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COMMISSION ON MACROMOLECULAR NOMENCLATURE*

**DEFINITIONS OF TERMS
RELATING TO
INDIVIDUAL MACROMOLECULES,
THEIR ASSEMBLIES, AND
DILUTE POLYMER
SOLUTIONS**

(Recommendations 1988)

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Definitions of terms relating to individual macromolecules, their assemblies, and dilute polymer solutions (Recommendations 1988)

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 (References 1–3). It is also the first of several documents that will be published dealing specifically with physico-chemical terminology in the polymer field. 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 'non-uniform polymer' which denote polymers composed of molecules that are uniform or non-uniform, respectively, with respect to relative molecular mass and constitution. These terms replace the widely used, but non-descriptive and self-contradictory, terms 'monodisperse polymer' and 'polydisperse polymer'.

1 INDIVIDUAL MACROMOLECULES

1.1 relative molecular mass molecular weight

recommended symbol: M_r

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

Notes

See 'Molar mass'.

1.2 molar mass

recommended symbol: M

Mass divided by amount of substance.

Notes

1 Molar mass is usually expressed in g/mol or kg/mol units. The g/mol 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.

2 Relative molecular mass (molecular weight) is a pure number and must not be associated with any units.

3 The use of the dalton as a unit of mass, identical with the atomic mass unit, is discouraged.

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

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

recommended symbol: X

recommended abbreviation: DP

The number of monomeric units in a molecule of a polymer.

1.4 thermodynamically-equivalent sphere

A sphere, impenetrable to other spheres, displaying the same excluded volume (see 3.1.9) 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 the chain.

Notes

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

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 the chain, that occasionally approach one another during molecular flexing.

Notes

1 This type of interaction is closely related to the excluded volume of a segment (see 3.1.8), the latter quantity reflecting interactions involving segments and solvent molecules.

2 If no confusion can occur, the word 'intramolecular' may be omitted.

1.7 unperturbed dimensions

The dimensions of an actual polymer random coil (see 1.15) in a theta state (see 3.1.5).

1.8 perturbed dimensions

The dimensions of an actual polymer random coil (see 1.15) not in a theta state (see 3.1.5).

1.9 radius of gyration

recommended symbols: s , $\langle s^2 \rangle^{1/2}$

A 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.,

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

Note

The subscript zero is used to indicate unperturbed dimensions (see 1.7), as in $\langle s^2 \rangle_0^{1/2}$.

1.10 end-to-end vector

recommended symbol: \mathbf{r}

The vector connecting the two ends of a linear polymer chain in a particular conformation.

1.11 end-to-end distance

recommended symbol: r

The length of the end-to-end vector (see 1.10).

1.12 root-mean-square end-to-end distance

recommended symbol: $\langle r^2 \rangle^{1/2}$

The square root of the mean-square end-to-end distance (see 1.11) of a linear polymer chain averaged over all conformations of the chain. For a freely-jointed chain (see 1.16) consisting of N segments each of length L , $\langle r^2 \rangle^{1/2} = N^{1/2}L$.

Notes

1 The subscript zero is used to indicate unperturbed dimensions (see 1.7), as in $\langle r^2 \rangle_0^{1/2}$.

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

recommended symbol: C_N (C_∞ when $N \rightarrow \infty$)

The ratio of the mean-square end-to-end distance (see 1.12), $\langle r^2 \rangle_0$, of a linear polymer

chain in the theta state (see 3.1.5) to $N \cdot L^2$, 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

The maximum end-to-end distance (see 1.11) of a linear polymer chain.

Notes

1 For a single-strand polymer molecule, this usually means the end-to-end distance of the chain extended to the all-trans conformation. For chains with complex structure, only an approximate value of the contour length may be accessible.

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 is discouraged.

1.15 random coil statistical coil

The 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 (see 3.1.5), the segments change mutual orientation only approximately randomly.

1.16 freely-jointed chain

A hypothetical linear chain molecule consisting of infinitely thin rectilinear segments uniform in length; each segment can take all orientations in space with equal probability, independently of its neighbours.

Note

For models in which the segments are not all uniform in length, the name **random-walk chain** has been used.

1.17 equivalent chain

A hypothetical freely-jointed chain (see 1.16) with the same mean-square end-to-end distance (see 1.11) and contour length (see 1.14) as an actual polymer chain in a theta state (see 3.1.5).

1.18 statistical segment

A segment of an actual polymer chain which behaves, with respect to some property, virtually as a segment of a freely-jointed chain (see 1.16).

1.19 freely-rotating chain

A hypothetical linear chain molecule, free from short-range and long-range interactions (see 1.5 and 1.6), 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

recommended symbol: σ

The ratio of the root-mean-square end-to-end distance (see 1.12) of a polymer chain with unperturbed dimensions (see 1.7), $\langle r^2 \rangle_0^{1/2}$, to that of a freely rotating chain (see 1.19) with the same structure, $\langle r^2 \rangle_{0,f}^{1/2}$, i.e., $(\langle r^2 \rangle_0 / \langle r^2 \rangle_{0,f})^{1/2}$, 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

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

Notes

1 The model describes the whole spectrum of chains with different degrees of chain stiffness from rigid rods to random coils (see 1.15), and is particularly useful for representing stiff chains.

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

1.22 persistence length

recommended symbol: a

The average projection of the end-to-end vector (see 1.10) 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 (see 1.21).

1.23 short-chain branch

An oligomeric offshoot from a macromolecular chain.

1.24 long-chain branch

A polymeric offshoot from a macromolecular chain.

1.25 branching index

recommended symbol: g

A parameter characterizing the effect of long-chain branches (see 1.24) on the size of a branched macromolecule in solution and defined as the ratio of the mean-square radius of gyration (see 1.9) 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 (see 1.1) in the same solvent and at the same temperature, i.e., $g = \langle s_b^2 \rangle / \langle s_l^2 \rangle$.

1.26 network

A 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

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.

1.27 microgel

A network of microscopic dimensions.

1.28 copolymer micelle

A micelle formed by one or more block of graft copolymer molecules in a selective solvent (see 3.1.14).

2 ASSEMBLIES OF MACROMOLECULES

2.1 compositional heterogeneity

The variation in elemental composition from molecule to molecule usually found in copolymers.

2.2 constitutional heterogeneity

The 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

A polymer composed of molecules uniform with respect to relative molecular mass (see 1.1) and constitution.

Notes

- 1 A polymer comprising a mixture of linear and branched chains, all of uniform relative molecular mass, is not uniform.
- 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).
- 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').
- 4 The adjective 'monodisperse' and 'polydisperse' (see 2.4) 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' (see 2.4) have been selected and they are now the preferred adjectives.

2.4 non-uniform polymer polydisperse polymer

A polymer comprising molecules non-uniform with respect to relative molecular mass (see 1.1) or constitution or both.

Note

See 2.3, Note 3.

2.5 molar-mass average

recommended symbol: \bar{M}_k

relative molecular-mass average molecular-weight average

recommended symbol: $\bar{M}_{r,k}$

In both symbols, k specifies the type of average.

Any average of the molar mass (see 1.2) or relative molecular mass (molecular weight) (see 1.1) for a non-uniform polymer.

Notes

- 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 (see 2.13) 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.

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

recommended symbol: \bar{M}_n

number-average relative molecular mass

number-average molecular weight

recommended symbol: $\bar{M}_{r,n}$

Definitions

$$\bar{M}_n = \frac{1}{\sum_i (w_i/M_i)} \quad \text{and} \quad \bar{M}_{r,n} = \frac{1}{\sum_i (w_i/M_{r,i})}$$

For explanation of symbols, see 'molar-mass average', 2.5.

2.7 mass-average molar mass

recommended symbol: \bar{M}_w

mass-average relative molecular mass

weight-average molecular weight

recommended symbol: $\bar{M}_{r,w}$

Definitions

$$\bar{M}_w = \sum_i w_i M_i \quad \text{and} \quad \bar{M}_{r,w} = \sum_i w_i M_{r,i}$$

For explanation of symbols, see 'molar-mass average', 2.5.

2.8 z-average molar mass

recommended symbol: \bar{M}_z

z-average relative molecular mass

z-average molecular weight

recommended symbol: $\bar{M}_{r,z}$

Definitions

$$\bar{M}_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \quad \text{and} \quad \bar{M}_{r,z} = \frac{\sum_i w_i M_{r,i}^2}{\sum_i w_i M_{r,i}}$$

For explanation of symbols, see 'molar-mass average', 2.5.

2.9 (z+1)-average molar mass

recommended symbol: \bar{M}_{z+1}

(z+1)-average relative molecular mass**(z+1)-average molecular weight**

recommended symbol: $\bar{M}_{r,z+1}$

Definitions

$$\bar{M}_{z+1} = \frac{\sum_i w_i M_i^3}{\sum_i w_i M_i^2} \quad \text{and} \quad \bar{M}_{r,z+1} = \frac{\sum_i w_i M_{r,i}^3}{\sum_i w_i M_{r,i}^2}$$

For explanation of symbols, see 'molar-mass average', 2.5.

2.10 viscosity-average molar mass

recommended symbol: \bar{M}_v

viscosity-average relative molecular mass**viscosity-average molecular weight**

recommended symbol: $\bar{M}_{r,v}$

Definitions

$$\bar{M}_v = \left[\sum_i w_i M_i^a \right]^{1/a} \quad \text{and} \quad \bar{M}_{r,v} = \left[\sum_i w_i M_{r,i}^a \right]^{1/a}$$

where a is the exponent in the Mark-Houwink equation (see 3.2.25), $[\eta] = K \cdot M^a$; for explanation of the other symbols, see 'molar-mass average', 2.5.

Note

The exponent a is not identical with the adjustable parameter of some of the distribution functions (see 2.16–2.20) or with the persistence length (see 1.22).

2.11 apparent molar mass

recommended symbol: M_{app}

apparent relative molecular mass**apparent molecular weight**

recommended symbol: $M_{r,\text{app}}$

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 (see 2.1), constitutional heterogeneity (see 2.2).

2.12 average degree of polymerization

recommended symbol: \bar{X}_k where k specifies the type of average
Any average of the degree of polymerization (see 1.3) for a polymer.

Note

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

2.13 distribution function

A 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.

Notes

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.

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).

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

A distribution function (see 2.13) 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.

2.15 mass-distribution function weight-distribution function

A distribution function (see 2.13) 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

A continuous distribution with the differential mass-distribution function (see 2.15) of the form

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

where x is a parameter characterizing the chain length, such as relative molecular mass (see 1.1) or degree of polymerization (see 1.3), a and b are positive adjustable parameters, and $\Gamma(b+1)$ is the gamma function of $(b+1)$.

2.17 most probable distribution

A discrete distribution with the differential mass-distribution function (see 2.15) of the form

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

For explanation of symbols, see ‘Schulz-Zimm distribution’, 2.16.

Notes

1 For large values of x , the most probable distribution converges to the particular case of the Schulz-Zimm distribution (see 2.16) with $b = 1$.

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

2.18 Poisson distribution

A discrete distribution with the differential mass-distribution function (see 2.15) of the form

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

For explanation of symbols, see ‘Schulz-Zimm distribution’, 2.16.

2.19 Tung distribution

A continuous distribution with the differential mass-distribution function (see 2.15) of the form

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

For explanation of symbols, see ‘Schulz-Zimm distribution’, 2.16.

2.20 logarithmic normal distribution

A continuous distribution with the differential mass-distribution function (see 2.15)

of the form

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

For explanation of symbols, see 'Schulz-Zimm distribution', 2.16.

2.21 polymolecularity correction

A correction applied to relationships between a property and the molar mass (see 1.2) or relative molecular mass (see 1.1), obtained from polymers non-uniform (see 2.4) with respect to relative molecular mass, in order to obtain the corresponding relationship for polymers strictly uniform (see 2.3) with respect to relative molecular mass.

3 DILUTE POLYMER SOLUTIONS

3.1 General and thermodynamic terms

3.1.1 dilute solution

A 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

recommended symbol: c^*

The 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

For the meaning of the term 'domain', see the note in 3.1.1.

3.1.3 polymer-solvent interaction

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

3.1.4 quality of solvent

thermodynamic quality of solvent

Qualitative characterization of the polymer-solvent interaction (see 3.1.3). A solution

of a polymer in a 'better' solvent is characterized by a higher value of the second virial coefficient (see 3.1.7) than a solution of the same polymer in a 'poorer' solvent.

3.1.5 theta state

The state of a polymer solution for which the second virial coefficient (see 3.1.7) is zero.

Notes

- 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.
- 2 In the literature, the theta state is also written '**θ state**'.
- 3 The solvent involved is often referred to as '**theta solvent**'.
- 4 It is assumed that the molar mass of the polymer is high.

3.1.6 theta temperature

The temperature at which a solution is in the theta state (see 3.1.5).

Note

In the literature, the theta temperature is also written '**θ temperature**'.

3.1.7 virial coefficients

virial coefficients of the chemical potential

recommended symbol: A_i , where $i = 1, 2$, etc.

The 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.,

$$\mu_s - \mu_s^0 = -\pi V_s = -RTV_s(A_1c + A_2c^2 + A_3c^3 + \dots),$$

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 (see 2.6), i.e., $A_1 = 1/\bar{M}_n$. The second and higher virial coefficients, A_2 , A_3 , ..., respectively, describe polymer-solvent (see 3.1.3) and polymer-polymer interactions.

Note

The factor RT is sometimes included in the virial coefficients.

3.1.8 excluded volume of a segment

The 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 (see 3.1.4), and is not a measure of the geometrical volume of that segment.

3.1.9 excluded volume of a macromolecule

The 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 (see 3.1.4), and is not a measure of the geometrical volume of that macromolecule.

3.1.10 expansion factor

recommended symbols: α_r , α_s , α_η

The 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 (see 3.1.5) at the same temperature. The most frequently used expansion factors are: expansion factor of the mean-square end-to-end distance (see 1.12), $\alpha_r = (\langle r^2 \rangle / \langle r^2 \rangle_0)^{1/2}$; expansion factor of the radius of gyration (see 1.9), $\alpha_s = (\langle s^2 \rangle / \langle s^2 \rangle_0)^{1/2}$; viscosity expansion factor $\alpha_\eta = ([\eta] / [\eta]_\theta)^{1/3}$, where $[\eta]$ and $[\eta]_\theta$ are the intrinsic viscosity (see 3.2.21) 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

A thermodynamic theory of polymer solutions, first formulated independently by Flory and by Huggins, 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 parameter’ (see 3.1.12).

3.1.12 χ parameter

recommended symbol: χ

A numerical parameter employed in the Flory-Huggins theory (see 3.1.11), which accounts in the main for the contribution of the non-combinatorial entropy of mixing and for the enthalpy of mixing.

3.1.13 preferential sorption selective sorption

An equilibrium phenomenon, operative in polymer solutions in multicomponent solvents and in polymer networks (see 1.26) 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

A 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

The 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)

recommended symbol: δ

A characteristic of a polymer used in predicting solubility of that polymer in a given solvent.

Notes

1 For a substance of low molecular weight, the value of the solubility parameter is often estimated from the enthalpy of vaporization; for a polymer, it is usually taken to be the value of the solubility parameter of the solvent producing the solution with maximum intrinsic viscosity (see 3.2.21) or maximum swelling of a network (see 1.26) of the polymer.

2 The solubility parameter is usually expressed in $(\text{cal}/\text{cm}^3)^{1/2}$ or, preferably, $(\text{J}/\text{cm}^3)^{1/2}$ units. The units must always be given; $1 (\text{cal}/\text{cm}^3)^{1/2} \approx 2.05 (\text{J}/\text{cm}^3)^{1/2}$.

3.1.17 isopycnic

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

3.2 Transport properties

3.2.1 frictional coefficient

recommended symbol: f

A 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 constant and $F = fu$.

3.2.2 hydrodynamically-equivalent sphere

A 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

The volume of a hydrodynamically-equivalent sphere (see 3.2.2).

3.2.4 bead-rod model

A 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

A 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

An 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

An 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

An 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 (see 3.2.6) macromolecule and a non-draining (see 3.2.7) macromolecule are two extremes of the concept of a partially-draining macromolecule.

3.2.9 streaming birefringence flow birefringence

The 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

A 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

recommended symbol: s

A 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., $s = u/(r \cdot \omega^2)$, where ω is the angular velocity and r the distance from the center of rotation.

Note

The unit 10^{-13} second is useful; this unit has been referred to as a 'svedberg' which, however, is not an SI-unit.

3.2.12 sedimentation equilibrium

The 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)

A 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 (see 3.2.12), and the results are interpreted in terms of molar masses (see 1.2) or their distribution, or both.

3.2.14 sedimentation velocity method

A 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) (see 3.2.11).

3.2.15 Archibald's method

A 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 direction and the equations characterizing the sedimentation equilibrium (see 3.2.12) 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

An equilibrium sedimentation (see 3.2.13) technique working with a multi-component solvent forming a density gradient in a centrifugal field.

3.2.17 relative viscosity viscosity ratio

recommended symbol: η_r

The 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

recommended symbol: η_i

The 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 explanation of symbols, see 'relative viscosity', 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 viscosity number

The ratio of the relative viscosity increment (see 3.2.18) to the mass concentration of the polymer, c , i.e., η_i/c .

Notes

- 1 The unit must be specified; cm³/g is recommended.
- 2 This quantity and those in 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 logarithmic viscosity number

recommended symbols: η_{inh} , η_{ln} , respectively

The ratio of the natural logarithm of the relative viscosity (see 3.2.17) to the mass concentration of the polymer, c , i.e.,

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

Notes

See notes under 'reduced viscosity', 3.2.19.

3.2.21 intrinsic viscosity limiting viscosity number

recommended symbol: $[\eta]$

The limiting value of the reduced viscosity (see 3.2.19) or the inherent viscosity (see 3.2.20) at infinite dilution of the polymer, i.e.,

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

Notes

- 1 This term is also known in the literature as the **Staudinger index**.
- 2 See notes under 'reduced viscosity', 3.2.19.

3.2.22 Huggins equation

The equation describing the dependence of the reduced viscosity (see 3.2.19), η_i/c , on the mass concentration of the polymer, c , for dilute polymer solutions (see 3.1.1) of the form

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

where k_H is the Huggins coefficient (see 3.2.23) and $[\eta]$ is the intrinsic viscosity (see 3.2.21).

3.2.23 Huggins coefficient

recommended symbol: k_H

A parameter in the Huggins equation (see 3.2.22).

3.2.24 viscosity function

recommended symbol: Φ

A coefficient connecting the intrinsic viscosity (see 3.2.21), the radius of gyration (see

1.9), and the molar mass (see 1.2) of a chain macromolecule, according to the equation $[\eta] = \Phi \sigma^{3/2} \langle s^2 \rangle^{3/2} / M$.

Note

The viscosity function is often referred to as the **Flory constant**.

3.2.25 Mark-Houwink equation

The equation describing the dependence of the intrinsic viscosity (see 3.2.21) of a polymer on its relative molecular mass (molecular weight) (see 1.1) and having the form

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

where K and a are constants, the values of which depend on the nature of the polymer and solvent as well as on temperature; M_r is usually one of the relative molecular-mass averages (see 2.5).

Notes

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 .

2 Kuhn and Sakurada have also made important contributions and their names are sometimes included, as, for example, in **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 document 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.

3.3.1 small particle

A 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

A 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 angle of observation

recommended symbol: θ

The 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

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

recommended symbol: q

The length of the scattering vector (see 3.3.4) is $q = (4\pi/\lambda) \cdot \sin(\theta/2)$ where λ is the wavelength of the scattered radiation in the medium and θ is the scattering angle (see 3.3.3).

3.3.6 refractive index increment

recommended symbol: $\partial n/\partial C$

The change of the solution refractive index, n , with solute concentration, C .

Notes

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.

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

3.3.7 Rayleigh ratio

recommended symbols: $R(\theta)$, R_θ

The quantity used to characterize the scattered intensity at the scattering angle θ (see 3.3.3), defined as $R(\theta) = i_\theta r^2/(I \cdot f \cdot V)$, 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. It depends on the type of radiation employed:

(i) for light scattering, dependent on 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 $\theta < \text{ca. } 5^\circ$.

Notes

1 The dimension of $R(\theta)$ is $(\text{length})^{-1}$ and the unit commonly used is cm^{-1} .

2 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

The difference between the Rayleigh ratio (see 3.3.7) 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

recommended symbol: τ

The apparent absorbance of the incident radiation due to scattering.

Note

For small particles (see 3.3.1), direct proportionality exists between turbidity and the Rayleigh ratio (see 3.3.7).

3.3.10 particle scattering function particle scattering factor

recommended symbols: $P(\theta)$, P_θ

The ratio of the intensity of radiation scattered at an angle of observation θ (see 3.3.3) to the intensity of radiation scattered at an angle zero, i.e., $P(\theta) \equiv R(\theta)/R(0)$.

3.3.11 Zimm plot

A diagrammatic representation of data on scattering from large particles (see 3.3.2), corresponding to the equation

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

and used for the simultaneous evaluation of the mass-average molar mass (see 2.7) \bar{M}_w , the second virial coefficient of the chemical potential (see 3.1.7) A_2 , and (usually) the z-average radius of gyration (see 1.9) $\langle s^2 \rangle_z^{1/2}$. c is the mass concentration of the solute, $\Delta R(\theta)$ the excess Rayleigh ratio (see 3.3.8), and $P(\theta)$ the particle scattering function (see 3.3.10) 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 (see 3.3.8) instead of the excess Rayleigh ratio.

3.3.12 Guinier plot

A diagrammatic representation of data on scattering from large particles (see 3.3.2), obtained at different angles but at the same concentration, constructed by plotting $\log \Delta R(\theta)$ or $\log P(\theta)$ versus $\sin^2(\theta/2)$ or q^2 , and (usually) used for the evaluation of the radius of gyration (see 1.9). $\Delta R(\theta)$ is the excess Rayleigh ratio (see 3.3.8), $P(\theta)$ the particle scattering function (see 3.3.10), θ the scattering angle (see 3.3.3), and q the length of the scattering vector (see 3.3.5).

3.3.13 Kratky plot

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

3.3.14 dissymmetry of scattering

recommended symbol: $z(\theta_1, \theta_2)$

The ratio of two Rayleigh ratios (see 3.3.7) for different angles of observation (see 3.3.3), i.e., $z(\theta_1, \theta_2) = R(\theta_1)/R(\theta_2)$, $\theta_1 < \theta_2$.

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

The phenomenon, due primarily to the anisotropy of the polarizability of the scattering medium, resulting from the fact that the electric vectors of the incident and scattered beams are not coplanar and that, therefore, light scattered from a vertically (horizontally) polarized incident beam contains a horizontal (vertical) component.

3.3.16 turbidimetric titration

The process in which a precipitant is added incrementally to a highly dilute polymer solution and the intensity of light scattered by, or the turbidity (see 3.3.9) due to, the finely dispersed particles of the polymer-rich phase (see 3.4.3) is measured as a function of the amount of precipitant added.

3.3.17 isorefractive

An 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

A process by means of which macromolecular species differing in some characteristic (chemical composition, relative molecular mass (see 1.1), branching, stereoregularity, etc.) are separated from each other.

3.4.2 polymer-poor phase dilute phase

That 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

That 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

A 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 (see 3.4.3).

3.4.5 extraction fractionation

A process in which a polymeric material, consisting of macromolecules differing in some characteristic affecting their solubility, is separated from a polymer-rich (see 3.4.3) 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 (see 3.4.2).

3.4.6 size-exclusion chromatography

recommended abbreviation: SEC

gel-permeation chromatography

recommended abbreviation: GPC

A separation technique in which separation mainly according to the hydrodynamic volume (see 3.2.3) 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.

Note

The term 'gel-permeation chromatography' should only be used when the porous non-adsorbing material is a gel. The term 'size-exclusion chromatography' is preferred.

3.4.7 molar-mass exclusion limit molecular-weight exclusion limit

The maximum value of the molar mass (see 1.2) or molecular weight (see 1.1) 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 (see 3.4.6).

Note

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

3.4.8 elution volume

The volume of a solvent passed, since the injection of the sample, through a size-exclusion chromatography (see 3.4.6) bed at the time at which a specified signal of the detector has been recorded.

3.4.9 retention volume

The elution volume (see 3.4.8) at the maximum concentration of an elution peak.

3.4.10 universal calibration

A calibration of a size-exclusion chromatography (see 3.4.6) set-up based on the finding that the retention volume (see 3.4.9) of a molecular or particulate species is 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 (see 3.2.21) and molar mass (see 1.2), $[\eta]M$, has been widely used as the size parameter.

3.4.11 spreading function

The normalized signal produced, as a function of elution volume (see 3.4.8), at the outlet of a size-exclusion chromatography (see 3.4.6) set-up, by an instantaneous injection of a uniform sample.

3.4.12 plate number

recommended symbol: N

A characteristic of the efficiency of a size-exclusion chromatography (see 3.4.6) set-up in terms of band broadening, defined as $N = (V_R/\sigma_V)^2$, where V_R is the retention volume (see 3.4.9) of an individual low-molecular-weight compound, and σ_V is the corresponding half width at 60.7% peak height of the elution peak.

3.4.13 plate height

recommended symbol: H

The length of a part of a size-exclusion chromatography (see 3.4.6) bed corresponding to one plate, i.e., the length of the bed, L , divided by its plate number (see 3.4.12), N , or $H = L/N$.

4 ALPHABETICAL INDEX OF TERMS

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