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TERMINOLOGY OF POLYMERS CONTAINING IONIZABLE OR IONIC GROUPS AND OF POLYMERS CONTAINING IONS

(IUPAC Recommendations 2004)

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TERMINOLOGY OF POLYMERS CONTAINING IONIZABLE OR IONIC GROUPS AND OF POLYMERS CONTAINING IONS

INTRODUCTION

The document defines the most commonly used terms relating to polymers containing ionizable or ionic groups and to polymers containing ions. Inorganic materials such as phosphates, silicates, etc., that also may be considered ionic polymers are excluded from the present document. Only those terms that could be defined without ambiguity are considered.

Terms subsidiary to the main terms, are printed in bold type in notes to the main terms.

1. ionic polymer
ion-containing polymer

Polymer composed of macromolecules containing ionic groups irrespective of their nature, content, and location.

Note:
Polymers composed of macromolecules containing groups that are not ionic but may undergo self-ionization under suitable conditions are customarily included in this class.

2. ionomer

Polymer composed of macromolecules in which a small but significant proportion of the constitutional units has ionic or ionizable groups or both.

Notes:
1. See Definition 1.66 in [2].
2. Ionic groups are present in sufficient amounts to cause the micro-phase separation of ionic domains from the continuous polymer phase. The ionic domains can act as physical crosslinks. Typically, “sufficient” means less than 10 % of constitutional units containing ionic or ionizable groups.

3. ionene

Polymer composed of macromolecules in which ionized groups are parts of main chains.

Note:
Most commonly, the ionized groups in ionenes are quaternary ammonium groups.

4. ionic aggregates in an ionomer

Domains enriched with ionic groups within an ionomer matrix.

5. critical ion-concentration in an ionomer

Concentration of ionic groups in an ionomer matrix, above which ionic aggregation occurs.

6. ionomer multiplet

Ionic aggregate, in a polymer matrix of low polarity, formed through the association of ion-pairs.

7. ionomer cluster

Ionic aggregate, in a polymer matrix of low polarity, formed through interactions of ionomer multiplets.

Notes:
1. The mobility of the polymer segments surrounding the multiplets is reduced relative to that of bulk material. With increasing ion content the number density of the multiplets increases leading to overlapping of the restricted mobility regions around the multiplets; those regions are referred to as clusters.
2. Typically an ionomer exhibits two glass transition temperatures (T_g), one for nonpolar matrix and the other for clusters.

8. polyelectrolyte

Polymer composed of macromolecules in which a substantial portion of the constitutional units contain ionic or ionizable groups, or both.

Notes:
1. See Definition 1.65 in [2]
2. A different definition, based on the properties of polyelectrolyte, is given in [1].
3. The terms **polymeric electrolyte** and **polymer electrolyte** are sometimes used for polyelectrolyte. They should not be confused with the term **solid polymer electrolyte** (see Definition 20).
4. Polyelectrolytes can be either synthetic or natural. Nucleic acids, proteins, teichoic acids, some polypeptides, and some polysaccharides are examples of natural polyelectrolytes.

9. polyelectrolyte network

Polymer network containing ionic or ionizable groups in a significant fraction of its constitutional units.

Notes:
1. A polyelectrolyte network is sometimes called a crosslinked polyelectrolyte. Use of the latter term is not recommended unless the polyelectrolyte network is formed by the crosslinking of existing polyelectrolyte macromolecules rather than by nonlinear polymerization (see Definition 1.59 in [2]).
2. In contrast to a polyelectrolyte (see Definition 8), a polyelectrolyte network is insoluble.
3. A polyelectrolyte network in contact with a solution of a salt is able to exchange counterions (cations or anions) with ionic components of the solution and act as an ion exchanger. Therefore, the term **ion-exchange polymer** (see Definition 10) is frequently used.

10. ion-exchange polymer

Polymer that has ionic groups, anionic or cationic, and is able to exchange counterions, cations or anions, with the ionic components of a solution.

Notes:
1. See definition 2.2 in [3]
2. Most commonly, ion-exchange polymers are polyelectrolyte networks (see Definition 9). They are often called **ion-exchange resins**; use of the term "resin" is discouraged (see Definition 2.13 in [3]).
3. Depending on the structure of their acid groups, cation-exchange polymers may be classified as strongly acidic (*e.g.*, containing sulfonic acid groups) or weakly acidic (*e.g.*, containing carboxylic acid groups).
4. Depending on the structure of their basic groups, anion-exchange polymers may be classified as strongly basic (*e.g.*, containing quaternary ammonium base groups) or weakly basic (*e.g.*, containing amino groups).

11. **polyampholyte**
amphoteric polymer
ampholytic polymer

Polyelectrolyte (see Definition 8) composed of macromolecules containing both cationic and anionic groups, or corresponding ionizable groups in the same macromolecule.

Notes:
1. See Definition 3.16 in [3].
2. A polyampholyte in which ionic groups of opposite sign are incorporated into one pendant group (betaine type structure) is called a **polymeric inner salt**, **zwitterionic polymer** or **polybetaine.**

12. polyelectrolyte complex

Polymer-polymer complex composed of macromolecules carrying charges of opposite sign causing the macromolecules to be bound together by electrostatic interactions.

Note:
Polyelectrolyte complex is also called polysalt. Use of this term is not recommended.

13. polyacid

Polyelectrolyte composed of macromolecules containing acidic groups on a significant fraction of the constitutional units.

Notes:
1. See Definition 3.16 in [3].
2. Most commonly, the acidic groups are –COOH, $-SO_3H$ or $–PO_3H_2$.

14. **polybase**

Polyelectrolyte composed of macromolecules containing basic groups on a significant fraction of the constitutional units.

Notes:
1. See Defition 3.16 in [3].
2. Most commonly, the basic groups are amino groups.

15. cationic polymer
polycation

Polymer composed of positively charged macromolecules.

Notes:
1. If a substantial fraction of constitutional units carries positive charges then a polycation is a polyelectrolyte.
2. The positive charges may be fixed on groups located in main chains as in an ionene (*cf.* Definition 3) or in pendant groups.
3. Each macromolecule of a cationic polymer is accompanied by its equivalent amount of counteranions.
4. The term cationic polymer should not be used to denote a polymer prepared by cationic polymerization.

16. anionic polymer
polyanion

Polymer composed of negatively charged macromolecules.

Notes:
1. If a substantial fraction of constitutional units carries negative charges then a polyanion is a polyelectrolyte.
2. Each macromolecule of an anionic polymer is accompanied by its equivalent amount of countercations.

3. The term anionic polymer should not be used to denote a polymer prepared by anionic polymerization.

17. halato-telechelic polymer

Polymer composed of linear macromolecules having ionic or ionizable end-groups.

Notes:
1. This term is used to denote a polymer composed of macromolecules having stable (long-lived) ionic or ionizable groups, such as carboxylate or quaternary ammonium groups, as chain ends. It should not be used to describe a polymer composed of macromolecules having chain ends that are transient intermediates in ionic polymerizations initiated by a difunctional initiators.
2. The term **halatopolymer** is used for linear polymers formed by the coupling of a halato-telechelic polymer having, *e.g.*, carboxylate groups with divalent metal cations [4].

18. electrically conducting polymer

Polymeric material that exhibits bulk electric conductivity.

Notes:
1. See Definition 3.2 in [3]
2. An important class of electrically conducting polymers are **intrinsically conducting polymers**. Such polymers are composed of macromolecules having fully conjugated sequences of double bonds along the chains. Upon acquiring positive or negative charges by oxidation or reduction with suitable electron acceptors or electron donors (charge-transfer agents), they show bulk electrical conductivity comparable to that of some metals.
3. Examples of conjugated, electrically conducting polymers are: polyacetylene, polythiophene, polypyrrole, poly(1,4-phenylene), poly(1,4-phenylene sulfide), poly(1,4-phenylenevinylene).
4. The oxidation or reduction processes referred to in Note 2 are termed **doping**. The charge-transfer agents used are termed **dopants**. Examples of dopants include AsF_5 or I_2 as oxidizing agents, generating cation-radicals on the chains (so-called holes), or a solution of sodium naphthalenide in tetrahydrofuran as a reducing agent, generating anion-radicals on the chains.
5. Unlike polymeric electrolytes in which charges are transported by dissolved ions, the charges in conjugated conducting polymers are transported along and between polymer molecules via generated charge carriers (*e.g.*, holes, electrons).
6. An intrinsically conducting polymer, should be distinguished from a **conducting polymer composite** (see Definition 19) and from a **solid polymer electrolyte** (see Definition 20).

19. conducting polymer composite1

Electrically conducting composite comprising a polymer and an electrically conducting material.

Note:
Most commonly the conducting material is a low-molecular-weight filler (*e.g.*, carbon black or metal particles).

20. solid polymer electrolyte

Electrically conducting solution of a salt in a polymer.

Notes:
1. An example of solid polymer electrolyte is a solution of a lithium salt in a poly(oxyethylene) matrix; the ionic conductivity of such material is due to the mobility of lithium cations and their counterions in an electric field.
2. Although the adjective "solid" is used, the material may be a liquid.
3. The term **solid polymer electrolyte** should not be confused with the term **polymeric electrolyte** (see Definition 8, Note 2).

References:

[1] IUPAC Compendium of Chemical Terminology, The Gold Book, Second Edition. A. D. McNaught and A. Wilkinson, Blackwell Science [ISBN 0865426848].

[2] Glossary of basic terms in polymer science (IUPAC Recommendations 1996) *Pure Appl. Chem.*, **68**, 2287-2311 (1996).

[3] Definition of terms relating to reactions of polymers and to functional polymeric materials (IUPAC Recommendations 2004) *Pure Appl. Chem.*, **76**, 889-906 (2004).

[4] Polymer Science Dictionary, M. S. Alger Ed., Elsevier Applied Science, London, New York, 1990.

Alphabetical Index of Terms: