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Recent trends in the synthesis of polyelectrolytes

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ABSTRACT

Recent developments in the synthesis of polyelectrolytes are highlighted, with respect to the nature of the ionic groups, the polymer backbones, synthetic methods, and additional functionality given to the polyelectrolytes. In fact, the synthesis of new polyelectrolytes is mostly driven by material aspects, currently. The article pays particular attention to strong polyelectrolytes, and the new methods of controlled polymerization. These methods and the so-called click reactions have enabled novel designs of polyelectrolytes. Nevertheless, the polymerization of unprotected ionic monomers is still challenging and limits the synthetic possibilities. The structural aspects are complemented by considerations with respect to the aspired uses of the new polyelectrolytes.

1. Introduction

The key feature of polyelectrolytes is the large number of electrically charged motifs chemically bound to the macromolecule, such that the charged groups dominate their physico-chemical behavior, in bulk as well as in solution. Albeit polyelectrolytes have been known for long and their chemistry—different from their theoretical understanding—might seem a mature field, new structures are still evolving continuously. At present, the motivation for creating new polyelectrolytes is mostly the desire to confer typical properties of polyelectrolytes to functional polymers, such as strong long-range interactions, ionic conductivity or hydrophilicity. The progress made in the past few years has thus been notable, even if the incremental innovation has been mostly gradual. Structural novelty can be encountered with respect to the nature of the ionic moieties bound to the polymer, to the nature of the polymer skeleton, or to the overall polymer architecture. The latter aspect is intimately interwoven with the upcoming of new synthetic methods for making charged polymers. Here the increasingly maturing techniques of the so-called controlled polymerization (CP), in particular of the controlled free radical polymerization (CFRP) methods, have provided a major thrust for creating new polyelectrolytes currently.

Let us recall that many difficulties in the synthesis of polyelectrolytes originate in the sensitivity, or even incompatibility, of most chemical reactions toward the simultaneous presence of electrophiles and nucleophiles. This however is the typical situation encountered not only for most monomers bearing ionic groups, but also for most solvents that are suited for polyelectrolytes, namely water, alcohols and other polar protic solvents. In order to minimize the arising problems, one may introduce the ionic moieties in a final post-polymerization modification step only, after the successful polymerization process. Obviously, this is often rather a makeshift, and direct pathways to polyelectrolytes are more desirable. Hence, there is, independent of the design of new polyelectrolyte structures, also a continuous effort in improving methods in order to obtain polyelectrolytes directly in the ionic form at the end of the polymerization step, even though the targeted polyelectrolyte structures have been already known, but have been prepared via a post-polymerization strategy.

2. New polyelectrolyte structures

2.1. New ionic moieties

2.1.1. Polycations

The majority of the hitherto reported cationic groups are based on amines or quaternary ammonium ions, because of their basicity (in the case of amines), relative stability, versatility and ease of access [1]. The variation of the substituents on the nitrogen is nearly unlimited. A structurally interesting facet of such variations is the use of multiply charged monomers to increase the local density of ionic groups in the resulting polymers (Fig. 1) [2–6], for example for boosting biocidal properties [2], or for boosting the threading of hollow host molecules in the synthesis of polyrotaxanes [5]. Beyond the focus on ammonium based polyelectrolytes, various attempts have been pursued to enlarge the scope of heteroions in the cationic moieties. Polymeric

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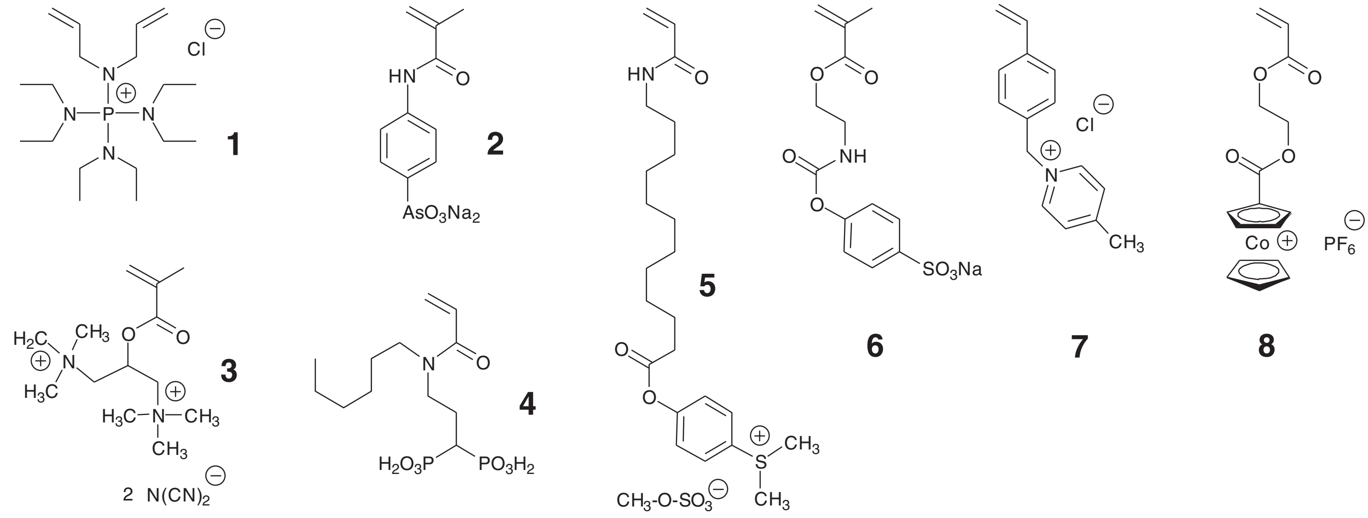

Fig. 1. Examples for new ionic monomers suited for free radical polymerization, characterized by unconventional ionic groups (**1**,**2**) [14,39], multiple ionic sites and ionic liquid character (**3**,**4**) [6,32], chemical reactive ionic moieties (**5**–**7**) [11,43,45], or metal-organic redoxactive moieties (**8**) [16].

phosphonium salts [4,7–10] are the most frequently studied alternatives, by virtue of their good chemical and thermal stability. Still, other examples, such as sulfonium (cf. Fig. 1, monomer 5) [11,12] and boronium [13] moieties have attracted some interest in addition, despite of their chemical sensitivity against nucleophiles, water included. A curiosity is the recent report on aminophosphonium polymers (Fig. 1, monomer 1) [14], the monomers of which behaving as ionic liquids (see below). A particular intriguing approach is the efforts to replace ionic groups based on a non-metallic hetero atom by charged metal-organic moieties. Cobaltocenes for instance were shown to be sufficiently stable to support polymerization processes, e.g. anionic as well as free radical polymerization (Figs. 1 and 2, compounds 8 and 9) [15••, 16]. Remarkably, these polymers are water-soluble, even when paired with the hydrophobic counterion hexafluorophosphate. Also, the charge density and thus the hydrophilicity of these polycations can be switched by electrochemical reduction/oxidation of the cobalt ion. In another remarkable development, difunctional monomers acting as potent chelating ligands allowed the stable incorporation of divers transition metal ions into the polymer backbones via a step growth polymerization (see Fig. 2, polymer 10). This led to a new class of high molar mass charged polymers, for which the name metallo-supramolecular polyelectrolytes (MEPEs) was coined [17••,18]. The opportunities for modular design of such MEPES are extremely versatile, comprise diverse metal ions, and allow for the tuning of e. g., their characteristic electrochromic behavior.

Polycations containing the imidazolium moiety have found strongly increasing interest over the past 10 years or so [1], due to the structural similarity of their constitutional repeat units to the most widely studied class of ionic liquids (ILs). The derived polymers are often referred to as poly(ionic liquid)s [19]. A number of poly(ionic liquid)s show highly interesting application profiles, e.g. as solid state electrolytes combining high ionic conductivities with good mechanical properties [6,20••,21•] as super absorbents for organic solvents or CO_2 [9,22], or for nanoporous organic and mesoporous carbon materials [4,20••,23•]. Thus, recent years have seen a plethora of classical low molar mass, and later on also of polymeric cationic structures, in which aliphatic ammonium groups or pyridinium groups were substituted by imidazolium residues and which were neutralized by rather hydrophobic counterions [19]. Concerning the synthetic procedures, the preparation of polymeric ILs has followed generally the established pathways and methods for preparing polycations, replacing only ammonium or pyridinium by imidazolium residues. Alternatively and even less painstaking, poly(ionic liquid)s have been prepared by exchanging the conventional negatively charged counterions in polycations against more “exotic” ones, e.g., hexafluorophosphate, dicyanamide, or bis(trifluoromethylsulfonimide) (cf. Fig. 1, monomer 3) [6]. Hence, though the number of chemical structures has been multiplied, and physical properties were varied, the majority of work on poly(ionic liquid)s has brought little innovation from the synthetic point of view. Also, it should be realized that polymerizable ILs, and thus the derived poly(ionic liquid)s, are not so new as often assumed. The elder literature is full of reports on cationic monomers, that do not solidify at room temperature, and of their polymerization. However, as the term ionic liquid has been

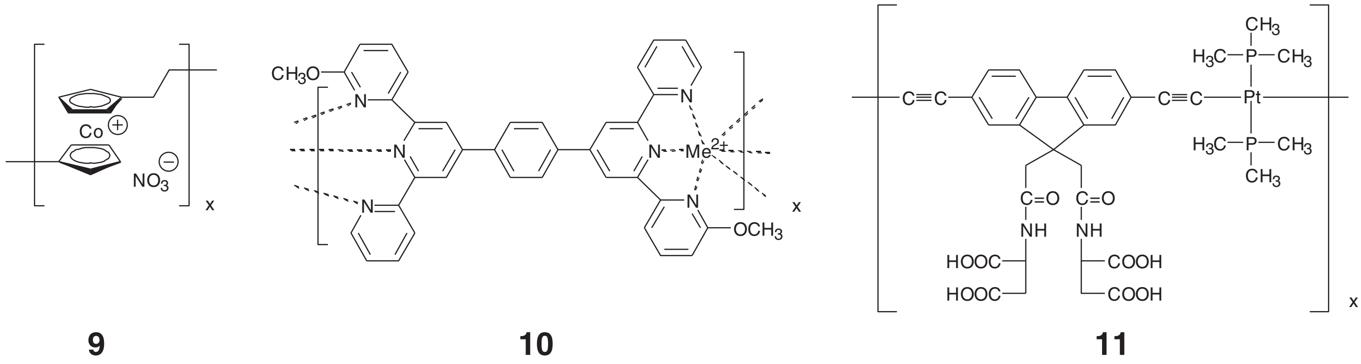

Fig. 2. Examples for metal-organic polyelectrolytes with the metal ions integrated into the polymer backbone based on cobaltocene (**9**) [15], MEPEs (**10**) with Me^{2+} = Fe(II), Co(II) and Ru(II) [17], and conjugated polyelectrolyte (**11**) [62].