

RECOVERY OF AMORPHOUS POLY(ETHYLENE TEREPHTHALATE) FILM UNIAXIALLY DRAWN JUST BELOW THE GLASS TRANSITION TEMPERATURE*

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Abstract Isothermal recovery in the macroscopic length of homogeneously deformed specimens of amorphous poly(ethylene terephthalate) (PET) film sample uniaxially drawn at 69°C to the draw ratios $\lambda_0 = 1.26\text{--}2.20$ were studied at temperatures around the glass transition temperature ($T_g = 73^\circ\text{C}$). Experimental results indicate that the length recovery took place in two distinct steps: a fast first step (fast relaxation) followed by a slow second step (slow relaxation). The relaxation processes were accompanied by the reversion of *trans*-conformers (1340 cm^{-1}) to *gauche*, and the dichroic function of the 1340 cm^{-1} band characterizing the segmental orientation along the chain direction decreased to a very low value at the end of the fast relaxation. This fact led us to assign the fast relaxation as the segmental orientation while the slow relaxation as relaxation of the global chain orientation. It was found that the slow relaxation follows a single exponential function, with relaxation times strongly dependent on the temperature resembling the glass transition process. The fast relaxation does not follow a single exponential decay, presumably a distribution of relaxation times is involved.

Keywords Poly(ethylene terephthalate), Uniaxial drawing, Recovery, Orientation

INTRODUCTION

Deformation of amorphous polymers below their glass transition temperature T_g , either under uniaxial drawing, hydrostatic extension, plane-stain compression, unidirectional compression and torsion could reach up to hundred percent or more after yielding. This has usually been termed the plastic deformation. However, when the drawn sample is heated above its glass transition temperature T_g , the sample will completely recover in a short time to its undeformed state^[1-5]. Consequently the nature of the large deformation observed is not of plastic deformation, but rubbery deformation of flexible chain polymers under stress, the recovery of which is so slow at temperatures below T_g that the deformation remained quasi-permanent. Therefore, it is not appropriate to understand this kind of "plastic deformation" from the viewpoints of dislocation and defects patterned from plastic deformation of metals. In fact, in the early forties this kind of deformation was correctly termed forced rubbery deformation^[6, 7]. The mechanism of stress induced glass to rubber transition is so far not understood. The rate of recovery of this strain induced rubbery deformation is of course highly temperature dependent. At temperatures below T_g it was observed that the slow recovery process took place in two stages^[4, 5, 8]. A fast component of recovery was found to be thermally activated at temperatures some 50 K or more below T_g , while the slow component of recovery was thermally activated around T_g ^[5, 8].

Because of craze formation leading to brittleness of amorphous polymers like polystyrene, polymethylmethacrylate, etc. on uniaxial drawing below T_g , the above mentioned studies were performed under unidirectional compression so that large deformation after yielding could be sustained without failure. In this

* This work was supported by the National Key Projects for Fundamental Research, "Macromolecular Condensed State", of Ministry of Science and Technology of China.

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Received June 7, 1999

paper amorphous poly(ethylene terephthalate) film is chosen for the study, which is ductile in cold drawing so that more than 100% deformation could be achieved by uniaxial drawing below T_g . Isothermal recovery of the drawn samples with different draw ratios was followed by changes in the length of the film strip and in the infrared spectrum and dichroism of the film at temperatures slightly above and below its T_g .

EXPERIMENTAL

Preparation of the Uniaxially Drawn Samples

PET pellets were dissolved in chloroform-trifluoroacetic acid (4:1 *V/V*) to a concentration of 9 wt%. A glass plate was dipped into the solution and drawn out, and then placed in an oven at 80°C to get a solution cast film of ca. 10 μm thickness. After the solvent was evaporated, the films were placed in a vacuum oven at 40°C for four days to remove the remaining solvent. The PET film thus prepared was shown to be amorphous by IR and wide-angle X-ray diffraction (WAXD) pattern^[9]. The dimensions of the specimens used for drawing were 20 (length) $\times$ 10 (width) mm. The specimen was heated to 92°C for 8 min then air quenched to room temperature. Then the specimen was uniaxially drawn on a tensile tester with a heating chamber made in this laboratory, at a constant crosshead speed of 30% min^{-1} to a series of draw ratios. Following drawing, the specimen was taken out immediately and air quenched to room temperature, so as to quench the dimensional shape. Draw ratios λ_0 were measured from a series of ink marks 1 mm apart, made on the specimen before drawing. The drawing temperature was 69°C and the draw ratio ranged from 1.26 to 2.20.

DSC Measurements

Thermal investigation was performed on a TA2910 Modulated DSC instrument with a data station. The heating rate was 10°C/min.

Measurement of Deformation Recovery

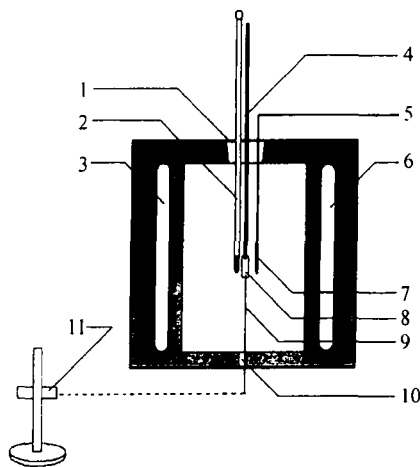


Fig. 1 Schematic diagram of the isothermal recovery oven
1) cork, 2) thermometer, 3) heating wire, 4) metal rod,
5) temperature control, 6) heating wire, 7) thermocouple,
8) sample, 9) silver wire, 10) slot, 11) cathetometer

Specimens of length 12 mm to 18 mm and width ~ 3 mm cut from the homogeneously deformed part of the uniaxially drawn film were used for the recovery experiments. Length recovery of the deformed specimen upon heating was carried out in an oven described schematically in Fig. 1, the temperature of which was controlled to $\pm 0.1^\circ\text{C}$. The metal rod could move up and down through the cork, but it would not slip down by gravity. The top end of the specimen was fixed at the end of the metal rod. A thin nichrome wire (diameter of 0.15 mm and length of 60 mm) was hooked at the bottom end of the specimen. The weight of the wire was so low (10.8 mg) that it would hardly affect the recovery of the sample. The rod, the specimen and the wire could move freely through a

slot of 3 mm in width and 10 mm in length, cut at the bottom of the oven, which did not affect the temperature in the oven significantly. The temperature difference was less than 2°C from the upper part to the bottom part in the oven.

When the temperature inside the oven has reached the recovery temperature, the metal rod was lowered so that its end came out of the slot in the oven. Then the specimen hooked with the wire was fixed to the end of the rod. The rod was then raised quickly into the oven and the recovery process of the specimen began. The deformation recovery of the specimen was directly measured through a cathetometer reading to 0.005 mm, focused to the position of the wire end.

In-situ FTIR Measurement of the Recovering Specimen

A Perkin-Elmer 2000 FTIR spectrometer was used. Every spectrum was the average of 16 scans with a spectral resolution of 4 cm⁻¹. A small oven with a heating equipment made in this laboratory was fixed in the sample compartment of the spectrometer. The polarizer used was a Perkin-Elmer AgBr wire grid polarizer with a polarization efficiency of 98%.

The drawn specimen was cut into three equal parts at the same position along the drawing direction. One part was used to obtain the isothermal recovery curve of the length in the draw direction of the specimen at a certain temperature T_{rec} . The other two parts were used to measure separately the *in-situ* polarization spectra with the electric field vector parallel and perpendicular to the drawing direction during recovery at the same T_{rec} . The 793 cm⁻¹ band which is insensitive to the chain conformation was used for thickness monitoring. The IR dichroic data were used only for the cases that the two parts of the specimen had the same A_{793} before and after relaxation. For uniaxially oriented film the dichroic function (DF) is defined as:

$$DF = [A_{//}/A_{\perp} - 1]/[A_{//}/A_{\perp} + 2] \quad (1)$$

where $A_{//}$ and $A_{\perp}$ are the absorbances of the radiation polarized parallel and perpendicular to the drawing direction, respectively. DF can be used to characterize the orientation of the sample, since the orientation function:

$$f = DF \times [2/(3\cos^2\alpha - 1)] \quad (2)$$

is proportional to DF , where α is the angle between the transition moment of the absorption and the chain direction.

In the IR spectrum of PET the 1340 cm⁻¹ and 1370 cm⁻¹ bands are characterized as *trans* and *gauche* conformers respectively of the —OCH₂CH₂O— segment of the PET chain^[10]. For uniaxially oriented film the structural absorbance A_0 of an IR band is given by:

$$A = (A_{//} + 2A_{\perp})/3 \quad (3)$$

The fraction of the *T* conformers can be obtained by^[11]

$$T = A_{1340}/(A_{1340} + 6.6 \times A_{1370}) \quad (4)$$

EXPERIMENTAL RESULTS

The DSC curve of the PET sample used is shown in Fig. 2, taken at a heating rate of 10°C/min. If the mid point of the endothermic step is taken as T_g , it is 73°C. The beginning of the endothermic step appears around 68°C. The sample is amorphous as shown by the presence of an endothermic step around T_g and an exothermic peak of cold crystallization at 132°C.

Typical isothermal deformation recovery curves expressed as the fraction of residual deformation, $[\lambda(t) - 1]/(\lambda_0 - 1)$, at time t on a logarithmic scale, for the specimens of the PET sample uniaxially drawn to a draw ratio, λ_0 , of 2.0 at 69°C are shown in Fig. 3 for T_{rec} of 68, 72, 75 and 79°C. The curves in the Figure were drawn solely to guide the eye. The nature of $\lg t$ plots should have the initial part of the curve running horizontal at very small t . In the case where the initial relaxation is fast, this horizontal part might not be observable. During drawing the specimen was not crystallizing as shown by the density values, 1.336 g/cm³ before drawing, 1.337 after drawing and 1.337 after complete relaxation, and also shown by 100% relaxation of the deformation at 68°C. The recovery curves clearly indicate a two-step process of relaxation. The first step relaxation, referred to

hereafter as fast relaxation, took place in short times, lasting for about 30,000, 2000, 1000 and 600 for T_{rec} at 68, 72, 75 and 79°C, respectively. The percentages recovered at the end of the fast relaxation step are roughly 30%, 40%, 65% and 90% for T_{rec} at 68, 72, 75 and 79°C, respectively. Although the initial period of recovery was followed with some uncertainty, it is quite sure that the first step of recovery was very fast. A special experiment to evaluate the time for the sample to reach the temperature of the oven after being raised into the oven showed that it took about 8 to reach the equilibrium temperature. In the experiments of deformation recovery after uniaxial compression mentioned in the introduction section the first step of recovery was impossible to obtain accurately owing to the relatively large dimensions of the sample used resulting in a slow temperature equilibration. Thus, in the isothermal recovery experiments of Chang *et al.*^[12] and Quison *et al.*^[4], the data of the initial 10 or more minutes during recovery were discarded. When the first step of recovery came close to be leveled off, the recovery proceeded again rather abruptly, signifying the beginning of the second step of recovery until the deformation recovered almost completely. The slow relaxation covered a long period of time. When T_{rec} was 84°C, the specimen recovered so fast that the process was completed in 2 min so that the recovery curve could not be recorded accurately.

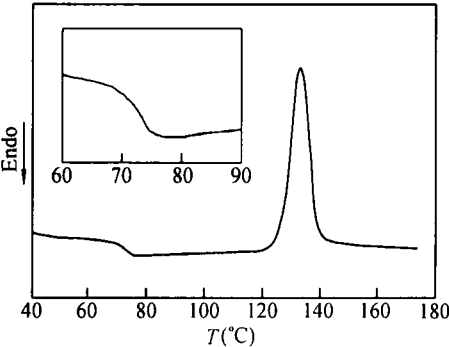


Fig. 2 DSC curve of the undeformed amorphous PET film

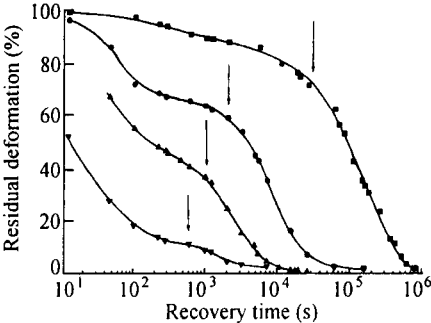


Fig. 3 Recovery of uniaxially drawn amorphous PET specimens at different temperatures
 $T_{def} = 69^\circ\text{C}$, draw ratio=2.00, T_{rec} : ■ 68°C, ● 72°C, ▲ 75°C, ▼ 79°C, the arrows indicating the end of the fast relaxation step

Curves of deformation recovery expressed as $[\lambda(t) - 1]/(\lambda_0 - 1)$ versus time t in log t scale, at $T_{rec} = 72^\circ\text{C}$ for specimens uniaxially drawn at 69°C to different draw ratios, $\lambda_0 = 2.20, 1.53$ and 1.26 , are shown in Fig. 4. The specimens recovered completely at almost the same time of about 10^5 s. It seems to indicate that the fast relaxation step went faster for smaller λ_0 and took a little longer time to reach the transition to the slow relaxation step, while the slow relaxation went slower for smaller λ_0 .

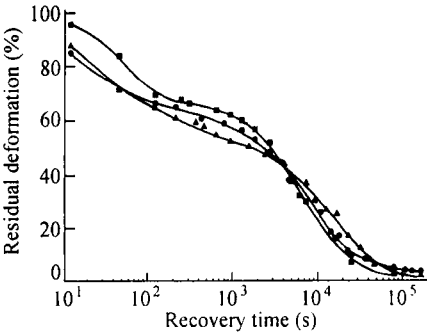


Fig. 4 Recovery of uniaxially drawn amorphous PET specimens at 72°C with different draw ratios
 $T_{def} = 69^\circ\text{C}$, draw ratios: ■ 2.20, ● 1.53, ▲ 1.26

The changes in *trans* population and *DF* for the band characterizing the *trans* (1340 cm^{-1}) conformer in the amorphous region during recovery at 75°C and 68°C for a specimen drawn at 69°C to a $\lambda_0 = 2.0$ are shown in Fig. 5. As the value of α for the 1340 cm^{-1} band is close to zero, the value of *DF* is close to the value of the orientation function.

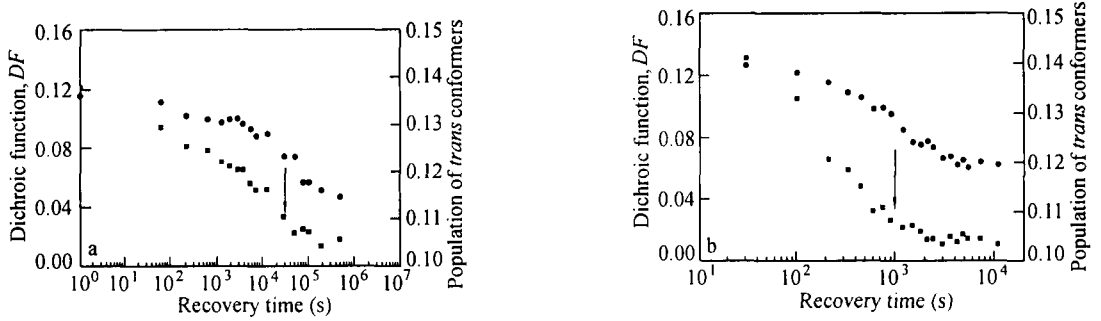


Fig. 5 Changes of the IR dichroic function *DF* of the 1340 cm^{-1} band (■) and population of *trans* conformers (●) during recovery process
 $T_{\text{def}} = 69^\circ\text{C}$, draw ratio = 2.0, T_{rec} : a) 68°C , b) 75°C

DISCUSSION

The complete recovery of large deformation of amorphous PET uniaxially drawn just below its T_g beyond yielding clearly shows that the nature of deformation is not plastic deformation but stress induced rubbery deformation. This rubbery deformation is frozen when the specimen under drawing is quenched to room temperature. When the specimen is heated to the temperature region of its glass transition the deformation will be recovered at a rate depending very much on the temperature T_{rec} as shown in the results of Fig. 3.

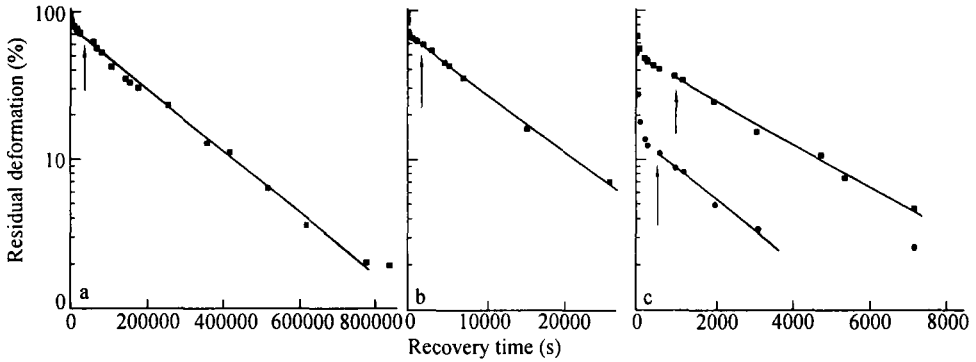


Fig. 6 The same results as in Fig. 3, residual deformation $[\lambda(t) - 1]/(\lambda_0 - 1)$ on a log scale, recovery time on a linear time scale
 T_{rec} : a) 68°C , b) 72°C , c) ■ 75°C , ● 79°C

It is interesting to note that the relaxation of large deformation at T_{rec} in the temperature region of the glass transition takes place in two distinct steps in succession, a fast relaxation step followed by a slow relaxation step. When the fraction of residual deformation, $[\lambda(t) - 1]/(\lambda_0 - 1)$, on a logarithmic scale is plotted versus t on a linear scale as shown in Fig. 6, it appears that the slow relaxation step follows a simple exponential decay for all T_{rec} given in Fig. 3. Because of the large time span from 10 to 8×10^5 s, separate plots are shown in Figs. 6a), b), c) with time axes $0 \sim 8 \times 10^5$ s, $0 \sim 3 \times 10^4$ s, $0 \sim 8 \times 10^3$ s, and $0 \sim 3 \times 10^3$ s, respectively. Best straight lines are drawn through the data points of the slow relaxation step, from which the values of relaxation time τ for the slow relaxation step are obtained as 2.2×10^5 , 1.5×10^4 , 3.0×10^3 and 2.1×10^3 s for T_{rec} of 68, 72, 75 and 79°C , respectively. The temperature dependence is remarkable, and a plot of $\lg \tau$ versus $1/T_{\text{rec}}$ is shown in Fig. 7, which

resembles the behavior of the glass transition in a small temperature span of 10°C, with an apparent activation energy for the process estimated to be 89 kJ·mol⁻¹·K⁻¹ at the high temperature end and 875 kJ·mol⁻¹·K⁻¹ at the low temperature end of the temperature interval.

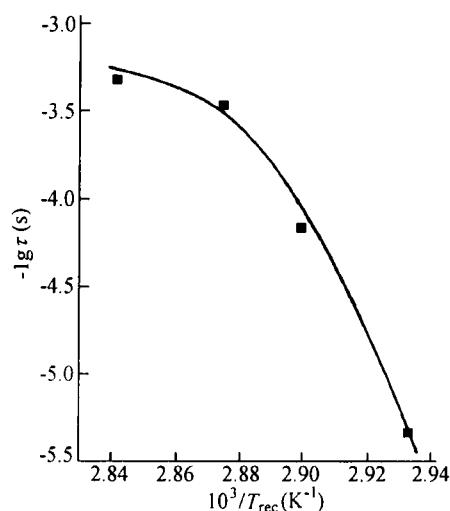


Fig. 7 Temperature dependence of the relaxation time τ of the slow relaxation step

The fast relaxation steps for T_{rec} at 75 and 79°C apparently do not follow a single exponential decay, presumably they involve a distribution of relaxation times. The time needed for the drop of residual deformation to 37% of its initial value, after the extrapolated slow relaxation is deducted from the data, is estimated to be approximately 10 s for both curves. So the fast relaxation is some 500 times faster than the slow relaxation. For T_{rec} at 68 and 72°C the amount of deformation recovery in the fast relaxation is too small to warrant further analysis. It is worth pointing out here that both fast and slow relaxation processes lead to the recovery of large deformation. In fact, at $T_{\text{rec}} = 79^\circ\text{C}$ the main part of deformation recovery was performed in the fast relaxation step, while at $T_{\text{rec}} = 68^\circ\text{C}$ the main part of deformation recovery was performed in the slow relaxation step.

During the relaxation of large deformation, *trans* conformers in the PET chain revert to *gauche* conformers. The decrease of the fraction of *trans* conformers shown in Fig. 5 does not show convincingly a two-step process and the dichroic function decreases to a very low value at the end of the fast relaxation step. As the molecular Gaussian coils in the bulk polymer deform affinely with the macroscopic deformation of the bulk specimen, as demonstrated experimentally by small angle neutron scattering^[13], the recovery of large stretching deformation of the specimen reflects the relaxation of affinely elongated Gaussian coils in a global sense, while the orientational relaxation as shown in the decrease of the *DF* of the 1340 cm⁻¹ IR band reflects the relaxation of local chain segments^[14]. In Fig. 5 it is clearly shown that the relaxation of local segmental orientation reaches a very low value, $DF < 0.03$, at the end of the fast relaxation of the recovery of large deformation. We can therefore assign the fast relaxation step of the recovery of large deformation as the relaxation of local chain segments. During the slow relaxation step of the recovery of large deformation the specimen is in the GOLR state, the state of high global chain orientation but nearly random segmental orientation of amorphous polymers^[14], and the relaxation is the relaxation of the global chain elongation. The difference in the corresponding relaxation times is about two to three orders of magnitude as discussed in the previous paragraph. The segmental relaxation comes from molecular chain motions involving presumably the coupling or cooperativity of internal rotation of chain backbone bonds of a few neighboring chain repeating units, or possibly also including the inter-chain coupling, leading to a spectrum of relaxation times, so that it could not be represented by a single exponential decay function. It is interesting to see that the global chain relaxation could be represented by a single relaxation time, despite the polydispersity in molar mass of the PET sample used. The molecular chain motion of global chain relaxation involves cooperative internal rotation of a longer length of the backbone bonds, presumably to a length

similar to that needed for the realization of rubbery state in glass-rubber transition. In the case of uniaxial drawing of polycarbonate at 170°C ($T_g = 148^\circ\text{C}$)^[15], the segmental relaxation at this temperature, as shown by the decrease of IR orientation function of 1364 cm^{-1} almost to zero, was completed at 10 s before the slow relaxation of the global chain deformation got started and complete recovery was observed after 10^4 s. It seems to be reasonable to expect that the excitation of cooperative internal rotation of the backbone bonds would increase in length as the temperature is increased towards T_g so that a significant amount of global chain relaxation results from segmental relaxation. This interpretation of the nature of two steps of large deformation recovery is also in agreement with the experimental results of temperature scanned relaxation of large deformation^[5, 8] that the first recovery step can be thermally activated at some 50°C below T_g while the second recovery step is thermally activated around T_g . Temperature scanned relaxation experiments^[5, 8] also show that when the deformation is carried out above T_g only one recovery step can be observed. This result can now be understood as the segmental relaxation being already completed during deformation and quenching of the specimen.

The relaxation time spectrum of a Gaussian coil as described by Rouse^[16] does not include the relaxation of local segments and is true only for a single coil as experimentally verified in dilute solutions. In the condensed state of interpenetrated Gaussian coils the relaxation time spectrum could be quite different. The present investigation showed that it consists of two distinct groups of relaxation times, one involving the segmental relaxation and the other the global chain relaxation. The former has a wider spectrum of relaxation time distribution and is at least two or three orders of magnitude faster than the latter. Both relaxation times are temperature dependent. For the global chain relaxation the temperature dependence of relaxation time is characterized by a large temperature dependence of activation energy in a rather short temperature interval which resembles the behavior of glass transition. For the segmental relaxation the extent of cooperativity of internal rotation of neighboring backbone bonds of the chain presumably extends in lengths with increasing temperature approaching T_g . It is not clear at the moment if this segmental relaxation is the same as the sub-Rouse mode observed in the viscoelastic behavior^[17] and photo correlation spectroscopy^[18].

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