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Thermochemical and deformational stability of microporous polyethylene films with polyaniline layer

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Abstract

Thermostability and structure transformations upon heating of composite systems consisting of a microporous polyethylene film and a conducting polyaniline (PANI) layer have been investigated by thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and wide-angle X-ray scattering (WAXS). Microporous polyethylene films were prepared by melt extrusion with subsequent annealing, uniaxial extension, and thermofixation. Polyaniline layers were formed by polymerizing aniline from solution in situ or by deposition of colloidal polyaniline dispersion on the polyethylene film surface. Composite systems have been found to demonstrate a considerably lower shrinkage upon heating than microporous polyethylene substrates. It has been discovered from DTA, DSC, and WAXS data that oriented phases in the polyethylene melt are formed in composite systems at melting temperature of polyethylene support. Oriented state in polyethylene melt is maintained at heating of composite samples up to the temperatures exceeding polyethylene melting point at several tens degrees. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline; Microporous polyethylene films; Composites; Thermostability

1. Introduction

Intrinsically conductive polymers, such as polyacetylene, polyaniline (PANI), polythiophene, and polypyrrole [1], attract considerable attention because of their unique electrical, optical, and electro-optical properties and numerous potential applications for batteries, electrochromic display devices, light-emitting diods, ion-exchange materials, membranes, sensors, corrosion protection, shielding of electromagnetic interference, microwave absorbers, antistatic materials, etc. Special interest was focused on PANI due to its low production cost, relatively high levels of electrical conductivity and good environmental stability (see, e.g. recent review articles [2–5]).

One of the key problems related to the potential application of PANI, like most of the electroactive polymers is, however, their poor processability and mechanical properties. The most promising approach to the solution of this problem is to prepare composite materials using conventional thermoplastic polymers. One of the most efficient techniques, particularly in preparation of composite membrane systems, consists

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in deposition of the conducting polymer into a porous polymeric substrate resulting in formation of a continuous conductive network both on the surface and in the bulk of a sample. Polycarbonate [6], polypropylene [7], and crosslinked polystyrene [8] have been used as porous substrates. Upon deposition of the rigid-chain conducting polymer layer, however, the polymer support often looses its elasticity to result in exfoliation of the coating.

In this work, the composite membrane systems consisting of a microporous polyethylene (PE) film coated with PANI layer have been investigated. Microporous PE films [9–11] were used as an elastic support for the conductive polymer layer. Owing to extremely high inertness to chemically aggressive media, PE can be employed in a wide diversity of systems; for instance, it can be used as membrane-separation material in power sources containing various organic and inorganic electrolytes. Composite membranes consisting of microporous PE film with a conducting polymer layer may serve simultaneously as a separator and one of the electrodes. In some cases (e.g. in lithium batteries), a conductive polymer layer which conducts Li ions acts as a protective coating for the Li cathode, thus preventing the direct contact between Li and the electrolyte and also the growth of lithium dendrites [12,13].

Since composite systems are subject to various types of deformational and thermal effects during their service, thermochemical transformation along with structural and phase transitions taking place at their heating were studied by TGA, DTA, thermomechanics, and X-ray analysis.

2. Experimental

2.1. Materials and techniques

Microporous PE films were prepared as described previously [9,11] by melt extrusion of linear HDPE ($M_w = 1.4 \times 10^5$, $M_w/M_n = 6$–8, and $T_m = 133°C$) at 200°C, with subsequent annealing for 30 min at 130°C. The pore-formation process was performed by uniaxial extension of the annealed films at room temperature. The obtained microporous PE films had a thickness of 10–15 μm and contained through-flow channels responsible for gas and liquid permeability. The size distribution of through-flow channels was determined by the filtration porosimetry technique involving measurements of the flow rate of a non-wetting liquid through a filtration cell. Sizes of the through-flow channels were described by the distribution function with a maximum corresponding to a size of 0.2 μm [10,11].

PANI was employed as an electroactive polymer in deposition of conducting layers onto porous PE films [14]. Two procedures were used for preparation of PE/PANI composite systems: (a) in situ oxidative polymerization of aniline in an acidic aqueous medium in the presence of a porous PE film, and (b) deposition of a previously prepared aqueous colloidal dispersion of PANI, which were prepared beforehand, onto a porous PE film.

In the first procedure a porous PE film was immersed in aniline for 2 h, and then weighed and placed in an aliquot of stirred aqueous 2.3 M hydrochloric acid and ammonium peroxydisulfate (equimolar ratio aniline/peroxydisulfate). All reagents were purchased from Fluka. Polymerization was carried out for 4 h at 5 or 20°C and was followed by vacuum drying of the film at room temperature. Percentage of PANI in the composite was 42%. The net PANI (PANI-HCl) powdered used in thermal analysis was prepared by using the same procedure at 5°C in the absence of PE.

In the second procedure the colloidal PANI dispersion was prepared as described previously [15]. To a stirred aqueous solution of dodecylbenzenesulfonic acid (0.1 M, 100 ml; purchased from Tokyo Kasei), 0.01 mol of aniline and a solution of 0.01 mol of ammonium peroxydisulfate in 5 ml of deionized water were successively added. Polymerization was carried out at 20–22°C for 4 h. The porous PE film was immersed for 4 h in the obtained colloidal dispersion, with subsequent drying at room temperature. Percentage of PANI in the composite was 72%. Net vacuum-dried "PANI dispersion" was also used for thermal analysis.

The thickness of the films with the PANI layer was 25 μm for the samples prepared by polymerization and 35 μm for the samples obtained by deposition of colloidal dispersion. The electrical conductivity measured by the conventional four-probe method and two-disk technique was 1.0–7.5 S/cm and $(1.5-8.0)\times 10^{-3}$ S/cm, respectively.

The porous PE films revealed a tensile strength of 200 MPa, elongation at break of 30%, and elastic modulus of 1000 MPa. They preserved their elasticity after deposition of the PANI layers. A high adhesion of PANI to the porous support was observed in all cases, and no peeling occurred even upon breakdown [14], while conventional PE films exhibit low adhesion to any kind of material (polymeric and nonpolymeric).

It was observed [11,16] that PE porous films are characterized by strongly developed relief-like surface. Conducting polymer layer is located both on the surface and on the walls of through-flow channels. As a result, the layer of rigid-chain conducting polymer forms a kind of "framework" on the surface and also inside the porous film. It was proved [17] that the specific features of the porous polyethylene films and composite structure are responsible for a high adhesion of conducting layer to PE support.

The thermodeformational behavior was investigated in standard thermomechanical tests and also by measuring the unloaded sample sizes at heating.

Wide-angle X-ray scattering (WAXS), thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were used to study structure transformations and phase transitions. X-ray diffraction patterns were taken on DRON-2.0 with Cu Kα radiation. TG and DTA analyses were performed on Derivatograph-C System (MOM, Budapest) at a heating rate of 10 K/min in a self-generating atmosphere; DSC data were obtained on a Perkin-Elmer DSC 7 at a heating rate 10 K/min in an argon atmosphere.

3. Results and discussion

3.1. Structure formation of porous PE films

The process of preparation of microporous PE films consists of several stages: extrusion, annealing, uniaxial extension, and thermal fixation (Fig. 1). At the extrusion stage, the initial oriented sample is formed by spin drawing. Its structure can be described as a system of parallel folded-chain lamellae disposed perpendicularly to the orientation direction and connected by tie molecules (Fig. 1a) [9,11,18].

At the second stage — annealing at temperature close to the melting point of PE — a considerable

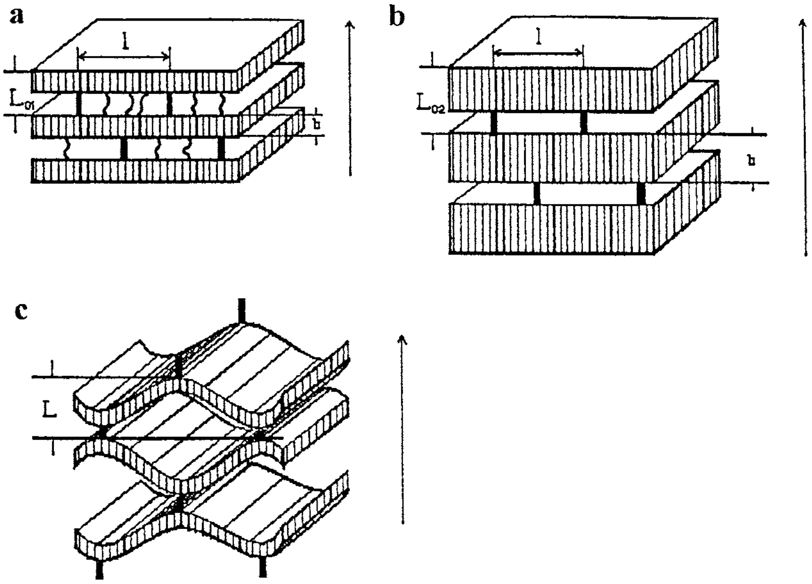

Fig. 1. Scheme of the sample structure formed at stages of extrusion (a), annealing (b), and uniaxial extension (c) — L_{01}: the long period in the initial (extruded) sample; L_{02}: the long period in the annealed sample; L: the long period in the porous film; b: lamella thickness; l: the distance between the "bridges" connecting the lamellae. Arrows show the orientation axis.

increase in the lamellae thickness occurs as a result of involvement of chains from amorphous regions into crystallites (Fig. 1b). At this stage, orientation of the sample becomes better since the annealing proceeds at fixed sample dimensions, i.e. under the conditions preventing its shrinkage [9,19].

Formation of the highly oriented structure is completed at the third stage of pore formation during the uniaxial extension of the annealed sample [11,19] when discontinuities (pores) appear due to moving apart and bending of the lamellae between the "bridges" consisting of stressed tie molecules (Fig. 1c). In the forth stage, thermal fixation, stabilization of the porous structure results from stress relaxation in the sample with fixed sizes at elevated temperatures which facilitates this process [20].

3.2. Thermodeformational behavior of PE films and composite systems

Studies of the thermodeformational behavior of composite PE/PANI systems have revealed that their shrinkage on heating is considerably smaller than that of the PE porous supports. Most importantly, they preserve their shape and do not exhibit any sign of fusion not only at the melting temperature of PE, but also at the temperatures exceeding it by several tens of Kelvins. The thermodeformational behavior was characterized by the value of shrinkage determined by variation in the geometrical dimensions of the sample on heating and calculated as $S = (l_0 - l_s)/l_0$, where l_0 is the initial length, and l_s the length after shrinkage. As evident from Fig. 2, the composite systems start shrinking at higher temperatures compared with the PE substrate. At 120°C, the shrinkage of PE support amounts to 60% (Fig. 2, curve 1), while the shrinkage of the PE/PANI system obtained by using the PANI dispersion is 30% (Fig. 2, curve 2), and for the composite systems prepared in situ by polymerizing aniline at 20 and 5°C (Fig. 2, curves 3 and 4, respectively), it equals 12 and 5%, respectively. It is important to note that a good adhesion of PANI to the PE support is maintained, and no exfoliation or destruction of the layer upon heating are observed.

This suggests that the layers of the rigid-chain conductive polymer "framework" in the composite system stabilizes the sample structure and shape upon heating, i.e. prevents its shrinkage. It was interesting therefore to find the reasons for such a behavior of the porous PE film inside the framework upon heating up to temperatures above T_m of PE. To this end, the thermoanalytical (TG and DTA) investigations of PE films and composite systems were performed.

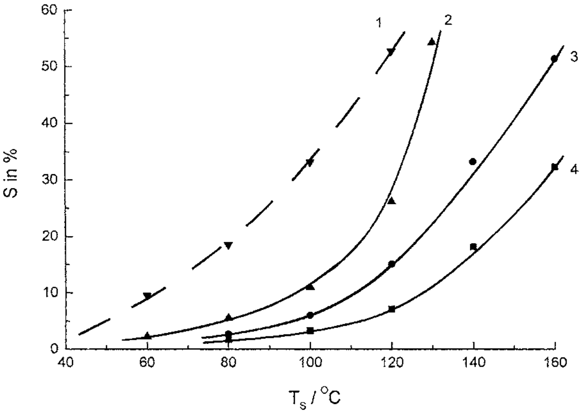

Fig. 2. Shrinkage S (%) vs. temperature for the PE support (curve 1) and composite samples PE/PANI prepared by deposition of dispersion (curve 2) and by in situ polymerizing aniline at 20°C (curve 3) and 5°C (curve 4).

3.3. Thermal analysis of porous PE films and composites

3.3.1. PE porous films

The films studied do not exhibit any destructive changes upon heating from RT to 246°C as evident from the absence of mass losses in the thermoanalytical curves (Figs. 3a and 4a, curve 1). DTA analysis (Fig. 3b, curve 1) has revealed that in this temperature range, melting of the sample with a pronounced endothermic effect at 136°C takes place.

A considerable exothermic effect with a maximum at 229°C (in the absence of mass losses in this temperature range) can be attributed to formation of hydroperoxides in result of oxidation processes in PE. A slow reduction in the sample mass with a constantly increasing thermal destruction rate starts above 246°C. Above 400°C, an avalanche-like process of PE total decomposition begins. Its mechanism was described in detail elsewhere [21–23]. The stage of intensive thermal destruction in the temperature range 400–500°C is completed by volatilization of all the fragments formed during degradation, which typically

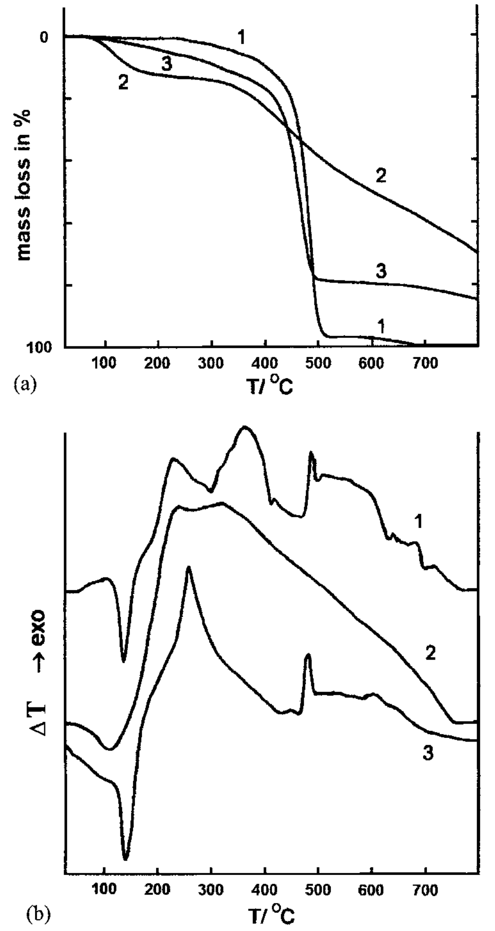

Fig. 3. TG (a) and DTA (b) curves for the porous PE film (curve 1), PANI-HCl (curve 2), and composite systems PE/PANI with the PANI layer obtained by in situ polymerizing aniline at 5°C (curve 3).

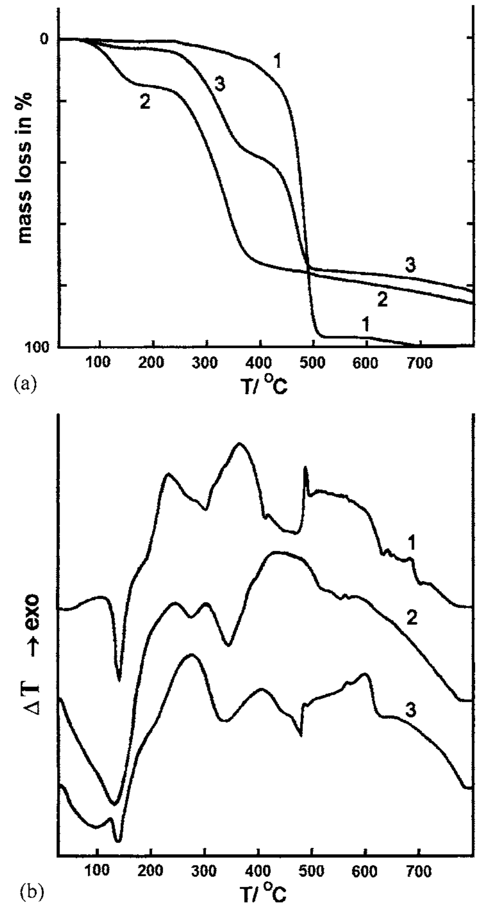

Fig. 4. TG (a) and DTA (b) curves for porous PE film (curve 1), PANI dispersion (curve 2), and composite systems PE/PANI with the PANI layer obtained by deposition of dispersion (curve 3).

consists of a set of hydrocarbons with one–six carbon atoms. A slow combustion of ca. 5% carbonized residue takes place between 500 and 700°C.

3.3.2. PANI and PE/PANI composite systems

1. The thermal destruction of powdered net PANI-HCl (Fig. 3a, curve 2) takes place in three stages in temperature ranges: 20–185, 185–320, and 320–800°C resulting in a carbonized residue of 35%.

   Thermal effects at destruction of PANI-HCl (Fig. 3b, curve 2) involve volatilization of aniline residues and its derivatives at the first stage of destruction (endopeak at 108°C) and considerable exo-effects of structure transformation in the temperature range 185–320°C. As temperature further increases, a gradual decrease in heat content in result of the carbonization processes is observed. Other way, these processes are accompanied by a decrease in heat capacity which is a typical feature for these processes in organic nitrogen-containing polymers [23,24].
2. The composite system PE/PANI prepared in situ by polymerizing aniline is similar to PE with regard to both kinetics of mass losses and thermal effects (Fig. 3a and b, curve 3). This is evident at the first heating stage when the sample looses no

more than 3–4% mass up to 250°C. The endothermic melting effect is nearly equal to the PE melting peak and its maximum is located at the same temperature on DTA curves of Fig. 3. We have carried out DSC investigations of our PE and composite samples, because DSC technique is the more correct for measurement of transition temperatures. According to DSC data, T_m of PE in composites is shifted (at 2.8 K) towards higher temperatures as compared with PE substrate.

At the subsequent thermal destruction stages, the characteristics of these composites approach those of PANI-HCl (up to 255–265°C), and of the PE support at the stage of carbonization with maximum mass losses at approximately 470°C. From 500 up to 800°C, mass losses are nearly nondistinguishable, and the carbonized residue is not more than 20% of the initial mass.

3. The thermodestruction process of "PANI dispersion" also consists of three degradation steps (Fig. 4a, curve 2), but each stage is characterized by much larger mass losses and considerable endo- and exothermic effects compared to PANI-HCl (Fig. 3a, curve 2). This indicates that thermostability of the PANI dispersion is much lower than that of PANI-HCl.
4. The comparison of thermograms of the PE film and PE/PANI dispersion composite (Fig. 4a and b, curves 1 and 3) reveals a perceptible difference in thermochemistry of the two systems. The data presented on TG instrument numerical records show that mass losses in PE/PANI start below 50°C, and by the onset of PE destruction (246°C) the composite sample has already lost 5% mass. Evolution of volatile products resulting from degradation of mainly PE and partially PANI, proceeds in the range 246–458°C. Above 460°C, the rate of mass losses fully corresponds to that of the net PE up to 477°C. Further temperature rise results in nearly 100% degradation of PE into volatile destruction products, whereas PE/PANI dispersion composite proves to be relatively thermostable in this range, and its rate of mass losses decreases sharply. This effect brings about the formation of carbonized residue amounting to 18% of the initial mass. It differs little from the value of the carbonized residue of PANI dispersion (Fig. 4, curve 2: 14%) obtained at the same temperature [25].

Consideration of the thermal effects related to the thermochemical processes taking place in a composite PE/PANI dispersion allows one to conclude that PANI affects PE up to the onset of PE thermal destruction. This is evident, first from the broad and relatively small endothermic peak with a maximum at 93°C (due to possible evacuation of residual solvent), and second from an appreciable decrease in the PE melting heat (compare curves 1 and 3 in Fig. 4b). Besides, DSC investigations demonstrate some increase in the melting temperature by 1.8 K. Variations in the magnitudes of the endothermic effects observed in the temperature range of thermal destruction also confirm the conclusion about the influence of the PANI dispersion layer on the thermal destruction processes in PE.

Decreasing of PE melting heat in composites in comparison with PE support is related to the fixation of PE chains with the rigid framework of conducting polymer which prevents the transition of PE chains into equilibrium conformations and formation of isotropic melt. Because the PE porous support was oriented, its melting leads to the transition into oriented melt which is characterized by the higher configuration entropy than for equilibrium melt, and consequently to decreasing of free energy changes at melting.

The stabilizing effect of the rigid-chain PANI layer on the PE support is also evident from the shift of the PE melting peak towards higher temperatures for both composite systems. Because of the fixation effect of the rigid framework, the PE chains are maintained stretched, and as a result the configuration entropy $\Delta S_{\text{crystal-melt}}$ decreases, thereby increasing $T_m = \Delta H/\Delta S$ as compared to the melting temperature of PE support.

Thus, the TG and DTA curves demonstrate that the thermal behavior of the PE/PANI systems is intermediate between those of their polymer constituents: the highest chemical stability is exhibited by PE below 500°C, while PANI appears to be most stable at higher temperatures, when PE totally decomposes.

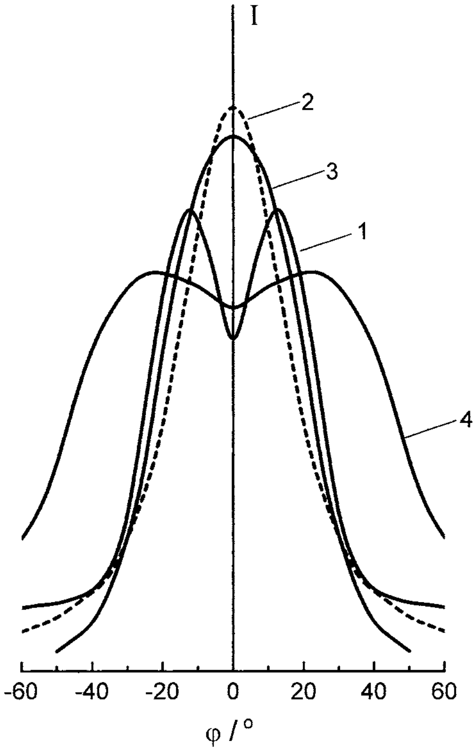

Fig. 5. Azimuthal distribution curves of X-ray scattering intensity I of the (1 1 0) equatorial reflection of polyethylene: initial (annealed) PE film (curve 1), porous PE film (curve 2), and PE/PANI composite system (obtained by in situ polymerizing aniline at 5°C) heated up to 140°C (curve 3) and 160°C (curve 4).

3.4. X-ray study of structure transformations upon heating of PE/PANI composites

In order to analyze the structure transformations upon heating of the composites, X-ray study of the samples preheated to the temperature higher than T_m of PE (up to 140 and 160°C) and then cooled to room temperature was performed. Azimuthal distribution curves of scattering intensity of (1 1 0) equatorial reflection for the initial (annealed) PE film, porous PE film, and composite systems are shown in Fig. 5.

Curve 1 corresponds to the PE samples biaxially oriented at the stages of extrusion and annealing, i.e. after two stages of structure formation (Fig. 1a and b); and curve 2 corresponds to more oriented systems with uniaxial orientation, i.e. porous films additionally oriented during uniaxial extension at the pore-formation stage (Fig. 1b). It is evident that after heating to 140°C, the composite samples are less oriented, but they maintain the uniaxial-type orientation inherent to porous membranes; upon heating to a higher temperature (160°C), the azimuthal distribution curve corresponds to the biaxial orientation which is characteristic for the initial PE films.

4. Conclusions

It was shown that the rigid framework of the conductive polymer constituent exerts a stabilizing effect on the thermodeformational behavior of the PE/PANI composite systems. They demonstrate a considerably lower shrinkage as compared to the PE support even at temperatures above T_m of PE. They also exhibit lower mass losses than powdered PANI-HCl and net "PANI-dispersion" up to the onset of intensive decomposition of PE at approximately 450°C.

WAXS, DTA, and DSC studies have revealed that upon heating of a porous PE films and especially of composites consisting of a porous PE film and PANI layer, oriented phase in PE melt is formed at melting temperature of PE.

It is noteworthy that formation of an ordered phase in the melts of flexible-chain polymers was also observed in heating of highly oriented PE and polypropylene fibers and films [26,27]. The superheating effect (melting at temperatures above equilibrium T_m) and melting accompanied by the transition into an induced oriented phase in the melt were discovered when the supermolecular structure of samples contained a rigid framework of extended-chain crystals embedded in the matrix of folded-chain crystals and amorphous phase [28]. Formation of the hexagonal-ordered phase in the melt was also revealed at melting of polyethylene samples consisting of extended-chain lamellae which were crystallized under high pressure [29,30]. Recently, the appearance of the hexagonal phase was observed for drawn samples of HDPE constrained to a constant length on heating up to the temperatures higher than equilibrium T_m [31].

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