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Terminology for aggregation and self-assembly in polymer science (IUPAC Recommendations 2013)*

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Abstract: In the past, aggregation and self-assembly have been associated principally with micellar and colloidal systems of molecules; however, with the advent of supramolecular chemistry, molecular self-assembly has been opened to a much wider understanding that has facilitated access to a variety of different shapes and sizes, along with the construction of new and fascinating molecular topologies. This document aims at defining more than 150 terms related to aggregation and self-assembly in the particular case of macromolecules. The list is restricted to the most commonly encountered terms.

Keywords: aggregation; IUPAC Polymer Division; polymers; recommendations; self-assembly; terminology.

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1. INTRODUCTION

Until quite recently, aggregation and self-assembly would have been associated principally with micellar and colloidal systems of molecules that would be viewed by polymer scientists as mainly oligomeric. However, with the advent of supramolecular chemistry, molecular self-assembly has been opened to a much wider understanding that has facilitated access to the construction of new and fascinating molecular topologies. The methodologies of polymer science have played a major part in securing these advances.

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Any burgeoning field brings with it a rapidly expanding terminology. Old terms take on new meanings, and new ones appear as the need arises. Some duplication is inevitable, and with the chemistry of aggregation and self-assembly sharing common ground with biological systems at the one extreme and with material physics at the other, there is considerable opportunity for confusion as to what different experts are seeking to convey. Accordingly, in this manuscript we have attempted to assemble a list of the most important terms that are in current use within the field. It is not an exclusive list but is one that should assist the reader who is unfamiliar with the concepts and serve as a guide to the use of standard terminology by those researching in these areas.

For consistency, where they are already satisfactorily defined in the context of polymer science, terms from other IUPAC publications have been used. However, the reader should be aware that some terms might have similar but nonetheless alternative definitions that apply in other contexts. In some instances, definitions of existing terms have been modified to achieve greater generality or else to improve the definitions. Otherwise, the terms and their definitions have been assembled in consultation with experts in the relevant fields.

For ease of reference, the terms are listed alphabetically and numbered sequentially. Cross-references to terms defined elsewhere in the document are denoted in italic typeface. If there are two or more terms on successive lines prior to a common definition, the later entries are accepted synonyms. In instances where two terms have similar though not identical meanings and it is essential that the distinction be recognised, each definition makes cross-reference to the other.

2. TERMINOLOGY

1 aggregate agglomerate

Irregular cluster of otherwise individual molecules or particles.

- *Note 1*: Adapted from definitions in [1-3] so as to emphasize the absence of order.
- *Note* 2: As to whether or not in the wider scientific context the terms "aggregate" and "agglomerate" are distinct from each other is contentious. Definitions of the terms as used within and without the polymer context are presented in [2]. That presented here, though a revised definition, is consistent with the former.

2 aggregation agglomeration

Process whereby otherwise discrete molecules or particles form aggregates.

- Note 1: See also association.
- *Note* 2: Adapted from the definition in [2] to accord with the revised definitions of aggregate and agglomerate.

3 amphiphile

Substance made up of molecules containing groups that are *solvophilic* and other groups that are *solvophobic* with respect to a given solvent.

Note 1: Depending upon the nature of the solvent, the solvophilic and solvophobic parts of the molecule may be ionic or non-ionic moieties.

- *Note* 2: The term is most commonly applied to molecules in aqueous media within which the existence of distinct polar (*hydrophilic*) and nonpolar (*hydrophobic*) regions in the molecule promotes the formation of *micelles*, *vesicles*, or *aggregates*.
- *Note 3*: Corrected from [1], in which the definition is restricted to molecules containing only anionic and cationic parts in an aqueous medium.

3.1 amphiphilic

Qualifier pertaining to amphiphiles.

Note: See also hydrophilic, fluorophilic, lipophilic, and organophilic.

3.2 boloamphiphile

Amphiphile, the constituent molecules of which have solvophilic groups at each end of a solvophobic chain.

4 anisotropic

Qualifier indicating directional dependence of the properties of molecules, molecular assemblies, and materials.

5 assembly

See *self-assembly*.

6 association

Assembly or aggregation of separate molecular or supramolecular entities.

- Note 1: The term is used especially, though not exclusively, for the aggregation of oppositely charged free ions into ion pairs or larger, and not necessarily well-defined, clusters of ions held together by electrostatic attraction.
- *Note* 2: The term signifies the reverse of dissociation, but is not commonly used for the formation of adducts by colligation or coordination (Gold Book online, 1994 entry [1]).
- Note 3: Modified from [1]. The definition proposed here is more general.

7 barotropic mesophase

Mesophase formed by varying the pressure at constant temperature.

8 biomimetic

Imitative of a natural process or material.

9 block

Portion of a macromolecule, comprising many constitutional units, that has at least one constitutional or configurational feature which is not present in the adjacent portions [4,5] (Gold Book online, 1996 entry [1]).

10 block copolymer

Polymer composed of block macromolecules [4].

11 block macromolecule

Macromolecule that is composed of blocks in a linear sequence (Gold Book online, 1996 entry [1]).

12 calamitic

Having a rod- or lath-like shape.

13 carceplex

Host-guest complex formed by a carcerand and a completely entrapped guest.

Note: See also *hemicarceplex*.

14 carcerand

Host molecule that completely entraps a guest molecule.

Note: See also *hemicarcerand*.

15 catenane

Mechanically interlocked molecular architecture consisting of two or more interlocked cycles or macrocycles.

Note: The interlocked rings cannot be separated without breaking covalent bonds.

16 charge-transfer complex

Electron-donor-electron-acceptor complex, characterized by electronic transition(s) to an excited state in which there is a partial transfer of electronic charge from the donor to the acceptor moiety (Gold Book online, 1994 entry [1]).

Note 1: Self-assembly is often driven by charge-transfer complexation.

Note 2: The terms donor-acceptor complex or electron-donor-acceptor complex, which are sometimes employed instead of charge-transfer complex or Lewis adduct, are obsolete terms.

17 clathrate

Inclusion compound in which the *guest* molecule is in a cage formed by the *host* molecule or by a lattice of *host* molecules (Gold Book online, 1994 entry [1]).

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18 co-assembly

Self-assembly of two or more self-assembling species that might or might not incorporate a non-assembling component into an ordered structure.

19 coil-to-globule transition

Change in conformation of a macromolecular chain in solution from that of a coil to a relatively compact structure in which the chain has collapsed upon itself in response to an external stimulus.

- *Note 1*: A coil-to-globule transition is the reverse of a *globule-to-coil transition*.
- *Note* 2: Typical external stimuli may be temperature, pH, electrolyte concentration, or solvent composition.

20 colloid

Synonym for a colloidal system (Gold Book online, 1972 entry [1]).

21 colloidal

Pertaining to a system containing particles of average dimensions between 1 nm and 1 μ m, or else discontinuities of that order, dispersed in an otherwise continuous phase.

- Note 1: The term "colloidal" is usually applied in the context in which the *supramolecular* species are dispersed in a medium.
- Note 2: Modification of the definition in [1], which is ungrammatical.

22 colloidal crystal

Two- or three-dimensional ordered array of molecules or nanoparticles having a dimension roughly between 1 nm and 1 µm in at least one direction.

Note: Examples of colloidal crystals are *photonic crystals* such as opal.

23 columnar phase

Cylindrical *assembly* of molecules within a distinct series of layers in which the axes of the molecules lie in the planes of the layers and are identically aligned and oriented in adjacent layers.

Note: A columnar assembly of discotic molecules, called a columnar mesophase, a columnar discotic mesophase, or a columnar discotic, is one of the class of liquid crystal mesophases [6].

24 complex

Molecular entity formed by the mutual attraction of two or more component molecular entities, ionic or uncharged.

- Note 1: The binding of the components is normally weaker than that of a covalent bond.
- Note 2: Modified from Gold Book online, 1994 entry [1].

25 core-crosslinked micelle

Core-shell structure formed by self-assembly of amphiphiles and subsequently covalently crosslinked through functionalities in the core.

- *Note 1*: The amphiphiles are often *amphiphilic block* copolymers
- *Note* 2: Such structures are used, for example, for drug delivery and dye or adulterant *encapsulation*.
- Note 3: See also shell-crosslinked micelle.

26 core-shell structure

Molecular entity of spherical, elliptical, or cylindrical symmetry in which the constitution of the interior, the core, differs from that of the external surface, the shell.

27 crystal lattice defect crystallographic defect

Interruption to the regular pattern of atomic arrangement in crystal lattices.

Note: In this context, the terms are commonly shortened to "defect".

28 cubic

Pertaining to assemblies of atoms, molecules, or ions with an overall three-dimensional order of cubic symmetry.

29 cubic mesophase

Mesophase with an overall three-dimensional order of cubic symmetry [6].

30 depletion

See negative adsorption.

31 dialysis

Separation of smaller molecular species from larger ones based on their ability to pass selectively through a membrane.

- Note 1: In this context, *supramolecules* are typical examples of relatively large molecular species.
- Note 2: Nanoprecipitation mediated by dialysis is one technique that can be used for the *self-assembly* of polymer nanoparticles.
- *Note 3*: Corrected from [1], in which the definition is restricted to the separation of *colloidal* species.

32 director, n

Local symmetry axis for the singlet, orientational distribution of the molecules of a mesophase [6].

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- *Note 1*: The director is defined as a unit vector, but directions +n and -n are arbitrary.
- *Note* 2: In uniaxial nematics, formed by compounds consisting of either rod- or disc-like molecules, the mean direction of the effective molecular symmetry axis coincides with the director.
- Note 3: The director also coincides with a local symmetry axis of any directional property of the *mesophase*, such as the refractive index or magnetic susceptibility.

33 discotic discoid

Having a disc-like shape.

34 discotic mesogen discoid mesogen

Mesogen composed of relatively flat, disc- or sheet-shaped molecules [6].

Note 1: Examples of discotic mesogens include (a) hexakis(acyloxy)benzenes, (b) hexakis(acyloxy)- and hexaalkoxy-triphenylenes, and (c) 10,15-dihydro-5*H*-diindeno [1,2-a:1',2'-c]fluorene derivatives.

Note 2: The adjective "discotic" is also employed to describe the *nematic mesophases* formed by discotic *mesogens*. The *mesophases* formed by a columnar *stacking* of disc-like molecules are described as *columnar mesophases*.

35 ditopic receptor

See receptor.

36 donor-acceptor complex

See *charge-transfer complex*.

37 double helix

Assembly of two interwined helices with the same axis, differing by a translation along the axis.

- Note 1: Two helices might typically be congruent.
- Note 2: The extent of translation may also vary resulting, typically, in the grooves that are found in DNA.

38 dynamer

Assembly or supramolecular assembly, the components of which are linked through reversible bondings that enable structural reassembly by reshuffling in response to changes in the chemical or physical environment.

Note: Examples include certain poly(acylhydrazones), polyazomethines, and many metallo-supramolecular species.

39 dynamic self-assembly

See self-assembly.

40 edge-face interaction

See *T-stacking*.

41 electroclinic polymer

Polymer with constitutional units that are susceptible to a change in orientation under the influence of an electric field that causes the system to have induced polarity.

42 encapsulation

Confinement of, or act of confining, guest molecules within a host.

- *Note 1*: The host matrix is often polymeric.
- Note 2: Guest materials include catalysts, enzymes, reagents, pharmaceuticals, dyes, fragrances, etc.

42.1 micro-encapsulation

Confinement of microscopic particles with a host.

42.2 molecular encapsulation

Confinement of an individual molecule within a larger molecule.

43 external field

Field surrounding a molecular or ionic species emanating from a source external to that species.

Note: Fields include electromagnetic, hydrodynamic, mechanical, etc.

44 ferroelectric polymer

Polymer that exhibits spontaneous polarization when dipoles become arranged parallel to each other by electric fields (Gold Book online, 2004 entry [1]).

- *Note 1*: See also *ferroelectric transition*.
- *Note* 2: Poly(1,1-difluoroethene) after being subjected to a corona discharge is an example of a ferroelectric polymer.

45 ferroelectric transition

Transition caused by the application of an electric field in which a crystal switches from one stable orientation state to another.

Note: A modification of the entry in [1] in which the transition is erroneously attributed specifically to an application of mechanical stress.

46 ferromagnetic polymer

Polymer that exhibits magnetic properties because it has unpaired electron spins aligned parallel to each other or electron spins that can easily be so aligned (Gold Book online, 2004 entry [1]).

47 ferromagnetic transition

Transition caused by application of magnetic field in which a crystal switches from one stable magnetic state to another.

48 fluorophilic

Qualifier indicating attraction to fluorous compounds.

49 fluorophilic interaction

Attractive interaction of *fluorous* structures.

50 fluorophobic

Qualifier indicating repulsion by *fluorous* compounds.

51 fluorophobic interaction

Repulsive interaction of *fluorous* and non-fluorous structures.

52 fluorous

Pertaining to the presence of a sufficient number of carbon–fluorine bonds as to cause a substance to be insoluble in water or common organic solvents but soluble in fluorocarbons.

53 foldamer

Polymer or oligomer molecule that adopts a *secondary structure* stabilized by noncovalent interactions.

Note: A helix, β -sheet, or *globule* are typical secondary structures.

54 functionality, f

Number of covalent bonds or noncovalent linkages that a monomer molecule, monomeric unit, or pendent group in a macromolecule or oligomer molecule can form with other reactants.

Note: Modification of the definition in [2].

55 gel microparticle

See microgel.

56 gel nanoparticle

See nanogel.

57 globule

Conformation of a macromolecule in which the constitutional units collectively arrange into a compact ovoid or spherical shape.

58 globule-to-coil transition

Reverse of a coil-to-globule transition.

59 guest

Atom, molecule, or ion that occupies a cavity, cleft, or pocket within the structure of a *host* entity.

Note 1: See also *carcerand*.

Note 2: Modified from [1]. The definition proposed here is recommended for its precision.

60 H bond

See hydrogen bond.

61 halogen bond

X bond

Attractive interaction of an electronegative atom and a halogen atom.

- Note 1: The halogen atom may be iodine, bromine, or chlorine but not usually fluorine.
- Note 2: A halogen bond is best considered as an electrostatic interaction between a Lewis base and an electrophilic halogen atom and is dependent on the polarisability and the presence of electronegative substituents on the latter.
- *Note 3*: Halogen bonds may be inter- or intra-molecular.

62 helicity

Chirality of a helical, propeller, or screw-shaped molecular or *supramolecular* entity.

Note: A right-handed *helix* is described as *P* (or plus), a left-handed one as *M* (or minus).

63 helix

Three-dimensional curve resembling a coiled cylindrical spring.

- Note 1: A helix possesses chirality.
- *Note* 2: Regularly repeating rotations around the *backbone* bonds of a macromolecule allow it to assume a helical conformation.
- Note 3: See also helicity.
- Note 4: Modification of the definitions in [9,10] which erroneously define the term through molecular conformation.

64 hemicarceplex

Complex formed by a hemicarcerand and an entrapped guest.

Note: See also carceplex.

65 hemicarcerand

Host molecule that allows *guest* molecules to enter and exit its cavities in accordance with a change in the equilibrium conditions.

Note: See also *carcerand*.

66 heterotopic

See receptor: ditopic receptor.

67 hexagonal mesophase

Columnar mesophase characterized by a hexagonal packing of the molecular column [6].

Note: For further detail, see ref. [5].

68 homotopic

See receptor: ditopic receptor.

69 honeycomb polymer film honeycomb polymer

Hexagonal array of holes in a polymer film.

Note 1: The cross-sectional dimensions of the holes of a hexagonal array are usually less than 1 mm.

Note 2: A method that utilizes the condensation of micrometer-size water droplets on the surface of solutions of block copolymers for the preparation of ordered micrometer-size honeycomb structures has led to the use of the extended term, honeycomb polymer from breath figures.

70 host

Molecular or supramolecular entity with the capacity to bind or trap a guest.

- Note 1: Examples of hosts that form *complexes* with guests include cryptands and crown ethers where there are ion-dipole attractions between heteroatoms and positive ions. Examples of polymers acting as hosts are molecularly imprinted polymers (see *molecular imprinting*).
- *Note* 2: Van der Waals forces and *hydrophobic* interactions bind the guest to the host in inclusion compounds such as *carcerands* and *clathrates*.
- Note 3: Steric factors often significantly influence the binding.
- Note 4: Modified from [1]. The definition presented here is more general.

71 hydrogen bond H bond

Attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation [11].

- Note 1: A typical hydrogen bond may be depicted as X–H···Y–Z, where the three dots denote the bond. X–H represents the hydrogen bond donor. The acceptor may be an atom or an anion Y, or a fragment or a molecule Y–Z, where Y is bonded to Z. In some cases, X and Y are the same. In more specific cases, X and Y are the same and X–H and Y–H distances are the same as well leading to symmetric hydrogen bonds. In any event, the acceptor is an electron-rich region such as, but not limited to, a lone pair of Y or π-bonded pair of Y–Z.
- Note 2: A hydrogen bond is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the periodic table, i.e., N, O, or F.
- *Note 3*: With a few exceptions, usually involving fluorine, the associated energies are less than (20–25) kJ·mol⁻¹.

72 hydrophilic

Qualifier indicating capacity of a molecular entity or of a substituent to interact attractively with polar molecules, in particular with water or with polar groups.

- Note 1: Literally translated as "water loving".
- Note 2: Modified from the definition [1]. The definition presented here is more precise.

73 hydrophilic interaction

Attractive interaction between hydrophilic groups, molecules, or substances.

74 hydrophobic

Qualifier indicating capacity of a molecular entity or of a substituent to interact repulsively with polar molecules, in particular with water or with polar groups.

Note: Literally translated as "water hating".

75 hydrophobic interaction

Repulsive interaction between polar and nonpolar groups, molecules, or substances.

- *Note 1*: The term arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons; however, the phenomenon is more properly attributable to the effect of the hydrocarbon-like groups disrupting the water—water interaction.
- Note 2: The misleading alternative term "hydrophobic bond" is discouraged.
- *Note 3*: Modified from [1]. The definition presented here is more precise.

76 inverse opal

Colloidal crystal of spherical voids with a periodic structure within a solid polymer continuum.

Note: An inverse opal is usually produced by assembling spheres, filling the interstitial spaces with solid, and removing the spheres.

77 ionic surfactant

See surfactant.

78 isotropic

Qualifier indicating directional non-dependence of the properties of molecules, molecular *assemblies*, and materials.

79 knedel

See shell-crosslinked micelle.

80 lamella

Organized structure extended in two dimensions and of uniform thickness resembling a thin layer, a plate, or a membrane.

80.1 lamellar block copolymer

Assembly of block copolymer molecules in which like blocks are segregated in lamella.

Note: Individual lamellae are usually of a thickness of 5–100 nm.

80.2 lamellar crystal

Type of crystal with a large extension in two dimensions and a uniform thickness [1].

Note: A lamellar crystal is usually of a thickness in the (5–100) nm range and may be found individually or in clusters.

81 Langmuir film

Monolayer of insoluble substance at a gas-liquid or liquid-liquid interface.

- *Note 1*: Monolayer formation is facilitated by the decrease in Gibbs energy upon *self-assembly* of the substance at the interface.
- *Note* 2: The term "Langmuir monolayer" has recently been coined for spread *monolayers*. This usage is not recommended because of its close association with Langmuir isotherms.

81.1 Langmuir-Blodgett film

One or more *monolayers* of substance assembled onto a solid substrate by repeated transfer from *Langmuir films* at air–water interfaces.

- *Note 1*: The transfer is achieved either by drawing the substrate through the interface or otherwise contacting it with the interface.
- Note 2: The adsorbed substance is commonly, though not exclusively, an organic amphiphile.
- *Note 3*: See also *layer-by-layer* assembly.

82 layer-by-layer assembly

Process whereby multilayered structures of molecules or particles of a substance are assembled on a solid substrate by sequential adsorption of *monolayers* held together by noncovalent interactions.

- Note 1: The material at the liquid surface need not necessarily be present as a solid monolayer.
- *Note* 2: Layer-by-layer assembly is often used to alternately transfer polyelectrolytes that are positively and negatively charged.
- Note 3: See also Langmuir-Blodgett film.

83 Lehn association

See supramolecular association.

84 ligand

Atoms or molecules joined to the central atom in a coordination compound.

- *Note 1*: The root of the word is often converted into other forms, such as to ligate, meaning to coordinate as a ligand, and the derived participles, ligating and ligated.
- Note 2: The terms "ligating atom" and "donor atom" are used interchangeably.
- Note 3: Adapted from the definition in [1] to accord with the definition of "ligands" on p. 145 of the Red Book [8].

85 lipophilic

Qualifier indicating attraction to or compatibility with nonpolar molecules, in particular hydrocarbons, or to nonpolar entities.

- *Note 1*: The term means "fat loving".
- Note 2: Modified from [1], within which the principle definition is the vagary given here as Note 1.

86 liposome

See vesicle.

87 liquid crystal

Substance in a *mesomorphic state* having long-range orientational order, and either partial positional order or complete positional disorder.

- *Note 1*: Liquid crystals are composed predominantly of rod- or disc-like molecules that can exhibit one or more different, ordered fluid phases as well as the isotropic fluid phase.
- Note 2: For further detail concerning liquid crystals, see ref. [5] or Chapter 7 of ref. [8].
- Note 3: Modified from [1] where the definition is through cross-reference to another term.

88 liquid-crystalline polymer liquid-crystal polymer polymer liquid crystal

Polymer that under suitable conditions of medium, temperature, pressure, and concentration, exists as a liquid-crystalline *mesophase* (Gold Book online, 2004 entry [1]).

- Note 1: See also liquid crystal.
- Note 2: A liquid-crystalline polymer can exhibit one or more liquid state(s) with one- or twodimensional, long-range orientational order over certain ranges of temperatures either in the melt (thermotropic liquid-crystalline polymer) or in solution (lyotropic liquidcrystalline polymer).
- *Note 3*: For further detail concerning liquid-crystalline polymers, see ref. [5] or Chapter 7 of ref. [8].

89 lyophilic

Qualifier indicating affinity for molecules of a solvent.

- *Note 1*: Literally translated as "solvent preferring".
- *Note* 2: Modified from [1] within which the definition is confused by the inclusion of terms for more specific solvent interactions.

90 lyophobic

Qualifier indicating lack of affinity for molecules of a solvent.

Note: Literally translated as "solvent hating".

91 lyotropic mesophase

Mesophase formed by dissolving a *mesogen* in a suitable solvent, under appropriate conditions of concentration, temperature, and pressure [6].

Note: Lyotropic mesophases are amongst the class of *liquid-crystal mesophases* [6].

92 main chain backbone

That linear *chain* to which all other *chains*, *long* or *short* or both, may be regarded as being pendent [1,4,9].

Note: Where two or more *chains* could equally be considered to be the *main chain*, the one that is selected is that which leads to the simplest representation of the molecule.

93 main-chain polymer liquid crystal

Liquid-crystalline polymer, the molecules of which have mesogenic units only in their main chains (Gold Book online, 2002 entry [1]).

94 mechanically interlocked molecular architecture

Supramolecular structure in which molecules are linked only as a consequence of their topology.

Note: Examples of mechanically interlocked molecular architectures include *catenanes* and rotaxanes.

95 mesogen

mesogenic compound mesogenic unit mesomorphic compound

Compound that under suitable conditions of medium, temperature, pressure, and concentration can exist as a *mesophase* or as a *liquid-crystalline phase* [6].

- *Note 1*: When the type of *mesophase* formed is known, more precisely qualifying terminology can be used, e.g., nematogen, chiral nematogen, and smectogen.
- *Note* 2: When more than one type of *mesophase* can be formed, more than one qualification could apply to the same compound and then the general term mesogen should be used.
- *Note 3*: For further detail, see ref. [5].

96 mesomorphic compound

See mesogen.

97 mesomorphic state

State of matter in which the degree of molecular order is intermediate between the perfect three-dimensional order found in crystals and the absence of long-range order found in isotropic liquids, gases, and amorphous solids [6].

Note: Modified from [1], in which the definition includes superfluous explanation of the order found in crystals.

98 mesophase

Phase occurring over a definite range of composition, temperature, and pressure within the *mesomor-phic state*.

Note: Adapted from the definition in [6].

99 metallomesogen

Mesogen composed of molecules incorporating one or more metal atoms.

Note: Metallomesogens may be either *calamitic* or *discotic mesogens* [6], respective examples of which include the following:

100 micellar rod

Rod-like *mesogens* with the capacity to form micellar *aggregates*.

101 micelle

Aggregate of amphiphilic molecules or ions of colloidal dimensions having a core-shell structure with the solvophilic parts directed outwards and the solvophobic parts directed inwards that, under specific conditions, exists in equilibrium with the molecules or ions from which it is formed.

- *Note 1*: Micelles are a particular subgroup of *supramolecules*.
- *Note* 2: "Specific conditions" under which micelles are formed are, e.g., concentration of the solute, nature or composition of the solvent, temperature, and pressure.
- *Note 3*: Examples of molecules that can form micelles are *surfactants* and amphiphilic block copolymers.
- Note 4: Modified from [1]. The definition proposed here is more general.

102 microgel gel microparticle

Particle of gel [2] of any shape with an equivalent diameter of approximately (0.1–100) µm [2].

103 microstructure

Structure of material in which at least one of the features repeats over distances of the order of micrometers.

104 molecular imprinting

Technique to create templated cavities in polymer matrices with memory of the template molecules to be used in *molecular recognition*.

105 molecular recognition

Specific interaction between two or more molecules through noncovalent bonding.

Note: Examples of interactions that facilitate molecular recognition include steric inter-

actions, hydrogen bonding, metal coordination, *hydrophobic* forces, van der Waals forces, π – π interactions, and other electrostatic or electromagnetic effects, or both.

106 molecular self-assembly

See self-assembly.

107 monolayer

Single layer of atoms or molecules.

- *Note 1*: The term "floating monolayer" is used for certain spread monolayers or films which are at an air–liquid interface.
- *Note* 2: Modified from the definition in [1], which stated that within monolayers the atoms or molecules had to be closely packed. That is not always the case.

108 morphology

Shape, optical appearance, or form of phase domains in substances.

- *Note 1*: Morphology is found in substances such as polymers, polymer blends, composites, and crystals.
- *Note* 2: For a polymer blend or composite, the morphology describes the structures and shapes observed, often by microscopy or scattering techniques, of the different phase domains present within the mixture.
- *Note 3*: Modified from [1], in which the definition is incorrectly extended to include the detail of Note 1.

109 nanocomposite

Composite in which at least one of the phase domains has at least one dimension of the order of nanometers (Gold Book online, 2007 entry [1]).

110 nanodomain

Region of a self-assembled entity with an equivalent diameter of approximately (1–100) nm.

111 nanogel

gel nanoparticle

Particle of gel of any shape with equivalent diameter of approximately (1–100) nm.

112 nanoscopic polymer film

Polymer film that has lateral dimensions in the range of (1–100) nm.

113 nanostructure

Structure in which at least one of the features repeats over distances of the order of nanometers.

114 negative adsorption

Depletion of one or more components in an interfacial layer [1].

Note: Because of its wider usage, the use of "depletion" as a synonym is discouraged.

115 nematogen

See mesogen.

116 nonionic surfactant

See surfactant.

117 order parameter, $\langle P_2 \rangle$

Parameter characterizing long-range orientational order with reference to the *director*, with $\langle P_2 \rangle = (3\langle \cos^2 \beta \rangle - 1)/2$, where β is the angle between the molecular symmetry axis and the director, and $\langle \rangle$ denotes an ensemble average [6].

118 organophilic

Qualifier indicating tendency of a molecular entity or of a pendent group thereof to interact favourably with nonpolar organic solvents.

- *Note 1*: The term is especially used of *colloids* that form solvates in organic solvents and thereby swell.
- Note 2: See also lipophilic.

119 organophilic interaction

Attractive interaction between organophilic molecules or materials.

120 orientation parameter

Order parameter applied to macroscopic assemblies of ordered materials, such as crystal assemblies in fibers.

121 pendent chain side-chain branch

Oligomeric or polymeric offshoot from a macromolecular chain.

- Note 1: An oligomeric branch may be termed a "short-chain branch".
- Note 2: A polymeric branch may be termed a "long-chain branch".

122 photonic crystal

Periodic optical *nanostructure* designed to affect the transmission of photons.

123 polyelectrolyte

Polymer composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both [7].

- Note 1: See definition 1.65 in [4].
- *Note* 2: The terms "polymeric electrolyte" and "polymer electrolyte" are sometimes used for polyelectrolyte. They should not be confused with the term "solid polymer electrolyte".
- *Note 3*: Polyelectrolytes can be either synthetic or natural. Nucleic acids, proteins, teichoic acids, some polypeptides, and some polysaccharides are examples of natural polyelectrolytes.

124 polyelectrolyte complex

Polymer–polymer *complex* composed of macromolecules carrying charges of opposite sign causing the macromolecules to be bound together by electrostatic interactions [7].

Note: A polyelectrolyte complex is also called a "polysalt". Use of this term is not recommended.

125 polymer crystal

Polymer domain exhibiting three-dimensional crystalline order at the atomic scale [10].

Note 1: Polymer crystals are usually much smaller and frequently do not display the perfection that is usual for low-molar-mass substances. Sizes range from 2–3 nm to a few μm, with more typical values, in one or more dimensions, around 10 nm.

Note 2: Polymer crystals can be twinned (twinned polymer crystals) or untwinned (polymer single crystals).

126 polymer liquid crystal

See *liquid-crystalline polymer*.

127 polymersome

Vesicle with radius ranging from 50 nm to greater than 5 μ m constructed from an amphiphilic synthetic block copolymer [12].

Note:

Most reported polymersomes serve as *hosts* for an aqueous solution and are useful for the accommodation or temporary trapping of molecules such as drugs, enzymes, and other proteins and peptides in in vivo applications.

128 polymolecular

Consisting of many molecules.

129 polyrotaxane

Polymer comprising *mechanically interlocked molecular architectures* typically of a macromolecule threaded through one or more macrocycles.

- Note 1: The macrocycle(s) may be threaded onto the polymer backbone or side-chains.
- *Note* 2: A polyrotaxane may also be composed of macromolecules comprising one or more macrocyclic main-chain or side-chain units threaded with linear chains.
- *Note 3*: A more detailed definition is presented in [13].

130 primary structure

Sequence of constitutional units in a macromolecule such as a protein, an oligomer molecule, or a block.

- *Note 1*: In proteins, by primary structure the sequential arrangement of amino-acid residues is meant, including crosslinking of chains.
- Note 2: See also secondary structure, tertiary structure, and quaternary structure.
- Note 3: Modified from [1], in which the definition confuses structure with formula.

131 quaternary structure

Defined organization of two or more macromolecules with tertiary structure.

- Note 1: Examples are protein molecules held together by hydrogen bonds, and van der Waals and coulombic forces.
- Note 2: See also primary structure, secondary structure, and tertiary structure.

132 random coil

Complete set of spatial arrangements of a chain molecule with a large number of segments that randomly change mutual orientation with time, under theta conditions in which it is free from external constraints that would affect its conformation [9].

Note 1: See also statistical coil.

Note 2: Modified from [1], in which the definition is that of a statistical coil.

133 receptor

Structural feature in or on a *host* molecule that specifically recognizes and thereby binds to a structural feature of a *guest* species.

Note: This definition is recommended as being more general than that in the Gold Book [1], which is set exclusively in the context of medicinal chemistry.

133.1 ditopic receptor

Receptor with two binding sites.

Note: Ditopic receptors can be either *homotopic* or *heterotopic* according to whether or not the binding sites are the same (typically, *self-complementary* binding sites) or different.

134 rod-coil copolymer

Copolymer the molecules of which consist of rigid and flexible blocks.

135 Scatchard equation

Equation used to calculate the association constant, K_a , of a *ligand* with a protein molecule.

Note 1: The Scatchard equation is

$$\frac{r}{c} = -K_{\rm a}r + K_{\rm a}n$$

in which r is the ratio of the concentration of bound ligand to the concentration of available protein binding sites, c is the concentration of free ligand, and n is the number of binding sites per protein molecule.

Note 2: The association constant, K_a , has units of reciprocal concentration.

136 Scatchard plot

Linear plot of r/c against r in accordance with the Scatchard equation.

137 secondary structure

Conformational arrangement of the *backbone* segments of a macromolecule without regard to the conformation of the side-chains or the relationship to other segments (Gold Book online, 1996 entry [1]).

Note 1: A typical example is the conformation of a polypeptide chain of a protein.

- *Note 2*: Typical conformations might be α -helices, β -pleated sheets, etc.
- *Note 3*: See also *primary structure*, *tertiary structure*, and *quaternary structure*.

138 self-assembled monolayer (SAM)

Ordered monolayer formed spontaneously on a surface by adsorption.

139 self-assembly self-organization molecular self-assembly dynamic self-assembly

Spontaneous and reversible organization of molecular entities by noncovalent interactions.

- *Note 1*: Typical noncovalent interactions are van der Waals interactions, π – π interactions, electrostatic interactions, and *hydrogen bonds*.
- Note 2: Self-assembly is a process in which a system of pre-existing components, under specific conditions, adopts a more organized structure through interactions between the components themselves.

139.1 main-chain self-assembly

Inter- or intra-molecular self-assembly of constitutional units within the backbones of polymer molecules.

139.2 side-chain self-assembly

Inter- or intra-molecular self-assembly of side-chains or constitutional units of polymer molecules.

140 self-complementary

See receptor: ditopic receptor.

141 self-organization

See self-assembly.

142 shell-crosslinked micelle knedel

Core-shell structure formed by self-assembly of amphiphiles and subsequently covalently crosslinked through functionalities in the shell.

- Note 1: The amphiphiles are often amphiphilic block copolymers.
- Note 2: Such structures are used, e.g., in drug delivery and dye encapsulation.
- Note 3: See also core-crosslinked micelle.

143 side-chain

See pendent chain.

144 smectic

Pertaining to the arrangement and orientation of molecules in a *smectic mesophase*.

145 smectic mesophase

Mesophase that has the molecules arranged in layers with a well-defined layer spacing or periodicity [6].

- *Note 1*: There are several types of smectic mesophases, characterised by a variety of molecular arrangements within the layers.
- Note 2: Although the total number of smectic mesophases cannot be specified, the following types have been defined: SmA, SmB, SmC, SmF, and SmI. The alphabetical order of suffixes merely indicates an order of discovery.
- Note 3: Smectic mesophases are amongst the class of liquid-crystal mesophases [6].
- Note 4: For further detail, see ref. [5].

146 spherand

Macrocyclic compound capable of completely enveloping a cation, having donor atoms (O, N, S) arranged such that they provide a solvation sphere to the encapsulated cation.

147 stacking

See assembly.

147.1 pi-pi stacking

π – π stacking

Inter- or intra-molecular alignment of aromatic groups within molecules induced by the interactional overlap of their π -orbitals.

Note: π - π Interactions become stronger as the number of π -electrons increases.

147.2 T-stacking

edge-face interaction

Orthogonal alignment of constitutional units within molecules that lead to favourable interactions.

Note: T-stacking is often seen in proteins where the partially positively charged hydrogen atom of one aromatic system points to the centre of the aromatic plane of another aromatic system.

148 static self-assembly

Self-assembly at equilibrium.

149 statistical coil

Complete set of spatial arrangements of a chain molecule with a large number of segments that change mutual orientation with time in accordance with statistical rules. In the absence of external constraints that would affect conformation, this would equate to a *random coil*.

Note 1: The terms "statistical coil" and "random coil" are often erroneously regarded as synonyms.

Note 2: See also random coil.

150 stereoblock macromolecule

Block macromolecule composed of blocks of differing stereoregularity.

Note: Modified from [1]. The definition presented here avoids cross-reference to two other related definitions.

151 stimuli-responsive polymer

Polymer that responds reversibly to external stimulus or stimuli.

Note: The external stimuli might be temperature, incident radiation, pH, etc., and responses would be manifest as changes in a physical property such as conformation, aggregation,

liquid-crystalline state, absorption spectrum, emission spectrum, etc.

152 solvophilic

Qualifier indicating an affinity for solvents.

153 solvophobic

Qualifier indicating a lack of affinity for solvents.

154 supramolecular assembly supramolecular species supramolecular structure supramolecule

Molecular system comprising two or more self-assembled molecular, or molecular and ionic, entities held together by means of noncovalent intermolecular binding interactions.

- *Note 1*: Modified from [1]. The definition proposed here more adequately covers all the synonyms that have entered usage since supramolecule was first defined.
- *Note* 2: While a supramolecular assembly may comprise only two molecular or molecular/ionic entities, for example, a DNA double helix or a *host–guest* complex, the term is more commonly used to denote larger constructs, typically with rod-, sheet-like, or spherical structures.
- Note 3: The dimensions of supramolecular assemblies can range from nanometers to micrometers
- Note 4: Use of the term "supramolecular polymer" is discouraged.

155 supramolecular association Lehn association

Self-assembly involving reversible, noncovalent, directional interactions of molecules that result in a high-molecular-mass entity.

Note: Use of the term "supramolecular polymerization" is discouraged.

156 surfactant

surface active agent

Substance that when dissolved in a medium is positively adsorbed at the interfaces, thereby lowering interfacial tensions with other phases.

- *Note 1*: Surfactants might be ionic or non-ionic substances.
- *Note* 2: Modified from [1], in which it is implied that the preferential adsorption of the surfactant is a consequence of the change in surface tension, and not the other way round.

157 template polymerization

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

158 tertiary structure

Spatial organization, including conformation, of an entire macromolecule.

- Note 1: See also primary structure, secondary structure, and quaternary structure.
- Note 2: The tertiary structure is essential for the function of protein molecules.
- Note 3: Corrected from [1] in which the definition is more restrictive.

159 thermotropic mesophase

Mesophase formed by heating a solid or cooling an isotropic liquid, or by heating or cooling a thermodynamically stable mesophase at constant pressure (Gold Book on-line, entry 2002 [1]).

160 vesicle

Surfactant-, amphiphilic-polymer-, or lipid-membrane-enclosed sac dispersed in a solvent.

Note: Most commonly, the dispersion medium is water.

160.1 lipid vesicle

liposome

Vesicle constructed from a lipid bilayer.

- Note 1: Liposomes have potential use in drug delivery.
- *Note* 2: Modified from [1], in which the definition refers only to phospholipid compartmentalization of a droplet.

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5. INDEX OF TERMS

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