



A comprehensive review on polyelectrolyte complexes

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Global research on polyelectrolytes at a fundamental and applied level is intensifying because the advantages of sustainability are being accepted in academia and industrial research settings. During recent decades, polyelectrolytes became one of the most attractive subjects of scientific research owing to their great potential in the areas of advanced technologies. Polyelectrolytes are a type of polymer that have multitudinous ionizable functional groups. Ionized polyelectrolytes in solution can form a complex with oppositely charged polyelectrolytes — a polyelectrolyte complex (PEC). The present article provides a comprehensive review on PECs and their classification, theory and characterization, as well as a critical analysis of the current research.

Introduction

Polyelectrolytes (PEs) have remained one of the most attractive subjects of scientific research in recent decades owing to their great importance in advanced technologies and molecular biology. A PE is defined as any macromolecular material that has repeating units and dissociates into a highly charged polymeric molecule upon being placed in any ionizing solvent (e.g., H₂O) forming either a positively or negatively charged polymeric chain [1]. The charge on the repeating units of the PE is neutralized by oppositely charged smaller counter ions that tend to preserve the electro neutrality. If any PE solution contains a positively charged electrolyte it can be accompanied by small negatively charged ions. In a similar way, negatively charged materials can be accompanied by small positively charged ions [2].

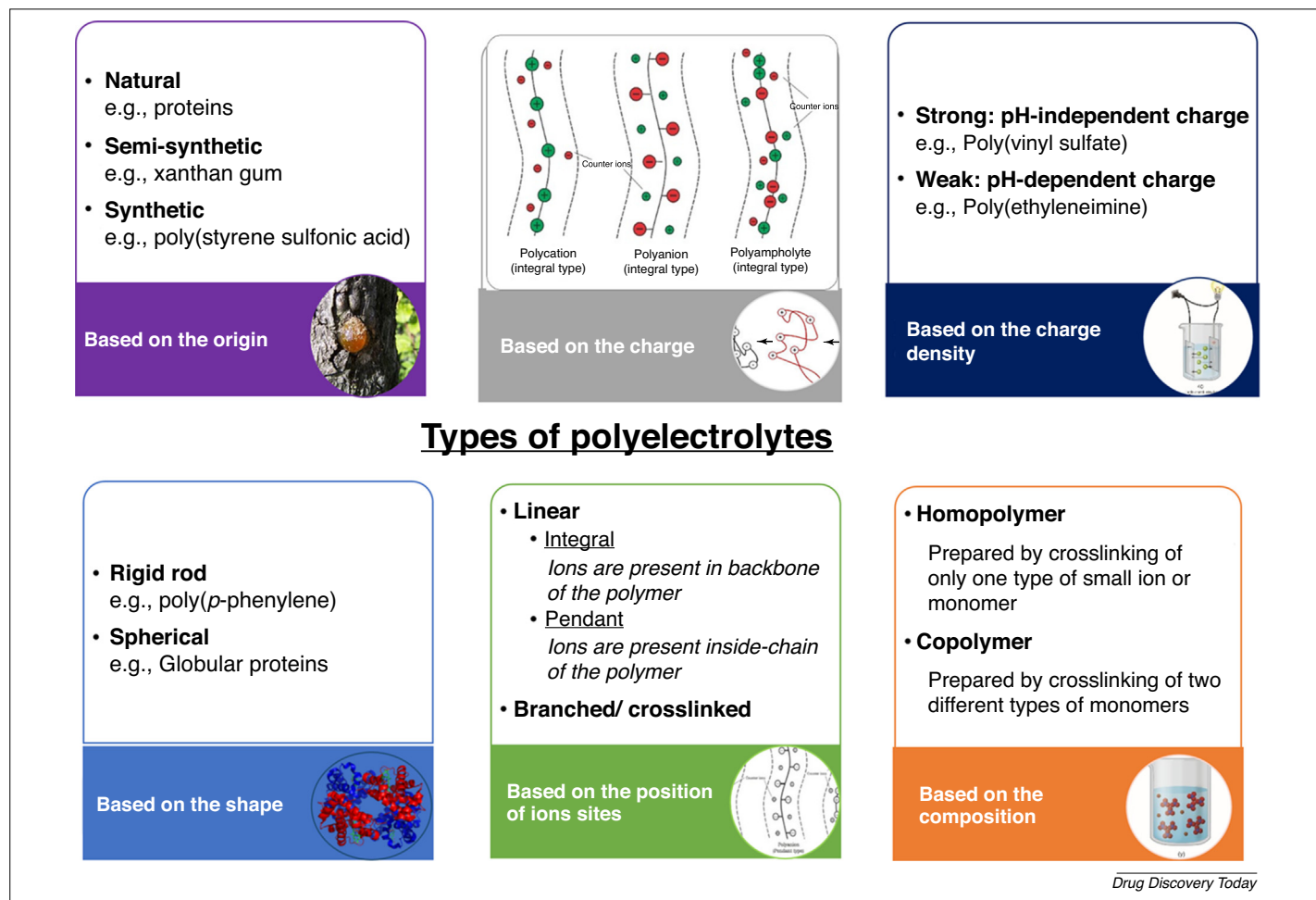
PEs in an uncharged state behave like normal macromolecules, however there might be some intense changes in their properties if there is a small dissociation of the ionic groups. Because of partial

or complete dissociation of ionic groups, electrostatic interactions can arise and could lead to deviations of polymer behavior. Properties of PEs such as viscosity, solubility, pH, ionization constant, ionic strength, diffusion coefficient, among others, can be altered if any new ionic groups introduced [3]. Ionic strength of the solution majorly influences the PE behavior. At lower ionic strength in solution PEs incline toward an extended form because of repulsion forces within the molecule. If ionic strength of the solution increases PEs will tend to become thicker. Because of this special nature, PEs have significant importance in various pharmaceutical and biomedical applications, because there can be different degrees of sizes, stability, viscosity or morphology for polyelectrolyte complex (PEC) dispersions [4].

Classification of PEs

PEs are a type of polymer bearing dissociated ionic groups and are a fascinating class of macromolecule, for a comprehensive review see [5]. These molecules exhibit interesting phenomena owing to their dual character of macromolecular chain plus high charge. The classification of the PEs is shown in Fig. 1 and some PEs are exemplified in Table 1 based on their nature.

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Types of polyelectrolytes

FIGURE 1

Classification of polyelectrolytes based on the charge and position of ionic sites in the polymer chain. Polycations ionize in solution and can form positive sites along the polymer molecule; polyanions ionize in solution and form negative sites along the polymer molecule; polyampholyte ionize in solution and form positive and negative charges.

TABLE 1

Some of the polyelectrolytes (PEs) and their ionic nature

PE type	Polyanion	Polycation
Natural	Nucleic acids, poly(L-glutamic acid), carrageenan, sodium alginate, hyaluronic acid, chondroitin sulfate, gellan gum, gum kondagogu, gum karaya, <i>Cieba pentandra</i> gum, <i>Termianlia catappa</i> gum, polygalacturonic acid	Poly(L-lysine), lysozyme, gelatin, chitosan, dextran, starch
Chemically modified/semi-synthetic	<i>N</i> -carboxymethyl chitosan, cellulose-based (sodium carboxymethyl cellulose), carboxymethyl konjac glucomannan, pectin, sodium dextran sulfate, xanthan gum	Chitosan (deacetylation of chitin), <i>N</i> -trimethyl chitosan, chitosan-g-poly(ethylene glycol) monomethyl ether
Synthetic	Poly(acrylic acid)/carbopol, poly(methacrylic acid), Eudragit [®] (Eudragit [®] L 100, Eudragit [®] S 100, Eudragit [®] FS 30 D), poly(acrylamide-2-methyl-propane sulfonate), poly(3-sulfopropyl methacrylate), dextran sulfate, poly(sodium styrene sulfonate), poly(vinyl sulfate), poly(acrylic acid-co-maleic acid), poly(<i>p</i> -styrenesulfonic acid), poly(<i>p</i> -styrenecarboxylic acid), poly(metaphosphoric acid), poly(4-methacryloyl oxyethyl trimellitate), poly(itaconic acid), poly(vinyloxy-4-butyric acid), poly(sodium 4-vinylbenzoate), poly(sodium acrylate)	Poly(ethyleneimine), poly(allylamine hydrochloride), Eudragit [®] E polymer (Eudragit [®] E PO, Eudragit [®] E 100), poly(<i>N,N,N</i> -trimethyl-2-methacryloyl ethyl ammonium) bromide, poly(diallyldimethyl ammonium chloride), poly(4-vinyl- <i>N</i> -methylpyridinium iodide), poly(acrylamide-co-dimethyldiallylammonium chloride), poly(vinylbenzyl trialkyl ammonium), poly(acryloyl-oxyalkyl-trialkyl ammonium), poly(acrylamidoalkyl-trialkyl ammonium), poly(2-vinylpyridine), poly(aminoethyl methacrylate), poly(2-ethyloxazoline), poly[4-(<i>N,N</i> -dimethylamino methylstyrene)], poly(β -amino ester), poly(sulfone-amine) hydrochlorate, poly(methacryloxyethyl trimethylammonium chloride)

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