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ИЛМИЙ-ТЕХНИКА ЖУРНАЛИ



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INVESTIGATION OF STRUCTURAL CHANGES OF POLYCAPROAMIDE UPON THERMAL TREATMENT

A.A. Khaydarov^a, S. Collins^b, S.Sh. Rashidova^c, N.R. Ashurov^c and M.Abdurazakov^c

^aFergana Polytechnic Institute, 150107, Fergana Street 86 A, Fergana, Uzbekistan;

^bInstitute for Particle Science and Engineering, SPEME, University of Leeds, Leeds LS29JT, UK; ^cInstitute of Polymer Chemistry and Physics, Academy of Science of Republic Uzbekistan, 700128, 7 b, A. Kadiri Street, Tashkent, Uzbekistan.

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Кенг бурчакли рентгенография методи билан дастлабки ва термик ишлов беришдан сўнги гидролитик ва анион полимерлаш усулида олинган поликапроамидни кристалл структураси ва айрим тузиллиш характеристикалари ўрганилган. Рентгенография натижалари термик ишлов беришда поликапроамидни кристалл структурасининг мукаммаллашуви аниқланди.

Таянч сўзлар: термик ишлов бериш, кристаллиниш, поликапроамид, рентгенография.

Методом широкоугольной рентгенографии исследованы кристаллическая структура и некоторые структурные характеристики исходных и термически обработанных образцов поликапроамида, полученных методами гидролитической и анионной полимеризации капролактама. Рентгенографические результаты показали на совершенствование кристаллической структуры поликапроамида при термической обработке.

Ключевые слова: отжиг, кристалличность, поликапроамид, рентгенография.

Wide angle x-ray scattering (WAXS) were used to study the crystalline structure and some structural properties of untreated and thermally treated samples of polycaproamide obtained by hydrolytic and anionic polymerisation of caprolactam. WAXS results showed an improvement in crystalline structure of the investigated samples of polycaproamide upon annealing.

Keywords: annealing, crystallinity, polycaproamide, WAXS.

1. Introduction

Aliphatic polyamides (e.g. polycaproamide (nylon 6)), are widely used in many applications as homopolymer, copolymers and blends [1]. In spite of a number of investigations on these polymers [2,3], there have been few papers dedicated to the fundamental investigation of the crystallisation process on the lamellar level [4,5].

These two methods of polymerisation of caprolactam lead to the formation of products having different final supermolecular structures. However, there is a shortage of reports which have detailed investigations into the supermolecular structure of polycaproamides synthesized by the two different methods of polymerisation.

In the present paper we report a thorough investigation of the formation of the crystalline and amorphous structure and some structural properties of polycaproamide samples (obtained using hydrolytic and anionic polymerisation methods) and their changes upon annealing using the techniques of wide angle X-ray scattering (WAXS). In addition the influence of temperature and duration of thermal treatment on the crystalline and amorphous structure was investigated.

2. Experimental

Samples of polycaproamide obtained using two different methods of polymerisation were used: hydrolytic polymerisation (commercial product (granular form) from China (HP1) and Germany (BASF) (HP2)) and laboratory samples synthesized by anionic activated

polymerisation of ϵ -caprolactam in block form (AP). For the AP, ϵ -caprolactam, $(\text{CH}_2)_5\text{NHCO}$, was purchased from ChPO Electrochimprom (Uzbekistan). 2,4-toluene diisocyanate (0.35 % molar mass) was used

as a activator and metallic sodium (0.35 % molar mass) was used as catalyst.

Samples were thermally treated in vacuum-treated ampoules under isothermal conditions using a variety of temperatures (150-190 °C) and times (6-72 hours).

The inherent viscosity $\eta_{inh} = \ln \eta_{rel} / C$, of polycaproamide samples was measured using an Ubbelohde viscometer with formic acid (85 %) at a temperature 20.0 ± 0.1 °C. The values of inherent viscosity are reported in Table 1 together with the viscosity-average molar mass M_v of each sample, calculated by the Mark-Houwink equation ($[\eta] = KM^a$), where $K = 22.6 \times 10^{-3}$ ml/g and $a = 0.82$ [6].

WAXS studies were carried out using a DRON-UM1 instrument with CuK_α radiation ($\lambda = 0.1542$ nm), a Cu anode, a voltage of 40 kV, a current intensity of 3 mA and a Ni filter. The scans were collected between $2\theta = 2^\circ$ and 30° with a scanning speed of 2° min^{-1} . Samples for WAXS experiments used on the form granule for polycaroamide synthesed by hydrolytic polymerisation an as chips for samples laboratory samples synthesed by anionic activated polymerisation.

3. Results and discussion

It is known that practical polymer characteristics such as melt viscosity, tensile modulus, and toughness are mostly defined by formation of the super molecular structure, as well as molecular-mass features. The inherent viscosity and viscosity-average molar mass determined for untreated and annealed samples of polycaproamide synthesed by anionic polymerisation (AP) and hydrolytic polymerisation (HP1, HP2) are presented in Table 1.

Intrinsic viscosity and molar mass of untreated and annealed samples of polycaproamide

Table 1.

Sample code	Sample	Untreated samples		ANNEALED SAMPLES (190 °C, 24 h)	
		$\eta_{inh} (\text{cm}^3 \text{g}^{-1})$	$M_v, (\text{GMOL-1})$	$\eta_{inh} (\text{cm}^3 \text{g}^{-1})$	$M_v, (\text{GMOL-1})$
AP	Anionic polymerisation	2.26	110500	1.35	54000
HP1	Hydrolytic polymerisation (China)	0.97	20000	0.95	19500
HP2	Hydrolytic polymerisation (BASF) (Germany)	0.84	17000	1.04	21000

Initial differences in viscosity-average molar masses values were observed for polycaproamide samples obtained by the different methods of polymerisation of caprolactam (anionic and hydrolytic) including differences for samples obtained by the same method of polymerisation (HP1, HP2). The differences in the viscosity-average molar mass for polycaproamide samples from the different sources can be explained by the different methods of polymerisation used. It is known that in anionic polymerization the molecular mass grows with practically no chain termination. The difference in molecular masses between the hydrolytic samples (HP1, HP2) is connected with the technological mode of their production. Comparing the viscosity-average molar mass of the untreated samples it is observed that anionic polymerisation has a better environment for growing long macromolecular chains.

The influence of annealing (190°C, 24h) on the viscosity-average molar mass of the investigated samples (Table 1) shows that for AP the molecular mass decreased by nearly half to 54000. This is probably connected to the "living" catalytic system of the sodium caprolactam remaining in the polymer after synthesis, which under high temperature is activated and brings

about cleavage of polycapraamide macromolecules. On annealing the viscosity-average molar masses for samples HP1 hardly changed but for HP2 there was a small growth in molecular mass presumably as a result of post condensation reactions [7]. The difference in the viscosity-average molar mass of samples obtained by hydrolytic polymerisation upon annealing may be connected to the specific conditions of the production of these polymers.

Most semicrystalline polymers exhibit the phenomenon of polymorphism. Polymorphic structures in polyamides vary in their spatial arrangement as a result of the hydrogen bonds between oxygens in the carbonyl groups of one polyamide molecular chain and the hydrogens attached to the nitrogens of the neighbouring molecular chain of polyamide. In polyamides there exist basically two crystalline structures: α - and γ - forms. The α -crystalline phase is described as a monoclinic lattice in which hydrogen bonds are made between antiparallel chains and the γ -crystalline is described as being formed by stacked parallel chains. There also exists an unstable γ^* -crystalline structure where hydrogen bonds have chaotic character, arising from low crystallisation temperatures or very high cooling rates of crystallisation of the polycapraamide. In X-ray diffraction patterns of polycapraamide, the α -form can be identified by two reflections at $\sim 4.4 \text{ \AA}$ for $\alpha_1(200)$ and 3.7 \AA for $\alpha_2(002/202)$, while the γ^* -crystalline form can be identified by a single strong reflection at $\sim 4.13 \text{ \AA}$ for $\gamma^*(001)$.

Figure 1 shows the WAXS patterns of the untreated samples of polycapraamide (AP, HP1, HP2). The presence of these three crystalline reflections indicates the presence of two crystalline structures, i.e. the coexistence of the stable α - crystalline monoclinic modification (at $2\theta = 20^\circ$ and 24°) and the unstable γ^* - pseudo hexagonal crystalline form (at $2\theta = 21^\circ$) that is typical of polycapraamide. It is interesting to note that these three crystalline reflections are present for all three investigated samples, independent of the method of polymerisation and (as will be shown later) duration of heat treatment.

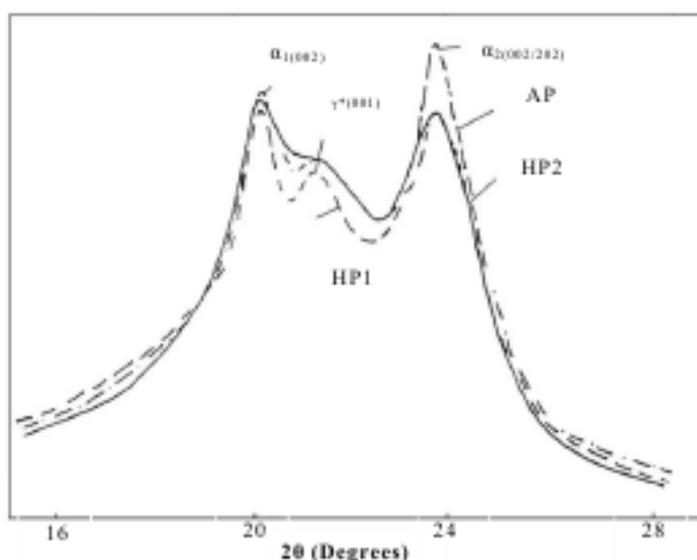


Fig.1. WAXS spectra of semicrystalline polycapraamide synthesized by anionic polymerization (AP) and hydrolytic polymerization (HP1, HP2).

Examination of the diffraction patterns for the untreated samples shows that the sample of polycapraamide obtained by anionic polymerisation (AP) (Fig.1) has a sharper and more intense crystalline reflection at scattering angle $2\theta=24^\circ$ (α - crystalline form) than for the samples obtained by hydrolytic polymerisation (HP1, HP2). This is attributed to the development of hydrogen bonds between chains of macromolecules of polycapraamide in the form of networked planes between anti-parallel chains of polycapraamide macromolecules.

The observed high intensity of the reflection at $2\theta=21^\circ$ for the polycapraamide obtained by hydrolytic polymerisation shows comparatively more γ^* -form content than in polycapraamide obtained by anionic polymerisation. However, it should be noted that the two hydrolytic polymers differ. For HP2 the peak at $2\theta=21^\circ$ has a lower resolution (compared with HP1) and is in the shape of a shoulder against a background diffraction at $2\theta=20^\circ$. This indicates that the initial content of the γ^* -form in HP2 is relatively high. Figure 1 shows the qualitative differences in the WAXS patterns for the untreated samples under investigation. The structural characteristics obtained confirm the qualitative conclusion from diffraction, showing a smaller content of the γ^* -form (R_{γ^*}) and a higher degree of crystallinity (χ) in the case of the sample obtained by anionic polymerisation (Table 2). There is a considerable difference in the parameters of crystalline structure between untreated samples of polycapraamide synthesized by the different methods. This is connected to the more rigid condition that occurs after hydrolytic polymerisation in comparison with that occurring after anionic polymerisation. Consequently, for anionic samples (with high initial molar mass), the conditions of crystallisation, which approximate to isothermal annealing and slow cooling of polymer, all favour the formation of a more perfect crystalline polycapraamide structure with less defects (in comparison with the hydrolytic samples).

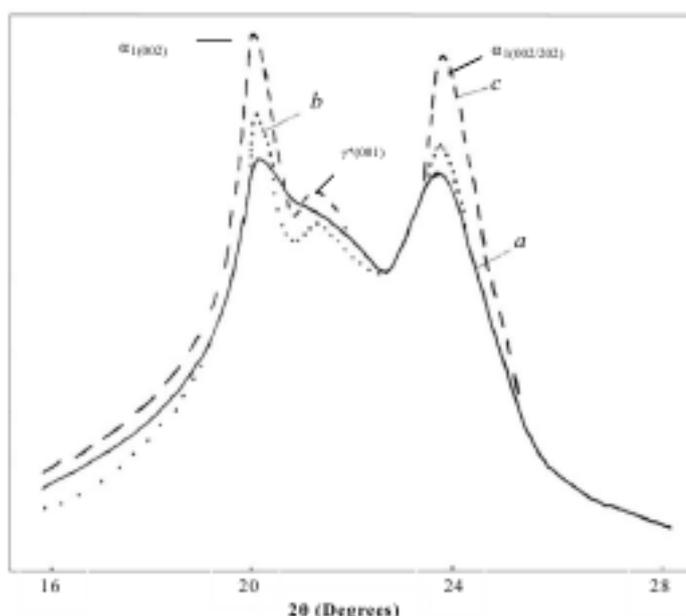


Fig.2. WAXS spectra of polycapraamide HP2: a) untreated; b) annealed at 150°C for 24 hours; c) annealed at 190°C for 24 hours.

Figure 1 shows the qualitative differences in the WAXS patterns for the untreated samples under investigation. The structural characteristics obtained confirm the qualitative conclusion from diffraction, showing a smaller content of the γ^* -form (R_{γ^*}) and a higher degree of crystallinity (χ) in the case of the sample obtained by anionic polymerisation (Table 2). There is a considerable difference in the parameters of crystalline structure between untreated samples of polycapraamide synthesized by the different methods. This is connected to the more rigid condition that occurs after hydrolytic polymerisation in comparison with that occurring after anionic polymerisation. Consequently, for anionic samples (with high initial molar mass), the conditions of crystallisation, which approximate to isothermal annealing and slow cooling of polymer, all favour the formation of a more perfect crystalline polycapraamide structure with less defects (in comparison with the hydrolytic samples).

Some structural characteristics of untreated and annealed samples of polycapraamide obtained from WAXS

Table 2.

Sample	Condition of annealing		Crystalline form						R_{γ^*}	χ
	$T_a, ^\circ\text{C}$	τ_a, hour	$\alpha_1(200)$		$\alpha_2(002/202)$		$\gamma^*(001)$			
			$2\theta_{\alpha_1}$	$d_{\alpha_1}, \text{\AA}$	$2\theta_{\alpha_2}$	$d_{\alpha_2}, \text{\AA}$	$2\theta_{\gamma^*}$	$d_{\gamma^*}, \text{\AA}$		
AP	-	-	$20^\circ10'$	4.23	$23^\circ50'$	3.78	$21^\circ13'$	4.20	0.27	0.38
HP1	-	-	$20^\circ10'$	4.23	$23^\circ50'$	3.78	$21^\circ24'$	4.18	0.29	0.32
HP2	-	-	$20^\circ09'$	4.25	$23^\circ48'$	3.79	$21^\circ10'$	4.21	0.30	0.34
AP	190	24	$20^\circ24'$	4.38	$23^\circ05'$	3.63	$21^\circ33'$	4.16	0.25	0.45
HP1	190	24	$20^\circ00'$	4.44	$23^\circ29'$	3.81	$21^\circ10'$	4.21	0.27	0.37
HP2	190	24	$20^\circ10'$	4.23	$23^\circ54'$	3.81	$21^\circ41'$	4.20	0.26	0.37

Notes: α_1, α_2 – monoclinic crystalline form, γ^* – pseudohexagonal crystalline form,

T_a = annealing temperature, τ_a =time of annealing, 2θ =scattering angle, d -distance between planes, R_{γ^*} =relative fraction of γ^* - crystalline form, χ =degree of crystallinity.

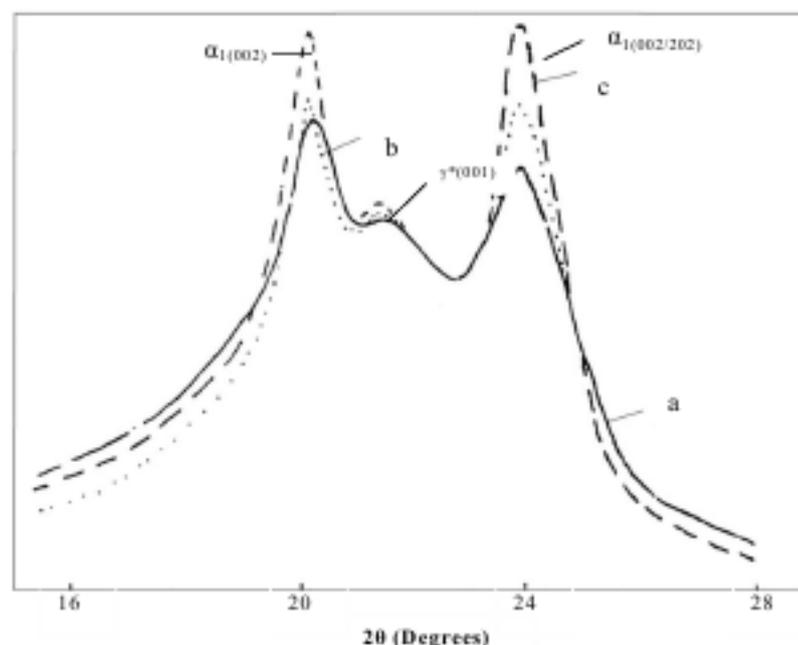


Fig. 3. WAXS spectra of polycapraamide HP1: a) untreated; b) annealed at 190°C for 24 hours; c) annealed at 190°C for 72 hours.

Figure 2 shows diffraction spectra for untreated and annealed samples (24hr, 150°C or 190°C) of polycapraamide obtained by hydrolytic polymerisation (HP2). Annealing at 150°C results in greater sharpness of the reflections and higher crystalline peaks of both the α and γ^* forms and an increased intensity of the α -crystalline maximum.

Increasing the temperature of isothermal annealing (from 150 to 190°C) increases these features. There are analogous changes in the diffraction patterns for HP1 annealed for increasing time at 190°C (Figure 3). The modification of structure was increased on increasing the annealing time. The WAXS patterns indicate changes occurring in the process of isothermal annealing with partial

removal of irregularity between chains and between associated sheets of macromolecules in the lamellae. By increasing the temperature (150 to 190°C) or duration of thermal treatment (at 190°C) an increased ordering is observed in terms of both α crystal size and/or perfection and crystallinity with a smaller, similar change in the γ^* form crystals. It has been reported that the largest change in these parameters was observed at an annealing temperature at the lower end of the melting point range of polycapraamide (between ~185 and 235 °C). Calculated quantitative structural parameters for the annealed samples are listed in Table 2. The degree of crystallinity was found to increase upon thermal treatment, becoming higher for all three samples investigated, but there was essentially no change in the R_{γ^*} of the specimens.

To help identify the polymorph modification occurring an approximation of the relative quantity of the crystalline phases was obtained. Fig. 4a shows a plot of the relative content of γ^* -crystalline form (R_{γ^*}) upon annealing temperature. It should be noted that in the unannealed samples, (initial points (at 20 °C) in Fig. 4a) the content of the γ^* -crystalline form was substantially lower in AP than in samples obtained by hydrolytic polymerisation of caprolactam (HP1, HP2). This indicates that different conditions of crystallisation exist during anionic and hydrolytic polymerisation, which has already been noted. The distinction in values of the γ^* -crystalline form obtained in samples using the same method but from different sources (HP1, HP2) can be explained by the particular technological features of the different production processes. HP2, presumably due to its rapid method of manufacture, results in a form less favourable for equilibrium crystallisation and more favourable to the formation of γ^* -crystalline form than HP1. Thermal treatment causes a decrease in the relative portion of the γ^* -crystalline form, increasing with increasing time annealing at low temperature. In the temperature range 170-190 °C the content of γ^* -crystalline form sharply decreases. This change may be explained by the chain mobility increasing in the crystalline structure at temperatures 170-190 °C which increases the intensity of the $\gamma^* \rightarrow \alpha$ polymorph transition.

Annealing temperature has a greater influence on HP2 along the whole temperature range considered (Fig. 4a), although the R_{γ^*} values are similar in the temperature range 150-170 °C. On further increasing the annealing temperature it was observed that R_{γ^*} increased and that this is a consequence of more intense restructuring in the crystalline phase of polycaprolactam samples. It must be noted that it has been reported that the unstable γ^* -crystalline form exhibits no changes up to 150 °C. However, it is possible that the temperature transition of the $\gamma^* \rightarrow \alpha$ polymorph transition for polycaprolactam can start at lower temperatures (~133°C). Our results agree with this second opinion, and indicate that the given transition probably starts at slightly less than 133°C. Increasing the duration of thermal treatment leads to a decrease in the content of the unstable form of crystallites in all the samples (Figure 4(b)). It should be noted that the relationship of R_{γ^*} to the logarithm of annealing time, for the AP and HP2 samples is linear, and for both samples of hydrolytic polymerisation (HP1 and HP2) there is observed a complex character dependence, with temperature having a comparatively larger effect than for AP.

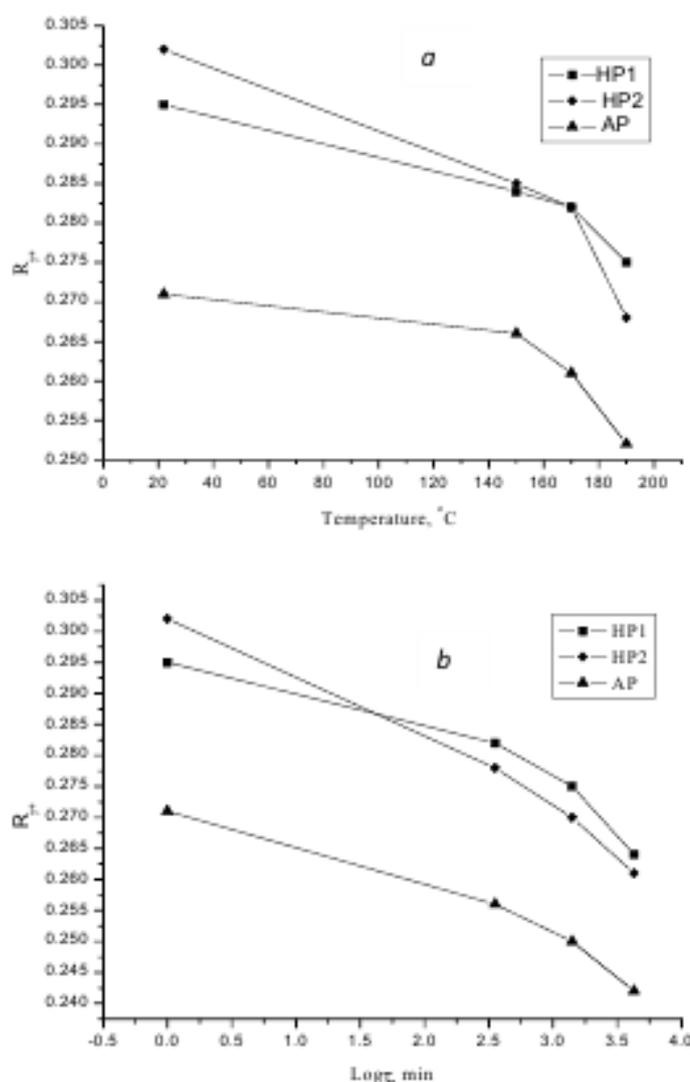


Fig. 4. The dependency of relatively content (R_{γ^*}) upon temperature for 24h annealing (a) and duration of annealing (b) at 190 °C.

The difference in values of R_{γ^*} for the hydrolytic polymerisation samples decreases upon annealing (Fig. 4b) and, after sufficiently long thermal treatment (72 hours), becomes almost identical. Comparison of the relationships in Figs 4(a) and (b) show that temperature and time have a similar effect upon R_{γ^*} . Control of the temperature-time factors of thermally treated samples of polycaprolactam allows better regulation of the process of the $\gamma^* \rightarrow \alpha$ polymorph transition. The experimentally observed polymorph transition $\gamma^* \rightarrow \alpha$ in the solid state of polycaprolactam samples upon annealing is due to the low value of free enthalpy of the more stable α -crystalline phase of polycaprolactam.

Figure 5 (a) shows the value of the thickness of α -crystalline lamellae as a function of the temperature of thermal treatment. It is observed that the value of the lamellae thickness (L) of anionic polymerisation samples considerably exceeds that for samples obtained by hydrolytic polymerisation (HP1, HP2) (see initial points of the curves). As was described above in the introduction, in the process of anionic polymerisation of caprolactam, the processes of polymerisation and crystallisation partly overlap. After partial polymerisation of caprolactam to form polymer the process of crystallisation has already started and the processes of polymerisation and crystallisation then occur in parallel until complete polymerisation of the monomer occurs. These conditions are favourable for the formation and growth, in a uniform distribution, of spherulites

comparable to hydrolytic polymerisation but with less crystalline defects. In the case of hydrolytic polymerisation the finished polymer is extruded using compressed nitrogen into a bath of water where it has the form of a ribbon or fibre, before being passed through draw-out equipment and cut in a granulator into very small pieces. Such a scheme creates very harsh and non ideal conditions for crystallisation. All this determines the difference in lamellar thickness in samples obtained using the different methods. This is confirmed by the observation that the lamellar thickness is similar in samples obtained by hydrolytic polymerisation from different sources.

It should be noted that the temperature of thermal treatment (Fig. 5a) has a different effect on samples obtained from anionic and hydrolytic polymerisation. For samples obtained by anionic polymerisation the untreated samples are mostly crystalline and isothermal annealing creates suitable conditions for crystallisation and helps further develop crystallisation. Therefore,

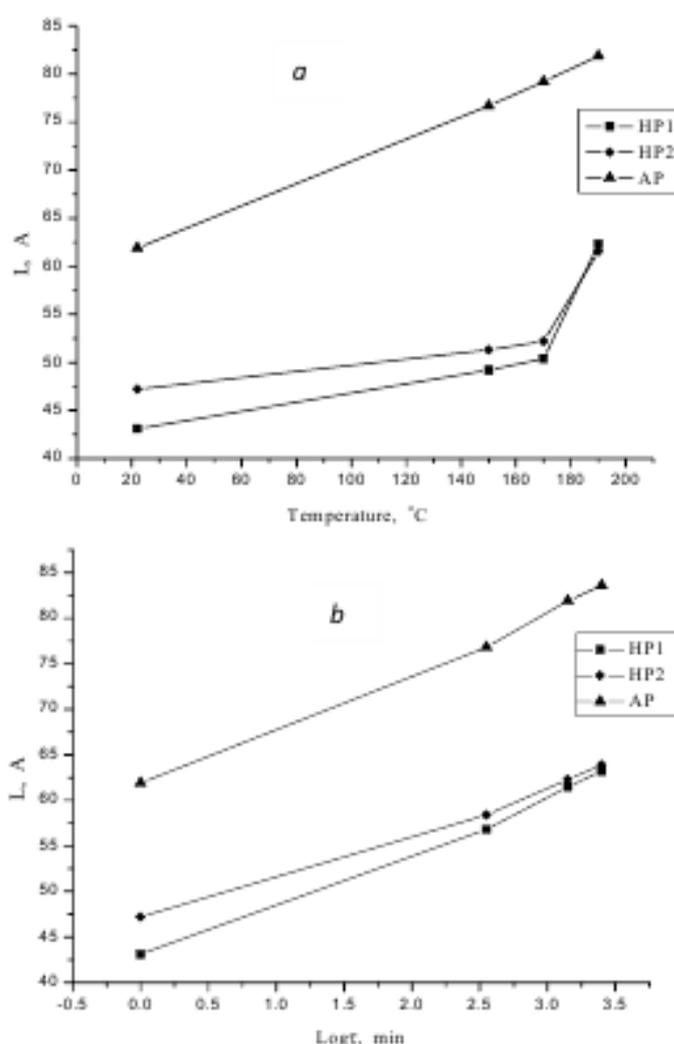


Fig.5. The dependency of lamellar thickness (L) upon a) temperature and b) duration of annealing at 190 °C.

there is a linear relationship of lamellae thickness with temperature of annealing. However, samples of polycaproatamide obtained by hydrolytic polymerisation of caprolactam exhibit a considerable increase in lamellar thickness observed over the annealing temperature range of 170-190°C. This is probably connected with the increasing kinetic mobility of macromolecules of polycaproatamide which leads to intensive reorganisation of the crystalline structure.

Figure 5(b) shows the effect of the duration of isothermal annealing at 190°C upon the lamellar thickness of polycaproatamide. It is observed that there is a linear relationship and that crystalline lamellae thicken steadily with increasing annealing time regardless of the method of polymerisation. The approximately parallel trend in increasing values of lamellar thickness suggests that there is a common mechanism of structural development in the different samples upon thermal treatment.

4. Conclusion

Using WAXS for the examination of untreated and thermally treated samples of polycaproatamide has shown considerable changes in the crystalline and amorphous phases. WAXS studies revealed that in all investigated samples of polycaproatamide, irrespective of their method of production and initial thermal histories, there is a co-existence of α -monoclinic and γ^* - pseudohexagonal crystalline forms. Anionic polymerisation results in a more ordered crystalline polycaproatamide structure than samples prepared by hydrolytic polymerisation with less γ^* - form. In the annealing process of polycaproatamide the crystalline phase of polymer increased (increasing lamellar size and degree of crystallinity) in contrast to R_{γ^*} which decreased. This suggests that increased ordering takes place not only due to the degree of crystallinity but also to the transformation of γ^* -form to α -form.

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КОРРЕЛЯЦИЯ СПЕКТРОВ НИЗКОТЕМПЕРАТУРНОЙ ФОТОЛЮМИНЕСЦЕНЦИИ И ФОТОВОЛЬТАИЧЕСКИХ СВОЙСТВ ТОНКИХ ПОЛИКРИСТАЛЛИЧЕСКИХ ПЛЕНОК CdTe

Б.Ж. Ахмадалиев, О.М. Маматов, Б.З. Полвонов, Н.Х. Юлдашев

Ферганский политехнический институт, uzferfizika@mail.ru

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Бурчак остида ўстирилган майда доғли ($d_{cr} \leq 1 \mu\text{m}$) CdTe плёнкарининг паст температурали ($T = 4.2 \text{ K}$) фотолюминесценция спектрларида кристалл доғлар чегарасидаги потенциал тўсиқлар тўғрисида юзага келадиган хусусий нурланиш ($e-h$)нинг асосий полосаси ва $e-h$ -полосанинг LO-фононли такрорланишидан иборат чегаравий