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On the relationship crystal structure – properties at flexible chain polymers. I. Polycaprolactam

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There are applied different methods as high temperature X–ray, microscopic, spectroscopic, calorimetrical, heat-mechanical etc. There are mostly studied the deformation and destruction of the elementary cells of the polycaprolactam basic crystal forms. By change of the intensity distribution of the powder X-ray diffraction there are controlled as the profile and angle deviation on different diffraction reflections, as well as the alterations in the packing of the macromolecular chain segments in the crystal phase. There are defined the critical deformation values caused the polymorphic transitions. The present results are connected with the crystal phase perfection and with the quantitative proportion of the simultaneously existed crystallographic modifications in the studied objects at the given conditions. There is supposed a mechanism of structural development connected with the specificity in the H-bonds redistribution at the polycaprolactam.

Key words: Polycaprolactam, thin films, structure, polymorphic transitions, X-ray diffraction.

INTRODUCTION

Undoubtedly the structure-properties relationship remains currently actually. At the strongly crystallizable flexible chain polymers and especially at polycaprolactam the studying of the relationship crystal structure/properties is particularly important. The influence of the hydrogen bonds between the amide groups as in the crystal as well as in the amorphous polycaprolactam regions fully defines its strength/deformation properties. The effect multiplies from the fact that the polycaprolactam structure/properties relation is consider in the borders crystal structure in isotropic state – deformation behaviour in orientated state, and includes basic stages as follows: nascent structure – forming conditions – isotropic structure – orientation drawing conditions – structure in orientated state at given drawing stage – utmost drawing conditions – utmost orientated structure – deformation behaviour of utmost orientated polycaprolactam. The studding of the relationships begins with temperature possibilities for optimal modifications of the initial isotropic structures and it can starts with investigation of the polycaprolactam polymorphism at cyclical repeatedly heating and cooling in the most wide possible temperature interval.

EXPERIMENTAL

There are used different modes polycaprolactam with different molecular masses and molecular-mass distribution (characteristic viscosity in 1% solution of H_2SO_4 $\eta_{rel} = 2.11 \div 2.83$), contents of low-molecular tie in the interval $1.0 \div 12.0\%$ mass, moisture content from 0,1 to 0,01% mass, as a necessary condition about the obtaining of crystal structures with different perfection. There are formed thin folios in a large diapason of forming conditions: $T_{pr.} = 483 \div 513$ K и $T_{c.} = 77 \div 473$ K. The high temperature X-ray investigations are 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. 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. Using

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an universal powder X-ray diffractmeters URD 6 ("Präzisionsmechanik – Freiburg", Germany) and ДРОН 3 equipped with a high temperature chamber УВД 2000 ("Буревестник – Санкт Петербург", Русия), at applying of $Cu_{K\alpha}$ radiation (β-filtered by Ni filter, $\lambda = 1.5418$ Å) there are obtained low- and high-temperature X-ray diffraction curves under different time/temperature conditions of simultaneous modification. 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]. The deformation/strength investigations are carried out at differen temperatures by an apparatus "Tiratest-102", Germany.

RESULTS AND DISCUSSION

The intensity distribution of the diffracted from isotropic structures X-ray beam is basically concentrated in the angle interval 18–19 ÷ 25–26 °2θ. In that interval appear the fundamental diffraction reflections of the all known polymorphous forms (α, α^*, β, β^*, γ, γ^*), the other possible meso-states, as well as the known as overcooling melt δ-phase [3–11]. Because of that the powder diffraction in the interval 15÷30 °2θ is fully sufficient about polymorphous phase investigations in the studying of its structure rearrangement. The relation structure – properties investigation needs of a detailed notion about the polycaprolactam crystal structure, because of the existence of direct connection with the morphology and determining of its mechanical behaviour amorphous regions. The obtained experimental data show that the most using morphologic structures cause the simultaneously existence of more than one crystal forms. Usually it can be observed the simultaneously existence of all possible polymorphous forms and mesophases in different

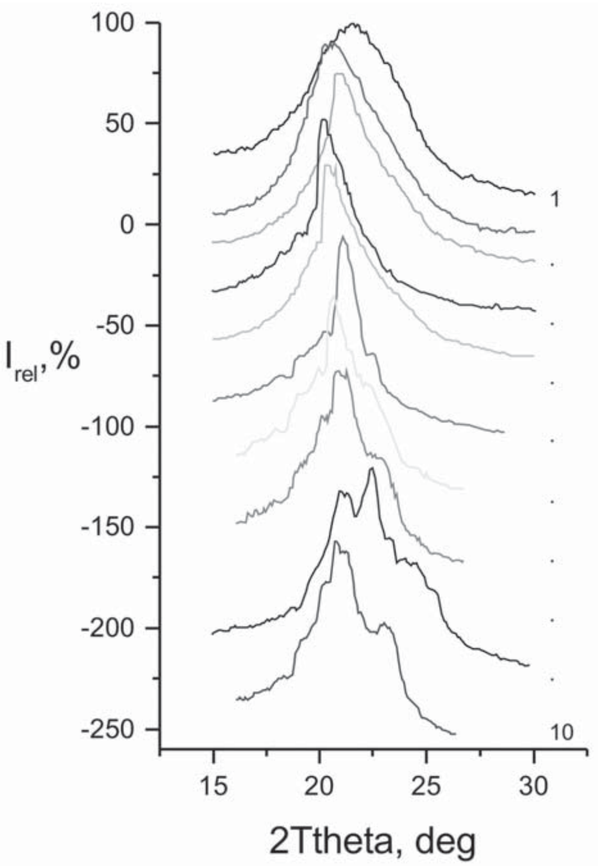

Fig. 1. High temperature X-ray diffractograms of thin PCL folios formed and scanned at different conditions:

1) PCL-2, Tpr = 220 °C, Tcool = 0 °C, Tsc = 20 °C;
2) PCL-2, Tpr = 230 °C, Tcool = 0 °C, Tsc = 20 °C;
3) PCL-2, Tpr = 240 °C, Tcool = 0 °C, Tsc = 20 °C;
4) PCL-1, Tpr = 240 °C, Tcool =20 °C, Tsc =180 °C;
5) PCL-2, Tpr = 240 °C, Tcool = 0 °C, Tsc = 20 °C;
6) PCL-2, Tpr = 240 °C, Tcool =20 °C, Tsc = 20 °C;
7) PCL-2, Tpr = 240 °C, Tcool =20 °C, Tsc =200 °C;
8) PCL-2, Tpr = 240 °C, Tcool =20 °C, Tsc =180 °C;
9) PCL-2, Tpr = 240 °C, Tcool =20 °C, Tsc =240 °C;
10) PCL-2, Tpr = 240 °C, Tcool =20 °C, Tsc =140 °C.

Table 1. Crystallographic and morphological information for some of the investigated objects

Object, №	$T_{pr.}$, K	$T_{cry.}$, K	$T_{sc.}$, K	α_c,%	α::γ:δ	Initial morphology	CPI*	ICP**
1. PCL-1	230	–196	120	4	3:8:89	Fine spherolitic Narrow size distribution	0.367	0.5
2. PCL-1	230	200	160	49	2:11:87	Large spherolitic lamellar Wide size distribution	0.704	1
3. PCL-2	240	20	180	41	19:38:43	Middle spherolitic Middle size distribution	0.604	0.846
4. PCL-2	240	200	210	1.5	94:2:4	Large spherolitic Wide size distribution	0.424	0.583

*Crystalline Perfection Index (CPI)
**Index of Chain Packing (ICP)

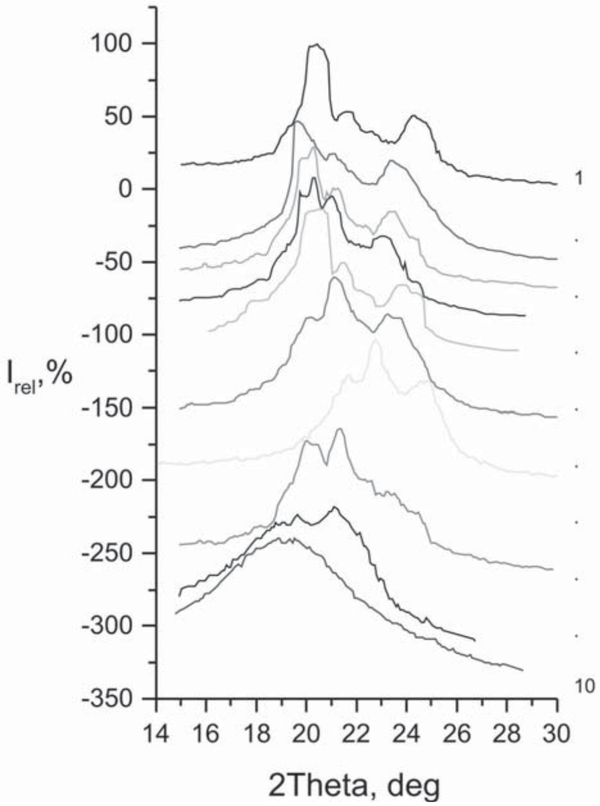

Fig. 2. High temperature X-ray diffractograms of thin PCL folios formed and scanned at different conditions:

1) PCL-2, Tpr = 200 °C, Tcool = 20 °C, Tsc = 20 °C;
2) PCL-2, Tpr = 240 °C, Tcool = 25 °C, Tsc = 25 °C;
3) PCL-2, Tpr = 240 °C, Tcool = 20 °C, Tsc = 100 °C;
4) PCL-2, Tpr = 240 °C, Tcool = 20 °C, Tsc = 140 °C;
5) PCL-2, Tpr = 240 °C, Tcool = 20 °C, Tsc = 50 °C;
6) PCL-1, Tpr = 240 °C, Tcool = 20 °C, Tsc = 20 °C;
7) PCL-2, Tpr = 245 °C, Tcool = 25 °C, Tsc = 30 °C;
8) PCL-2, Tpr = 240 °C, Tcool = 20 °C, Tsc = 20 °C;
9) PCL-1, Tpr = 215 °C, Tcool = 20 °C, Tsc = 210 °C;
10) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc = 20 °C.

quantitative proportions. The specific conditions just strongly increase the content of some of them (Table 1). So by changing of the forming conditions of different structures is possible to affect strongly the properties of the polycaprolactam materials and products. It is possible by reason of the fact that every determining the mechanical behaviour morphology is genetically connected with own crystallographic content. For example the known with the better mechanical behaviour fine spherolitic structure with not so large as a size of the morphological components distribution (Fig. 4d) is described with significant presence of almost every polycaprolactam polymorphous forms and mesophases and approximately equally content of α- and γ-forms (Curve 1, Fig. 2; Fig. 4c; Table 1, № 3).

The large-spherolitic structures with narrow size-distribution possess high (490 MPa) and lower strength characteristics (31–37 MPa). The large-spherolitic structures with very widely size-distribution of the morphological components are characterized with better mechanical features (E_{el} = 430 MPa, σ_{ext} = 42 MPa) in comparison with the structures having whopping morphological components but with narrow size-distribution. The biggest spherolitic and lamellar polycaprolactam structures (Fig. 4a) with a little dispersion show very high modulus (1.6 GPa) only in the little deformations range ($\varepsilon = 0.01\div0.5\%$).

It was found, that it is easy to find out forming conditions for every kind of polycaprolactam with purpose to obtain the desired isotropic structure with crystallographic modifications in the crystal phase are connected with the morphologi-

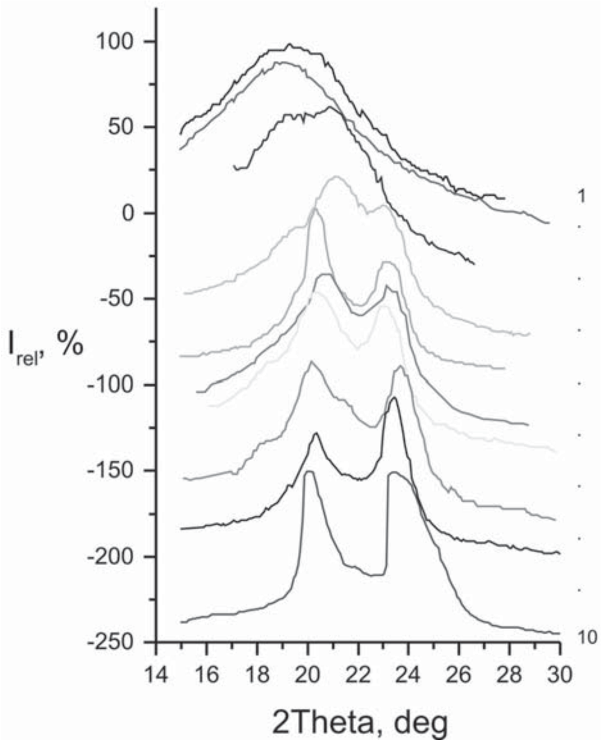

Fig. 3. High temperature X-ray diffractograms of thin PCL folios formed and scanned at different conditions:

1) PCL-1, Tpr = 240 °C, Tcool = 20 °C, Tsc =230 °C;
2) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =230 °C;
3) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =200 °C;
4) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =160 °C;
5) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =220 °C;
6) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =140 °C;
7) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =100 °C;
8) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =20 °C;
9) PCL-1, Tpr = 220 °C, Tcool = –95 °C, Tsc =120 °C;
10) PCL-1, Tpr = 230 °C, Tcool = –196 °C, Tsc =20 °C.

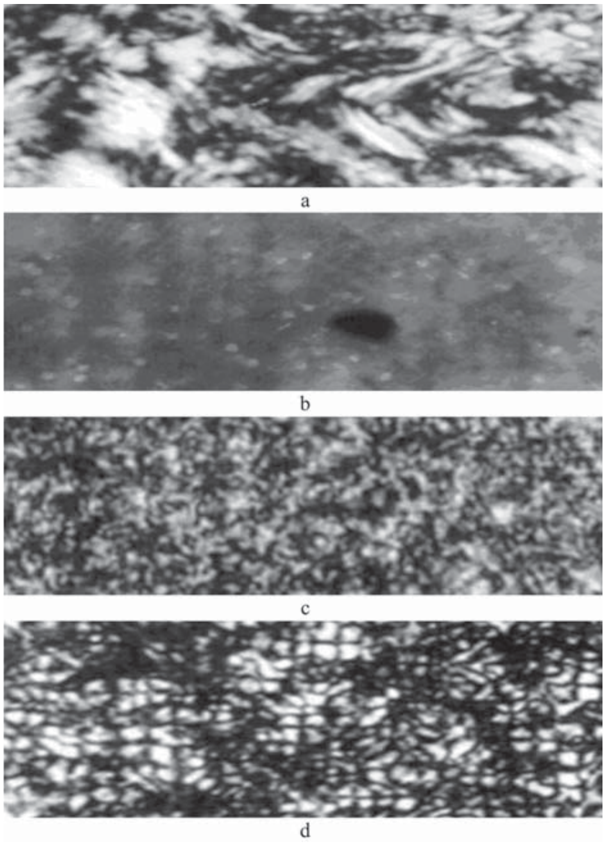

Fig. 4. Polarization microphotos of thin PCL folios Formed by pressing at: a) Tpr =240 °C, Tcool = 0 °C; b) Tpr = 240 °C, Tcool = 20 °C; c) Tpr = 200 °C, Tcool = 20 °C; d) Tpr = 230 °C, Tcool = –196 °C. Micr. magnification 200×.

cal type, and respectively with the mechanical behaviour, too. On the basis of the initial isotropic structure 3 (Table 1, Curve 1, Fig. 2, Fig 4c) subjected to gradually orientated drawing in the temperature interval from 393 K to 433 K were reached $E_{el.}$ = 1.1 GPa and σ_{ext} = 350 MPa at 7.2 multiple extension. Besides, every structure can be easy temperature modified in other desired one using different modes. It is most important the circumstance that at one and the same conditions it can be formed different structures (with different quantitative proportion of crystal forms) or at different conditions – identical structures, depending on the objects preliminary history. As a result of heating, for example of the amorphous δ-phase forming itself γ-modification, turns into the polycaprolactam α-form. Up to 140–160 °C there are running improving processes of the both co-existence modification. At farther temperature raising begins increase of the γ-form contents. Over 180 °C starts the crystal phase melting that is finish around 220–230 °C. The first cooling forms first of all the α-form that is perfecting up to room temperature.

At variance of the time/temperature modification conditions at different temperatures and different heating and cooling cycles it can be obtain different structures with different perfection (Fig. 1–3, Table 1). Namely the different quantity and quality of the crystallographic modifications determine the suitable density and mode of the segments packing for different structural reorganizations depending on the implement conditions. Their big multiform and complexity should to be investigated concrete in detail for all used in the practice polycaprolactam materials. On Figures 1–3 are present a number of powder diffractograms of thin polycaprolactam folios formed under different conditions. Accepting the β-form [3] as an α- and γ-forms blend, supplemented up to 100% with the δ-phase, we can characterize the roughly presented isotropic structures in first approach by the quantitative proportion of the α- and γ-forms. If accept the basic peaks of the crystal forms appears in the angle intervals 20.1–20.2° ± 0.4–0.8° 2θ for 200_α, 21.6–21.8 ± 0.4–0.8° 2θ for 100_γ and 23.4–23.8^0 ± 0.4–0.8° 2θ for 002_α, 020_α we can interpret qualitative, or with some approximation, their quantitative content in the experimental powder diffractograms. As it can be seen from the shown diffractograms there are observed one-, two-, three- and multilineal polycaprolactam models in the studied diffraction interval 18–19÷25–26°. It is not easy to interpret similar multiplicity in the light of the polycaprolactam complicated polymorphism, that is strongly dependent on different physics influences. By the realizing of different degrees and modes of overcooling during the initial isotropic structure forming, is possible to obtain various variants of the diffracted beam intensity distribution. It turned out, that the same or similar pictures can be obtained by means of different hating and cooling modes. I.e., from every one obtained initial isotropic structure, using different modes of temperature modification, it is possible to receive another possible from that group isotropic structure. Moreover, with different degree of perfection.

CONCLUSION

Depending on the forming conditions of thin folios by pressing and basically, from the overcooling ratio at the recrystallization processes it is possible to obtain strongly different isotropic structures, that contains all known polycaprolactam polymorphous phases, with differently quantitative proportion and perfection. By different modes of heating and cooling of the initial polycaprolactam phases it can be received various desired isotropic structures;

There are observed at first sight illogogical polymorphous transitions, namely – form more steadily to less steadily crystal modifications, depending on the initial structure, time-temperature pre-history and the transition scheme, as well as from the perfection of the α- and γ-crystal modification at the moment of the polymorphic transition. The present diffractograms, connected with the relevant forming conditions, can be obtained with a good repetition at consecutively heating and cooling cycles in the temperature interval 20–240 °C.

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ВЪРХУ ВРЪЗКАТА МЕЖДУ КРИСТАЛНАТА СТРУКТУРА И СВОЙСТВАТА ПРИ ГЪВКАВОВЕРИЖНИТЕ ПОЛИМЕРИ. I. ПОЛИКАПРОЛАКТАМ

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(Резюме)

Използвани са високотемпературни рентгенови, микроскопски и деформационно-якостни методи и методики за изследване полиморфизма на поликапролактама. Изучавани са, основно, деформацията и разрушението на елементарните клетки на основните кристални форми на поликапролактама при прехода им в други кристални модификации. Контролирани са, посредством изменение на интензитетното разпределение на праховата рентгенова дифракция, профила и ъгловата девиация на определени дифракционни отражения, отразяващи промените в опаковката на макромолекулните верижни сегменти в кристалната фаза. Резултатите са свързани със съвършенството на кристалната фаза и с количественото съотношение на едновременно съществуващите кристалографски модификации в изследваните обекти при дадените условия.