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Polycaprolactam crystal structure. II. Crystal phase perfection

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An attempt was made to optimize the valuation methods of the polycaprolactam crystalline phase perfection. Criteria for the evaluation of the perfection of the alpha form are established.

It is proposed a methodology for the practical determination of the alpha-form perfection. Formulas are derived for its quantification.

Approaches have been proposed for the evaluation of other polymorphic forms of the polycaprolactam. The intensity ratio of the main diffraction reflections is used to determine the quantitative assessment of the presence and perfection of the beta form. Changes in angular displacement of the main diffraction reflection of the gamma-form in the powder diffractograms were analyzed to determine the perfection of gamma crystalline form.

Key words: polycaprolactam, crystal phase, perfection.

INTRODUCTION

The perfection of the crystalline phase in the polymer has different dimensions than that of low molecular weight substances. Partly this is due to skeletal chemical bonds in long-chain polymer molecules. Restricting the freedom of the nearest neighbors in the base of elementary crystal cells, they significantly affect the far order in the grid. They are the basis and for the specific type of defects in the polymers, too. This necessitated the creation of the theory of polymer pseudocrystal. All factors affecting the quality of the crystalline phase otherwise impact in varying degrees to perfection pseudocristal polymer lattice. And they are very complex and their simultaneous impact is ambiguous. An additional complicating factor in polycaprolactam (PCL) are dynamically changing balances arising from shatter and recombine hydrogen bonds (H-bonds). These may be other chemical, physical or purely complex networks or just any steric factor and geometric specificity. Especially in the process of crystallization, recrystallization, and any type of structural reorganization of the atomic-molecular level in terms of thermal, thermo-mechanical or other type of complex physical fields. And these are all real thermal fluctuation processes of structural adjustment and fine-crystal crystallographic and morphological level.

Fortunately, most accurate and complete uniformity in the definition of similar processes and structures is rarely attainable and seldom necessary. For example, in the study of polymorphic transitions PCL, knowledge and ability to control the perfection of the crystalline phase is required. Because the wide variety of polymorphic transitions is not nothing but a permanent process of improvement of the crystal structure of the PCL. And just tracking the change of the lattice perfection we can study the polymorphism of PCL. To do so, however, is not complete determinism of the studied physical reality. We need to know only what quality (crystalline perfection – CP) structure, respectively, way and packing density (chain packing density – CPD) of macro-molecular chain segments arises a crystalline phase, under what conditions and how does it change. When and how to improve and to what extent violates the order to destroy the crystal structure of phase or move to another crystallographic modification.

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EXPERIMENTAL

High-temperature powder X-ray diffractometers are best suited for the study of temperature-initiated restructuring of the crystalline phase of PCL. Structural changes are controlled by changes in the geometry of the intensity distribution of X-ray radiation. Angular positional deviations, intensity variations and profile changes of the diffraction reflections have been observed and compared. They specify the dimensions and distances between structural elements, the quantity and type of packaging in the different structures of the polymer. Key structural elements are chain segments in the elementary crystal cell. Usually they are the symmetrical version or parts from it in the basis of the cell.

The behavior of α-, β-, γ- and δ-PCL forms were studied in a wide temperature range (20–240 °C) and in more detail in the range 160–190 °C. The temperature dependences of the angular deviations of all major diffraction reflections of polymorphic forms and above all $(200)_\alpha$, $(100)_\gamma$ and $(002)_\alpha/(202)_\alpha$ are controlled. By using suitable software such as "ORIGIN" decomposition of multiply peaks was performed to establish the statistical characteristics of the actual characteristics of the diffraction reflections. Experienced subjects were scanned at speeds 1, 2 and 3° 2θ/min, if necessary, in the interval 20–24 °2θ, 15–30 °2θ 2–60 °2θ and a URD-6 (Freiburg "Precizionsmechanik", Germany), and DRON-3 ("Burevestnik", St. Petersburg, Russia) equipped with a high-temperature chamber ATM-2000. Used $Cu_{K\alpha av.}$ = 1.5418 Å radiation filtered β-nickel filter.

Different types of polycaprolactam (PCL-1 with $\eta_{rel.1\%\ sol.\ H2SO4} = 2.64$; $W_{mass.\%} = 1.0$ and PCL-2 with $\eta_{rel.1\% sol.}$ $H_2SO_4 = 2.32$; $W_{mass.\%} = 0.01$) with different molecular masses and molecular-mass distribution (characteristic viscosity in 1% solution of H_2SO_4 $\eta_{rel} = 2.11–2.83$) were used with contents of low-molecular tie in the interval 1.0–12.0% mass, moisture content W from 0.1 to 0.01 mass%, as a necessary condition about the obtaining of crystal structures with different perfection. Thin folios were formed in a large diapason of forming conditions: $T_m = 210–240$ and $T_c = –196–200$ °C.

The high temperature X-ray investigations were carried out by repeated cyclical heating and cooling in the temperature interval from 293 K to 513 K with heating rate of 5 K/min and 5 min tempering for every scanned temperature at interval of 5 K. A software package "Origin 5.0" was used for decomposition of multiple peaks in determining polymorphic forms of PCL.

The initial isotropic structure of the pressed folios was characterized by light-microscopy, electron-microscopy and with powder X-ray diffraction methods using a polarization light-microscopy Amplival Pol, Karl Zeiss, Jena, Germany, SEM BS – 340, Tesla, Brno, Cheh Republic, TEM Opton 10B, Feintechnik, Oberkochen, Germany.

The crystal phase perfection was defined by the packing compactness of the macromolecular chain segments in the crystal phase of the α-crystal modification [1, 2].

RESULTS AND DISCUSSION

It is impossible to talk about precise and unambiguous quantitative and even qualitative structural study of the polymers, if there is not an opportunity to identify and assess the quality of their crystalline phase. For chain-flexible polymers and PCL not much information on similar research is available [1–8]. The main quantitative criterion in the X-ray structural studies is the integral diffraction intensity of the X-ray radiation in a given crystallographic direction. On the other hand, the integral intensity is strongly connected with the quality of the studied structure at the atomic-molecular level. This kind of "dualism" can lead to ambiguous experimental solutions. In the more perfect low molecular crystal lattices the polymorphic resolution is better. In some cases, depending on the conditions and objectives of the study, the profile of diffraction effects can successfully arbitrate and decide such dualism.

Mathematical and statistical characteristics of the profile distributions as a design may be sufficient for this. Moreover, if they are representatives of various relevant statistics such as Gauss, Lorentz, Lorentz quadratic, Void, Pseudo-Void, Pearson VII, etc., for polymers, in particular PCL, such a decision is unthinkable. All major diffraction reflections of his polymorphic diversity are nesting in the range of 1–2 Bragg degrees. This strongly hampers the qualitative and quantitative analysis of the diffraction pattern. But the study of polymorphic transitions requires precise control of the qualitative and quantitative simultaneous polymorphic composition. This requires the creation of a criteria basis for recognition, separation, correction, evaluation and comparison of the diffraction reflections of co-existing in different proportions polymorphic modifications of PCL. At first glance, the undeniable correlation between the quality and quantity of each polymer crystallographic modifications looks facilitating the identification of real forms in the crystalline phase of PCL. It seems that the existing relations lower degrees of freedom and the apparent ambiguity in permanently changing structures studied. In practice, however, this is not so. The limited selection of practical approaches and techniques for detection of the crystalline forms in PCL would not allow its use even in synchronous excellent knowledge.

It appears unlikely the exact establishment of the moment of polymorphic transition relation by the quantity–quality of the polymorphic crystal forms. The definition of the polymer polymorphic transitions as a continuous process of change in the packaging of the macromolecular chain segments, and the technical difficulties in the experimental implementation of the evaluations guarantee this. What is the system of approaches and techniques for implementation of the planned experiment? The main objective is the study of polymorphic transformations of PCL in a wide range of conditions. This can be investigated with high-temperature X-ray powder diffraction under different conditions of thin films of PCL with different starting structure. The need to be thin foils is determined by the low coefficient of thermal conductivity of the polymer that must be heated and cooled quickly and homogeneously. A detailed interpretation of the geometry of the intensity distribution of high-temperature powder diffraction, especially in the angle range from 20 to 24 °2θ of diffraction scan. The basic diffraction reflections of the known polymorphic crystal forms of the polymer are in this interval. To them the proportion between the crystal forms in simultaneous coexistence may be established. By varying temperatures in different modifications can be studied the geometry, mechanism and kinetics of the polymorphic transitions. For this purpose is needed data for the angular deviation, intensity and profile modification of the diffraction reflections. It can be obtained after splitting of the overlap in complex multiple peak of diffraction reflections of individual alpha- beta-and gamma-crystalline forms of PCL. The processing of the multiple peaks can be done with a computer program Origin. As supporting information can be used theoretical diffraction curves of known crystal forms of PCL and simulation of particle diffraction images with their software as, for example, Crystallographica, Material Studio, etc.

The alpha form perfection can be defined as a CPP (crystalline phase perfection) = $83(d_{(200)}/d_{(002),(202)})$, [%], and the density of the chains packing as a CPD (chains packing density) = $137(d_{(200)} - d_{(002),(202)})$, [%]. Thus, through the angular deviation of the main diffraction reflections can be controlled quantitatively, evaluated and compared the changes in the crystalline phase quality and the distance between the chains.

The normalizing coefficients estimated, namely "83" (in front of the ratio of the distances between the planar) and "137" (in front of the their difference) determine the maximum value (100%), respectively of perfection and density. Of course, the values of the normalizing coefficients have been estimated at the maximum possible experimentally reachable values of the used ratio and difference of the distance between the planar, at the angular positions values of the diffraction reflection $(200)_{\alpha}$ – 20.00 °2θ and of $(002)_{\alpha}$,$(202)_{\alpha}$ – 24.00 °2θ.

It is established that within the boundaries of possible deviation of reflections CPP is between 91–100%, a CPD varies in the range of 54–100%. The perfection climate out these borders means critical deformation of the unit cell, polymorphic transition and the crystalline phase destruction, depending on conditions.

The change of the density of packing of the chains has no direct sense of a change in the distance between them, and the percentage of the maximum difference between the planar distances of family's crystallographic planes that lie in the chains.

This indicator shows rather tendencies to increase or decrease of distances in trigonometric relationships. It can be seen that the perfection decrease of the alpha form leads to a percentage lower of the chains packing density in times fast for the defined range.

Intensity ratio (the linear intensities) of (200) to (002)/(202) in the alpha form is about 3/2 = 1.5. In beta form, it is back to 2/3 ~ 0.667. So the most easily recognized and percentage calculation can be done using intensity ratio $CPP^{\beta} = 150(I_{(200)\alpha\beta}/I_{(002)\alpha\beta/(202)\alpha,\beta})$, [%]. The detailed justification and output of the analytical dependence is as follows.

The simulation of the theoretical powder diffraction of the known PCL polymorphic forms shows the declared above dependencies of the intensity ratios.

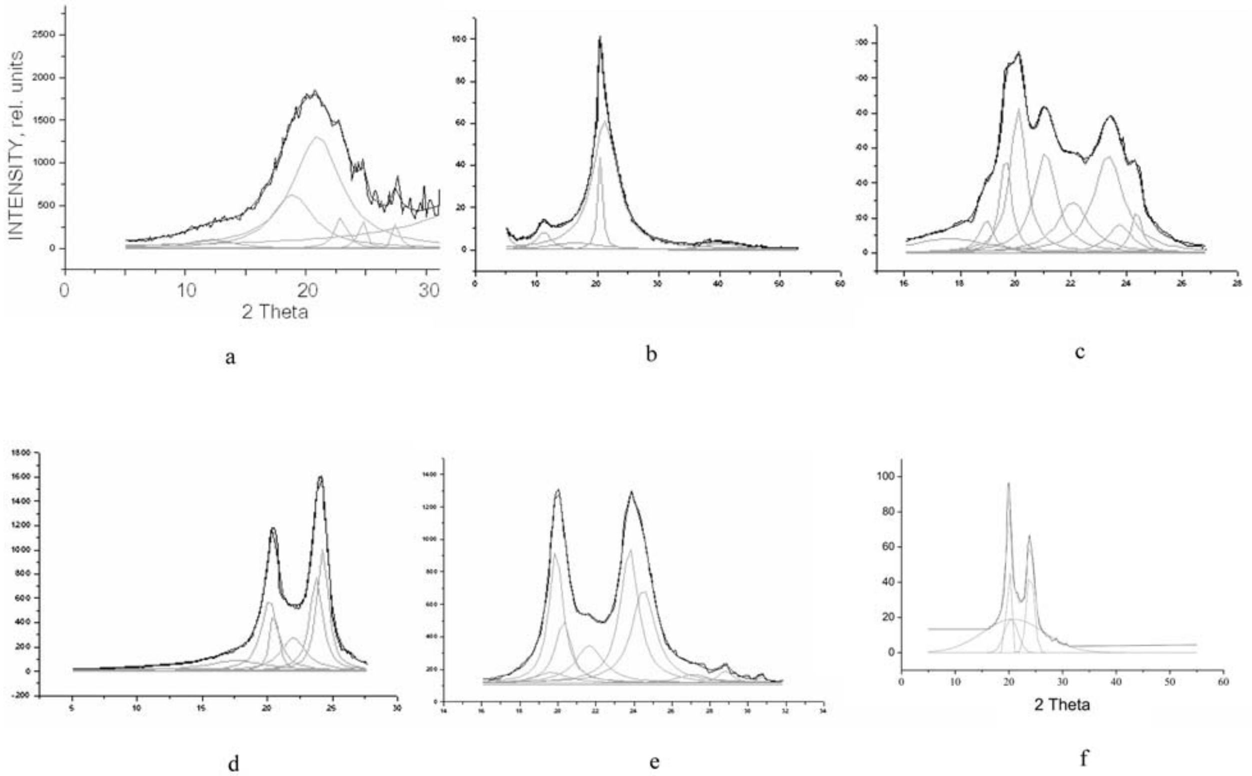
After simulation and experimental confirmation was considered as the maximum of the beta form on scanned objects is $I_{(200)\alpha\beta}/I_{(002)\alpha\beta/(202)\alpha\beta} = 0{,}667$. After the standardization it to 100% as $(I_{(200)\alpha\beta}/I_{(002)\alpha\beta/(202)\alpha\beta})/0{,}667).100$, [%], the expression was a little simplistic to $150(I_{(200)\alpha\beta}/I_{(002)\alpha\beta/(202)\alpha\beta})$, by introducing a correction coefficient 150 ~ 0.00667. Coefficient 150 is connected with the idea of 150% intensity of the second line to the first PCL peak in the powder diffraction of the monoclinic crystallographic alpha and beta modifications.

It is easy to reduce in percentage the beta-crystalline phase. Higher accuracy is possible, but in most cases it is not necessary. In the remaining cases are used the algorithms for the alpha form. It should be noted that alpha and beta forms always coexist in different proportions and perfection. When we talk about 100 percentage of beta-form, that means their 100% possible participation in such polymorphic mixture.

Determination of the gamma-form perfection is reasonable in the light of the clarification of the so-called Brill transition (gamma–alpha, or gamma–beta–alpha transition). From maximum amorphized (deep hardened) condition close to ideal

Table 1. Dependence of d-spacing of PCL-2 thin foil in cyclic thermal modification and simultaneous X-ray scan

$T_{sk.}$, °C	Alpha crystal form of PCL								Beta crystal form of PCL								Gamma crystal form of PCL			
	$T^{\circ\uparrow}$	$T^{\circ}_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$	$T^{\uparrow}$	$T_{\downarrow}$
	(200)	(002)	(200)	(002)	(200)	(002)	(200)	(002)	(200)	(002)	(200)	(002)	(200)	(002)	(200)	(002)	(100)	(100)	(100)	(100)
	4.42	3.72	4.36	3.79	4.42	3.72	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.69	3.99	3.99	3.99	3.99
	4.42	3.72	4.36	3.79	4.42	3.72	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.69	3.99	3.99	3.99	3.99
	4.42	3.72	4.36	3.79	4.42	3.72	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.69	3.97	3.99	3.98	3.99
	4.42	3.72	4.36	3.79	4.42	3.72	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.70	3.97	3.99	3.97	3.99
	4.42	3.73	4.36	3.79	4.42	3.73	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.70	3.95	3.99	3.96	3.99
	4.42	3.73	4.36	3.79	4.42	3.73	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.70	3.95	3.99	3.96	3.99
	4.41	3.73	4.36	3.79	4.42	3.73	4.36	3.79	4.44	3.70	4.42	3.70	4.44	3.70	4.42	3.70	3.95	3.99	3.96	3.99
	4.41	3.73	4.36	3.79	4.42	3.73	4.36	3.79	4.44	3.70	4.42	3.70	4.44	3.70	4.41	3.70	3.93	3.99	3.95	3.99
	4.41	3.73	4.36	3.79	4.41	3.73	4.36	3.79	4.43	3.70	4.42	3.70	4.44	3.70	4.41	3.70	3.92	3.99	3.94	3.99
	4.41	3.73	4.36	3.80	4.41	3.73	4.36	3.80	4.43	3.70	4.42	3.70	4.44	3.70	4.41	3.70	3.90	3.99	3.92	3.98
	4.41	3.73	4.35	3.80	4.41	3.73	4.35	3.80	4.43	3.70	4.41	3.70	4.43	3.70	4.41	3.70	3.90	3.99	3.91	3.98
	4.40	3.74	4.35	3.80	4.41	3.74	4.35	3.80	4.42	3.71	4.41	3.70	4.43	3.71	4.40	3.70	3.90	3.99	3.91	3.98
	4.39	3.75	4.35	3.80	4.39	3.75	4.35	3.80	4.42	3.71	4.40	3.70	4.43	3.71	4.40	3.70	3.89	3.99	3.91	3.98
	4.38	3.77	4.35	3.81	4.38	3.77	4.35	3.81	4.42	3.71	4.40	3.70	4.43	3.71	4.40	3.71	3.89	3.99	3.90	3.98
	4.36	3.79	4.35	3.81	4.37	3.79	4.35	3.81	4.42	3.71	4.39	3.70	4.42	3.71	4.40	3.71	3.88	3.99	3.90	3.98
	4.35	3.80	4.35	3.81	4.36	3.80	4.33	3.81	4.41	3.71	4.39	3.71	4.42	3.71	4.39	3.72	3.88	3.99	3.89	3.98
	4.34	3.82	4.35	3.81	4.35	3.82	4.33	3.81	4.41	3.72	4.39	3.72	4.42	3.72	4.39	3.74	3.88	3.99	3.88	3.98
	4.33	3.83	4.34	3.82	4.34	3.83	4.32	3.81	4.39	3.74	4.38	3.74	4.42	3.74	4.38	3.75	3.87	3.99	3.88	3.98
	4.32	3.85	4.33	3.83	4.33	3.85	4.30	3.83	4.38	3.75	4.37	3.75	4.41	3.75	4.37	3.77	3.87	3.99	3.87	3.98
	4.31	3.87	4.32	3.87	4.30	3.87	4.29	3.86	4.37	3.77	4.36	3.77	4.39	3.77	4.36	3.79	3.86	3.99	3.86	3.98
	4.30	3.88	4.31	3.88	4.29	3.88	4.29	3.88	4.36	3.79	4.35	3.79	4.36	3.79	4.34	3.80	3.86	3.98	3.86	3.98
	4.29	3.90	4.30	3.90	4.28	3.90	4.27	3.90	4.35	3.80	4.33	3.80	4.35	3.80	4.32	3.82	3.86	3.98	3.86	3.98
	4.28	3.92	4.29	3.92	4.27	3.92	4.26	3.91	4.33	3.82	4.31	3.82	4.34	3.82	4.31	3.84	3.85	3.95	3.85	3.95
	4.27	3.93	4.28	3.93	4.26	3.93	4.26	3.92	4.32	3.83	4.29	3.83	4.33	3.83	4.28	3.85	3.85	3.92	3.85	3.91
	4.26	3.95	4.26	3.95	4.26	3.95	4.25	3.95	4.31	3.85	4.29	3.85	4.29	3.85	4.29	3.86	3.84	3.89	3.84	3.89
	4.25	3.97	4.26	3.97	4.25	3.97	4.25	3.97	4.30	3.87	4.28	3.87	4.30	3.87	4.28	3.87	3.84	3.86	3.84	3.86
	4.24	3.98	4.24	3.98	4.25	3.98	4.25	3.98	4.29	3.88	4.27	3.88	4.29	3.88	4.28	3.88	3.83	3.83	3.83	3.83
	4.23	3.99	4.23	3.99	4.25	3.99	4.25	3.99	4.27	3.88	4.27	3.88	4.28	3.88	4.28	3.88	3.82	3.82	3.82	3.82
	4.42	3.72	4.36	3.79	4.42	3.72	4.36	3.79	4.44	3.69	4.42	3.69	4.44	3.69	4.42	3.69	3.99	3.99	3.99	3.99



a b c

d e f

Fig. 1. High temperature X-ray powder diffraction of thin films of PCL-2, pressed at 225 °C (T_m = 225 °C), crystallized at 0 °C (T_c = 0 °C). X-ray scans temperatures: a – 20 °C; b – 170 °C; c – 165 °C after heating (V_{heat} = 5°/min) to 225, then cooling (V_{cool} = 5°/min); d – 145 after heated (V_{heat} = 5°/min) to 225, then cooling (V_{cool}=5 °/min); e – 120 °C after heating (V_{heat} = 5°/min) to 225, then cooling (V_{cool} = 5°/min); f – 20 °C after heating (V_{heat} = 5°/min) at 165 °C for 5 min, and 225 °C for 5 min, then cooling to 165 °C for 5 min and cooling (V_{cool} = 1°/min) to 20 °C.

super cooled melt of PCL called delta-form up to gamma-transition has no structural secrets. This transition occurs secret, as well as the beta-alpha transition with improvement of the more stable and perfect form.

In contrast to the gamma-alpha transition consisting of a significant structural adjustment and cardinal modification of the hydrogen bonds between the segments. In the delta-form the segments packaging showed an average statistical distance between the chains around 4.20–4.22 Å. The appearance of the minimum sufficient for structural formation segmental mobility at the expense of recombination of the hydrogen bonds compacts container to 4.17–4.18 Å. The trend is stable, albeit within the margin of uncertainty. Perfecting, the gamma form compacts the segment package by mutual hydrogen bonding of all neighbors to 3.90 Å (22.770 °θ).

The newly established system of hydrogen bonds is dynamically changing and the distances fluctuate greatly. With temperature modification under certain conditions, in the range 160–1900 S stable alpha form starts forming. It forms two spacing of chain segments and, more specifically, between the crystallographic planes in which they lie. 4.44 Å – the distance between the targeted alternative circuits in the plains of folding. It is fixed to free from tension, conveniently located hydrogen bonds [Holms] and least varying in temperature modification. 3.71 Å – distance crystallographic axis "c" between stitched by hydrogen bonds sheets (planes of segments folding).

Sewing together by hydrogen bonds between alternative targeted segments (folds) in the same chain is folded and sewn together between neighboring segments, defining the width of the folds. Because on a number of thermodynamic and geometric reasons, they are extremely stable and large enough, 4.44 Å, can slipping through each other (in the direction perpendicular to the "b" molecular axes – i.e. a crystallographic axis "a") to wedge each other their Van-der-Waals interactions. This further helps compaction of stitched leaves and small lattice periodicity in the direction of "c".

It is clear that in this situation, a more imperfect and unstable, but more homogeneous and isotropic

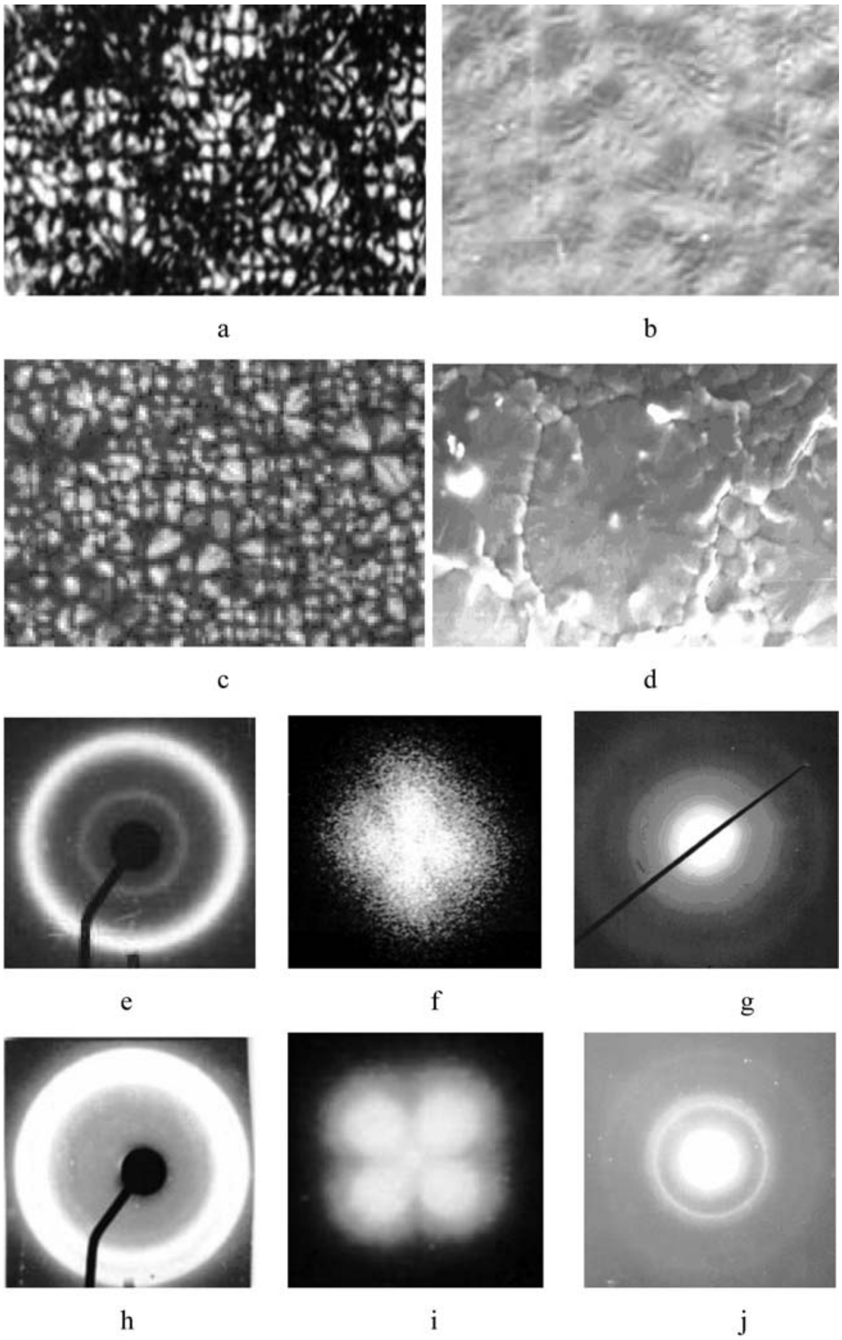


Fig. 2. Polarization (a, c) and scanning (b, d) photomicrography, X-ray (e, h), light (f, i - Small Angle Light Scattering, SALS) and electron (g, j) photo diffraction of thin films of PCL-2 (T_m = 225 °C; T_c = 20 °C): crystallization temperature 20 °C after free cooling (a, b, e, f, g); crystallization temperature 200 °C (c, d, h, I, j).

perpendicular to the macromolecular axes structure with average distances between the chains around 3.90 Å should be transformed into more non isometric the plain "ac" with periods in the crystallographic directions [200] and [002] 4.44 Å and 3.71 Å, respectively. This can occur spontaneously in increased segmental mobility due to thermal modification by pulling in an appropriate direction of dynamic equilibrium in the processes of fragmentation and recombination of hydrogen bonds between the amide groups of adjacent segments.

The appropriate direction in this case is between the different directions oriented segments of the same chain in the plains of folding them. That is, the realization of hydrogen bonds (H-bonds) between the amide groups of the two neighboring alterna-

Table 2. Perfection in % for thermal modification of the crystalline phase of the films of 50 microns PCL-2, 225 °C when pressed and crystallized at 200 °C

№	$T_{modif.}$, °C	Perfection of alpha form of PCL				Perfection of gamma form of PCL			
		V = 5 °C/min		V = 10 °C/min		V = 5 °C/min		V = 10 °C/min	
		heating	cooling	heating	cooling	heating	cooling	heating	cooling
1	20	98.48	95.63	98.48	95.59	99.66	99.75	99.66	99.62
2	30	98.48	95.55	98.48	95.51	99.66	99.75	99.66	99.62
3	40	98.48	95.55	98.48	95.51	99.22	99.75	99.53	99.62
4	50	98.43	95.51	98.48	95.51	99.22	99.75	99.31	99.62
5	60	98.39	95.46	98.39	95.42	98.79	99.75	99.00	99.62
6	70	98.39	95.42	98.39	95.42	98.79	99.71	98.96	99.62
7	80	98.30	95.42	98.39	95.42	98.79	99.71	98.92	99.62
8	90	98.26	95.33	98.35	95.33	98.36	99.71	98.74	99.62
9	100	98.21	95.29	98.26	95.29	97.93	99.71	98.57	99.62
10	110	98.13	95.25	98.22	95.25	97.50	99.71	98.10	99.57
11	120	98.04	95.13	98.18	95.17	97.46	99.71	97.84	99.57
12	130	97.60	95.09	97.88	95.13	97.38	99.71	97.76	99.53
13	140	96.95	95.05	97.05	95.05	97.29	99.71	97.67	99.53
14	150	96.31	94.80	96.46	94.80	97.21	99.66	97.59	99.40
15	160	95.68	94.80	95.87	94.80	97.08	99.66	97.42	99.49
16	165	95.05	94.80	95.28	94.43	97.00	99.66	97.17	99.49
17	170	94.42	94.66	94.60	94.26	96.88	99.66	97.08	99.44
18	175	93.79	94.28	94.02	93.99	96.75	99.62	96.88	99.44
19	180	93.17	93.75	93.44	93.28	96.63	99.62	96.67	99.40
20	185	92.55	92.64	92.32	92.35	96.54	99.62	96.54	99.40
21	190	91.93	92.06	91.75	91.91	96.46	99.53	96.46	99.44
22	195	91.31	91.40	91.14	91.00	96.38	99.44	96.38	99.40
23	200	90.70	90.88	90.49	90.55	96.30	98.79	96.30	98.74
24	205	90.09	90.35	89.88	90.03	96.21	97.89	96.21	97.80
25	210	89.49	89.49	89.40	89.52	96.09	97.29	96.09	97.25
26	215	88.88	89.14	88.97	89.05	95.97	96.59	95.97	96.59
27	220	88.48	88.52	88.73	88.73	95.76	95.81	95.76	95.81
28	225	88.07	88.07	88.49	88.49	95.40	95.40	95.40	95.40

tively targeted segments (branches) of a fold. Such connections are steric favorable to the molecular geometry and form thermodynamically favorable structures. The slightly folded sheets stitched also fit comfortably on matrix van-der-Waals curves planar contours using small fluctuation cooperative untangling. The latter, according to the common or micro local conditions may be replaced by other mechanisms.

For example, first may be adjusted the relief, and then to be fixed the network by suitable H-bonding, etc. in the space and time as one not a quick process, but thermodynamically favorable and therefore stable trend. The relatively isotropic gamma structure should be slightly deformed, forming H-bonds in stitched sheets and, more importantly, congesting these lists – improve packaging segments approximating crystallographic planes which lie in stable (200) of monoclinic alpha form 3.71 Å distance.

In practice, the distance increases with 0.54 Å from 3.90 up to 4.44 Å and the reduction with 0.19 Å from 3.90 to 3.71 Å within specified crystallographic directions are realized at the expense of minor reorganizations in basis of the unit cell. Like less permanent change in the partial coordinates of the basis change the structural amplitude so that the $(100)_\gamma$ migrates slightly from item 21.3 °θ (4.17 Å) up to 21.1 °2θ, in reaching the distance between the chaotically adjacent chains around 4.21 Å, then gradually migrate to 22,85 °2θ (3.89 Å). Then: BRILL (gamma–alpha) (γ↔α) = ($d_{(100)\gamma}$/3.88).100, [%], – 0.258$d_{(100)\gamma}$, %, 25$d_{(100)\gamma}$, [%].

The delta form, present always and everywhere as a transitional phase between amorphous others may present average statistical distances between segments axes about 4.0 and 4.5 Å, an average of 4.22 Å. Rarely implemented in practice so deep hardening to form in the pure state.

Sometimes, the apparent displacement of the center of gravity of the amorphous halo of the most frequently observed angular position 21.05 °2θ, corresponding to the distance of 4.22 Å, probably due to the different quantitative relationship between the other polymer forms. Because the delta-form in the transition zones around the crystalline of different polymorphic forms with different perfection has a different density and different geometric statistical properties. It is difficult to find adequate criteria, however, for such assessments. Such precision is not necessary.

CONCLUSION

1. It was found that the control on the perfection change of the crystalline phase as the density of chain segments packing is adequate and convenient method about study of the PCL polymorphic transitions and their mechanism.

2. Algorithm and methodology for convenient practical control of the PCL crystalline phase perfection have been created. Analytical dependences of quantitative evaluation of the packing density and the perfection of its main polymorphic forms have been proposed.

3. The obtained results allow the assumption that the rich polymorphism and the transitions between the polymorphic phases are the most natural and thermodynamically entropy most comfortable steps in improving of the PCL crystal structure.

4. The assumptions and conclusions give reason to plan a detailed study of the specifics of segment packaging of all meso phases and phases of PCL from the structure of super cooled melt up to the perfect state of the stable crystalline α-form in practical the widest possible range of conditions. The need for such a study is determined by the requirement for the formation of an appropriate structure for obtaining the desired performance properties. Refinement and extension of the results of these studies show that this possibility is feasible.

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КРИСТАЛНА СТРУКТУРА НА ПОЛИКАПРОЛАКТАМА. II. СЪВЪРШЕНСТВО НА КРИСТАЛНАТА ФАЗА

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(Резюме)

Посредством комплексен анализ на интензитетни, профилни и позиционни характеристики на пиковете на дифракционните отражения от праховите рентгенови дифрактограми на поликапролактама се търсят подходи за определяне количественото съдържание и качествено състояние на кристалографските модификации в кристалната му фаза, като способ за оценка степента на завършеност на полиморфните му преходи при кристализация и рекристализация.

Установено е, че за обективност, адекватност и сравнимост на резултатите при определяне механизма и кинетиката на структурна реорганизация е необходима гарантирана условна еднозначност при събиране геометрично-чувствителната дифракционна експериментална информация посредством високо-температурната прахова рентгенова дифрактометрия. Необходима е адекватна еднозначна декомпозиция на интегрално-интензитетната дифрактометрична крива. Еднозначно разделяне и разпознаване на фазите, индексация на дифракционните отражения. Подобен подход би гарантирал точното определяне на количественото и качествено съотношение на полиморфните форми, определящо степента на реализиране на полиморфните преходи с близката предистория и перспектива. Точността на прогнозата зависи от това.

Направен е опит да се оптимизират методите за оценка съвършенството на кристалната фаза при поликапролактама. Установени са критерии за оценка на съвършенството на алфа формата му. Предложена е методика за практическото му определяне. Изведени са формули за неговата количествена оценка. Предложени са подходи за оценяване и на други полиморфни форми на поликапролактама. Интензитетното съотношение на основните дифракционни отражения се използва за количествена оценка и усъвършенстването на бета формата. Измененията в ъгловите девиации на основното дифракционно отражение на гама формата се анализират за определяне съвършенството ѝ.