



**Glossary of Terms Related to Kinetics, Thermodynamics and Mechanisms  
of Polymerization**

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

POLYMER DIVISION

COMMISSION ON MACROMOLECULAR NOMENCLATURE\*

and

SUB-COMMITTEE ON POLYMER TERMINOLOGY\*\*

## GLOSSARY OF TERMS RELATED TO KINETICS, THERMODYNAMICS AND MECHANISMS OF POLYMERIZATION

(IUPAC Recommendations 2007)

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# GLOSSARY OF TERMS RELATED TO KINETICS, THERMODYNAMICS AND MECHANISMS OF POLYMERIZATION

## (IUPAC Recommendations 2007)

*Abstract:* This document presents recommended definitions of basic terms related to polymerization processes, principally to the kinetics, thermodynamics, and mechanisms of polymerization.

### INTRODUCTION

This document presents recommended definitions of basic terms related to polymerization processes, principally to the kinetics, thermodynamics, and mechanisms of polymerization. Polymerization processes have their specific features and, in some instances, the definitions presented here differ from the corresponding general definitions in the *Compendium of Chemical Terminology* (the “Gold Book”) [1]. It should be noted that the Gold Book is now available on-line at <http://goldbook.iupac.org/>. The process of revising the Gold Book, i.e., adding terms from post-1995 IUPAC recommendations to this website, is in progress but no new hard-copy version is contemplated.

Some terms defined in the present document were also included in previous IUPAC recommendations, particularly in the *Glossary of Basic Terms in Polymer Science* (the “Glossary”) [2] and the *Basic Classification and Definitions of Polymerization Reactions* [3]. In many cases, the previously-given definitions have been retained but, in other cases, the development of the field has required some changes. Lists of those Definitions from the Gold Book and the Glossary that have been changed are provided as appendices to the present document.

The terms defined in this document are presented in alphabetical sequence. Italic type is used for cross-references to terms defined elsewhere in the document.

## RECOMMENDED DEFINITIONS

### 1. activated monomer

Cationic or anionic species generated reversibly from a monomer.

See also *activated-monomer polymerization*.

### 2. activated-monomer polymerization

*Chain polymerization* in which *propagation* involves reaction between a neutral growing chain-end and an *activated monomer*.

See also *activated monomer*.

### 3. acrylic diene metathesis polymerization, ADMET

*Metathesis polymerization* of an acrylic diene monomer.

### 4. active centre (in a polymerization)

active site, kinetic-chain carrier

Site on a *chain carrier* at which reaction occurs

Note: In [1], the terms “active centre” and “active site” are defined with reference to heterogeneous catalysis and the term “reactive site” is used within the definition of *chain polymerization*.

### 5. active site

See *active centre*

### 6. alternating copolymerization

*Copolymerization* in which an alternating copolymer is formed [1,2].

Note 1: An alternating copolymer is a copolymer consisting of linear macromolecules comprising two species of monomer units in alternating sequence.

Note 2: See also *periodic copolymerization*.

### 7. anionic polymerization

*Ionic polymerization* in which the *active centres* are anions.

Note 1: The anions may be free, paired, or aggregated.

Note 2: Modified from the definition in [1,2]

## 8. apparent rate constant of polymerization, $k_p^{\text{app}}$

Measured *rate of polymerization* divided by the concentration of the reactant (if there is only one) or the product of concentrations of the presumed reactants.

Note 1: SI unit:  $\text{s}^{-1}$  or  $\text{dm}^{-3} \text{mol s}^{-1}$

Note 2: The apparent rate constant of a *polymerization* should not be confused with the rate coefficients or the rate constants of the elementary reaction steps (compare the definitions of these in [1]).

## 9. auto-acceleration

Increase in the *rate of polymerization* with increasing conversion of the reactant(s).

Note: In a *polymerization*, auto-acceleration may be due to a variety of causes. An example of auto-acceleration in a *polymerization* is the Norrish-Trommsdorf effect (gel effect) which leads to a significant increase in the rate of a bulk *radical polymerization* with conversion. The effect is due to the rate of termination decreasing with increasing viscosity of the system, causing an increasing concentration of propagating *radicals*.

## 10. azeotropic copolymerization

*Binary copolymerization* in which the two *monomer reactivity ratios*,  $r_{12}$  and  $r_{21}$ , are not both equal to unity yet the copolymerization forms a copolymer with its molar ratio of monomer units equal to the molar ratio of monomers in the monomer feed.

Note 1: An *azeotropic polymerization* occurs at only one specific molar ratio of monomers in the feed.

Note 2: Although, in its equality of copolymer and monomer-feed compositions, an *azeotropic polymerization* has the same feature as an *ideal binary copolymerization* in which  $r_{12} = r_{21} = 1$ , it is not an *ideal copolymerization* as it has  $r_{12}r_{21} \neq 1$ .

## 11. backbiting

intramolecular chain transfer

*Chain transfer* from an *active centre* on a macromolecule to another part of the same macromolecule.

Note 1: An *active centre* may be located anywhere along a macromolecular chain.

Note 2: Often branching occurs or cyclic structures are formed as a result of backbiting.

Note 3: See also chain transfer and intermolecular chain transfer.

## 12. bead polymerization

See *suspension polymerization*.

### 13. binary copolymerization

*Copolymerization* involving two species of monomer.

### 14. bulk polymerization

*Polymerization* of an undiluted liquid monomer.

### 15. cage effect

General term referring to reactions between reactant molecules trapped transiently in a restricted volume of molecular dimensions.

Note 1: In polymerizations, the best-known example of the cage effect is the reduced efficiency of initiation of a *radical polymerization* due to a fast reaction between the two *radicals*, formed by the homolytic dissociation of initiator, within a transient cage of molecules. The reaction occurs before the *radicals* are able to diffuse apart.

Note 2: Modified from the definition in [1].

### 16. cationic polymerization

*Ionic polymerization* in which the *active centres* are cations.

Note 1: The cations may be free, paired, or aggregated.

Note 2: Modified from the definition in [1,2]

### 17. ceiling temperature, $T_c$

Lowest temperature at which the concentration of monomer in equilibrium with its polymer is essentially equal to the initial monomer concentration and therefore the Gibbs energy change accompanying *polymerization* becomes positive.

Note 1: Usually, a ceiling temperature is observed when  $\Delta H < 0$ , where  $\Delta H$  is the enthalpy change per mole of monomer units reacted.

Note 2:  $T_c$  is given by the standard enthalpy change,  $\Delta H^\circ$ , divided by the entropy change,  $\Delta S$ , per mole of monomer reacted, i.e.,  $T_c = \Delta H^\circ / \Delta S$ . If the standard state refers to unit concentration and the monomer behaves ideally,  $\Delta S = \Delta S^\circ + R \ln([M]_0 / c^\circ)$ , where  $\Delta S^\circ$  is the entropy change in the standard state,  $[M]_0$  denotes the starting monomer concentration and  $c^\circ = 1 \text{ mol dm}^{-3}$  is the standard concentration.

Note 3:  $T_c$  can be raised by increasing the concentration of monomer when a solvent is present.

Note 4: The symbol  $T_c(c^\circ)$  is used to define the ceiling temperature when the starting monomer concentration,  $[M]_0$ , is equal to  $c^\circ$ .

Note 5: The symbol  $T_c(\text{bulk})$  is used to define the ceiling temperature when the starting monomer concentration is equal to its undiluted concentration.

**18. chain activation**

See *chain reactivation*.

**19. chain carrier**

Intermediate species bearing an *active site* for the propagation of a chain reaction.

Note 1: If an *active site* is on the terminal monomer unit of a chain, the *chain carrier* is represented by the symbol ...-m\*.

Note 2: Modified from the definition in [1].

**20. chain copolymerization**

*Chain polymerization* in which a copolymer is formed.

**21. chain deactivation**

Conversion of a *chain carrier* to an inactive species.

Note 1: Chain deactivation, unlike *chain termination*, may be reversible; see *reversible chain deactivation*.

Note 2: The reverse of chain deactivation is *chain reactivation*.

**22. chain depropagation**

depropagation

Chemical reaction that results in the formation of a monomer molecule from an *active centre* on the terminal unit of a *chain carrier* and reduces the *degree of polymerization* of the *chain carrier* by one.

Note 1: *Chain depropagation* is the reverse of *chain propagation*

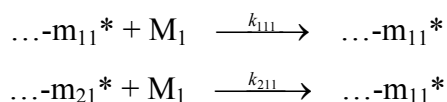
Note 2: See also *depolymerization* and *unzipping*

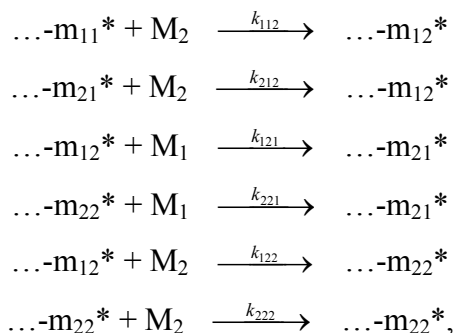
**23. chain-end reactivity ratio,  $s_1$  and  $s_2$** 

radical reactivity ratio

In a *binary copolymerization*, the ratio of two rate constants defining the relative activity of an *active centre* on a given type of terminal unit of a *chain carrier* towards one type of monomer, in the two cases where the penultimate unit of the *chain carrier* is identical to and different from the terminal unit.

Note 1: The reactions involved are defined in accordance with the *penultimate-unit effect*, namely,





where  $M_1$  and  $M_2$  are the two monomers involved in the binary copolymerization and  $\dots -m_{ij}^*$  ( $i, j = 1, 2$ ) denotes a *chain carrier* having an *active site* on its terminal monomer unit of type  $M_j$  and having the adjacent, penultimate monomer unit of type  $M_i$  (See *chain carrier*).

Note 2: The *chain-end reactivity ratios* are defined by the equations

$$s_1 = k_{211}/k_{111}; s_2 = k_{122}/k_{222}$$

Note 3: The *monomer reactivity ratios*, defined in accordance with the *penultimate-unit effect*, are

$$r_{112} = k_{111}/k_{112}; r_{212} = k_{211}/k_{212}; r_{221} = k_{222}/k_{221}; r_{121} = k_{122}/k_{121}.$$

The symbols for the *monomer reactivity ratios* are often abbreviated to  $r_1$ ,  $r_1'$ ,  $r_2$  and  $r_2'$ , respectively (See *monomer reactivity ratios* for the definitions of  $r_1$  and  $r_2$  ignoring the *penultimate-unit effect*).

## 24. chain initiation (in a polymerization)

initiation

Chemical reaction in which *primary radicals* add to monomer to form *chain carriers*.

Note 1: The recommended symbol for the rate constant for *chain initiation* in a *polymerization* is  $k_i$ .

Note 2: Modified from the definition in [1].

## 25. chain polymerization

Chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and *active site(s)* on the polymer chain with regeneration of the *active site(s)* at the end of each growth step.

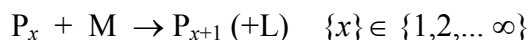
Note 1: A *chain polymerization* consists of *chain initiation* and *chain propagation* reactions, and may also include *chain deactivation* or *chain transfer* reactions, or both.

Note 2: The adjective “chain” in *chain polymerization* denotes “chain reaction” rather than a “polymer chain”.

Note 3: Propagation in *chain polymerization* usually occurs without the formation of small molecules. However, cases exist where a low-molar-mass by-product is formed, as in the *polymerization* of oxazolidine-2,5-diones derived from amino acids

(commonly termed amino-acid *N*-carboxy anhydrides). When a low-molar-mass by-product is formed, the additional adjective condensative is recommended to form the term “condensative *chain polymerization*”.

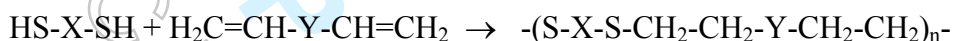
Note 4: The growth steps are expressed by:



where  $P_x$  denotes the growing chain of *degree of polymerization*  $x$ ,  $M$  a monomer, and  $L$  a low-molar-mass by-product formed in the case of condensative *chain polymerization*.

Note 5: The term “*chain polymerization*” may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g., ring-opening *chain polymerization*, cationic *chain polymerization*.

Note 6: There exist, exceptionally, some *polymerizations* that proceed *via* chain reactions that, according to the definition, are not *chain polymerizations*. For example, the *polymerization*.



proceeds *via* a radical chain reaction with intermolecular transfer of the radical centre. The growth step, however, involves reactions between molecules of all *degrees of polymerization* and, hence, the *polymerization* is classified as a *polyaddition*. If required, the classification can be made more precise and the *polymerization* described as a chain-reaction *polyaddition*.

Note 7: Modified from the definition in [1,2].

## 26. chain propagation (in a polymerization)

propagation

Chemical reaction between a *chain carrier* and a monomer that results in the growth of a polymer chain and the regeneration of at least one *chain carrier*.

Note 1: The recommended symbol for the rate constant for *chain propagation* in a *homopolymerization* is  $k_p$ .

Note 2: For *chain propagation* in *copolymerization* see *cross-propagation*.

Note 3: Modified from the definition in [1].

## 27. chain reactivation

chain activation

Conversion of an inactive chain into a *chain carrier*.

Note 1: The term is usually used to refer to the reactivation of previously deactivated chains.

Note 2: *Chain reactivation* can be reversible or irreversible.

Note 3: The reverse of chain reactivation is *chain deactivation* or *reversible chain deactivation*.

**28. chain scission**

Chemical reaction resulting in the breaking of skeletal bonds in a polymer chain.

Note: Modified from the definition in [1, 2].

**29. chain termination (in a polymerization)**

irreversible chain deactivation, termination

Chemical reaction in which a *chain carrier* is converted irreversibly into a non-propagating species without the formation of a new *chain carrier*.

Note 1: The recommended symbol for the rate constant or coefficient for *chain termination* in a *homopolymerization* is  $k_t$ .

Note 2: The term “*chain deactivation*” is often used to stress that, in contrast to termination, the formation of non-propagating species may be reversible; see *chain deactivation* and *reversible chain deactivation*.

Note 3: See also *combination*, *cross-termination*, *disproportionation* and *spontaneous termination*.

Note 4: Modified from the definition in [1].

**30. chain transfer (in a polymerization)**

Chemical reaction occurring during a *chain polymerization* in which an *active centre* is transferred from a growing macromolecule or oligomer molecule to another molecule or to another site on the same molecule.

Note 1: See also *intermolecular chain transfer*, *intramolecular chain transfer* and *backbiting*.

Note 2: The recommended symbol for the rate constant of *chain transfer* in a *homopolymerization* is  $k_{tr}$ .

Note 3: Modified from the definition in [1].

**31. chain-transfer agent**

Substance able to react with a *chain carrier* by a reaction in which the original *chain carrier* is deactivated and a new *chain carrier* is generated.

Note: In a *polymerization*, the common occurrence is that a new *chain carrier* of lower molar mass is generated.

**32. chain-transfer constant,  $C_{tr}$** 

In a *homopolymerization*, rate constant for *chain transfer*,  $k_{tr}$ , divided by the rate constant for *chain propagation*,  $k_p$ , i.e.,  $C_{tr} = k_{tr}/k_p$ .

### 33. combination

*Chain termination*, in a *chain polymerization*, between two propagating macromolecules that gives rise to a single macromolecule of molar mass equal to the sum of the molar masses of the two macromolecules.

Note 1: *Combination* is often incorrectly called “recombination”.

Note 2: Radical combination is also called colligation [1].

### 34. comonomer

Monomer used in *copolymerization*.

### 35. connectivity (in polymer science)

See *functionality*.

### 36. controlled polymerization

Term indicating control of a certain kinetic feature of a *polymerization* or structural aspect of the polymer molecules formed, or both.

Note 1: The expression *controlled polymerization* is sometimes used to describe a *radical* or *ionic polymerization* in which *reversible deactivation* of the *chain carriers* is an essential component of the mechanism, increasing the time of propagation to secure control of one or more kinetic features of the *polymerization* or one or more structural aspects of the macromolecules formed, or both.

Note 2: The expression *controlled radical polymerization* is sometimes used to describe a *radical polymerization* conducted in the presence of reagents that lead to, *e.g.*, atom-transfer *radical polymerization* (ATRP), *polymerization* mediated by nitroxyl radicals (NMP), or reversible-addition-fragmentation-chain transfer (RAFT) *polymerization*.

Note 3: Generally, the adjective “controlled” should not be used without specifying the particular kinetic or structural feature that is subject to control.

### 37. coordination polymerization

*Chain polymerization* that involves the preliminary coordination of a monomer molecule with a *chain carrier*.

Note: *Coordination polymerization* often occurs by *pseudo-ionic polymerization*.

### 38. copolymerization

Polymerization in which a copolymer is formed [1,2].

Note: A copolymer is a polymer derived from at least two species of monomer [1,2].

### 39. copolymerization composition equation

Equation relating the instantaneous composition of a binary copolymer to the *monomer reactivity ratios* and the ratio of instantaneous monomer concentrations.

Note 1: The instantaneous composition of copolymer generally changes during the course of a *copolymerization* due to the changing composition of the monomer mixture (but see *azeotropic polymerization*).

Note 2: See also *chain-end reactivity ratio, monomer reactivity ratios*.

Note 3: Integrated forms of the *copolymer composition equation* have been developed to relate polymer composition to *monomer reactivity ratios* and monomer conversions.

Note 4: The copolymer composition equation is known also as the Mayo-Lewis equation.

### 40. counter-ion

Ion that carries a charge opposite to that carried by an ionized group of an ionic macromolecule (ionomer or polyelectrolyte) or by an ionized group of the *chain carrier* of an *ionic polymerization*, thus maintaining overall electrical neutrality.

Note: Modified from the definition in [1].

### 41. coupling reaction

Linking of two macromolecules through chemical reaction.

Note: The coupling may proceed with or without an added coupling agent.

### 42. cross-propagation

Propagation reaction in a *copolymerization* in which a *chain carrier*, bearing at its active end a monomer unit of one kind, reacts with a monomer molecule of another kind.

Note: The recommended symbol for the rate constant of cross-propagation in a *binary copolymerization* is  $k_{ij}$ , in which i and j refer to (a) the type of terminal monomer unit of the *chain carrier* and (b) the reacting monomer molecule, respectively.

### 43. cross-termination

Termination reaction in a *copolymerization* between two *chain carriers* of different chemical natures.

Note 1: Usually only the chemical natures of the units at the active centres are considered.

Note 2: Cross-termination may occur by *combination* or *disproportionation*.

**44. cyclopolymerization**

*Polymerization* in which the number of cyclic structures in the constitutional units of the resulting macromolecules is larger than that in the monomer molecules [1, 2].

**45. dead-end polymerization**

*Radical polymerization* that stops, as a consequence of the depletion of the initiator, before the monomer has reacted fully.

**46. degenerate chain transfer**

See *degenerative chain transfer*.

**47. degenerative chain transfer**

*Chain transfer* reaction that generates a new *chain carrier* and a new *chain-transfer agent* with the same reactivity as the original *chain carrier* and *chain-transfer agent*.

**48. degradative chain transfer**

*Chain-transfer* reaction that generates a new *chain carrier* of much lower reactivity than that of the original *chain carrier*.

**49. degree of polymerization**

Number of monomeric units in a macromolecule, an oligomer molecule, a block, or a chain [1, 2].

**50. depolymerization**

Process of converting a polymer into a monomer or a mixture of monomers [1,2].

Note: See also *chain depropagation* and *unzipping*.

**51. depropagation**

See *chain depropagation*.

Note: See also *unzipping*.

**52. diffusion-controlled termination**

*Chain termination* in a *chain polymerization* in which the rate-controlling step is a diffusion process.

### 53. disproportionation (in a chain polymerization)

*Chain termination*, in a *chain polymerization*, between two propagating macromolecules that results in two macromolecules, one carrying an unsaturated chain-end, the other carrying a saturated chain-end.

Note: Modified from the definition in [1].

### 54. emulsion polymerization

Process whereby monomer(s), initiator, dispersion medium (and possibly colloid stabilizer) are mixed, forming initially an inhomogeneous system conducive to the *polymerization* of the monomer(s), and resulting in particles of colloidal dimensions.

Note: The term “*emulsion polymerization*” is a misnomer because historically it was thought that the *polymerization* occurred within the droplets of a monomer emulsion.

### 55. end-capping

Reaction in which *end-groups* of a desired structure are intentionally added to polymer chains.

### 56. end-group

Structural unit that is an extremity of a macromolecule or oligomer molecule [2].

### 57. enthalpy of polymerization, $\Delta H$ or $\Delta_{ab}H$

Change of enthalpy in a *homopolymerization* associated with the conversion of one mole of monomer into polymer under isobaric and isothermal conditions.

Note 1: SI unit:  $\text{J mol}^{-1}$

Note 2: Under defined standard conditions the enthalpy of polymerization is designated  $\Delta H^\circ$ .

Note 3: The subscripts in  $\Delta_{ab}H$  denote (a) the state of the monomer and (b) the state of polymer, as follows:

- g - gaseous state (hypothetical in the case of polymer)
- l - liquid state (must be specified in the case of a mesophase)
- s - in solution (solvent and mesophases, if any, must be specified)
- c – (condensed) amorphous, glassy states
- c' - crystalline or partly crystalline state

e.g.,  $\Delta_{lc}H$  means: from liquid state to amorphous or glassy state;  $\Delta_{ss}H$  means from monomer in solvent to polymer in solvent.

Note 4: Under certain conditions the enthalpy of polymerization is equal to the *heat of polymerization*.

Note 5: The symbol  $\Delta H_{ab}$ , in common usage in polymer chemistry, is discouraged as the IUPAC recommended symbol is  $\Delta_{ab}H$  [4].

### 58. entropy of polymerization, $\Delta S$ or $\Delta_{ab}S$

Change of entropy in a *homopolymerization* associated with the conversion of one mole of monomer into polymer under isobaric and isothermal conditions.

Note 1: SI unit:  $\text{J mol}^{-1} \text{K}^{-1}$

Note 2: Under defined standard conditions the entropy of polymerization is designated  $\Delta S^\circ$ ; thus, if the standard state refers to unit concentration, and the monomer behaves ideally,  $\Delta S = \Delta S^\circ + R \ln [M]$ .

Note 3: The subscripts in  $\Delta_{ab}S$  denote the state of the monomer (a) and the state of polymer (b) (see Notes to *enthalpy of polymerization*).

### 59. floor temperature, $T_f$

Highest temperature at which the concentration of monomer in equilibrium with its polymer is essentially equal to the initial monomer concentration, and therefore the Gibbs energy change accompanying *polymerization* becomes positive.

Note 1: SI unit: K

Note 2: Usually, a *floor temperature* exists when  $\Delta H > 0$ .

Note 3:  $T_f$  is equal to the standard enthalpy change divided by the entropy change on *polymerization*: *i.e.*,

$$T_f = \Delta H^\circ / \Delta S = \Delta H^\circ / (\Delta S^\circ + RT \ln ([M]_0/c^\circ))$$

(see Note 2 under *ceiling temperature*).

Note 4:  $T_f$  can be decreased by increasing the concentration of monomer when solvent is present.

Note 5: The symbol  $T_f(c^\circ)$  is used to define the floor temperature when the starting monomer concentration,  $[M]_0$ , is equal to  $c^\circ = 1.0 \text{ mol dm}^{-3}$ .

Note 6: The symbol  $T_f(\text{bulk})$  is used to define the floor temperature when the starting monomer concentration is equal to the concentration of monomer in bulk.

### 60. free ion

Ion that is independent of the influence of a *counter-ion*.

Note: A free ion is a distinct kinetic entity, and its reactivity is usually different from that of an *ion-pair*.

### 61. functionality, $f$

connectivity (in polymer science)

Number of chemical bonds that a monomeric or polymeric reactant can form with other reactants.

Note 1: There are no monofunctional monomers.

Note 2: If  $f = 2$ , a linear chain macromolecule or a macrocycle (see Definition 1.57 in [2]) can be formed.

Note 3: If  $f > 2$ , a branch point can be formed leading to a branched macromolecule, a network or a micro-network.

Note 4: Ethene and ethylene glycol are examples of difunctional monomers, glycerol is an example of a trifunctional monomer, and divinylbenzene and pentaerythritol are examples of tetrafunctional monomers.

## 62. gelation point

See *gel point*.

## 63. gel point

gelation point

Point of incipient network formation in a process forming a chemical or physical network.

Note 1: In both network-forming polymerization and the crosslinking of polymer chains, the *gel point* is expressed as an extent of chemical reaction.

Note 2: At the *gel point* a solid (network) material spanning the entire system is formed.

Note 3: The *gel point* is often detected using rheological methods. Different methods can give different gel points because viscosity is tending to infinity at the gel point and a unique value cannot be measured directly.

## 64. heat of polymerization, $Q$

Heat resulting from the conversion of a specified amount of monomer into polymer.

Note 1: SI unit:  $\text{J mol}^{-1}$

Note 2: The molar heat of polymerization is denoted by the symbol  $Q_m$  and is the heat of polymerization of 1 mole of monomer.

Note 3: The heat of polymerization is equal to the *enthalpy of polymerization* only under isobaric and isothermal conditions.

## 65. homopolymerization

Polymerization in which a homopolymer is formed [1,2].

Note: A homopolymer is a polymer derived from one species of (real, implicit, or hypothetical) monomer [2].

### 66. homopropagation

Addition of a monomer to a *chain carrier* bearing a terminal group derived from the same monomer species.

### 67. ideal binary copolymerization

*Binary copolymerization* in which the relative rates of incorporation of the two types of monomer into the copolymer are independent of the nature of the monomer unit at the end of a propagating chain.

Note 1: See *monomer reactivity ratios*. In an *ideal binary copolymerization*,  $k_{11}/k_{21} = k_{12}/k_{22}$  and  $r_{12}r_{21} = 1$ .

Note 2: In the special case of an *ideal binary copolymerization* in which  $r_{12} = r_{21} = 1$ , the two monomers show equal reactivities toward both types of propagating species. Thus,  $k_{11} = k_{21}$  and  $k_{12} = k_{22}$ . Hence, *copolymerization* of a mixture of two monomers with any ratio of monomer concentrations in the monomer feed gives rise to a copolymer in which the molar ratio of monomer units is identical to that in the monomer feed. (See also *azeotropic copolymerization*.)

### 68. ideal copolymerization

*Copolymerization* in which all types of propagating species show the same relative reactivity towards the monomers present.

### 69. inhibitor

Additive that reacts so rapidly with the *chain carriers* that it reduces the observed rate of *polymerization* to zero.

Note 1: Long-chain macromolecules cannot be formed until virtually all the inhibitor is consumed.

Note 2: Modified from the definition in [1].

### 70. initiator

Substance introduced into a reaction system in order to cause *chain initiation*.

Note 1: In contrast to a catalyst, an initiator is consumed in the reaction.

Note 2: Modified from the definition in [1].

**71. initiator efficiency,  $f$** 

Number of growing chains initiated divided by the number of *active centres* generated from *initiator* molecules.

Note 1: In a *radical polymerization*, the rate of radical production from an initiator that provides two similar radicals is  $2k_d f$ , where  $k_d$  is the rate constant for initiator decomposition.

Note 2: In some texts the initiator efficiency is defined as the fraction of radicals that escapes the cage (see *cage effect*).

**72. initiation (in a chain polymerization)**

See *chain initiation*.

**73. interchange reaction**

Reaction between functional groups within polymer molecules that causes a redistribution of structural units.

Note: *Transamidation* and *transesterification* are the best-known examples of interchange reactions.

**74. interfacial polycondensation**

*Polycondensation* involving two monomers separately dissolved in immiscible solvents, forming a two-phase system, with *polycondensation* taking place at (or near) an interface between the two phases.

**75. intermolecular chain transfer**

*Chain transfer* from an *active centre* on a macromolecule to a different macromolecule.

Note 1: An *active centre* may be located anywhere along a macromolecular chain.

Note 2: See also *chain transfer*, *backbiting*.

**76. intramolecular chain transfer**

See *backbiting*.

**77. ionic copolymerization**

*Copolymerization* that is an *ionic polymerization* [2].

**78. ionic polymerization**

*Chain polymerization* in which *active centres* are ions or ion-pairs.

Note 1: Usually the chain-ends are ions, although ions can also be located on the monomer molecules, as in an *activated-monomer polymerization*.

Note 2: The ions may also be present in the form of higher aggregates that usually are less reactive than non-aggregated species.

Note 3: Modified from the definition in [2].

**79. ion-pair**

Pair of oppositely charged ions, held together by Coulombic attraction.

Note: Modified from the definition in [1].

**80. irreversible chain deactivation**

See *chain termination*.

**81. kinetic-chain carrier**

See *active centre*.

**82. kinetic-chain length**

In a *chain polymerization*, the rate of *chain propagation* divided by the sum of the rates of all of the *chain-termination* processes.

Note 1: *Chain-termination* processes include termination by *combination* or *disproportionation* but do not include *chain transfer*.

Note 2: In the absence of *chain transfer*, the kinetic chain length will be equal to the degree of polymerization.

**83. living copolymerization**

*Copolymerization* that is a *living polymerization* [1,2].

**84. living polymerization**

*Chain polymerization* in which *chain termination* and irreversible *intermolecular chain transfer* are absent.

Note 1: In many cases, the rate of *chain initiation* is fast compared with the rate of *chain propagation*, so that the number of *kinetic-chain carriers* is essentially constant throughout the reaction.

Note 2: In living polymerization, the reversible (temporary) deactivation of *active centres* can take place (See *reversible chain deactivation*).

Note 3: In a living polymerization, essentially all the macromolecules possess the potential for further growth.

Note 4: Use of the adjectives “pseudo-living”, “quasi-living”, and “immortal” for “living” is discouraged.

Note 5: Modified from the definition in [1,2].

### 85. macromonomer

Polymer or oligomer composed of molecules, each of which has at least one chain-end or other site bearing a functional group capable of undergoing polymerization.

Note 1: The *homopolymerization* or *copolymerization* of macromonomer molecules, each of which has a single functional group capable of undergoing polymerization, gives rise to graft copolymers.

Note 2: Modified from the definition in [1,2].

### 86. metathesis polymerization

Polymerization in which olefinic monomers are transformed into unsaturated polymers by a process of bond rearrangement.

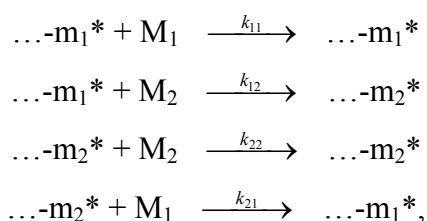
Note 1: Metathesis polymerization is most often metal-catalysed and the *kinetic-chain carriers* alternate between metal carbenes and metallocyclobutanes or metal carbynes and metallocyclobutenes.

Note 2: The two most common forms of metathesis polymerization are *ring-opening metathesis polymerization* (ROMP) and *acyclic diene metathesis polymerization* (ADMET).

### 87. monomer reactivity ratios, $r_{12}$ , $r_{21}$

In *binary copolymerization*, (a) the ratio ( $r_{12}$ ) of the rate constant ( $k_{11}$ ) for the *homopropagation* of monomer  $M_1$  to the rate constant ( $k_{12}$ ) for the *cross-propagation* of the *chain carrier*  $\dots-m_1^*$  with the monomer  $M_2$  and (b) the ratio ( $r_{21}$ ) of the rate constant ( $k_{22}$ ) for the *homopropagation* of monomer  $M_2$  to the rate constant for the *cross-propagation* ( $k_{21}$ ) of the *chain carrier*  $\dots-m_2^*$  with monomer  $M_1$ . Thus:  $r_{12} = k_{11}/k_{12}$ ,  $r_{21} = k_{22}/k_{21}$ .

Note 1: The reactions involved are:



where  $M_1$  and  $M_2$  are the two monomers involved in the *binary copolymerization* and  $\dots-m_i^*$  ( $i = 1,2$ ) denotes a *chain carrier* having an *active site* on its terminal monomer unit of type  $M_i$ .

Note 2: The symbols  $r_{12}$  and  $r_{21}$  are often abbreviated to  $r_1$  and  $r_2$ , respectively.

Note 3: See also *chain-end reactivity ratios*.

Note 4: The present definition ignores the penultimate-unit effect. For the definition of monomer reactivity ratios accounting for the penultimate-unit effect, see Note 3 of chain-end reactivity ratios.

### 88. monomer reactivity scale

Relative scale defined by the values of the rate constants for the addition of monomers to a reference *active centre*.

Note: See also *patterns of reactivity scheme*, *Q-e scheme*.

### 89. oligomerization

Process of converting a monomer or a mixture of monomers into an oligomer [1,2].

Note 1: An oligomer is a substance composed of oligomer molecules, the structure of which essentially comprises a small number of units derived, actually or conceptually, from molecules of lower molar mass.

Note 2: See also *telomerization*.

### 90. patterns of reactivity scheme

Method for the prediction of monomer reactivity ratios in *binary copolymerization*, based exclusively on experimentally-determined parameters.

Note 1: The parameters may be the monomer reactivity ratios for the separate *copolymerizations* of the monomers concerned, namely 1 and 2, with a non-polar monomer, e.g., styrene (S), and a polar monomer, e.g., acrylonitrile (A). The equations for the desired monomer reactivity ratios,  $r_{12}$  and  $r_{21}$ , are then as follows:

$$\log r_{12} = \log (r_{1S}.r_{S2}) - [\log (r_{AS}.r_{S2}/r_{A2})][\log (r_{SA}.r_{1S}/r_{1A})]/\log (r_{AS}.r_{SA})$$

$$\log r_{21} = \log (r_{2S}.r_{S1}) - [\log (r_{AS}.r_{S1}/r_{A1})][\log (r_{SA}.r_{2S}/r_{2A})]/\log (r_{AS}.r_{SA})$$

Note 2: The patterns of reactivity scheme is known also as Jenkins' scheme

### 91. pearl polymerization

See *suspension polymerization*.

### 92. penultimate-unit effect

Phenomenon that the penultimate monomer unit preceding the *active centre* on the terminal unit of an active polymer chain affects the reactivity of that *active centre*.

Note: See also *chain end reactivity ratio*.

### 93. periodic copolymerization

*Copolymerization* in which a periodic copolymer is formed [1,2].

Note: A periodic copolymer is a copolymer consisting of macromolecules comprising more than two species of monomeric units in regular sequence [1,2].

### 94. photopolymerization

*Polymerization* initiated by visible or ultra-violet light, typically in the presence of a light-sensitive compound known as a photo-initiator.

Note: Depending on the mechanism of decomposition of the photo-initiator upon irradiation and the structure of the monomer, photopolymerization may proceed by either a radical or an ionic mechanism.

### 95. polyaddition

*Polymerization* in which the growth of polymer chains proceeds by addition reactions between molecules of all *degrees of polymerization* [1,2].

Note 1: The growth steps are expressed by



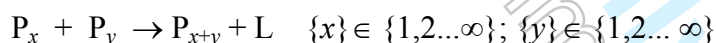
where  $P_x$  and  $P_y$  denote chains of *degrees of polymerization*  $x$  and  $y$ , respectively.

Note 2: The earlier term “addition polymerization”, defined previously [5], embraced both the current concepts of *polyaddition* and *chain polymerization*, but did not include condensative *chain polymerization*. (See Note 3 under *chain polymerization*).

### 96. polycondensation

*Polymerization* in which the growth of polymer chains proceeds by condensation reactions between molecules of all *degrees of polymerization* [1,2].

Note 1: The growth steps are expressed by:



where  $P_x$  and  $P_y$  denote the chains of *degree of polymerization*  $x$  and  $y$ , respectively, and  $L$  a low-molar-mass by-product.

Note 2: The terms “polycondensation” and “condensation polymerization”, defined previously [5], were synonymous. It should be noted that the current definitions of *polycondensation* and condensative *chain polymerization* (see Note 3 under *chain polymerization*) were both embraced by the previous term “polycondensation”.

### 97. polymerization

Process of converting a monomer or a mixture of monomers into a polymer [1,2].

Note: A polymer is a substance composed of macromolecules [1,2].

### 98. primary radical

*Radical* that is formed from an *initiator* or monomer molecule and that is capable of initiating *polymerization*.

Note 1: A primary *radical* may be formed by the action of heat or radiation.

Note 2: The recombination of primary radicals and their reactions with other species may lead to reduced *initiator efficiency*.

Note 3: *Radicals* that are formed by rearrangement or fragmentation of *radicals* formed from an *initiator* that are capable of initiating *polymerization* are sometimes called secondary radicals.

### 99. primary-radical termination

Termination reaction involving a radical *chain carrier* and a *primary radical*.

### 100. propagation (in a chain polymerization)

See *chain propagation*

### 101. pseudo-ionic polymerization

*Polymerization* proceeding by insertion of a monomer into a polar bond without the generation of ions.

Note 1: Most *pseudo-ionic polymerizations* involve concerted (e.g., four-centre or multi-centre) mechanisms of propagation.

Note 2: See also *coordination polymerization*.

### 102. pulsed-laser polymerization, PLP

Polymerization initiated by successive pulses of laser light.

Note: In a *radical polymerization*, PLP allows determination of the propagation rate constants.

### 103. Q-e scheme

Empirical equations expressing the *monomer reactivity ratios* in a *binary radical copolymerization*,  $r_{12}$  and  $r_{21}$ , in terms of the empirical parameters  $Q$  and  $e$ , with

$$r_{12} = (Q_1/Q_2)\exp[-e_1(e_1-e_2)] \text{ and } r_{21} = (Q_2/Q_1)\exp[-e_2(e_2-e_1)]$$

Note 1: Although both parameters are empirically derived, the parameter  $Q$  is considered to be a measure of the stabilization by conjugation of a monomer and the

radical derived from it, while the parameter  $e$  is considered to be a measure of the polar effects of substituents on the monomer and the radical derived from it.

Note 2: The  $Q$ - $e$  scheme is known also as the Alfrey-Price scheme

#### 104. radical

Molecular entity possessing an unpaired electron.

Note 1: The use of term “free radical” is discouraged.

Note 2: Modified from the definition in [1].

#### 105. radical copolymerization

*Copolymerization* that is a radical polymerization.

Note: Modified from the definition in [1,2].

#### 106. radical polymerization

Chain polymerization in which the *active centres* are radicals.

Note 1: Each active chain-end bears an unpaired electron.

Note 2: Modified from the definition in [1,2].

#### 107. radical reactivity ratio

See *chain-end reactivity ratio*.

#### 108. radical reactivity scale

Scale of the values of the rate constants for the reaction of *radicals* with a reference monomer.

#### 109. random copolymerization

*Copolymerization* in which a random copolymer is formed [1,2].

Note 1: A random copolymer is a copolymer consisting of macromolecules in which the probability of finding a given monomer unit at any given site in the chain is independent of the nature of the adjacent units [2].

Note 2: *Random copolymerization* should not be confused with *statistical copolymerization*.

#### 110. rate of polymerization

Rate of consumption of monomers in a *chain polymerization*, or the rate of consumption of the functional groups in the reaction mixture of a *polycondensation* or *polyaddition*.

### 111. reversible chain deactivation

Deactivation of a *chain carrier* in a *chain polymerization*, reversibly converting the *active centre* into an inactive one and then, within the average lifetime of a growing macromolecule, regenerating an *active centre* on the same *original carrier*.

Note 1: The temporarily deactivated species created in this process are often described as dormant.

Note 2: Reversible deactivation often involves reversible *coupling* or reversible *chain transfer*.

### 112. ring-opening copolymerization

*Copolymerization* that is a ring-opening polymerization with respect to at least one monomer [2].

### 113. ring-opening metathesis polymerization

**Recommended abbreviation:** ROMP

*Metathesis polymerization* in which an unsaturated cyclic monomer is converted into an unsaturated monomeric unit that is either acyclic or contains fewer cycles than the cyclic monomer.

### 114. ring-opening polymerization

Polymerization in which a cyclic monomer yields a monomeric unit that contains fewer cycles than the cyclic monomer.

Note 1: If the monomer is polycyclic, the opening of a single ring is sufficient to classify the polymerization as a *ring-opening polymerization*.

Note 2: Modified from the definition in [1,2].

### 115. self-initiated polymerization

*Polymerization* in which initiating species are formed exclusively from the monomer.

### 116. solid-state polymerization

*Polymerization* of a crystalline monomer.

Note 1: The initiating species is usually formed by the action of heat or radiation.

Note 2: A *solid-state polymerization* may involve significant atomic or molecular motions leading to a semi-crystalline polymer having a crystal structure different from that of the crystalline monomer, or alternatively it may proceed as a *topochemical polymerization*.

Note 3: A *solid-state polymerization* is usually initiated by irradiation of the monomer with, e.g., ultraviolet light or  $\gamma$ -rays; chemical initiation with a vapour-phase *initiator* is used less frequently.

Note 4: Depending on the *initiation* mode and the structure of the monomer, a *solid-state* polymerization may proceed by a *radical* or an ionic mechanism.

Note 5: The term "*bulk polymerization*" refers exclusively to the polymerization of undiluted liquid monomer.

### 117. spontaneous termination

*Chain termination* proceeding as a unimolecular process.

### 118. statistical copolymerization

*Copolymerization* in which a statistical copolymer is formed [1,2].

Note 1: A statistical copolymer is a copolymer consisting of macromolecules in which the sequential distribution of the monomeric units obeys known statistical laws [1,2].

Note 2: *Statistical copolymerization* should not be confused with *random copolymerization*.

### 119. stereospecific polymerization

*Polymerization* in which a tactic polymer is formed [5].

Note 1: A tactic polymer is composed of tactic macromolecules [1,2].

Note 2: A tactic macromolecule is a regular macromolecule, in which essentially all the configurational repeating units are identical [1,2].

Note 3: Modified from the definition in [1].

### 120. suspension polymerization

*Polymerization* that takes place in particles that exceed colloidal dimensions dispersed in an inert liquid medium.

Note: The initiator of a *suspension polymerization* is soluble in the dispersed monomer phase and essentially insoluble in the inert-liquid dispersing phase.

Synonyms: *pearl polymerization*, *bead polymerization*.

### 121. telomerization

*Oligomerization* by *chain polymerization* in the presence of a large amount of *chain-transfer agent*, so that end-groups are essentially fragments of the *chain-transfer agent* [2].

**122. template polymerization**

*Polymerization* of a monomer adsorbed or oriented, or both, (a) on a surface, (b) in a polymer lattice, or (c) on a polymer in solution, whereby the structure of the polymer chains formed is *controlled* by the orientation of the monomer molecules.

**123. termination (in a chain polymerization)**

See *chain termination*

**124. topochemical polymerization**

*Solid-state polymerization*, resulting in the formation of a polymer having essentially the same crystal structure as that of the monomer.

Note 1: A *topochemical polymerization* is usually initiated by irradiation of the crystalline monomer with, *e.g.*, ultraviolet light,  $\gamma$ -rays, or by chemical initiators.

Note 2: A *topochemical polymerization* does not involve significant atomic or molecular motions.

**125. transamidation**

*Interchange reaction* involving amide groups that occurs during a polymerization forming a polyamide.

**126. transesterification**

*Interchange reaction* involving ester groups that occurs during a polymerization forming a polyester.

**127. unzipping**

*Depolymerization* occurring by a sequence of reactions, progressing along a macromolecule and yielding products, usually monomer molecules, at each reaction step, from which macromolecules similar to the original can be regenerated.

Note: See also *chain depropagation*.

**128. zwitterionic copolymerization**

*Copolymerization* that is a *zwitterionic polymerization*.

Note: A *zwitterionic copolymerization* usually involves a nucleophilic monomer and an electrophilic monomer, and it may produce an alternating copolymer.

**129. zwitterionic polymerization**

*Chain polymerization* in which a growing macromolecule bears two ionic chain carriers of opposite signs, at one or both of its ends.

Note: Chains in a *zwitterionic polymerization* may grow from one or both of their ends.

**REFERENCES**

1. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.
2. Glossary of Basic Terms in Polymer Science (IUPAC Recommendations 1996), *Pure Appl. Chem.* **68**, 2287 (1996). Online version at <http://www.iupac.org/reports/1996/6812jenkins/6812basicterms.pdf>
3. Basic Classification and Definitions of Polymerization Reactions (IUPAC Recommendations 1994). *Pure Appl. Chem.* **66**, 2483 (1994).
4. IUPAC. Quantities, Units and Symbols in Physical Chemistry. 2<sup>nd</sup> ed. Prepared for publication by I. Mills, T. Cvitaš, K. Homann, N. Kallay, K. Kuchitsu. Blackwell Scientific Publications, Oxford (1993).
5. Compendium of Macromolecular Nomenclature (the Purple Book) (1<sup>st</sup> Edn) Blackwell Scientific Publications, Oxford (1991).

## APPENDICES 1 AND 2

Changes to some of the terms in the Gold Book [1] and the "Glossary of Basic Terms in Polymer Science" [2] have been necessitated by developments in polymer science and, in other cases, by the existing definitions not being specifically directed toward macromolecular terminology. Appendices 1 and 2 list the definitions from the Gold Book [1] and from the "Glossary of Basic Terms in Polymer Science" [2] that have been modified in this document. These Appendices are enclosed so that interested readers have the information readily available without the need to cross-reference other documents.

### Appendix 1

#### Relevant Definitions from the Gold Book [1] that have been modified.

##### **anionic polymerization**

An *ionic polymerization* in which the kinetic-chain carriers are anions.

##### **cage effect**

When in a condensed phase, or in a dense gas, *reactant* molecules come together, or species are caged in by surrounding molecules, they may undergo a set of collisions known as an *encounter*; the term "cage effect" is then applied.

##### **cationic polymerization**

An *ionic polymerization* in which the kinetic-chain carriers are cations.

##### **chain carrier**

A species, such as an atom or free radical, which is involved in *chain-propagating reactions* is known as a chain carrier.

##### **chain initiation**

The process in a *chain reaction* that is responsible for the formation of a *chain carrier*

##### **chain polymerization**

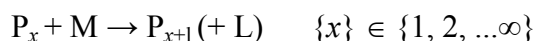
A chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.

Note 1: A chain polymerization consists of initiation and propagation reactions, and may also include termination and chain-transfer reactions.

Note 2: The adjective "chain" in "chain polymerization" denotes "chain reaction" rather than "polymer chain".

Note 3: Propagation in chain polymerization often occurs without the formation of small molecules. However, cases exist where, at each propagation step, a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed amino-acid N-carboxyl anhydrides). When a low-molar-mass by-product is formed the adjective *condensative* is recommended to give the term "condensative chain polymerization".

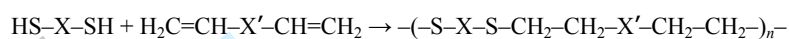
Note 4: The growth steps are expressed by



where  $P_x$  denotes the growing chain of degree of polymerization  $x$ ,  $M$  a monomer and  $L$  a low-molar-mass by-product formed in the case of condensative chain polymerization.

S. The term "chain polymerization" may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g. ring-opening chain polymerization and cationic chain polymerization.

Note 5: There exist, exceptionally, some polymerizations that can proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization



proceeds via a radical chain reaction with intermolecular transfer of the radical centre. The growth step, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition. If required, the classification can be made more precise and the polymerization described as a chain-reaction polyaddition.

### chain-propagating reaction

A *chain-propagating reaction*, or more simply a *propagating reaction*, is an elementary step in a *chain reaction* in which one *chain carrier* is converted into another. The conversion can be a *unimolecular* reaction or a *bimolecular* reaction with a reactant molecule.

### chain scission (of a polymer)

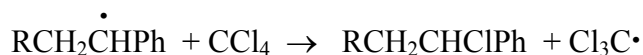
A chemical reaction resulting in the breaking of *skeletal bonds*.

### chain-termination reaction

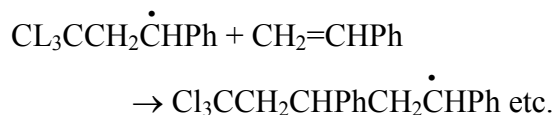
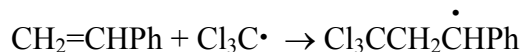
See *termination*.

### chain transfer

The abstraction, by the *radical* end of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization, is simultaneously created. For the example of alkylene polymerization cited for a *chain reaction*, the reaction:



represents a chain transfer, the radical  $\text{Cl}_3\text{C}\cdot$  inducing further polymerization:



The phenomenon occurs also in other chain reactions such as a cationic polymerization.

### counterions

1. (in an ion exchanger): the mobile exchangeable ions.

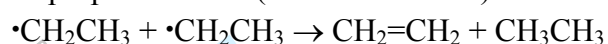
2. (in colloid chemistry): ions of low relative molecular mass, with a charge opposite to that of the colloidal ion.

### disproportionation

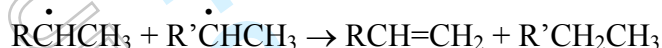
1. Any chemical reaction of the type  $A + A \rightarrow A' + A''$ , where A, A' and A'' are different chemical species. For example:



The reverse of disproportionation is called comportionation. A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by:



Reactions of the more general type:



are also loosely described as radical disproportionations.

### inhibitor

A substance that diminishes the rate of a chemical reaction; the process is called *inhibition*. Inhibitors are sometimes called negative catalysts, but since the action of an inhibitor is fundamentally different from that of a *catalyst*, this terminology discouraged. In contrast to a catalyst, an inhibitor may be consumed during the course of a reaction. In enzyme-catalysed reactions an inhibitor frequently acts by binding to the enzyme, in which case it may be called an *enzyme inhibitor*.

### initiator

A substance introduced into a reaction system in order to bring about an *initiation* reaction.

### ionic polymerization

A *chain polymerization* in which the kinetic-chain carriers are ions or ion pairs. Usually, the growing chain ends are ions.

### ion pair

A pair of oppositely charged ions held together by Coulomb attraction without formation of a *covalent bond*. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance:

$$q = 8.36 \times 10^6 \frac{z^+ z^-}{\epsilon_r T} \text{ pm}$$

are considered to constitute an ion pair ('Bjerrum ion pair'). [ $z^+$  and  $z^-$  are the charge numbers of the ions, and  $\epsilon_r$  is the relative permittivity (or dielectric constant) of the medium].

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a 'tight ion pair' (or 'intimate' or 'contact ion pair'). A tight ion pair of  $X^+$  and  $Y^-$  is symbolically represented as  $X^+Y^-$ .

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a 'loose ion pair', symbolically represented as  $X^+2Y^-$ . The members of a loose ion pair can readily interchange with other free or

loosely paired ions in the solution. This interchange may be detectable (*e.g.*, by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In 'solvent-shared ion pairs' the ionic constituents of the pair are separated by only a single solvent molecule, whereas in 'solvent-separated ion pairs' more than one solvent molecule intervenes. However, the term 'solvent-separated ion pair' must be used and interpreted with care since it has also widely been used as a less specific term for 'loose' ion pair.

### living polymerization

A chain polymerization from which chain transfer and chain termination are absent. In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the reaction.

### macromonomer

A polymer composed of macromonomer molecules.

### macromonomer molecule

A macromolecule that has one end-group which enables it to act as a monomer molecule, contributing only a single monomeric unit to a chain of the final macromolecule

### oligomerization

The process of converting a *monomer* or a mixture of monomer into an *oligomer*. An oligomerization by chain reaction carried out in the presence of a large amount of *chain-transfer* agent, so that the *end groups* are essentially fragments of the chain transfer agent, is termed *telomerization*.

### radical

A *molecular entity* such as  $\cdot\text{CH}_3$ ,  $\cdot\text{SnH}_3$ ,  $\text{Cl}\cdot$  possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible). Paramagnetic metal ions are not normally regarded as radicals. However, in the 'isolobal analogy' the similarity between certain paramagnetic metal ions and radical becomes apparent.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective 'free' in the general name of this type of *chemical species* and *molecular entity*, so that the term 'free radical' may in future be restricted to those radicals which do not form parts of radical pairs.

Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred radicals. If the unpaired electron occupies an orbital having considerable s or more less pure p character, the respective radicals are termed  $\sigma$ - or  $\pi$ -radicals.

In the past, the term 'radical' was used to designate a *substituent group* bound to a molecular entity, as opposed to 'free radical', which nowadays is simply called radical. The bound entities may be called *groups* or *substituents*, but should no longer be called radicals.

**radical polymerization**

A *chain polymerization* in which the kinetic-chain carriers are radicals. Usually, the growing chain end bears an unpaired electron.

**stereospecific polymerization**

*Polymerization* in which a *tactic polymer* is formed. However, polymerization in which stereoisomerism present in the *monomer* is merely retained in the *polymer* is not to be regarded as *stereospecific*. For example, the polymerization of a chiral monomer, *e.g.*, D-propylene oxide (D-methyloxirane), with retention of *configuration* is not considered to be a stereospecific reaction; however, selective polymerization, with retention, of one of the *enantiomers* present in a mixture of D- and L-propylene oxide molecules is so classified.

**termination**

The steps in a chain reaction in which reactive intermediates are destroyed or rendered inactive, thus ending the chain.

## Appendix 2

### Relevant Definitions from the Glossary of Basic Terms in Polymer Science (2) that have been changed or modified.

#### 3.19 anionic polymerization

An ionic polymerization in which the kinetic-chain carriers are anions.

#### 3.20 cationic polymerization

An ionic polymerization in which the kinetic-chain carriers are cations.

#### 3.6 chain polymerization

A chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.

Note 1: A chain polymerization consists of initiation and propagation reactions, and may also include termination and chain transfer reactions.

Note 2: The adjective “chain” in “chain polymerization” denotes “chain reaction” rather than “polymer chain”.

Note 3: Propagation in chain polymerization often occurs without the formation of small molecules. However, cases exist where, at each propagation step, a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed amino-acid N-carboxyl anhydrides).

When a low-molar-mass by-product is formed the adjective *condensative* is recommended to give the term “condensative chain polymerization”.

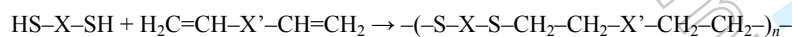
Note 4: The growth steps are expressed by



where  $P_x$  denotes the growing chain of degree of polymerization  $x$ ,  $M$  a monomer and  $L$  a low-molar-mass by-product formed in the case of condensative chain polymerization.

Note 5: The term “chain polymerization” may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g. ring-opening chain polymerization and cationic chain polymerization.

Note 6: There exist, exceptionally, some polymerizations that can proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization



proceeds via a radical chain reaction with intermolecular transfer of the radical center. The growth step, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition. If required, the classification can be made more precise and the polymerization described as a chain-reaction polyaddition.

#### 3.24 chain scission

A chemical reaction resulting in the breaking of skeletal bonds.

#### 3.17 ionic polymerization

A chain polymerization in which the kinetic-chain carriers are ions or ion-pairs.

Note: Usually, the growing chain ends are ions.

### 3.21 living polymerization

A chain polymerization from which chain transfer and chain termination are absent.

Note: In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization.

### 2.35 macromonomer

A polymer composed of macromonomer molecules.

### 1.9 macromonomer molecule

A macromolecule that has one end-group which enables it to act as a monomer molecule, contributing only a single monomeric unit to a chain of the final macromolecule.

### 3.2 oligomerization

The process of converting a monomer or a mixture of monomers into an oligomer.

Note: An oligomerization by chain reaction carried out in the presence of a large amount of chain-transfer agent, so that the end-groups are essentially fragments of the chain-transfer agent, is termed telomerization.

### 3.15 radical polymerization

A chain polymerization in which the kinetic-chain carriers are radicals.

Note: Usually, the growing chain end bears an unpaired electron.

### 3.13 ring-opening polymerization

A polymerization in which a cyclic monomer yields a monomeric unit which is acyclic or contains fewer cycles than the monomer.

Note: If the monomer is polycyclic, the opening of a single ring is sufficient to classify the reaction as a ring-opening polymerization.