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Study of the conformations of poly(ε-caprolactam) and poly(ε-caprolactam)–polybutadiene block copolymers by *FT* i.r. spectroscopy with photoacoustic detection and by micro-Raman confocal spectroscopy

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The conformations of poly(ε-caprolactam) and of poly(ε-caprolactam)-block-polybutadiene copolymers were investigated by Fourier Transform infrared spectroscopy with photoacoustic detection (PA-*FT*i.r.) and by micro-Raman confocal spectroscopy. The lowering of the planar conformation content with increasing concentration of butadiene units was confirmed. In the surface layers formed by rapid saw-cutting and in the islands probably formed by microtome cutting, the content of the planar conformation was reduced. The content of the planar conformation increases on water treatment. © 1997 Elsevier Science Ltd.

(Keywords: ε-caprolactam–butadiene block copolymers; *FT*i.r. spectroscopy with photoacoustic detection; micro-Raman spectroscopy)

INTRODUCTION

For many years it has been known that the chains of poly(ε-caprolactam) (PCL) can exist in two different conformations[1,2]. In the planar conformation, stabilized in the monoclinic α-crystalline lattice, the amide groups are coplanar with the methylene parts of the chains[3]. In the nonplanar conformations, present either in mesomorphous forms[4] or in the hexagonal γ-crystalline form[5], the planes of the amide groups are twisted with respect to the planes of the methylene chains. Thermal and mechanical conditions of preparation, thermal treatment, and swelling by water vapour, liquid water or by other chemical agents, can influence the populations of these conformations[1,2,6,7]. Because each of the different conformations gives characteristic vibrational bands, the mentioned conformational changes can be followed by i.r.[1] and Raman[8] spectra.

Recently, block copolymers of ε-caprolactam and butadiene (PCL–PBD) were prepared[9] and their *FT* Raman spectra were investigated[8]. It was found that the ratio of the populations of planar and nonplanar conformations of poly(ε-caprolactam) chains depends both on the concentration of butadiene units in PCL–PBD copolymers and on the temperature regime during the preparation of these copolymers.

We wanted now to estimate more accurately the content of the planar conformation in the copolymers. We also wanted to know how the structural forms are affected by cutting the material, and how the physical structure is influenced by water treatment. Fourier transform infrared spectroscopy with photoacoustic detection (PA-*FT*i.r.), not demanding any sample preparation which could affect the physical structure, promised to be very useful for this type of analysis. For determining the microscopical distribution of different conformations in our samples, we also used the micro-Raman confocal spectroscopy and imaging in our study.

EXPERIMENTAL

Poly(ε-caprolactam) (PCL) and poly(ε-caprolactam)–polybutadiene block copolymers (PCL–PBD) were prepared by hand casting of plates in an Al mould at 150°C, using a polymerization mixture containing ε-caprolactam

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(CL), α,ω-dihydroxyterminated polybutadiene (PBD), potassium salt of CL and an aromatic diisocyanate as functionalization agent; for details see ref. 9. In ref. 10, the composition of PCL–PBD copolymers is given.

The samples were prepared in the form of plates 4 mm thick. They were then rapidly transversally cut with an electrical saw (velocity 7.9 m s^{-1}) into the form of strips. The surface layers of these strips affected by this rapid cutting (see *Figure 1*) were measured by PA-*FT*i.r.—a method sensitive only for a surface layer ~10–20 μm thick. For the study of the original (as-polymerized) sample, the outer layers affected by the saw-cutting were gently removed. The samples were also treated by immersing into distilled water at room temperature for 24 h, or by boiling in distilled water at 100°C for 2 h (see *Table 1*). After the water treatment, the samples were held in a desiccator over P_2O_5. For the PA-*FT*i.r. measurements, the samples were cut from the original strips to fit into the vessel of the photoacoustic cell with the diameter of 10 mm.

For the micro-Raman confocal measurement and imaging, slices about 100 μm thick were cut by a microtome transversally to the longer dimension of the strip (see *Figure 1*). The velocity of cutting was 50 mm s^{-1}.

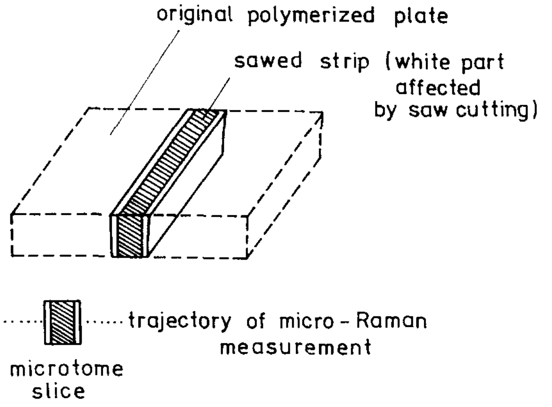

Figure 1 Preparation of samples for spectroscopic measurements

Table 1 Fraction of planar PCL conformation in PCL and PCL–PBD copolymers: PA-*FT*i.r. results

Sample No.	Composition	Part	H_2O treatment	S	A_{1201}	A_{1170}	x_A
1	PCL homopolymer	*u*	—	251	0.139	0.120	0.54
		s	—	631	0.087	0.161	0.35
		s	25°C	309	0.147	0.210	0.41
		s	100°C	315	0.190	0.174	0.52
2	PCL-PBD copolymer 15 wt.% PBD	*u*	—	259	0.120	0.133	0.47
		s	—	282	0.091	0.170	0.35
		s	25°C	284	0.138	0.213	0.39
		s	100°C	307	0.179	0.184	0.49
3	PCL-PBD copolymer 25 wt.% PBD	*u*		252	0.101	0.165	0.38
		u	25°C	271	0.118	0.143	0.45
		u	100°C	274	0.139	0.133	0.51

u, 'as-polymerized' part of the material, unaffected by saw-cutting
s, saw-cut part of the material
S, integral area under the spectral curve between 2430–2995 cm^{-1}
A_{1201}, A_{1170}, intensities in maxima of the respective bands
x_A, fraction of planar conformation of PCL as calculated by equation (3)

PA-*FT*i.r. spectra were measured on a spectrometer Mattson Cygnus 100 equipped with a MTEC PA cell, in a stream of helium at 20 ml min^{-1}. Powdered charcoal as delivered by the producer was used as background. The spectral resolution was 4 cm^{-1}, the velocity of the shift of the mirror was 0.11 cm s^{-1}; 1120 scans (122 min) were recorded for the sample and 208 scans (22 min) for the background.

Micro-Raman spectra of the samples were measured on a Raman microspectrometer DILOR Labram Confocal, using a He–Ne laser with laser power of 16 mW, a ×100-objective, a pinhole of 100 μm and a slit of 100 μm. The scanning time was 30 s; five spectra were accumulated. Raman imaging was performed by the method of global illumination for the band at 1079 cm^{-1} with a slit of 1000 μm (spectral resolution 20 cm^{-1}) and a ×100-objective; two scans of 300 s each were added.

D.s.c. measurement of PCL was performed on a Mettler TC 11 calorimeter, using the value 26.0 kJ mol^{-1} as the heat of melting of an ideal monoclinic crystal of PCL (see ref. 11).

RESULTS AND DISCUSSION

*PA–*FT *i.r. spectroscopy*

Besides the differences in the intensity ratios, the PA-*FT*i.r. spectra remind us very closely of the usual transparent i.r. spectra of PCL (see ref. 1). The spectra show the bands of the characteristic amide vibrations: the stretching N–H vibration at 3300 cm^{-1}, harmonic amide II vibration in Fermi resonance with the stretching N–H near 3070 cm^{-1}, amide I vibration near 1640 cm^{-1}, amide II vibration near 1550 cm^{-1}, amide V vibration near 700 cm^{-1} and amide VI vibration near 600 cm^{-1}. The

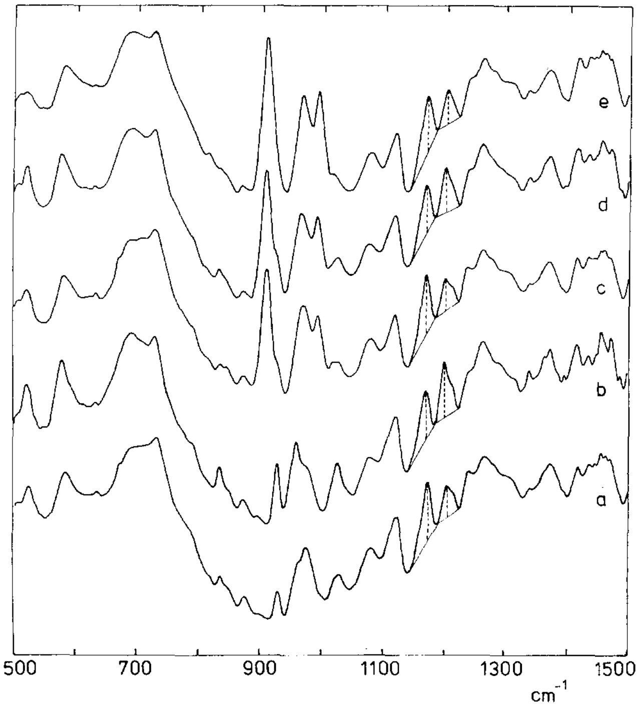

Figure 2 Photoacoustic *FT*i.r. spectra; (a) Sample 1 (PCL–homopolymer), saw-cut surface, (b) Sample 1, unaffected part; (c) Sample 2 (copolymer with 15 wt% PBD blocks) saw-cut surface, (d) Sample 2, unaffected part; (e) Sample 3 (copolymer with 25 wt% of PBD blocks), unaffected

exact positions of these bands are to some extent dependent on the intermolecular order and conformational structure[11]. In addition to this, the spectra also show the bands corresponding to the aliphatic parts of PCL chains, particularly the CH_2 scissoring vibration bands between 1500–1400 cm^{-1}, wagging vibration bands between 1210 and 1150 cm^{-1} and skeletal vibration bands between 1000–900 cm^{-1} which are very sensitive to changes in conformation[1,2,8,12].

In our previous work, the differences between the i.r. spectra of planar and non-planar conformations have been discussed[1,2]. We were able to calculate the concentration of the planar and non-planar conformation of PCL from the absorbances of the bands characteristic of each conformation in the i.r. transparence spectra[6,13]. For the PA-*FT*i.r. spectra, the saturation effect plays an important role for the majority of the bands (see, e.g. ref. 14); as a result, in PCL–PBD copolymers a linear relation between the concentration and intensity of the bands, similar to that observed by transparence spectroscopy, generally does not hold[10]. Nevertheless the situation can be simplified if we compare the changes in

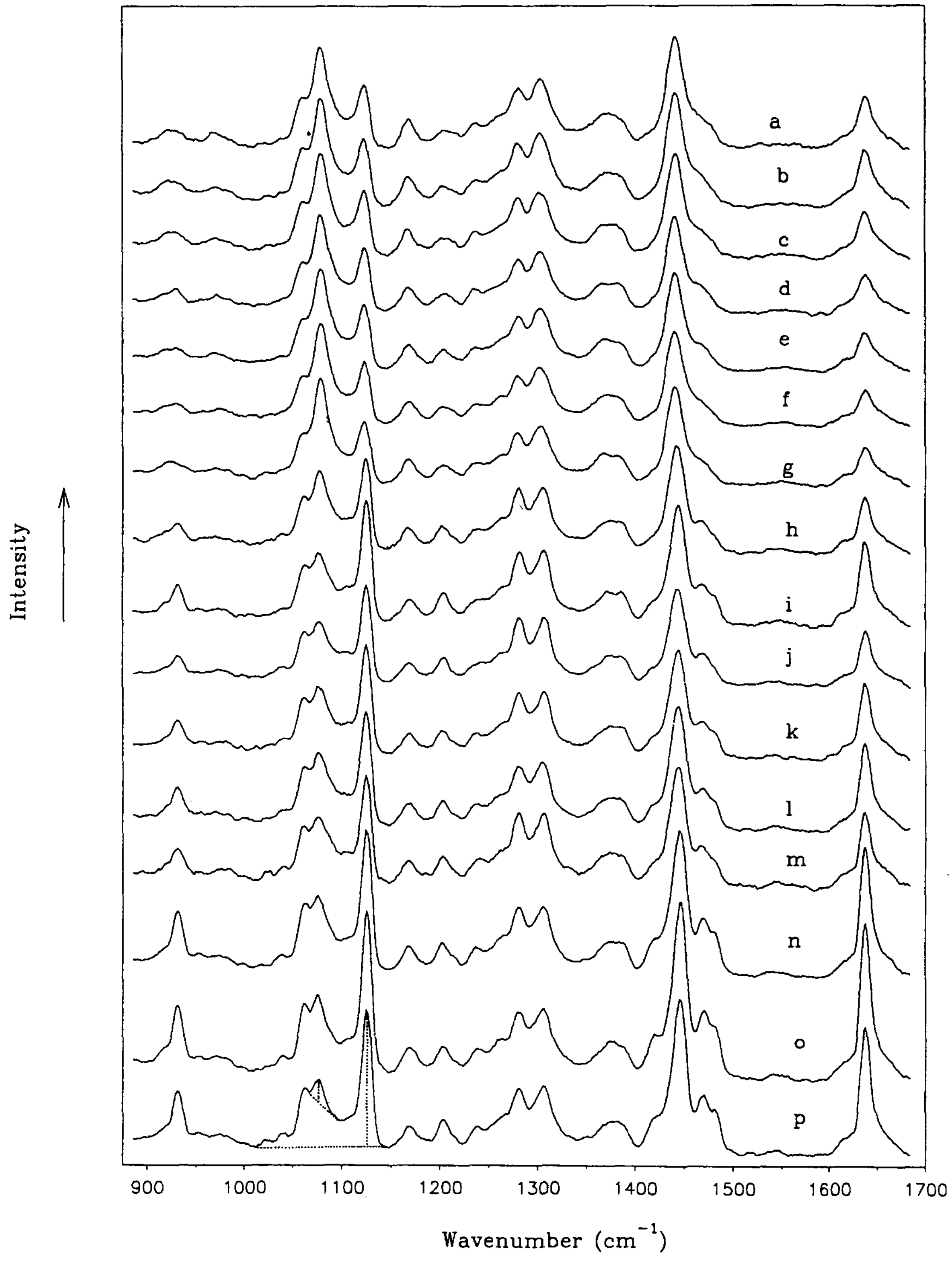

Figure 3 Micro-Raman confocal spectra of the microtome section of Sample 1 (PCL–homopolymer); (a) saw-cut surface, (b)–(p) 2–30 μm from the saw-cut surface

intensity ratios of approximately equally strong bands. Then both of them are similarly influenced by saturation effects and a relation analogous to the case of transparence spectroscopy can be used for the calculation of concentration ratios. We have used this procedure for all our calculations in this study.

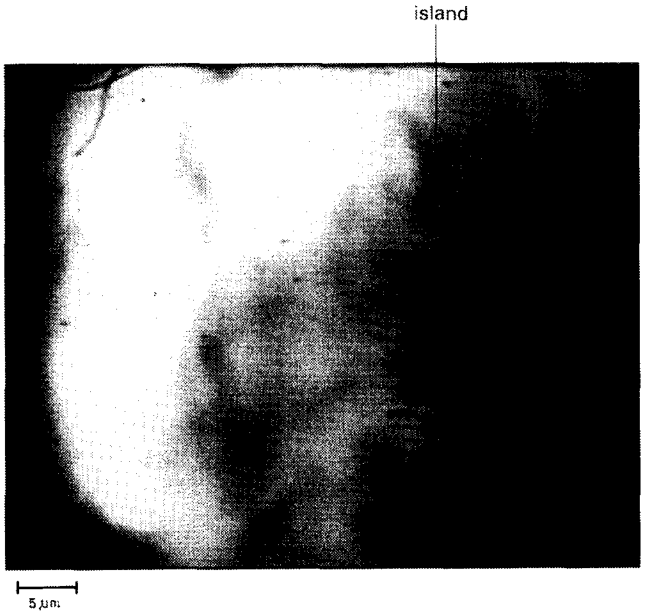

Figure 4 Television image of the less crystalline island in Sample 1 (PCL–homopolymer)

PA-*FT*i.r. spectra of PCL-homopolymer and of PCL–PBD copolymers were found to differ in the intensities of bands sensitive to the conformations of the PCL blocks (see *Figure 2*). The band situated at 1201 cm^{-1} was used as characteristic of the planar and the band at 1170 cm^{-1} of the non-planar conformation. The intensities of these bands were measured from the baselines, as shown in *Figure 2*. As a standard of the whole photoacoustic intensity of a given sample reflecting the measured sample volume, we used the value of the integral area S under the spectral curve between 2430–2995 cm^{-1} (C–H aliphatic stretching vibrations), which practically does not change either with the content of conformations, or with the content of the butadiene units in the measured material.

In *Table 1*, the characteristics and the treatment of the samples, the values of S and the photoacoustic absorbances A of the bands at 1201 and 1170 cm^{-1} are summarized. Assuming the presence of two conformational fractions in the PCL material, the planar x_A and the nonplanar x_B with $x_A + x_B = 1$, we can use the relations

$$A_{1201}/S = \varepsilon_{1201} \cdot x_A \qquad (1)$$

$$A_{1170}/S = \varepsilon_{1170} \cdot (1 - x_A) \qquad (2)$$

where A are the values of photoacoustic absorbances, S is the integral intensity of the standard photoacoustic signal, and ε are the relative absorbance coefficients. These relations could be used in the calculation of the

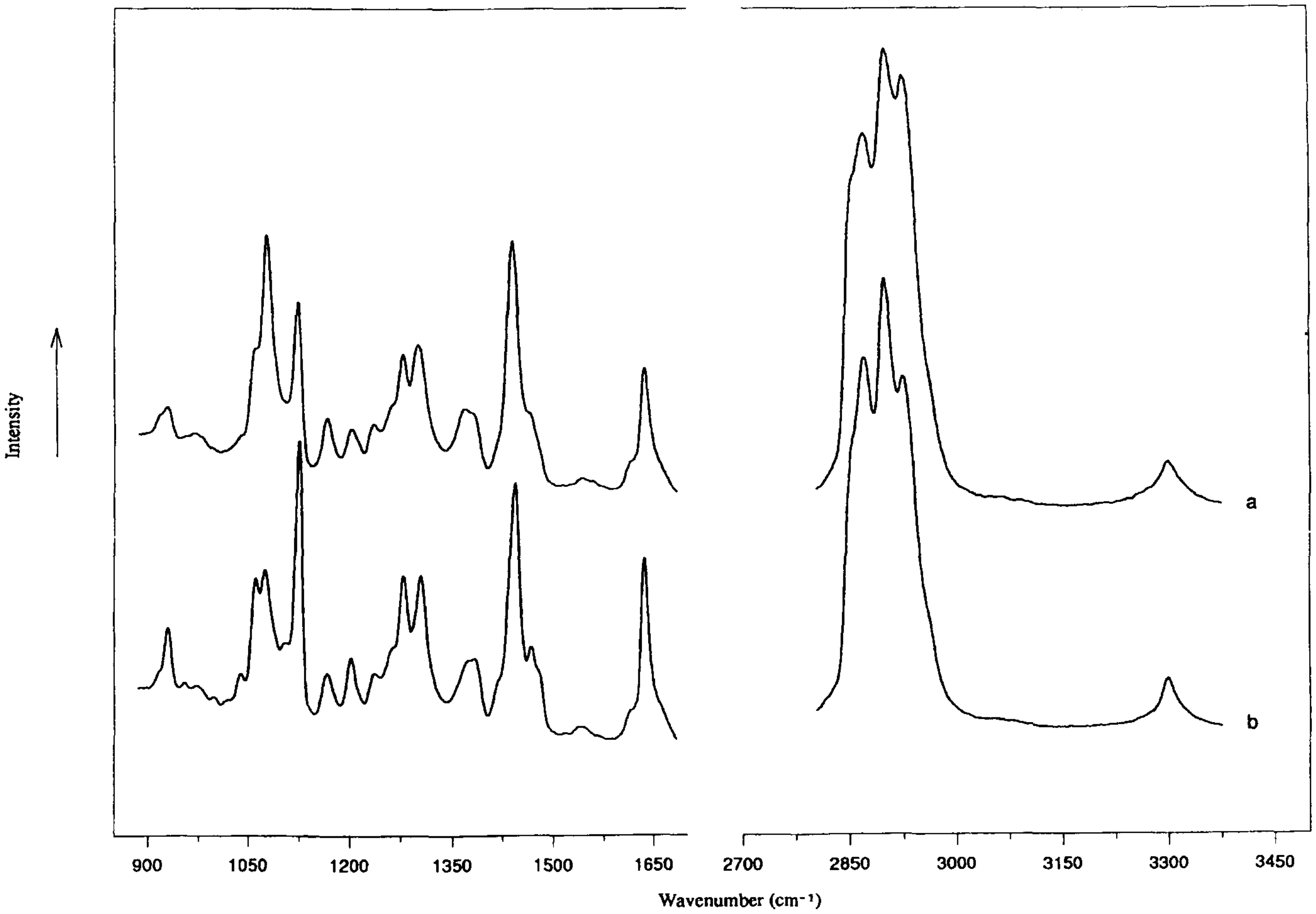

Figure 5 Micro-Raman confocal spectra of sample 1 measured (a) inside and (b) outside the island

ratios of absorbance coefficients, ε_{1201} and ε_{1170}, for the surface or inner parts of the samples prepared by various treatments. Using the baseline shown in *Figure 2*, we found that the value of the ratio of the absorbance coefficients $\varepsilon_{1170}/\varepsilon_{1201} = 1$ is a good approximation for all the studied samples, similarly to the previously studied case[6,13]. This approximation was therefore used for the calculation of the fractions of the planar conformation in all the PCL samples, according to the simplified relation

$$x_A = A_{1201}/(A_{1201} + A_{1170}) \qquad (3)$$

In the PA-*FT*i.r. spectra of PCL–PBD copolymers there also appear absorptions corresponding to PBD blocks in the polymer chain. Nevertheless, only very weak PBD absorptions appear in the region 1100–1300 cm^{-1}[10]; therefore, the same relation (3) could serve also for the investigation of conformations of the CL part in the PCL–PBD copolymers. All the results of these calculations for pure PCL and for the PCL–PBD copolymers are given in *Table 1*.

In *Figure 2*, two different PA-*FT*i.r. spectra of sample 1 (PCL–homopolymer) are shown: the spectrum of unaffected as-polymerized inner part of the polymer plate and the spectrum of the saw-cut surface. An important difference can be found between these two spectra: the spectrum of the inner part (*Figure 2b*) corresponds to a material with a higher concentration of the planar conformation of PCL than that observed for the surface affected by saw-cutting (see *Figure 2a*) (compare also *Table 1)*.

It is known that the PA-*FT*i.r. technique reflects the spectral characteristics of the material of approx. 15 μm from the measured surface (see, e.g. ref. 14); thus, on the saw-cut surface of sample 1 a layer with a smaller concentration of the planar conformation of PCL is formed, compared with the unaffected inner part of the sample. Apparently, during the rapid saw-cutting, the material melted and then rapidly cooled, so that the monoclinic α-crystalline structure could not be fully developed.

Similar results were obtained also for sample 2 containing 15 wt% of PBD blocks in the chains. Nevertheless, in the unaffected part of sample 2, the concentration of the planar conformation is slightly lower than in the respective part of sample 1 discussed above (see *Figure 2c,d* and *Table 1*). This is the result of the presence of PBD blocks in the block copolymer chains, which decreases the possibility of the formation of the planar conformation (see ref. 8). Also here the rapid saw-cutting further decreases the amount of the planar conformation in the surface layer of the sample.

In the non-treated sample 3, the presence of 25 wt% of PBD blocks strongly decreases the concentration of the planar conformation in the PCL blocks down to $x_A < 0.4$ in all the volume (see *Figure 2e* and *Table 1*). As in this case the saw-cutting did not cause a further decrease in the content of the planar conformation, we did not examine the saw-cut surface layer of sample 3.

In a previous i.r. study of physical structure of PCL, we have shown that treatment with water increases the concentration of the planar conformation in PCL[6]. For the samples studied here, the influence of water treatment is also apparent. It can be seen from *Table 1*, that the surface layers of samples 1 and 2 (with the content of the planar conformation reduced due to the presence of PBD blocks and/or due to the saw-cutting) and all the volume of sample 3 show a slight increase in the concentration of the planar conformation in consequence of water treatment at room temperature; after boiling the samples in water, the effects are much stronger.

D.s.c. measurement

To confirm the formation of the surface layers by saw-cutting, we compared the d.s.c. crystallinity of the average material of our sample 1 with the crystallinity of the material carefully removed from the saw-cut surface of the same sample. The average d.s.c. crystallinity of that sample was found to be 54%, the d.s.c. crystallinity of the material taken from the surface was 46%. The d.s.c. results reflect mainly the melting of the monoclinic α-crystalline phase[15]. Thus, previous PA-*FT*i.r. spectroscopic findings about the formation of a layer with a smaller content of planar PCL chains seem to be confirmed.

Micro-Raman spectroscopy and spectral imaging

In a previous *FT* Raman study of PCL and PCL–PBD copolymers, we identified the Raman bands which are characteristic of the planar and non-planar conformation of PCL chains[8]. For the micro-Raman study we have used two of those bands for estimating the conformational structure of our samples: the band at 1125 cm^{-1} characterizes the planar and the band at 1079 cm^{-1} the non-planar conformation.

The high spatial resolution of the micro-Raman confocal technique enabled us to follow the distribution of regions with different conformational composition in the cross-section of our samples. In *Figure 3*, the Raman spectra of PCL–homopolymer (sample 1), obtained from the measurements in steps of 2 μm across the microtome section are given. Small changes in the intensity ratio between the bands characteristic of the planar and non-planar conformation in the region near to the saw-affected surface can be observed. At a distance of about 12 μm, the intensity of the bands characteristic of the non-planar conformation rapidly decreases, whereas that of the bands characteristic of the planar conformation exhibits a rapid increase. Such a behaviour confirms our previous assumption from PA-*FT*i.r. that the less crystalline surface layer of this sample is approximately 10–20 μm thick. In the Raman spectra measured deeper than

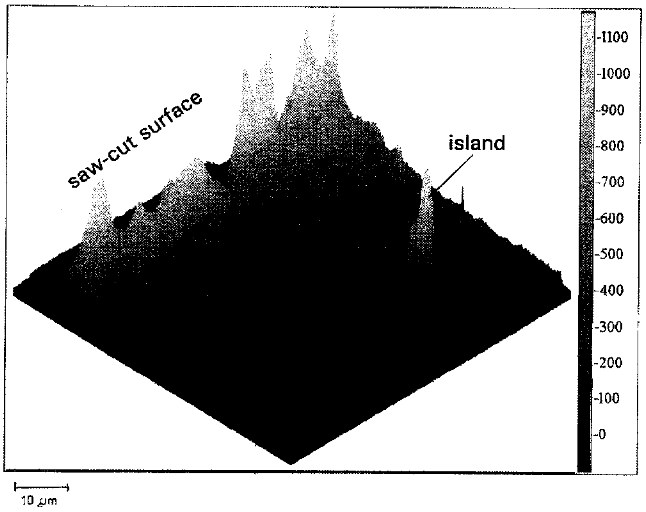

Figure 6 Raman image of the microtome section of sample 1 centred on the band at 1079 cm^{-1}

20 μm from the surface of the sample, the intensities of the bands characteristic of the planar conformation of the PCL chain are prevailing. Nevertheless, in some positions in the inner part of the sample, great fluctuations can be found in the measured intensity ratios, with higher relative intensities of the bands of the non-planar and smaller for the planar conformations. This indicates that the majority of the material unaffected by saw-cutting exhibits a higher monoclinic crystallinity, but that also some less crystalline 'islands' can be detected in the inner part of the material.

These islands could be revealed by means of the television camera of the micro-Raman instrument. Their average diameter is about 10 μm. In *Figure 4* a television image of such an island is presented. In *Figure 5*, curve a shows a Raman spectrum taken in the centre of the island, curve b a spectrum taken outside, but in the close vicinity of the island. The Raman spectrum from the inside of the island corresponds to the material with a lower concentration of planar conformation of PCL chains. Apparently these islands were formed during the microtome cutting, similarly to the layer during the saw-cutting, so that the monoclinic α-crystalline structure could not be formed properly.

Other evidence on the formation of the regions with a lower monoclinic crystallinity can be obtained by Raman imaging. In *Figure 6*, a typical Raman image of a part of the microtome slice monitored by the intensity of the Raman band at 1079 cm^{-1}, demonstrating the presence of the surface layer formed by saw-cutting and of an island, both having smaller crystallinity is shown.

Samples of PCL–PBD copolymers, besides the bands of the PCL part, exhibit in their Raman spectra additional bands corresponding to BD units in the PBD blocks of the polymer chains, as expected[8,10]. Nevertheless, the bands at 1125 and 1079 cm^{-1} are not much affected by the presence of the BD units and they can therefore be used for the estimation of the conformation of the CL units in the chain, similar to PCL homopolymer.

The micro-Raman spectra of sample 2 (copolymer with 15 wt% of PBD blocks) (see *Figure 7*) reflect the formation of a surface layer and of 'islands' in the inner part with a lower concentration of the planar conformation of PCL parts of the chains, similarly to that found for sample 1, but with a smaller difference between the less and more crystalline parts. The intensity of the bands of the butadiene part of block copolymers at 3080 and 3020 cm^{-1} is practically the same in the saw-cut surface layer, in the bulk (*Figure 7*) and also in the inner and in the outer parts of the islands. It appears that the distribution of the PBD blocks, unaffected by rapid cutting, is homogeneous in all the volume of the sample.

In *Figures 8* and *9* are plotted the ratios of the intensities of the Raman bands I_{1125}/I_{1079} for samples 1 and 2 against the distance from the surface of the sample. These figures give also a qualitative information on the fraction of planar conformation x_A obtained from the results of the PA-*FT*i.r. measurements.

According to the Raman spectrum of sample 3 (copolymer with 25 wt% PBD blocks) (*Figure 10*) and in accordance with previous results using the PA-*FT*i.r. technique, the presence of 25 wt% of PBD strongly reduces the content of the planar conformation of PCL

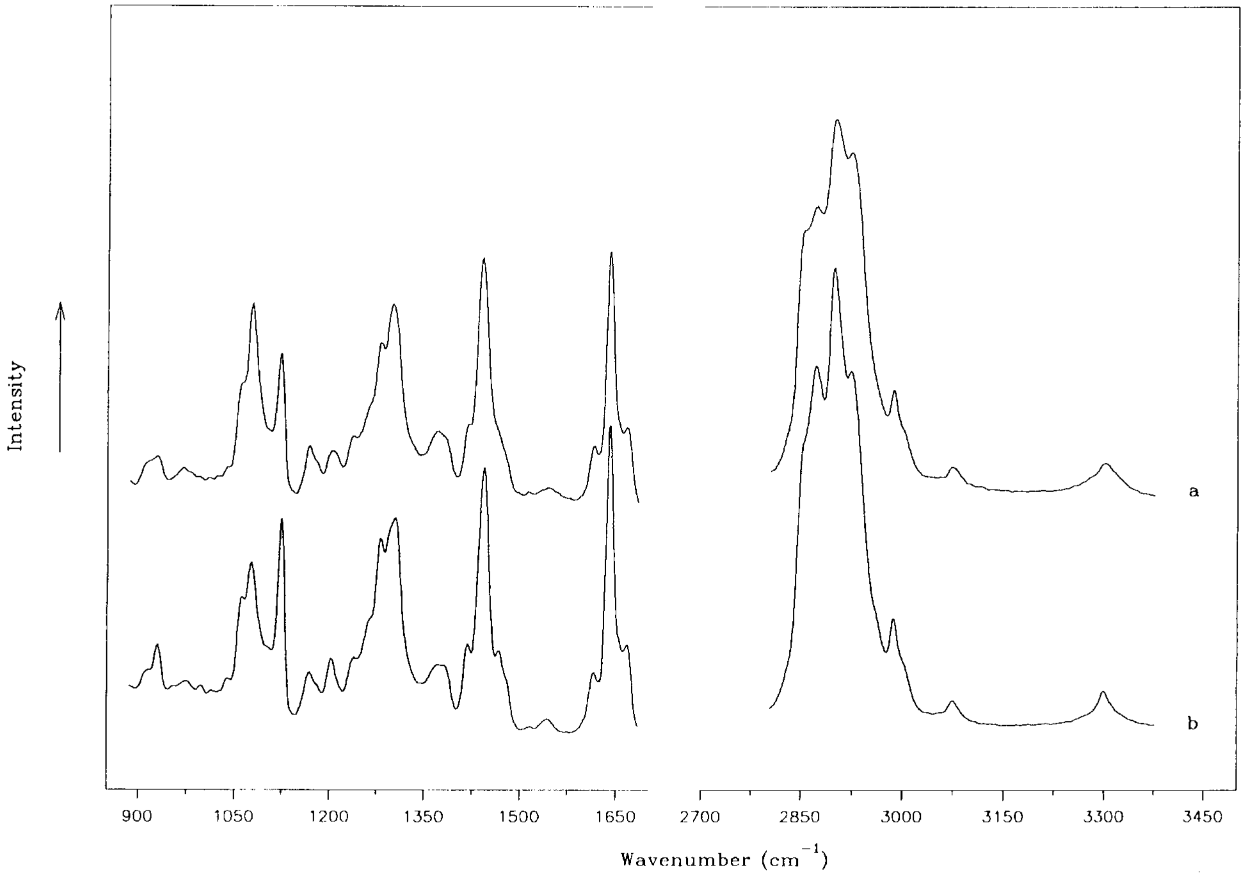

Figure 7 Typical micro-Raman spectra of sample 2 (block copolymer with 15 wt% of PBD blocks). (a) saw-cut layer, (b) unaffected part

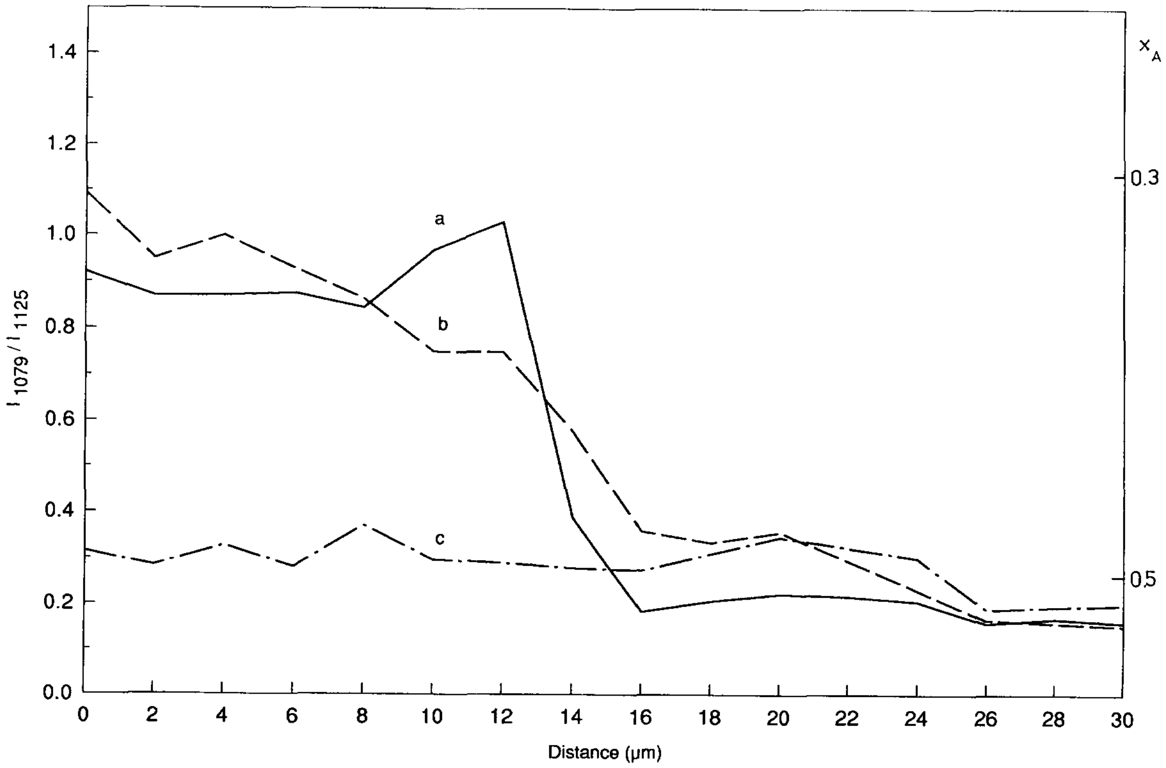

Figure 8 Dependence of the intensity ratios of the Raman bands on the distance from the saw-cut surface for sample 1 (PCL–homopolymer) (a) non-treated, (b) after water treatment at 25°C and (c) at 100°C

chains in all the material; neither a surface layer after saw-cutting nor islands after microtome cutting with different conformational composition seem to exist. The sample is homogeneous in all its volume from the point of view of both chemical composition and its conformational structure.

As follows from the curves also given in *Figures 8* and *9*, the treatment of the samples with water at room

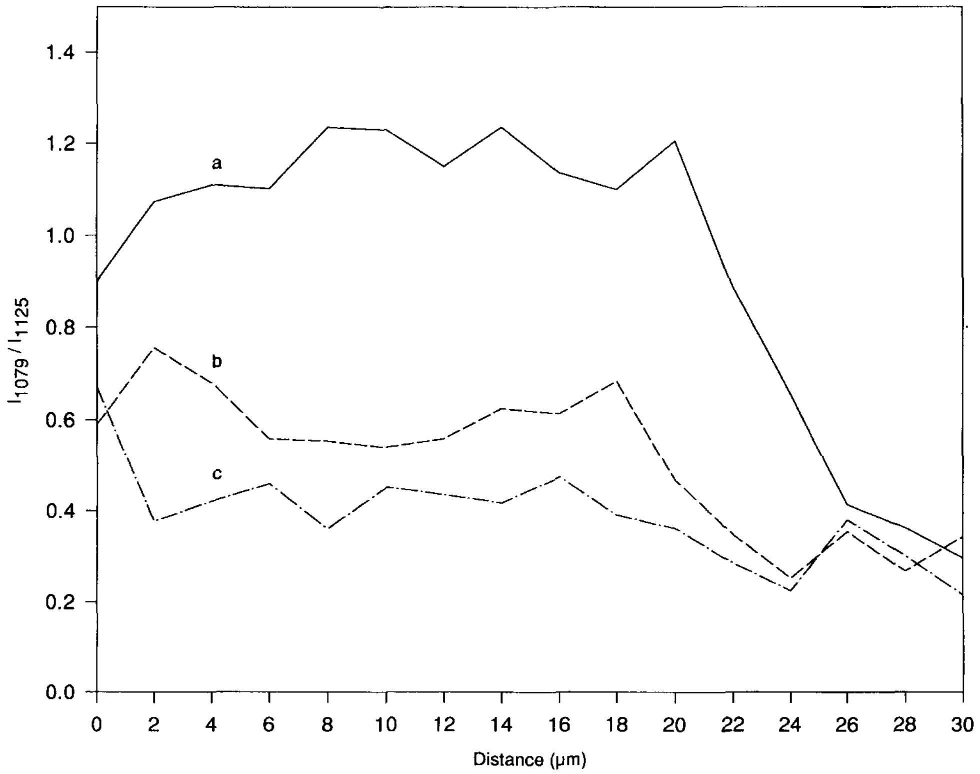

Figure 9 Dependence of the intensity ratios of the Raman bands on the distance from the saw-cut surface for the sample 2 (PCL–PBD copolymer with 15 wt% of PBD blocks) (a) non-treated, (b) after water treatment at 25°C and (c) at 100°C

temperature increases slightly the fraction of the planar conformation x_A in the saw-affected surface layers of samples 1 and 2. On the other hand, boiling of these samples in water at 100°C completely destroys the surface layers of those samples, increasing the fraction of the planar conformation near the surface to the values which the material had before the saw-cutting.

As follows from the micro-Raman measurement of sample 3 and in accordance with our PA-*FT*i.r. measurement, boiling in water increased the fraction of the planar conformation x_A in all the volume of the material (see *Figure 10*).

CONCLUSIONS

1. In the PCL–PBD block copolymers prepared by anionic polymerization, the resulting fraction x_A of the planar conformation of poly(ε-caprolactam) chains decreases with the increasing content of PBD blocks, from the value 0.5–0.6 for the PCL homopolymer down to 0.3–0.4 for the copolymer with 25 wt% of PBD blocks.
2. By saw-cutting of the samples with the higher mean value of x_A (PCL homopolymer and copolymer with 15 wt% of PBD blocks), 10–15 μm thick surface layers with lower values of x_A are formed. Islands of similar size and character are formed by cutting these samples with a microtome.
3. The content of the planar conformation, lowered in the copolymers and in the saw-cut surface, can be substantially increased by water treatment, especially at elevated temperatures. In the copolymer with 25 wt% PBD blocks, the contents of the planar conformation almost equal to the PCL–homopolymer can be reached in this way.
4. PA-*FT*i.r. spectroscopy appears to be a useful tool for the study of the physical structure of amide polymers, as no sample preparation possibly changing the physical structure is needed here; this method is particularly suitable for determining the mean population of the planar conformation.
5. The micro-Raman confocal method together with the Raman imaging are very suitable for estimating variations in conformational structure at dimensions of micrometer order; nevertheless, care must be taken of possible changes in the physical structure caused by microtome cutting.

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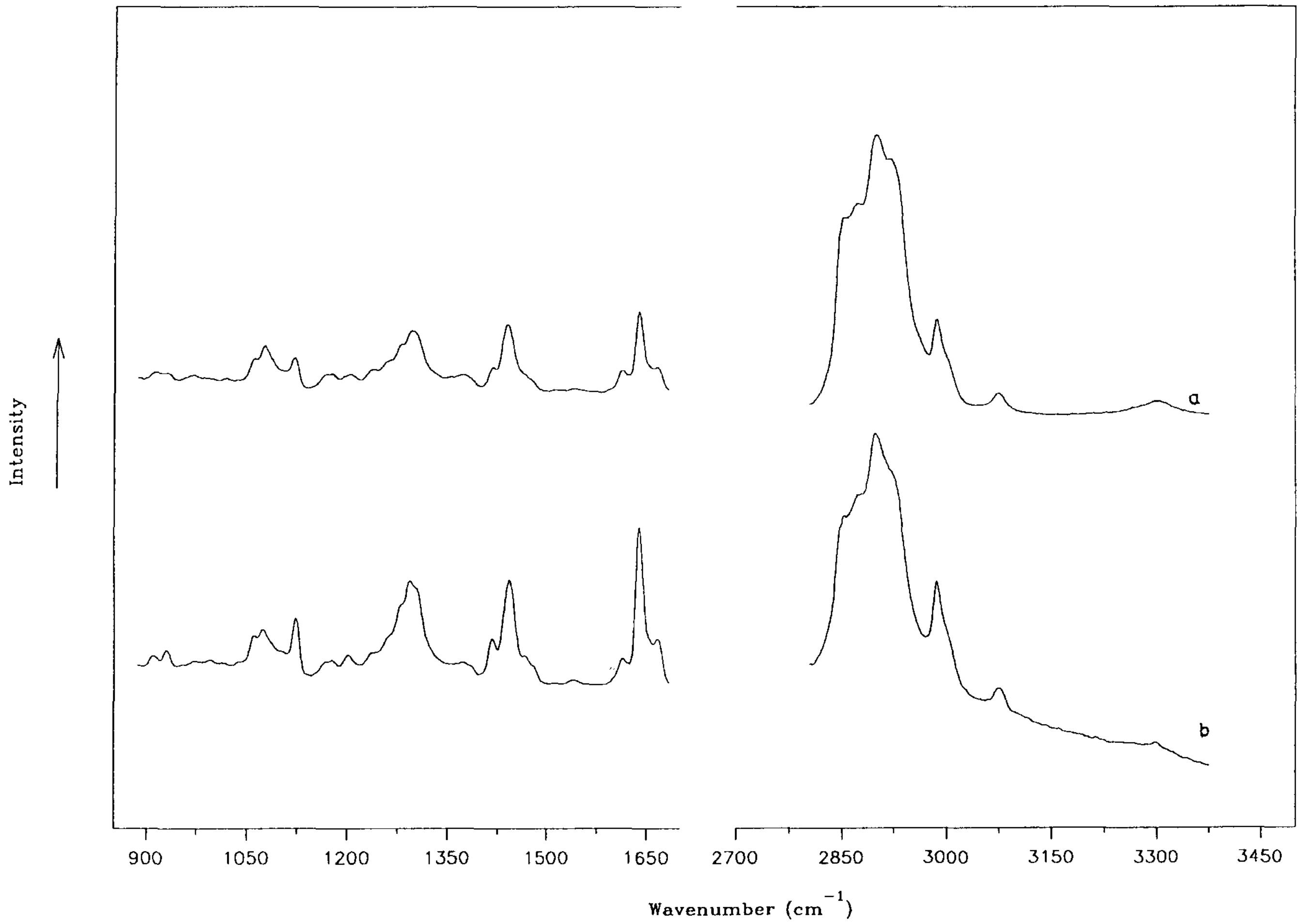

Figure 10 Typical micro-Raman spectra of sample 3 (copolymer with 25 wt% of PBD blocks) inside the sample (a) non-treated (b) after water treatment at 100°C

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