Influence of Temperature on Molecular Regroupings and Chain Rupture under Stretching Deformation of High-Oriented Linear Polyethylene

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Summary: Conformational regrouping and rupture of macromolecular chains at different stretching deformation temperatures of highly oriented linear polyethylene samples (monofilaments) were studied. Measurements of the relative concentration of rotational isomers and chain rupture were determined by IR spectroscopy. Regroupings occur in the highly oriented polymer when elastic stretching of the sample exceeds a threshold value, irrespective of deformation temperature; this is assumed to be due to steric conditions that influence the cooperative transition of coiled-chain isomers in the extended isomeric conformational state.

Polymer stretching at elevated temperatures, in comparison with room temperature, occurred at considerably lower loads and showed increases in elastic deformation, extent of conformational regroupings of molecular segments and reduction in the number of macromolecular ruptures. Deformation at identical values was accompanied by a smaller decrease in concentration of coiled-chain rotational isomers. The number of molecular chain ruptures, which is proportional to stress load, appeared to be unaffected by temperature.

It is proposed that the small decreases observed in the content of coiled-chain isomers and of chain rupture with deformation are facilitated by macromolecular slippage processes that occur through polymer crystallites.

Introduction

Polymer deformation and fracture processes have been found to be highly sensitive to the changes in temperature, pressure, and strain rates[1-3]. The role of individual chains on polymer deformation and chain stretching was also studied[4] as well as the role of tie molecules on yielding deformation of isotactic polypropylene[5].

Based on the conformational structure of flexible macromolecular chains[6-8], stretching (extensional) deformation of crystalline polymers would be expected to be accompanied by a re-distribution in the amount of the different rotational isomers and by extended conformations of the macromolecular chain.

Studies on polymer chain ruptures and molecular regroupings during orientation drawing and elastic deformation of linear polyethylene at room temperature has revealed[9,10] that the importance of the conformation mechanism of elastic deformation in oriented flexible-chain

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crystalline polymers. Orientation drawing and elastic deformation of linear polyethylene films are accompanied by a decrease in the content of coiled-chain isomers, and an increase in the extension of the *trans*-isomer segment of the molecular chain, mainly in the amorphous region of the polymer. Molecular regroupings depend on ordering and the conformation state of the amorphous region of the polymer. It has been shown[7] that a decrease in the number of coiled-chain isomers is linearly dependent on the extent of orientation stretching.

The purpose of the present study is to clarify the influence of temperature on the mechanical stimulation of molecular regroupings and on chain ruptures during orientation stretching of linear polyethylene samples (monofilaments).

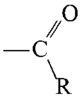
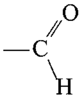
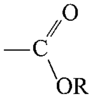
Experimental

Fibers of highly oriented linear polyethylene were used. Fibres were oriented at elevated temperature using local heating to prevent thermal degradation of the polymer. Previously described[9-11] infrared spectroscopic methodologies were used to measure the relative number of macromolecular segments with different rotational isomers and the extent of chain ruptures that occurred at different temperatures. IR spectra of the monofilaments were recorded, over 30min, using a specially constructed oven for a micro- attachment to the IR Spectrometer [11].

Results and Discussion

IR spectra in the region of CH_2 wagging vibration modes for the different coiled-chain isomeric molecular segments and changes in the stretching deformation of the highly oriented linear polyethylene filament at 80°C are shown in Figure1. Changes in the concentration of polymer segments in the coiled-chain isomer state was defined in terms of changes in the intensity of infrared absorption bands of the methylene wagging vibration modes[12]. The amount of chain rupture was defined in terms of the increase in the concentration of the terminal groups; these groups and their corresponding IR bands are shown in Table 1.

Table 1. Molecular groups and their corresponding infrared vibration modes [13-17].

Wavenumber, cm^{-1}	Molecular group	Vibration mode
910	$=CH_2$	out-of-plane deformation mode of CH_2 (terminal $-CH=CH_2$)
965	R-CH=CH-R'	out-of-plane deformation mode of CH (trans-in-chain, -CH=CH-)
1070	R-OH	stretching mode of C-O bond
1379	$-CH_3$	deformation mode of CH_3
1715	 $-C(=O)R$	stretching mode of C=O bond (ketones, saturated carboxylic acids and their dimers)
1735	 $-C(=O)H$	stretching mode of C=O bond (saturated aldehydes and esters)
1745	 $-C(=O)OR$	stretching mode of C=O bond (saturated esters and ketoesters)

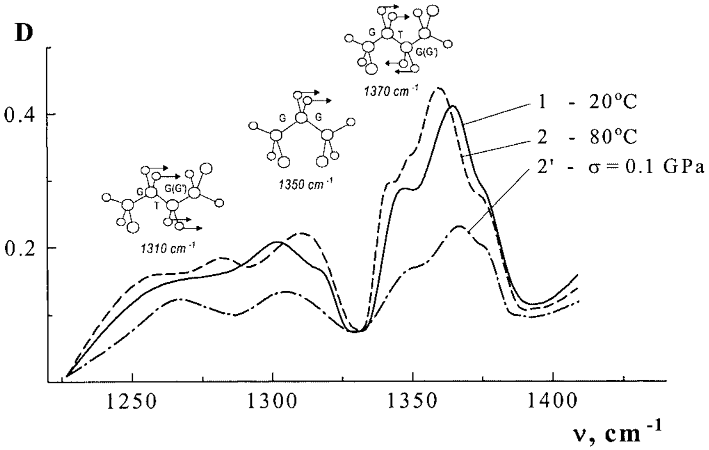


Figure 1. IR absorption spectra of highly oriented linear polyethylene monofilament, with corresponding molecular segments of different coiled-chain rotational isomers; 1- unloaded initial sample, 2- sample 1 at 80° C , 2'- deformed sample at 80°C.

Changes in the relative concentration of coiled-chain rotational isomers are shown in Figures 2 and 3, respectively; the absorption bands were deconvoluted graphically[17].

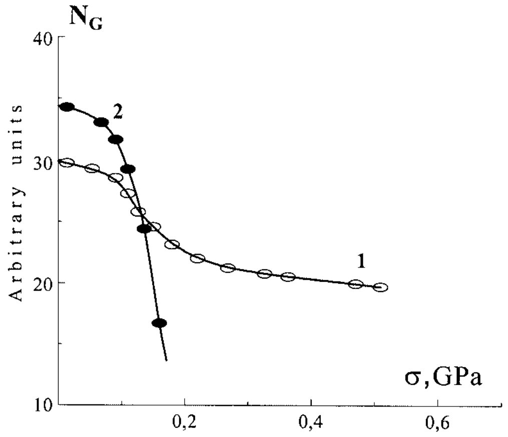


Figure 2. Changes in the relative content (N_G) of coiled-chain rotational isomers as a function of extensional load (σ) at 20°C (1) and 80°C (2).

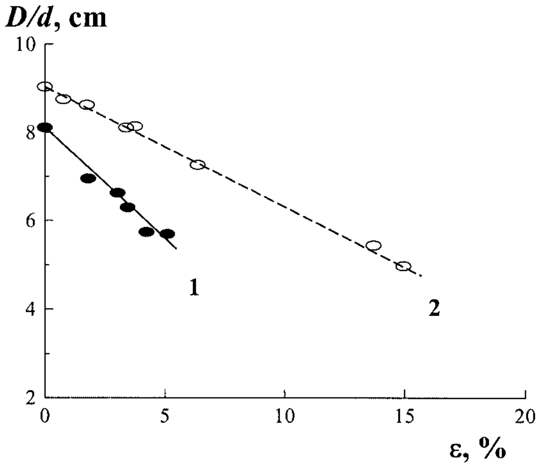
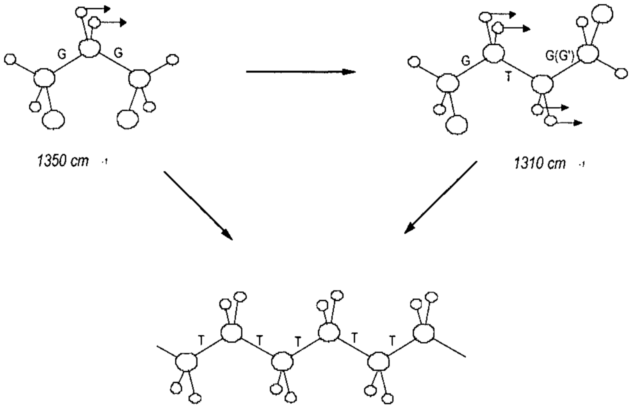


Figure 3. Changes in the intensity of absorption band at 1350 cm^{-1} as a function of elastic deformation (% strain, ε) at 20°C (1) and 80°C (2).

The molecular regrouping of the -GG- rotational isomers to -TG- and to -TT- isomers may be represented as follows



The infrared data (see Figure 1) show that, in oriented linear polyethylene, conformational reorganization takes place after exceeding a threshold value of elastic stretching for the sample irrespective of temperature. This preliminary extension creates steric conditions for cooperative transition of the kink-isomers in the extended *trans*-isomeric states. As a result of this deformation, the highly oriented polymer sample acquires greater mobility. Limits of loads of deformation within which conformational regrouping takes place characterize dispersions in length and conformation structure of amorphous segments. The more homogeneous and ordered the molecular structure of a polymer is the greater is the tendency for conformational regrouping that corresponds with the deformation. Additional extension of amorphous regions is necessary for further conformational reorganization; longer amorphous segments with kink-isomers are obtained following the extension of relatively short amorphous regions of the macromolecular structure. Extension is achieved through an increase in the extensional load or by slippage and rupture of the short linear macromolecular segments under stress. Under constant external load, further conformational reorganization could take place only if slippage or rupture of extended interconnecting molecular segments can occur. Macromolecular chain slippage in an already extended amorphous segment is a further reason for deformation to occur at high temperature with slower decrease in the concentration of coiled-chain isomers. Polymer chain slippage is further facilitated by weakening intermolecular interactions and by increasing molecular mobility. Molecular chain rupture occurs mainly after extending the conformation of the relatively short amorphous molecular segments (Figure 4).

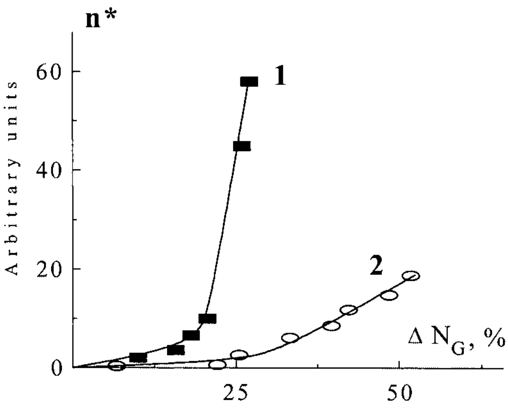


Figure 4. Changes in the relative number of chain ruptures (**n***) as a function of change (decrease) in coiled-chain molecular segments (ΔNG) with gauche-isomers under stretching of polyethylene monofilaments at 20° C (1) and 80° C (2).

Slippage at room temperature is harder and the process demands high local loads; enhanced local loads lead to increased probability of polymer chain ruptures. It is clear from Figure 5 that, given identical initial molecular and supramolecular structure, the number of chain ruptures is proportional to the stress load irrespective of the temperature during extension.

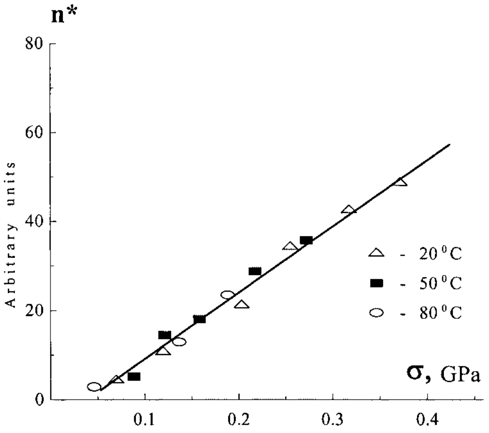


Figure 5. Number of relative chain ruptures (**n***) as function of deformation load (σ) at different temperatures.

Weakening of intermolecular interactions and increasing molecular mobility, with increasing temperature, facilitates polymer chain slippage; at elevated temperature, polymer stretching occurs at considerably lower loads causing fewer macromolecular ruptures. On the other hand, rupture of overstrained macromolecular segments leads to an increasing number of chain slippage. However, as only few localized chain ruptures take place, chain-slippage processes play a major role in this type of deformation.

Molecular regroupings, chain slippage and chain rupture during polymer deformation depends on ordering and the conformational state of interconnecting macromolecules in amorphous regions, and in folds and loops on crystalline surfaces and in entanglements. A biphasic model of deformation for linear highly oriented flexible-chain crystalline polymers of fibrillar microstructure with alternating amorphous and crystalline regions is shown in Figure 6.

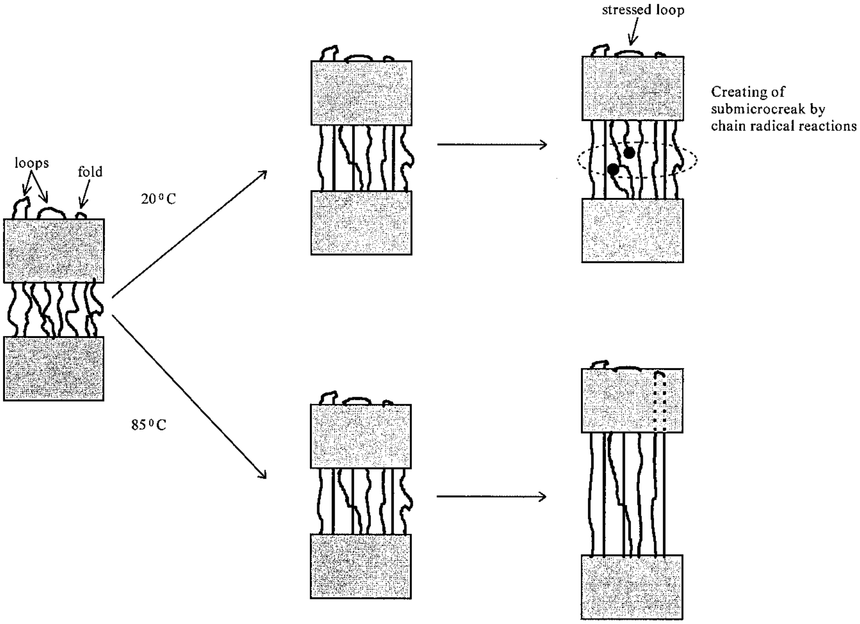


Figure 6. Scheme for a fibrillar structure fragment of a loaded highly oriented semi-crystalline polymer.

Different conformation states, kink-isomers of macromolecular sections are found in the amorphous regions of the polymer. There is definite amount of chain-folding, with regular adjacent re-entry of the chain into polymer crystallites' surfaces, as observed in the crystal structure of polymer single crystals, in addition to the main loops and interconnecting chains[18-20]. Molecular folding in polyethylene crystallites has been observed by atomic force microscopy[21].

Chain folding with regular adjacent re-entry of the chain into polymer crystallites' surfaces can be shifted into polymer crystallites under conditions of high temperature extensional deformation. The relatively shorter interconnecting polymer chain in *trans*-extended conformation states undergoes slip and ruptures. Maximal loads on a chain are limited by the amount of load that causes macromolecular slippage out of crystallites. Thus, an unconstrained macromolecule would not rupture. A favorable condition for chain rupture is realized in stressed sections of a macromolecule fixed on polymer crystallite surfaces or in entanglements. Chain ruptures can also stimulate chain radical reactions and formation of microcrack[2]. Molecular segments, with coiled-chain isomeric links, have relatively low modulus of elasticity and require very little load for deformation; chain slippage out of crystallites can then be ignored.

Conclusion

Our study shows that conformation regrouping and reorganisation in highly oriented polymers occur in a sample, after exceeding a definite value of elastic stretching, irrespective of deformation temperature. The initial chain extending creates the steric conditions for cooperative transition of the kink-isomers in the extended *trans*-isomeric states. As a result of this deformation, such highly oriented polymer sample acquires additional mobility. By comparison with room temperature, polymer stretching at elevated temperatures occurs at considerably lower load values, showing increases in elastic deformation value, extent of conformational regrouping of molecular segments and a decrease in the number of macromolecular ruptures. The deformation observed, under the same load, was accompanied by a smaller decrease in the concentration coiled-chain rotational isomers.

Chain rupture occurs mainly after conformation extending of relatively short interconnecting molecular chains. The number of molecular chain ruptures appears to be proportional to the stress load value irrespective of the temperature of the polymer sample during stretching. Slippage of macromolecular chains, with an already extended amorphous segment, at relatively small deformation loads is another reason that would explain the observation that deformation at higher temperature takes place with a slower decrease in the concentration of coiled-chain isomers and with a significant decrease in the number of chain ruptures.

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