AB Block-copolymers poly(oxyethylene)-*block*-poly(dicyclohexyl itaconate): temperature dependence of the morphology

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Abstract: The paper deals with AB block-copolymers poly(oxyethylene)-*block*-poly(dicyclohexyl itaconate) (POE/PDCHI) containing 2000 and 5000 g/mol of the flexible POE. The study aims at revealing the thermal effect on the copolymer morphology in the 20 - 200°C range. Optical microscopy investigations were performed. The results confirm our previous X-ray studies. A liquid crystalline state is observed in the 90 - 180°C range. It is characterized by birefringence and is determined by the chair-chair conformation, a dominating structure of the cyclohexyl rings. A condiscrystal state is observed at cooling in the interval 90°C to room temperature. It is characterised by a variety of cyclohexyl conformations and, therefore, by a lack of birefringence. The PEO component in the copolymer starts crystallising into small local spherulites at about room temperature. The results obtained allow the conclusion that the presence of PDCHI is a determining factor for the mesomorphic state of the copolymers discussed.

Introduction

Copolymers of itaconic derivatives are supposed to be a starting material for the preparation of coagulants, high adhesive coatings, and emulsifiers [1]. Itaconic acid monomers with one or two cyclohexyl rings are known as thermally stabile materials [2,3]. Poly(dicyclohexyl itaconate) (PDCHI) has two cyclohexyl rings acting as a steric barrier to free rotation of the polymer chain. The block copolymers, investigated in this article, have the following chemical structure:

Fig. 1. Chemical structure of POE/PDCHI block-copolymer

Such a structure classifies PDCHI as a polymer with a rigid chain and a relatively high value of the steric parameter σ (2.99) [4]. This polymer is characterized by its high glass transition temperature [5-7]. Information about PDCHI in the crystal state and its structural transitions is quite scarce [5,7]. The existence of this polymer in another mesomorphous state (LC, condis-crystal) has not been reported previously.

Poly(oxyethylene) (POE) presents as a second component in the block-copolymer. It differs from PDCHI in its flexibility [9], capability of crystallisation and high degree of crystallinity, viz., 65 - 70% [10]. Normally, POE crystallises into a monoclinic lattice [11]. However, the crystallisation under stress leads to the formation of a triclinic phase [11].

The copolymer POE/PDCHI (Fig. 1) possesses both a flexible and a rigid part. The difference in their nature supposes a structure with interfacial separation of the components, which gives rise to the formation of a peculiar mesomorphous phase [12]. The different structural changes typical of each polymer are summarized in Figs. 2 and 3, respectively.

POE is a model sample for studying the crystallisation of polymers because of its large crystal formations occurring in solution and melt [13,14]. The ability of this polymer to crystallise also as component of other block-copolymers has been recently reported [15]. It has been found that in this case the distortion of its monoclinic phase is due to the formation of crystal lamellae proceeding under stress [15].

POE forms lamellae easily and quickly in the presence of primary nuclei. The crystallisation may be nucleation- or diffusion-controlled. The former process is observed more frequently. The mechanism of secondary nucleation determines its whole rate. The appearance of hedrites results from larger defect structures or twins; their manner of growth corresponds to the screw dislocation mechanism [16]. In the same way spherulites grow from smaller defects situated on the lamellae surface [16]. The negative hedrites built of b-lamellae grow during crystallisation in the range from 50 to 60°C. The positive spherulitoides, formed of [401]-lamellae having straight molecules (perpendicular to the lamellae surface), predominate in the 50 - 37°C range. Negative spherulites of the same [401]-lamellae are observed below 37°C [16]. The transition temperature (50°C) is attributed to the solid-plastic crystal transition in POE [16].

The glass-transition temperature and/or the existence of a crystal arrangement of poly(mono-n-alkyl itaconate)s have been investigated in a calorimetric study of comb-like polymers with long side chains [8]. Transition between the alpha-hexagonal form of crystallisation and the liquid state has been found. This phenomenon takes place not only in poly(monoalkyl itaconate)s, but in poly(dialkyl itaconate)s as well.

Cowie et al. [7] described the chair-chair conformational transition to the cyclohexyl derivatives of poly(itaconic ester)s. It occurs at about -88°C, i.e., at the glass-transition (Fig. 3). The temperature of the glass-transition T_g is strongly affected by the distance between the backbone and the rings on the side chains. The shorter the distance, the higher the T_g values [7].

The aim of the study is to reveal the crystalline and mesomorphous structure of POE-*b*-PDCHI block-copolymer via detailed investigations by optical microscopy. We presume that the morphology and crystallisation properties of this copolymer are influenced by the presence of rigid PDCHI blocks. A liquid crystal (LC) state as well as a condis-crystal one are observed both in the structure of the block-copolymer and in that of the PDCHI homopolymer.

Fig. 2. Scale of the temperature transitions of POE

Experimental part

Materials

AB block-copolymers were synthesised via free-radical polymerisation as described in ref. [17] using macro-azo-initiators containing PEO blocks. The synthesis of PDCHI homopolymer was performed by radical polymerisation run with *tert*-butyl hydroperoxide as an initiator [17].

Fig. 3. Scale of temperature transitions of PDCHI

The studied AB block copolymers are poly(oxyethylene)-*block*-poly(dicyclohexyl itaconate)s where A is the rigid chain such as PDCHI and B the flexible substance POE. They comprise different amounts of flexible blocks. Such are AB₂₀₀₀ and AB₅₀₀₀, which contain 2000 and 5000 g/mol PEO, respectively. The molecular characteristics of the synthesised block- and homopolymers are shown in Tab. 1:

Tab. 1. Molecular characteristics of the used materials

Sample	$M_n \times 10^{-3}$ in g/mol	$M_w \times 10^{-3}$ in g/mol	M_w/M_n	T_g in °C	Refs.
AB ₂₀₀₀	12	24	2	-36.4	[12,34]
AB ₅₀₀₀	10	20	2	-21.5	[12,34]
PEO-1	-	2	-	-67	[12]
PEO-2	-	5	-	-58	[12]
PDCHI	31	116	3.7	-75	[12,33]

Methods

Light microscopy

The morphology of the samples was investigated on a hot-stage optical microscope Reichert Zetopan. Thin films of about 30 - 40 μm thickness were obtained from 10% chloroform solution of the copolymer. The nascent samples were also used for microscopy investigation. The samples were heated between slide and cover glasses. The hot film could be easily moved on a usual microscope stage. It was possible to apply the creep tension on the cover glass during the heating to obtain a film of regular uniform thickness and texture.

It is hard to prepare the film below 140°C because of the highly viscous medium. Below 180°C solid state PDCHI undergoes different low temperature transitions [5,7]. The copolymer starts to flow above 140°C [5,7]. However, a thermal destruction occurs simultaneously with the flowing over 180°C on the microscopic hot stage. Formation of numerous bubbles was found to be a result of the degradation process over 180°C and it was revealed as formation of bubbles with gaseous product. Furthermore, the quantity of bubbles increased dramatically with increasing the temperature over 200°C. Such phenomenon was also observed for PDCHI homopolymer. Hence, there was no need to make experiments at higher temperatures. Previous experimental data concerning the thermal stability of PDCHI show a decomposition around 190°C [5]. POE decomposition begins at about 190°C, too [18]. Thus, the process of bubble formation is assumed to be caused by the decomposition of both components.

At first, thermally non-treated samples were subjected to optical observation. They are optically empty. In order to observe some structural arrangement three thermal procedures were applied to the samples (Fig. 4):

- 1) Heating to 200°C on the microscopic hot stage and quick replacement into cold medium until room temperature was reached.
- 2) Heating to 200°C followed by tempering at 115, 105, 90, 80, 70, 40°C for 20 h before cooling to room temperature. The purpose was to achieve isothermal crystallisation.
- 3) Heating to 200°C followed by slow cooling (20 h) to room temperature.

The rate of cooling below 40°C was 0.2 °/min and further the cooling progress was non-linear.

It is worth noting that the transitions from mesomorphous into crystal state took place in a very narrow temperature range. The degree of crystallinity was relatively low, so

that it could not be measured. That fact confirmed optical microscopy to be the most suitable method for observation.

Fig. 4. Different temperature treatment of samples: heating is followed by fast and by slow cooling

Wide angle X-ray scattering (WAXS)

WAXS in transmission mode

The principal state of copolymers was assigned to be mesomorphous in a smectic phase. WAXS was used in transmission mode in order to confirm the presence of some ordered formation corresponding to the mesomorphous state [12]. A Philips WAXS diffractometer with Cu-K α radiation was used in transmission mode (Fig. 5a).

WAXS in reflection mode

WAXS in reflection mode was used to prove the presence of quite a small crystalline phase simultaneously to the mesomorphous phase. A Siemens WAXS diffractometer was used in reflection mode regime (Fig. 5b). The thickness of samples was about 1 mm. The nascent material was pressed in order to obtain a homogeneous scattering surface. The observed reflection was a result from the superficial 100 μ m. Because of the low crystallinity of the copolymer (less than 10%) the X-ray results are presented in Tab. 2. Each of the patterns has a reflex with maximum intensity found previously; all other intensities are settled in relation to it.

Results

Results from the WAXS studies

Tab. 2 presents the results from X-ray patterns obtained in transmission mode (Fig. 5A). The patterns show the dominant mesomorphous state (90 - 95%). Fig. 5A.A shows the typical high crystalline state of pure POE. Fig. 5A.B corresponds to AB₂₀₀₀, 5A.C to AB₅₀₀₀. The mesomorphous state for PDCHI is demonstrated in Fig. 5A.D. As seen, its pattern does not differ essentially from those of the copolymers. It means

that such a mesomorphous state of the PDCHI component provokes the observed mesomorphous state of the copolymers.

The low degree of crystallinity of the samples was studied by WAXS in reflection mode. Fig. 5B exhibits consecutively the following samples: Fig. 5B.A - POE/PDCHI blends 80\20, 5B.B-E - AB₅₀₀₀ and AB₂₀₀₀ - nascent samples and samples obtained from the melt. Noteworthy are the numerous reflexes in the nascent samples in comparison with the others. Fig. 5B.F shows the X-rays patterns of nascent powder PDCHI homopolymer. Such reflexes (Fig. 5B.F) confirm the ability of PDCHI to crystallise into its own crystalline lattice. This lattice, which has not been reported so far, was observed with quite a low degree of crystallinity.

Fig. 5A. Transmission mode WAXS patterns of: A - POE; B - AB₂₀₀₀; C - AB₅₀₀₀; D - PDCHI

Fig. 5B. Reflection mode WAXS patterns

As a whole, the reflexes of POE and PDCHI are common to all patterns of AB copolymers (Fig. 5A.B - 5A.E). However, those of the former component are less pronounced. These results lead to the important conclusion that at first PDCHI crystallises or its structure gets arranged. The degree of crystallinity is quite low (4 - 5%). The arrangement observed could be adopted as a matrix for further crystallisation of POE.

Tab. 2. WAXS calculations of crystal dimensions by Sherrer and interplanar distances

Substance	Interplanar distances	Crystal dimensions by Sherrer	
		low-angle reflex	
		reflexes $2\theta = 6^\circ$	reflexes $2\theta = 17.5^\circ$
PDCHI	13.0 Å	44.9 Å	68.6 Å
AB ₂₀₀₀	13.6 Å	67.9 Å	68.75 Å
AB ₅₀₀₀	15.2 Å	67.9 Å	68.6 Å

where the following relations are used: $2d_{hkl} \sin \theta = n\lambda$ – interplanar distance, and $D = 0.9 \lambda / (W \cos \theta)$ – crystal dimensions by Sherrer.

Hot stage microscopy studies of the phase transitions

Up to 90°C, the samples heated according to the first thermal procedure were optically empty. They were not lightened during the rotation between crossed polarizers. Anisotropy was absent, too. The whole film had no uniform texture. However, a polygonal structure was observed in case of parallel polarizers (Fig. 6). Similar textures for low molecular liquid crystals have been described in refs. [19,20]. Anyway, the real state of our high molecular weight substances observed under the described conditions remains still open.

Fig. 6. Polarising micrographs taken at room temperature; AB₅₀₀₀ film, parallel polarizers, 320x

According to the DSC data an endothermic peak is observed near 60°C [12]. It corresponds to the melting of the formed crystals and is present for both AB₂₀₀₀ and

AB₅₀₀₀ copolymers. This melting peak is observed following all thermal procedures. Conversely, during cooling the respective crystallization peaks disappear. The crystallisation can be realised at relatively low temperature and after slow cooling [12].

The samples observed between crossed polarizers become brighter if the temperature increases over 90°C. Optical anisotropy with positive character appears when the sample is rotated between crossed polarizers using a gypsum plate.

Furthermore, above 180°C the film becomes gradually darker. The colours due to the optical birefringence of the whole film disappear. Several bubbles occur and grow simultaneously as an indication of thermal destruction.

The above-described process of brightening in the 90 - 180°C range is reversible. The same transitions will be observed in reverse order during cooling. A temperature transition at about 90°C is also found by DSC studies [12]. There is such second order transition described as a change in the slope of c_p . This dark mesomorphous state is supposed to exist below 90°C. The phenomenon has been confirmed by thermomechanical studies as well [5,7].

The first thermal procedure is not followed by crystal growth: either these structures are absolutely absent, or their appearance is quite rare. Our results are in accordance with those obtained by DSC [12].

The heating process according to the other procedures is analogical. In the course of tempering at 115, 105 and 90°C the optical birefringence is well manifested. Thermal treatment at lower temperatures does not show birefringence. Anyway, the second procedure does not result into isothermal crystallisation, even after such long lasting thermal treatments.

The discussed transition at 90°C also occurred during the treatment according to the last procedure. The cooling rate was quite slow. 20 h later it resulted into crystals as described bellow. A thin layer of crystallised material can be seen. Obviously, it has been accumulated on the cracks and bubbles borders. Clear spherulitic forms are mainly distinguished. The crystallisation process during the final slow cooling can be assumed as nearly isothermal.

The thermal treatment of the homopolymer PDCHI was the same. However, the crystallisation process started below 20°C. It was observed after a long time and after very slow cooling.

Crystalline structures obtained according to the third thermal procedure

POE and PDCHI are incompatible. In the structure of the copolymers their chains are located in two separated phases. The phase boundaries are in fact the chemical bonds between these different blocks. The presence of such phases, phase boundaries and their alternation supposes the presence of the mesomorphous state [12]. The rigid PDCHI macromolecules are set perpendicularly to the phase boundary. The flexibility of the POE block is strongly influenced by its bounding to the rigid PDCHI segments. Thus, POE crystallisation will be seriously hindered, too.

The dominant mass of the samples is not crystalline. It is cracked and bubbled. Crystal formation is located amongst the cracks and the bubbles. These crystallites could be centres of primary nucleation. The cracks separate the different polygonal regions crystallising independently from each other (Fig. 7). The copolymers AB₂₀₀₀

and AB₅₀₀₀ show reduced numbers of crystals. Negative spherulites are discovered on the boundaries of the cracks and bubbles (Figs. 8 and 9).

Fig. 7. The dominant mass of the samples is crossed by bubbles and cracks. Crossed polarizers; gypsum plate; 9x10

Fig. 8. Negative POE spherulites appear on the boundaries of the bubbles and cracks. Crossed polarizers; gypsum plate; 9x10

Fig. 9. Typical POE spherulite; crossed polarizers; gypsum plate; 9x10

In this case the crystals fill up the given polygonal structure and do not go out of it (Fig. 10). Generally, primary nucleation appears on the cracks and the polylamellar structures formed expand either to the end of the polygonal area (Figs. 9, 10 and 11) or to the bubbles boundaries (Fig. 12). Their formation presented in Figs. 8 - 12 is assumed to result from the crystallisation of mobile POE segments in the copolymer. Such crystalline forms originate from primary nucleation. Spherulite-like formations grow by the mechanism of secondary nucleation.

POE layers are situated in the polygonal structures among the PDCHI ones. PDCHI layers disposition determines the shape of the spherulite-like structures. PDCHI models the spherulites lamellae. POE molecules are folded into lamellae covering the whole given crack-free domains. The lamellae grow up to the polygonal boundary, i.e., the crack. Both lamellae growth and spherulite formation (i.e., secondary nucleation) are diffusion controlled. So is the primary nucleation. Diffusion controlled crystallisation is the most probable consequence of the hindrance of rigid PDCHI segments.

Fig. 10. POE crystallisation is limited to the polygonal structure. Crossed polarizers; gypsum plate; 9x10

Fig. 11. Polylamellar structures finish at the end of the polygonal structure. Crossed polarizers; gypsum plate; 9x10

Fig. 13 shows the availability of dendrites, i.e., secondary nucleation on tertiary nuclei in hardly flowing melt is realised. As known, the growth of dendrites is caused by secondary nucleation. The molecules (or blocks of them) unable to crystallise are pushed out of the crystallisation front. In that way every 'branch' is enabled to reach the regions capable of crystallising. This is quite surprising in our non-flowing melt. May be it is a result of chain scission caused by the earlier destruction process.

The birefringence of the described structures is due to their thickness and/or to the orientation of their optical indicatrix toward the object glass. The crystals are built of edge-on lamellae (Fig. 14) or of nearly edge-on (Fig. 15). However, domains with weak birefringence and mainly flat-on orientation prevail. In the process of thermal and mechanical treatment the edge-on position is achieved as a consequence of the slipping as well of the rotation of whole lamellae groups (Fig. 14).

In fact, edge-on (90°) (Fig. 13), flat-on (0°) (Fig. 16) or some intermediate lamellae position ($0^\circ < \alpha < 90^\circ$) (Fig. 15) have been set previously by disposition of the POE-PDCHI layers into the hardly flowing melt. These positions seem to be equally probable depending on the stresses applied previously. However, POE lamellae remain [401]-type in all of these cases. Anyway, PDCHI layers are not crystalline.

Fig. 12. Spherulitic grow is limited at bubbles appearance. Crossed polarizers; 9x10

Fig. 13. Dendrites are found at the samples' ends in limited regions only. Crossed polarizers; 9x10

Fig. 14. Edge-on position of lamellae. Clear birefringence is observed. Crossed polarizers; gypsum plate; 9x10

Fig. 15. Nearly edge-on lamellae towards the crystal in the centre. Crossed polarizers; 9x10

Fig. 16. Flat-on lamellae are characterised by weak birefringence. Crossed polarizers; gypsum plate; 9x10

Fig. 17. Owing to the disposition of PDCHI layers, tree differently oriented crystal regions are detected. Crossed polarizers, 9x10

Actually, POE crystallisation is hindered quite often owing to the presence of PDCHI. So the process is limited only to certain layers of the copolymer. The birefringence intensity is different in the different regions (Fig. 17). As mentioned already, the phenomenon is determined by the disposition of PDCHI layers.

It is worth noting an interesting case resulting of the heating at high temperatures (nearly 180°C) when a certain mobility of PDCHI blocks is accomplished. Then a twisting of all copolymer layers in the polygonal structure is observed (Figs. 18, 19). Further the lamellae bands thus twisted crystallise during cooling. A succession of appearance and extinction in brightening is well observed. This case shows another effect of PDCHI upon the crystallisation of POE. It leads to the formation of so-called banded spherulites. Such crystalline forms are not known for POE. Obviously, the crystallisation capability and the obtained structures depend on the length of the block-segments as discussed above (Fig. 5B).

There are unusual rod-like or ribbon-like crystalline structures with different birefringence (Figs. 18, 19), as well as grain-like ones (Figs. 21, 22). An explanation for such crystalline formations can be the way of obtaining a uniform layer of the initial

powder-like copolymer. During the slipping of the slide and the cover glass statistical mixing of layers by the non-flowing melt in some regions is achieved. The mesomorphous regions with small dimensions are randomly oriented and each one of them crystallises autonomously. The growth of spherulites ceases because of the occurrence of disorder.

Fig. 18. Banded spherulites. The twisting period is well distinguishable. Crossed polarizers; gypsum plate; 9x10

Fig. 19. Banded ribbon-like crystallisation. Crossed polarizers; gypsum plate; 9x10

Fig. 20. Rod-like crystalline forms. Crossed polarizers; gypsum plate; 9x10

Fig. 21. Unusual grain-like structures. Crossed polarizers; 9x10

Fig. 22. The 'Milky Way': small grain-like structures. Crossed polarizers; 9x10

Bubbles occur in the sample, too, when cooling the PDCHI homopolymer from 200°C and after a long stay at room temperature. There are crystal structures in the shape of straight sticks with dominant positive birefringence. They are positioned among the bubbles (Figs. 23, 24). The fibrils fit within the limits of polygonal structures and are mostly parallel (Figs. 23, 25).

Fig. 23. PDCHI crystallisation in straight sticks: the birefringence is positive. Crossed polarizers; 9x10

Fig. 24. Rare PDCHI crystallisation; positive birefringence. Crossed polarizers; 9x10

Fig. 25. PDCHI fibrils. Crossed polarizers; 9x10

Discussion

Our attention has been focused upon the availability of a mesomorphous state in both AB block-copolymers and PDCHI homopolymer. Surplus, second-order transitions depending on the temperature are observable in these samples. The transitions occur in the temperature interval from 190°C to room temperature and can be recognised by a change in the birefringence. The mesomorphous transitions from liquid crystal (LC) to condic crystal (CC) at 90°C and from CC to low crystallinity (glass state) at about room temperature are consecutively detected.

Temperature variation leads to special arrangements in both the block-copolymer and pure PDCHI. These arrangements are related to the cyclohexyl substituents essentially. The rings can exist in two specific conformations (Fig. 26). Transitions between these two conformations are accomplished repeatedly and are possible even at room temperature [27]. Such transitions are normally accompanied by a few intermediate states with potential energy somewhat higher than the chair one. An intermediate conformation during the chair-chair transition is the 'boat' form (Fig. 27).

However, the high-temperature states (up to 90°C) are characterised by the dominating chair-conformation. The boat-one is not representative of this interval [28].

Fig. 26. Transition between two chair-conformations

Fig. 27. 'Boat' intermediate conformation

On the other hand, each of the chair-forms can be bounded to the side chain both in *trans*- and *cis*- position (Fig. 26). The *trans*-substituted chair-conformations are dominant in the case of a mixture where *cis*- and *trans*-bounding are equally probable [27]. The *trans*-ones are more favourable from the point of view of potential energy especially at higher temperatures [28]. Also, same *trans*-position of the cyclohexyl rings has been found to be present in the liquid crystal [28]. The boat conformation is assumed to be incompatible for this state. In fact, the *trans*-ring connection enables a relative tilt of the PDCHI side chain. Therefore, the birefringence is well pronounced (Fig. 28). The tilt is identical for all side chains.

Fig. 28. A tilt in side chain is realised at temperatures over 90°C; one chair-conformations is dominant, *trans*-bounded; clear birefringence is detected

Fig. 29. Smectic-type LC

Worth noting is another important condition to observe birefringence (LC, respectively): the priority of one only chair-form over the other. According to Wunderlich et al. [29] the liquid crystal state is characterized by orientational long-range order as well as by dynamic and positional disorder. Actually, this is the present case: on one hand, the *trans*-bounded uniform chair-conformation is dominant; on the other, different longitudinal and transversal oscillations of side chains are possible. As

known, at 144°C (Fig. 3) the alpha-transition is realized and, therefore, below this temperature the flip-flop torsional movement of the main chain is frozen. However, this alpha-transition does not affect the birefringence caused by the tilt of side chains.

The incompatibility of the components and their manner of arrangement in the copolymer structure suppose a liquid crystal state of smectic type (Fig. 29). The WAXS patterns of the same plane-oriented smectic crystals exhibit two halos. Such a crystalline type normally shows pseudo-hexagonal packing of its molecules [28]. Such is the packing accomplished in PDCHI (Fig. 30), which is an indication of orientational order. Moreover, literature data define this state as smectic B-type [30]. The presence of numerous phase boundaries is also an indication for the long-range orientational order. The boundaries are determined by PDCHI mainly (Fig. 31). In respect of them, during the high temperature treatments, 180°C could be adopted as critical, i.e., disintegration of phase boundaries occurs up to 180°C as a result of the degradation process.

Fig. 30. Hexagonal packing determines an orientational order

Fig. 31. Phase boundaries: an indication for long-range orientation

According to the literature, the boat-conformation is not stable in the LC state and exists usually at low temperature [28]. The birefringence disappears after the temperature decreases below 90°C. This case is characterized by dynamic and conformational disorder [29], i.e., both chair-conformations can exist simultaneously as well as intermediate ones. In addition a failure to usual *trans*-bonding of the rings is quite possible (Fig. 32). Moreover, at temperatures lower than T_g (PDCHI) all these states are frozen. However, the phase boundaries and the pseudo-hexagonal packing of molecules exist and determine the available orientational order (Figs. 30, 31). According to Wunderlich [29] this is the CC state.

The real crystallization process here is quite limited and is detected for POE only. Both positional and conformational orders exist in the samples and are expressed in the crystalline lattice and the typical POE helix 7_2 type, respectively [31]. The crystallisation of POE in the copolymer begins at about room temperature. Such crystallisation could be recognised by the typical negative spherulites. The relatively short POE molecules fold into low-dimensional lamellae [32]. The *c*-axis of these lamellae is perpendicular to the phase boundary. According to the literature, the AB₂₀₀₀ copolymer has one folding only; for AB₅₀₀₀ there are two [32] (Fig. 33 a,b).

The mesomorphous homopolymer can turn into genuine crystal, too, but this phenomenon is less possible. Indeed, only molecules preserving their LC-state are

engaged in the crystalline process with quite low degree of crystallinity. The observed birefringence is positive.

Usually PDCHI is tenacious to crystallisation. The greater part of it remains in the glass state containing different ring conformations.

Fig. 32. Conformational disorder causes extinction of birefringence

Fig. 33. Short POE molecules fold into lamellae, which are parallel to the phase boundaries. A - AB₂₀₀₀; B - AB₅₀₀₀

Conclusions

The morphological changes of POE/PDCHI block-copolymers and pure PDCHI homopolymer have been studied in the 20 - 200°C temperature range. In the range from 180 to 90°C the liquid crystalline state is observed both in the block-copolymer and the homopolymer samples. Long-range orientational order and positional disorder are typical of the LC state. It is detected by the positive birefringence. The cyclohexyl rings in the PDCHI side chains are in a uniform chair conformation, which is *trans*-bounded to the COO-group.

The condiscrystal state is observed in the range below 90°C to room temperature. It is characterised by long-range positional order and conformational disorder. The birefringence disappears. Simultaneous existence of different ring conformations (both of chairs and even the boat-intermediate ones) is quite probable. They could be bounded equally at *trans*- and in *cis*-positions.

POE crystallisation in block-copolymers takes place at about room temperature. Negative spherulites are observed at limited places. Probably the primary nuclei are small PDCHI crystalline formations. However, such phase in the copolymers discussed is very rare.

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