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MALDI TOF Mass Spectrometry for the Characterization of Phosphorus-Containing Dendrimers. Scope and Limitations

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Neutral phosphorus-containing dendrimers with aldehyde groups at the periphery have been analyzed using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOFMS) up to generation four. Although the expected quasi-molecular ion is generally observed, the mass spectral pattern, presence of fragments and adducts related to the original skeleton, is highly relevant to the sample preparation (nature of the matrix: 2-5-dihydroxybenzoic acid (2.5-DHB), 1,8-dihydroxy-9[10*H*]-anthracenone (dithranol), 6-azathiothymine, 2,4,6-trihydroxyacetophenon, 7-hydroxycoumarin or 2-anthramine, and addition of alkali metal salts). The dithranol matrix with addition of LiI offers milder conditions; however, abundant fragments are still observed for the higher generation dendrimers. Investigation of these effects in connection with SEC, NMR, and MALDI-TOFMS studies of UV preirradiated dendrimers allows the assumption to be made that fragmentation occurs in MALDI due to the relatively strong absorption of the dendrimers at 337 nm. Fragmentations and formation of adducts involve nitrogen−nitrogen bond cleavage, imine metathesis, and reaction of aldehyde groups with internal imino groups.

The design of monodisperse polyfunctionalized macromolecules as dendrimers is a field of considerable growing interest, these macromolecules possessing a number of specific properties (solubility, viscosity, thermal stability...) different from those of more classical polymers. These properties are generally due to the presence of a large number of functional groups on the surface and of internal cavities and to the fact that dendrimers have a very narrow molecular weight distribution.[1−9] Full characterization of dendrimers includes a variety of techniques: ^{1}H,^{13}C,^{29}Si NMR (however not useful for higher generations), size exclusion chromatography (SEC), laser-light scattering, osmometry and mass spectrometry using mainly electrospray ionization (ESI),[10−15] and matrix-assisted laser desorption ionization (MALDI).[16−23] A few structures, concerning only small dendrimers (up to generation two), have been determined by X-ray diffraction.

In the case of phosphorus-containing dendrimers, the main characterization was done by ^{31}P NMR. Indeed, ^{31}P NMR spectroscopy has been shown to be an extraordinary tool for following the growth of these macromolecules and for controlling the progress of all reactions performed either in the internal layers or on the surface.[24−37] Fast-atom bombardment (FAB) mass

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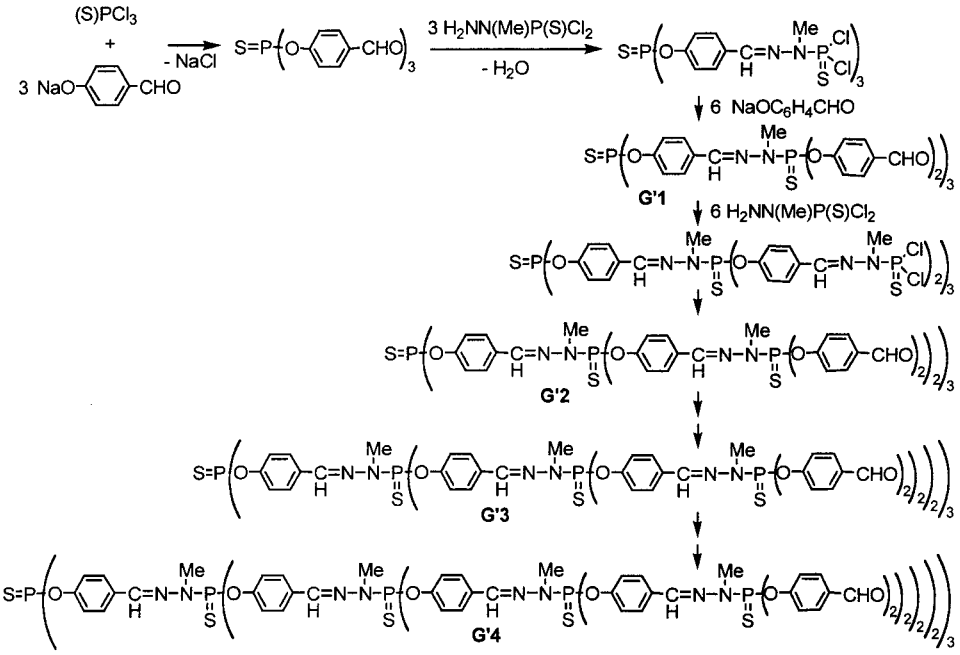
Scheme 1. Synthesis of Dendrimers G′1−G′4



spectrometry (limited to lower generations) and size-exclusion chromatography were the other techniques used for this special class of dendrimers. Therefore, it is clear that there is a lack of knowledge and information concerning the characterization and physicochemical properties of these dendrimers.

In this paper, we report efforts to characterize phosphorus-containing dendrimers using MALDI-TOFMS. In particular, possible fragmentation occurring during the MALDI processes has been investigated.

EXPERIMENTAL SECTION

Dendrimer Synthesis. Phosphorus-containing dendrimers of generations one to four were prepared by the conventional divergent approach[38] (Scheme 1).

Size Exclusion Chromatography (SEC). SEC was performed using a Waters (Milford, MA) 515 pump, a Waters 410 differential refractometer working at room temperature with tetrahydrofuran (THF) eluent at a flow rate of 5 mL min^{-1} and equipped with a set of 100, 500, 10^3, and 10^4 Å Ultrastyragel columns (19 × 300 mm). Molecular weights were derived from a calibration curve based on polystyrene standards.

MALDI-TOF Mass Spectrometry. MALDI mass spectra were recorded with a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflection modes. The mass spectra shown represent an average over 256 consecutive laser shots (3 Hz repetition rate). Peptides were used to calibrate the mass scale using the two points calibration software 3.07.1 from PerSeptive Biosystems. Mentioned m/z values correspond to monoisotopic masses except for dendrimers G′3 and G′4 where average masses are given. The dendrimer solutions (10^{-3} M) were prepared in tetrahydrofuran (THF). Matrix compounds were from Sigma (France) and used without further purification. The matrixes, 2-5-dihydroxybenzoic acid (2.5-DHB), 1,8-dihydroxy-9[10*H*]-anthracenone (dithranol), 6-azathiothymine, 2,4,6-trihydroxyacetophenon, 7-hydroxycoumarin, or 2-anthramine, were also dissolved in THF (10 g L^{-1}). One microliter of dendrimer solution was mixed with 50 μL of matrix solution. Ten microliters of alkali iodide (LiI, NaI) solution (5 g L^{-1} in THF) were added in some experiments to induce cationization. One microliter of the final solution was deposited onto the sample stage and allowed to dry in air.

Irradiation Experiments. $CDCl_3$ solutions of dendrimers G′1 to G′4 (20 g L^{-1}) were irradiated at 350 nm for 12 h using the Rayonet photochemical reactor RPR 100.

RESULTS AND DISCUSSION

These compounds were first characterized by size exclusion chromatography (SEC) which shows a narrow distribution of molecular weight (Figure 1). The width of the signals obtained by SEC confirms the good purity of these dendritic systems. However, it is possible to detect for the dendrimers of generations 1 (G′1) and 2 (G′2) a second signal corresponding to higher molecular species. In addition, a tailing toward the higher retention times is observed for G′3 and G′4, possibly indicating presence of structure defects. A plot of the SEC elution time versus the

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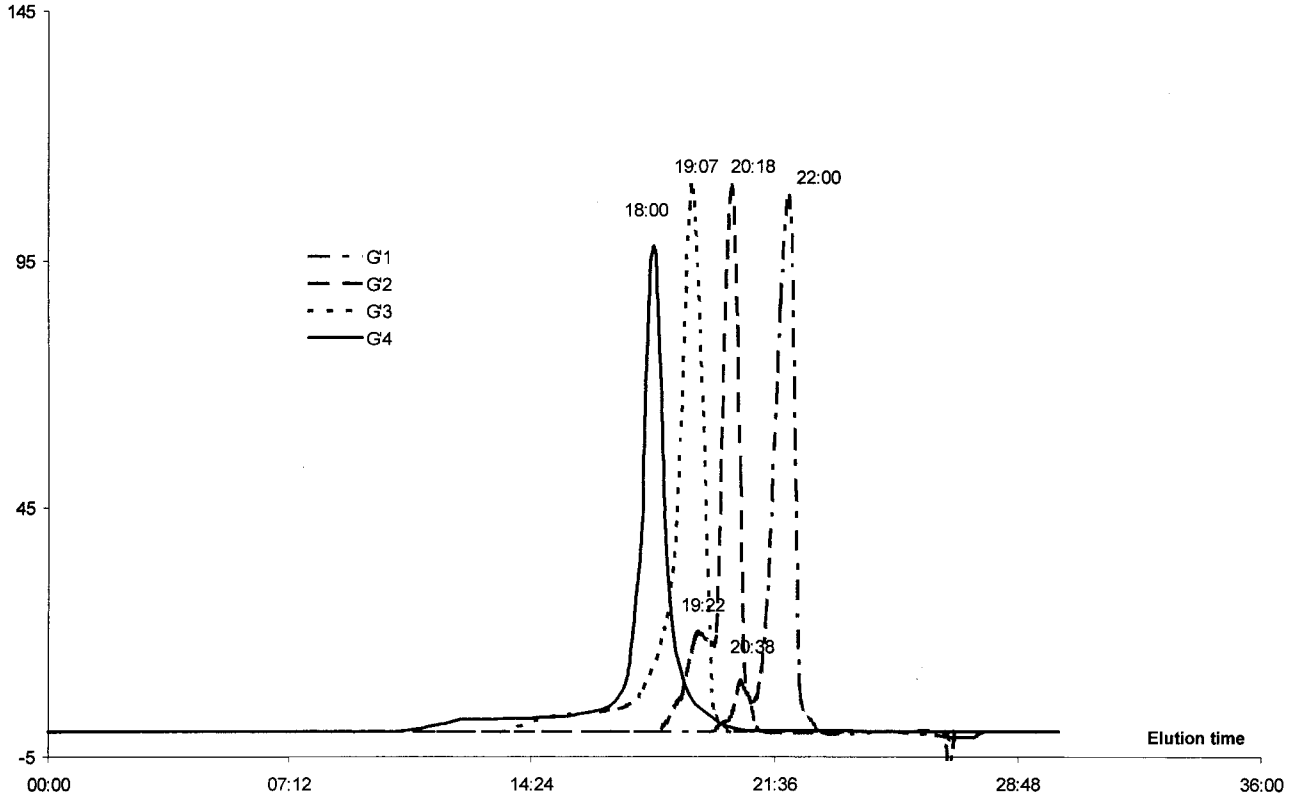

Figure 1. Size exclusion chromatography (SEC) of dendrimers G′1−G′4.

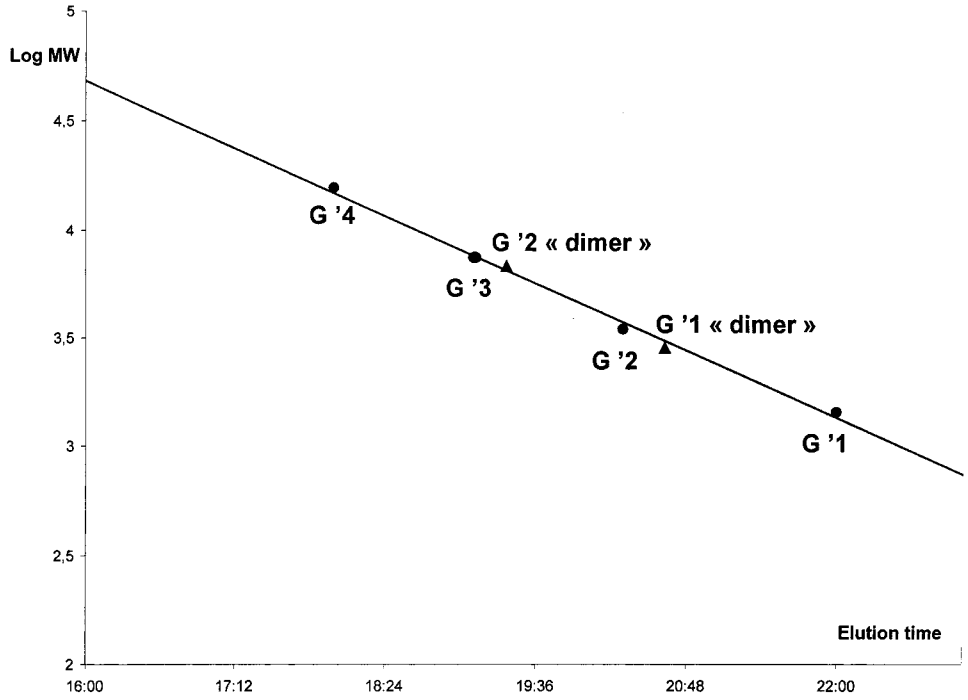

Figure 2. Elution time of dendrimers G′1−G′4 versus logarithm of the molecular weight.

logarithm of the molecular weight of G′1−G′4 gives a straight line (Figure 2); this is in agreement with what was observed for different other dendrimers.[6] The value of the elution time observed for the minor signals detected for G′1 (20.38 min) or G′2 (19.22 min) can be attributed to species resulting from self-assembly of two dendrimers of generation 1 or generation 2, respectively. This can be shown in Figure 2 where values of the elution time of the minor signals allowed us to determine a molecular weight of 6786 g mol^{-1} for the "G′2 dimer" (theoretical molecular weight 6834 g mol^{-1}) and of 3197 g mol^{-1} for the "G′1 dimer" (theoretical molecular weight 2846 g mol^{-1}). However, characterization by SEC is generally of limited value since the dendrimers themselves are less polydisperse than the polymer standards used to calibrate the columns (polydispersity of polystyrene used in this work: 1.03) and it does not provide information on the structure of the species. Therefore there was a need to characterize more carefully our

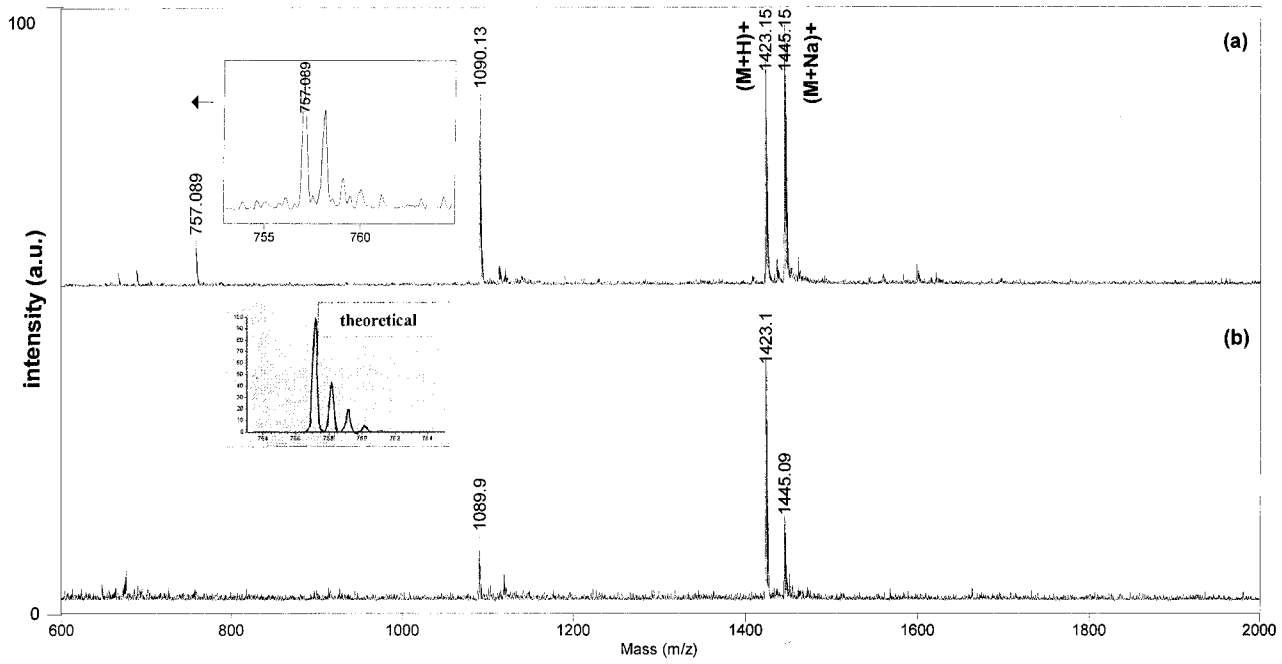

Figure 3. Positive-ion MALDI mass spectra of G′1: 2,5-DHB matrix (a) and dithranol matrix (b).

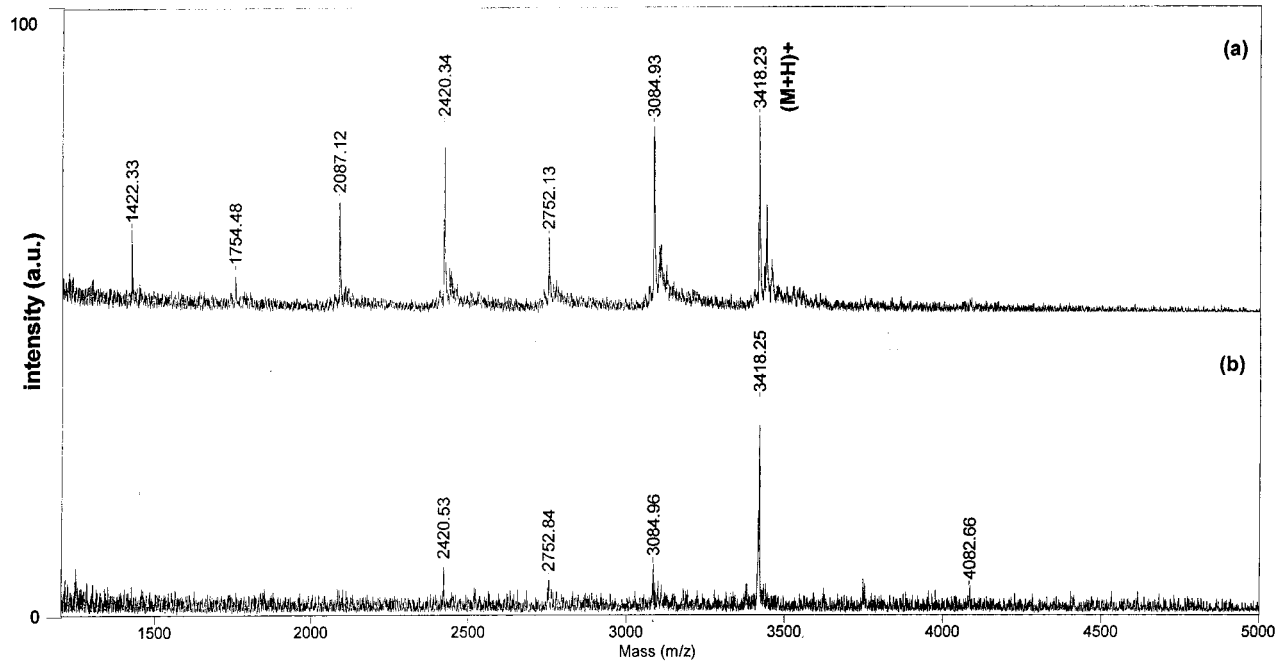

Figure 4. Positive-ion MALDI mass spectra of G′2: 2,5-DHB matrix (a) and dithranol matrix (b).

dendrimers by the MALDI-TOFMS technique which should be the best mass spectrometry method for this category of neutral dendrimers.

Since experimental conditions (matrix, metal salt addition, fluence, etc.) can strongly influence mass spectral characteristics,[16] they have been optimized using generation 1 (G′1) and 2 (G′2) dendrimers. MALDI mass spectra of G′1 using 2,5-DHB and dithranol matrixes are shown in Figure 3a,b. Besides the peaks at m/z 1423.1 and 1445.1 attributed to protonated and sodium cationized molecules, respectively, fragment ions at m/z 1090.1 (2,5-DHB and dithranol) and m/z 757.1 (2,5-DHB) are observed. Fragmentation is enhanced with the 2,5-DHB matrix. Loss of 333 u from the protonated molecule and further loss of 333 u occurs with this matrix. In addition, examination of the isotopic cluster at m/z 757.1 shows that it does not fit with a single species and that a second species corresponding to a loss of 332 u from m/z 1090.1 is present. This phenomenon is more pronounced for G′2 as shown in Figure 4a,b. With the dithranol matrix, in addition to loss of 333 u (m/z 3085) from the protonated molecule at m/z 3418.2, further losses of 332 u are also observed (m/z 2752.8 and 2420.5, Figure 4b). With the 2,5-DHB matrix, these fragmentations are considerably reinforced and the protonated molecule is not the dominant peak of the mass spectrum (Figure 4a). Thus, a milder desorption is observed with dithranol compared with that with 2,5-DHB. In addition, adducts (+332 u) are also observed in the case of dithranol (Figure 4b). Experiments have been carried

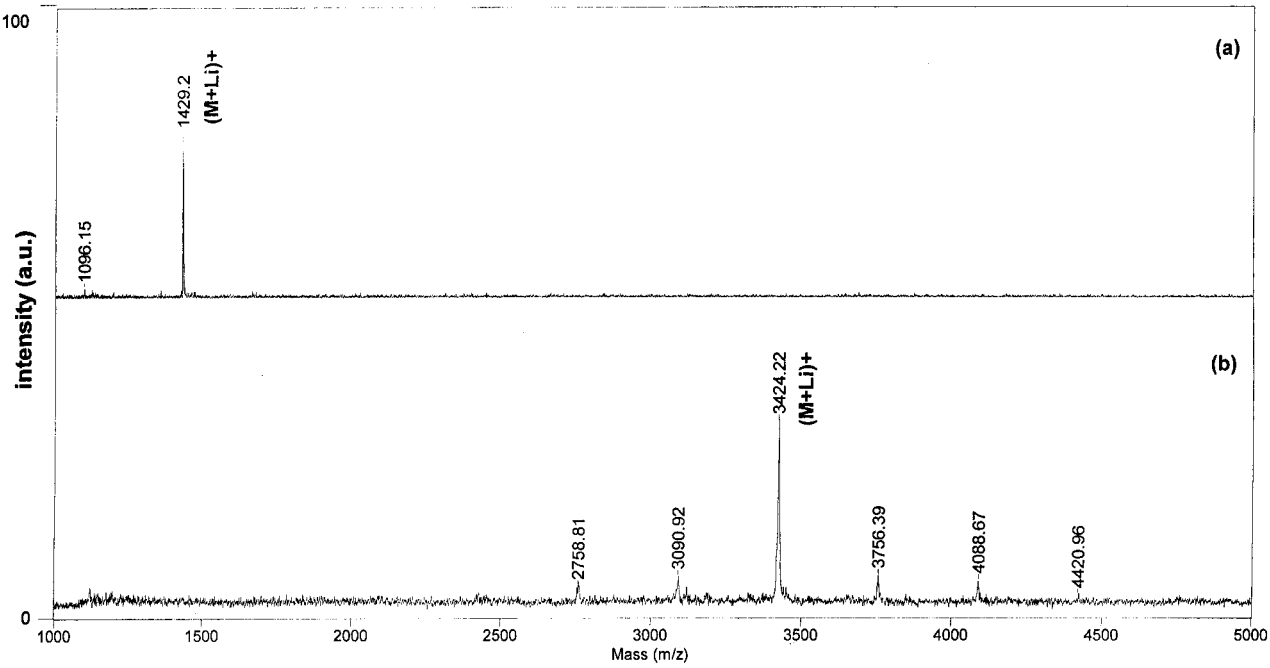

Figure 5. Positive-ion MALDI mass spectra of G′1 (a) and G′2 (b) in the presence of LiI (dithranol matrix).

out with other matrixes (in particular, less acidic matrixes such as 6-azathiothymine, 2,4,6-trihydroxyacetophenon, 7-hydroxycoumarin, or 2-anthramine). The highest quasi-molecular ion yields and the lowest fragmentation were observed with dithranol, and modification of the laser fluence does not change this behavior. As alkali ion cationization is known to reduce fragmentation, the same experiments have been carried out with addition of alkali metal salts (LiI and NaI) to the sample to induce cationization. In the presence of LiI, protonation is completely suppressed, which is not the case with NaI. Thus, LiI addition has been preferred. Under such experimental conditions, the fragmentation is dramatically reduced as shown in Figure 5a,b. The G′1 mass spectrum exhibits essentially the Li^+ cationized molecule at m/z 1429.2, while for G′2, fragments at m/z 3090.9 (loss of 333 u from the lithiated molecule at m/z 3424.2) and 2758.8 (loss of 332 u from m/z 3090.9) are of low abundance. It can be noted that G′2 was also characterized by FAB mass spectrometry.[38]

The dithranol matrix, offering milder desorption/ionization conditions than other tested matrixes for G′1 and G′2 analysis, has been used to analyze higher generation dendrimers. For G′3, in the absence or presence of LiI, the quasi-molecular ion ($[M+H]^+$ at m/z 7406 or $[M+Li]^+$ at m/z 7411.9) is again the dominant peak in the mass spectrum but, even in the presence of LiI offering milder conditions, two sets of abundant fragments (losses of 333 and/or 332 u and 664 u) and adducts (+332 u) are detected (Figure 6a,b). Within this mass range, due to a lack of resolution, it is not possible to distinguish loss of 333 u from loss of 332 u. The situation starts to be much more complicated for G′4: peaks are observed along the 2000−18 000 m/z range with the expected quasi-molecular ion $[MLi]^+$ at m/z 15 383 and sets of fragment ions (−332 and −664 u) and adducts (+332 u) (Figure 7).

It is clear that these fragments, and of course these adducts, appear not to correspond as a whole to the existence of a number of structure defects. Such an abundance of structure defects would be detected by ^{31}P NMR[4] without any doubt. However, presence of side products or chemical degradation products cannot be excluded. Moreover it is interesting to note that mass spectrometry does not reveal the presence of chlorine atoms, thus allowing us to reject the presence of $P(S)Cl_2$ or $P(S)(Cl)(OC_6H_4CHO)$ groups either on the surface or within the cascade structure of the dendrimers G′1−G′4.

Therefore, one can assume that degradation occurs during MALDI analysis, either in the course of sample preparation or during and/or after UV laser irradiation. Decomposition during sample preparation is not likely since it is very fast (less than 30 s) and an extended stay (4 h) of the dendrimer in a THF/H_2O (20:1 v/v) solution containing the matrix and LiI does not modify the mass spectrum. On the other hand, degradation consecutive to laser irradiation is more likely. UV spectra of dendrimers G′1−G′4 in THF show a very broad absorption band between 210 and 360 nm, with a red shift for the highest generations (Figure 8). At 337 nm, the extinction coefficient, ϵ, of G′1 has been evaluated to 1400 L mol^{-1} cm^{-1}. Indeed, irradiation of G′1−G′4 in chloroform for 12 h at 350 nm provokes serious damages as can be seen by ^{31}P and ^{1}H NMR, SEC, and MALDI-TOFMS. NMR spectra recorded after irradiation exhibit broader signals than before and new peaks corresponding to the degradation of the dendrimer. Such a dramatic effect can be also visualized by SEC, which shows an important broadening of the distribution of mass for each generation, indicating the formation of decomposition products and also adducts. MALDI-TOF mass spectra of the irradiated samples corroborate such a decomposition. Two main sets of peaks can be observed for G′1, corresponding to successive losses of 332 u from the quasi-molecular ion $[M+Li]^+$ and losses of 94 u from these species. Adducts (+332 u) are also observed. For dendrimers G′2, G′3, G′4, signals are only observed in the low mass range (m/z < 3000). It must be emphasized that a nonsoluble residue was present in the irradiated solutions of these higher generation dendrimers.

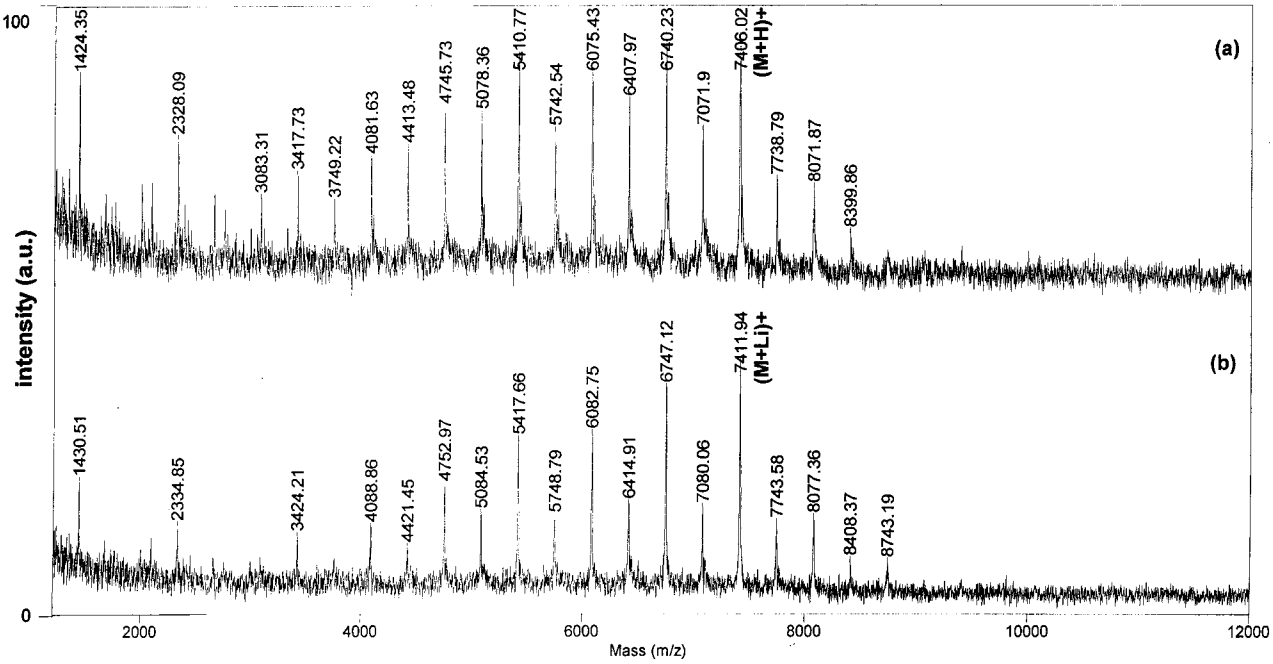

Figure 6. Positive-ion MALDI mass spectra of G′3 in the absence (a) or presence (b) of LiI (dithranol matrix).

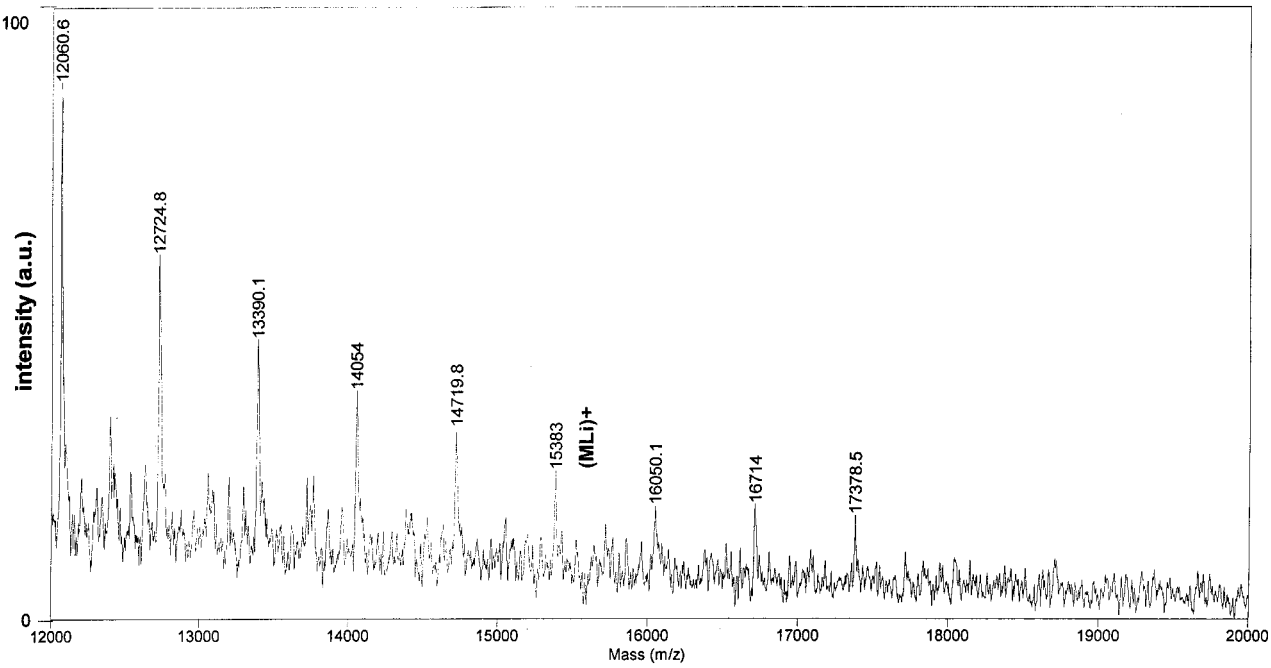

Figure 7. Positive-ion MALDI mass spectra of G′4 in the presence of LiI (dithranol matrix).

Although irradiation conditions are quite different in MALDI analysis (solid phase and presence of an absorbing matrix, short laser pulse), it is evident that UV irradiation at 337 nm (the extinction coefficient being higher for the dendrimer at 337 nm than at 350 nm) can induce decompositions. Indeed, a laser desorption ionization (LDI) mass spectrum (Figure 9) of the neat G′2 (absence of matrix) shows abundant fragments (losses of 333 and 332 u). The presence of the matrix would not completely protect the dendrimer from degradation during MALDI analysis. Now a question arises: how to explain such fragmentations as losses of 333, 332, and 664 u and also the formation of adducts +332 and +664 u, these phenomena being enhanced when moving from generation one to generation four? Losses of 333 u (Scheme 2) can be attributed to charge-induced gas-phase fragmentation of protonated or lithiated species. Such a fragmentation pathway has been observed in post-source-decay (PSD)[40] experiments with G′1 (results not shown). Considering the PA of matrixes, the fragmentation should not be significantly increased with dithranol (PA = 209 kcal mol^{-1})[41] compared with 2,5-DHB (PA = 204 kcal mol^{-1})[41] since the exothermicity of the protonation reaction with both matrixes is very close. Thus, other parameters

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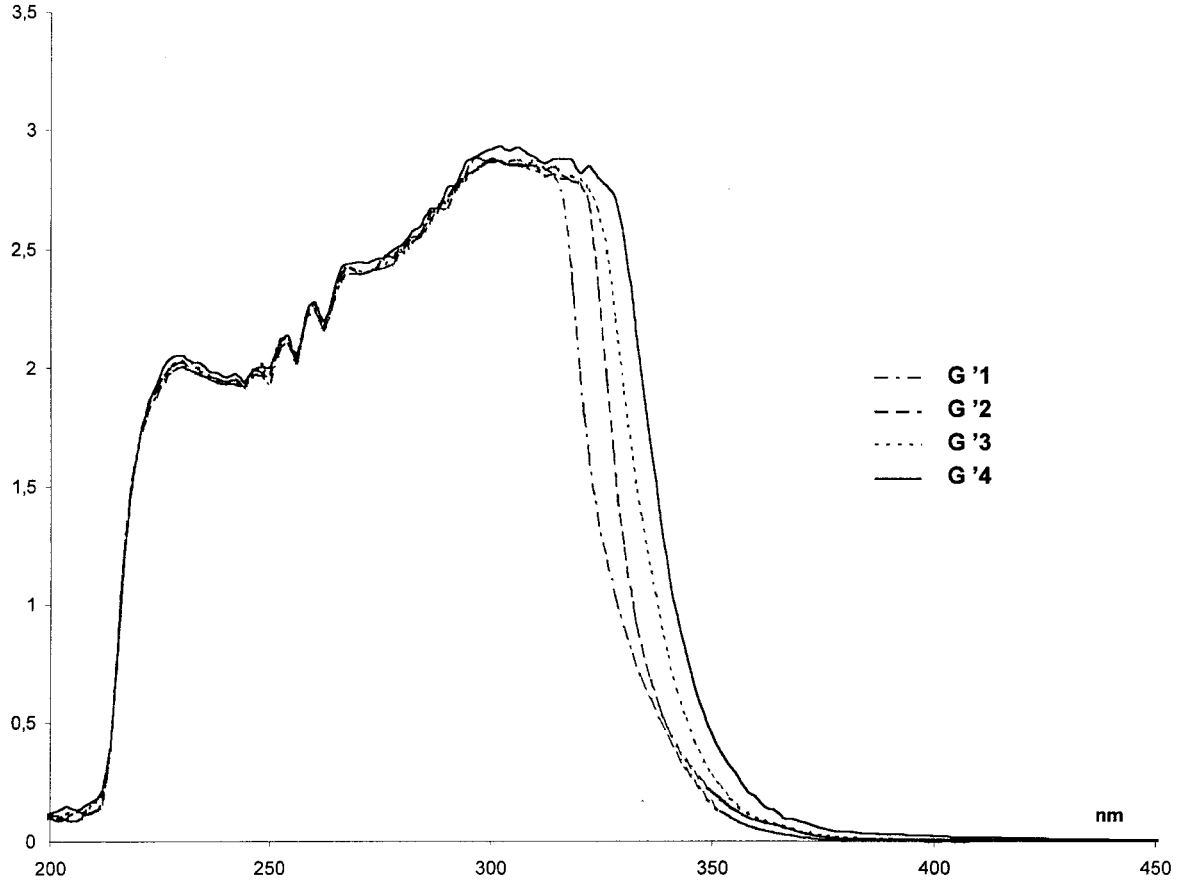

Figure 8. UV spectra of dendrimers G′1−G′4 in THF.

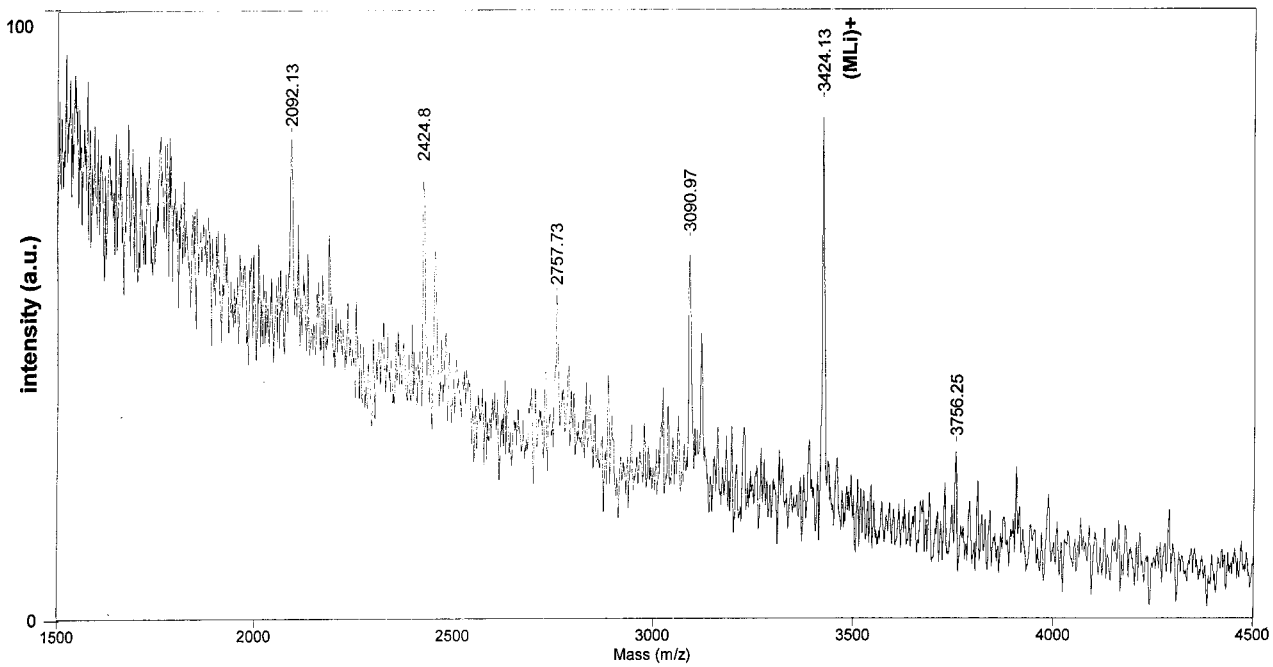

Figure 9. Laser desorption ionization mass spectrum of neat G′2.

should be taken into consideration. For instance, higher laser fluence is used with 2,5-DHB compared with dithranol due to lower extinction coefficients at 337 nm ($\epsilon_{\text{dithranol}} = 7300$ L mol^{-1} cm^{-1} and $\epsilon_{\text{DHB}} = 4400$ L mol^{-1} cm^{-1} in solution).[42] The higher fluence used with 2,5-DHB could increase the internal energy of the desorbed dendrimer and thus the fragmentation yields. For more packed structures, proton migration is favored, which possibly leads to consecutive losses. It must be pointed out that this enhancement of fragmentation with 2,5-DHB has also been observed for dendritic polypyridine.[16]

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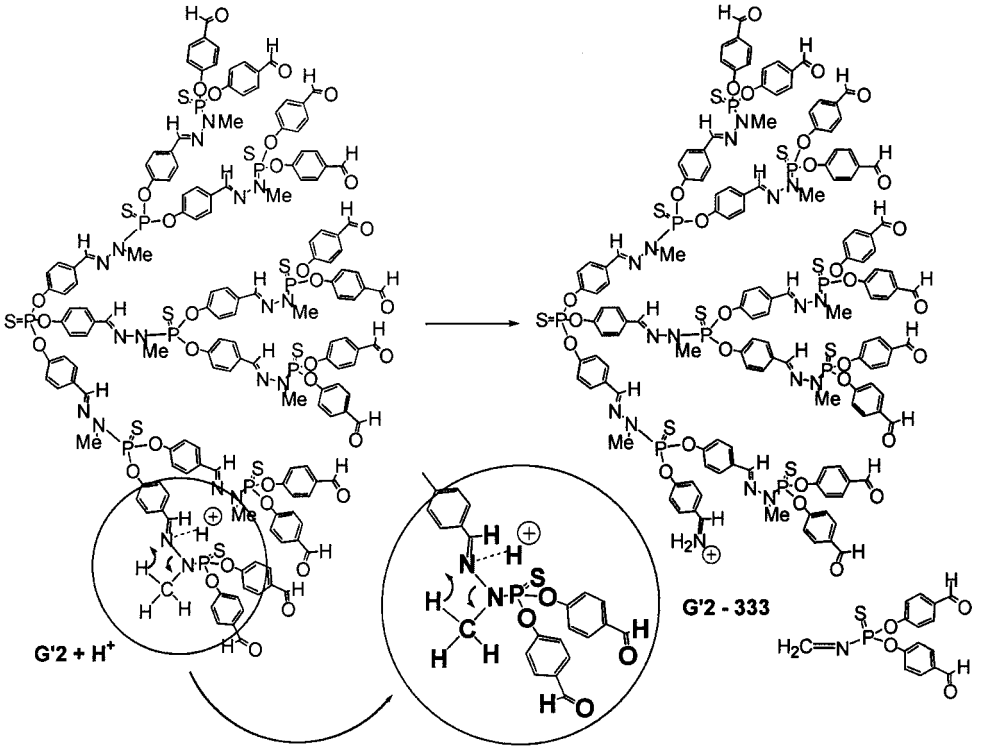
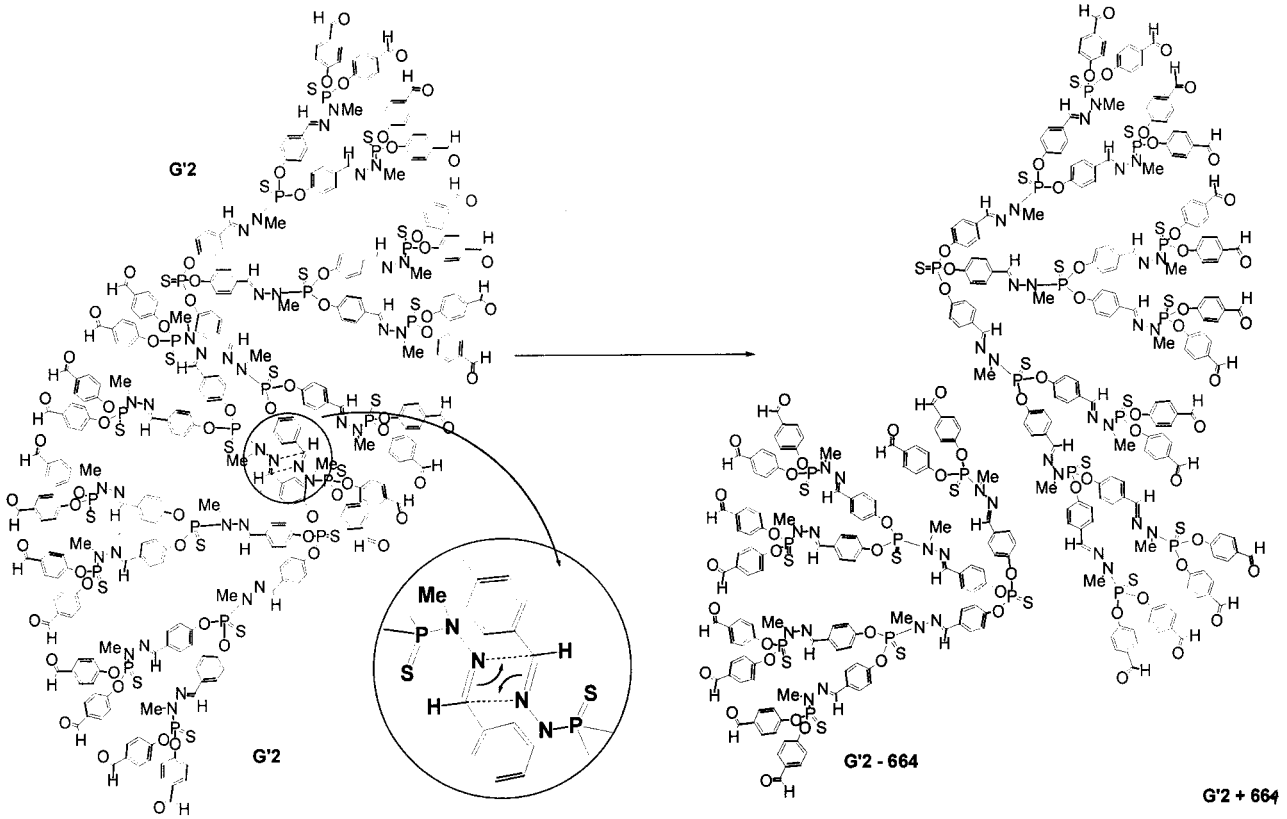
Scheme 2. Proposed Mechanism of Charge-Oriented Gas-Phase Fragmentation of Protonated or Lithiated Species

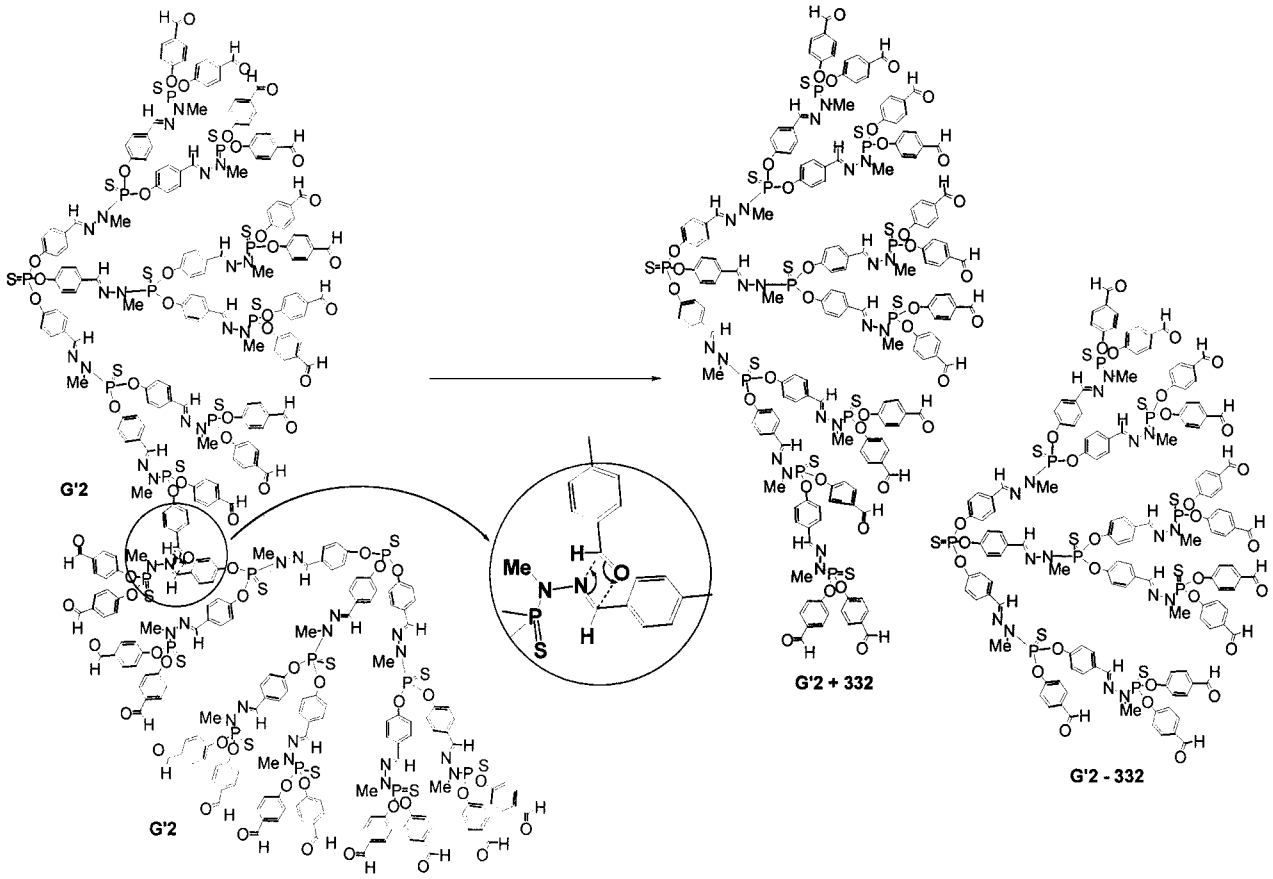


Scheme 3. Fragmentation Involving Imine Metathesis



On the other hand, losses of 332 u/664 u and formation of adducts probably originate from a fragmentation mechanism involving a rearrangement. Two types of rearrangement can be postulated: imine metathesis or reaction of terminal aldehyde groups with internal imino groups. Metathesis of imines requires generally more drastic conditions than olefin metathesis. It has been known for a long time that such a process can be acid-catalyzed,[43] and recently it was found that such a reaction can be

Scheme 4. Fragmentation Involving Reaction of Terminal Aldehyde Groups with Internal Imino Groups



catalyzed by imido molybdenium complexes.[44] In the present case, it can be assumed that under irradiation such an imine metathesis, or more precisely such an hydrazone metathesis, takes place between two dendrimers of a given generation with, as a consequence, the formation of "unperfect" dendritic species (see Scheme 3) with concomitant loss of 664 u for one macromolecule and gain of 664 u for the other. The second mechanism of degradation consists of the reaction of internal hydrazone groups with aldehyde groups located at the outer shell. Such an exchange can afford fragments and adducts with loss and gain, respectively, of 332 and 664 u (or multiples of 332 u) (see Scheme 4). To check this last assumption, a dendrimer of generation three with 24 phenoxy groups, instead of 24 aldehyde groups, located on the outer shell was prepared. As a result, losses and adducts of 304 u (corresponding to 332 u for the terminal aldehyde group) disappear, and only losses and gains of 608 u (corresponding to 664 u for the terminal aldehyde group) were observed; this clearly indicates that reaction of terminal hydrazone groups with aldehyde groups is the cause of the fragmentations observed. Intramolecular rearrangements can also occur for the higher generations. A possible mechanism could be the decomposition of neutral species induced by UV irradiation followed by gas-phase ionization of neutrals in the plume. Such mechanisms involve inter- or intramolecular interactions which could be favorized for higher generation dendrimers. Interactions should be reduced in the presence of the matrix; however, we have not experimentally observed any dilution effect (molar ratio of matrix/dendrimer varying from 150 to 15 000) on the fragmentation yields. The stability decrease observed for higher generation dendrimers could also be related to a higher steric strain energy.

CONCLUSION

Phosphorus-containing dendrimers constituted by the repetition of $POC_6H_4CH{=}NN(CH_3)$ fragments appeared very sensitive to UV MALDI conditions. Even if molecular peaks are detected for dendrimers of generations one to four, it is clear that fragmentations occur due to the relatively strong UV absorption of these dendrimers at 337 nm. These fragmentations involve nitrogen−nitrogen bond cleavage, imine metathesis, or reaction of terminal aldehyde groups with internal imino groups.

As a consequence, such a technique cannot be used to fully characterize structure defects in the case of these phosphorus-containing dendrimers. However, the presence of chlorine atoms was never detected, allowing us to reject structure defects involving remaining P−Cl bonds. These defects, if any, might only come from incomplete Schiff reactions between terminal aldehyde groups and methylhydrazinodichlorophosphine sulfide.

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