Large Dipole Moments of Phosphorus-Containing Dendrimers

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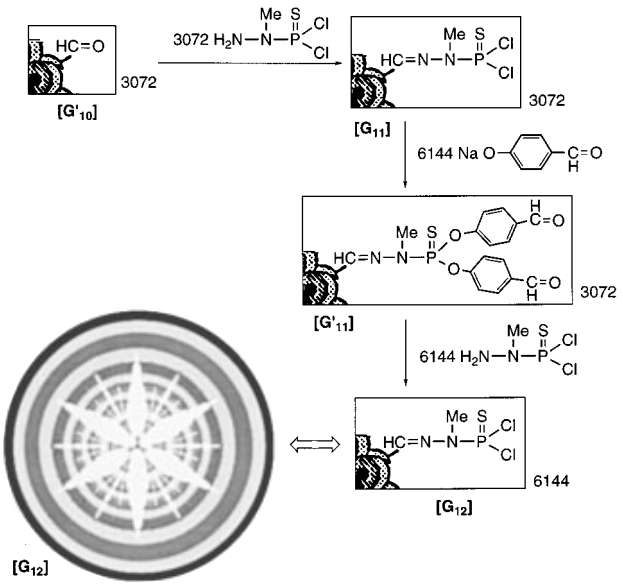
Dipole moments of linear polymers increase with the increasing degree of polymerization. Such an observation applied to dendrimers[1] should lead to experimental high dipole moments for these macromolecules: flexibility of the branches especially at lower sizes and rotation about any of the many bonds in the structure destroying the symmetry may facilitate alignment of the polar units of the structure in the direction of the field. Consequently, each of the polar units should significantly contribute to the overall dipole moment of the dendrimer. However, enhancement of the observed dipole moments can be expected to be smaller for high generations due to steric effects and to the compact globular shape generally adopted by dendritic structures: this should result in a drastic reduction of the dipole moment of these macromolecules in comparison to linear or less sterically confined systems.

Recently,[2] it was demonstrated that plots of dipole moments versus molecular weight for organic dendrimers of generation 1−5 were not linear and that dipole moments of dendrimers containing electron-withdrawing and electron-donating groups at the chain ends were much larger than those measured for symmetrical structures: from 4.54 (generation 1) to 17.6 (generation 5) D for the former and from 2.66 (generation 1) to 12.1 (generation 5) D for the latter.

This prompts us to measure dipole moments of a set of phosphorus-containing dendrimers incorporating strong P═S polar units and for which higher generations can be prepared. We describe here such a study with emphasis on the extremely high dipole moment values observed for such species. The first X-ray diffraction studies of a phosphorus-containing dendrimer are also reported.

Dendrimers of generation 1−10 with phosphorus−chlorine bonds **[G$_1$]**−**[G$_{10}$]** or with terminal aldehyde groups **[G′$_1$]**−**[G′$_{10}$]** were already described up to generation 10.[3] Dendrimers of generation 11, **[G$_{11}$]** and **[G′$_{11}$]**, and 12 **[G$_{12}$]** (theoretical molecular weight 3 030 289, 12 288 P−Cl bonds) are prepared from generation 10 using the strategy outlined in Scheme 1. Dense packing effects prevent the formation of **[G′$_{12}$]**, and therefore of higher generations; only insoluble unidentified material was formed when **[G$_{12}$]** was heated with the sodium salt of hydroxybenzaldehyde. **[G$_{11}$]**, **[G′$_{11}$]**, and **[G$_{12}$]** are characterized by means of ^{31}P, ^{1}H, and ^{13}C NMR and elemental analysis.[4] Indeed, ^{31}P NMR appears to be the method of choice to follow rigorously the construction of these macromolecules: condensation reactions result in the appearance of a new signal due to the phosphorus atoms of the upper generation $n + 1$ and a slight deshielding effect for the phosphorus atom of generation n, whereas substitution

Scheme 1



reactions induce a shielding of the signal due to the phosphorus atoms of the upper generation (Figure 1). Of course, structure defects cannot be totally ruled out but can be reasonably limited to the precision of ^{31}P NMR. Dendrimers **[G$_{11}$]** and **[G′$_{11}$]** are easily soluble in most organic solvents while **[G$_{12}$]** appears less soluble but soluble enough to be characterized in $CDCl_3$ solution.

An X-ray diffraction study[5] of dendrimer **[G$_1$]** was undertaken in order to understand why it is possible to obtain such large phosphorus macromolecules.

The ORTEP drawing of this compound is depicted in Figure 2. Three main features can be emphasized: (i) Each OC_6H_4CH═N−N(Me)P arm is planar (maximal deviation from 0.06 to 0.193 Å to the average plane, depending on the atom being considered). The molecule as a whole looks like a three blade propeller when examined in the direction of terminal P═S groups: (ii) The distance between terminal P═S groups is very large (17 Å). (iii) The length of each arm is 9 Å.

All these observations suggest that steric congestion does not disturb the construction of dendrimers even for the highest generations and that terminal groups are readily available for further reactions.

Dipole moments for dioxane solutions of both CHO or P−Cl terminated dendrimers were measured at 25 °C[6] (Table 1). Remarkably, values of dipole moment versus generation increase exponentially from 8.43 (**[G$_1$]**) to 258 (**[G$_{10}$]**) and from 8.27 (**[G′$_1$]**) to 328 (**[G′$_{11}$]**) D (Figure 3), the highest dipole moment values reported up to now for dendritic structures. Dipole moments[7] are not totally dependent on the nature of chain ends, since close values are obtained for CHO- and P−Cl-terminated dendrimers of a given generation. The dipole moment of these phosphorus-containing dendrimers versus molecular weight does not increase in a linear fashion, as was previously observed for organic dendrimers.[2] However, a plot of the dipole moments as a function of the square root of molecular weights is a straight line. This is in perfect agreement with previous calculations on statistical mean dipole moments of polymers.[8] Moreover, the dipole moment ratio D ($D = \mu^2/N(\mu_0)^2$ where μ is the dipole moment of the dendrimer, N is the number of monomer units, and μ_0

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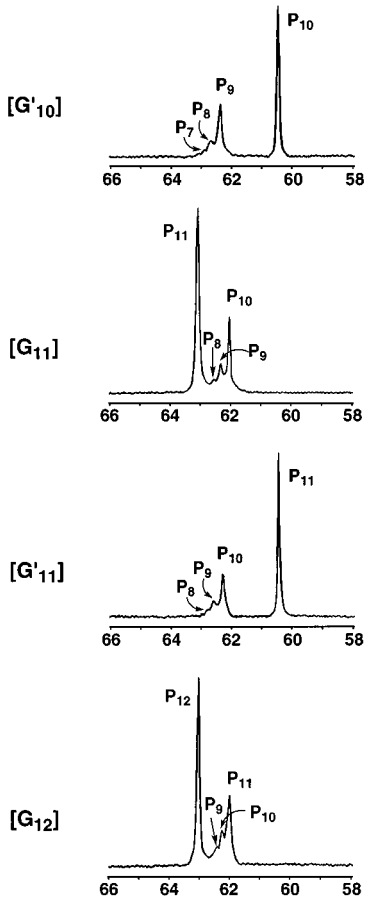

Figure 1. Variation of ^{31}P NMR chemical shifts for the dendrimers of highest generations: **[G′$_{10}$]**, **[G$_{11}$]**, and **[G′$_{11}$]** in $CDCl_3$ and **[G$_{12}$]** in THF-d_8.

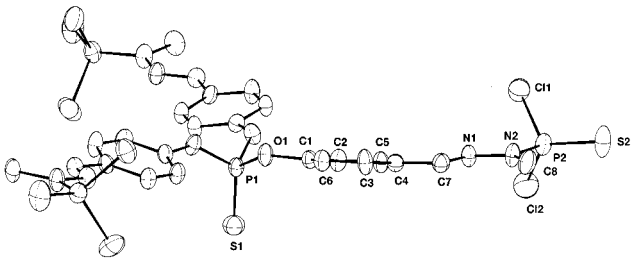

Figure 2. Molecular structure of **[G$_1$]**. Selected bond lengths (Å) and bond angles (deg): P(1)−O(1) 1.580(4); C(7)−N(1) 1.270(6); N(1)−N(2) 1.401(6); P(2)−N(2) 1.623(5); P(1)−O(1)−C(1) 130.7(3); N(1)−N(2)−P(2) 112.7(3); C(7)−N(1)−N(2) 119.3(4).

is the dipole moment of the monomer unit) versus molecular weight is a constant ($D = 2.3$) (Figure 4). This unusually large value indicates considerable local correlation between neighboring dipoles, as might be expected.

Remarkably too, the contribution of each polar unit, the P═S group, to the global dipole moment decreases exponentially from 2.1 (**[G$_1$]**) or 2.07 (**[G′$_1$]**) to 0.08 (**[G$_{10}$]**) or 0.05 (**[G$_{11}$]**) D. Therefore, a strong compensation (98.5% for **[G$_{11}$]**!) takes place. One can postulate that this strong compensation might be due to steric hindrance restricting the orientation of individual dipole vectors: consequently, the contribution of each polar unit is largely attenuated. Nevertheless, obtaining rather sharp resonances in solution spectra in ^{31}P NMR demonstrates that conformational flexibility, which determines the correlation times of the nuclei, is still high even at the **[G$_{10}$]**−**[G$_{12}$]** levels; otherwise, well-resolved signals would not be obtained. This can explain why the contribution of each polar unit although weak is not equal to zero and why that even at high generations a maximum of μ is not observed in spite of the globular shape of these dendrimers.

Investigations concerning other physical properties of these macromolecules are underway.

Table 1. Dipole Moment Values μ (D) for Dendrimers [G$_1$]−[G$_{10}$] and [G′$_0$]−[G′$_{11}$]

compd	μ	compd	μ
		[G′$_0$]	3.03
[G$_1$]	8.43	**[G′$_1$]**	8.27
[G$_2$]	14.24	**[G′$_2$]**	14.63
[G$_3$]	20.00	**[G′$_3$]**	20.26
[G$_4$]	30.36	**[G′$_4$]**	32.24
[G$_5$]	41.66	**[G′$_5$]**	41.27
[G$_6$]	61.84	**[G′$_6$]**	66.65
		[G′$_7$]	90.65
[G$_8$]	138.5	**[G′$_8$]**	132.3
[G$_9$]	169.8	**[G′$_9$]**	168.2
[G$_{10}$]	258.0		
		[G′$_{11}$]	328.0

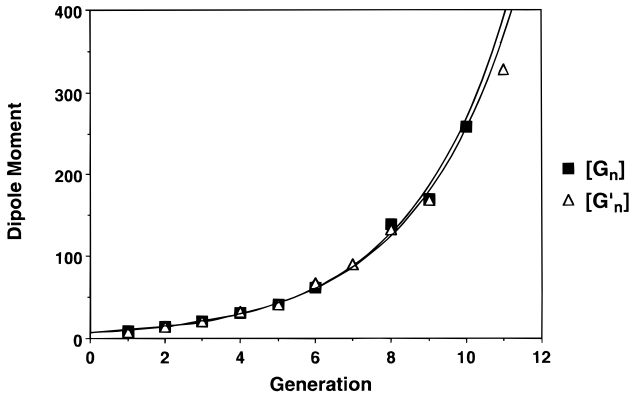

Figure 3. Plots of dipole moments vs generation for dendrimers **[G$_1$]**−**[G$_{10}$]** and **[G′$_1$]**−**[G′$_{11}$]**.

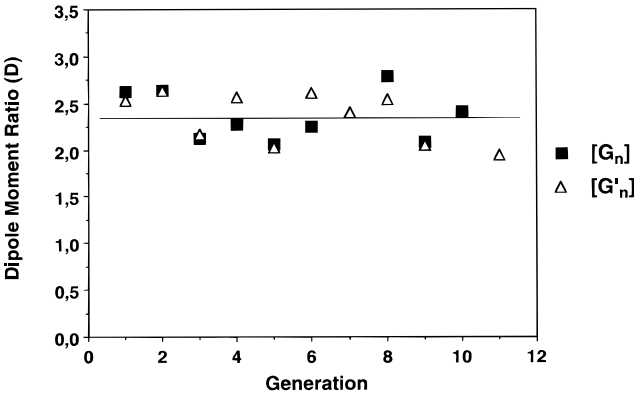

Figure 4. Dipole moment ratio vs generation $D = \mu^2/N(\mu_0)^2$ (N = number of momomer unit, $\mu_0 = 3.03$ for **[G′$_0$]**).

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Supporting Information Available: Selected spectroscopic data for compounds **[G′$_{10}$]**, **[G$_{11}$]**, **[G′$_{11}$]**, and **[G$_{12}$]**; full crystallographic data for **[G$_1$]** including an ORTEP diagram, crystal data, atomic coordinates, interatomic distances and angles, and thermal parameters; plots of the variation of dipole moments with molecular weight for dendrimers **[G$_1$]**−**[G$_{10}$]** and **[G′$_1$]**−**[G′$_{11}$]**; plots of dipole moment vs square root of molecular weight for dendrimers **[G$_n$]** (n = 1−10) and **[G′$_n$]** (n = 1−11); and plots of the contribution of each P═S group to the global dipole moment vs generation for the dendrimer

[G_1]−[G_{10}] and **[G'_1]−[G'_{11}]** (14 pages). Structure factors for **[G_1]** (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For a review on dendrimers, see, for example: Newkome, G. R.; Moorefield, C. N.; Vögtle, F. In *Dendritic Molecules*; VCH: Deerfield Beach, FL, 1996.

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(5) Crystallographic data for **G_1**: $C_{24}H_{24}O_3N_6PS$, $M = 909.33$, rhombohedric, space group $R3$, $a = b = 16.746$ (3) Å, $c = 11.910$ (2) Å, $V = 2892.7$ Å, $Z = 1$, $\rho_{calcd} = 1.57$ g·cm^{-3}, $\mu = 8.56$ cm^{-1}, crystal size (mn) 0.60 × 0.30 × 0.07 mm, 7718 measured reflections (1980 independent), $R_m = 0.043$, $R_m = 0.0326$, and $R_w = 0.0339$ from 1278 reflections used with a criterion [$I > 3\sigma(I)$]. The data collection was performed at room temperature ($T = 293$ K) on a IPDS STOE using graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods using SIR92[9] and subsequent difference Fourier maps. The refinement of the model was performed by using the full-matrix least-squares techniques with the aid of the package CRISTALS.[10] All hydrogen atoms were found on difference Fourier maps, but they were introduced in the process of refinement as fixed contributors with (C−H = 0.96 Å) and isotropic thermal parameters fixed 20% higher than those of the carbon atoms to which they were attached; their positions were recalculated after each cycle of refinement. All non-hydrogen atoms were anisotropically refined. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Rd, GB-Cambridge CB21EZ, U.K. on quoting the full journal citation.

(6) Dipole moments were measured in dioxane at 25 °C. The D formula was used as the Halverstadt and Kumler[11] extrapolation method for calculation of the total polarization with $\alpha = (d\epsilon/d\omega_2)_{\omega_2 \to 0}$, $\beta = (dv/d\omega_2)$, and $0.0001 < \omega_2 < 0.050$, where ϵ is the dielectric constant, ω_2 is the mass fraction of the sample, and v is the mass volume. Electronic polarization can be replaced by molecular refraction R_{MD}.

(7) The dipole moment of the starting "monomer" P(S)(OC_6H_4-CHO)$_3$ was found to be 3.03 D. This value is in agreement with those measured for thiophosphines and related compounds. See, for example: Fayet, J. P.; Mauret, P.; Labarre, M. C.; Labarre, J. F. *J. Chim. Phys.* **1968**, *65*, 722.

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