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# Correlation between crystallization and mechanical stress revealed by chain scission of segmented amide copolymer

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Thermoplastic elastomer

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## A B S T R A C T

By tuning hydrolysis duration of a segmented ether-amide copolymer (PEBA), a range of specimens presenting various macromolecular structures has been produced. Knowing that scissions occur predominantly at the bond between hard and soft blocks, for a given hard phase structure we study the impact of phase interconnection changes on strain-induced crystallization (SIC) occurring during tensile loading. The consequences of chain scissions on the structural reorganization involving SIC measured with in situ X-ray diffraction is considered here for the first time. A close correlation between stress and crystallinity induced under strain is highlighted whatever the chain scission number, i.e. the number of phase interconnections. As a result, the stress decrease observed at a given elongation can be interpreted as a consequence of a SIC weakening with the chain scission process.

## 1. Introduction

Strain-induced crystallization (SIC) is at the origin of the remarkable mechanical properties of many elastomers such as natural polyisoprene [1–5], polychloroprene rubbers [6,7] or some polyurethane elastomers. It results from the alignment of amorphous molecular chains in the stretching direction, lowering the crystallization entropy cost [8]. In thermoplastic elastomers (TPEs), the crystallization of the soft phase upon stretching is accompanied by a reorganization of the hard domains. These complex morphological transformations have been particularly studied on urethane segmented copolymer (TPU) [9–11] and poly(ether-block-amide) (PEBA) [12–15].

PEBA is composed of alternating flexible soft polyether segments and rigid hard polyamide segments. By modifying the weight ratio or the length of the respective segments, it is possible to tune the physico-chemical properties of the material. Grades can thus exhibit a mechanical behaviour ranging from rubber, for low PA content, to homopolymer-like PA, for high PA content [16,17]. They exhibit a micro-phase separated morphology, consisting of hard microdomains dispersed throughout a soft phase matrix [18]. Some amorphous PA

segments remain isolated into the soft phase, as covalent bonding between both blocks prevent a perfect segregation. In case of soft PEBA grades as considered here, the extent of PA crystallization is limited by the low PA content [15,17–19].

The PEBA reorganization under stretching has been described in the literature as a three-stage process [19,20]. Starting from the quiescent state (macroscopic elongation  $\lambda = 1$ ), drawing up to  $\lambda = 2$  simply results in an extension of the soft segments. PA lamellae start to rotate at higher draw ratio and become oriented in a tilted direction with respect to the draw axis (observation of a cross-like SAXS pattern [20]). Lamellae start to break at around  $\lambda = 4$ , leading to the formation of fibrils oriented in the tensile direction. It also induces some relaxation of the soft polyether segments, from thereon orienting at a lower rate with increasing elongation [19]. This progressive lamellae break-up, moderate soft chains orientation and crystallization, proceed up to high elongation.

This study is part of a project investigating the ageing behaviour of thermoplastic elastomers in marine environment [21–23]. The immersion of samples in natural seawater leads to hydrolysis, resulting in molecular chain scissions. We used this framework as an opportunity to study the strain-induced crystallization of PEBA through a novel

approach. Indeed, a common approach for TPEs is to compare grades with different hard/soft ratios [13,15,17,19]. However, many parameters are affected by this ratio, such as soft segment length, crystalline domain size or the global organization of the material. This method is then not best suited to separate the respective contribution of each parameter. More recently, the effect of crosslinking networks on SIC has been studied in PTMO [24]: crosslinking has a weak effect on the onset of SIC itself but it promotes the extend of crystallization during deformation. By inducing chain scission through hydrolysis, our approach enables us to produce samples with an essentially preserved structure where the only changing parameter is the degree of connections between the soft and hard blocks associated with the chain scission number generated by hydrolysis.

According to this approach, we propose here to study the SIC process for samples submitted to different degrees of hydrolysis. The macromolecular, structural, and mechanical changes induced by chain scissions and stretching are presented and discussed here with the aim to propose a new relationship between strain-induced crystallization and mechanical properties.

## 2. Experimental section

### 2.1. Materials

The Pebax® 2533 grade was purchased from Arkema in granular form. The specific 2533 SD 02 grade has been selected due to the incorporation of specific stabilizers that prevent oxidation. It ensures that degradation is essentially due to hydrolysis and not oxidation during water aging. Granules were dried at 80 °C for 15 h before processing. Injection of 2.5 mm-thick plates was performed according to supplier specifications on a DK CODIM 175/410 injection molding machine. The Pebax® chemical structure and composition are recalled in Fig. 1. The number of repeating units of soft and hard blocks ( $n$  and  $m$  respectively), the degree of polymerization  $N$  and the different number average molar masses are averaged from data found in the literature on Pebax® 2533 [25–27]. The total molar mass is about  $55\,000\text{ g mol}^{-1}$  and the polyamide weight ratio is 23%.

### 2.2. Hydrolysis conditions

Before starting the chemical degradation process, plates were annealed at 110 °C for 15 h under vacuum to stabilize the microstructure. Slow cooling to ambient was simply obtained by turning off the oven. Differential scanning calorimetry analysis (not shown here) confirmed a stable microstructure (no additional melting peak) up to 110 °C. Samples were then immersed in tanks filled with continuously renewed natural seawater at four temperatures: 40, 60, 80, and  $90 \pm 2$  °C. They were removed from the tanks after a definite time and carefully wiped with a paper towel. To avoid further hydrolysis, samples were fully dried in a desiccator filled with silica gel (i.e., RH close to 0) at 40 °C for 48 h prior to testing. A special attention was paid to ageing conditions and sample geometry to ensure that the samples were hydrolyzed homogeneously through the thickness, in others words to ensure that water diffusion was much faster than hydrolysis kinetics. In fact,

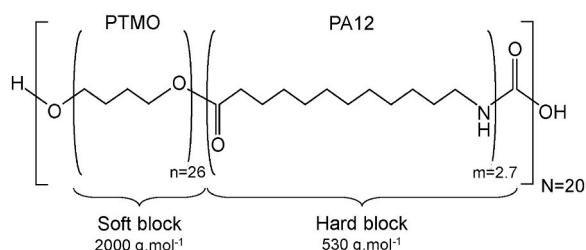


Fig. 1. Pebax® 2533 chemical structure and composition.

considering water diffusion in Pebax at 80 °C, a typical Fickian behaviour is observed with a time to reach saturation within the material about 0,1 day. In the meantime, it can be seen that the amount of chain scission after 7 days at 80 °C is very low (about 0,01 mol/kg). It means that de water diffusion is much faster than the hydrolysis rate (at least by a factor of 10) and so degradation is homogeneous through thickness during ageing. The same behaviour is observed for all ageing temperature.

Finally, it is noteworthy that characterizations were performed with dried samples, to be in the same state for all tests (i.e. tensile tests, DSC, X Ray, GPC). Tensile tests have been performed with and without drying, no major changes in mechanical behaviour were observed.

### 2.3. Chain scission measurement

Molar mass was measured with gel permeation chromatography by the PeakExpert Company. Analyses were performed at 20 °C using a mixture of hexafluoroisopropanol and 0.1 M potassium trifluoroacetate as eluent. The apparatus was equipped with a pre-column and two columns packed with  $7\text{ }\mu\text{m}$  PFG particles of 1000 Å and 100 Å pore size, respectively. The detection was performed using a Waters 2414 differential refractive index detector. The calibration was performed with poly(methyl methacrylate) samples.

### 2.4. Conventional tensile test

Uniaxial tensile tests were performed at a rate of 50 mm/min on a 10 kN capacity Instron machine in a room regulated at  $21 \pm 1$  °C and 50% relative humidity. A 500 N load cell was used. Dogbone samples were cut according to ISO 37:2005 type 3 (50 mm overall length, 2.5 mm thickness) and two duct tape marks were placed at the gauge length, 15 mm apart. A camera coupled to a specific software developed at IFREMER allows the relative displacement of the two tape markers to be tracked. The tensile modulus ( $E$ ) was estimated from the initial slope of the stress-strain curve.

### 2.5. Static small and wide X-Ray scattering (SAXS and WAXS)

SAXS and WAXS analysis were performed without any mechanical load applied on the high brilliance SWING beamline at the Soleil Synchrotron facility. A wavelength  $\lambda_{XR} = 0.0775\text{ nm}$  is selected by three monochromator. Patterns were recorded at room temperature, with a CCD detector located at 6 m from the sample for SAXS, and 0.5 m for WAXS. 1D curves were obtained by circular averaging of 2D patterns, using the Foxtrot software. Thanks to the fast processing here, 10 images are collected for the same position of a sample. Resulting WAXS and SAXS curves are respectively plotted as function of the scattering angle  $2\theta$  and the wave vector  $q$ , with  $q = 4\pi \cdot \sin(\theta) / \lambda_{XR}$ . The long period  $L$  corresponding to the diffraction peak observed in SAXS was calculated as  $L = 2\pi/q$ , considering the Lorentz correction. Fityk software was used for signal treatment, enabling a crystallinity index to be determined as the ratio of peak area attributed to Bragg diffraction to the signal total area.

### 2.6. In situ X-ray diffraction under mechanical load

Tests were performed on a symmetric tensile device mounted on a rotating anode X-ray generator (focus size:  $0.2 \times 0.2\text{ mm}^2$ ; 40 kV, 40 mA) equipped with a copper anode whose  $K_\alpha$  radiation (wavelength 0.1542 nm) is selected by a doubly curved graphite monochromator [28]. The sample is located at the focalization point close to the collimator exit, which ensures maximum diffracted intensity. Diffraction patterns are recorded with an indirect illumination CCD camera. A beam-stop is fixed close to the camera and contains a photodiode that delivers a photocurrent proportional to the X-ray intensity transmitted through the sample. The exposure time was set at 10 s. An optical

camera was used to measure elongation, following the same method as for conventional tensile tests (section 2.4). ISO 37:2005 Type 2 dogbone tensile samples were tested (75 mm overall length, 2.5 mm thickness), at a rate of 10 mm/min, at 20 °C. A detailed description of the apparatus used here can be found in [1–7].

## 2.7. In situ X-ray data processing

Relevant data are retrieved from two angular scans, one centered on the equatorial Bragg lobes forming upon stretching, the other centered more inwards to only include diffraction by the pure amorphous phase (Fig. 2). This procedure enables to separate the respective contributions of the crystalline and amorphous phases. 1D azimuthal profile corresponding to each scan was obtained by radially integrating the signal between the  $2\theta$  bounds of the scan area, for  $-80^\circ < \varphi < 80^\circ$ .

The azimuthal profile of the pure amorphous phase (containing the PTMO and some amorphous PA blocks not contributing to the crystalline phase) was fitted with a  $A + B \cos^2 \varphi$  function, following the Gaussian theory of rubber elasticity. The associated Legendre coefficient  $\langle P_2^{RX} \rangle = (3\langle \cos^2 \varphi \rangle + 1)/2$  is assumed to be proportional to the Herman coefficient  $\langle P_2 \rangle$  for the segmental orientation function of the molten polymer chains. It is recalled that  $\langle P_2 \rangle = (\lambda^2 - 1/\lambda)/5N$  within the framework of the Gaussian model, where  $\lambda$  is the draw ratio and  $N$  is the average number of freely jointed statistical segments per chain.

A crystallinity index (CI) was determined by fitting the Bragg peak observed in the first azimuthal profile with a Pearson VII function; the amorphous contribution was accounted for by a square cosine function

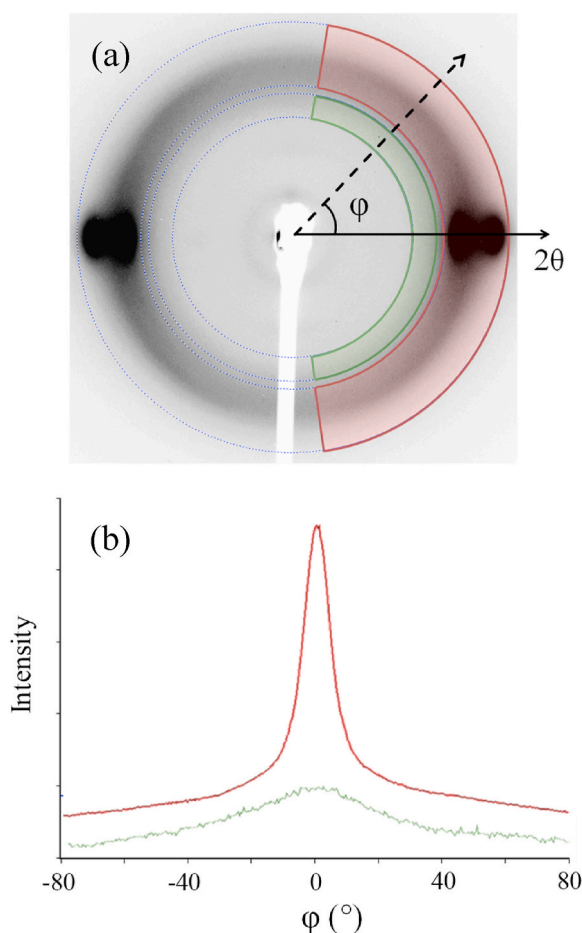


Fig. 2. (a) Diffraction pattern of a stretched sample with the two integration areas, one including the diffraction lobes and the other including a pure amorphous phase. In (b) the corresponding diffractograms are plotted, resulting from the radial integration in the respective areas.

similar to what is done with the inner angular scan. Indeed, the outer scan captures most of the diffracted intensity and the ratio of Pearson VII function surface by the total integrated intensity is expected to be close to the crystallinity. To avoid any ambiguity this CI was normalized by setting to unity its maximum value, all samples considered (it corresponds to the sample with scissions =  $0.6 \times 10^{-2} \text{ mol kg}^{-1}$ ).

## 3. Results and discussion

### 3.1. Chain scission process

A chain scission process was induced by hydrolysis to produce a range of poly(ether-block-amide) (PEBA) samples with various macromolecular structures. The mechanism responsible for the chain scission process is discussed later. Scission directly affects the average molar mass, and this last was measured with GPC so as to estimate the chain scissions concentration. This last parameter is calculated according to:  $Scissions = \frac{1}{M_n(t)} - \frac{1}{M_{n0}}$  where  $M_{n0}$  is the initial average molar mass and  $M_n(t)$  its value after immersion time  $t$ . Samples were immersed at different temperatures from 40 to 90 °C, for up to 700 days. The chain scission kinetics occurring in the PEBA are reported in Fig. 3 and a clear effect of the ageing temperature on the scission kinetics is actually observed. Results for scissions up to  $7 \times 10^{-2} \text{ mol kg}^{-1}$  are shown here, but an important brittleness is already observed for scission contents above  $4 \times 10^{-2} \text{ mol kg}^{-1}$ . Further observations will thus be limited to this maximum value. Finally, polydispersity remains unchanged for all ageing conditions and close to 2 (data not shown).

Regarding the degradation mechanism, two sites are particularly susceptible to hydrolysis in PEBA: the amide group in the hard segment and the ester group located at the junction of hard and soft segments. This ester group results from the polycondensation of alcohol-terminated PA block and acid-terminated PTMO block. Since the ether segment of PTMO is known to be much less sensitive [29], hydrolysis is expected to occur at the amide or ester sites. To identify the weakest group, a homopolymer PA12, which constitutes the PEBA's hard segments, was also immersed at 80 °C for comparison. In Fig. 3 we can see that, at 80 °C, the PA12 chain scissions rate is significantly lower than observed for the PEBA. As this grade only contains 23 %<sub>w</sub> of PA hard segments, we can conclude here that scissions marginally occur in the hard segments. The ester group is consequently the primary site of hydrolysis. This observation is consistent with other hydrolytic degradation studies of poly(ester-amide) segmented copolymers [30,31].

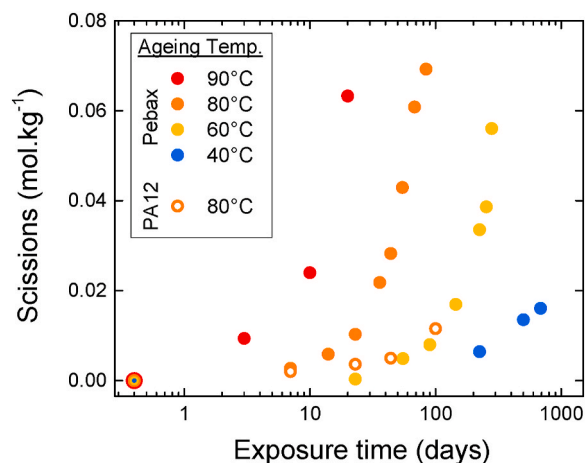


Fig. 3. Chain scission kinetics of the PEBA and the PA12 homopolymer constituting PEBA's hard segments aged at different temperatures in water.

### 3.2. Undeformed PEBA microstructure

To investigate potential morphological changes induced by chain scissions, SAXS and WAXS measurements were performed in the undeformed state (no mechanical load applied) for the PEBA samples presenting increasing chain scission concentrations (Fig. 4). Both SAXS and WAXS results show that there is no major impact of the chain scission process on the morphology of the PEBA. Nevertheless, if we look at the results in detail, the following comments can be made:

i) The initial WAXS diffractogram (Fig. 4-a) shows a large broad peak, characteristic of a predominant amorphous organization. The small broad peaks at shorter ranges (7.9 and 16.8 Å) are related to the well-ordered PA12 domains, and more precisely to a long-range order of amide groups along the chain [32–34]. For low degradation level, i.e. when scissions equal to  $2.2 \times 10^{-2} \text{ mol kg}^{-1}$ , we observe a peak growing at 4.2 Å, that corresponds to the  $\gamma$ -crystalline phase of PA12 [32–34]. From  $2.8 \times 10^{-2} \text{ mol kg}^{-1}$  on, the soft segment crystallization is evidenced by two peaks growing at 3.7 and 4.5 Å that are related to the thermal crystallization of PTMO [35]. This means that the PTMO crystalline phase is stabilized by chain scissions. However, this stabilization occurs at a degree of scissions where the PEBA has lost most of its initial mechanical properties (see Fig. 5 and Fig. 6). PTMO crystallization can explain the embrittlement of PEBA at a high level of degradation but is not involved in the changes of the strain induced crystallization process that will be highlighted later on.

ii) SAXS data corrected for the Lorentz factor  $q^2$  are plotted in Fig. 4-b. A broad peak is observed, characteristic of some stacking order: it may be associated to the PA inter-lamellar order [20]. The corresponding long period  $L$ , calculated from the position of the peak maximum, is initially ca.13 nm, consistent with data reported in the literature for similar PEBA grades [14–20]. A slight peak shift towards lower  $q$ -values is observed at high scission degrees, reflecting an increase of the long period by about 10%. This 10% increase during chain scission is considered minor in comparison with the increase of  $L$  that occurs during stretching; for example, a 100% increase is observed by stretching at  $\lambda = 2$  [20].

Overall, we consider here that the PEBA morphology in the undeformed state remains unchanged for scissions less than  $4.3 \times 10^{-2} \text{ mol kg}^{-1}$ , for higher degradation levels differences can be observed but the material is brittle and cannot be stretched anymore. Let us now focus on changes in the strain induced crystallization process in the following sections.

### 3.3. Mechanical behaviour

In what follows, the tensile modulus  $E$  is defined by the initial slope of the stress-strain curve. Its dependence upon scission concentration is

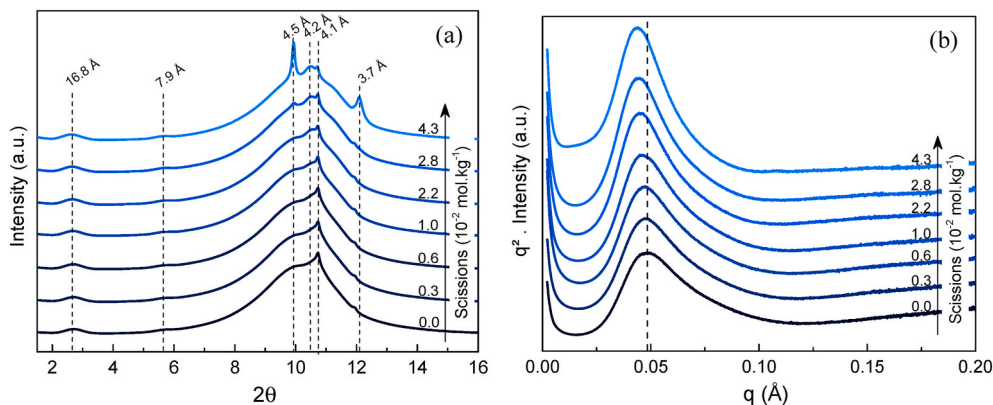


Fig. 4. Effect of chain scissions on the PEBA morphology: (a) WAXS and (b) SAXS diffractograms resulting from measurements in the quiescent state (no mechanical load applied) at room temperature.

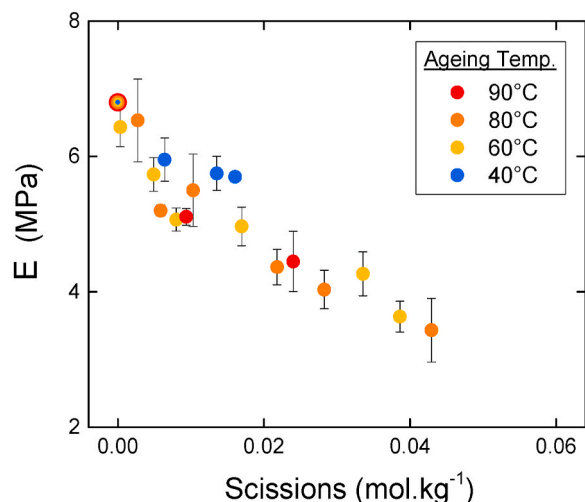


Fig. 5. Change in the PEBA modulus with chain scissions induced by hydrolysis. The tensile modulus  $E$  is defined as the slope for  $1 < \lambda < 1.2$ .

reported in Fig. 5. We see that  $E$  decreases almost linearly up to a concentration  $4.3 \times 10^{-2} \text{ mol kg}^{-1}$ . The data obtained at different ageing temperatures superpose well, forming a master curve, even though the scission kinetics are greatly affected by temperature (as seen in Fig. 3). Although a correlation between scissions and modulus can be assumed according to rubber theory, this point will not be further investigated here since chain scissions cannot rigorously be considered as random in the soft phase. Moreover, hydrolysis can also create new physical crosslinking or modify the entanglement density within the polymer leading to complex interpretation of results presented in Fig. 5.

The data for the nominal stress at break  $\sigma_b$  and elongation at break  $\lambda_b$  also exhibit master curves whatever the chain scission kinetics (Fig. 6).  $\lambda_b$  presents at first a slight increase and a plateau, followed by a drop (Fig. 6-a). On the other hand, the global  $\lambda_b$  behaviour is similar to what is observed in conventional linear thermoplastic polymers where fracture properties remain constant above a specific molar mass  $M_n$  and sharply drop below that value. A critical molar mass  $M'_c$ , related to the ability of the amorphous chains to form entanglements is thus identified. The relationships between fracture properties and molar mass of segmented urethane and amide copolymers have been addressed in detail in a previous publication [23]. We see in Fig. 6-b that  $\sigma_b$  decreases almost linearly with scissions. This point is discussed below, in regard of the SIC contribution to the nominal stress upon stretching.

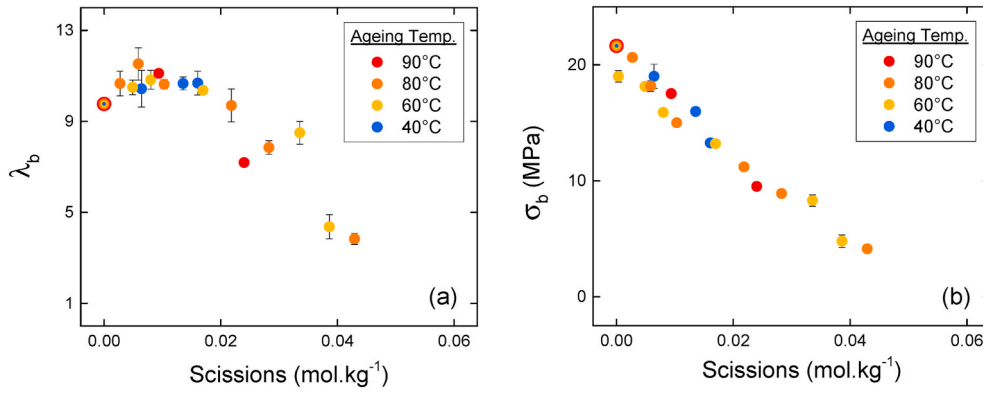


Fig. 6. Effect of chain scissions induced by immersion at different temperatures on the PEBA's (a) elongation at break and (b) nominal stress at break.

### 3.4. Strain-induced morphological change

In situ X-ray diffraction measurements were performed to investigate the morphological changes occurring in PEBA upon stretching up to break. For the sake of clarity, the patterns are displayed with two different levels of contrast (upper and lower rows), Fig. 7. The corresponding tensile curve is presented in Fig. 8. In the undeformed state, a broad halo is observed, characteristic of an isotropic amorphous organization. On the low brightness image (lower row), we can discern two inner rings, corresponding to lower 2 $\theta$ , related to the long-range order of PA segments (visible at 7.9 and 16.8 Å in Fig. 4) [36]. On the high brightness shot (upper row), a thin, intense ring can be discerned on the outer part of the amorphous halo, corresponding to the 4.1 Å Bragg peak previously observed. Overall, the in-situ X-ray patterns for  $\lambda = 1$  are consistent with static XRD analyses.

As PTMO chains orient in the stretching direction, the amorphous halo gradually concentrates in the equatorial direction, due to inter-chain positional correlations. From  $\lambda = 1.7$  on, two well-defined spots become visible in equatorial position and continuously grow in intensity. The angular positions of these spots correspond to the d-spacings of the diffraction peaks of thermally grown PTMO crystallites (3.7 and 4.5 Å, see Fig. 4). The two inner rings, associated to the long-range order along the PA chains, concentrate in azimuthal position to form intense spots clearly visible above  $\lambda = 2.9$ . This was linked to scattering by PA fibrils that results from lamellae breaking [20]. These spots grow in intensity, which reflects the increasing number of fibrils as stretching proceeds.

As detailed in section 2.7, the two relevant parameters that can be derived from the diffraction patterns are a PTMO normalized crystallinity index  $CI_{norm}$  and the amorphous phase orientation parameter  $P_2^{RX}$ .

Let us recall here that  $CI_{norm}$  values are normalized with respect to the maximum measured value when considering all samples (sample with Scissions =  $0.6 \times 10^{-2}$  mol kg<sup>-1</sup>, see experimental part).  $P_2^{RX}$ ,  $CI_{norm}$  and the engineering stress are plotted in Fig. 8 as a function of the draw ratio for a sample with a scission concentration  $1.0 \times 10^{-2}$  mol kg<sup>-1</sup>. The  $P_2^{RX}$  increase reflects the progressive alignment of the soft segments along the draw direction. The orientation rate diminishes above  $\lambda = 2.5$ , that corresponds to the point where lamellae start to breakup. The onset of PTMO strain-induced crystallization matches with the upturn in stress, demonstrating its reinforcing effect. All parameters increase steadily up to  $\lambda = 6$ , as PA lamellae progressively break up and soft PTMO segments orientate and crystallize, leading to the PEBA strengthening. Interestingly, above  $\lambda = 6$ , the CI exhibits a plateau, suggesting that SIC has reached a saturation or an equilibrium, even though the soft segments still orientate up to break, as evidenced by the continuous  $P_2^{RX}$  increase. To our knowledge, this phenomenon was not previously reported, possibly since most studies were confined to low to medium deformations.

### 3.5. Effect of scissions on the SIC process and mechanical behaviour

The scissions have a dramatic effect on tensile properties (Fig. 9), already described in section 3.1. We bring to the reader's attention that the results presented in section 3.1 come from conventional uniaxial tensile tests, while data in Fig. 9 come from in situ XRD combined with tensile testing. All crystallinity curves present a sigmoidal shape (Fig. 9). For a given elongation, CI decreases with increasing scissions. At high scission levels ( $4.3 \times 10^{-2}$  mol kg<sup>-1</sup>), the SIC is significantly reduced, and mechanical properties dramatically drop. The SIC onset, determined as the intersection of the x-axis with the CI- $\lambda$  linear fit for CI between 0.1

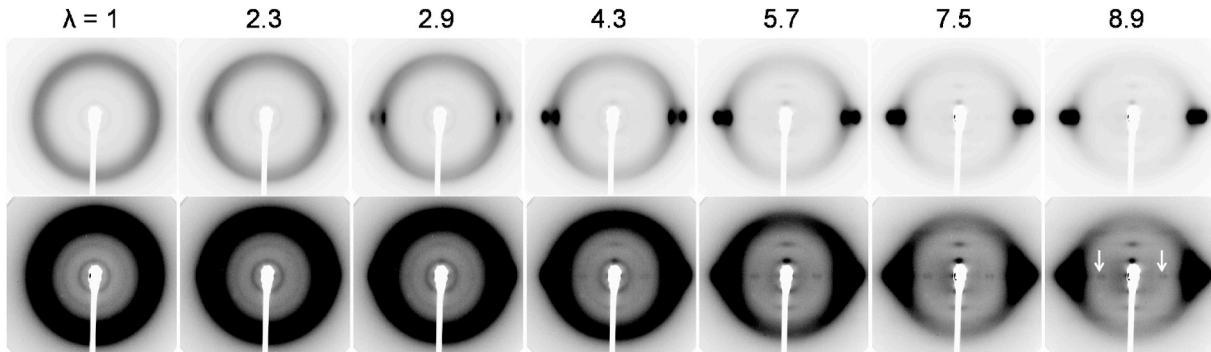
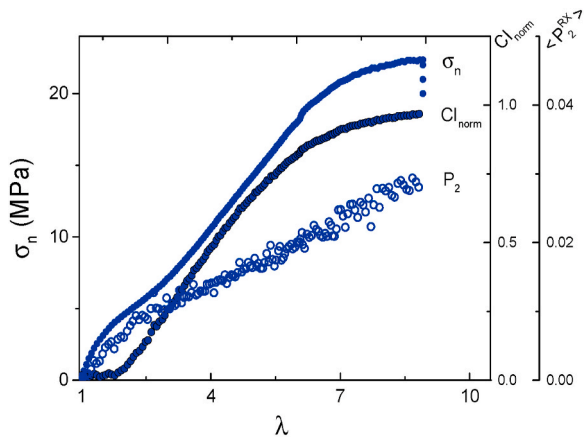


Fig. 7. In situ WAXS patterns of a PEBA sample under uniaxial tension (draw direction is vertical). The sample subjected to  $1.0 \times 10^{-2}$  mol kg<sup>-1</sup> scissions induced by immersion at 80 °C was here arbitrarily chosen as representative. For the sake of clarity, the patterns are displayed with two different levels of contrast (upper and lower rows). The corresponding tensile curve is presented in Fig. 8. Spots indicated with arrows (visible for  $\lambda \geq 4.3$ ) are experiment artefacts, not related to any morphological feature.

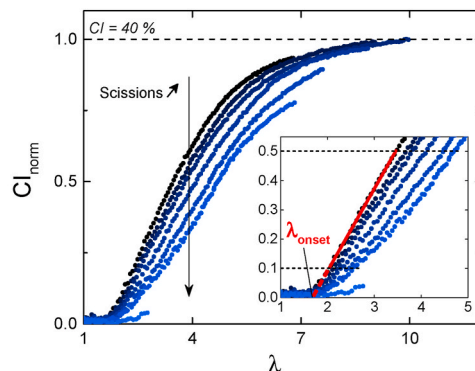
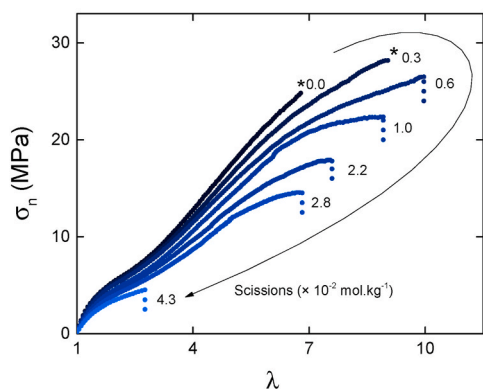


**Fig. 8.** Mechanical and structural changes under stretch of the PEBA sample presenting  $1.0 \times 10^{-2} \text{ mol kg}^{-1}$  scissions induced by immersion at  $80^\circ\text{C}$  (sample arbitrarily chosen as representative). The nominal stress  $\sigma_n$ , the normalized crystallinity index  $CI_{norm}$ , and the amorphous phase orientation parameter  $P_2^{RX}$  are superimposed to highlight structural changes along with their impact on the mechanical behaviour of the PEBA. Corresponding in situ WAXS patterns from which  $CI_{norm}$  and  $P_2^{RX}$  are determined are presented in Fig. 7.

and 0.5, increases with scissions. A slow-down in crystallization kinetics seems common to all samples and  $CI_{norm} = 1$  seems to be close to a plateau value. Further treatment enabled us to estimate that this crystallinity index corresponds to a PTMO crystallinity index of 40%.

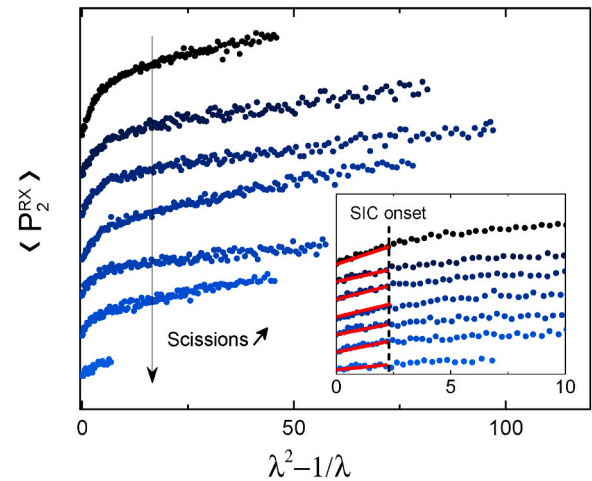
Following a common approach used for thermoset elastomers,  $P_2^{RX}$  is plotted as function of  $(\lambda^2 - \lambda^{-1})$  (Fig. 10). According to the theory of rubber elasticity, the slope, determined between  $\lambda = 1$  and the SIC onset elongation, is directly linked to the crosslink density of these materials. Though the PEBA morphology differs from thermoset elastomers, we can consider that the PA hard domains, where PTMO amorphous chains interconnect, may be viewed as mechanically similar to crosslinks in rubbers (TPEs are frequently described as physically crosslinked elastomers). Besides, we previously showed in section 3.4 that, at low strain, the PA crystalline domains do not undergo any major morphological change upon stretching. The  $P_2^{RX}$  slope decrease observed in Fig. 10 was caused by scissions occurring between hard and soft segments (section 3.1). These scissions globally lead to a decrease in the interconnections between hard and soft phases.

We have also shown in Fig. 9 that the crystallinity index measured at a given elongation between the SIC onset and the high-strain CI plateau, decreases with increasing scissions. This can be illustrated by considering the elongation necessary to reach a specific crystallinity index, arbitrarily chosen as  $CI = 0.5$  in the present case (Fig. 11). It is interesting to note that this elongation is significantly more sensitive to

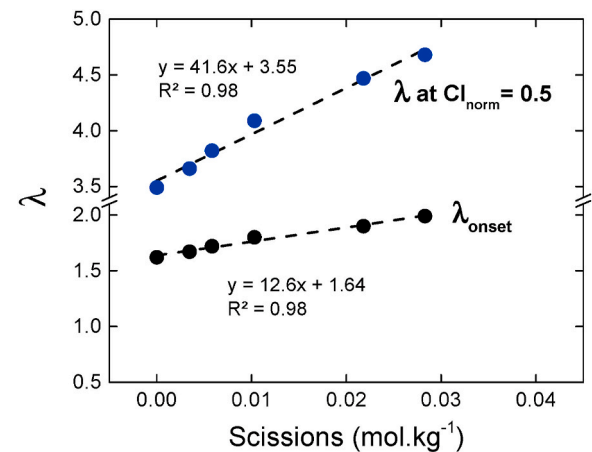


**Fig. 9.** Effect of scissions induced by immersion at  $80^\circ\text{C}$  on the stress and crystallinity of the PEBA. Stars (\*) on the  $\sigma_n$ - $\lambda$  curves indicate that failure was not reached for samples subjected to none and  $0.3 \times 10^{-2} \text{ mol kg}^{-1}$  scissions, due to slippage of the specimen out of clamps. All crystallinity index data were normalized to the highest CI value reached; all samples considered. The SIC onset was determined as the intersection of the x-axis with the  $CI_{norm}$ - $\lambda$  curve linear fit for  $0.1 < CI_{norm} < 0.5$ .

scissions than  $\lambda_{onset}$  (slope of 2.8 against 0.8). The fact that the crosslinking density influences slightly  $\lambda_{onset}$  has already been shown in the literature [24,37]. We can then deduce that the increased elongation required to reach  $CI_{norm} = 0.5$  is not only due to the  $\lambda_{onset}$  increase. In other terms, while scissions cause a SIC onset delay, they also affect the ability of the PTMO segments to crystallize at a given elongation. This is



**Fig. 10.** Effect of scissions induced by immersion at  $80^\circ\text{C}$  on the soft segment orientation behaviour of the PEBA. The  $P_2^{RX}$  slope was determined for  $1 < \lambda < \lambda_{onset-min}$ ,  $\lambda_{onset-min}$  being the smallest  $\lambda_{onset}$  measured (all samples considered).



**Fig. 11.** Effect of chain scission, on the strain-induced crystallization onset and on the elongation required to reach a normalized crystallinity index of 0.5. Data presented here correspond to samples immersed at  $80^\circ\text{C}$ .

illustrated by a slope decrease of the central part of the  $CI$ - $\lambda$  sigmoidal curve (Fig. 9). Consequently, with increasing scissions, a higher strain is required to reach a given crystallinity. A possible interpretation is that the chains that underwent scission, being now pendant or free, are not mechanically active anymore, and thus do not stretch. Consequently, they do not contribute to the SIC.

### 3.6. SIC contribution to the stress

SIC is known to reinforce elastomers and increase their properties at break, hindering fracture propagation. Though this phenomenon is commonly admitted, it is complicated to actually evaluate the crystal-lites contribution to the mechanical behaviour. In an attempt to address this point, the stress was plotted as a function of the crystallinity index, for all samples (Fig. 12). All curves accurately overlap up to  $CI_{norm} = 0.7$ , whatever the degree of scissions. At first, the stress value increases without any change in crystallinity, as the low strain behaviour is driven by the amorphous phase (stretching of the soft segments). Once SIC initiates, a steady stress increase is observed with increasing CI. This remarkable correlation between stress and crystallinity demonstrates that the strain-induced crystallization of the soft segments is the primary phenomenon driving the stress response of the PEBA under uniaxial tension. The stress decrease observed with increasing scissions at a given elongation (Fig. 9) then results from a weakening of the SIC.

To further test this relationship, another parameter than chain scissions was considered: the testing temperature. In situ XRD tests upon stretching were performed at different temperatures, from 20 to 50 °C, on unaltered PEBA samples. Increasing the temperature significantly affects the SIC phenomenon, increasing the energy barrier that SIC needs to overcome in order to occur. Though the temperature significantly influences the mechanical behaviour and the PTMO crystallization upon stretching, the corresponding  $\sigma$ - $CI$  curves overlap with the results obtained from varying the chain scissions (Fig. 12). This strengthens our observation: whatever the degree of scissions or the testing temperature, and even though both parameters greatly affect mechanical and SIC behaviors, a strong correlation is found between stress and crystallinity content.

Conclusions are less straightforward regarding the stress at break (reported in Fig. 6 for conventional tensile testing). At high elongation (or high CI), another phenomenon seems to overtake the SIC contribution, resulting in the curve discrepancy from  $CI_{norm} = 0.7$  in Fig. 12. This phenomenon is scissions-dependent, as it is the most substantial for the unaltered sample, and then decreases with increasing scissions. At high elongation, the CI was observed to present a plateau, as SIC seemed to reach an equilibrium or a saturation point (Fig. 9). Meanwhile,  $P_2^{RX}$  still increases above  $CI_{norm} = 0.7$ , reflecting those amorphous chains keep orienting. The sharp stress increase seems thus to originate from these chains, possibly reaching their full stretch conformation.

Hydrolysis was used to selectively modify the macromolecular structure a poly(ether-block-amide) copolymer (PEBA) and to investigate the strain-induced crystallization (SIC) contribution to the mechanical behaviour. Hydrolytic scissions were shown to predominantly occur at the ester function located between PA hard and PTMO soft segments, in the soft phase. This approach is particularly relevant, as scissions do not affect the PA crystalline domains, which was confirmed with static XRD analysis. It enables the behaviour of a range of PEBA samples presenting a given hard phase to be investigated, as they only differ by their soft phase macromolecular structure, that depends on their scission extend.

In situ XRD analysis combined with uniaxial testing enabled a remarkable correlation between stress and crystallinity to be highlighted, whatever the scission degree PEBA to which samples were

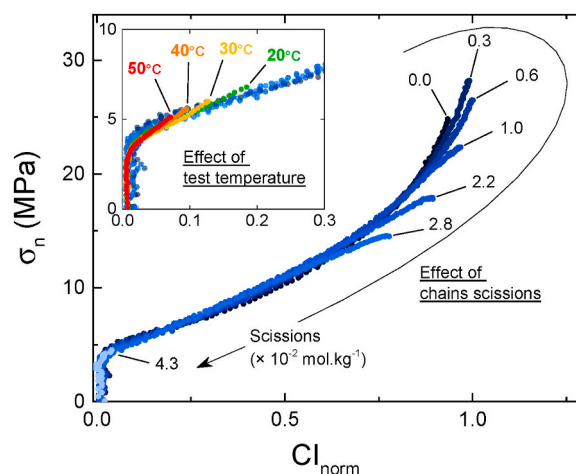


Fig. 12. Master curve between nominal stress and normalized crystallinity index of the PEBA presenting varying scission levels induced by immersion at 80 °C. Unaltered samples (not subjected to any scissions) were also tested at different temperatures.

subjected. This demonstrates that SIC is the driving phenomenon determining the PEBA stress response upon stretching. Consequently, with increasing scissions, the stress decrease observed at a given elongation can be fully interpreted as a consequence of a SIC weakening. Further tests, performed at different testing temperatures, confirmed this observation: even though the testing temperature and the chain scissions both significantly affect the SIC phenomenon and the PEBA mechanical properties, a strong correlation between stress and crystallinity is still observed. Overall, strain-induced crystallization is identified as a major phenomenon in understanding the mechanical behaviour of PEBA.

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### Notes

The authors declare no competing financial interest.

### CRediT authorship contribution statement

**Antoine Bardin:** Investigation, Data curation, Writing – original draft, Writing – review & editing. **Pierre-Yves Le Gac:** Conceptualization, Writing – review & editing, Visualization, Supervision. **Pierre-Antoine Albouy:** Conceptualization, Writing – review & editing, Visualization, Supervision. **Hervé Bindi:** Conceptualization, Writing – review & editing, Visualization, Supervision. **Bruno Fayolle:** Conceptualization, Writing – review & editing, Visualization, Supervision.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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