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MESOMORPHISM IN POLYMERS AND ITS MECHANOTROPIC VARIETY FOR POLYETHYLENE IN BINARY POLYMER BLENDS BASED ON IT

E. M. Antipov[a] **and J. W. M. Noordermeer**[b]

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For the first time, an attempt has been made to illustrate the diversity of different forms of mesomorphism in flexible- and rigid-chain linear polymers whose macromolecules do not contain mesogenic groups. The emphasis has been on description of new structural varieties that are equilibrium mesophases from the thermodynamic viewpoint. Concrete examples of unusual two-dimensional and one-dimensional forms of ordering, recently found by the authors for a number of high-molecular-weight compounds, have been given.

The originality of modern concepts of the structure of high-molecular-weight compounds (HMWCs) lies in the increasingly greater departure of researchers from the two-phase model, according to which there can exist only two physical states — the crystalline state (3D — long-range order) and the amorphous state (3D — near-range order).

It is surprising how common the universally accepted viewpoint of the single-step fusion of a crystal as of the process typical of the condensed state of a substance has become. We consider the actual situation from a somewhat different viewpoint.

The simplest crystals constructed from spherically shaped elements (for example, metals) are known to be characterized by the long-range position order in three independent dimensions. If the elements constituting the crystal lattice have an anisotropy of shape (rods or disks), orientation elements of order are added to the three position degrees of freedom. If such rods or disks have lateral substitutes, one should also take into account the rotation forms of ordering. Thus, the structural hierarchy of even a low-molecular-weight crystal can appear rather complex and can possess a rich combinatorics of different "degrees of freedom" or elements of order. As far as polymers whose macromolecules have a complex structure in themselves, possess a pronounced shape anisotropy, and are often characterized by cylindrical symmetry, here one should expect dramatic thermodynamic events "on the path from a crystal to a liquid."

The question arises: from where does it follow that the entire rich hierarchy of order must be destroyed suddenly, simultaneously, at a single temperature point (and, needless to say, for a certain fixed value of pressure) in heating to form a totally "structureless" melt or, more precisely, a state characterized only by the near-range order in all three dimensions? It is much more natural to expect a step-by-step "melting" of some degrees of freedom or others in heating of the system, which means a multistep process of disordering, each step of which is separated from another by a phase transition of the first kind. This, in turn, points to the possibility of observing a sequence of polymorphic transformations of intermediate but simultaneously equilibrium structures in the temperature series (or on the pressure scale) with a gradual but discrete loss of the solid-state properties of a truly crystalline substance and approach to a truly liquid state. And that is the case. Each of such structures was considered first as an "exception to this rule," as an unusual kind of partially "spoiled" crystal, or as a liquid with an "excessively" high level of organization. In modern terminology, such equilibrium phases belong to mesomorphic states or are simply called mesophases ("meso" is "intermediate" in Greek).

Tens of varieties of equilibrium mesomorphic states in both low- and high-molecular-weight compounds have been found at present [1–3]; the process of accumulation of information in this field is intensely continuing. According

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[a] A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Lenin Ave., Moscow, 119991, Russia; email: antipov@ips.ar.ru; [b] University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 5, pp. 10–18, September–October, 2005. Original article submitted October 13, 2004.

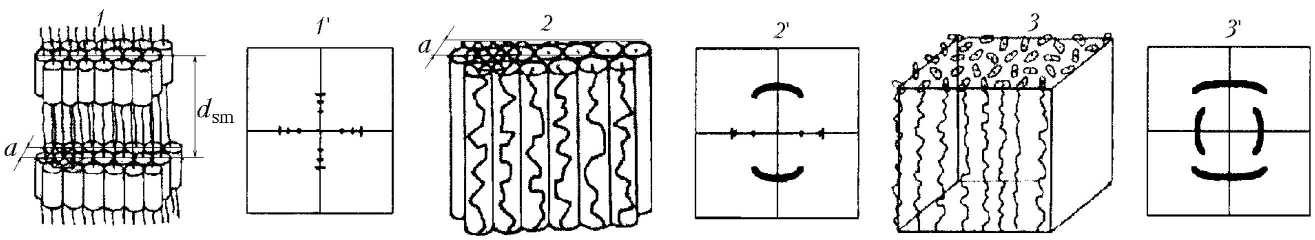

Fig. 1. Diagrammatic representation of possible equilibrium mesomorphic states in polymers and of the contours of corresponding x-ray photographs: 1) smectic LC state (orientation order + layer periodicity + two-dimensional long-range position order); 2) columnar mesophase (orientation order + two-dimensional long-range position order + conformation disorder); 3) nematic LC state (orientation order + position and conformation disordering); 1–3) models; 1′–3′) contours of the x-ray photograph.

to the classification of 1988–1994 [1, 3], the existing mesophases were subdivided (in order of diminishing liquid properties and growing solid-state ones) into three classes:

1. Liquid *crystals* (LCs) have been studied most adequately; tens of their varieties have been found; hundreds or even thousands of examples, including those for polymers, are known.

2. Plastic *crystals* (PCs) are characteristic of molecules with a slight anisotropy of shape; they do not occur in polymers.

3. Conformation-disordered (condis) *crystals* (CCs) or, according to the modern terminology, columnar mesophases, are at the stage of being intensely studied at present, particularly, in the field of polymer physics and chemistry.

We note that the term "crystal" has been used in each of the names of these three classes of mesomorphic states; needless to say, this has been established chronologically and is inconsistent with the strict meaning of the name. Despite the obvious incorrectness of such terminology, everyone has become accustomed to it and has used it thus far. All this diversity of partially disordered crystals was mainly discovered in low-molecular-weight substances. However, it has turned out that the polymer world is capable of introducing additional beauty and an even greater wealth of forms into it.

We give just a few examples based on the experimental experience of our researchers gained over a period of nearly twenty years in this field; our research team has been able to find a number of interesting new varieties of equilibrium mesophases in flexible- and rigid-chain polymers of both organic and element-organic structure.

Results and Their Discussion. For polymer systems, we have the following (fairly rigorous) simple scheme of possible mesomorphic states (Fig. 1). The transition from a typical crystal to an isotropic melt according to the scheme "3D crystal → 2D LC smectic B → 2D CC → 1D-LC nematic → 3D liquid" is accompanied by the discrete loss of one level of order, with the remaining levels being preserved. An x-ray structural analysis is the basic means of finding and identifying the structural features of different mesophases; therefore, in the figure, we give x-ray photographs, which are their unusual kind of show window. This simple structural classification of mesophase polymers was supplemented with a number of structurally new mesophases found in the course of this cycle of investigations. Figure 2 gives mainly the "unusual" varieties of LC and CC mesophases found by us for the first time and not known earlier for polymers.

It is noteworthy that all the HMWCs we are dealing with do not contain the so-called mesogenic groups in their chains. This is significant, since the situation is simple for the polymers containing them: necessary and sufficient conditions for realization of mesomorphism are observed for them, i.e., the anisotropies of macromolecular shape and the rigidity of mesogenic fragments contained in the chain are found. As was to be expected, it is precisely for such systems that a set of varieties of LC mesomorphic states in all their diversity was primarily found. Tens of monographs and thousands of publications on this subject have appeared in the scientific press in the last three decades.

However, in our opinion, of special interest are polymers whose macromolecules do not contain mesogenic groups, i.e., the systems in which the occurrence of mesomorphic groups looks like a certain paradox inconsistent with modern theoretical concepts.

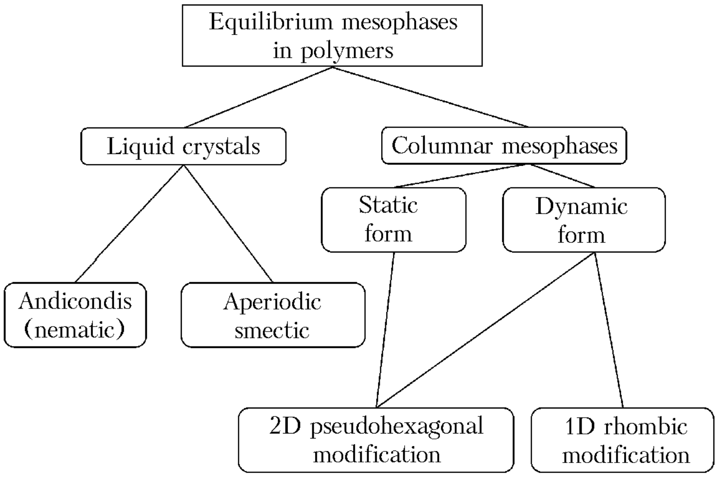

Fig. 2. Mesophases found for the first time in this investigation.

Let us consider first rigid-chain HMWCs not containing mesogenic groups in the main or side chains. More than 10 families of totally aromatic copolyesters of statistical structure of both domestic and foreign make have been investigated in detail at present [4–8]. A comparative analysis of the phase composition and temperature evolution of the structure of this class of rigid-chain HMWCs in which the chain is constructed based on monomer links of different architecture, which destroy the regular packing of macromolecules in both the longitudinal direction and that perpendicular to the chain axes, with monomers of equal and different length, and containing and not containing side groups has shown the following:

1. It has turned out that, despite the fundamentally irregular structure of such copolymers, all of them are capable of crystallizing with any ratio of the components, forming at least a two-phase partially crystalline material.

2. In the presence of a massive lateral substitute, we observe such a "fine" thermodynamic effect as phase layering with the formation of two crystalline structures coexisting in a single material, similar in type but differing in the parameters of an elementary cell.

3. When the monomer links of a copolymer are equally long, the crystalline phase is a typical 3D crystal, even if strongly imperfect. If comonomers differ in length, the crystalline phase can be described by a paracrystalline model or a model of aperiodic layers with a two-dimensional order in the plane perpendicular to the macromolecular axes. The structure of such systems more resembles the liquid-crystalline structure than the structure of a true 3D crystal.

4. Very unusual was the structure of the noncrystalline phases in these polymer objects; a detailed analysis and identification of this structure led to the discovery of the so-called aperiodic LC smectics, mesomorphic structures not known earlier for polymers. It is significant that the noncrystalline-phase part of such systems always contains an LC smectic component in addition to the LC nematic component. Depending on what kind of monomer links (of equal or different length) constitutes a polymer chain, a regular periodic layer structure or an unusual aperiodic one are formed in the system. It is precisely the aperiodic smectic mesophase (and its content always prevails) that is responsible for the operating and, in particular, mechanical characteristics of a material, including its rheological behavior.

Figure 3 shows three kinds of polymer LC smectics. The first (trivial) type (Fig. 3a) is for chains containing mesogenic groups. The second kind (Fig. 3b) is for mesogen-containing polymers in which the monomer links, however, are equally long and, as a consequence, we observe a periodic alternation of smectic layers. If the monomer links are differently long (Fig. 3c), from the formal viewpoint, such a structure must be called LC smectic, as previously, but with an aperiodic alternation of layers rather than with a periodic one (Fig. 3c).

5. In most cases, such systems demonstrate, in heating, reversible transformation from the crystalline state into a CC mesophase (with a 2D pseudohexagonal packing) with the characteristic features of phase transition of the second kind. Such a phase transformation is not always capable of being realized; in this case it is "virtual" in character. The latter means that we could have a phase transition, but the fusion and isotropy or even destruction of the material are observed long before a possible, hypothetical, transition temperature.

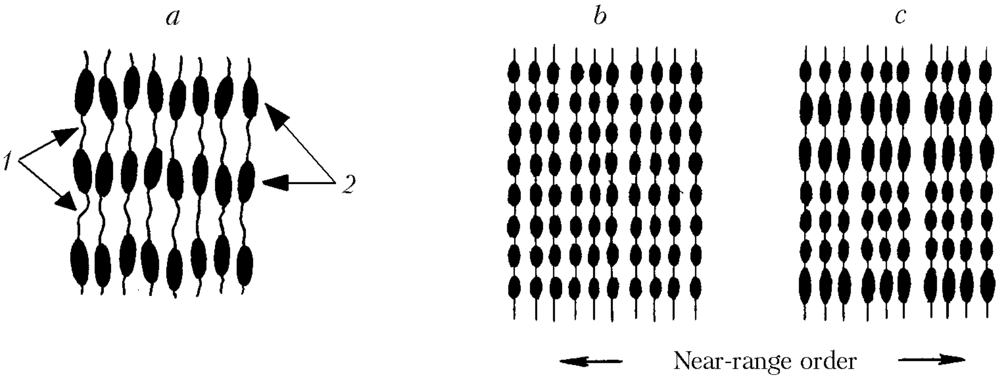

Fig. 3. Diagrammatic representation of the structure of "usual" (a) and "unusual" periodic (b) and aperiodic (c) LC smectics: 1) flexible decoupling; 2) mesogenic groups.

6. This class of polymer systems is unusual not only structurally but also in such an important (for polymers) phenomenon as the process of vitrification. In heating of the polymer in a glassy state, local mobilities of some groups or others in a monomer link are usually successively unfrozen. After the unfreezing of the latter, the polymer must additionally be heated by approximately 100°C, as a rule, for the cooperative motion of macromolecular segments to occur. This instant corresponds to the vitrification temperature.

In the case of thermotropic LC copolyesters the situation is significantly different. At the instant of unfreezing of the local mobility of the most heat-resistant structural unit of the chain, a segmental mobility immediately occurs, i.e., we have the devitrification of the entire polymer. Thus, we have proposed for the first time a new concept of the process of vitrification; this concept has turned out to be generally universal for LC rigid-chain HMWCs.

Indeed, the array of experimental data accumulated at present enables us to infer that the conclusions formulated are universal not only for the class of totally aromatic copolyesters of statistical structure but also for the adjacent classes of rigid-chain polymers whose macromolecules do not contain monomer groups. We give just a few examples for copolyamides and copolyesteramides [9].

The most popular representative of this class is KEVLAR, a regular (alternating) copolyamide of foreign make, which is widely used in practice, in particular, for production of high-strength, high-modulus fibers intended for bullet-proof jackets, superstrong ropes, etc. The destruction temperature of the polymer lies below its melting temperature. Because of their high refractoriness, high-strength fibers are produced by the method of solution (the solvent is sulfuric acid) technology. The domestic analogs of this polymer are represented, first, by SVM fiber and, second, by an ARMOS statistical copolyesteramide which, even if much more expensive, surpasses KEVLAR in mechanical characteristics.

It has turned out that aperiodic Bragg reflexes are present on the meridian of the texture x-ray photographs of the fiber of both the copolyesteramides of statistical structure and the thermotropic LC copolyesters. But unlike the copolyesters, statistical copolyamides are uncapable of crystallizing. They do not crystallize even in heat treatment above a vitrification temperature of ~300°C. However, in annealing above the vitrification temperature, a new, more ordered phase is formed from the single-phase LC nematic structure of the starting newly formed fiber; this phase is nothing but an aperiodic LC smectic — a mesophase characteristic of statistical copolyesters and found for them by us for the first time. Thus, unlike the copolyesters, the higher form of ordering for copolyamides is an aperiodic smectic coexisting in the annealed material with the LC nematic mesophase up to the disintegration temperature of the material.

Let us pass to flexible-chain polymers not containing mesogenic groups in the main or side chains. We begin with heteroorganic polyfluoroalkoxyphosphazenes [10–16].

It is noteworthy that the introduction of a fluorine atom into the chain of a flexible-chain polymer leads to unexpected results. Indeed, if we substitute fluorine in a PE macromolecule for the hydrogen, the polymer, nonmesophase-type, under normal conditions, becomes polytetrafluoroethylene in which the crystalline phase changes to a columnar one even at 300 K and exists in equilibrium in a temperature interval of the order of 300 degrees. Its

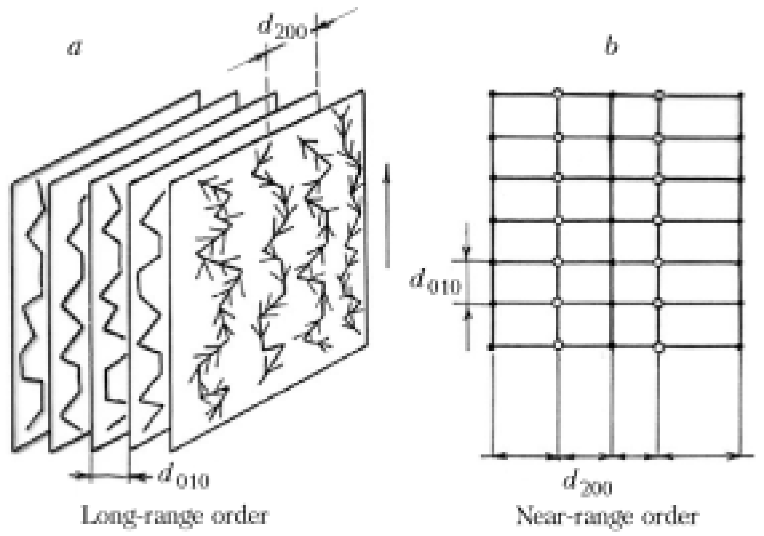

Fig. 4. One-dimensional CC mesophase of polybistrifluoroethoxyphosphazene: a) isometric projection; b) projection in the basal plane.

derivatives — polyvinylidene fluoride and others — are also mesophase-type. The same is true of polyphosphazenes: in the absence of a fluorine atom, the polymers are nonmesophase-type, whereas polyfluoroalkoxyphosphazenes demonstrate a pronounced mesophase character with an interval of its existence of 150–250°C. In particular, depending on the prehistory of preparation of the sample, polybistrifluoroethoxyphosphazene is capable of existing in three crystalline α-, β-, and γ-modifications; the β-modification crystallizes with straight chains, whereas the other two crystallize with folded chains. Accordingly, two varieties of CC mesomorphic structures — δ_1 and δ_2 — can be formed in the crystal-mesophase transition in the process of heating of the polymer. The second form is the already-mentioned mesophase with a 2D pseudohexagonal structure, and the first variety is unique (Fig. 4).

In a one-dimensional layer model, the crystallographic system is close to a pseudorhombic modification. The prefix "pseudo" means the absence of the long-range order along the chain. The macromolecules are conformationally disordered but preserve orientation and, similarly to a "sagged" band or thread, lie in the planes arranged in space with a strict periodicity. Only the near-range order is realized within the layer. That is why the structure is one-dimensional (in terms of long-range position ordering).

Such a mesophase type was found by us for the first time in 1993. Subsequently, the works of other scientists confirmed the existence of 1D varieties of condis crystals and their static and dynamic modifications (we will be dealing with them below) using other polymer objects: polyorganosiloxanes.

Unusual, even if simpler, appears the chain of phase transformations for the second term of the homologous series of polyfluoroalkoxyphosphazenes. In heating of the polymer, first we observe the transition of a 3D monoclinic crystal to a typical LC smectic characteristic of comb-shaped polymers, in which the side framing of macromolecules is well packed but the chains themselves are conformationally disordered. At higher temperatures, we observe the transition to a 2D pseudohexagonal mesophase and only thereafter a true melting of the polymer. Crystallization turned out to be completely impossible for the third homolog since its vitrification temperature is higher than the crystallization temperature of the polymer. Therefore, for this polymer we observed for the first time an effect of great interest: the transition of the high-temperature form of the mesophase to its low-temperature variety.

In cooling of the polymer from the state of a high-temperature CC mesophase, we observe the "amorphism" of the pattern of x-ray scattering, accompanied by a very slight (~1 J) thermal effect on the thermogram obtained by the method of differential scanning calorimetry (DSC). This is paradoxical, since, as it would seem, no deterioration of the order can be observed in cooling. Nonetheless, such is the case, since the high-frequency, rotation–vibration mobility of macromolecular segments relative to the intrinsic axis is "frozen out" with decrease in the temperature. It is precisely these motions that result in the cylindrical symmetry of bodies of revolution at elevated temperatures, and the closest packing of them is known to be hexagonal. Hence, columnar mesophases in most cases possess a pseudohexagonal structure.

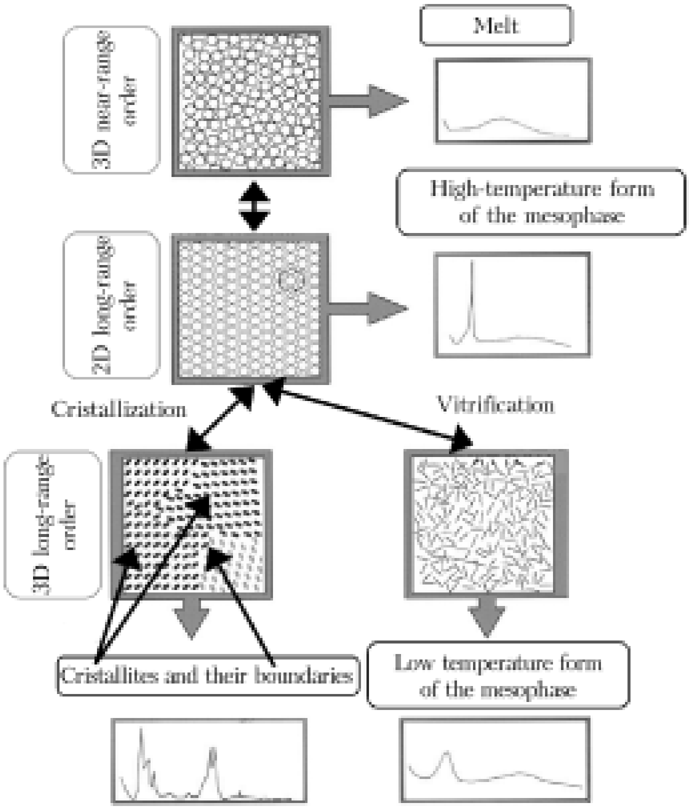

Fig. 5. Diagram of possible phase transformations in mesophase polymers not containing mesogenic groups (using polyfluoroalkoxyphophazenes as an example), including the high-temperature-to-low-temperature transition of the CC mesomorphic state.

As can be seen from the diagram presented (Fig. 5), there are three pathways from the dynamic state or the high-temperature form of a mesophase. The first is further heating and formation of an isotropic melt. The second is cooling: if crystallization is possible, the mesophase–crystal transition is realized; if crystallization is impossible for some reasons or is hindered, the high-temperature-to-low-temperature transition of a mesophase is realized.

It has turned out that this diagram of transitions is universal and also suitable for other mesophase polymers of this type, such as polyorganosiloxanes [17], polytetrafluoroethylene and its derivatives [2], 1,4-*trans*-polybutadiene (TPB) (one of the oldest representatives of the class of polyelastomers, studied in great detail, it would seem, in the last five decades [18–20]), and others. We will be dealing with some of them below.

Quite recently we have developed new catalysts [21] intended for synthesis mainly of polymers — PEs, PPs, and higher poly-α-olefins — widely used in practice. These are the so-called binucleus metal-complex catalytic systems distinguished by their high activity, their stereospecificity of action, and a sharp reduction in the by-product yield, i.e., environmentally safe ones.

We do not know of attempts to apply such catalysts to the synthesis of polydienes. Varying the composition of a catalytic system and the conditions of the reaction, we obtained a maximum regular polymer — 1,4-*trans*-PB or 1,4-*cis*-PB, or the mechanical mixtures of 1,4-*trans*-, 1,4-*cis*-, and 1,2-vinylhomopolymer, or a number of statistical copolymers of a wide range of compositions, whose macromolecules are constructed from 1,4-*trans*- and 1,2-links.

1,4-*trans*-polybutadiene is known to be one of the few flexible-chain polymers demonstrating two-step melting. At 70–80^{o}C, monoclinic crystals change to a mesomorphic state with a 2D pseudohexagonal structure (columnar mesophase), whereas at 140^{o}C, the mesophase is melted to form an isotropic melt.

Curiously, the newly produced polymer (polymer with a nascent structure) demonstrates the doublet character of the endomaximum for high-temperature transition in heating. This doubling rapidly disappears with the introduction of foreign links into the regular chain. Both low- and high-temperature transitions shift toward lower temperatures; the temperature interval between them decreases down to its complete disappearance.

A detailed analysis of the diffraction pattern of scattering of a regular TPB has shown that a nascent polymer (obtained directly from the chemical reactor) possesses a three-phase structure and not a two-phase one, as it usually does. In addition to 50% of the crystalline-phase component and to 28% of the amorphous one, the material contains 22% of not a crystalline-phase component and not an amorphous component; it has turned out in further consideration that this component is a low-temperature form of a columnar mesophase (or, in other words, its static variety).

In heating of the polymer, it is clearly seen how the low-temperature form of the mesophase is transformed into a high-temperature one; then the crystalline fraction is melted, which corresponds to the second endopeak of the doublet on the DSC curve, and finally we observe a melting of the high-temperature (dynamic) mesophase to form an isotropic melt. In cooling, the transitions are ressumed in the reverse sequence, with the exception of the reduction of the low-temperature mesophase form inherent only in a polymer with a nascent structure.

As has already been noted, the temperature interval of existence of the mesophase becomes narrower with increase in the concentration of defect links (1,2-groups) disturbing the regularity of the TPB chain. The mesophase ceases to exist for a critical value of ~36 mol. %, and the polymer loses its capacity for crystallizing with a concentration of ~40 mol. % (unlike rigid-chain LC copolyesters which, as has been mentioned above, crystallize for any ratio of monomer links from which their chains are constructed).

The conclusion on reduction in the tendency of a polymer toward mesomorphism with increase in the imperfection of the structure of its chains is far from being trivial and could not be predicted *a priori*. This principle has been confirmed at present for several families of statistical copolymers (PEs/PPs, mesophase copolyphosphazenes, and copolysiloxanes).

Another example of experimental observation of the static variety of columnar mesophases is provided by polyvinyl silanes and polyvinyl germanes [22, 23]. By virtue of their stereoirregularity, these polymers do not crystallize, in principle. But the nearly spiral macromolecular conformation of such polymers as polyvinyl trimethylsilane or polyvinyl trimethylgermane possesses cylindrical symmetry, whereas the closest packing of cylinders is hexagonal, as has already been mentioned. Therefore, the higher form of ordering of such systems is a 2D pseudohexagonal packing. Such a CC mesophase in its static variety occurs only at long times of annealing of a maximum oriented polymer. These polymers are unique in their membrane properties and are used for separation of oxygen and nitrogen. It is not improbable that the good gas-separating properties of these systems are related to their mesophase structure.

In the previous discussion, we have been dealing mainly with one variety of mesomorphism, i.e., a thermotropic variety. It has turned out, however, that a barotropic variety compares well with it in the context of thermodynamics. An example of realization of the barotropic variety was provided experimentally by the simplest PE polymer, which is seemingly far from being mesophase, as far back as the 1970s. Beginning with a pressure of 4 kbar, rhombic PE crystals change to the so-called rotation phase with a pseudohexagonal 2D structure which is a typical columnar mesophase from the modern viewpoint [24]. It is precisely in crystallization from this phase state that the "famous" straight-chain crystals, or SCCs, are formed.

In addition to the two varieties, thermotropic and barotropic, we have found another form of realization of mesomorphism in polymers: a mechanotropic form. Indeed, another parameter corresponding to the action of a field (e.g., a mechanical field) on the system can be introduced into the generalized equation of free energy in addition to the temperature and the pressure. We realized this approach in practice using the same PE [25].

If PE is dispersed into the matrix of another more refractory polymer, e.g., PP, to a fairly high level and both components are mutually inoculated to an extent, the situation observed in subsequent uniaxial orientation of the system is as follows.

If such an extension is carried out at a temperature higher than the melting point of the dispersed polymer (when PE already flows, being molten) but lower than the melting temperature of the matrix (when PP is still deformed following the laws of plastic deformation of a rigid body), we observe a straightening of the PE chains and their holding in this state in cooling of the material due to the action of contacts with the matrix. In this case, in heating of a sample with fixed ends (isometric conditions, which is equivalent to the action of the mechanical field on the sample), we observe three new endomaxima, instead of the "usual" endoeffect corresponding to the melting of PE with folded chains (167°C), on the DSC thermograms.

According to the data of the temperature x-ray structural analysis, it has unambiguously been established that the first peak at 140–150^{o}C corresponds to the phase transition of the first kind "rhombic crystal–2D pseudohexagonal mesophase," the second maximum at 160^{o}C corresponds to the phase transformation "CC mesophase–oriented melt (LC nematic state)," and only the third endoeffect at 167^{o}C reflects the true melting of PE to form an isotropic melt. The PP matrix of the binary blend composition begins to melt at this temperature, too.

An analogous chain of phase transformations was also observed for fibers of an ultrahigh-molecular weight (higher than a million) PE in heating of the sample under isothermal conditions, as previously [26]. However, in this case the temperature range of existence of the columnar mesophase was much wider. The polymer melted at ~200^{o}C.

Finally, we give another intriguing example. Among the higher poly-α-olefins, there is an unusual kind of polymer, poly(4-methylpentene-1) (P4MP1) for which a density anomaly is known to be observed: its noncrystalline phase component turns out to be denser than its crystalline one, depending on its prehistory. This polymer was synthesized about 40 years ago, and it always belonged to the classical crystallizable HMWCs with a typical "single-act" character of melting.

Using the new catalytic systems mentioned above, we have synthesized a highly stereoregular polymer (98%) P4MP1 [27] on whose DSC curve we observe, in addition to the peak of melting of the crystalline phase, another weak endomaximum 15–20^{o}C higher than the principal one. This peak corresponds to an abrupt change in the temperature dependence of the angular position of the diffuse maximum on the scattering curve. According to the data of x-ray structural analysis, after classical melting, this polymer is still preserved in the form of a certain one-dimensionally ordered structure in a fairly long temperature interval (15^{o}C). This mesophase is characterized by the presence of the long-range order along the axis of uniaxially oriented macromolecules and by the absence of it in two perpendicular dimensions. In other words, this is essentially the anticondis mesomorphic state, which can be recognized as one new variety of polymer LC nematics. But conceivably this might be an LC smectic, i.e., a mesophase analogous to the mesomorphic structure of the thermotropic LC copolyesters mentioned earlier, in which the macromolecules consist of equally long monomer links.

Work on creating a new classification of equilibrium mesophases in polymers is being actively continued.

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NOTATION

a, parameter of the elementary cell; d_{sm}, interplane distance between smectic layers; d_{010} and d_{200}, interplane distances in different crystallographic directions.

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