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Water-soluble phosphorus-containing dendrimers

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Abstract

In most cases, the water solubility of phosphorus-containing dendrimers is mainly due to the presence of hydrophilic end groups, which bear either positive or negative charges. In the first part of this paper, several methods of synthesis and functionalization of phosphorus dendrimers are described leading to the grafting either of ammonium groups or carboxylate groups, which ensure the water-solubility. The structural conflict between the hydrophobic interior and the hydrophilic exterior of these dendrimers leads to special properties, which are emphasized in a second part. For instance, some of them behave like nanometric sponges toward lipophilic substances; whereas, others form supramolecular arrangements leading to vesicles or hydrogels. Some of these dendrimers also possess interesting biological properties and can be used as in vitro DNA transfecting agents or in vivo anti-prion agents.
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Keywords: Phosphorus; Dendrimers; Water-solubility; Hydrogels; Transfection; Anti-prion

Contents

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1. Introduction

Amongst all the special properties of dendrimers [1,2], their high solubility constitutes a major difference when compared to linear polymers. This special behavior has been noted for several types of dendrimers for which the corresponding linear analogs are available, in particular for polyphenylene [3], polyarylether [4], and polyamide dendrimers [5]; differences in solubility between branched and linear compounds can be of several orders of magnitude, up to 10^6 times in some cases. Even very high generations of dendrimers (generation 10 [6] or 12 [7]) remain soluble despite a molecular weight close to one or several millions. The type of solvent that is able to dissolve a dendrimer is highly dependant on the type of end group of the dendrimer, even if though the structure may play a role in some cases. Amongst all the solvents used for dissolving dendrimers, one is especially important, particularly when envisaging biological applications, that is water. Most of the work dealing with water-soluble dendrimers has been carried out with PAMAM (polyamidoamine) dendrimers [8] and their derivatives, and to a lesser extent with PPI (polypropyleneimine) dendrimers [9–11] and their derivatives. However, and especially in recent years, the importance of water-soluble phosphorus-containing dendrimers begins to increase. In most cases, the water solubility of these compounds depends mainly on the type of end groups they carry, but with some exceptions. This paper will first describe how to synthesize water-soluble phosphorus dendrimers followed by special properties and unique applications that have already been reported for this very special class of dendrimers.

2. Syntheses

It is noteworthy, that the solubility of the first water-soluble phosphorus-containing dendrimers ever reported (1-Gn), was mainly due to their internal structure in which each branching point is a phosphonium site [12]. The synthesis was carried out up to the third generation, but only the first and second generations are soluble in water (Fig. 1). The solubility of the nucleic acid derived dendrimers 2-Gn based on tymidine bridged by a phosphoramidite reagent and synthesized in the solid phase either by a convergent [13] (Fig. 2) or a divergent [14] process is also due mainly to their internal structure. However, these first examples are actually exceptions; in that the water solubility of most phosphorus-containing dendrimers is only due to the hydrophilicity of their end

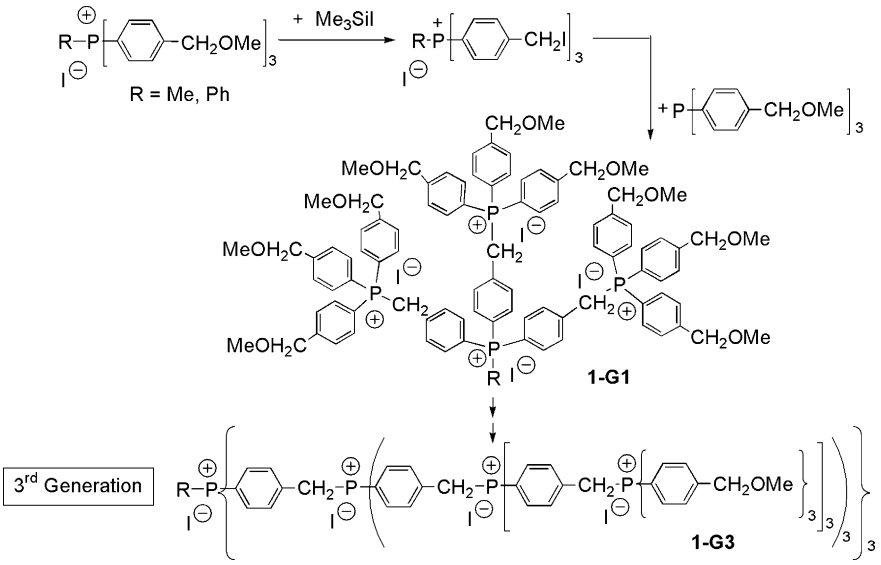

Fig. 1. Synthesis of the first water-soluble phosphorus-containing dendrimers (1-G1 and 1-G2).

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