than those of PO₄H₃, and, as a result, it is easy to show that about 85% of the As must be in the AsO₄^{3–} form, the balance being AsO₄H^{2–}.

All reagents were purchased from Aldrich and used as received. In a typical preparation, 1.2 mmol of As₂O₅ was placed in 20 mL of deionized water in a high-density polyethylene bottle (HDPE). To this suspension, 0.0375 mmol of DAB-

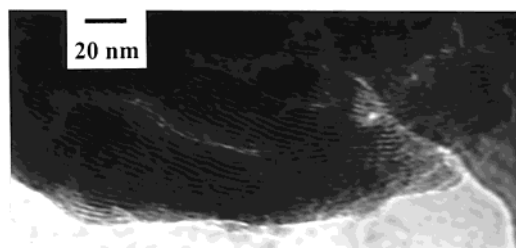


Figure 1. TEM image of ZAsO/G5.

Am-64 dendrimer (–NH₂ terminal groups, 2.4 mmol) in 4 mL of water and 1.2 mL of CsOH (50 wt %) were added. The HDPE bottle was placed in an oven at 70 °C until the oxide phase was completely dissolved. Then, the solution was cooled to room temperature and 2.4 mmol of Zn(NO₃)₂·6H₂O in 5 mL of water were added. At this stage, formation of a white, or white/yellow, precipitate took place. This suspended solid in the HPDE container was shaken for a few seconds and subsequently placed in an oven at 70 °C for 5 more days. Even at slightly lower pH values, significantly longer aging times were required. The solid material was filtered, washed with water, and finally allowed to dry on a warm metal surface (35–45 °C) exposed to ambient air. All samples are labeled as ZAsO/G*n*, where “*n*” denotes the generation number of the dendrimer.

Characterization. Powder X-ray diffraction experiments were carried out on a computer-interfaced Rigaku (The Woodlands, TX) instrument with a Cu K α source. Transmission electron microscopy experiments were performed on a JEOL JEM2010 (Sheboygan, WI) microscope at 200 keV beam energy. Chemical analysis was done at Galbraith Laboratories (Knoxville, TN).

Temperature-programmed oxidation studies were run with the aid of a computer-interfaced MKS residual gas analyzer. The powdered material (150 mg) was mechanically mixed with coarse (0.1–1 mm) nonporous silica (250 mg) and placed in a quartz U-tube reactor containing a preheating bed of low surface area α -alumina (1–2 m²/g). Instrument grade air was used. A linear temperature ramp of 7 h was applied from room temperature to 700 °C, followed by a 1 h plateau at 700 °C. The product gases from these temperature-programmed decomposition experiments were sampled into the quadrupole via a capillary stainless steel tubing placed immediately above the powdered sample bed inside the quartz reactor, and up to 16 different masses were monitored continuously.

Results and Discussion

On thorough inspection of these materials particles with transmission electron microscopy (TEM), it is possible to eventually obtain a “side view” that shows their layered structures. Figure 1 shows a TEM image for the sample prepared from DAB-Am-64 (ZAs/G5). The low-temperature synthesis adopted in our work yields solids that display some level of folding of the ZnAs/dendrimer sheets and, occasionally, defects such as sheet branching. This is not surprising, as high levels of crystallinity are not expected to occur in the temperature range that resulted in the observation of lamellae.

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Inspection of magnified TEM images in several regions, where layer stacking is close to perfect, reveals a repetitive distance of 26.5 Å (i.e., one solid ZnAs layer plus the dendrimer-filled interlayer spacing) in the G5-based material. Despite this estimate of interlayer distance being more crude than the data obtained from XRD analysis (see below) given the relatively lower TEM resolution, Figure 1 provides direct confirmation of the presence of a lamellar phase.

The question of dendrimer diameter once sandwiched between the ZnAs layers is of fundamental interest. The PAMAM dendrimers have been found to adopt oblate shapes when adsorbed on silicon surfaces,¹⁹ a fact that points to the flexibility of these amine and aminoamine quasi-spheres. Scherrenberg et al.²⁰ studied the DAB-Am-*n* family in D₂O solutions by means of small-angle neutron scattering (SANS), viscosimetry, and molecular dynamics (MD) studies. With regard to their MD computations, these authors found pronounced diameter increases (c.a. 27–29%) when only repulsive van der Waals (VDW) interatomic (intramolecular) energy terms (instead of including both Coulombic and VDW attractive and repulsive contributions) are allowed. Furthermore, rather broad radial density distribution functions were also found in all cases.²⁰ These observations point to the remarkable ability of dendrimers to adjust their size and shape to their immediate chemical environment. In fact, the so-called “dense core” structure (extensive back-folding of the branches) is favored at high ionic strength, whereas the “dense shell” (branches nearly fully stretched out) conformation is observed in the absence of an environment incapable of producing strong local electric fields.²¹

These issues are especially relevant to that of dendrimer state in our materials. Given that, in D₂O solutions DAB-Am-64 has an experimentally determined diameter of 39.6–27.8 Å (from viscosity and SANS measurements, respectively), or a theoretically predicted one (from MD) of 31.8–25.0 Å,²⁰ it is apparent that the G5 dendrimer trapped between ZnAs layers is forced to adopt a distorted, possibly oblate, conformation to interact more efficiently with the inorganic layers.

These distortions in the dendrimer conformation leading to compressed structures are even more pronounced during the intermediate stages of solid formation (see Figure 2). A rather vitreous, yet amorphous, xerogel-type solid is collected at relatively short reaction times. Interestingly, an unstable intermediate with a relatively smaller interlayer distance progressively gives way to the final, more expanded lamellar structure. To account for the presence of a metastable phase with the dendrimer in a dense-core or highly compressed state, we must realize that these polyamines are excellent buffers for both pH and ionic strength control, via complexation reactions through their many amine ligands. When dissolved ionic precursors are still present in the reaction media at relatively high concentrations, the dendrimer is expected to react to such an environment by back-folding its lipophilic groups (thereby

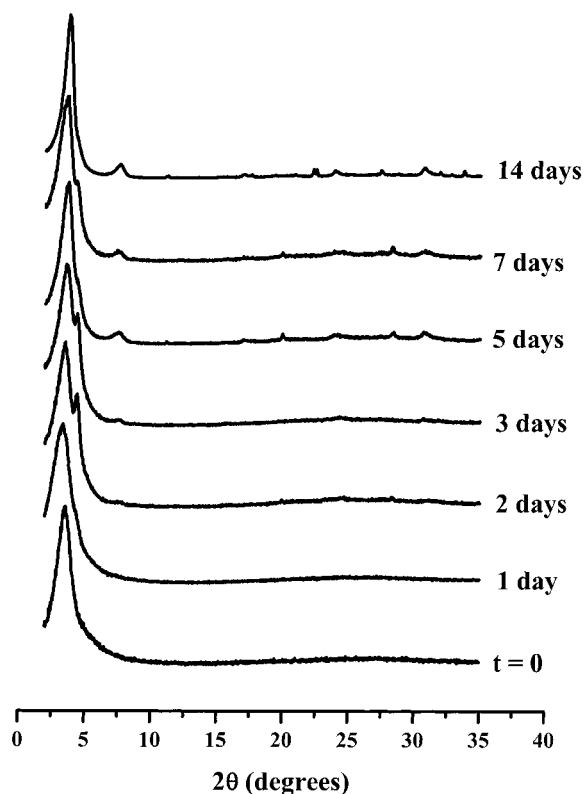


Figure 2. Effect of aging time on the structure of ZnAsO/G5, as monitored by XRD. In this case, the pH was adjusted to 9.5 at the start and was found to be equal to 10.0 after 14 days.

preventing the access of polar and ionic species to its core), while maximizing exposure of its $-NH_2$ ends. Once the solid becomes more organized and oligomeric species condense, the dendrimer structure is allowed to relax.

The XRD patterns of the whole series of materials are shown in Figure 3. The XRD pattern of the dendrimer-free, blank material, which lacks the typical low-angle reflection of the dendrimer-loaded samples, is shown in Figure A of the Supporting Information. For G1 and G2, contamination of the final solid with a nonlamellar, crystalline phase could not be entirely avoided, regardless of pH, temperature, and reactant ratios. However (as is also the case for the sequence in Figure 2, which was done at pH values below the optimum range), several reflections corresponded to those of a “blank” material obtained by carrying out the synthesis in the absence of dendrimer. Indeed, a minor contaminant fraction of particles with a high degree of crystallinity can be separated (not without effort) from the lamellar phase, and the two phases are also distinguishable by TEM. The issue of characterization of these 3-D crystalline impurities will not be dealt with here.

To obtain a quantitative description of these layered materials by XRD, all observable $00k$ reflections (typically 4–6) were employed to derive the interlayer spacings. Plots of $1/k$ vs d_k^{obs} (where d_k^{obs} is the Bragg distance calculated for each $00k$ reflection) were obtained. The slope of these plots is the calculated interlayer distance, in angstroms. Again, interlayer spacing slowly increases with dendrimer generation (Figure 4), i.e., slower than the expected average diameter increase with generation number in solution.²⁰ This flexibility

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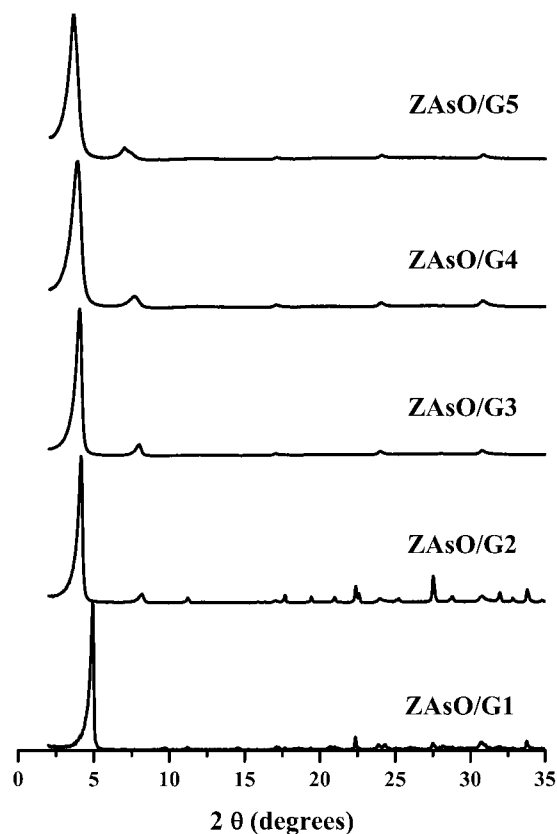


Figure 3. XRD patterns of the ZAsO/*G_n* series (made as prescribed in Table 1).

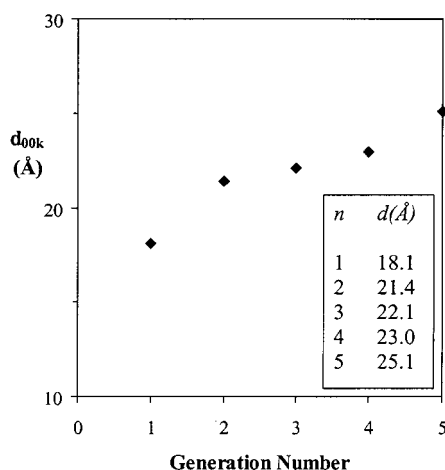


Figure 4. Interlayer spacing vs dendrimer generation.

is inherent in the DAB-Am-*n* group: One of the key features of the theoretical results on DAB-Am-*n* diameters by Scherrenberg et al.²⁰ is that very broad radial density distributions are obtained for all generations. It is not unreasonable to propose that “fully stretched” conformations are required to maximize the interaction between terminal amine groups and the inorganic layers (as well as packing efficiency) with the lower generations. By the same token, adoption of oblate shapes by the more globular, high-generation members would maximize such interactions, a situation that would explain the apparently slow increase in interlayer spacing with generation number.

Table 2 shows the chemical analysis results. The oxygen weight percent was inferred by difference. With

Table 2. Chemical Analysis

ZAsO/G5				
	wt %	mol/100 g	mol of G5/100 g	(Zn or As)/-NH ₂
H ₂ O ^a	2.07	0.115		
C	17.96	1.497	0.003 99	
N	6.88	0.491	0.003 90	
H	4.12	4.120	0.004 68	
H(corr.) ^b	3.52	3.520	0.004 00	
Zn	32.4	0.495		1.99
As	15.4	0.206		0.82
Cs	0.13	9.78 104		
Oc	21.17	1.323		
ZAsO/G4				
	wt %	mol/(100 g)	mol of G4/(100 g)	(Zn or As)/-NH ₂
H ₂ O ^a	1.76	0.098		
C	17.56	1.463	0.007 95	
N	6.52	0.466	0.007 51	
H	4.02	4.020	0.009 30	
H(corr.) ^b	3.24	3.240	0.007 50	
Zn	32.6	0.498		2.07
As	15.3	0.204		0.85
Cs	0.34	2.56 103		
Oc	22.33	1.396		
ZAsO/G3				
	wt %	mol/(100 g)	mol of G3/(100 g)	(Zn or As)/-NH ₂
H ₂ O ^a	1.33	0.074		
C	15.92	1.327	0.015 08	
N	5.51	0.394	0.013 12	
H	3.78	3.780	0.018 17	
H(corr.) ^b	2.91	2.910	0.014 00	
Zn	33.9	0.518		2.47
As	15.9	0.212		1.01
Cs	0.25	1.88 103		
Oc	23.7	1.481		
ZAsO/G2 ^d				
	wt %	mol/(100 g)	mol of G2/(100 g)	(Zn or As)/-NH ₂
H ₂ O	3.35	0.186		
C	8.36	0.697	0.003 99	
N	3.06	0.219	0.003 90	
H	2.41	2.41	0.004 68	
H(corr.)	—	—	—	
Zn	29.6	0.453		3.62
As	17.6	0.235		1.88
Cs	12.8	0.096		
O	—	—		

^a Karl Fischer-titratable water. ^b Once the O²⁻ necessary to neutralize the As⁵⁺ and Zn²⁺ is subtracted from the total O wt %, the residual O²⁻ is assumed to be water of crystallization, and H(corr.) reflects the H wt % solely due to the dendrimer. ^c Calculated by difference, neglecting the Cs content (i.e., assuming that Cs is a physically trapped impurity). ^d For the ZAs/G2 material, an effort to correct the H wt % was not made, since there is more than one phase detected by XRD.

the exception of the sample based on G2 (which is impure), Cs is essentially not incorporated in these materials. Chemical analysis was not done on the G1-based material since, just like with the sample made from G2, departure from a purely lamellar phase was apparent.

The Zn/As ratios exceed those used in the synthesis medium and are also slightly larger than the 1.5 value commonly found in hydrothermally prepared (nonporous) zinc arsenates.²² Another observation is that a very small amount of loosely bound water is detected

by the Karl Fischer method (see Table 1). This is expected, as sample drying was only effected at 45 °C. On the other hand, we believe for reasons discussed below that the Karl Fischer technique is incapable of extracting and titrating water molecules that could in principle be termed "structural".

From the C and N weight percent, one can estimate the number of moles of dendrimer in each material. Being the number of moles of dendrimer predicted from either element roughly equal, it is apparent that nitrate from the Zn precursor is not trapped in the layered structure. Furthermore, this precludes complexation of extraframework Zn^{2+} by the dendrimers, since NO_3^- ions would be needed to counter-balance the excess positive charge from chelated Zn^{2+} . Thus, an explanation for the Zn-rich nature of these materials is not likely to come from the presence of dendrimer-chelated (extraframework) Zn^{2+} .

There is still the question of why the H content needs to be "corrected" (see Table 2). Once the amount of O^{2-} needed to neutralize the As^{5+} and Zn^{2+} derived from chemical analysis is calculated, it is possible to account for the "excess" H: When an apparent excess of O found in all cases is tied to a fraction of the total H content to give water (not titrated by the Karl Fischer method), the moles of dendrimer calculated from (nonwater, labeled as H (corr.) in Table 2) hydrogen match very closely the stoichiometry from C and N analysis.

The calculated number of Zn ions per terminal amine group is close to two in ZAs/G3, ZAs/G4, and ZAs/G5. In solution, the DAB-Am-*n* family has a Zn^{2+} complexation capacity of one cation per every two terminal amine groups.^{23a} In fact, in polar liquids this is an important property of DAB-Am-*n* dendrimers: the primary amine groups are responsible for metal ion-dendrimer interactions, not the tertiary N centers located at the core of the dendrimer.^{23a} Such a property would give a DAB-Am-*n* molecule great flexibility (as suggested earlier) once sandwiched between ZnAs layers, since the core would be nonionic. Polyamidoamine (PAMAM) dendrimers, on the other hand, will indiscriminately interact with transition metal ions at both core and shell locations, unless the outer amine groups are protected or replaced.^{23b} While Zn^{2+} centers are the expected point of dendrimer/inorganic layer interaction via $\text{Zn}^{2+}\cdots\text{NH}_2\text{R}$ coordination, it is clear that there are more Zn^{2+} ions in these solids than those capable of interacting with the dendrimers' outer shells. This need not be surprising: unless an extremely thin inorganic layer is formed (which is clearly not the case according to Figure 1), a fraction of the Zn^{2+} ions is expected to be used for charge neutralization inside the ZnAs layers; i.e., such a type of Zn^{2+} does not directly interact with amine groups from the dendrimer.

In Table 2, once the entries for the nondendrimer elements are rounded off to the smallest set of integers, the following chemical formulas for ZAs/G5, ZAs/G4, and ZAs/G3 are obtained: $\text{G5}_{0.039}\text{As}_2\text{O}_{10}\text{Zn}_5\cdot 3\text{H}_2\text{O}$, $\text{G4}_{0.074}\text{As}_2\text{O}_{10}\text{Zn}_5\cdot 4\text{H}_2\text{O}$, and $\text{G3}_{0.13}\text{As}_2\text{O}_{10}\text{Zn}_5\cdot 4\text{H}_2\text{O}$, respectively.

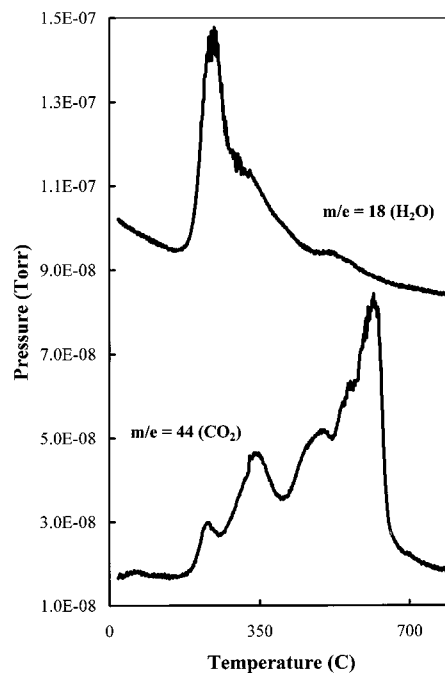


Figure 5. ZAsO/G5 temperature-programmed oxidation pattern (wherein, for example, "1.5E-07" represents 1.5×10^{-7}).

The temperature-programmed decomposition pattern of ZAs/G5 shown in Figure 5 exemplifies the thermal behavior of these materials in air. Water evolution starts at ca. 200 °C, which marks the onset of structural collapse, as confirmed by XRD. Assuming that metastable Zn or As carbonate species form and subsequently decompose at low temperatures, the high-temperature CO_2 peak must be due to hydrogen-deficient carbonaceous residues from the dendrimer. Note that the late release of CO_2 is not accompanied by water evolution. Given the sample:air flow ratio employed (150 mg:100 mL/min) in our studies, it was not possible to detect any significant negative deflection in the $m/e = 32$ (O_2 consumption signal, shown in Supporting Information, Figure B).

Conclusions

The DAB-Am-*n* dendrimers were found to form layered structures with zinc arsenates via hydrothermal syntheses in a relatively narrow pH window, rather than by conventional intercalation of preformed layered solids. The structural flexibility of DAB-Am-*n* dendrimers allows their higher generations to presumably locate between the ZnAs layers in oblate or compressed structures.

Despite the inherently low thermal instability of these layered materials, the DAB-Am-*n* dendrimers are nevertheless able to self-assemble with inorganic precursors, opening up a number of opportunities. First, "folding sheet" mechanisms²⁴ might exist to ultimately synthesize 3-D structures that could potentially lead to new porous (once dendrimer removal is effected) materials. Second, layered structures can still be utilized to produce more stable, pillared materials since the higher generation dendrimers have the ability to chelate dozens of Cu^{2+} , Ni^{2+} , Co^{2+} (or better, Co^{3+}), and other catalytic

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cally interesting transition metal ions with affinity for nitrogen ligands.

Acknowledgment. We acknowledge support from the National Science Foundation (Grant CTS-9733756) and Kraft Foods Inc.

Supporting Information Available: Figures A and B showing low-angle reflection of dendrimer-loaded samples and O₂ consumption signal (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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