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

(IUPAC Recommendations 2006)

Prepared by a Working Group consisting of

M. HESS¹, R. G. JONES², J. KAHOVEC³, T. KITAYAMA⁴, P. KRATOCHVÍL³, P. KUBISA^{5,‡},
W. MORMANN⁶, R. F. T. STEPTO⁷, D. TABAK⁸, J. VOHLÍDAL⁹, AND E. S. WILKS¹⁰

¹Universität Duisburg-Essen, Duisburg, Germany; ²University of Kent, Canterbury, Kent, UK;

³Ústav Makromolekulární Chemie, Akademie věd České Republiky, Praha, Czech Republic; ⁴Osaka University, Toyonaka, Osaka, Japan; ⁵Centrum Badan Molek. i Makromolek., Polska Akademia Nauk, Łódź, Poland; ⁶Universität Gesamthochschule Siegen, Siegen, Germany; ⁷University of Manchester and UMIST, UK; ⁸Praca Pio X, Candelaria, Rio de Janeiro, Brazil; ⁹Universita Karlova, Praha, Czech Republic; ¹⁰113 Meriden Drive, Canterbury Hills, Hockessin, DE 19707, USA

*Membership of the Commission on Macromolecular Nomenclature (extant until 2002) during the preparation of this report (1996–2005) was as follows:

Titular Members: M. Barón (Argentina, TM from 1996, *Secretary* from 1998); K. Hatada (Japan, to 1997, AM to 1999); M. Hess (Germany, AM from 1996, TM from 1998, *Chairman* from 2000); K. Horie (Japan, AM from 1996, TM from 1998); R. G. Jones (UK, Pool TM to 1997, TM from 1998); J. Kahovec (Czech Republic, to 1999); P. Kubisa (Poland, AM from 1996, TM from 2000); E. Maréchal (France, TM to 1999, AM 2000–2001); I. Meisel (Germany, AM from 1998, TM from 2000); W. V. Metanomski (USA, to 1999); C. Noël (France, to 1997); V. P. Shibaev (Russia, AM to 1999); R. F. T. Stepto (UK, *Chairman* to 1999); E. S. Wilks (USA, AM from 1998, TM from 2000); W. J. Work (USA, *Secretary* to 1997).

**Other Members of the Subcommittee on Macromolecular Terminology who contributed to this report:

M. Barón (Argentina, *Secretary* until 2003); G. Allegra (Italy); A. Fradet (France); J. He (China); K.-H. Hellwich (Germany); K. Horie (Japan); A. D. Jenkins (UK); J.-I. Jin (Korea); R. G. Jones (UK); I. Meisel (Germany); W. V. Metanomski (USA); G. Moad (Australia); S. Penczek (Poland); M. Rinaudo (France); S. Słomkowski (Poland); W. J. Work (USA).

Others contributing to this report: B. Grady (USA).

‡Corresponding author: E-mail: pkubisa@bilbo.cbmm.lodz.pl

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Terminology of polymers containing ionizable or ionic groups and of polymers containing ions

(IUPAC Recommendations 2006)

Abstract: This document defines the terms most commonly encountered in the field of polymers containing ionizable or ionic groups and polymers containing ions. The scope of the document has been limited to organic polymers. Inorganic materials, such as certain phosphates, silicates, etc., which also may be considered ionic polymers, are excluded from the present document.

The terms selected are those that are widely used in the field of polymers containing ionizable or ionic groups and polymers containing ions. Only those terms that could be defined without ambiguity are considered.

The terms are listed in alphabetical order, and cross-references to definitions given in other documents are provided.

Keywords: ionic polymers; polyelectrolytes; ionomers; polyacid; polybase.

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INTRODUCTION

This document defines the most commonly used terms relating to polymers containing ionizable or ionic groups and to polymers containing ions. Inorganic materials, such as certain 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.

Cross-references to terms defined elsewhere within the document are printed in italic type.

LIST OF TERMS

1. ampholytic polymer

Polyelectrolyte composed of macromolecules containing both cationic and anionic groups, or corresponding ionizable groups.

Note:

An *ampholytic* polymer in which ionic groups of opposite sign are incorporated into the same pendant groups is called, depending on the structure of the pendant groups, a *zwitterionic polymer*, *polymeric inner salt*, or *polybetaine*.

Synonym: *polyampholyte*

2. anion-exchange polymer

See also *ion-exchange polymer*.

3. anionic polymer

Polymer composed of negatively charged macromolecules and an equivalent amount of countercations.

Notes:

1. If a substantial fraction of constitutional units carries negative charges, then an *anionic polymer* is a *polyelectrolyte*.
2. The term *anionic polymer* should not be used to denote a polymer prepared by anionic polymerization.

4. cation-exchange polymer

See also *ion-exchange polymer*.

5. cationic polymer

Polymer composed of positively charged macromolecules and an equivalent amount of counteranions.

Notes:

1. If a substantial fraction of constitutional units carries positive charges, then a *cationic polymer* is a *polyelectrolyte*.
2. The positive charges may be fixed on groups located in main chains as in an *ionene* or in pendant groups.
3. The term *cationic polymer* should not be used to denote a polymer prepared by cationic polymerization.

6. conducting polymer composite

Electrically conducting composite comprising a non-conducting polymer matrix and an electrically conducting material.

Note:

Examples of the electrically conducting materials are carbon black and metal particles.

See also *solid polymer electrolyte*.

7. critical ion-concentration in an ionomer

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

8. dopant

Charge-transfer agent used to generate, by oxidation or reduction, positive or negative charges in an intrinsically conducting polymer.

Note:

Examples of dopants include AsF_5 or I_2 as oxidizing agents, generating cation radicals on the chains of an *intrinsically conducting polymer* (so-called holes), or a solution of sodium naphthalenuidyl in

tetrahydrofuran as a reducing agent, generating anion radicals on the chains of an *intrinsically conducting polymer*.

9. doping

Oxidation or reduction process brought about by a *dopant*.

10. electrically conducting polymer

Polymeric material that exhibits bulk electric conductivity.

Note:

Definition same as definition 3.2, ref. [1].

11. halatopolymer

See *halato-telechelic polymer*.

12. halato-telechelic polymer

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

Notes:

1. The term *halato-telechelic polymer* 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 difunctional initiators.
2. The term *halatopolymer* is used for a linear polymer formed by the coupling of halato-telechelic polymer molecules, for example, for the linear polymer formed by the coupling of carboxylate end-groups with divalent metal cations [2].

13. intrinsically conducting polymer

Electrically conducting polymer composed of macromolecules having fully conjugated sequences of double bonds along the chains.

Notes:

1. The bulk electrical conductivity of an *intrinsically conducting polymer* is comparable to that of some metals and results from its macromolecules acquiring positive or negative charges through oxidation or reduction by an electron acceptor or donor (charge-transfer agent), termed a *dopant*.
2. Examples of *intrinsically conducting polymers* are polyacetylene, polythiophene, polypyrrole, or polyaniline.
3. Unlike *polymeric electrolytes*, in which charge is transported by dissolved ions, charge in *intrinsically conducting polymers* is transported along and between polymer molecules via generated charge carriers (e.g., holes, electrons).
4. An *intrinsically conducting polymer* should be distinguished from a *conducting polymer composite* and from a *solid polymer electrolyte*.

14. ion-containing polymer

See *ionic polymer*.

15. ionene

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

Note:

Most commonly, the ionic groups in ionenes are quaternary ammonium groups.

16. ion-exchange membrane

See *ion-exchange polymer*.

17. ion-exchange polymer

Polymer that is able to exchange ions (cations or anions) with the ionic components in solution.

Notes:

1. Definition same as definition 2.2, ref. [1]
2. See ref. [4] for ion exchange.
3. Depending on which ion can be exchanged, the polymer is referred to as an *anion exchange polymer* or *cation exchange polymer*.
4. An ion-exchange polymer in ionized form may also be referred to as a *polyanion* or *polycation*.
5. Synthetic ion-exchange organic polymers are often network *polyelectrolytes*.
6. A membrane having ion-exchange groups is called an ion-exchange membrane.
7. Use of the term *ion-exchange resin* for *ion-exchange polymer* is strongly discouraged.

18. ionic aggregates in an ionomer

Domains enriched with ionic groups within an ionomer matrix.

19. ionic polymer

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

Synonym: *ion-containing polymer*

20. 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. Definition same as definition 1.66, ref. [3].
2. Ionic groups are usually present in sufficient amounts (typically less than 10 % of constitutional units) to cause micro-phase separation of ionic domains from the continuous polymer phase. The ionic domains act as physical crosslinks.

21. 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 ionomer multiplets increases, leading to overlapping of the restricted mobility regions around the multiplets and the formation of clusters.
2. Typically, an ionomer exhibits two glass transition temperatures (T_g), one for the nonpolar matrix and the other for clusters.

22. ionomer multiplet

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

23. polyacid

In polymer terminology, polyelectrolyte composed of macromolecules containing acid groups on a substantial fraction of the constitutional units.

Note:

Most commonly, the acid groups are $-COOH$, $-SO_3H$, or $-PO_3H_2$.

24. polyampholyte

See *ampholytic polymer*.

25. polybase

In polymer terminology, polyelectrolyte composed of macromolecules containing basic groups on a substantial fraction of the constitutional units.

Note:

Most commonly, the basic groups are amino groups.

26. polybetaine

Ampholytic polymer in which pendant groups have a betaine-type structure.

Notes:

1. For the definition of a betaine-type structure, see ref. [4].
2. A *polybetaine* is a type of *zwitterionic polymer*.

27. polyelectrolyte

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

Notes:

1. Definition 24 is consistent with definition 1.65, ref. [3] and supersedes the definition given in [4].
2. The terms polyelectrolyte, polymer electrolyte, and *polymeric electrolyte* should not be confused with the term *solid polymer electrolyte*.
3. Polyelectrolytes can be either synthetic or natural. Nucleic acids, proteins, teichoic acids, some polypeptides, and some polysaccharides are examples of natural polyelectrolytes.

Synonyms: *polymer electrolyte*, *polymeric electrolyte*

28. polyelectrolyte complex

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

Note:

A *polyelectrolyte complex* is also called a polysalt. Use of this term is not recommended.

29. polyelectrolyte network

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

Notes:

1. A polyelectrolyte network is sometimes called a cross-linked polyelectrolyte. Use of the latter term is not recommended unless the polyelectrolyte network is formed by the cross-linking of existing polyelectrolyte macromolecules rather than by nonlinear polymerization. (See the definition of a crosslink, definition 1.59, ref. [3].)
2. In contrast to a *polyelectrolyte*, a polyelectrolyte network is always insoluble, although swelling or contraction can occur when it is immersed in a solvent.
3. A polyelectrolyte network in contact with a solution of a salt is able to exchange counterions (cations or anions) with ionic species in the solution and act as an ion exchanger. Therefore, a polyelectrolyte network is frequently described as an ion-exchange polymer.

30. polymer electrolyte

See *polyelectrolyte*.

31. polymeric electrolyte

See *polyelectrolyte*.

32. polymeric inner salt

See *zwitterionic polymer*.

33. solid polymer electrolyte

Electrically conducting solution of a salt in a polymer.

Notes:

1. An example of a *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*.
4. See also *conducting polymer composite*.

34. zwitterionic polymer

Ampholytic polymer containing ionic groups of opposite sign, commonly on the same pendant groups.

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