

## Polycaprolactam crystal structure. I. Gamma–alpha polymorphic transition

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It was examined the polycaprolactam gamma–alpha transition as its major structural transformation. The specific behavior of the polymer in the reversible alpha–gamma transition was established. It was found that the transition progress was accompanied by a critical deformations of the crystal cells. The gamma–alpha transition is presented as the first stage of the polycaprolactam crystalline phase development by forming of a stable configuration in the package of the macromolecular chain segments. The influence of the quantitative accumulation of gamma phase and its development during the transition in the alpha phase has been also investigated. It is proposed a methodology for the realization of the study and criteria for evaluation. A mechanism of the structural transitions has been suggested.

**Key words:** polycaprolactam, crystal structure, polymorphism.

### INTRODUCTION

Crystal structure of poly( $\epsilon$ -caprolactam) (PCL) examination has been intensified since 1942 [1, 2]. It is known for its polymorphic great diversity [1–21]. However, the results are very inconsistent, conflicting and sometimes controversial [1–35]. This applies particularly for thermal initiated polymorphic transitions. They are highly dependent on the conditions of implementation. Most of these conditions are difficult to be controlled precisely. This makes it difficult to predict the structure and performance properties of materials and products.

To establish the relation between structure and properties is necessary to know well the structure. The structural diversity to be well defined. To describe accurately and unambiguously polymorphism of PCL it is necessary to assess the quality of polymorphic forms. Only then its polymorphic transitions can be precisely clarified.

So, first, it is necessary to clarify the terms of the alpha–gamma transition, i.e. to assess the perfection

of the crystalline phase of PCL. Only then the perfection of the crystal forms can be evaluated and its structural diversity thoroughly described.

### EXPERIMENTAL

Different types of polycaprolactam (PCL) with different molecular weight and molecular mass distribution (characteristic viscosity in 1%-ile sol.  $N_2SO_4$   $\eta_{\text{opt.}} = 2.11\text{--}2.83$ ) were used with a content of low molecular weight compounds in the range 1.0–12.0% fat. and moisture content of 0.1 to 0.01% mass as a prerequisite to obtaining crystal structures of varying sophistication. Thin films were formed in a wide range of molding conditions:  $T_m = 215\text{--}240$  °C and  $T_{\text{cool.}} = -196\text{--}200$  °C.

Using universal powder X-ray diffractometers URD-6 (“Präzisionsmechanik – Freiburg”, Germany) and DRON-3 with a high temperature camera ATM-2000 (“Burevestnik – St. Petersburg”, Russia) using  $Cu_{K\alpha}$ -radiation ( $\beta$ -filtered with Ni-Filter,  $\lambda = 1,5418$  Å), low and high temperature X-ray diffraction at different temperature-time regimes of simultaneous modification was received

Software package “Origin 5.0” was used for decomposition multiply peaks in determining polymorphic forms of PCL.

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## RESULTS AND DISCUSSION

The experiment involves heating and cooling under different conditions of thin films of PCL. The main purpose of the experiment is to study the polymorphic forms of PCL and transitions between them, mainly gamma–alpha transition. This is the main polymorphic transition in PCL between the unstable gamma and the stable alpha-crystalline polymorphic modifications. The degree of completeness of the transition forms the structure that determines the operating properties of the polymer. This is the structure on which the possibility for further processing and modification of polymeric material depends in order to optimize its operational properties. The content of the unstable gamma form enhances the compressibility of the structures in terms of thermal, mechanical, heat-mechanical and others complex physical fields. This is extremely important for the tape, foil and fiber-forming materials.

According to recent literature and our data, the heat of a super cooled melt of PCL forms initially its gamma form. The continuation of the process leads to improvement of the crystal structure to the stable alpha form. In this transition, beta form inevitably presents in detectable amounts, regardless of its strong conditional dependence. The impression is of its buffer, intermediate, facilitating role in the gamma–alpha transition. On the other hand, its satellite presence in the advanced stable structure is observed after the apparent depletion of the gamma form. It is not certain that there no traces of the beta-form remain even after prolonged annealing, because it is structurally very similar to the alpha form [8, 24].

For the first time the beta-form is mentioned by Holmes and coworkers'1955 together with the alpha-form definition [8]. In this sense, the beta-form can be called alpha-imperfect form. Because of its presence and influence on the determination of the partial coordinates of the basic alpha-form by Holmes it is necessary their later correction by Simon [24].

It is not accidental that some authors have assumed its presence in the form of a mixture from alpha and gamma forms. Thus, the transition delta–gamma–beta–alpha can be represented as a continuous process of improvement of the PCL crystalline phase. The whole structural reorganization occurs without cardinal displacement and geometrical modifications, while the delta–gamma and beta–alpha stages are realized permanently and almost unnoticed. Therefore, in first approximation, we can say that the compaction of the PCL structure through repacking of chain segments in the crystalline phase is realized by gamma–alpha transition. This transition is realized through the redistribution of hydro-

gen bonds (H-bonds) from the nearest neighboring segments in different crystallographic directions, especially in the plains of molecular folding.

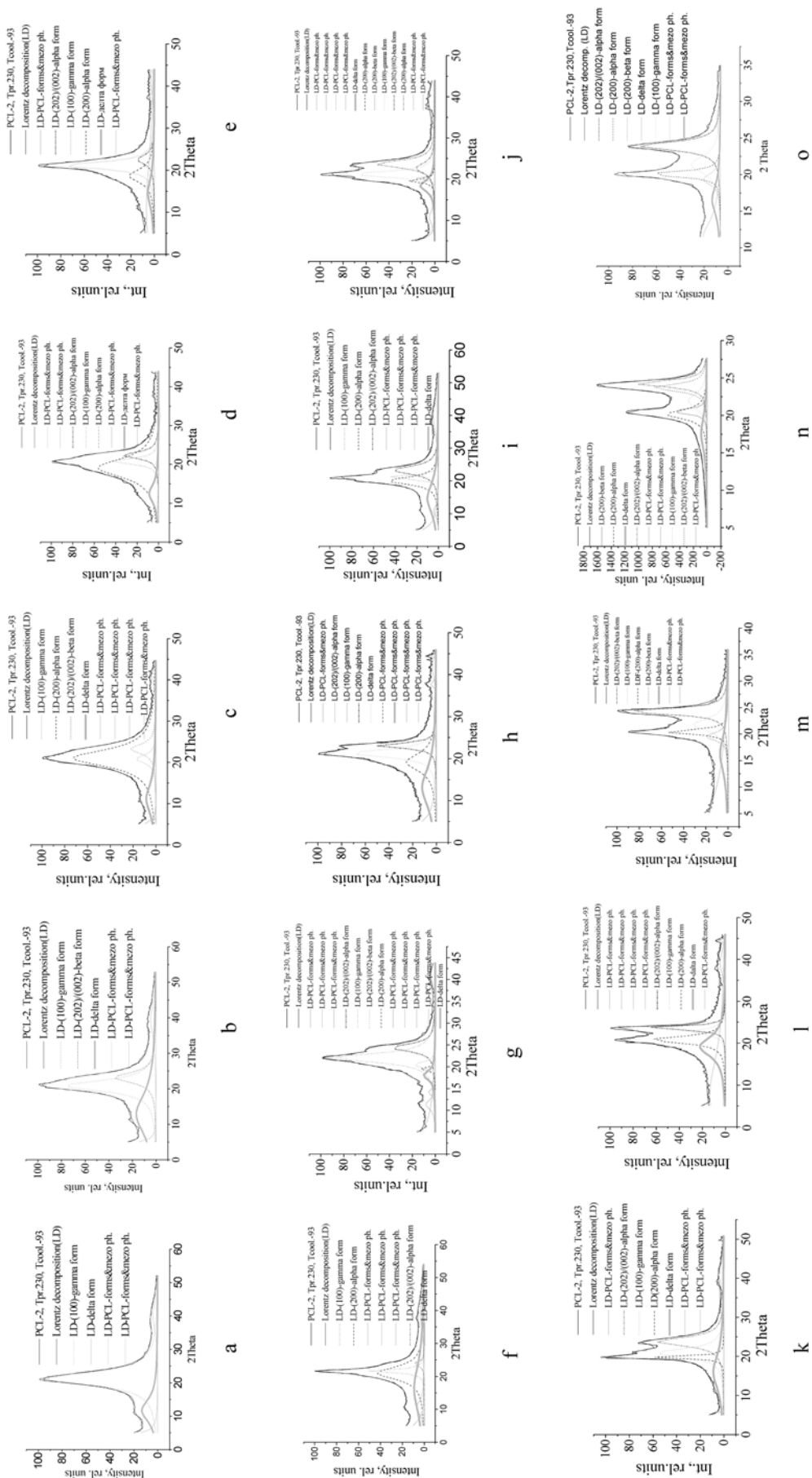
The carried out experiments showed the presence of extremely rich possibilities of structural conversions. Depending on the type of polymer, the geometry of the samples, their starting structures, schemes and the conditions of temperature modification and simultaneous X-ray scanning and so on, get the impression of infinite structural diversity and ambiguous reorganization behavior.

This sets the need for criteria and systems of quantitative evaluation of the crystalline phase perfection. The need for such qualifying of the crystalline phase quality at each stage and every moment of the structural adjustment comes from the need to assess the degree of completion of polymorphic transitions. Moreover, the characterization of the crystalline phase is necessary for elucidation of simultaneous presence of the possible PCL crystal forms with different amounts and perfection. This fact determines the possibility and necessity of the simultaneous running of the possible polymorphic transitions. Under different conditions, however, it can change the direction of the various processes and increase the ambiguity of the results and their interpretation.

Some of the results from the study on the gamma–alpha transition of PCL are shown in Fig. 1 and in Table 1. When heating the  $\delta$ -form (super cooled melt) from 20–30 °C to 70–80 °C with heating rate of 50 °C/min no significant changes in its dust diffraction occur. It is observed the appearance of  $\gamma$ -form in the range from 80–90 °C to 100–110 °C. Its improvement continued up to 160 °C. The diffraction reflection ( $100\gamma$ ) is migrating into the diffraction of about 21.1 to about 22.6–22.7  $\theta$ . The gamma–alpha transition is realized within the interval 160–190 °C.

The intensity of overlaid reflections  $(200)_{\beta,\alpha}$  and  $(002)_{\beta,\alpha}/(202)_{\beta,\alpha}$  grows and their positions divide noticeably at a temperature about 180 °C. The angular positions at the time of occurrence are about 20, 60  $^{\circ}2\theta$  and 22.85  $^{\circ}2\theta$ , respectively. At the same time, the position of the reflection ( $100\gamma$ ) started reverse migration to the value of 21.15  $^{\circ}\theta$ . The probable cause of the observed effects is the started redistribution of the hydrogen bonds from all closest neighboring segments in different crystallographic directions only in the plains of folding of the macromolecular chains.

The position 21.15  $^{\circ}2\theta$ , of  $(100)_{\gamma}$  corresponds to the largest (about 4.2 Å) achievable for gamma-form distance between the segments axes in the crystalline phase. It is probably possible because of the optimal heating speed of 5 °C/min up to that temperature, the tempering during the X-ray scanning and the appropriate objects geometry. This dis-



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**Fig. 1.** Some of the high-temperature powder X-ray diffraction, showing gamma–alpha transition in PCL: a) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 20 °C. The main single peak of the decomposed doublet, almost coinciding with the diffraction curve at the distribution about 21 °2 $\theta$  can be accepted as an equivalent to a 100 $\gamma$  on the diffuse halo of the super cooled melt ( $\delta$ -phase); b) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 120 °C, after heating from 20 °C with a speed of 5°/min and tempering for 3 min. Minor change of the profile of the multiple experimental peak after decomposition shows the appearance of additional peak (right to larger diffraction angles), corresponding to possible 202/002 $\beta,\alpha$ ; c) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C and scanned at 140 °C (after 120 °C). Again, minor modification of the profile of the multiple peak does not hide, however, the possibility for significant structural changes through repackaging of chain segments and possible decomposition of 200 $\alpha,\beta$ , 100 $\gamma$ , 202/002 $\alpha,\beta$ , respectively; d) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C and scanned at 160 °C (after 140 °C) shows a strong change in the proportion of co-existing with different perfection phases; e) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C and scanned at 180 °C (after 160 °C) already shows a strong increase with the temperature increasing of the amount of  $\gamma$ -crystalline form; f) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C and scanned at 190 °C (after 180 °C). It is observed a picture of approximation and intensity decrease of reflections of different phases at the expense of maintaining priority wheelbase of around 4.22 Å (priority baseline condition for obtaining  $\alpha$ -perfect shape after polymorphic transition  $\gamma$ - $\beta$ - $\alpha$  at sufficient cooling); g) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 180 °C (after cooling from 220, 200 and 190 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; h) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 160 °C (after cooling from 220, 200, 190, 180 and 170 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; i) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 150 °C (after cooling from 220, 200, 190, 180, 170 and 160 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; j) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 140 °C (after cooling from 220, 200, 190, 180, 170, 160 and 150 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; k) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 130 °C (after cooling from 220, 200, 190, 180, 170, 160, 150 and 140 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; l) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 120 °C (after cooling from 220, 200, 190, 180, 170, 160, 150, 140 and 130 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; m) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 110 °C (after cooling from 220, 200, 190, 180, 170, 160, 150, 140, 130 and 120 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; n) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 100 °C (after cooling from 220, 200, 190, 180, 170, 160, 150, 140, 130, 120 and 110 °C with a speed of 5°/min and tempering for 3 min). Shows improvement (away of the decomposed peaks corresponding to the reflections about 20 and 24 °2 $\theta$ ) and quantitative growth of  $\alpha$ - and  $\beta$ -forms; o) Lorentz decomposition of part of the powder diffraction curve from thin isotropic PCL film, molded by pressing at 235 °C and tempered at –93 °C, scanned at 20 °C (after cooling from 220, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110 and 100 °C with a speed of 5°/min and tempering for 3 min). Multiply peaks observed in the geometry of the intensity distribution in the diffraction experiments are decomposed by Gaussian and Lorentzian distributions corresponding to the main polymorphic forms of PCL.; This allows control of the polymorphic composition of PCL during thermal modification.

**Table 1.** Illustratively represent a double cycle of heating and cooling of 50  $\mu\text{m}$  PCL-2 foil, pressed at 498 K and cooled to 293 K in air

No	$T_{\text{ex}},$ $^{\circ}\text{C}$	Angle deviation on thermal modification of the diffraction reflections of the PCL																							
		Alpha-form												Beta-form*											
		$V = 5^{\circ}\text{C}/\text{min}$						$V = 10^{\circ}\text{C}/\text{min}$						$V = 5^{\circ}\text{C}/\text{min}$						$V = 10^{\circ}\text{C}/\text{min}$					
		heating		cooling		heating		cooling		heating		cooling		heating		cooling		heating		cooling		heating		cooling	
(200)	2 $\theta$	(002)/(202)	2 $\theta$	(200)	2 $\theta$	(002)/(202)	2 $\theta$	(200)	2 $\theta$	(002)/(202)	2 $\theta$	(200)	2 $\theta$	(002)/(202)	2 $\theta$	(200)	2 $\theta$	(002)/(202)	2 $\theta$	(200)	2 $\theta$	(002)/(202)	2 $\theta$		
1	20	20.10	23.90	20.36	23.50	20.10	23.90	20.36	23.49	20.00	24.11	20.08	24.11	20.00	24.10	20.09	24.09	20.09	24.09	20.09	24.09	20.09	24.09	20.09	24.09
2	30	20.10	23.90	20.37	23.49	20.10	23.90	20.37	23.48	20.00	24.10	20.08	24.10	20.00	24.10	20.09	24.09	20.10	24.08	20.10	24.08	20.10	24.08	20.10	24.08
3	40	20.10	23.90	20.37	23.49	20.10	23.90	20.37	23.48	20.00	24.10	20.09	24.10	20.00	24.10	20.09	24.09	20.10	24.07	20.10	24.07	20.10	24.08	20.10	24.07
4	50	20.11	23.90	20.37	23.48	20.10	23.90	20.37	23.48	20.01	24.09	20.09	24.09	20.01	24.09	20.09	24.09	20.10	24.08	20.10	24.08	20.10	24.08	20.10	24.07
5	60	20.11	23.89	20.38	23.48	20.11	23.89	20.38	23.47	20.01	24.09	20.09	24.09	20.01	24.09	20.09	24.09	20.10	24.08	20.10	24.08	20.10	24.08	20.10	24.07
6	70	20.11	23.89	20.38	23.47	20.11	23.89	20.38	23.47	20.01	24.09	20.10	24.09	20.01	24.09	20.10	24.09	20.11	24.07	20.10	24.07	20.10	24.08	20.10	24.07
7	80	20.12	23.88	20.38	23.47	20.11	23.89	20.38	23.47	20.01	24.08	20.10	24.08	20.01	24.08	20.10	24.08	20.11	24.07	20.10	24.07	20.10	24.08	20.10	24.07
8	90	20.12	23.87	20.39	23.46	20.11	23.88	20.39	23.46	20.02	24.07	20.10	24.08	20.02	24.07	20.10	24.07	20.12	24.06	20.10	24.06	20.10	24.07	20.10	24.06
9	100	20.13	23.87	20.39	23.45	20.12	23.87	20.39	23.45	20.03	24.07	20.10	24.08	20.02	24.07	20.10	24.07	20.13	24.05	20.10	24.05	20.10	24.07	20.10	24.05
10	110	20.14	23.86	20.39	23.44	20.12	23.86	20.39	23.44	20.04	24.06	20.11	24.07	20.02	24.06	20.10	24.06	20.14	24.05	20.10	24.05	20.10	24.06	20.10	24.05
11	120	20.15	23.85	20.40	23.42	20.12	23.85	20.40	23.43	20.06	24.05	20.13	24.07	20.03	24.05	20.10	24.05	20.16	24.05	20.10	24.05	20.10	24.06	20.10	24.05
12	130	20.20	23.80	20.40	23.41	20.14	23.80	20.40	23.42	20.08	24.00	20.15	24.07	20.04	24.00	20.17	24.04	20.17	24.04	20.17	24.04	20.17	24.04	20.17	24.03
13	140	20.25	23.70	20.40	23.40	20.23	23.70	20.40	23.40	20.09	24.00	20.17	24.07	20.05	24.00	20.18	24.03	20.18	24.03	20.18	24.03	20.18	24.03	20.18	24.02
14	150	20.30	23.60	20.41	23.35	20.27	23.60	20.41	23.35	20.10	24.00	20.19	24.06	20.06	24.00	20.19	24.02	20.19	24.02	20.19	24.02	20.19	24.02	20.19	24.02
15	160	20.35	23.50	20.41	23.35	20.31	23.50	20.41	23.35	20.11	24.00	20.21	24.05	20.07	24.00	20.20	24.01	20.20	24.01	20.20	24.01	20.20	24.01	20.20	24.01
16	165	20.40	23.40	20.41	23.35	20.35	23.40	20.49	23.35	20.12	24.00	20.22	24.00	20.08	24.00	20.22	23.95	20.22	23.95	20.22	23.95	20.22	23.95	20.22	23.95
17	170	20.45	23.30	20.44	23.35	20.41	23.30	20.52	23.34	20.16	23.90	20.25	23.90	20.09	23.90	20.25	23.82	20.25	23.82	20.25	23.82	20.25	23.82	20.25	23.82
18	175	20.50	23.20	20.48	23.30	20.45	23.20	20.58	23.34	20.22	23.80	20.29	23.80	20.11	23.80	20.30	23.75	20.30	23.75	20.30	23.75	20.30	23.75	20.30	23.75
19	180	20.55	23.10	20.51	23.20	20.49	23.10	20.65	23.24	20.28	23.70	20.32	23.70	20.16	23.70	20.32	23.61	20.32	23.61	20.32	23.61	20.32	23.61	20.32	23.61
20	185	20.60	23.00	20.58	23.00	20.65	23.00	20.69	23.05	20.33	23.60	20.39	23.60	20.25	23.60	20.35	23.50	20.35	23.50	20.35	23.50	20.35	23.50	20.35	23.50
21	190	20.65	22.90	20.62	22.90	20.69	22.90	20.70	22.95	20.39	23.50	20.44	23.50	20.36	23.50	20.46	23.39	20.46	23.39	20.46	23.39	20.46	23.39	20.46	23.39
22	195	20.70	22.80	20.68	22.80	20.74	22.80	20.79	22.82	20.44	23.40	20.51	23.40	20.43	23.40	20.55	23.27	20.55	23.27	20.55	23.27	20.55	23.27	20.55	23.27
23	200	20.75	22.70	20.71	22.70	20.80	22.70	20.85	22.77	20.49	23.30	20.61	23.30	20.48	23.30	20.63	23.15	20.63	23.15	20.63	23.15	20.63	23.15	20.63	23.15
24	205	20.80	22.60	20.74	22.60	20.85	22.60	20.87	22.66	20.55	23.20	20.69	23.20	20.52	23.20	20.78	23.09	20.78	23.09	20.78	23.09	20.78	23.09	20.78	23.09
25	210	20.85	22.50	20.85	22.50	20.87	22.50	20.88	22.54	20.60	23.10	20.72	23.10	20.69	23.10	20.73	23.03	20.73	23.03	20.73	23.03	20.73	23.03	20.73	23.03
26	215	20.90	22.40	20.84	22.40	20.88	22.40	20.88	22.42	20.66	23.00	20.77	23.00	20.65	23.00	20.74	22.97	20.74	22.97	20.74	22.97	20.74	22.97	20.74	22.97
27	220	20.95	22.35	20.94	22.35	20.89	22.35	20.89	22.35	20.72	22.95	20.79	22.95	20.71	22.95	20.76	22.93	20.76	22.93	20.76	22.93	20.76	22.93	20.76	22.93
28	225	21.00	22.30	21.00	22.30	20.90	22.30	20.90	22.30	20.79	22.90	20.79	22.90	20.77	22.90	20.77	22.90	20.77	22.90	20.77	22.90	20.77	22.90	20.77	22.90

\* Note: Often the angular deviations of the beta-form are within the boundaries of the method uncertainty and methodology of recording of the peak positions as compared with the same peaks of the alpha-form. But the gravity center of the integrated intensity of the delta-form coincides with the position of the gamma form peak. Furthermore, gamma and alpha forms fully characterized the PCL structure. Therefore, beta and delta forms can not be illustrated.

tance is close to the thermodynamic advantageous fold width during the PCL chains folding. Thus it makes possible to create H-bonds between the opposite targeted segments in the folding planes that forms its alpha form.

After this point, the amount of the gamma form reduces and it loses its perfection. The smaller the peak of the diffraction reflection  $(100)_\gamma$  is, so much the visual reporting position is inaccurate.

In the geometry of the intensity distribution of the high-temperature powder diffraction, it is highly

overlapping with  $(200)_{\beta,\alpha}$ . If the heating rate is higher, the gamma–alpha transition is realized later and on smaller average statistically distances between the segments in the polymer volume. Then it gets mainly the beta form that improved in alpha.

This is indicated by the increased intensity of the  $(002)_{\beta,\alpha}/(202)_{\beta,\alpha}$  [8]. Then, the near located peak  $(100)_\gamma$  overlaps and geometric “draws” from the higher intensity. Decomposition, however, shows the true positions of the diffraction reflections in the Table. They allow the definition of some, albeit rel-

**Table 2.** An illustrative example of the formation of same structures (Fig. 1, h) by different ways

Object formation and measurement	Thermal modification				
	$V_{\text{modification}},$ °C/min	$\tau_{\text{tempering}},$ min	n, number of full cycles	$\uparrow\downarrow,$ heating cooling processes	$\sim\alpha:\beta:\gamma:\delta,$ %
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=-93$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=165$	5	3	3	3	9:37:45:9
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=20$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=170$	4	4	2	2	9:37:45:9
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=200$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=175$	3	5	1	1	9:37:45:9
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=-93$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=180$	5	3	3	3	9:37:45:9
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=20$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=185$	4	4	2	2	9:37:45:9
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=200$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=185$	3	5	1	1	9:37:45:9

**Table 3.** An illustrative example of the formation of different structures by the same ways

Object formation and measurement	Thermal modification				
	$V_{\text{modif.}},$ °C/min	$\tau_{\text{tempering}},$ min	n, number of full cycles	$\uparrow\downarrow,$ heating cooling processes	$\sim\alpha:\beta:\gamma:\delta,$ %
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=-93$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=165$	10	1	5	2	34:34:24:8
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=20$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=170$	10	1	5	2	36:33:23:8
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=200$ PCL – 1 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=175$	10	1	5	2	38:36:19:7
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=-93$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=180$	10	1	5	2	37:33:22:8
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=20$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=185$	10	1	5	2	38:34:21:7
$T_{\text{mold.}}=235$ $T_{\text{crystall.}}=200$ PCL – 2 $T_{\text{modif.}}=120-220$ $T_{\text{scann.}}=185$	10	1	5	2	39:35:19:7

ative temperature-time intervals of the transitions. We can come in many other ways to similar reflections positions, for example, via other schemes, speeds of heating and X-ray scan, other times and exposures of tempering, using other PCL, source structures and geometry of its objects, other combinations etc.

The best justifications for that are the different results by different authors [1–35]. It is therefore necessary to create a unified system for study of the structural reorganization of PCL, with the ability to quantitative assessment of the crystalline phase quality. This would allow an unambiguous and accurate assessment of the implementation of the polymorphic transition.

### CONCLUSION

1. It was found that the structural diversity in PCL temperature modification in a wide range of conditions is difficult to be realized by X-ray diffraction interpretation and evaluation. It is proposed simultaneous control with a high temperature powder diffraction and interpretation of information obtained from the structural studies of thin films of PCL with different initial structure after the necessary corrections and decomposition of multiple intensity distribution.

2. Detailed information about the temperature dependence of the possible angular deviations, intensity proportions and profile changes of the polymorphic diffraction reflections in the observed experimental peaks has been obtained. An attempt to analyze the polymorphic reorganizations and especially the main alpha-gamma transition in PCL has been made. Difficulties in the interpretation of the observed effects related to their qualitative and quantitative ambiguities have been shown.

3. The impossibility for precise and positive interpretation of the diffraction (powder diffraction) results from the structural changes in PCL without satisfactory quantitative evaluation of the quality and quantity of polymorphic forms has been assumed. It is very difficult without a quantitative assessment of their perfection as a measure of the completeness of the polymorphic transitions.

4. A conclusion has been drawn about the need to establish the basis of criteria and methodology for practical assessment of the crystalline phase perfection of the main polymorphic forms.

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## КРИСТАЛНА СТРУКТУРА НА ПОЛИКАПРОЛАКТАМА. I. ГАМА–АЛФА ПОЛИМОРФЕН ПРЕХОД

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(Резюме)

На база предположението за перманентна реорганизация на опаковката на макромолекулните верижни сегменти на поликапролактама, вследствие динамично изменящите се равновесни мрежи от водородни връзки при температурна или термомеханична модификация, е изучаван богатия му полиморфизъм в интервала 20–240 °С.

Изследван е основният гама–алфа полиморфен преход на поликапролактама. Установено е специфично поведение на полимера при обратимия алфа–гама преход. Установено е, че прехода се съпровожда с достигане на критични деформации на елементарните кристални клетки. Гама–алфа преходът е представен като първи етап от развитието на кристалната фаза на поликапролактама при формирането на стабилна конфигурация в опаковката на макромолекулните верижни сегменти. Изследвано е влиянието на количественото натрупване и усъвършенстване на гама формата върху прехода и в алфа форма. Предложена е методика за провеждане и критерии за оценка на изследванията. Предположен е механизъм за реализиране на структурните преходи.

Установено е едновременното съвместно съществуване в различно количествено съотношение и с различно съвършенство на алфа, бета, гама и делта формите му в комплексни структури в зависимост от вида на полимера, предисторията на обектите, начина и условията на водене на кристализационния или рекристализационния процес. В зависимост от начина и пътя на температурна модификация е разгледана възможността за получаване на подобни комплексни структури при различни условия или различни комплексни структури при еднакви условия на формирането им. Това затруднява силно изучаване на полиморфизма и полиморфните му преходи.