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Interphases and Mesophases in Polymer Crystallization II

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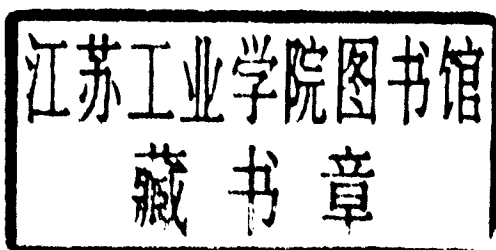
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This series presents critical reviews of the present and future trends in polymer and biopolymer science including chemistry, physical chemistry, physics and material science. It is addressed to all scientists at universities and in industry who wish to keep abreast of advances in the topics covered.

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Preface

Polymer crystallisation is a field of science whose widespread practical and technological implications add to its scientific relevance. Unlike most molecular substances, synthetic polymers consist of long, linear chains usually covering a broad distribution of molecular lengths. It is no surprise that only rarely may they give rise to regularly shaped crystals, if at all. As a rule, especially from the bulk state, polymers solidify as very tiny crystals interspersed in an amorphous matrix and randomly interconnected by disordered chains. How do these crystals form? Do they correspond to a state of thermodynamic equilibrium, or are the chains so inextricably entangled that equilibrium is virtually impossible to reach? There is currently a widespread consensus on the latter conclusion, which only makes the problem more interesting as well as more difficult to handle. The perspective at the base of the present endeavour can be summarised with two questions: What are the key structural steps from the original non-crystalline states to the semi-crystalline organization of the polymer? Do these different stages influence the resulting structure and to what degree?

As demonstrated by the collection of review articles published within three volumes of *Advances in Polymer Science* (Volumes 180, 181 and 191), this problem may be approached from very different sides, just as with the related topic of polymer melting, for that matter. Morphological and atomistic investigations are carried out through the several microscopic and scattering techniques currently available. X-ray, neutron and electron diffraction also provide information to unravel the structure puzzle down to the atomistic level. The same techniques also allow us to explore *kinetic* aspects. The fast development of molecular simulation approaches in the last few decades has given important answers to the many open problems relating to kinetics as well as morphology; in turn, statistical-mechanical studies try to make sense of the many experimental results and related simulations. In spite of several successes over 60 years or more, these studies are still far from providing a complete, unambiguous picture of the problems involved in polymer crystallisation. As one of the authors (an outstanding scientist as well as a very good friend) told me a couple of years ago when we started thinking about this project, we should not regard this book as the solution to our big problem – which it is not – but rather

as a sort of “time capsule” left to cleverer and better-equipped scientists of generations to come, who will make polymer crystallisation completely clear.

Thanks to all the authors for making this book possible. Here I cannot help mentioning one of them in particular, Valdo Meille, who helped with planning, suggesting solutions and organising these volumes. Thank you, Valdo, your intelligent cooperation has been outstandingly useful.

Milan, February 2005

Giuseppe Allegra

Contents

Solid Mesophases in Semicrystalline Polymers: Structural Analysis by Diffraction Techniques F. Auriemma · C. De Rosa · P. Corradini	1
Flow-Induced Mesophases in Crystallizable Polymers L. Li · W. H. de Jeu	75
Stepwise Phase Transitions of Chain Molecules: Crystallization/Melting via a Nematic Liquid-Crystalline Phase A. Abe · H. Furuya · Z. Zhou · T. Hiejima · Y. Kobayashi	121
Motional Phase Disorder of Polymer Chains as Crystallized to Hexagonal Lattices P. Sozzani · S. Bracco · A. Comotti · R. Simonutti	153
Author Index Volumes 101–181	179
Subject Index	201

Solid Mesophases in Semicrystalline Polymers: Structural Analysis by Diffraction Techniques

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1	Introduction	2
2	Disorder in Crystals of Low Molecular Mass Molecules: Limit Models of Mesophases	5
3	Disorder in Semicrystalline Polymers: Limit Models of Mesophases	6
3.1	General Principles	6
3.2	Classification of Disordered Systems	9
4	Calculation Methods of the X-ray Diffraction Intensities from Disordered Model Structures	14
5	Solid Mesophases with Long-Range Positional Order in Three Dimensions of Not-Point-Centered Structural Features	22
5.1	1,4-tans-poly(1,3-butadiene)	22
5.2	Poly(ϵ -caprolactame) (nylon 6)	25
5.3	Poly(acrylonitrile)	30
5.4	Ethylene-Propylene Random Copolymers	37
5.5	Alternating Ethylene-Norbornene Copolymers	42
5.6	Pseudo-Hexagonal Form of Polyethylene at High Pressure and Temperature	48
5.7	Poly(tetrafluoroethylene)	51
5.8	Alternating Ethylene-Tetrafluoroethylene Copolymers	57
6	Solid Mesophases with Long-Range Positional Order in Two or One Dimensions	59
6.1	Poly(ethylene terephthalate)	59
6.2	Isotactic Polypropylene	64
6.3	Other Mesophases Characterized by Conformationally Ordered Polymer Chains and No Order in the Lateral Packing	65
7	Conclusions	66
	References	68

Abstract Crystalline polymers may be affected by various kinds and amounts of structural disorder. Lack of order in polymer crystals may arise from the presence of defects in the chemical constitution, configuration and conformation and defects in the mode of packing of chains inside the crystals. Polymeric materials characterized by long range order in the parallel arrangement of chain axes and a large amount of structural disorder may be considered as solid mesophases. The different kinds and amount of disorder present in the solid mesophases of semicrystalline polymers and the possible types of solid mesophases are discussed in terms of idealized limit models of disorder. These models imply maintenance of long-range positional order, at least along one dimension, of structural features which are not necessarily point centered. Structural features, which are not point centered, are for instance chain axes, the center of mass of special groups of atoms or bundles of chains and so on. Structural aspects emerging from the X-ray diffraction analysis of several solid mesophases discussed so far in the literature are reviewed, in the light of the present analysis.

Keywords Solid mesophases · Disordered structures · Diffuse scattering · X-ray diffraction · Structure modeling

1

Introduction

The term “mesomorphic” was proposed by Friedel in 1922 for materials of “middle” (Greek: *mesos*) “form” (Greek: *morphe*) to address materials in a condensed phase having intermediate characteristics between liquids and crystals [1]. More generally, the term “mesomorphic” may be used to address all the states of matter, which may be considered as intermediate between the crystalline and the liquid (or amorphous) state, as for instance “positionally disordered” crystals or “orientationally ordered” liquids and/or glasses [2].

A tentative classification of mesophases was reported by Wunderlich [2], who divided mesophases into six different types of phases: liquid crystals (LC), condensation crystals (CD), plastic crystals (PC) and the corresponding LC, CD and PC glasses.

Liquid crystals are materials characterized by long-range orientational order of molecules as in crystals but absence of three-dimensional positional order as in liquids. In these “positionally disordered” crystals or “orientationally ordered” liquids, large-scale molecular motion is possible [3–5]. The name “liquid crystals” was given by Lehman in 1907 [6] because of their optical anisotropy and the liquid-like flow of these materials.

Plastic crystals are characterized by orientational disorder but positional order of the structural motif. Molecules of plastic crystals are close to spherical, which are generally packed in body- or face-centered cubic structures [7]. Typical examples are provided by the structure of ball-like hydrocarbon molecules as adamantane and norbornane. The name “plastic crystals” derives from the softness and easy of deformation of these materials, due to the large number of slip planes in close packed structures [5, 7].

The term “condis crystals” has been used to identify “conformationally disordered” crystals, i.e. structures characterized by disorder in the conformation of molecules [2].

Plastic crystals and condis crystals are two kinds of solid mesophases, whereas liquid crystals are essentially liquids. The differences between these three mesophases are largely based on the geometry of the molecules: the molecules of liquid crystals always have a rigid, mesogenic group which is rod- or disk-like and causes a high activation barrier to rotational reorientation [3, 5]. The molecules of plastic crystals are compact and rather globular, so that there is no high activation barrier to their reorientation [5, 7]. Condis crystals consist of flexible molecules which can easily undergo changes in the conformation without losing positional or orientational order [2].

According to Wunderlich [2], positionally disordered or LC-glasses, orientationally disordered or PC-glasses and conformationally disordered or CD-glasses, are terms identifying glasses obtained by quenching liquid crystals or the melt of plastic crystals and condis crystals, respectively, at temperatures below the glass transition, preventing crystallization.

As discussed in [2], in a condis crystal cooperative motion between various conformational isomers is permitted, whereas in the CD-glass this motion is frozen, but the conformationally disordered structure remains. In the case of polymers, a condition for formation of condis crystals is that the macromolecules exist in conformational isomers of low energy, which leave the macromolecules largely in extended conformations so that the parallelism of chain axes is maintained.

Condis crystals include a large number of solid mesophases of polymers, as for instance the high-temperature crystalline forms of 1,4-*trans*-poly(1,3-butadiene) [8, 9] and poly(tetrafluoroethylene) [10–12]. In both cases, the chains are conformationally disordered; long-range order is maintained as far as the parallelism of chain axes and the pseudo-hexagonal placement of chain axes are concerned.

More in general, solid mesophases not only include crystalline forms of polymers containing a large amount of disorder in the conformation of chains and long-range order in the position of chain axes as in condis crystals, but also crystalline polymers characterized by disorder in the lateral packing of conformationally ordered chains [13, 14].

A notable difference between the solid mesomorphic forms and the ordered liquid mesophases is that the solid mesomorphic forms are crystalline modifications generally characterized by the typical feature of crystalline order, that is, the packing of parallel chains. The long-range order in the correlations between the atoms of the parallel chains is absent because of the presence of disorder. The long-range order may be lost in one or two dimensions, for example, when conformationally disordered chains are packed with long-range order in the position of chain axes or for conformationally ordered chains packed with a high degree of disorder in the lateral pack-

ing [13, 14]. The presence of these kinds of disorder generally prevents the definition of a unit cell. Typical features in the X-ray diffraction patterns of solid mesophases are the presence of a large amount of diffuse scattering and a few (if any) Bragg reflections [13].

Solid mesophases are extremely frequent in polymers. For instance, at high pressure the orthorhombic form of polyethylene transforms into a hexagonal mesophase, characterized by a high degree of disorder (conformational disorder) [15–17]. In some cases, the amorphous phase may transform into a mesophase by stretching at temperatures lower than the glass transition temperature (e.g. in poly(ethylene terephthalate) [18–20], syndiotactic polystyrene [21, 22], nylon 6 [23, 24]) or by quenching the melt at low temperatures (isotactic [25–27] and syndiotactic [28, 29] polypropylene). Copolymers of ethylene/propylene with a propylene content in the range of 15–35 mol % are amorphous at room temperature and in the unstretched state, but crystallize into a pseudo-hexagonal mesomorphic form, by cooling at low temperatures or by stretching at room temperature [30–38]. In the case of atactic polyacrylonitrile, the crystalline pseudo-hexagonal polymorph is actually a mesophase [39–48]. The already mentioned high-temperature forms of poly(tetrafluoroethylene) [10–12, 49–54] and of 1,4-*trans*-poly(1,3-butadiene) [8, 9, 55–58] may also be considered mesophases. Some, but not all, of the above listed mesophases are “condis crystals” in the sense of Wunderlich [2].

It is very difficult to classify the various kinds of solid mesophases of polymers described so far in the literature in a simple and general way, because in the crystals different kinds and different degrees of disorder may be present at the same time; often it is not easy to identify which kind of disorder mainly characterizes a given mesophase.

Because of the presence of structural disorder, the X-ray diffraction patterns of mesophases show a large amount of diffuse scattering and need a special care for a quantitative evaluation. Paracrystalline distortions of the lattice [59, 60] usually affect the shape and the width of the diffraction peaks to a large extent. The analysis of disorder necessarily implies a multidisciplinary approach, in order to unravel the complicated nature of disorder in disordered crystalline materials [61].

In this review, we attempt to present the subject of solid mesophases of polymers mainly in relation to structural aspects emerging from diffraction experiments. The relationships between the structure and properties of these materials are analyzed and related to the amount and kind of disorder present in the crystals. The study of disorder in solid mesophases, indeed, allows a deep comprehension of phenomena subtending their chemical and physical properties.

In line with arguments of [13], with the terms “solid mesophase” we identify states of matter falling “in between” amorphous and crystalline states, characterized by long-range order in the parallel arrangement of chain axes.

We will attempt to outline possible classes of solid mesophases, not based on the different kinds and amount of disorder present in the crystals, but rather in terms of idealized limit models of disorder. These models imply maintenance of long-range positional order, at least along one dimension, of structural motifs, which are not necessarily point centered [13].

2

Disorder in Crystals of Low Molecular Mass Molecules: Limit Models of Mesophases

A model of ideal crystal consists in a three-dimensional array of identical units. Such an “ideal” crystal gives rise to calculated diffraction patterns consisting of only discrete diffraction peaks (called Bragg reflections). Thermal movements are disregarded in this definition.

The definition of crystal as a periodic array of identical motifs corresponds to the mathematical concept of lattice. Under this assumption, crystallography has developed powerful methods for allowing crystal structure determination of different materials, from simple metals (where the asymmetric unit may be the single atom) to protein crystals (containing thousands of atoms per cell) [62].

However, real crystalline materials only approximate this ideal model. Departures from the ideal periodic array of identical units may usually occur in a variety of different ways and implies presence of disorder [63, 64]. The presence of disorder in the crystals gives rise to a diffuse, continuous scattering in diffraction patterns. Disorder, indeed, may cause broadening of Bragg reflections and a decrease of the maximum height of the peak intensity; for a given Bragg reflection, however, the intensity which is lost because of the presence of disorder is found in the background and represents the diffuse scattering [61, 63, 64].

First of all, disorder in crystals arises from thermal motion of atoms around their equilibrium positions (thermal disorder). Disorder may also originate from the presence of defects in the lattice, due, for instance, to substitution of atoms (or group of atoms) with atoms (or group of atoms) of a different chemical nature, inclusion of structural motifs in interstitial lattice positions, or when structural units may pack in the same basic crystal lattice in different orientations or in a different conformation [63, 64]. The presence of defects in the crystals, in turn, may induce local deformation of the lattice (due to small displacements of atoms from their average positions), which helps relaxation of local stresses, and causes diffuse scattering.

According to Hosemann [59, 60], the lattice distortions, in addition to those due to thermal vibrations of atoms, may be classified as of a) first kind if the long-range periodicity is preserved with respect to the average positions over all the lattice points, and of b) second kind if the position of each lattice

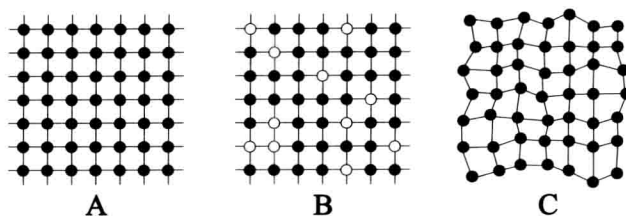


Fig. 1 (A) an ideal two-dimensional lattice. (B) first-kind distortions implying substitution type disorder; filled and empty balls indicate different chemical structural units. (C) Lattice distortions of second kind (paracrystal)

point deviates statistically only with respect to its nearest neighbors instead of respect to the ideal lattice points. As an example, lattice distortions of the first and second kind in a bidimensional lattice are schematically represented in Fig. 1.

The presence of lattice distortions of the first kind induces a decrease of the intensities of X-ray diffraction reflections with increasing diffraction order, whereas the width of reflection spots does not vary. Lattice distortions of the second kind, instead, result in both a diminution of reflection intensity and an increase in reflection breadth, with increasing reflection order [59, 60]. They are also called paracrystalline distortions [60].

3

Disorder in Semicrystalline Polymers: Limit Models of Mesophases

3.1

General Principles

Disregarding thermal motion, the concept of an ideal crystal requires long-range positional order for all atoms. For polymers, this ideal condition implies an infinite chain length, regular constitution, regular configuration and regular conformation [65].

The requirement of a regular constitution implies that all repeating units have the same chemical structure. The requirement of a regular configuration implies that whenever a monomeric unit may assume different configurations, the succession of configurations must be regular. The requirement of a regular conformation implies that the conformation assumed by polymer chains of a given constitution and configuration in the crystalline state can be defined as a succession of structural units which occupy geometrically (not necessarily crystallographically) equivalent positions with respect to a chain axis (equivalence principle) [65, 66]. The chain axis is generally parallel to a crystallographic axis of the crystal.

The geometrical equivalence of structural units along an axis allows defining types of geometrical symmetry that a linear macromolecule may achieve in the crystalline state. The conformation of a macromolecule is generally defined in terms of its symmetry and, precisely, of the line repetition symmetry group [65, 67–69].

In the framework of the allowed symmetries, that is under the restrictions imposed by the need of having an axis of repetition, the conformation of the chain will tend to approach one of minimum conformational energy for the isolated chain [65, 70–72]. Packing effects generally do not influence the conformation of the chains as long as the conformational energy of the isolated chain corresponds to a deep energy minimum. Crystal packing effects may influence the choice among conformations of nearly equal energy for the isolated chain [73].

Of course, none of the above requirements concerning infinite chain length, the regularity in constitution, configuration and conformation, can be fulfilled in the crystals of real polymers, which are then disordered [14, 65].

Some kinds of disorder are as follows: First of all, polymers (as well as oligomers, in general) are materials consisting of molecules of non-uniform molecular mass [74]. At variance with biological macromolecules, as nucleic acids and polypeptides, which are known to be uniform at least with respect to the molecular structure of the core (that is, sequence arrangement of constitutional units, stereoregularity and overall conformation), the macromolecular chains in a given polymer may be similar, but, certainly, not all alike [74, 75].

In polymers, examples of constitutional faults with respect to an idealized model include mistakes in the head-to-tail succession of monomeric units, the presence of units derived from a different monomer and in any case, the chain ends [65].

Copolymers of different monomeric units that are able to cocrystallize in the same lattice may be considered as a possible exception to the need of regularity in the chemical constitution. For instance, in the case of vinyl polymers it is possible to accommodate into the crystalline lattice different comonomeric units having lateral groups with different shape and dimensions. Copolymers of butene and 3-methylbutene [76] or copolymers of styrene and *o*-fluorostyrene [77] are crystalline over the whole range of composition, provided that the copolymers are isotactic whereas propene and 1-butene also are able to cocrystallize at any composition in syndiotactic copolymers [78, 79]. Isomorphism of comonomeric units also occurs in copolymers of acetaldehyde and *n*-butyraldehyde [80], which are crystalline over the whole range of composition. Analogous isomorphism of comonomeric units has been observed in *trans*-1,4-copolymers of butadiene and 1,3-pentadiene [81] and in copolymers of vinylidenefluoride and vinylfluoride [82].

An example of a configurational mistake is the possible presence, in an isotactic polymer, of racemic diads in place of all *meso*-diads. In several cases, the presence of configurational defects in chains of stereoregular polymers does not prevent crystallization; their possible inclusion in the crystals may be energetically feasible, provided that the portion of chain close to the defect adopt a low-energy conformation which does not disrupt the packing of close neighboring chains [83–86]. Moreover, even stereoirregular polymers are able to crystallize; classical examples are poly(vinyl alcohol) [87, 88], poly(vinyl chloride) [89–94] and poly(acrylonitrile) [39–48, 95–97].

For polymers with a regular constitution and configuration, the conformation adopted by chains in the crystalline state is generally regular. However, some three-dimensional, long-range crystalline order may be maintained even when disorder is present in the conformation of polymer chains. The term conformational isomorphism refers to the more or less random occurrence in the same lattice site of different, but almost isoenergetic, conformers of the same portion of a molecule [58]. A classification of the possible cases of conformational isomorphism in polymers can be made on the basis of the following two possibilities [98, 99]:

1. The chain may assume, in the same crystal and more or less at random, different (although nearly isosteric) conformations.
2. If the geometry of the main chain is fixed, the lateral groups may assume different conformations in the same crystal, more or less at random.

Crystalline polymers characterized by disordered conformations of the chains are, for instance, polytetrafluoroethylene [10–12, 49–54], *cis*-1,4-poly(isoprene) [100–102] and *trans*-1,4-poly(1,3-butadiene) [8, 9, 55–58]. In these cases, disorder does not destroy the crystallinity because of the similar shape of the various conformational units. The occurrence of cases of conformational isomorphism of the first kind demonstrates that a polymer chain can remain straight, as if it was constrained to run inside the walls of a tight cylinder, while its conformational freedom remains of the same order of magnitude as that in the melt.

The case of conformational isomorphism of lateral groups occurs, for instance, in the crystal structure of isotactic poly(*S*-3-methyl-pentene), characterized by the presence of fourfold helices of only one sense (left-handed), with lateral groups which may adopt statistically two conformations of minimum energy [99, 103].

In addition, conformational disorder in polymer crystals may give rise to point and line defects which are tolerated in the crystal lattice at a low cost of free energy as kinks [104, 105], jogs [106, 107] and dislocations [108, 109]. Such crystallographic defects arise whenever portions of chain adopt conformations different from the conformation assumed by the chains in the crystal state [99], and have been widely discussed in the literature, in the case of polyethylene [108, 109] and some aliphatic polyamides [99, 106]. Point and