

3: Definitions of Terms Relating to Individual Macromolecules, Their Assemblies, and Dilute Polymer Solutions

CONTENTS

Preamble

1. Individual macromolecules
2. Assemblies of macromolecules
3. Dilute polymer solutions

References

PREAMBLE

This document is part of a series published by the Commission on Macromolecular Nomenclature dealing with definitions for the important terms in polymer science [1-3]. The recommendations presented here deal with such key areas of the physical chemistry of macromolecules as individual macromolecules, their assemblies and dilute polymer solutions; they include recommended terminology for molecular weight, molecular-weight averages, distribution functions, radius of gyration, the Flory-Huggins theory, viscosity of solutions, scattering of radiation by polymers, fractionation, etc.

The reader's attention is especially directed to the new terms 'uniform polymer' and 'nonuniform polymer' which denote polymers composed of molecules that are uniform or nonuniform, respectively, with respect to relative molecular mass and constitution. These terms replaced the widely used, but non-descriptive and self-contradictory terms 'monodisperse polymer' and 'polydisperse polymer'.

1 INDIVIDUAL MACROMOLECULES

1.1 relative molecular mass, M_r molecular weight

Ratio of the average mass per formula unit of a substance to 1/12 of the mass of an atom of nuclide ^{12}C .

Note: See Definition 1.2.

1.2 molar mass, M

Mass divided by amount of substance.

Note 1: Molar mass is usually expressed in g mol^{-1} or kg mol^{-1} units. The g mol^{-1} unit is recommended in polymer science, since then the numerical values of the molar mass and the *relative molecular mass* of a substance are equal.

Originally prepared by a working group consisting of P. Kratochvíl (Czech Republic) and U. W. Suter (Switzerland). Reprinted from *Pure Appl. Chem.* **61**, 211-241 (1989), with changes and corrections (2006).

Note 2: *Relative molecular mass* (relative molar mass, *molecular weight*) is a pure number and must not be associated with any units.

Note 3: The dalton, symbol Da, is an alternative name for the unified atomic mass unit, m_u , symbol u, i.e., $m_u = 1$ u.

Note 4: The terms ‘molar’ and ‘molecular’ may also be used for particles consisting of more than one molecule, such as complexes, aggregates, micelles, etc.

Note 5: If there is no danger of confusion, the subscript r in the recommended symbol for the relative molecular mass, M_r , may be omitted.

1.3 degree of polymerization (DP), X

Number of monomeric units in a macromolecule or an oligomer molecule, a block, or a chain.

1.4 thermodynamically equivalent sphere

Sphere, impenetrable to other spheres, displaying the same *excluded volume* as an actual polymer molecule.

1.5 short-range intramolecular interaction

Steric or other interaction involving atoms or groups or both situated nearby in sequence along a polymer chain.

Note 1: The interacting atoms or groups are typically separated by fewer than ten consecutive bonds in a chain.

Note 2: If no confusion can occur, the word ‘intramolecular’ may be omitted.

1.6 long-range intramolecular interaction

Interaction between segments, widely separated in sequence along a polymer chain, that occasionally approach one another during molecular flexing.

Note 1: This type of interaction is closely related to the *excluded volume of a segment*, the latter quantity reflecting interactions involving segments and solvent molecules.

Note 2: If no confusion can occur, the word ‘intramolecular’ may be omitted.

1.7 unperturbed dimensions

Dimensions of an actual polymer *random coil* in a *theta state*.

1.8 perturbed dimensions

Dimensions of an actual polymer *random coil* not in a *theta state*.

1.9 radius of gyration, s , $\langle s^2 \rangle^{1/2}$

Parameter characterizing the size of a particle of any shape.

For a rigid particle consisting of mass elements of mass m_i , each located at a distance r_i from the centre of mass, the radius of gyration, s , is defined as the square root of the mass-average of r_i^2 for all the mass elements, i.e.,

$$s = \left(\frac{\sum_i m_i r_i^2}{\sum_i m_i} \right)^{1/2}$$

For a non-rigid particle, an average over all conformations is considered, i.e.,

TERMINOLOGY

$$\langle s^2 \rangle^{1/2} = \langle \sum_i m_i r_i^2 \rangle^{1/2} / \left(\sum_i m_i \right)^{1/2}$$

Note: The subscript zero is used to indicate *unperturbed dimensions* as in $\langle s^2 \rangle_0^{1/2}$.

1.10 end-to-end vector, $r \rightarrow \underline{r}$

Vector connecting the two ends of a linear macromolecular chain in a particular conformation.

1.11 end-to-end distance, r

Length of the *end-to-end vector*.

1.12 root-mean-square end-to-end distance, $\langle r^2 \rangle^{1/2}$

Square root of the mean-square *end-to-end distance* of a linear macromolecular chain averaged over all conformations of the chain. For a *freely jointed chain* consisting of N segments each of length L , $\langle r^2 \rangle^{1/2} = N^{1/2} L$.

Note 1: The subscript zero is used to indicate *unperturbed dimensions*, as in $\langle r^2 \rangle_0^{1/2}$.

Note 2: If this term is used repeatedly, and if it is not confusing, the abbreviated name 'end-to-end distance' may be used.

1.13 characteristic ratio, C_N (C_∞ when $N \rightarrow \infty$)

Ratio of the mean-square *end-to-end distance*, $\langle r^2 \rangle_0$, of a linear macromolecular chain in a *theta state* to NL^2 , where N is the number of rigid sections in the main chain, each of length L ; if all of the rigid sections are not of equal length, the mean-square value of L is used, i.e.,

$$L^2 = \sum_i \overline{L_i^2} / N$$

Note: In simple single-strand chains, the bonds are taken as the rigid sections.

1.14 contour length

Maximum *end-to-end distance* of a linear macromolecular chain.

Note 1: For a single-strand polymer molecule with skeletal bonds all joined by the same value of valence angle, the contour length is equal to the *end-to-end distance* of the chain extended to the all-trans conformation. For chains of complex structures, only approximate values of the contour length may be accessible.

Note 2: The sum of the lengths of all skeletal bonds of a single-strand polymer molecule is occasionally termed 'contour length'. This use of the term in this sense is discouraged.

1.15 random coil, statistical coil

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

Note: If the solution of the chain molecules is not in a *theta state*, the segments change mutual orientation only approximately randomly.

1.16 freely jointed chain

Hypothetical linear chain consisting of infinitely thin rectilinear segments uniform in length, each of which can take all orientations in space with equal probability, independently of its neighbours.

Note 1: For models in which the segments are not all uniform in length, the name ‘random-walk chain’ has been used.

Note 2: In the freely-jointed-chain approach, two or more segments can occupy the same volume simultaneously.

1.17 equivalent chain

Hypothetical *freely jointed chain* with the same *mean-square end-to-end distance* and *contour length* as an actual macromolecular chain in a *theta state*.

1.18 statistical segment

Segment of an actual macromolecular chain which behaves, with respect to some property, virtually as a segment of a *freely jointed chain*.

1.19 freely rotating chain

Hypothetical linear chain molecule, free from *short-range* and *long-range interactions*, consisting of infinitely thin rectilinear segments (bonds) of fixed length, jointed at fixed bond angles; the torsion angles of the bonds can assume all values with equal probability.

1.20 steric factor, σ

Ratio of the *root-mean-square end-to-end distance* of a macromolecular chain with *unperturbed dimensions*, $\langle r^2 \rangle_0^{1/2}$, to that of a *freely rotating chain* with the same structure, $\langle r^2 \rangle_{0,f}^{1/2}$, i.e., $\left(\langle r^2 \rangle_0 / \langle r^2 \rangle_{0,f} \right)^{1/2}$ in the limit of infinite chain length.

Note: The steric factor reflects the effect of hindrance to free rotation.

1.21 worm-like chain continuously curved chain

Hypothetical linear macromolecule consisting of an infinitely thin chain of continuous curvature; the direction of curvature at any point is random.

Note 1: The model describes the whole spectrum of chains with different degrees of chain stiffness from rigid rods to *random coils*, and is particularly useful for representing stiff chains.

Note 2: In the literature this chain is sometimes referred to as Porod-Kratky chain.

1.22 persistence length, a

Average projection of the *end-to-end vector* on the tangent to the chain contour at a chain end in the limit of infinite chain length.

Note: The persistence length is the basic characteristic of the *worm-like chain*.

1.23 short-chain branch

Oligomeric offshoot from a macromolecular chain.

1.24 long-chain branch

Polymeric offshoot from a macromolecular chain.

TERMINOLOGY

1.25 branching index, g

Parameter characterizing the effect of *long-chain branches* on the size of a branched molecule in solution and defined as the ratio of the mean-square *radius of gyration* of a branched molecule, $\langle s_b^2 \rangle$, to that of an otherwise identical linear molecule $\langle s_l^2 \rangle$, with the same *relative molecular mass* in the same solvent at the same temperature, i.e., $g = \langle s_b^2 \rangle / \langle s_l^2 \rangle$.

1.26 network

Highly ramified polymer structure in which each constitutional unit is connected to each other constitutional unit and to the macroscopic phase boundary by many permanent paths through the structure, their number increasing with the average number of intervening bonds; these paths must on the average be coextensive with this structure.

Note 1: Usually, and in all systems that exhibit rubber elasticity, the number of distinct paths is very high, but some constitutional units exist, in most cases, which are connected by a single path only. Sometimes, a structure without any multiple path has also been called a network.

Note 2: If the permanent paths through the structure of a network are all formed by covalent bonds, the term covalent network may be used.

Note 3: The term physical network may be used if the permanent paths through the structure of a network are not all formed by covalent bonds but, at least in part, by physical interactions, such that removal of the interactions leaves individual macromolecules or a macromolecule that is not a network.

Note 4: See also Definition 4.1.21 in Chapter 11.

1.27 microgel

Particle of a *gel* of any shape with an equivalent diameter of approximately 0.1 to 100 μm .

1.28 copolymer micelle

Micelle formed by one or more block or graft copolymer molecules in a *selective solvent*.

2 ASSEMBLIES OF MACROMOLECULES

2.1 compositional heterogeneity

Variation in elemental composition from molecule to molecule usually found in copolymers.

2.2 constitutional heterogeneity

Variation in constitution from molecule to molecule in polymers with molecules uniform with respect to elemental composition.

Note: An example is a polymer composed of linear and branched molecules; another example is a statistical copolymer comprising two isomeric constitutional units.

2.3 uniform polymer monodisperse polymer

Polymer composed of molecules uniform with respect to *relative molecular mass* and constitution.

Note 1: A polymer comprising a mixture of linear and branched chains, all of uniform *relative molecular mass*, is not uniform.

Note 2: A copolymer comprising linear molecules of uniform relative molecular mass and uniform elemental composition, but different sequence arrangement of the various types of monomeric units, is not uniform (e.g., a copolymer comprising molecules with random arrangement as well as block arrangement of monomeric units).

Note 3: A polymer uniform with respect only to either relative molecular mass or constitution may be termed ‘uniform’, provided a suitable qualifier is used (e.g., ‘a polymer uniform with respect to relative molecular mass’).

Note 4: The adjectives ‘monodisperse’ and ‘polydisperse’ are deeply rooted in the literature despite being non-descriptive and self-contradictory. They are in common usage and it is recognized that they will continue to be used for a certain time, nevertheless more satisfactory terms are clearly desirable. After an extensive search for possible replacements, the new terms ‘uniform’ and ‘non-uniform’ have been selected and they are now the preferred adjectives.

2.4 non-uniform polymer polydisperse polymer

Polymer comprising molecules non-uniform with respect to *relative molecular mass* or constitution or both.

Note: See Definition 2.3, Note 3.

2.5 molar-mass average, \overline{M}_k , relative-molecular-mass average/molecular-weight average, $\overline{M}_{r,k}$

Any average of the *molar mass* or *relative molecular mass* (*molecular weight*) for a non-uniform polymer. In both symbols, k specifies the type of average.

Note 1: An infinite number of molar-mass averages can in principle be defined, but only a few types of averages are directly accessible experimentally. The most important averages are defined by simple moments of the *distribution functions* and are obtained by methods applied to systems in thermodynamic equilibrium, such as osmometry, light scattering and sedimentation equilibrium. Hydrodynamic methods, as a rule, yield more complex molar-mass averages.

Note 2: Any molar-mass average can be defined in terms of mass fractions or mole fractions. In this document only a few of the important molar-mass averages are given in terms of the mass fractions, w_i , of the species with molar mass M_i . These definitions are most closely related to the experimental determination of molar-mass averages.

2.6 number-average molar mass, \overline{M}_n

$$\overline{M}_n = \frac{1}{\sum_i (w_i / M_i)}$$

number-average relative molecular mass
number-average molecular weight, $\overline{M}_{r,n}$

$$\overline{M}_{r,n} = \frac{1}{\sum_i (w_i / M_{r,i})}$$

For definitions of symbols, see Definition 2.5.

TERMINOLOGY

2.7 mass-average molar mass, \overline{M}_w

$$\overline{M}_w = \sum_i w_i M_i$$

**mass-average relative molecular mass, $\overline{M}_{r,w}$
weight-average molecular weight**

$$\overline{M}_{r,w} = \sum_i w_i M_{r,i}$$

For definitions of symbols, see Definition 2.5.

2.8 z-average molar mass, \overline{M}_z

$$\overline{M}_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i}$$

**z-average relative molecular mass, $\overline{M}_{r,z}$
z-average molecular weight**

$$\overline{M}_{r,z} = \frac{\sum_i w_i M_{r,i}^2}{\sum_i w_i M_{r,i}}$$

For definitions of symbols, see Definition 2.5.

2.9 (z + 1)-average molar mass, \overline{M}_{z+1}

$$\overline{M}_{z+1} = \frac{\sum_i w_i M_i^3}{\sum_i w_i M_i^2}$$

**(z + 1)-average relative molecular mass, $\overline{M}_{r,z+1}$
(z + 1)-average molecular weight**

$$\overline{M}_{r,z+1} = \frac{\sum_i w_i M_{r,i}^3}{\sum_i w_i M_{r,i}^2}$$

For definitions of symbols, see Definition 2.5.

2.10 viscosity-average molar mass, \overline{M}_v

$$\overline{M}_v = \left[\sum_i w_i M_i^\alpha \right]^{1/\alpha}$$

viscosity-average relative molecular mass, $\overline{M}_{r,v}$
viscosity-average molecular weight

$$\overline{M}_{r,v} = \left[\sum_i w_i M_{r,i}^a \right]^{1/a}$$

where a is the exponent in the *Mark-Houwink equation*, $[\eta] = KM^a$; For definitions of the other symbols, see Definition 2.5.

Note: The exponent a is not identical with the adjustable parameter of some of the *distribution functions* or with the *persistence length*.

2.11 apparent molar mass, M_{app}
apparent relative molecular mass, $M_{r,app}$
apparent molecular weight

Molar mass, relative molecular mass, or molecular weight calculated from experimental data without the application of appropriate corrections, such as for finite polymer concentration, association, preferential solvation, *compositional heterogeneity*, *constitutional heterogeneity*.

2.12 average degree of polymerization, \overline{X}_k

Average of the *degree of polymerization* for a polymer, where k specifies the type of average.

Note: Definitions 2.5-2.10 apply directly to averages of the degree of polymerization when X is substituted for M in the formulae.

2.13 distribution function

Normalized function giving the relative amount of a portion of a polymeric substance with a specific value, or a range of values, of a random variable or variables.

Note 1: Distribution functions may be discrete, i.e., take on only certain specified values of the random variable(s), or continuous, i.e., take on any intermediate value of the random variable(s), in a given range. Most distributions in polymer science are intrinsically discrete, but it is often convenient to regard them as continuous or to use distribution functions that are inherently continuous.

Note 2: Distribution functions may be integral (or cumulative), i.e., give the proportion of the population for which a random variable is less than or equal to a given value. Alternatively they may be differential distribution functions (or probability density functions), i.e., give the (maybe infinitesimal) proportion of the population for which the random variable(s) is (are) within a (maybe infinitesimal) interval of its (their) range(s).

Note 3: Normalization requires that: (i) for a discrete differential distribution function, the sum of the function values over all possible values of the random variable(s) be unity; (ii) for a continuous differential distribution function, the integral over the entire range of the random variable(s) be unity; (iii) for an integral (cumulative) distribution function, the function value at the upper limit of the random variable(s) be unity.

2.14 number-distribution function

Distribution function in which the relative amount of a portion of a substance with a specific value, or a range of values, of the random variable(s) is expressed in terms of mole fraction.

TERMINOLOGY

2.15 mass-distribution function weight-distribution function

Distribution function in which the relative amount of a portion of a substance with a specific value, or a range of values, of the random variable(s) is expressed in terms of mass fraction.

2.16 Schulz-Zimm distribution

Continuous distribution with the *differential mass-distribution function* of the form

$$f_w(x) dx = \frac{a^{b+1}}{\Gamma(b+1)} x^b \exp(-ax) dx,$$

where x is a parameter characterizing the chain length, such as *relative molecular mass* or *degree of polymerization*, a and b are positive adjustable parameters, and $\Gamma(b+1)$ is the gamma function of argument $(b+1)$.

2.17 most probable distribution

Discrete distribution with the *differential mass-distribution function* of the form

$$f_w(x) = a^2 x (1-x)^{x-1},$$

For definitions of symbols, see Definition 2.16.

Note 1: For large values of x , the *most probable distribution* converges to the particular case of the *Schulz-Zimm distribution* with $b = 1$.

Note 2: In the literature, this distribution is sometimes referred to as the Flory distribution or the Schulz-Flory distribution.

2.18 Poisson distribution

Discrete distribution with the *differential mass-distribution function* of the form

$$f_w(x) = \frac{x e^{-a} a^{x-1}}{(a+1)(x-1)!},$$

For definitions of symbols, see Definition 2.16.

2.19 Tung distribution

Continuous distribution with the *differential mass-distribution function* of the form

$$f_w(x) dx = abx^{b-1} \exp(-ax^b) dx,$$

For definitions of symbols, see Definition 2.16.

2.20 logarithmic normal distribution

Continuous distribution with the *differential mass-distribution function* of the form

$$f_w(x) dx = \frac{1}{ax\sqrt{\pi}} \exp\left(-\frac{1}{a^2} \left[\ln\left(\frac{x}{b}\right)\right]^2\right) dx$$

For definitions of symbols, see Definition 2.16.

2.21 polymolecularity correction

Correction applied to relationships between a property and the *molar mass* or *relative molecular mass*, obtained from polymers *non-uniform* with respect to *relative molecular mass*, in order to obtain the corresponding relationship for polymers strictly *uniform* with respect to *relative molecular mass*.

3 DILUTE POLYMER SOLUTIONS

3.1 General and Thermodynamic Terms

3.1.1 dilute solution

Solution in which the sum of the volumes of the domains occupied by the solute molecules or particles is substantially less than the total volume of the solution.

Note: The term ‘domain’ refers to the smallest convex body that contains the molecule or particle in its average shape.

3.1.2 cross-over concentration, c^* overlap concentration

Concentration range at which the sum of the volumes of the domains occupied by the solute molecules or particles in solution is approximately equal to the total volume of that solution.

Note 1: For the meaning of the term ‘domain’, see the note in Definition 3.1.1.

Note 2: Cross-over concentration is defined as a range because different measurement techniques give different values. The symbol c^* refers usually to amount concentration, but in polymer science it is generally used for mass concentration.

3.1.3 polymer-solvent interaction

Sum of the effects of all intermolecular interactions between polymer and solvent molecules in solution that are reflected in the values of the Gibbs and Helmholtz energies of mixing.

3.1.4 thermodynamic quality of solvent quality of solvent

Qualitative characterization of the *polymer-solvent interaction*. A solution of a polymer in a ‘better’ solvent is characterized by a higher value of the *second virial coefficient* than a solution of the same polymer in a ‘poorer’ solvent.

3.1.5 theta state θ state

State of a polymer solution for which the *second virial coefficient* is zero.

TERMINOLOGY

Note 1: In some respects, a polymer solution in the theta state resembles an ideal solution and the theta state may be referred to as a pseudo-ideal state. However, a solution in the theta state must not be identified with an ideal solution.

Note 2: The solvent involved is often referred to as ‘theta solvent’ or ‘ θ solvent’.

Note 3: It is assumed that the *degree of polymerization* of the polymer is high.

3.1.6 theta temperature; θ , SI unit: K θ temperature

Temperature at which a solution is in the *theta state*.

3.1.7 virial coefficients, A_i where $i = 1, 2$, etc. virial coefficients of the chemical potential

Coefficients in the expansion of the chemical potential of the solvent, μ_s , in powers of the mass concentration, c , of the solute, i.e.,

$$\mu_s - \mu_s^0 = -\pi V_s = -RTV_s (A_1 c + A_2 c^2 + A_3 c^3 + \dots),$$

where μ_s^0 is the chemical potential of the solvent in the reference state at the temperature of the system and ambient pressure, π is the osmotic pressure and V_s is the partial molar volume of the solvent. In solvents comprising more than one component, the definition applies to any solvent component. The first virial coefficient is the reciprocal *number-average molar mass*, i.e., $A_1 = 1/\overline{M}_n$. The second and higher virial coefficients, A_2, A_3, \dots , respectively, describe *polymer-solvent* and *polymer-polymer* interactions.

Note: The factor RT is sometimes included in the virial coefficients.

3.1.8 excluded volume of a segment

Volume from which a segment of a macromolecule in solution effectively excludes all other segments, i.e., those belonging to the same macromolecule as well as those belonging to other macromolecules.

Note: The excluded volume of a segment depends on the Gibbs and Helmholtz energies of mixing of solvent and polymer, i.e., on the *thermodynamic quality of the solvent*, and is not a measure of the geometrical volume of that segment.

3.1.9 excluded volume of a macromolecule

Volume from which a macromolecule in a dilute solution effectively excludes all other macromolecules.

Note: The excluded volume of a macromolecule depends on the Gibbs and Helmholtz energies of mixing of solvent and polymer, i.e., on the *thermodynamic quality of the solvent*, and is not a measure of the geometrical volume of that macromolecule.

3.1.10 expansion factor $\alpha_r, \alpha_s, \alpha_\eta$

Ratio of a dimensional characteristic of a macromolecule in a given solvent at a given temperature to the same dimensional characteristic in the *theta state* at the same temperature. The most frequently used expansion factors are: expansion factor of the *mean-square end-to-end distance*, $\alpha_r = (\langle r^2 \rangle / \langle r^2 \rangle_0)^{1/2}$; expansion factor of the *radius of gyration*, $\alpha_s = (\langle s^2 \rangle / \langle s^2 \rangle_0)^{1/2}$; *relative viscosity*, $\alpha_\eta = ([\eta] / [\eta]_0)^{1/3}$, where $[\eta]$ and $[\eta]_0$ are the *intrinsic viscosity* in a given solvent and in the *theta state* at the same temperature, respectively.

Note: Expansion factors defined by different dimensional characteristics are not exactly equal, nor need they have a constant ratio as a function of relative molecular mass.

3.1.11 Flory-Huggins theory

Flory-Huggins-Staverman theory

Statistical thermodynamic mean-field theory of polymer solutions, first formulated independently by Flory, Huggins, and Staverman, in which the thermodynamic quantities of the solution are derived from a simple concept of combinatorial entropy of mixing and a reduced Gibbs-energy parameter, the χ *interaction parameter*.

3.1.12 χ parameter, χ

χ interaction parameter

Numerical parameter employed in the *Flory-Huggins theory*, to account for the contribution of the noncombinatorial entropy of mixing and the enthalpy of mixing to the Gibbs energy of mixing.

3.1.13 preferential sorption selective sorption

Equilibrium phenomenon, operative in polymer solutions, in multicomponent solvents, and in *polymer networks* swollen by multicomponent solvents, that produces differences in solvent composition in the polymer-containing region and in the pure solvent which is in thermodynamic equilibrium with that region.

3.1.14 selective solvent

Medium that is a solvent for at least one component of a mixture of polymers, or for at least one block of a block or graft polymer, but a non-solvent for the other component(s) or block(s).

3.1.15 co-solvency

Dissolution of a polymer in a solvent comprising more than one component, each component of which by itself is a non-solvent for the polymer.

3.1.16 solubility parameter (of a polymer), δ , SI unit: $\text{Pa}^{1/2} = \text{J}^{1/2} \text{m}^{-3/2}$

Parameter used in predicting the *solubility* of non-electrolytes (including polymers) in a given *solvent*. For a substance B:

$$\delta_B = \left(\Delta_{\text{vap}} E_{\text{m,B}} / V_{\text{m,B}} \right)^{1/2}$$

where $\Delta_{\text{vap}} E_{\text{m}}$ is the molar energy of vaporization at zero pressure and V_{m} is the molar volume.

Note 1: Alternative units are $\mu\text{Pa}^{1/2} = \text{J}^{1/2} \text{cm}^{-3/2}$ and $\text{cal}^{1/2} \text{cm}^{-3/2}$, where $1 \text{ J}^{1/2} \text{cm}^{-3/2} \approx 2.045 \text{ cal}^{1/2} \text{cm}^{-3/2}$.

Note 2: For a polymer, the value of the solubility parameter is usually taken to be the value of the solubility parameter of the solvent producing the solution with maximum *intrinsic viscosity* or maximum swelling of a *network* of the polymer.

Note 3: For a substance of low molecular weight, the value of the solubility parameter can be estimated most reliably from the enthalpy of vaporization and the molar volume.

TERMINOLOGY

Note 4: The solubility of a substance B can be related to the square of the difference between the solubility parameters for supercooled liquid B and solvent at a given temperature, with appropriate allowances for entropy of mixing. Thus a value can be estimated from the solubility of the solid in a series of solvents of known solubility parameter.

3.1.17 isopycnic

Adjective describing components of a multicomponent system with equal partial specific volumes.

3.2 Transport Properties

3.2.1 frictional coefficient, f , SI unit: kg s^{-1}

Tensor correlating the frictional force, F , opposing the motion of a particle in a viscous fluid and the velocity u of this particle relative to the fluid.

Note: In the case of an isolated spherical particle in a viscous isotropic fluid, f is a scalar and $F = fu$.

3.2.2 hydrodynamically equivalent sphere

Hypothetical sphere, impenetrable to the surrounding medium, displaying in a hydrodynamic field the same frictional effect as an actual polymer molecule.

Note: The size of a hydrodynamically equivalent sphere may be different for different types of motion of the macromolecule, e.g., for diffusion and for viscous flow.

3.2.3 hydrodynamic volume

Volume of a *hydrodynamically equivalent sphere*.

3.2.4 bead-rod model

Model simulating the hydrodynamic properties of a chain macromolecule consisting of a sequence of beads, each of which offers hydrodynamic resistance to the flow of the surrounding medium and is connected to the next bead by a rigid rod which does not. The mutual orientation of the rods is random.

3.2.5 bead-spring model

Model simulating the hydrodynamic properties of a chain macromolecule consisting of a sequence of beads, each of which offers hydrodynamic resistance to the flow of the surrounding medium and is connected to the next bead by a spring which does not contribute to the frictional interaction but which is responsible for the elastic and deformational properties of the chain. The mutual orientation of the springs is random.

3.2.6 freely draining

Adjective referring to a chain macromolecule the segments of which produce such small frictional effects when moving in a medium that the hydrodynamic field in the vicinity of a given segment is not affected by the presence of other segments. Thus, the solvent can flow virtually undisturbed through the domain occupied by a freely draining macromolecule.

3.2.7 non-draining

Adjective describing a chain macromolecule that behaves in a hydrodynamic field as though the solvent within the domain of the macromolecule were virtually immobilized with respect to the macromolecule.

3.2.8 partially draining

Adjective describing a chain macromolecule that behaves in a hydrodynamic field as though the solvent within the domain of the macromolecule were progressively more immobilized with respect to the macromolecule in the direction from its outer fringes inward.

Note: A *freely draining* macromolecule and a *non-draining* macromolecule are two extremes of the concept of a partially draining macromolecule.

3.2.9 streaming birefringence flow birefringence

Birefringence induced by flow in liquids, solutions and dispersions of optically anisotropic, anisometric or deformable molecules or particles due to a non-random orientation of the molecules or particles.

3.2.10 rotational diffusion

Process by which the equilibrium statistical distribution of the overall orientation of molecules or particles is maintained or restored.

Note: Rotational diffusion may be compared to translational diffusion, through which the equilibrium statistical distribution of position in space is maintained or restored.

3.2.11 sedimentation coefficient, s , SI unit: s

Parameter characterizing the motion of a particle in a centrifugal field and defined as the velocity of motion u due to unit centrifugal acceleration, i.e., $s = u/(r\omega^2)$, where ω is the angular velocity and r the distance from the centre of rotation.

Note: The unit 10^{-13} s is useful; this unit has been referred to as a 'svedberg' (Sv). $1 \text{ Sv} = 10^{-13} \text{ s} = 0.1 \text{ ps}$.

3.2.12 sedimentation equilibrium

Equilibrium established in a centrifugal field when there is no net flux of any component across any plane perpendicular to the centrifugal force.

3.2.13 equilibrium sedimentation (method)

Method by which the distribution of the concentration of the solute or dispersed component in a dilute solution or dispersion along the centrifuge cell is measured at *sedimentation equilibrium*, and the results are interpreted in terms of *molar masses* or their distribution, or both.

3.2.14 sedimentation velocity method

Method by which the velocity of motion of solute component(s) or dispersed particles is measured and the result is expressed in terms of its (their) *sedimentation coefficient(s)*.

3.2.15 Archibald's method

Sedimentation method based on the fact that at the meniscus and at the bottom of the centrifuge cell there is never a flux of the solute across a plane perpendicular to the radial

TERMINOLOGY

direction and the equations characterizing the *sedimentation equilibrium* always apply there, even though the system as a whole may be far from equilibrium.

Note: The use of the term ‘approach to sedimentation equilibrium’ for Archibald’s method is discouraged, since it has a more general meaning.

3.2.16 equilibrium sedimentation in a density gradient

Equilibrium sedimentation technique working with a multi-component solvent forming a density gradient in a centrifugal field

3.2.17 relative viscosity, η_r viscosity ratio

Ratio of the viscosity of the solution, η , to the viscosity of the solvent, η_s , i.e., $\eta_r = \eta/\eta_s$.

3.2.18 relative viscosity increment, η_i

Ratio of the difference between the viscosities of solution and solvent to the viscosity of the solvent, i.e., $\eta_i = (\eta - \eta_s)/\eta_s$. For definitions of symbols, see Definition 3.2.17.

Note: The use of the term ‘specific viscosity’ for this quantity is discouraged, since the relative viscosity increment does not have the attributes of a specific quantity.

3.2.19 reduced viscosity, SI unit: $\text{m}^3 \text{kg}^{-1}$ viscosity number

Ratio of the *relative viscosity increment* to the mass concentration of the polymer, c , i.e., η_i/c .

Note: This quantity and those in Definitions 3.2.20 and 3.2.21 are neither viscosities nor pure numbers. The terms are to be looked on as traditional names. Any replacement by consistent terminology would produce unnecessary confusion in the polymer literature.

3.2.20 inherent viscosity, η_{inh} , SI unit: $\text{m}^3 \text{kg}^{-1}$ logarithmic viscosity number, η_{ln}

Ratio of the natural logarithm of the *relative viscosity* to the mass concentration of the polymer, c , i.e.,

$$\eta_{\text{inh}} \equiv \eta_{\text{ln}} = (\ln \eta_r)/c.$$

Note: See note under Definition 3.2.19.

3.2.21 intrinsic viscosity, $[\eta]$, SI unit: $\text{m}^3 \text{kg}^{-1}$ limiting viscosity number Staudinger index

Limiting value of the *reduced viscosity* (or the *inherent viscosity*) at infinite dilution of the polymer, i.e.,

$$[\eta] = \lim_{c \rightarrow 0} (\eta_i/c) = \lim_{c \rightarrow 0} \eta_{\text{inh}}$$

Note: See note under Definition 3.2.19.

3.2.22 Huggins equation

Equation describing the dependence of the *reduced viscosity*, η_i/c , on the mass concentration of the polymer, c , for *dilute polymer solutions* of the form

$$\eta_i/c = [\eta] + k_H [\eta]^2 c$$

where k_H is the *Huggins coefficient* and $[\eta]$ is the *intrinsic viscosity*.

3.2.23 Huggins coefficient, k_H

Parameter in the *Huggins equation*.

3.2.24 viscosity function, ϕ

Flory constant

Coefficient connecting the *intrinsic viscosity*, the *radius of gyration* and the *molar mass* of a chain macromolecule, according to the equation

$$[\eta] = \Phi 6^{3/2} \langle s^2 \rangle^{3/2} / M$$

3.2.25 Mark-Houwink equation

Equation describing the dependence of the *intrinsic viscosity* of a polymer on its *relative molecular mass (molecular weight)* and having the form

$$[\eta] = K M_r^a$$

where K and a are constants, the values of which depend on the nature of the polymer and solvent as well as on temperature, and M_r is usually one of the *relative molecular-mass averages*.

Note 1: The use of this equation with the *relative molecular mass (molecular weight)* is recommended, rather than with *molar mass* (which has the dimension of mass divided by amount of substance), since in the latter case the constant K assumes awkward and variable dimensions owing to the fractional and variable nature of the exponent a .

Note 2: Kuhn and Sakurada have also made important contributions and their names are sometimes included, as, for example, in the Kuhn-Mark-Houwink-Sakurada equation.

3.3 coherent elastic scattering of radiation

A beam of radiation traversing a medium may be attenuated and partially scattered. The definitions below are for those cases in which the attenuation of the incident beam is due only to scattering, the energy of scattering quanta is the same as that of quanta in the primary beam (elastic scattering) and phase relationships between independent scatterers are retained (coherent scattering). This section deals with light scattering (LS), small-angle x-ray scattering (SAXS), and small-angle neutron scattering (SANS). In light scattering the polarization of light is relevant; plane-polarized light is considered here only, and it is called vertically polarized (v) if the electric vector of the beam is perpendicular to the plane containing the source, sample and detector, and horizontally polarized (h) if the electric vector lies in that plane. Unpolarized light is considered to be a mixture of equal parts of v and h light.

TERMINOLOGY

3.3.1 small particle

Particle much smaller than the wavelength of the radiation in the medium. In practice, all dimensions of a particle considered small must be less than about one-twentieth of the wavelength employed.

3.3.2 large particle

Particle with dimensions comparable with the wavelength of the radiation in the medium or larger. In practice a particle must be treated as large, if its largest dimension exceeds about one-twentieth of the wavelength employed.

3.3.3 scattering angle, θ angle of observation

Angle between the forward direction of the incident beam and a straight line connecting the scattering point and the detector.

3.3.4 scattering vector; q

Vector difference between the wave propagation vectors of the incident and the scattered beam, both of length $2\pi/\lambda$, where λ is the wavelength of the scattered radiation in the medium.

3.3.5 length of the scattering vector, q

Length of the *scattering vector* is $q = (4\pi/\lambda) \sin(\lambda/2)$, where λ is the wavelength of the scattered radiation in the medium and θ is the *scattering angle*.

3.3.6 refractive index increment, $\partial n/\partial c$

Change of the solution refractive index, n , with solute concentration, c .

Note 1: The solute concentration is most frequently expressed in terms of mass concentration, molality or volume fraction. If expressed in terms of mass concentration or molality, the corresponding refractive index increments are referred to as specific or molal refractive index increments, respectively.

Note 2: Following use of the full name, the abbreviated name refractive increment may be used.

3.3.7 Rayleigh ratio, $R(\theta)$ or R_θ , SI unit: m^{-1}

Quantity used to characterize the scattered intensity at the *scattering angle*, θ , defined as $R(\theta) = i_\theta r^2/(I f V)$, where I is the intensity of the incident radiation, i_θ is the total intensity of scattered radiation observed at an angle θ and a distance r from the point of scattering and V is the scattering volume. The factor f takes account of polarization phenomena.

Note 1: The value of f depends upon the type of radiation employed:

(i) for light scattering, depending upon the polarization of the incident beam, $f = 1$ for vertically polarized light, $f = \cos^2 \theta$ for horizontally polarized light, $f = (1 + \cos^2 \theta)/2$ for unpolarized light;

(ii) for small-angle neutron scattering $f = 1$;

(iii) for small-angle x-ray scattering $f \approx 1$, if $\theta < \text{ca } 5^\circ$.

Note 2: In physics, the factor, f , may not be included in the definition of the Rayleigh ratio.

Note 3: In small-angle neutron scattering, the term cross-section is often used instead of $R(\theta)$; the two quantities are identical.

3.3.8 excess Rayleigh ratio

Difference between the *Rayleigh ratio* for a dilute solution and for pure solvent.

Note: If the scattering intensity is not reduced to the *Rayleigh ratio*, the difference between the scattering intensities for a dilute solution and that for pure solvent is named ‘excess scattering’.

3.3.9 turbidity, τ

Apparent absorbance of the incident radiation due to scattering.

Note: For *small particles* direct proportionality exists between turbidity and the *Rayleigh ratio*.

3.3.10 particle scattering function, $P(\theta)$ or P_θ particle scattering factor

Ratio of the intensity of radiation scattered at an angle of observation θ to the intensity of radiation scattered at an angle zero, i.e., $P(\theta) \equiv R(\theta)/R(0)$.

3.3.11 Zimm plot

Diagrammatic representation of data on scattering from *large particles*, corresponding to the equation

$$\frac{Kc}{\Delta R(\theta)} = \frac{1}{\overline{M}_w P(\theta)} + 2A_2c + \dots$$

and used for the simultaneous evaluation of the *mass-average molar mass*, \overline{M}_w , the *second virial coefficient of the chemical potential*, A_2 , and (usually) the *z-average radius of gyration*; c is the mass concentration of the solute, $\Delta R(\theta)$ the *excess Rayleigh ratio*, and $P(\theta)$ the *particle scattering function* that comprises (usually) the *z-average radius of gyration*. K depends on the solute, the temperature and the type of radiation employed.

Note: Several modifications of the Zimm plot are in frequent use; the most common one uses the *excess scattering* instead of the *excess Rayleigh ratio*.

3.3.12 Guinier plot

Diagrammatic representation of data on scattering from *large particles*, obtained at different angles but at the same concentration, constructed by plotting $\lg[\Delta R(\theta)]$ or $\lg[P(\theta)]$ versus $\sin^2(\theta/2)$ or q^2 , and (usually) used for the evaluation of the *radius of gyration*, $P(\theta)$ the *particle scattering function*, θ , the *scattering angle* and q , the length of the *scattering vector*.

3.3.13 Kratky plot

Diagrammatic representation of scattering data on *large particles*, obtained at different angles but at the same concentration, constructed by plotting $\sin^2(\theta/2)\Delta R(\theta)$ versus $\sin(\theta/2)$, or $q^2\Delta R(\theta)$ versus q , and used for the determination of molecular shape. For definitions of symbols, see Definition 3.3.12.

3.3.14 dissymmetry of scattering, $z(\theta_1, \theta_2)$

Ratio of two *Rayleigh ratios* for different *angles of observation*, i.e.,

TERMINOLOGY

$$z(\theta_1, \theta_2) = R(\theta_1)/R(\theta_2), \theta_1 > \theta_2.$$

Note: The angles must be specified; in light scattering it is customary to let $\theta_2 = 180^\circ - \theta_1$, and, most frequently, $\theta_1 = 45^\circ$ and $\theta_2 = 135^\circ$.

3.3.15 depolarization of scattered light

Phenomenon consequent upon the electric vectors of the incident and scattered beams being non-coplanar, such that light scattered from a vertically (horizontally) polarized incident beam contains a horizontal (vertical) component.

Note: The phenomenon is due primarily to the anisotropy of the polarizability of the scattering medium.

3.3.16 turbidimetric titration

Process in which a precipitant is added incrementally to a highly dilute polymer solution and the intensity of light scattered by, or the *turbidity* due to, the finely dispersed particles of the *polymer-rich phase* is measured as a function of the amount of precipitant added.

3.3.17 isorefractive

Adjective describing components of a multicomponent system having zero refractive index increments with respect to each other.

3.3.18 Mie scattering

Scattering of light by particles with size larger than approximately one-half of the wavelength of incident light.

Note: For homogeneous spheres, this phenomenon is rigorously described by the theory developed by Mie.

3.4 Separation

3.4.1 fractionation

Process by means of which macromolecular species differing in some characteristic (chemical composition, *relative molecular mass*, branching, stereoregularity, etc.) are separated from each other.

3.4.2 polymer-poor phase dilute phase

Phase of a two-phase equilibrium system, consisting of a polymer and low-molecular-weight material, in which the polymer concentration is lower.

Note: The use of the name 'sol phase' is discouraged.

3.4.3 polymer-rich phase concentrated phase

Phase of a two-phase equilibrium system, consisting of a polymer and low-molecular-weight material, in which the polymer concentration is higher.

Note: The use of the name 'gel phase' is discouraged.

3.4.4 precipitation fractionation

Process in which a polymeric material, consisting of macromolecules differing in some characteristic affecting their solubility, is separated from solution into fractions by successively decreasing the solution power of the solvent, resulting in the repeated

formation of a two-phase system in which the less soluble components concentrate in the *polymer-rich phase*.

3.4.5 extraction fractionation

Process in which a polymeric material, consisting of macromolecules differing in some characteristic affecting their solubility, is separated from a *polymer-rich phase* into fractions by successively increasing the solution power of the solvent, resulting in the repeated formation of a two phase system in which the more soluble components concentrate in the *polymer-poor phase*.

3.4.6 size-exclusion chromatography (SEC)

Separation technique in which separation mainly according to the *hydrodynamic volume* of the molecules or particles takes place in a porous non-adsorbing material with pores of approximately the same size as the effective dimensions in solution of the molecules to be separated.

3.4.7 gel-permeation chromatography (GPC)

Size-exclusion chromatography in which the porous non-adsorbing material is a gel.

3.4.8 molar-mass exclusion limit

molecular-weight exclusion limit

Maximum value of the *molar mass* or *molecular weight* of molecules or particles, in a specific polymer-solvent system, that can enter into the pores of the porous non-adsorbing material used in *size-exclusion chromatography*.

Note: For particles with molar mass or molecular weight larger than the exclusion limit the separation effect of the size-exclusion chromatography vanishes.

3.4.9 elution volume, V_{el} , SI unit: m^3

Volume of a solvent passed, since the injection of the sample, through a *size-exclusion chromatography* bed at the time at which a specified signal of the detector has been recorded.

3.4.10 retention volume, V_R

Elution volume at the maximum concentration of an elution peak.

3.4.11 universal calibration

Calibration of *size-exclusion chromatography* columns based on the finding that the *retention volume* of a molecular or particulate species is usually a single-valued function of an appropriate size parameter of this molecule or particle, irrespective of its chemical nature and structure.

Note: The product of the *intrinsic viscosity* and *molar mass*, $[\eta] M$, has been widely used as a size parameter.

3.4.12 spreading function

Normalized signal produced, as a function of *elution volume*, at the outlet of a *size-exclusion chromatography* set-up, by an instantaneous injection of a uniform sample.

TERMINOLOGY

3.4.13 plate number, N

Characteristic of the efficiency of a *size-exclusion chromatography* set-up in terms of band broadening, defined as $N = (V_R/\sigma_V)^2$, where V_R is the *retention volume* of an individual low-molecular-weight compound, and σ_V is the corresponding full width at 60.7% peak height of the elution peak.

3.4.14 plate height, H

height equivalent to a theoretical plate

Length of a part of a *size-exclusion chromatography* bed corresponding to one plate, i.e., the length of the bed, L , divided by its *plate number*, N , or $H = L/N$.

REFERENCES

1. IUPAC. 'Glossary of basic terms in polymer science (IUPAC Recommendations 1996)', *Pure Appl. Chem.* **68**, 2287-2311 (1996). Reprinted as Chapter 1 this volume.
2. IUPAC. 'Stereochemical definitions and notations relating to polymers (Recommendations 1980)', *Pure Appl. Chem.* **53**, 733-752 (1981). Reprinted as Chapter 2 this volume.
3. IUPAC. 'Note on the terminology for molar masses in polymer science', *Makromol. Chem.* **185**, Appendix to No. 1 (1984); *J. Polym. Sci., Polym. Lett. Ed.* **22**, 57 (1984); and in other journals.
4. 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 version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.