

Rigidity of Heat-Treated Oriented Isotactic Polypropylene

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Received 23 February 2006; accepted 29 June 2006

DOI 10.1002/app.25010

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Uniaxially oriented commercial films of isotactic polypropylene were strained with ends keeping fixed and subjected to the heat treatment at temperatures from 50 to 200°C. The rigidity of annealed samples was characterized by the value of tangent modulus, E_t , determined graphically at the initial portions of stress–strain curves. The structural changes in the samples were studied with the help of the IR and low-frequency Raman spectroscopies. The smallest E_t values were

obtained for the low-strained films, while the tangent moduli measured for highly strained samples exceeded the value for the original (untreated) film. The most prominent positive effect was achieved after annealing the samples at 90°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6074–6080, 2006

Key words: Raman spectroscopy; mechanical properties; polyolefins; infrared spectroscopy

INTRODUCTION

The rigidity of polymers is related directly to the supermolecular structural ordering. A routine way that is commonly used to gain the rigidity of polymeric materials is the orientation drawing, which results in both axial and transverse ordering of macromolecular segments. However, during the working life of polymeric products, the elements of so constructed regular structure undergo the stress and temperature impacts that cause, respectively, the mechano- and termodestruction of polymer chains. The chain breaking, on the one hand, reduces the connectedness of the structural units with worsening the mechanical properties of a polymer, and, on the other hand, facilitate some structural rearrangements that lead to the formation of harder elements, such as conjugated double bonds that increase the rigidity of the macromolecules¹ at the molecular level, and “bridging” structures^{2,3} at the level of supermolecular organization. Therefore, the effects of strain and heat exposition (which are commonly occurring in various applications of polymeric materials) on the mechanical properties depend on many structural parameters, whose contribution to the final result could be estimated reliably only from experimental studies.

This work concerns with the heat- and strain-induced modifications in the properties and structure of oriented isotactic polypropylene (i-PP). The i-PP is

used in many applied areas. The world production of this material is about 2 millions tonnes per year. The i-PP has a range of remarkable features that distinguish it from other commonly used polymers: low specific density (~ 0.92 g/cm³), good elastic properties under short-time action, high chemical resistance, almost zero hygroscopicity, and good dielectric properties. At the same time, there are certain restrictions for its application in some fields issued from its relatively low glass transition temperature and noticeable creep under long-term loading.^{4,5} The i-PP is highly vulnerable to all types of degradation because of its chemical structure with a labile tertiary carbon atom in the main chain.⁵ One should expect significant changes in its structure and mechanical properties after heating and straining. In this connection, the rigidity is one of the important parameters that determine the behavior of the i-PP-made films and fibers under real conditions.

In a previous work,⁶ the transformation of the supermolecular structure of axially-oriented i-PP films was studied under condition of isometric stress relaxation at the room temperature. It was shown that the process of stress relaxation is accompanied by both breakage of chemical bonds and redistribution of lengths of straight segments. In this study, some structural factors that determine the rigidity of uniaxially-strained i-PP were considered in dependence of the heat treatment conditions imposed on stretched films.

The results of mechanical tests were interpreted in terms of changes in the molecular structure, observed with the help of the IR and low-frequency Raman spectroscopies.

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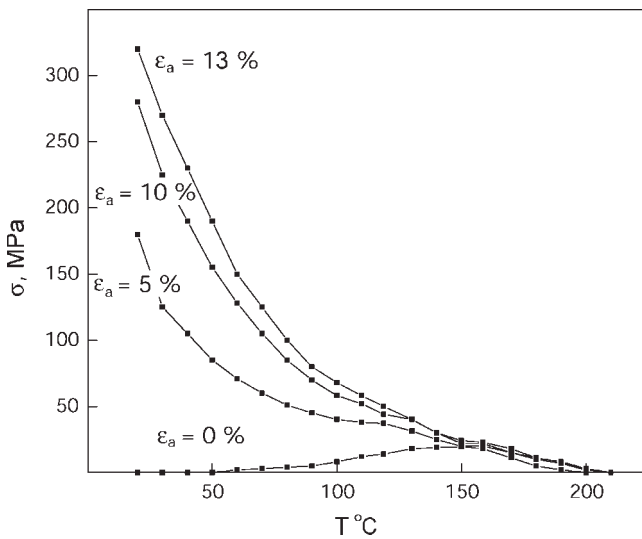


Figure 1 Isometric heat curves for strained i-PP films. ϵ_a denotes the strain applied during the annealing procedure.

SAMPLES AND TECHNIQUES

The commercial films of 60 μm thick with draw ratio (λ) equal to 6 were strained up to the relative elongation from 2.5% to ultimate strain ($\epsilon_r \sim 20\%$) and annealed with their ends keeping fixed at temperatures up to $T_a = 220^\circ\text{C}$ for 1 h, in air. Molecular weight (M_w) of the polymer was 2×10^5 , the ultimate strength $\sigma_r = 580$ MPa.

The mechanical tests of the original and heat-treated films were performed on a universal Instron 1122 Tensile Tester. The strain rate was 50 mm/min. The rigidity of samples was estimated from the values of the tangent modulus $E_t = \partial\sigma/\partial\epsilon$ (here σ is the tensile stress), determined from the slope of stress-strain (σ versus ϵ) curves at the initial stage of straining.

The IR experiments were carried out on a Perkin-Elmer Fourier spectrometer Model "Spectrum One" in a transmission mode.

The Raman spectra in the range of longitudinal acoustic modes (LAM) were measured on a Raman spectrometer Spex Model 1401, equipped with a third monochromator. The spectra were recorded in 90° geometry using XX light polarization, and with the film axis collinear to X direction.

Mechanical tests

The effect of heat treatment on the tensile relaxation in strained, ends-fixed films is shown in Figure 1. The case $\epsilon_a = 0$ represents the result of isometric annealing of the unstrained sample. The tensile stress caused by the shrinkage of 6–8% of the sample grows gradually as the temperature increases up to the melting point (160–170°C); the value of σ decreases at higher temperatures. The tensile stress in the strained samples ($\epsilon_a \neq 0$) relaxes dramatically with the temperature

increase; the behavior of all variously strained samples at $T_a > 130^\circ\text{C}$ is very similar.

The initial portions of some stress-strain curves for the original sample and samples annealed at 70, 90, and 130°C are shown in Figure 2; the temperature 130°C is close to the upper processing limit for i-PP. The starting portions of these curves (and similar ones for other ϵ_a) were used for graphical determination of the values of initial tangent moduli displayed in Figure 3 as functions of the strain. One can see a common decrease of the E_t at small deformations, which is changed by a significant increase of the values at

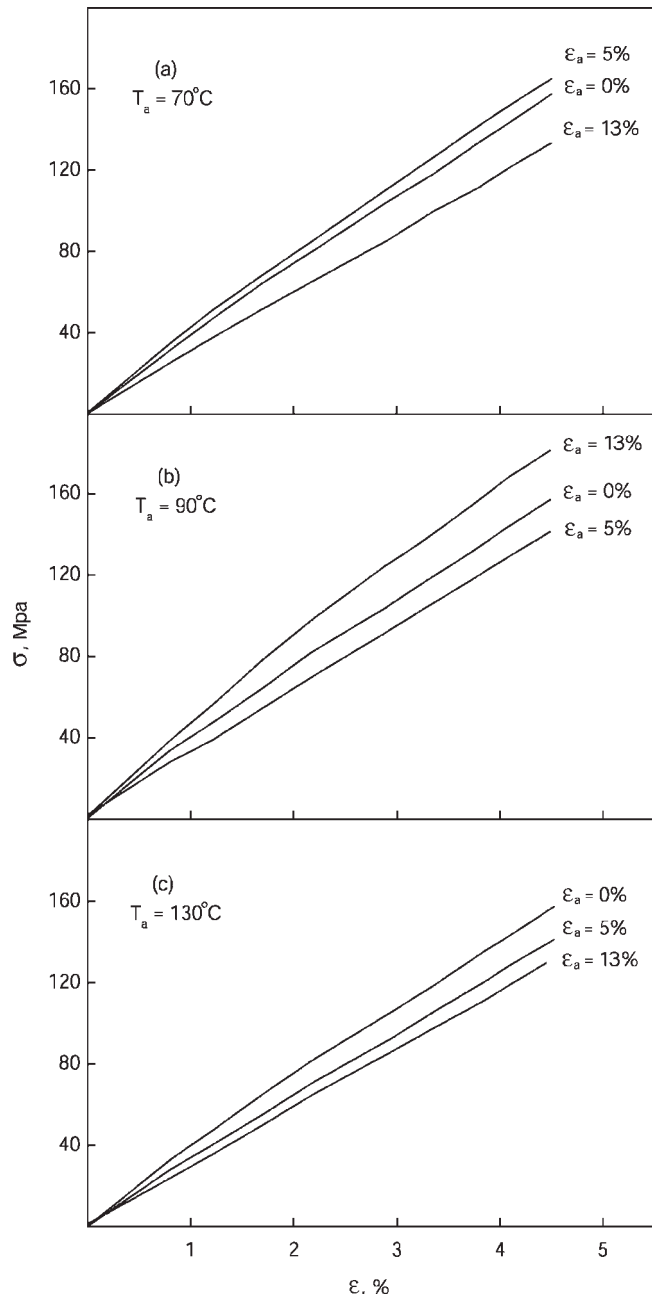


Figure 2 Initial portions of the σ versus ϵ curves for films annealed at (a) 70°C , (b) 90°C , and (c) 130°C under different tensile strain.

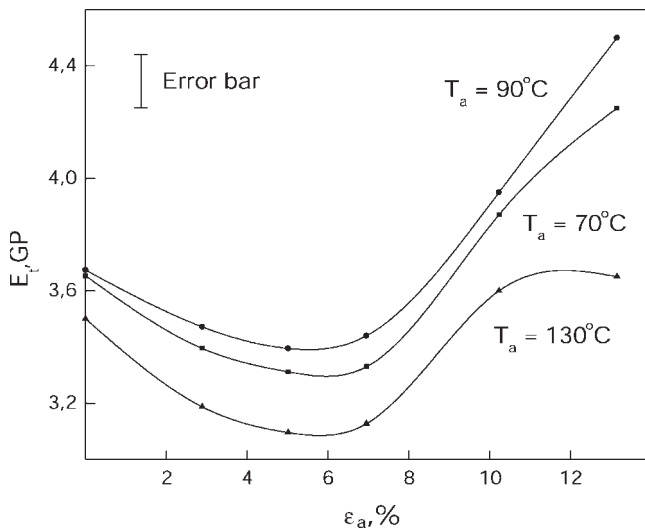


Figure 3 Initial tangent modulus as a function of strain applied (ϵ_a) to samples during the isometric heat treatment performed at different temperatures.

higher strain. The temperature dependences of the E_t values (Fig. 4) demonstrate a gradual growth up to $\sim 90^\circ\text{C}$, and it drops as it approaches the ultimate working temperature ($\sim 130^\circ\text{C}$).

A variable response of the tangent modulus to the changes in the thermal and mechanical conditions of the applied treatment signals the presence of competitive processes that affect the physical properties of i-PP. Obviously, the main (but not exclusive) processes triggered by the heat treatment in strained samples are the degradation of chemical structure and chain coiling/straightening. The corresponding structural modifications occurring in our treated samples were studied using the IR spectroscopy (chain break-

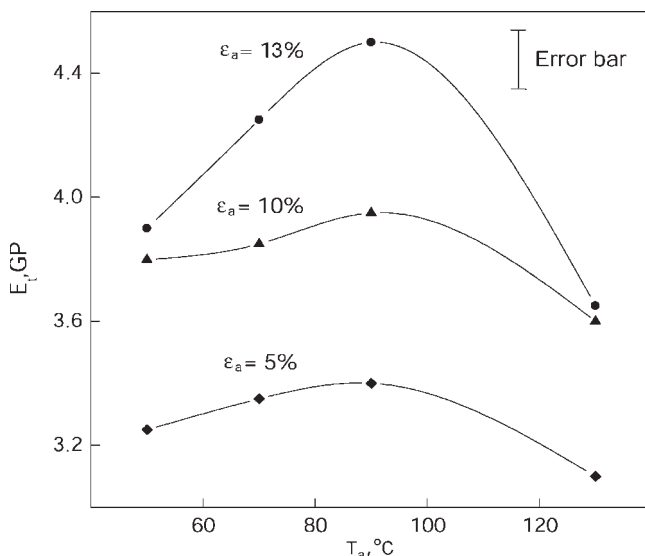


Figure 4 Initial tangent modulus as a function of annealing temperature in samples heated under different tensile strain ϵ_a .

ing) and the low-frequency Raman spectroscopy (chain straightening).

Chain breaking

The IR transmission spectra were recorded in the range of $1800\text{--}1400\text{ cm}^{-1}$, where the bands at 1735 , 1640 , and 1595 cm^{-1} are situated. The former one belongs to oxygen-containing terminal groups, while the two latter bands are referred to the diene groups in, respectively, terminal ($-\text{CH}=\text{CH}_2$) and conjugated ($-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$) positions.⁷ Figure 5 shows the changes in the spectra of samples annealed at 130°C . The intensity of the 1735 cm^{-1} band was not sensitive to the sample treatment because its formation in destructive processes is limited by the accessibility of the air oxygen. The optical densities of the newly appeared bands at 1640 and 1595 cm^{-1} (D_{1640} and D_{1595}), which are proportional to the concentration of oxygen-free products of the chain breakage in i-PP, were measured as ratios to the optical density of the band at 1445 cm^{-1} (D_{1445}) used as a reference. The latter band is due to vibrations localized on the CH_2 groups,⁷ the concentration of which is, in fact, independent on the destruction process.

The intensity of the oxygen-free "defect" bands in the untreated sample is very small. The heat treatment

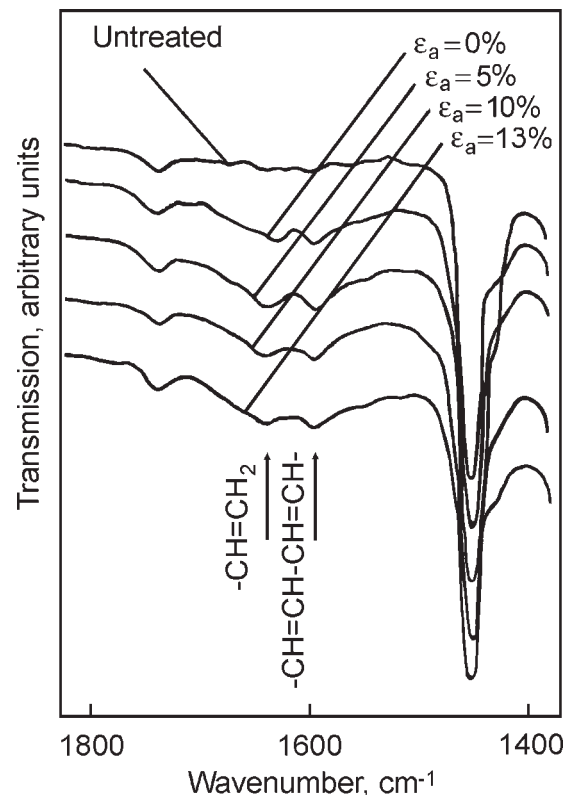


Figure 5 IR transmission spectra of samples annealed at 130°C under different tensile strain in the range of breakage products absorption.

TABLE I
Relative Optical Densities of the "Defect" Bands in the Samples Annealed at 130°C

ε_a (%)	D_{1640}	D_{1600}	D_{1445}	$\frac{D_{1640}/D_{1445}}{+ D_{1600}/D_{1445}}$
0 ^a	0.011	0.009	0.075	0.26
0 ^b	0.004	0.004	0.049	0.15
5	0.011	0.009	0.047	0.42
10	0.006	0.005	0.060	0.18
13	0.008	0.007	0.054	0.25

^a Annealing with keeping ends free.

^b Annealing with keeping ends fixed.

causes the appearance of both these bands in the spectrum of the unstrained sample; even greater increase of the band intensity was observed for the annealed strained samples. The calculated optical densities are given in Table I. The spectral changes in the samples heated at 90 and 70°C were qualitatively similar to those detected in the 130°C sample but their absolute values were insufficient to make numerical estimations.

In all cases, the strongest effect of the accumulation of degradation products was observed in the samples strained with $\varepsilon_a = 5\%$, while the amount of newly-formed "defect" groups in the $\varepsilon_a = 10\%$ sample was intermediate between the $\varepsilon_a = 0$ and $\varepsilon_a = 13\%$ samples.

The result of the IR spectroscopic study is in good agreement with the lowest values of the tangent modulus found for the $\varepsilon_a = 5\%$ sample: really, the higher the degree of degradation, the lower the E_t . However, the fact of reduced chain breakage in the most strained $\varepsilon_a = 13\%$ sample remains unclear without taking into account the role of the competitive process:

Chain straightening

The Raman measurements were carried out in the spectral range 5–30 cm^{-1} , where the longitudinal acoustic

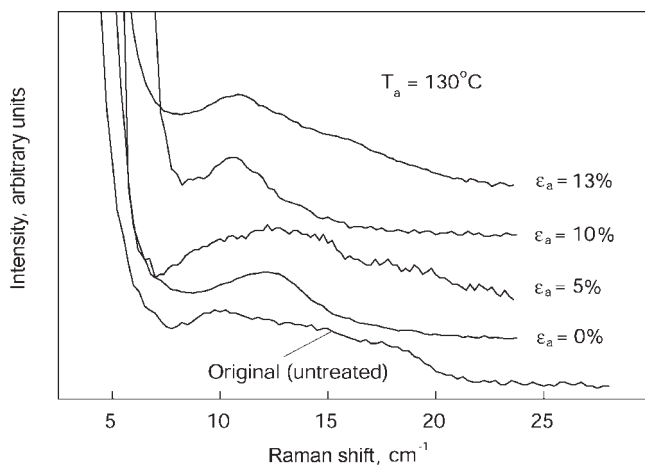


Figure 6 Low-frequency Raman spectra of samples annealed at 130°C under different tensile strain. The spectra are arbitrary shifted along the vertical axis.

modes (LAM) localized along the straight chain segments (SCS) yield a band whose shape is determined by the SCS length distribution. The SCS of different

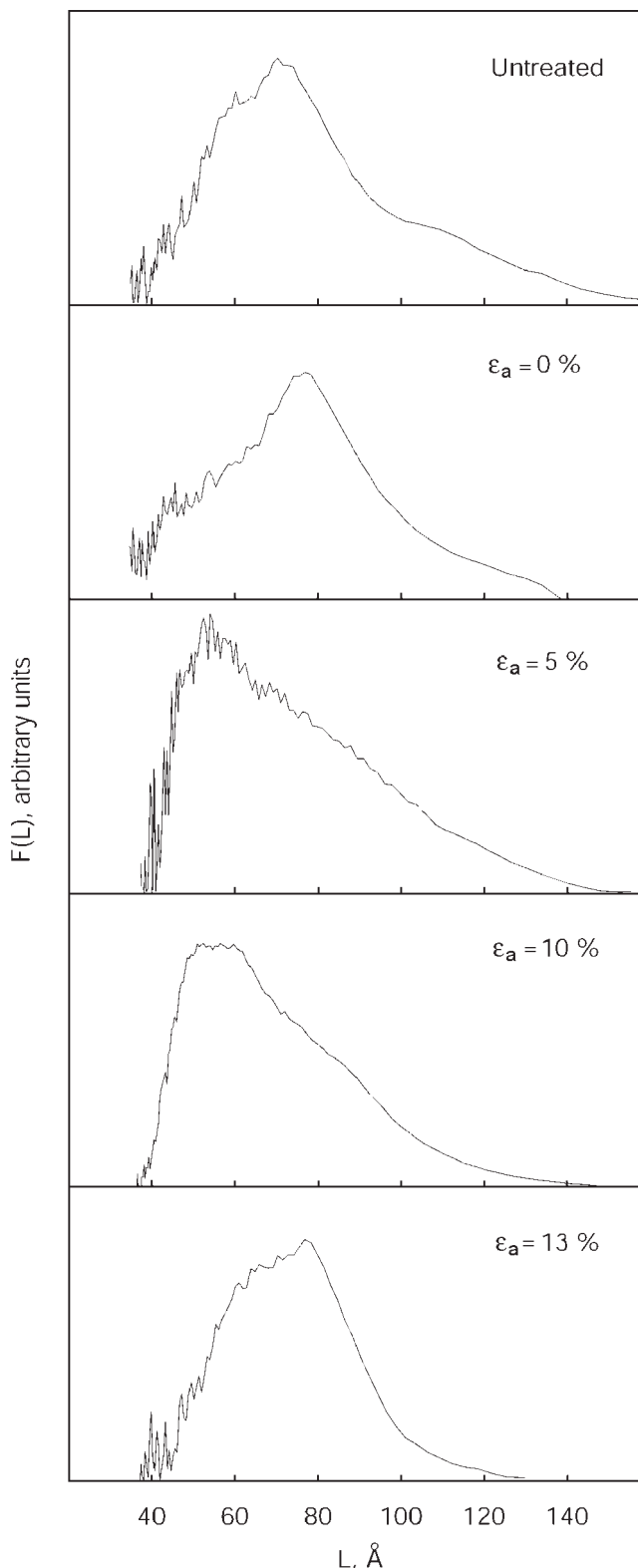


Figure 7 SCS length distributions in samples annealed at 130°C under different tensile strain.

length situated in crystalline or amorphous regions contribute to the LAM spectrum in a similar manner.

The average number fraction of the SCS of length L is given by the distribution function $F(L)$ that corresponds to the Raman intensity of the LAM band, $I_{\text{LAM}}(\omega)$, as:⁸

$$F(L) \propto n(\omega)\omega_L^2 I_{\text{LAM}}(\omega), \quad (1)$$

where ω is the Raman shift measured in cm^{-1} ; $n(\omega) = 1 - \exp(-hc\omega/kT)$ is the Boltzmann factor; $\omega_L = (2cL)^{-1}(E/\rho)^{1/2}$ is the frequency of acoustic vibrations localized on SCS of length L ; c is the speed of light; ρ is the density; E is the Young's modulus in the chain direction.

The Raman spectra of the samples annealed at 130°C are depicted in Figure 6; Figure 7 shows the SCS length distributions calculated from these spectra.

The SCS distributions in all samples are represented by functions $F(L)$, whose asymmetric profiles vary in dependence of the applied treatment. The actual positions of the main maxima are determined by the most probable length of straight segments, L_0 . In oriented samples this value exceeds, as a rule, the thickness of crystal core for account of the contribution of the unfolded SCS penetrating into the amorphous regions. The position of the main peak at $\sim 70 \text{ \AA}$ remains unchanged after the annealing of the unstrained, fixed-ends sample but in the samples subjected to the

strain exposition $\varepsilon_a = 5\%$, the peak shifts to $\sim 50 \text{ \AA}$. At higher strain, the main peak shifts to longer SCS lengths reaching $L_0 \cong 80 \text{ \AA}$ in the $\varepsilon_a = 13\%$ sample.

The longest SCS contributes to the right-hand edge of the distribution. One can see that their maximum length, L_{max} , decrease gradually from $\sim 160 \text{ \AA}$ in the original sample to $\sim 140 \text{ \AA}$ in annealed unstrained one, and the to $\sim 130 \text{ \AA}$ in the $\varepsilon_a = 13\%$ sample.

The SCS distributions in the samples annealed at 90 and 70°C are given in Figure 8 (the original spectra are not shown). The changes with the strain increase in the samples heated at 90°C are similar to those observed after heating at 130°C . However, the final position of the main peak in this case exceeds only slightly the value L_0 for the original sample (75 \AA against 70 \AA).

The changes in the SCS length distribution in samples heated at 70°C are insignificant, however, the left-hand side shift of the main maximum in the $\varepsilon_a = 5\%$ sample is also noticeable.

DISCUSSION

The thermal and mechanic destruction in heated fixed-ends strained films, on the one hand, is gained by the action of tensile stress (both imposed and shrinkage-induced) and, on the other hand, the stress stimulates the chain straightening process facilitated by thermally-enhanced mobility. The rigidity of the polymer

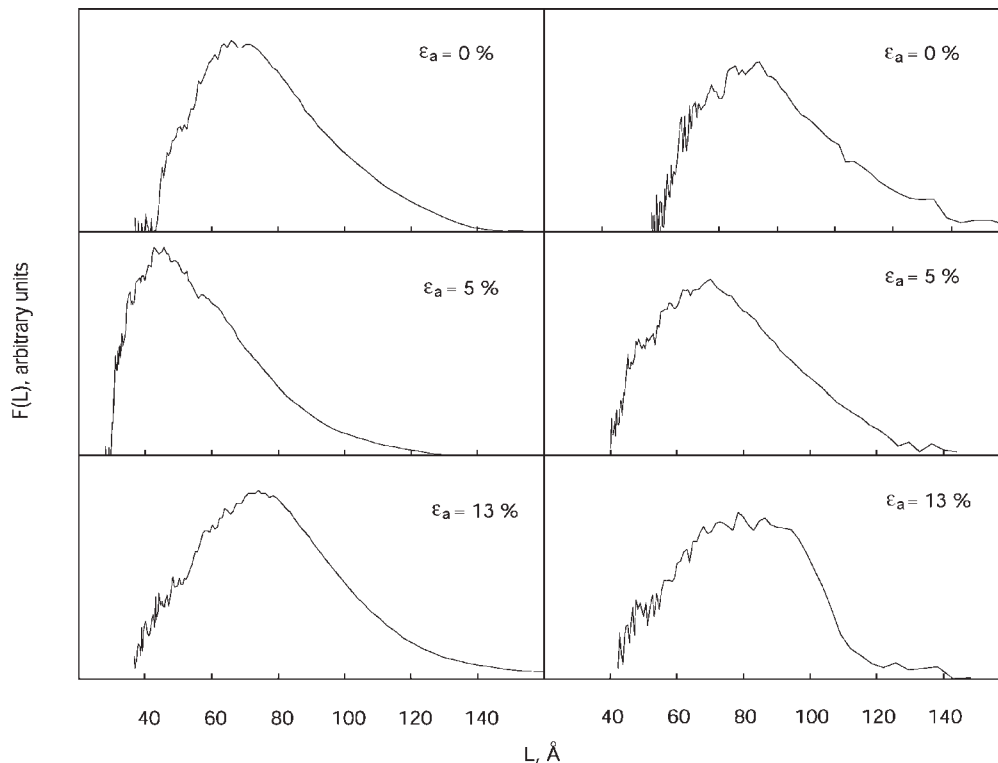


Figure 8 SCS length distributions in samples annealed at 90°C (left column) and 70°C (right column) under different tensile strain.

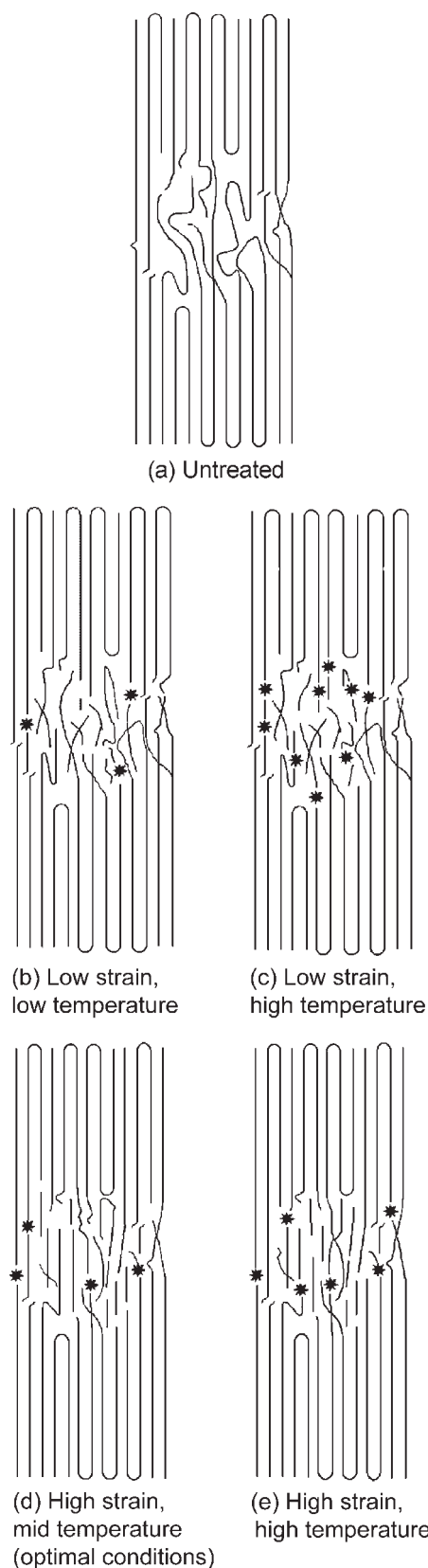


Figure 9 Schematic representation of structural rearrangements in the amorphous regions of oriented i-PP sample in dependence of a particular combination of the applied strain and temperature during the annealing with keeping ends fixed (asterisks denote newly-formed broken chains).

is determined by both these trends. The smallest values of E_t were detected in the samples strained to $\epsilon_a = 5\%$ at all temperatures of annealing (Fig. 5). The $\epsilon_a = 5\%$ samples were the most vulnerable for thermal destruction (Table I), and multiple chain scissions cause the decrease of the rigidity of their molecular structure. Moreover, these samples underwent the most significant reduction of the SCS lengths after the heat treatment (Figs. 7 and 8). The latter effect is also directly related with the breakage of the longest SCS situated partially in the amorphous regions that carries the largest load. The longest chains are the most affected by thermomechanical degradation.⁹

At higher deformation ($\epsilon_a = 10$ and 13%), the action of relaxing tensile stress would be more destructive but the chain breakage becomes hindered by molecular ordering in the amorphous regions. The enhanced process of chain orientation produces zones of parallel arrangement of macromolecules in a form of rigid insertions that lay obstacle for chain scissions due to more uniform stress distribution over individual chain and restricted mobility of macromolecular segments in partially ordered domains.¹⁰ The difference between the types of degradation, which take place in low- and high-strained samples is shown in Figure 9.

In terms of the bridge model introduced by Ward and coworkers,^{2,3} the chain orientation in sufficiently strained semicrystalline polymers promotes the formation of elongated rigid structures, which are characterized by a lateral order (parallel arrangement) of the chains without longitudinal uniformity due to the length variability of the involved SCS.

Unlike the polyethylene, where the bridging structures are constructed, predominantly, by taut-tie molecules (TTM) that link two or more adjacent crystallites,¹¹ in the drawn PP the amorphous regions consist of relatively short SCS which form so-called "rigid amorphous phase" (RAP).⁶

The results obtained in this work confirm this model. The most rigid structures in heated strained sample of i-PP arise at 90°C and under the strain close to its ultimate value (Fig. 3). Under these conditions, the highly developed RAP ("defect bridges") provides the optimal conditions for the formation of a sufficiently rigid molecular framework in the absence of TTM. A complicated effect of the temperature and stress application should be taken in account in some practical applications, both at the stage of processing, and in the working life of a variety of products made of oriented i-PP.

CONCLUSIONS

A practically important case of heating the strained polymeric products was considered in connection with its impact on the mechanical and structural properties of uniaxially drawn i-PP films. The main molecular

processes during the stress relaxation under these conditions involve chain breakage and chain straightening. Both the temperature and strain stimulate the chain destruction; at the same time, heating facilitates the stress-induced chain straightening with forming certain ordered structures in the amorphous regions. The optimal combination of the heat-and-strain action from the viewpoint of gaining the rigidity of oriented films of i-PP was found to be $\varepsilon_a = 13\%$ and $t = 90^\circ\text{C}$. The lowest values of the tangent modulus were obtained under $\varepsilon_a = 5\%$ at all temperatures in the range of 20–130°C.

References

1. La Mantia F. P. In *Frontiers in the Science and Technology of Polymer Recycling*; Akevali, G., Bernardo, C. A., Leidner, J., Utracki, L. A., Xanthos, M., Eds.; Kluwer: Dordrecht, 1998; p 249.
2. Al-Hussein, M.; Davies, G. R.; Ward, I. M. *Polymer* 2001, 42, 3679.
3. Amornsakchai, T.; Olley, R. H.; Bassett, D. C.; Unwin, A. P.; Ward, I. M. *Polymer* 2001, 42, 4117.
4. Karger-Kocsis, J. *Polypropylene: An A-Z Reference*. Kluwer: Dordrecht; 1999; Vol. 1–3.
5. White, G. L.; Choi, D. D. *Polyolefins: Processing, Structure, Development and Properties*. Hansen: Munich, 2005.
6. Tsobkallo, K.; Tikhomirov, A.; Tshmel, A. *Polymer* 2004, 45, 1689.
7. Dechant, J. *Ultrarotspektroskopische Untersuchungen an Polymeren*. Akademischer Verlag: Berlin; 1972.
8. Capaccio, G.; Wilding, M. A.; Ward, I. M. *J Polym Sci Polym Phys Ed* 1981, 19, 1489.
9. Andreassen, E. *Polymer* 1999, 40, 3909.
10. Incarnato, L.; Scarfato, P.; Acierno, D. *Polym Eng Sci* 1999, 39, 749.
11. Pakhomov, P. M.; Khizhnyak, S.; Golitsyn V.; Ruhk, E.; Vasil'eva, V.; Tshmel, A. *J Macromol Sci Phys* 2002, B41, 229.