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Linear, Hyperbranched, and Dendrimer-Like Polymers Containing Phosphorus: Synthesis and Properties

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SUMMARY: A strategy allowing the synthesis of linear, hyperbranched and dendritic polymers containing phosphorus is reported. A comparative study of the physical properties of these new polymers is presented.

Introduction

Phosphorus-containing dendrimers have attracted more and more attention this last decade for various reasons [1)]. First, the synthesis of these macromolecules can be controlled not only using the classical methods of characterization of organic polymers but also by ^{31}P NMR which appeared to be a quite efficient tool to monitor the reiteration of the sequence of reactions allowing the construction of each generation [1a)]. Second, the possibility to perform selective reactions directly on phosphorus or on internal phosphorus-nitrogen-phosphorus-sulfur linkages offers the opportunity to modify the skeleton of dendrimers exactly where and when desired within the cascade structure [2)]. Indeed a large number of functional groups can be incorporated either on the surface but also within the internal branches. Third, functionalization of the core, i.e. preparation of dendrons, allows the preparation of new "polydendritic" systems such as for example surface-block dendrimers, layer-block dendrimers, layered surface-block dendrimers, via core-core or core-surface coupling reactions between dendrons or between dendrons and dendrimers [3)] (Scheme 1).

Fourth, as it is recently illustrated, the presence of phosphino or diphosphino groups on the surface of dendrimers allows the synthesis of a number of metallodendrimers incorporating Pd, Pt, Au, Rh, Ru, etc which appear to be excellent catalysts for a number of reactions in organic chemistry [1u,4)]. Last but not least, the use of phosphorus-containing dendrimers as efficient DNA transfecting agents [1g)] or for the preparation and the stabilization of $(Au_{55})_\infty$ microcrystals [1s)] was also reported.

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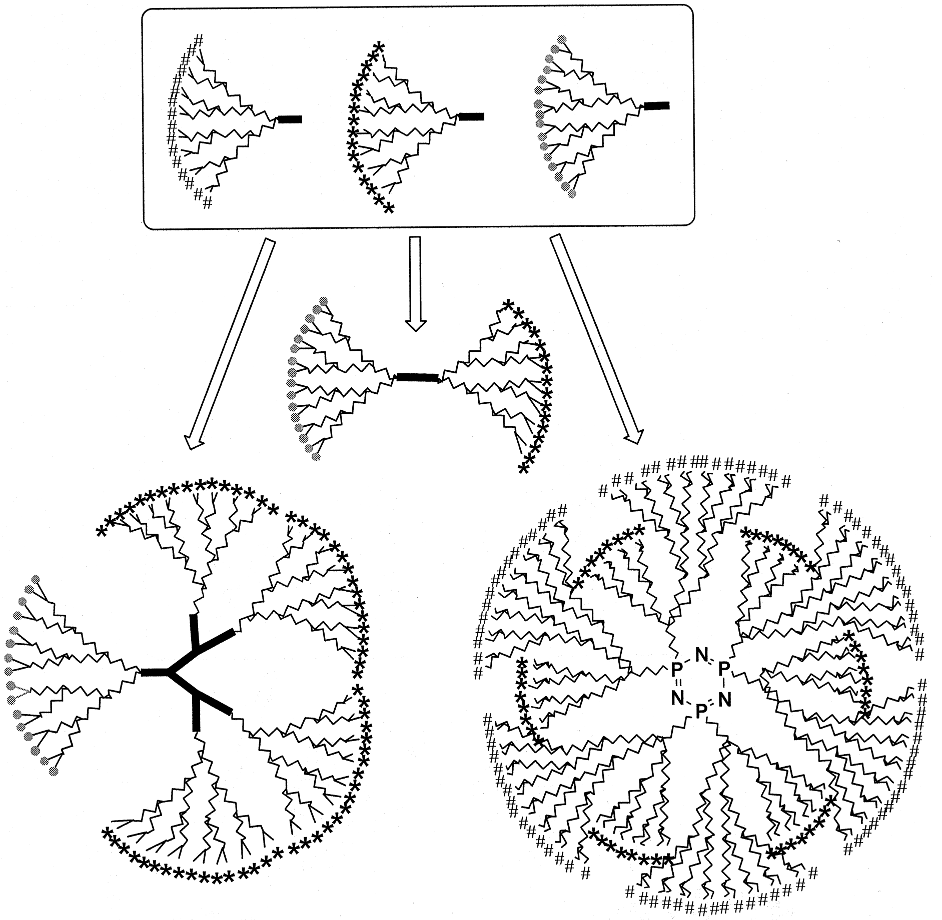


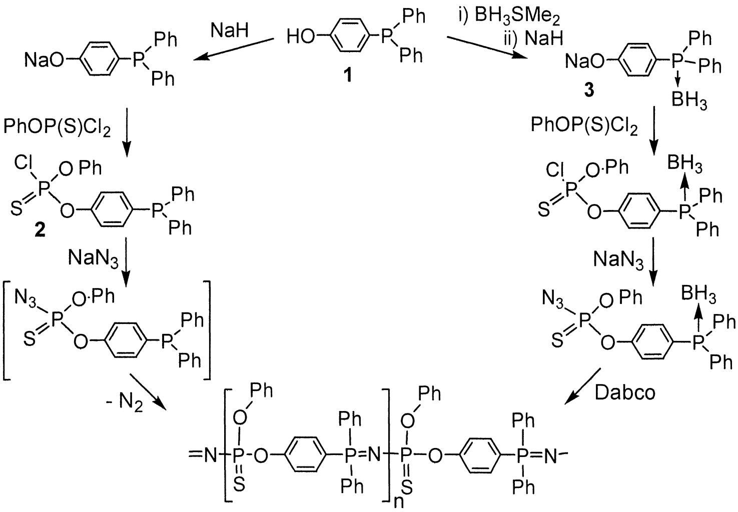
Scheme 1: New polydendritic polymers prepared via coupling reactions between dendrons or between dendrons and dendrimers.

Therefore, phosphorus-containing dendrimers appear as promising polymers for a number of applications, due to their versatile reactivity, their thermal stability or their solubility in different solvents including water.

On the other hand, phosphorus linear polymers, i.e. mainly polyphosphazenes (linear polymers that possess a backbone of alternating phosphorus and nitrogen atoms linked through P=N type units) present properties seldom found in organic polymers(5). Surprisingly, no hyperbanched phosphorus polymers are reported. Having that in mind, we focused our efforts to the preparation of these macromolecules in order to compare their properties with that of linear polymers or dendrimers. The presence of a same repeating unit within the structure of these different macromolecules should permit a better comparison of their respective properties. Consequently, we prepared new series of linear, hyperbranched and dendritic polymers elaborated from the same phosphorus reagent $HOC_6H_4P(Ph)_2$ **1** and entirely formed of $OC_6H_4P(Ph)_2=N-P(S)$ units.

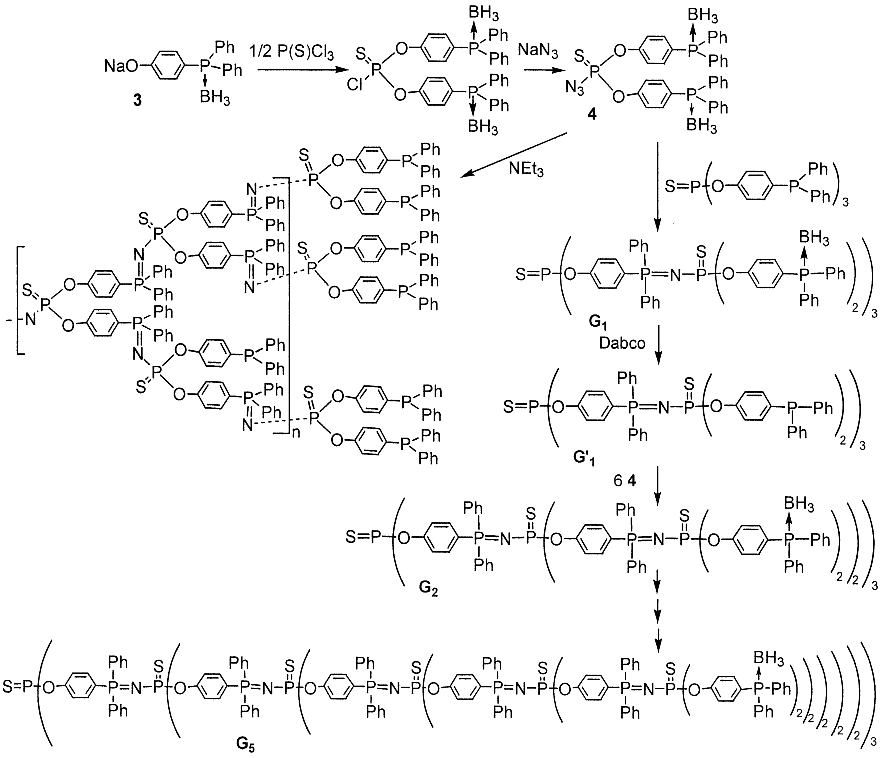
Results and discussion

The key reagent for all these syntheses is the sodium salt of the 4-hydroxyphenyldiphenylphosphine **1** which was reacted with phenoxythiodichlorophosphine to give the precursor **2**; substitution reaction with sodium azide of the P-Cl bond, and Staudinger reaction between the free phosphine and the resulting azide allow to prepare the linear polymers. Another way consists to react the phosphine borane adduct **3** with phenoxythiodichlorophosphine, then the corresponding complex is deprotected allowing the Staudinger reaction to take place with formation of linear polymers (Scheme 2).



Scheme 2: Synthesis of linear phosphorus containing polymers.

It was also possible to prepare the corresponding hyperbranched and dendritic polymers from the phosphine borane adduct of the sodium salt of **1**, i.e. **3**, using as halogenated thiophosphine $(S)PCl_3$ (Scheme 3).



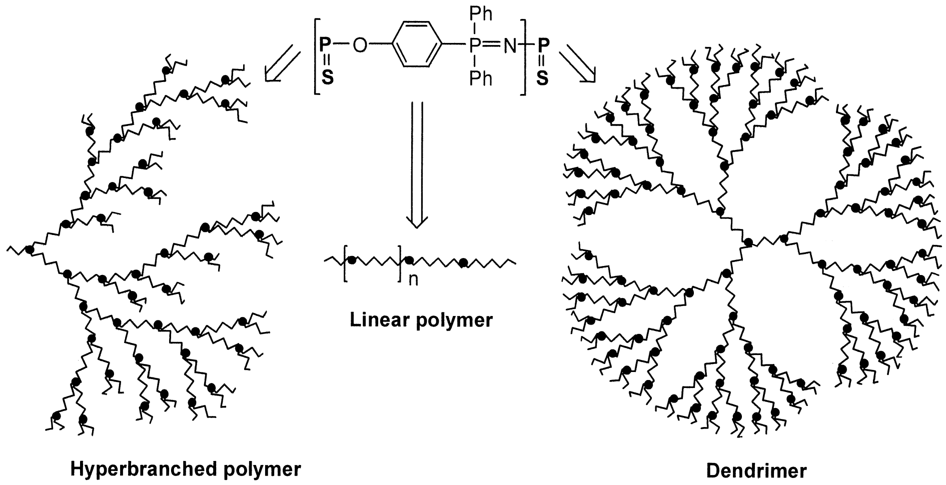
Scheme 3: Synthesis of hyperbranched polymers and dendrimers from the same building block.

In all case, the key step was a Staudinger reaction between a phosphorus azide and a free phosphine. Such a reaction allows the quantitative formation of an iminophosphorane linkage P=N-P(S) characterized in ^{31}P NMR by two doublets at 13.5 - 14.5 (P=N) and 49.0 - 50.5 (P=S) ppm with $^{2}J_{PP} \approx 30$ Hz. Remarkably, this reaction proceeds in very mild conditions with evolvement of nitrogen as the only formed by-product.

Solution behavior (molar masses and molar masses distribution, intrinsic viscosity) and thermal behavior of all the new polymers were studied, allowing us to point out similarities between purely organic hyperbranched and dendritic polymers and their corresponding phosphorus analogs. The characterization of these phosphorus-based macromolecules in solution revealed marked differences in their respective behavior. For example, a bell-shaped curve can be established for the [η] behavior of the dendrimers, whereas the [η] of hyperbranched polymers was found to vary moderately with the molar mass. Indeed they were shown to depend on the nature of the terminal functions, as the Tg's of these branched architectures. Unexpected high value of degree of branching (DB > 0.8) was observed for hyperbranched phosphorus polymers.

Conclusion

A Staudinger reaction between phosphines and phosphorus azides has been found to be the key step in all reactions leading to the formation of linear, hyperbranched and dendritic polymers (Scheme 4). Such a reaction is quantitative with removal of dinitrogen. These phosphorus-containing polymers present analogous properties to that observed for purely organic dendrimers.



Scheme 4: Three types of polymers having the same repeating units

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