PHOSPHORUS-CONTAINING DENDRIMERS

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Abstract : Synthesis of dendrimers incorporating phosphorus groups at each generation are reported. The presence of these phosphorus fragments allows to develop a rich and versatile chemistry on the surface and within the cascade structure. Some applications are also described.

Dendrimers are three-dimensional, highly ordered polymers formed by reiterative reaction sequences starting from smaller molecules. There is a few phosphorus-containing dendrimers¹ and the first neutral species of this type possessing either P-N and P-O bonds², or P-C bonds³ were described in 1994.

SYNTHESIS

In a pioneering work we reported the synthesis of phosphorus-containing dendrimers, first up to the fourth generation² then up to generation 12, the highest generation described in dendrimer chemistry⁴ (scheme 1).

Another very efficient way of construction of dendrimers should be emphasized. It is outlined in scheme 2. Dendrimers **3-G₁-3-G₄** and **3-G'₁-3-G'₄** can be prepared in high yield. They possess a number of P=N-P=S groups, and the O-C₆H₄CH=N-N(CH₃)P=S fragment functions as the linker between each generation in all these new macromolecules (scheme 2).

REACTIVITY

Reactivity within the cascade structure of these new phosphorus-containing dendrimers will be presented⁵.

Scheme 1

Scheme 2

Up to 322 charges can be chemoselectively incorporated in the skeleton through the selective alkylation of the thiophosphoryl groups of the $\text{Ph}_2\text{P}=\text{N}-\text{P}=\text{S}$ units. The remaining macromolecules remain fairly soluble in different solvent⁶.

Regioselective gold complexation into the internal layers of dendritic and polydendritic macromolecules takes place not only on $\text{P}=\text{N}-\text{P}=\text{S}$ groups but also on $\text{P}=\text{N}-\text{P}=\text{N}-\text{P}=\text{S}$ fragments as well as on more classical CH_2PPh_2 moieties which can be incorporated within the cascade structure⁷.

The first example of the formation of multidendritic macromolecules can be proposed through the regioselective stepwise growth of six dendrimer units into the internal voids of a main dendrimer⁸ (fig.1).

Internal $\text{P}=\text{N}-\text{P}<$ groups can be easily generated through cleavage of the phosphorus sulfur bond of the internal $\text{Ph}_2\text{P}^+=\text{N}-\text{P}(\text{SR})<$ linkages. The resulting aminophosphite groups reacted with a variety of reagents, ie for example functionalized azides, allowing the formation of neutral dendrimers possessing functional groups such as amines, isothiocyanates... chemoselectively grafted within the cascade structure.

Aldehyde groups incorporated into the internal voids of dendrimers remain reactive. Indeed treatment of a dendrimer possessing 12 internal aldehyde groups with for example 4'-aminobenzo-15-crown-5 (12 equiv.) leads to the corresponding dendrimer bearing 12 crown ether units within the cascade structure (fig.2).

Applications of some of these dendrimers in different fields will be underlined.

REFERENCES

- 1 For a review see : J.P. Majoral, A.M. Caminade, Chem. Rev., **99**, 845 (1999).
- 2 N. Launay, A.M. Caminade, R. Lahana, J.P. Majoral, Angew. Chem. Int. Ed. Engl., **33**, 1589 (1994).
- 3 A. Miedaner, C.J. Curtis, R.M. Barkley, D.L. Dubois, Inorg. Chem., **33**, 5482 (1994).
- 4 M.L. Lartigue, B. Donnadieu, C. Galliot, A.M. Caminade, J.P. Majoral, J.P. Fayet, Macromolecules, **30**, 7335 (1997).
- 5 C. Larré, B. Donnadieu, A.M. Caminade, J.P. Majoral, J. Am. Chem. Soc., **120**, 4029 (1998).
- 6 C. Larré, A.M. Caminade, J.P. Majoral, Angew. Chem. Int. Ed. Engl., **36**, 596 (1997).
- 7 C. Larré, B. Donnadieu, A.M. Caminade, J.P. Majoral, Chem. Eur. J., **4**, 2031 (1998).
- 8 C. Galliot, C. Larré, A.M. Caminade, J.P. Majoral, Science, **277**, 1981 (1997).

Figure 1

Figure 2