

ELENA RUSU^{1)*}, GHEORGHE RUSU¹⁾, DANA-ORTANSA DOROHOI²⁾

Influence of temperature on structures of polymers with ϵ -caprolactam units studied by FT-IR spectroscopy

Summary — Some films obtained from poly(ϵ -caprolactam) (polyamide 6) and its copolymers with laurolactam (copolyamides 6/12) were submitted to thermal treatment. The most versatile method for characterization of polyamide and its copolymers, *i.e.*, FT-IR spectroscopy, was chosen as a tool in order to determine the possible changes in the structures of polymers. It was observed that the polymers films showed Brill transition during heating.

Key words: ϵ -caprolactam, laurolactam, polyamide 6, copolyamide, FT-IR spectrum, Brill transition.

BADANIA ZA POMOCĄ SPEKTROSKOPII FT-IR WPŁYWU TEMPERATURY NA STRUKTURĘ POLIMERÓW ZAWIERAJĄCYCH JEDNOSTKI ϵ -KAPROLAKTAMOWE

Streszczenie — Zsyntetyzowano poli(kaprolaktam) (poliamid 6) i jego kopolimery z laurolaktamem (kopoliamid 6/12) stosując do 50 % mas. laurolaktamu (CLL0, CLL5, CLL10, CLL20 i CLL30). Przygotowane z tych polimerów folie o grubości 40 μm poddano działaniu temperatury w zakresie od 20 do 180 $^{\circ}\text{C}$ w czasie 30 min. Następnie próbki charakteryzowano za pomocą jednowymiarowej i dwuwymiarowej spektroskopii FT-IR (rys. 1—7). Zaobserwowano, że przemiana fazowa kryształ-kryształ tzw. przemiana Brill'a zachodzi w przypadku poliamidu 6 w temp. 160 $^{\circ}\text{C}$, a w przypadkach kopoliamidów 6/12 w temp. 120 $^{\circ}\text{C}$.

Słowa kluczowe: ϵ -kaprolaktam, laurolaktam, poliamid 6, kopoliamid, widmo FT-IR, przemiana Brill'a.

The aliphatic polyamides belong to the largest class of the engineering plastics. They contain structural units similar to natural polymers — proteins, namely, polar amide groups (CO-NH) and methylene segments $(\text{CH}_2)_n$. However, despite their simple structures they have many desirable features (elasticity, dyeability, resistance, rigidity, dimensional stability, *etc.*). The properties of aliphatic polyamides are correlated with both the density of the amide groups and the hydrogen bonds between CO-NH units, representative for this type of polymers. These polymers are preferred for a variety of applications ranging from fibres and automotive industry to biological and medical fields [1—7]. The studies related to these polymers could contribute to the development of academic research.

Poly(ϵ -caprolactam) (polyamide 6 or nylon 6) with $[-(\text{CH}_2)_5\text{NHCO}]_n$, as repeating units, is a semicrystalline polymer and has a sheet-like structure favored by H-bonds between the NH and CO groups and arrangements of polymer chains. Usually it is regarded as a dual-phase system consisting of crystalline and amorphous regions. Its crystalline structure belongs to the α , β and γ phase types which generally coexist in various amounts in correlation with the requirement to maxi-

mize the number of H-bonds [8, 9]. In the α and γ forms the molecular chains are organized in parallel sheets, stabilizing the hydrogen bonds. The stable monoclinic α phase is dominant in the structure of polyamide 6 and it has an extended planar chain conformation, with H-bonds lying between parallel but oppositely directed chains. In the γ form the hydrogen bonding occurs between parallel chains in adjacent sheets rather than within the sheets. This form is unstable and it can be transformed into the α form by annealing. The metastable β form is regarded as an intermediate structure with variable degrees of disorder [10—13].

Anionic activated monomer polymerization of ϵ -caprolactam by rotational molding is a preferred route of the syntheses of the homopolymer and copolymers. This solvent-free process proceeds at a significantly faster rate, reaching equilibrium conversion in only a few minutes, compared to the classical hydrolytic polymerization (12—24 h) and at 140—170 $^{\circ}\text{C}$, well below the melting temperature of polymer (~ 220 $^{\circ}\text{C}$) [14—20]. The copolymerization of ϵ -caprolactam with another lactam can give new polymers suitable for particular applications due to the modification of amide groups density along the polymer chains [20—26]. In this sense one could take into account the properties of poly(laurolactam) (polyamide 12) that has a lower moisture uptake (1.8 %), excellent ductility, good electrical properties, and significant chemical and impact resistance but lower melting temperature (172 $^{\circ}\text{C}$) compared to polyamide 6

¹⁾ "Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Grigore Ghica Voda, Iasi, RO-700487.

²⁾ "Al. I. Cuza" University, Faculty of Physics, 11 Carol I Bdv., Iasi, RO-700056.

^{*)} Correspondence author: Elena Rusu, e-mail: eerusu@yahoo.com

(220—225 °C) due to the presence of longer aliphatic segments between the amide groups [20, 27—29].

Polyamides undergo various heat setting processes during fabric finishing and their use. Firstly, Brill reported (in 1942) that a crystal to crystal transition occurred during the heating process of polyamide 6,6 and then many aliphatic polyamides showing such behavior have been observed. This phenomenon is so-called Brill transition and it can be considered as a result of increasing mobility of alkanes segments [30]. The FT-IR spectroscopy may be useful to get information about the changes in the structure of the polyamides [3—7, 31—33].

Some polyamides, namely polyamide 6 and its copolymers with different contents of lauro lactam obtained by rotational molding *via* anionic polymerization were submitted to thermal treatment. It was expected that during the heating of films of thus obtained polyamides structural modification and Brill transition could appear. The paper describes the study of the structural modification of polyamides films by FT-IR spectroscopy in order to evidence the Brill transition.

EXPERIMENTAL

Materials

The commercially available monomers (technical grade), ϵ -caprolactam and lauro lactam were supplied by Fibrex S.A. (Savinesti, Romania) and Hüls (Germany), respectively. For further processing, in order to remove the moisture, ϵ -caprolactam was dried by distilling off about 5 % by weight of monomer under low pressure at 140 °C. Also, the lauro lactam was dried for 16 h in a vacuum at 20 mm Hg and 90 °C.

The solution of 3.0 mol L⁻¹ of ethyl magnesium bromide (EtMgBr) in diethyl ether was used as a polymerization initiator (as received).

The activator, *N,N*-isophthaloyl-*bis*- ϵ -caprolactam was synthesized in our laboratories from isophthaloyl dichloride and ϵ -caprolactam and then it was repeatedly crystallized from dry diethyl ether. Melting temperature of the product, determined by differential scanning calorimetry, was 141 °C.

Formic acid (98 %) applied as a solvent for the films preparation was purchased from Fluka and used as received.

Synthesis and sample preparation

The poly(ϵ -caprolactam) (polyamide 6) and its copolymers with lauro lactam (copolyamides 6/12) were synthesized as constituent polymers of the parts made by activated anionic ring-opening copolymerization of ϵ -caprolactam (CL) with lauro lactam (L) in a laboratory rotational molding installation. The initial content of L varied between 0.0 and 50.0 wt. % with respect to the

total monomers' feed. The syntheses and purification of products were described in detail previously [12, 14].

The processing of polymers as films was performed by casting of formic acid solutions (10 wt. %) of polymers on glass plates followed by drying in an oven at 120 °C for 30 min. The thickness of polymeric films, determined by micrometer measurements, was about 40 μ m. Thus obtained film samples are denoted as CLL0, CLL5, CLL10, CLL20, CLL30, CLL50, where numbers 0, 5, 10, 20, 30 and 50, respectively refer to wt. % of lauro lactam in the mixture of monomers. The polyamide films were submitted to thermal treatment in the range of 20—180 °C for a period of 30 min.

Methods of testing

Infrared spectra (FT-IR) were recorded using a JASCO FT/IR-670 apparatus, at 400—4000 cm⁻¹ range, resolution of 4 cm⁻¹ and co-addition of 100 scans. The influence of temperature on the characteristic absorption bands was investigated using a Jasco Spectra Manager Software (Jasco Corp.).

The two-dimensional correlation FT-IR spectroscopy (2D FT-IR Correlation), originally proposed by Noda and Ozaki [34, 35] let evidence the correlations among the vibrations of different structural groups and the modifications induced under external perturbations. The 2D FT-IR technique is a useful tool for the interpretation of complex one-dimensional (1D) spectra, especially spectra with broad, multiply overlapped bands commonly encountered in vibrational spectroscopy. The changes in the structures of polyamide films by variation of the lauro lactam concentration (as a perturbation factor) in the mixture were observed. The dynamic spectrum was obtained by subtracting a reference spectrum from each spectrum of copolyamides.

RESULTS AND DISCUSSION

In the mid-infrared region polyamide 6 displays stretching and bending vibrations originating both from the secondary amide group -HN-C(O)- and the methylene sequences. The functional group acting as acceptor in the hydrogen bonding with NH is the polyamide carbonyl (C=O). The relation among the arrangement of hydrogen bonds and certain vibration modes can be also identified in FT-IR spectra. There are nine IR frequency regions that can be used in the study of the amide groups, namely amide A, B and amide I—VII (amide I — C=O stretch; amide II — in plane N-H bend coupled with C-N stretch; amide III — coupled N-H bend and C-N stretch as in amide II, but in an opposite phase; amide IV — in plane C=O bend; amide V — out of plane N-H bend; amide VI — out of plane C=O bend; amide VII — C-N torsional vibration). The infrared spectra taken for non-heated polyamide 6 sample are shown in Figure 1.

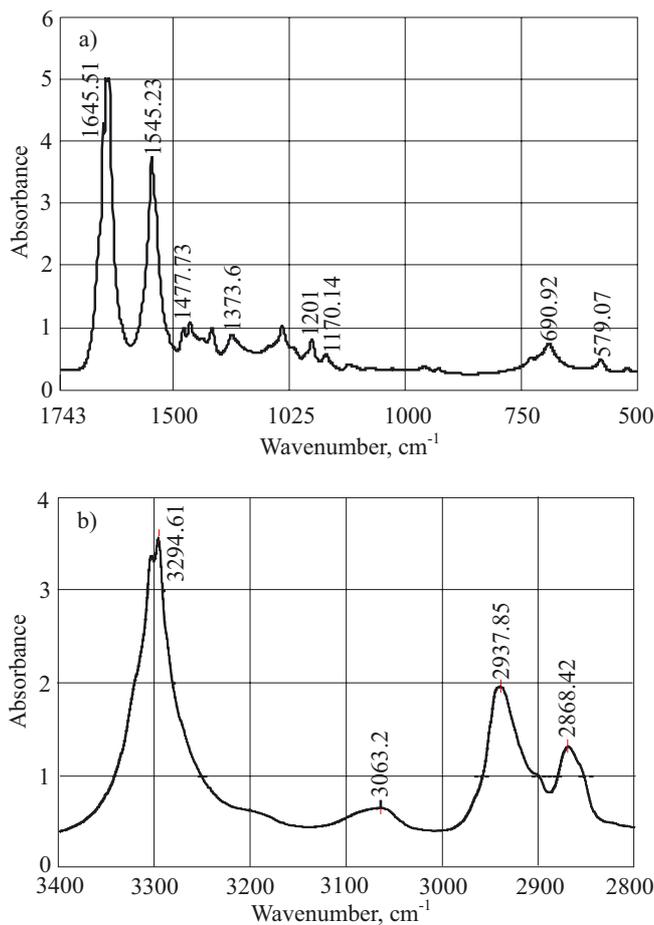


Fig. 1. FT-IR spectra of polyamide 6 in wavenumber ranges: a) 1743—500 cm^{-1} , b) 3400—2800 cm^{-1}

Polyamide 6 has three strong IR absorption bands at about 3294 cm^{-1} (amide A, $\nu_{\text{NH}} = \text{N-H}$ stretch identified vibration), 1645 cm^{-1} (amide I) and 1545 cm^{-1} (amide II) that can be influenced by the hydrogen bonding interactions. In the 500—1400 cm^{-1} region of the IR spectra the absorptions attributed to methylene sequences and crystalline forms of polyamide 6 film can be distinguished. This film presents the bands at 692 cm^{-1} and 579 cm^{-1} (out of plane bends of NH and C=O), 929 and 960 cm^{-1} (CO-NH in plane vibration), 1201 cm^{-1} (CH_2 twist-wagging vibration), 1374 cm^{-1} (amide III and CH_2 wagging vibration), 1417 cm^{-1} and 1477 cm^{-1} (CH_2 scissors vibration). These show that the studied sample consist predominantly of α crystalline form with a small amount of γ crystalline form. Other peaks also appear in the spectrum of polyamide 6: for the CO-NH group at 1170 cm^{-1} (CO-NH, skeletal motion), 1264 cm^{-1} (N-H bending and C-N stretching), 3083 cm^{-1} (NH stretching) and CH_2 sequences at 1305 cm^{-1} (CH_2 wagging), 2937 and 2868 cm^{-1} (antisymmetric and symmetric $-\text{CH}_2-$ stretching), 3294 cm^{-1} (amide A H-bonded N-H stretching), 3063 cm^{-1} (amide B overtone of amide II). The band assignments are in agreement with those reported in the literature [5, 36—40].

The FT-IR spectra of polyamide 6 film in the 500—1743 cm^{-1} range recorded after annealing for 30 min at

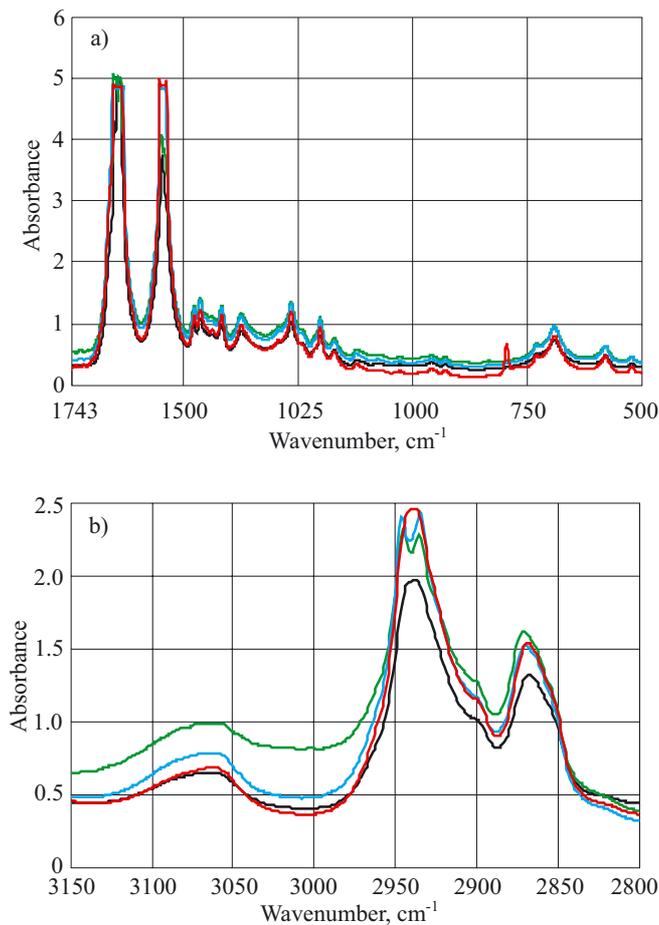


Fig. 2. FT-IR spectra of polyamide 6 after annealing for 30 min to different thermal treatment temperature (20 $^{\circ}\text{C}$ — black, 140 $^{\circ}\text{C}$ — green, 160 $^{\circ}\text{C}$ — blue, 180 $^{\circ}\text{C}$ — red) in wavenumber ranges: a) 1743—500 cm^{-1} , b) 3150—2800 cm^{-1}

different temperatures are shown in Figure 2. The behavior of investigated films submitted to thermal treatment is reflected in the spectra as modifications in the relative intensity and frequency shifts of some absorption bands. Several bands show splitting when temperature increases. All these indicate the changes in the structures of polymers or environments around the polyamide films during thermal treatment. The temperature changes influence both the structures of the aliphatic segments and hydrogen bonding. The bands appearing in 500—1400 cm^{-1} range did not change significantly when the films were heated up to 160 $^{\circ}\text{C}$.

A decrease in the intensities of the bands assigned to α crystalline form positioned at 692 cm^{-1} and 579 cm^{-1} (out of plane bends of NH and C=O) and at 960 and 930 cm^{-1} (CO-NH in plane vibration) was not observed. The small red shifts of the band at 1477 cm^{-1} evidenced at heating could be associated with the reorganization of H-bonding. Under the influence of temperature on polyamide crystals the intersheet distance enlarges as the temperature increases, whereas the interchain spacing within H-bonded sheets slightly decreases [41]. However, when annealing temperature increases from 20 $^{\circ}\text{C}$

to 140 °C an up shift of zero line of the spectrum was observed, while at 160 and 180 °C [close to the melting temperature of poly(ϵ -caprolactam), ~220 °C] a progressive downshift of this band occurred. This behavior can be explained by the increase in heterogeneity of the system up to 140 °C that determines an increase in the scattered radiation as a result of increasing mobility of alkane segments. In the same time the up shift of the spectra comes from the weakening of hydrogen bond. Over 140 °C the polymer begins to soften and the homogeneity of the system increases. This leads to a decrease in the scattered radiation. In Fig. 2 it is evidenced that the onset of the Brill transition of poly(ϵ -caprolactam) occurs at 160 °C. The "Brill temperature" (T_B) is defined as the lowest temperature at which the projected inter-chain distance within an H-bonded sheet equals the inter-sheet spacing [42]. It is commonly accepted that the origin of the Brill transition is the conformational motion due to the temperature increasing. The changes in packing within the crystal occur and the ordered crystalline structure at low temperature gets into a less ordered crystalline form at high temperature [31, 42]. The CH₂ sites in the crystal regions underwent an increase in the rates and angles of spatially heterogeneous liberation motions, while the N-H sites began to undergo restricted liberation motions. In the FT-IR spectrum obtained after annealing of the polymer film at 180 °C the appearance of two new bands at 795 cm⁻¹ and 775 cm⁻¹ was observed. The origin of these bands is not clear and cannot be assigned to -CH₂- rocking band. The amide I is a relatively sharp band and it splits into three components — free, ordered and disordered H-bonded carbonyl groups. The amide II band shifted to blue and splitted into two components when temperature increased. At 180 °C, close to the melting temperature of polyamide 6, the homogeneity of the system increases and only a single band appears. This behavior is related to the modification in the hydrogen bonds between amide groups. The free C=O and NH groups are associated with the peaks which appear next to amide I at higher frequency and next to amide II at lower frequency, respectively. The temperature changes not only influence the hydrogen bonding between amide groups but also the structures of aliphatic chains. The intensities of the three highest frequency bands observed in FT-IR spectra at 2868, 2937 and 3294 cm⁻¹ (Fig. 2b) increases. The origin of the small shift toward high wavenumbers while heating from an ambient temperature to 160 °C for the observed symmetric -CH₂- stretching band at 2868 cm⁻¹ could arise from an increase in repulsive forces exerted by neighbour groups. At the same time the band corresponding to antisymmetric CH₂ stretching vibration positioned at 2937 cm⁻¹ splits at 140 and 160 °C into two components, separated by 10 cm⁻¹ and 12 cm⁻¹ with intensity ratio of 1.3:1 and 1:1.3, respectively. The vibration state of -CH₂- units is changed when the heterogeneity of system increases due to increase in temperature. However, at 180

°C the split disappears and a single band appears. When temperature increases the bandwidths become broad. The band at 3294 cm⁻¹ (N-H stretch in resonance with amide II overtone) associated with amide A exhibits the same behavior. The crystal structure at room temperature was found to be the so-called α form. The structure that appears after annealing of polymer sample is probably due to β crystalline form similar to α form, because the FT-IR spectra show almost similar forms. The β phase is a high-temperature phase, the existence of which has been taken as an evidence of Brill transition in polyamide 6 [43].

The copolyamide 6/12 contains -NH(CH₂)₅CO- and -NH(CH₂)₁₁CO- units from CL and L monomers, respectively. Incorporation of L moieties into polyamide 6 chains, changes the amide density, the crystallinity decreases and therefore some of polyamide 6 properties are improved [23, 44, 45]. A reduction in the intermolecular forces among the chains also occurs due to higher content of -CH₂- units. As the number of methylene units increases, the more efficient packing of CH₂ groups compensates the slightly poorer hydrogen bonds in the γ form [46]. It is known that copolyamides 6/12 with L lower content (<20 wt. %) crystallize well since the CL segments are high enough in number and length to form the H-bonds, have strong dipole-dipole interactions and force L random sequences into the amorphous phase [23]. In the case of copolymers it is difficult to determine the characteristic bands of L *co*-units from IR absorption spectra because of the general similarity of the spectra of polyamide 6 and polyamide 12 [21]. Infrared spectra taken for polyamide 6 (CLL0), copolyamides CLL20 and CLL50 at 20 °C are shown in Figure 3.

However, some characteristic bands appear at around 700 cm⁻¹ and 950–980 cm⁻¹ for copolymers with high content of CL. The characteristic bands of polyamide 12 at 1080, 1190 cm⁻¹ are not given by copolymers with less than 50 wt. % of L units [21]. It is known that the crystalline structures of copolymers with < 20 mol. % of L are in α phase [47]. The bands at 690 cm⁻¹ and 579 cm⁻¹ initially increase slightly but then decrease when L content becomes higher than 20 wt. %. In addition the bands at 929 and 960 cm⁻¹ increase in intensity for copolymers with up to 20 wt. % of L. Then these bands disappear while the band at 973 cm⁻¹ increases with increasing L content. This later peak is associated with γ crystalline form of polymer. Moreover the bands at 1437 cm⁻¹, 1374 cm⁻¹, 1201 cm⁻¹ and 1237 cm⁻¹ decrease when the amount of the γ crystalline form increases. The changes observed for the absorption bands mentioned above have consistently been interpreted as being due to change of crystallinity degree in the case of copolyamides 6/12 when L content increases in the range of 20–50 wt. %.

FT-IR spectra of copolyamide CLL10 after annealing for 30 min at different temperatures are presented in Figure 4. In the cases of copolyamides with less than

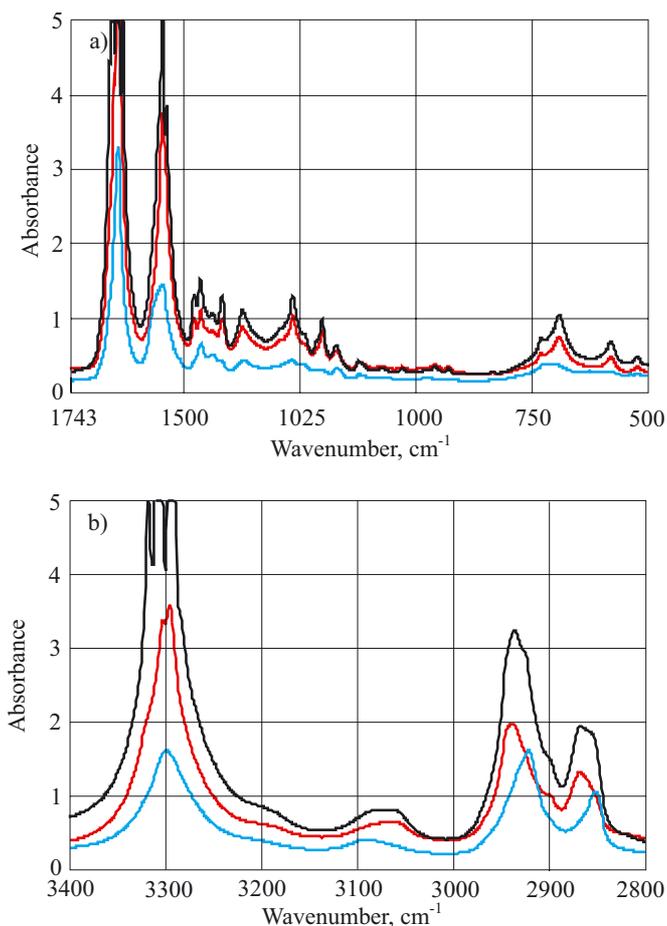


Fig. 3. FT-IR spectra of polyamide 6 (CLL0 — red) and copolyamides CLL20 (black) and CLL50 (blue) at 20 °C in wavenumber ranges: a) 1743—500 cm^{-1} , b) 3400—2800 cm^{-1}

50 wt. % of L units it was observed that the exposure to different thermal treatments is accompanied by the decrease in FT-IR bands intensities, but significant changes in the shapes of bands were not observed. The band at 3294 cm^{-1} splits into three components with the increasing L content up to 20 wt. % but a single band appears when L content becomes higher than 20 wt. %. The blue shift of the band at 3063 cm^{-1} is larger than 25 cm^{-1} for copolymer CLL50 while the red shift of both 2937 cm^{-1} band and 2968 cm^{-1} band is larger by 17 cm^{-1} in relation to CLL0. The shifts of these bands are anticipated by the shoulder which develops at 2925 and 2855 cm^{-1} . The split of band positioned at 2937 cm^{-1} was not observed. The onset of Brill transition of polyamide 6 was observed at 160 °C, for copolymer with L content up to 20 wt. %.

When the content of L increases to 50 wt. % the onset of Brill transition appear at 120 °C. This behavior is associated with the formation of the high temperature pseudo-hexagonal γ modification. The shape of spectrum becomes narrow when temperature rises at 180 °C as it can be seen in Figure 5. More bands become large and some bands split. The bands at 929 and 960 cm^{-1} which can be barely noticed at 140 °C become sharp and increase for the samples annealed at 180 °C. It seems that

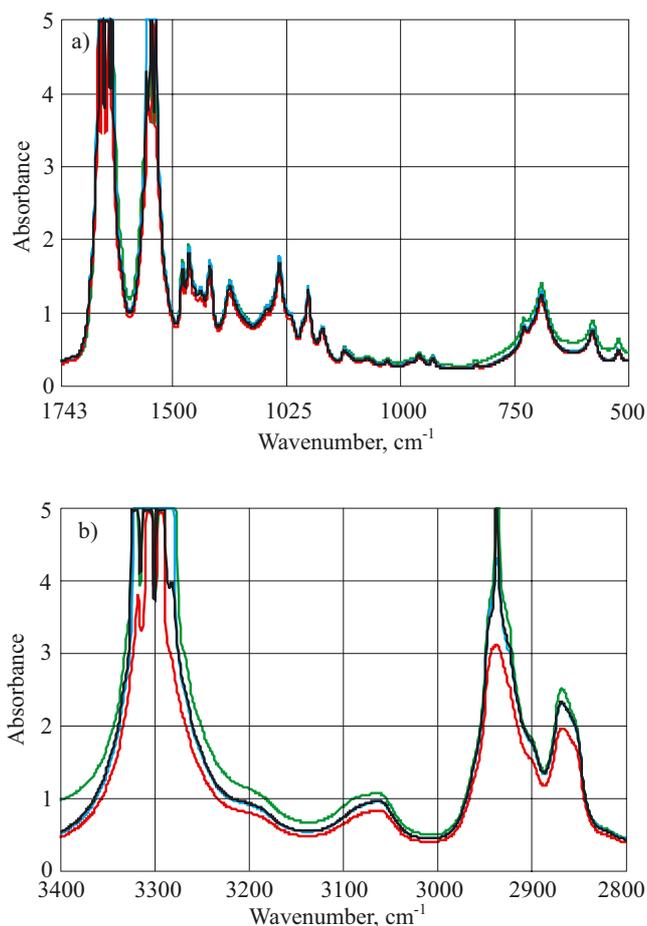


Fig. 4. FT-IR spectra of CLL10 after annealing for 30 min to different thermal treatment temperature (20 °C — green, 140 °C — blue, 160 °C — red, 180 °C — black) in wavenumber ranges: a) 1743—500 cm^{-1} , b) 3400—2800 cm^{-1}

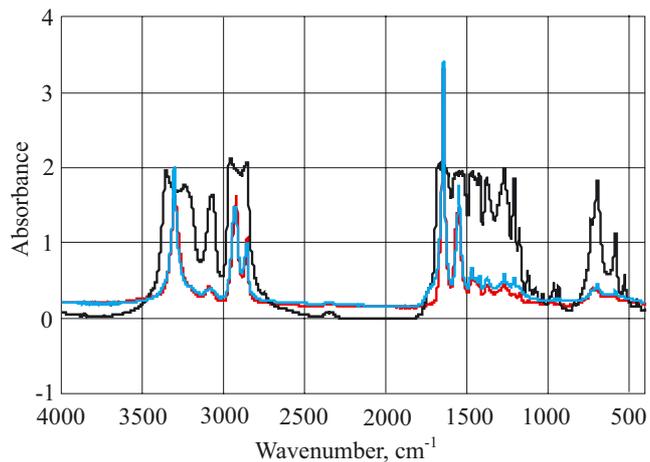


Fig. 5. FT-IR spectra of CLL50 after annealing for 30 min to different thermal treatment temperature (20 °C — red, 140 °C — blue, 180 °C — black)

the increase in temperature favours the reorientation of CH_2 segments from L.

Two-dimensional (2D) correlation FT-IR spectroscopy was used in order to confirm the change in the

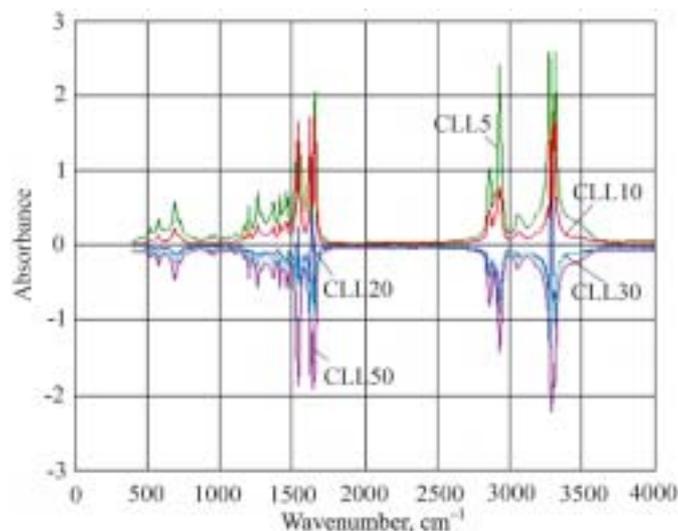


Fig. 6. Dynamic FT-IR spectra of copolymers

structure of copolyamide chains when content of L was modified. The dynamic spectra corresponding to the L content perturbation in the range 0–50 wt. % were obtained. The dynamic spectra presented in Figure 6 show that the copolymers with L content up to 20 wt. % have a positive variation related to media while those correspondent to copolymers with L content higher than 20 wt. % have a negative variation. It was observed that higher variation of relative intensities of bands occurred in 1000–1700 cm^{-1} and 2600–3300 cm^{-1} ranges. From the observation of the different dynamic behavior of the copolymers it is clear that they are organized differently in the studied films. All these suggest that more or less isotropic arrangement, due to the presence of L segments, occurs.

Figure 7 shows the synchronous and asynchronous 2D FT-IR spectra of copolymers in the spectral region of 3500–500 cm^{-1} . According to Noda [34] in synchronous spectra, the positive cross peaks indicate simultaneously increasing or decreasing features at the two corresponding frequencies, while the negative peaks are associated with the variation in opposite directions of the two components. The synchronous correlation spectrum shows the correspondence for the changes in vibration with the same phase (in-phase) and is symmetrical with respect to the diagonal line. In the synchronous spectrum (Fig. 7a) the diagonal positions referred as auto-peaks reveal autocorrelations among the spectral intensities of variations of CH_2 segments and amide bands and L content in the copolymers. These auto-peaks indicate the functional groups that give an orientational response to the perturbation. The strong auto-peaks from 2D synchronous spectrum that indicate autocorrelated changes are positioned at 3294 cm^{-1} , 2937 cm^{-1} , 1645 cm^{-1} and 1545 cm^{-1} . The off-diagonal peaks in the Fig. 7a represent the simultaneous changes in the intensities of bands from the two mentioned above spectral ranges when L content increases in the studied samples. The crosspeaks

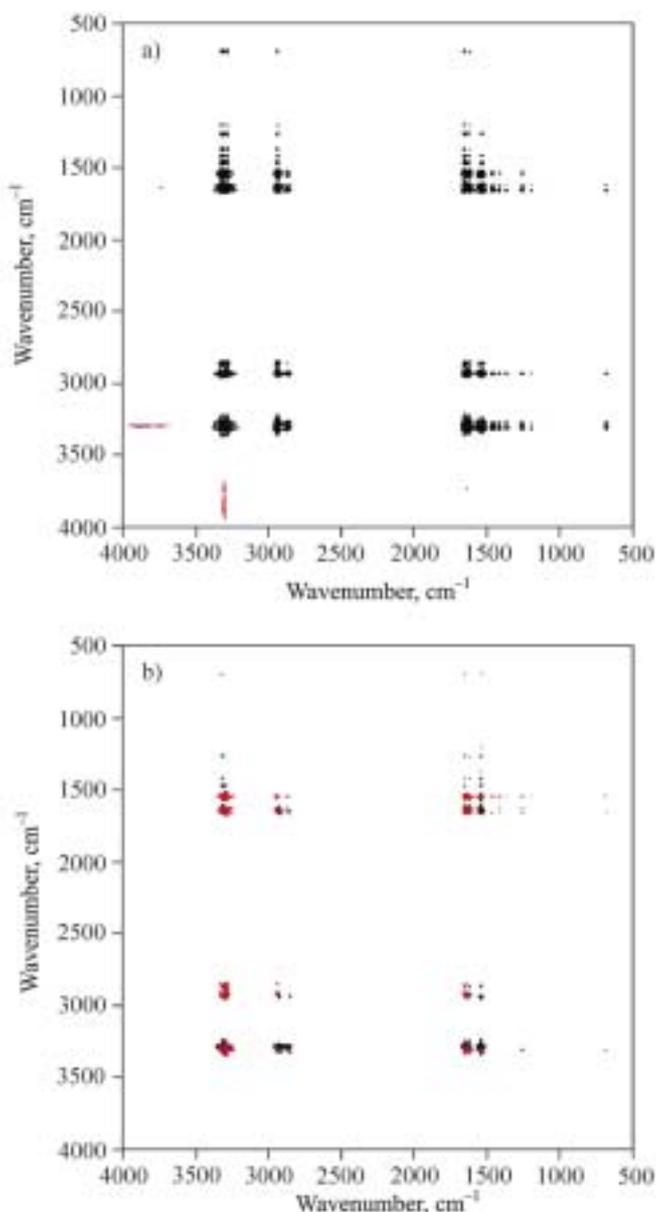


Fig. 7. Contour map for synchronous (a) and asynchronous (b) 2D FT-IR of copolymers

from 2D synchronous spectrum have positive sign revealing a concomitant increase or decrease of the bands intensities as function of the L content. The presence of asynchronous peaks (Fig. 7b) indicates that the intensity responses of corresponding bands occur at different rates. The positive asynchronous peaks at ν_1 , ν_2 (i.e. about 2937 cm^{-1} and 3294 cm^{-1} , 2868 cm^{-1} and 3294 cm^{-1}) can be associated with faster changes of the intensity at ν_1 compared to that at ν_2 . This is due to the changes in the mobility of methylene segments. In the same time the negative asynchronous peaks are related to the opposite behavior. The cross peaks from 2D asynchronous spectrum reveal that the intermolecular H-bonds among the amide groups weaken when L content increases. The information from 2D FT-IR spectra can be associated to the splitting of the bands corresponding to amide groups