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DEFINITIONS OF BASIC TERMS RELATING TO POLYMER LIQUID CRYSTALS

(IUPAC Recommendations 2001)

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Definitions of basic terms relating to polymer liquid crystals

(IUPAC Recommendations 2001)

Abstract: The document first gives definitions of basic terms related to liquid-crystalline and mesomorphic states of matter and then terms specific to the classification of liquid-crystal polymers. The terms have been restricted to those most commonly encountered in the structural description of the latter class of materials.

The terms have been selected from the recently published comprehensive document "Definitions of basic terms relating to low-molar-mass and polymer liquid crystals" [*Pure and Applied Chemistry* **73** (5), 845–895 (2001)] and are intended to form a readily usable guide for the reader interested in the structural description of polymer liquid crystals. The more comprehensive document should be used for terminology associated with types of mesophases and the optical and physical characteristics of liquid-crystalline materials.

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1 INTRODUCTION

This document provides definitions of the basic terms that are commonly used in the field of liquid-crystalline polymers.

The recommendations made are concerned with terminology relating to the structure of liquid-crystal polymers. General terms relating to liquid-crystalline and mesomorphic states are defined first followed by terms specific to the classification of liquid-crystal polymers.

In view of the rapid growth of the field, the present document has been restricted to established terms presently in common usage [1–39].

Implied definitions, occurring in Notes to the main definitions, are indicated by using bold type for the terms so defined.

The terms have been selected from the recently published, more comprehensive document [40] "Definitions of basic terms relating to low-molar-mass and polymer liquid crystals" [*Pure and Applied Chemistry* **73** (5), 845–895 (2001)] and are intended to form a readily usable guide for the reader interested in the structural description of polymer liquid crystals. The more comprehensive document should be used for terminology associated with mesophases, and the optical textures and physical characteristics of liquid-crystalline materials. Section 2 of this guide corresponds essentially to Section 2 of the comprehensive document and Sections 3 to 6 of the comprehensive document.

The numbering of the terms in the present document is sequential within each section. When the number of a term is different from that in the more comprehensive document, the number of the term

in the comprehensive document is given in square brackets, e.g., 2.7 [2.10] mesogenic group indicates that the term 2.7 in the present document is the same as 2.10 in the comprehensive document.

2 GENERAL DEFINITIONS

2.1 mesomorphic state mesomorphous state

A state of matter in which the degree of molecular order is intermediate between the perfect three-dimensional, long-range positional and orientational order found in solid crystals and the absence of long-range order found in isotropic liquids, gases, and amorphous solids.

Notes:

1. The term “mesomorphic state” has a more general meaning than “liquid-crystal state” (see Definition 2.2), but the two are often used as synonyms.
2. The term is used to describe orientationally disordered crystals, crystals with molecules in random conformations (i.e., conformationally disordered crystals), plastic crystals, and liquid crystals (see Definition 2.3).
3. A compound which can exist in a mesomorphic state is usually called a **mesomorphic compound** (see Definition 2.8 [2.11]).
4. A vitrified substance in the mesomorphic state is called a **mesomorphic glass** and is obtained, for example, by rapid quenching or by cross-linking.

2.2 liquid-crystal state liquid-crystalline state *Recommended abbreviation: LC state*

A mesomorphic state having long-range orientational order and either partial positional order or complete positional disorder.

Notes:

1. In the LC state, a substance combines the properties of a liquid (e.g., flow, ability to form droplets) and a crystalline solid (e.g., anisotropy of some physical properties).
2. The LC state occurs between the crystalline solid and the isotropic liquid states on varying, for example, the temperature.

2.2.1 liquid-crystalline phase *Recommended abbreviation: LC phase*

A phase occurring over a definite temperature range within the LC state.

2.3 liquid crystal *Recommended abbreviation: LC*

A substance in the LC state.

Note: A pronounced anisotropy in the shapes and interactions of molecules, molecular moieties, or molecular aggregates is necessary for the formation of liquid crystals.

2.4 mesophase

A phase occurring over a definite range of temperature, pressure, or concentration within the mesomorphic state.

2.4.1 enantiotropic mesophase

A mesophase that is thermodynamically stable over a definite temperature or pressure range.

Note: The range of thermal stability of an enantiotropic mesophase is limited by the melting point and the clearing point of an LC compound (see Definition 2.6) or by any two successive mesophase transitions.

2.4.2 thermotropic mesophase

A mesophase formed by heating a solid or cooling an isotropic liquid, or by heating or cooling a thermodynamically stable mesophase.

Notes:

1. The adjective “thermotropic” describes a change of phase with a change of temperature. “Thermotropic” may also be used to qualify types of mesophase (e.g., thermotropic nematic).
2. Analogous changes can also occur on varying the pressure in which case the mesophase may be termed **barotropic mesophase**.

2.4.3 lyotropic mesophase

A mesophase formed by dissolving an amphiphilic mesogen in a suitable solvent, under appropriate conditions of concentration, temperature, and pressure.

Notes:

1. The essential feature of a lyotropic liquid crystal is the formation of molecular aggregates or micelles as a result of specific interactions involving the molecules of the amphiphilic mesogen and those of the solvent.
2. See Definition 2.8.1 [2.11.1] for the definition of an amphiphilic mesogen.
3. The mesomorphic character of a lyotropic mesophase arises from the extended, ordered arrangement of the solvent-induced micelles. Hence, such mesophases should be regarded as based not on the structural arrangement of individual molecules (as in a nonamphiphilic or a thermotropic mesophase), but on the arrangement of multimolecular units.

2.4.4 amphitropic compound

A compound that can exhibit thermotropic as well as lyotropic mesophases.

Note: Examples are nonbranched potassium alkanooates, lecithin, certain polyisocyanates, cellulose derivatives with long side-chains, such as (2-hydroxypropyl)cellulose, and cyanobiphenyl derivatives of alkyl(triethyl)ammonium bromide.

2.4.5 monotropic mesophase

A metastable mesophase that can be formed by supercooling an isotropic liquid or an enantiotropic mesophase at a given pressure to a temperature below the melting point of the crystal.

2.5 transition temperature

Recommended symbol: T_{XY}

SI unit: K

The temperature at which the transition from mesophase X to mesophase Y occurs.

Note: Mesophase X should be stable at lower temperature than phase Y. For example, the nematic-isotropic transition temperature would be denoted as T_{NI} .

2.6 clearing point

clearing temperature

isotropization temperature

Recommended symbol: T_{cl} or T_i

SI unit: K

The temperature at which the transition between the mesophase with the highest temperature range and the isotropic phase occurs.

Note: The term should only be used when the identity of the mesophase preceding the isotropic phase is unknown.

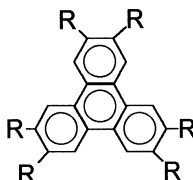
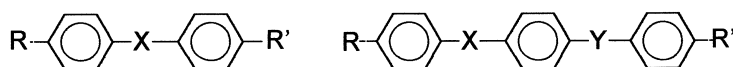
**2.7 [2.10] mesogenic group
mesogenic unit
mesogenic moiety**

A part of a molecule or macromolecule endowed with sufficient anisotropy in both attractive and repulsive forces to contribute strongly to mesophase or, in particular, LC mesophase formation in low-molar-mass and polymeric substances.

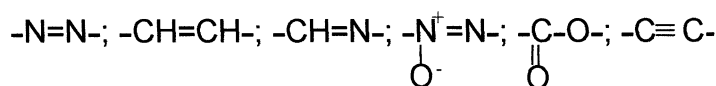
Notes:

1. "Mesogenic" is an adjective that in the present document applies to molecular moieties that are structurally compatible with the formation of LC phases by the molecular system in which they exist.
2. Mesogenic groups occur in both low-molar-mass and polymeric compounds.
3. A majority of mesogenic groups consists of rigid rod- or disc-like molecular moieties.

Examples of mesogenic groups



where X and Y are covalent bonds or linking units such as:



**2.8 [2.11] mesogen
mesogenic compound
mesomorphic compound**

A compound that under suitable conditions of temperature, pressure, and concentration can exist as a mesophase or, in particular, as an LC phase.

Notes:

1. When the type of mesophase formed is known, more precisely qualifying terminology can be used, e.g., **nematogen**, **smectogen**, and **chiral nematogen**.
2. When more than one type of mesophase can be formed, more than one qualification could apply to the same compound and then the general term mesogen should be used.

2.8.1 [2.11.1] amphiphilic mesogen

A mesogen composed of molecules consisting of two parts of contrasting character that are hydrophilic and hydrophobic or lipophobic and lipophilic.

Notes:

1. Examples of amphiphilic mesogens are soaps, detergents, and some block copolymers.
2. Under suitable conditions of temperature and concentration, similar parts of amphiphilic molecules cluster together to form aggregates or micelles (see Definition 2.4.2).

2.8.2 [2.11.2] nonamphiphilic mesogen

A mesogen that is not of the amphiphilic type.

Notes:

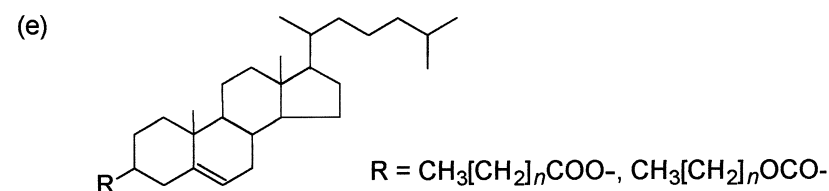
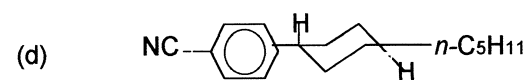
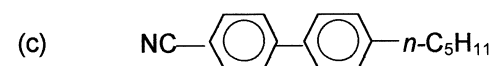
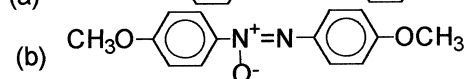
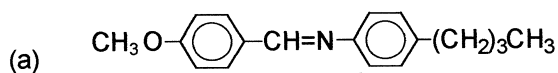
1. At one time it was thought that a nonamphiphilic molecule had to be long and rod-like for mesophase formation, but it has now been established that molecules of other types and shape, for example, disc-like and banana-shaped molecules, may also form mesophases. (See ref. 6).
2. A selection of the types of nonamphiphilic mesogens is given in Definitions 2.8.2.1–2.8.2.10 [2.11.2.1–2.11.2.10].

2.8.2.1 [2.11.2.1] calamitic mesogen

A mesogen composed of rod- or lath-like molecules.

Note: Examples are:

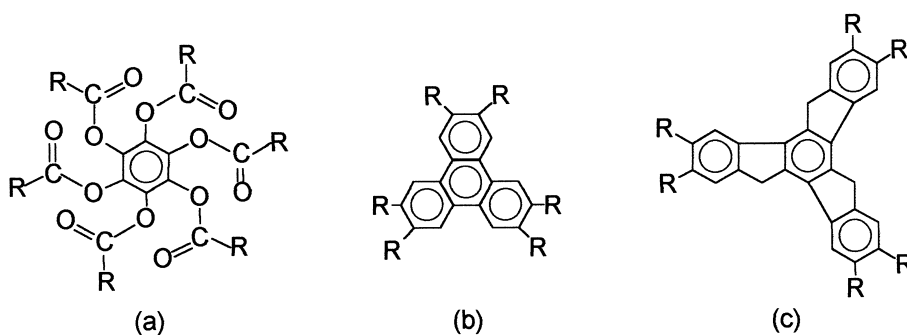
- 4-butyl-*N*-(4-methoxybenzylidene)aniline (BMBA) (a)
- 4,4'-dimethoxyazoxybenzene (b)
- 4-cyano-4'-pentylbiphenyl (c)
- 4-(trans-4-pentylcyclohexyl)benzotrile (d)
- cholesterol and cholest-5-ene-3-carboxylic acid esters (e).

**2.8.2.2 [2.11.2.2] discotic mesogen
discoid mesogen**

A mesogen composed of relatively flat, disc- or sheet-shaped molecules.

Notes:

1. Examples are: hexa(alkanoyloxy)benzenes (a), hexa(alkanoyloxy)- and hexa-alkoxytriphenylenes (b), 5*H*,10*H*,15*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene derivatives (c).



Examples of some substituents are:

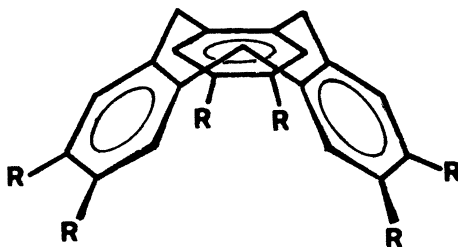
R = alkyl, alkoxy, alkanoyl, (*n*-alkylbenzoyl)oxy groups

- The adjective “discotic” is also employed to describe the nematic mesophases formed by discotic mesogens. The mesophases formed by a columnar stacking of disc-like molecules are described as columnar mesophases. These terms refer to Definitions 3.2 in the comprehensive document [40].

**2.8.2.3 [2.11.2.3] pyramidic mesogen
conical or cone-shaped mesogen
bowlic mesogen**

A mesogen composed of molecules containing a semi-rigid conical core.

Note: Examples are hexasubstituted 5*H*,10*H*,15*H*-tribenzo[*a,d,g*][9]annulenes.




2.8.2.4 [2.11.2.4] sanidic mesogen

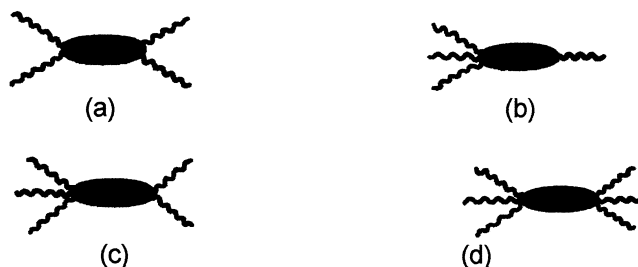
A mesogen composed of board-like molecules with the long-range orientational order of the phase reflecting the symmetry of the constituent molecules.

2.8.2.5 [2.11.2.5] polycatenary mesogen

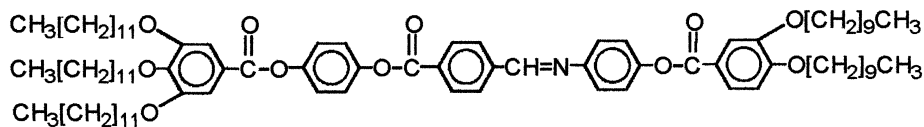
A mesogen composed of molecules each having an elongated rigid core with several flexible chains attached to its end(s).

Notes:

- The flexible chains are usually aliphatic.
- The numbers of flexible chains at the ends of the core can be indicated by using the term *m,n*-polycatenary mesogen.
- There exist several descriptive names for these mesogens. Examples are: (a) **biforked mesogen** (2,2-polycatenary mesogen), (b) **hemiphasmidic mesogen** (3,1-polycatenary mesogen), (c) **forked hemiphasmidic mesogen** (3,2-polycatenary mesogen), and (d) **phasmidic mesogen** (3,3-polycatenary mesogen). Examples of each type with the core represented by  are given together with a specific example of a forked hemiphasmidic mesogen (c).



A specific example of (c) is



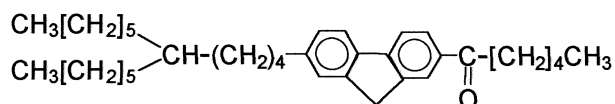
2.8.2.6 [2.11.2.6] swallow-tailed mesogen

A mesogen composed of molecules with an elongated rigid core with, at one end, a branched flexible chain, having branches of about the same length.

Note: A sketch of the structure of a swallow-tailed mesogen is



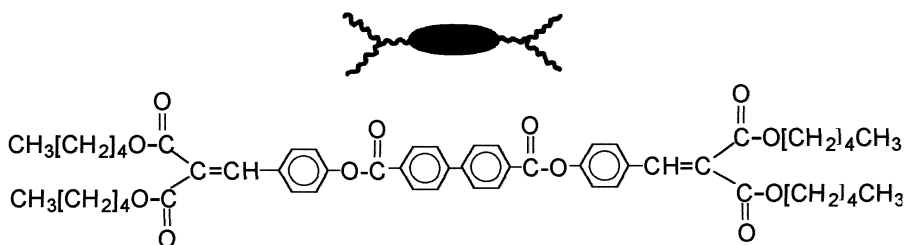
and an example is the fluorene derivative



2.8.2.7 [2.11.2.7] bis-swallow-tailed mesogen

A mesogen composed of molecules with an elongated rigid core and a branched flexible chain, with branches of about the same length, attached at each end.

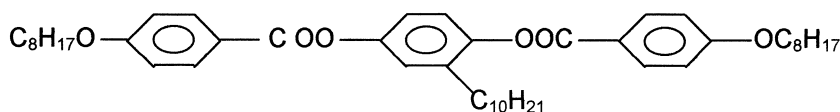
Example:



2.8.2.8 [2.11.2.8] laterally branched mesogen

A mesogen composed of rod-like molecules with large lateral branches such as alkyl, alkoxy, or ring-containing moieties.

Example:

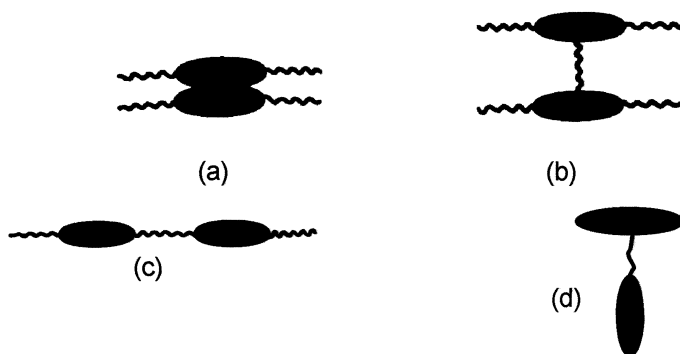


2.8.2.9 [2.11.2.9] liquid-crystal oligomer mesogenic oligomer

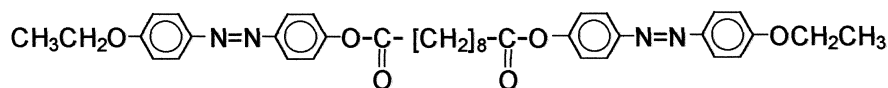
A mesogen constituted of molecules, each with more than one mesogenic group.

Notes:

1. The mesogenic groups usually have identical structures.
2. A **liquid-crystal dimer** or **mesogenic dimer** is sometimes known as a **twin mesogen**. Use of the terms “dimesogenic compounds” and “Siamese-twin mesogen” for “liquid-crystal dimer” or “mesogenic dimer” is not recommended.
3. Examples of mesogenic dimers are: (a) **fused twin mesogen**, where the mesogenic groups are linked rigidly by a (usually fused) ring system; (b) **ligated twin mesogen**, in which the mesogenic groups are connected by a **spacer** (see Definition 3.4. [6.4]) at a central position; (c) **tail-to-tail twin mesogen**, which has a flexible spacer linking the two groups; and (d) **side-to-tail twin mesogen**. The structures of these different types of liquid-crystal dimers are illustrated with the mesogenic groups are represented by



A specific example of type (c), a tail-to-tail liquid-crystal dimer is



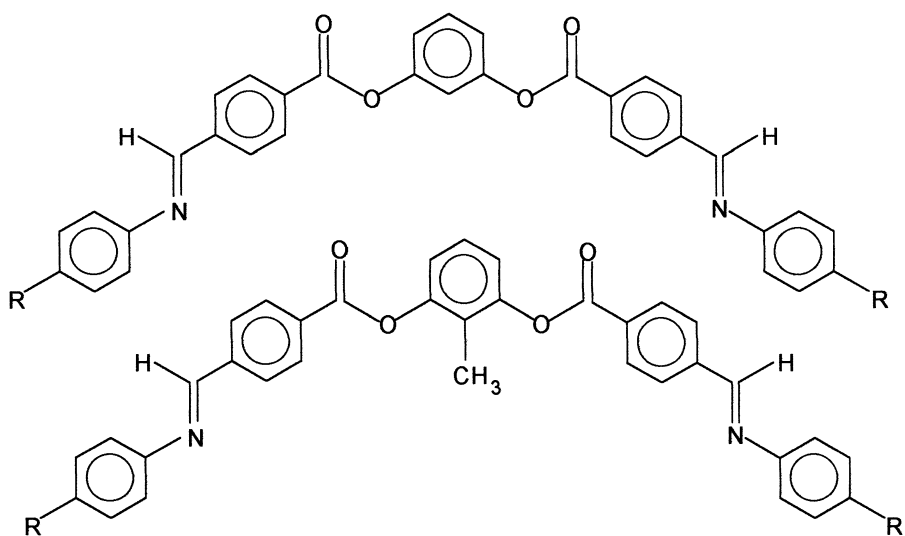
wherein $-\text{[CH}_2\text{]}_8-$ is the flexible spacer linking the two mesogenic groups.

4. A liquid-crystal dimer with different mesogenic groups linked by a spacer is known as an **asymmetric liquid-crystal dimer**.
5. A liquid-crystal dimer with flexible hydrocarbon chains having an odd number of carbon atoms is called an **odd-membered liquid-crystal dimer**, whereas one with hydrocarbon chains having an even number of carbon atoms is called an **even-membered liquid-crystal dimer**.

2.8.2.10 [2.11.2.10] banana mesogen

A mesogen constituted of bent or so-called banana-shaped molecules in which two mesogenic groups are linked through a semi-rigid group in such a way as not to be colinear.

Note: Examples of such structures are



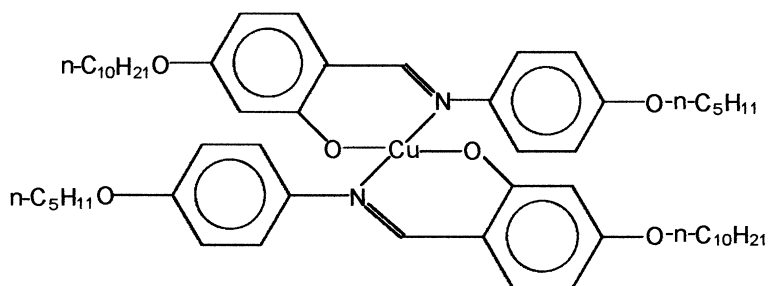
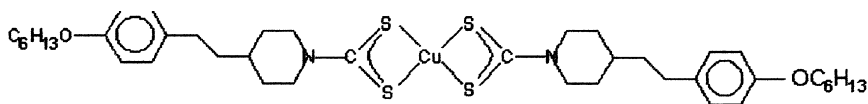
with the substituent group R being an alkoxy group.

2.8.3 [2.11.3] metallomesogen

A mesogen composed of molecules incorporating one or more metal atoms.

Notes:

1. Metallomesogens may be either calamitic (see Definition 2.8.2.1 [2.11.2.1]) or discotic (see Definition 2.8.2.2 [2.11.2.2]).
2. Examples of such compounds are



3 [6] LIQUID-CRYSTAL POLYMERS

3.1 [6.1] liquid-crystal polymer polymer liquid-crystal liquid-crystalline polymer

Recommended abbreviations: LCP and PLC

A polymer material that, under suitable conditions of temperature, pressure, and concentration, exists as an LC mesophase.

**3.2 [6.2] main-chain polymer liquid-crystal
main-chain liquid-crystalline polymer**
Recommended abbreviation: MCPLC or MCLCP

A polymer, whose molecules have mesogenic units only in their main chains.

Notes:

1. An MCPLC is formed by linking together suitable relatively rigid units directly or through appropriate functional groups (see Fig. 1).
2. The linkage between the rigid units (I) may be (a) direct or (b–g) via flexible spacers (II) (see Definition 3.4 [6.4]).
3. A MCPLC with cross-shaped mesogenic groups (b) or (g) is known as a **cruciform (or star) polymer liquid-crystal**.
4. The rigid units may, but often do not, possess intrinsic mesogenic character.

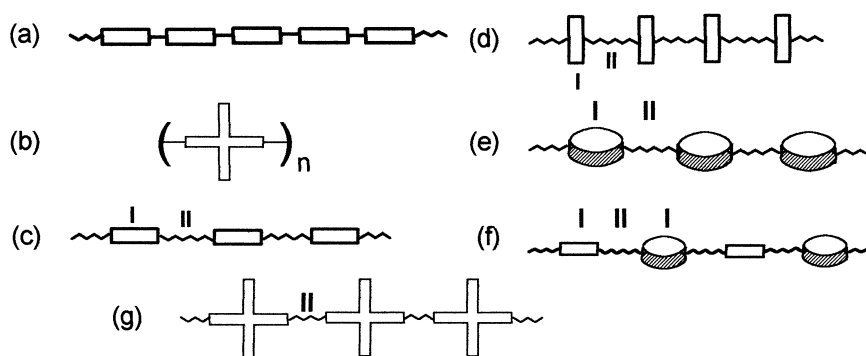


Fig. 1 Examples of main-chain polymer liquid-crystals: I - mesogenic group; II - spacer.

**3.3 [6.3] side-group or side-chain polymer liquid-crystal
side-group or side-chain liquid-crystalline polymer**
polymer with mesogenic side-groups or side-chains
comb-shaped (comb-like) polymer liquid-crystal
Recommended abbreviations: SGPLC, SCPLC, SGLCP, SCLCP

A polymer, the molecules of which have mesogenic units only in the side-group's side-chains.

Notes:

1. The mesogenic groups (I) in an SGPLC can be connected to the backbone (III) either (a) directly or (b,c) via flexible spacers (II) (see Fig. 2).
2. The structures as in Fig. 2 can also be used with the proviso that the side-group units are replaced by chains containing mesogens.
3. Examples of polymer backbones are polyacrylates, polymethacrylates, and polysiloxanes; the spacers are usually polymethylene, poly(oxyethylene), or polysiloxane fragments.
4. The pendant groups in these polymers have structures compatible with liquid-crystal formation, that is, they are mesogenic but not intrinsically mesomorphic. See the examples given in Definitions 2.7 [2.10]; 2.8.2.1 [2.11.2.1].
5. If the mesogenic side groups are rod-like (calamitic), the resulting polymer may, depending upon its detailed structure, exhibit any of the common types of calamitic mesophases: nematic, chiral nematic, or smectic. Side-on fixed SGPLC, however, are predominantly nematic or chiral nematic in character. Similarly, disc-shaped side-groups tend to promote discotic nematic or columnar

mesophases, while amphiphilic side-chains tend to promote amphiphilic or lyotropic mesophases.

6. A plethora of types of copolymers can be produced. For example, nonmesogenic side-groups may be used in conjunction with mesogenic side-groups and the polymer backbone may be substituted, to various degrees, with side-groups or chains.

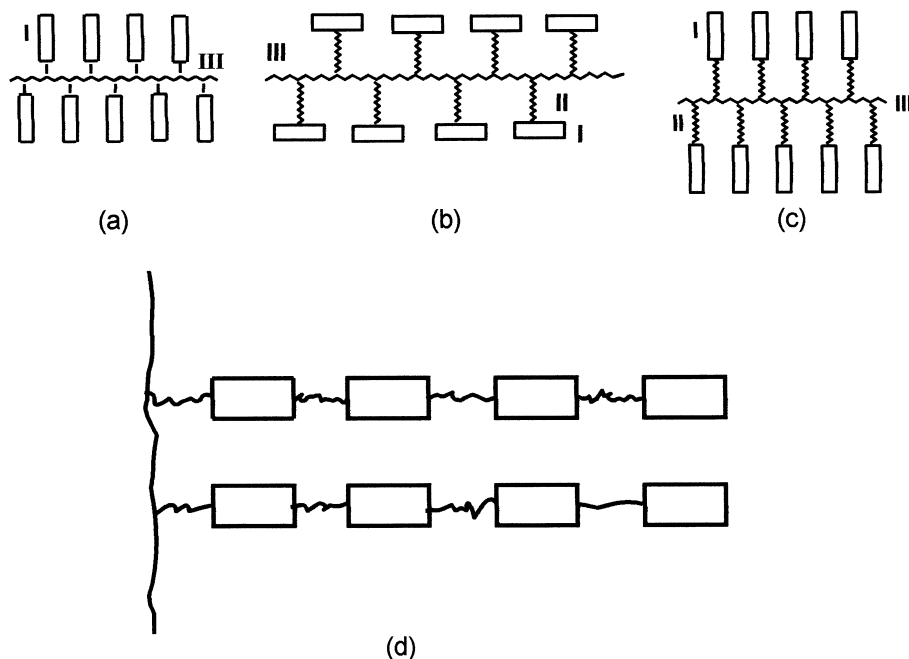


Fig. 2 Examples of side-group polymer liquid-crystals: I - mesogenic group; II - spacer; III - backbone. The terminology “**side-group**” is used for (a), “**side-on fixed**” is used for (b), “**end-on fixed**” for (c), and “**side-chain**” for (d).

3.4 [6.4] spacer

A flexible segment used to link successive mesogenic units in the molecules of MCPLCs or to attach mesogenic units as side-groups onto the polymer backbone of SGPLCs.

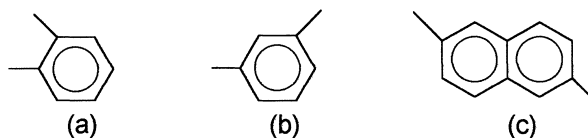
Notes:

1. Examples of spacers are: polymethylene, poly(oxyethylene) or polysiloxane chains.
2. The term is also used for the group linking two or more mesogenic units in liquid-crystal oligomers (see Definition 2.8.2.9 [2.11.2.9]).

3.5 [6.5] disruptor

A chemical group used to disrupt the linearity of the backbone of molecules of MCLCPs.

Note: Examples are (a,b) rigid-kink or (c) crankshaft units.



3.6 [6.6] combined liquid-crystalline polymer

A liquid-crystalline polymer consisting of macromolecules in which mesogenic groups are incorporated both in the main-chain and in the side-groups.

Note: See Fig. 3. The mesogenic side-groups can be attached either as lateral substituents to the backbone mesogenic moieties that are connected to each other either (a) directly or (b) by spacers or (c) they can be attached to the spacer incorporated into the main-chain.

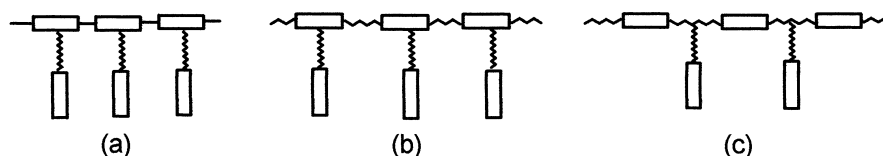


Fig. 3 Examples of combined liquid-crystalline polymers.

3.7 [6.7] rigid chain

The rod-like chain of a MCPLC with direct links between the mesogenic groups for which the persistence length is at least comparable with the contour length and much greater than the diameter.

Notes:

1. The persistence length is a characteristic of the stiffness of a chain in the limit of infinite chain length [see *Compendium of Macromolecular Nomenclature*, W. V. Metanovski (Ed.), p. 47, Blackwell Scientific Publications, Oxford, 1991].
2. A polymer composed of molecules that have rigid rod-like groups or chains usually does not show thermotropic mesomorphic behavior because decomposition occurs below its melting point.
3. A polymer composed of molecules that have rigid rod-like groups or chains may form LC mesophases in solution under suitable conditions. These are sometimes described as lyotropic but, as the solvent does not induce the formation of aggregates or micelles, this term is not appropriate.

3.8 [6.8] semi-rigid chain

A chain for which the contour length is greater than the persistence length but for which their ratio is still below the Gaussian limit.

Note: Some polymers composed of semi-rigid chains form amphiphilic mesogens (see Definition 2.8.1 [2.11.1]).

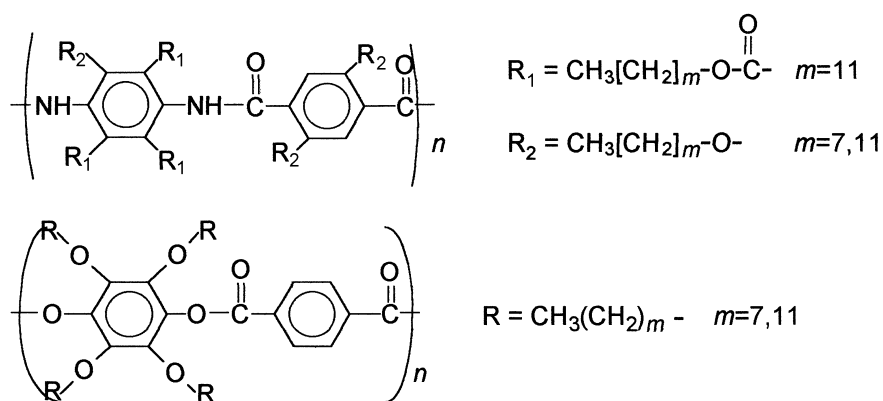
Examples: Polyisocyanates and (2-hydroxyethyl)cellulose.

3.9 [6.9] board-shaped polymer

A polymer chain composed of a rigid backbone to which a large number of lateral side groups is attached, giving the repeat unit a board-like shape.

Notes:

1. The rigid backbone often has a polyester, polyamide, or poly(ester-co-amide) type of structure. Examples are:



2. A polymer LC consisting of macromolecules of board-like shape can be called a board-shaped polymer LC. Such polymers can form sanidic mesogens (see Definition 2.8.2.4. [2.11.2.4]).

3.10 [6.10] liquid-crystal dendrimer dendrimeric liquid-crystal dendritic liquid-crystal

A highly branched oligomer or polymer of dendritic structure containing mesogenic groups that can display mesophase behavior.

Notes:

1. See Fig. 4. The mesogenic groups can be located along the chains of the molecule (a) or can occur as terminal groups (b).
2. The mesogenic groups can be, e.g., rod- or disc-like, and can be attached laterally or longitudinally to the flexible spacers.

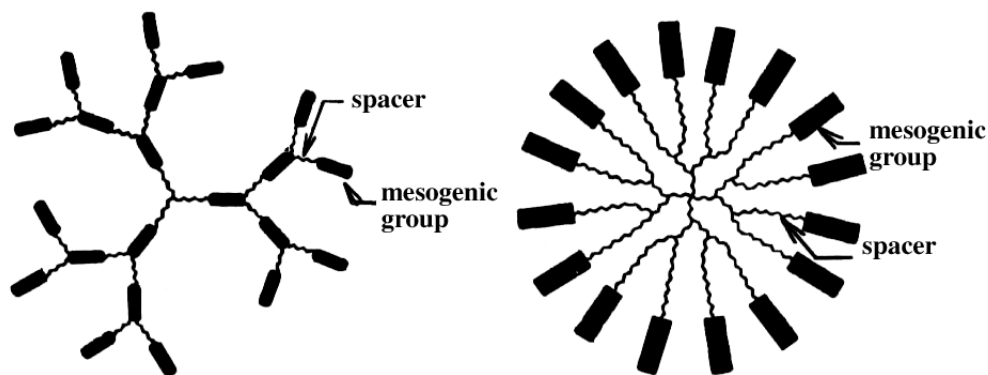


Fig. 4 Liquid-crystal dendrimers: (a) with mesogenic groups in the whole volume of a macromolecule, (b) with terminal mesogenic groups.

3.11 [6.11] hyperbranched-polymer liquid-crystal

A polymer composed of highly branched macromolecules containing mesogenic groups of which any linear subchain generally may lead in either direction, to at least two other subchains.

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