Strain Hardening of Polycarbonate in the Glassy State: 
Influence of Temperature and Molecular Weight

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Received 2 October 2003; revised 14 January 2004; accepted 15 January 2004 
DOI: 10.1002/polb.20095
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study is concerned with the temperature and molecular weight dependence of the strain-hardening behavior of polycarbonate. It is shown that the strain-hardening modulus reduces with increasing temperature and decreasing molecular weight. This result is interpreted in terms of temperature accelerated relaxation of the entanglement network. Moreover, it is shown that frozen-in orientations, induced by homogeneous deformations above the glass transition temperature, lead to anisotropic yield behavior that can be fully rationalized (and modelled) in terms of a superimposed stress contribution of the prestrained network. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 2041–2049, 2004
Keywords: polymer glasses; polycarbonate; anisotropic yielding; strain hardening; viscoelasticity

INTRODUCTION

An important aspect of the mechanical behavior of polymers is the strain-hardening response during large strain plastic deformation. It is now well recognized that the molecular description of strain-hardening in glassy polymers involves a rubber–elastic response of the entangled covalent bonded chains. In a hallmark paper, Haward and Thackray1 captured the essence of the large strain deformation behavior of glassy polymers in a one-dimensional constitutive equation combining a nonlinear viscosity, to model the stress-activated yield, process, and a finite extensible rubber–elastic spring, the so-called “Langevin spring,” to describe the subsequent chain orientation hardening. The Haward-Thackray model was extended to the three-dimensional “BPA-model,”2 in which the strain-hardening is described by the three-chain model.3,4 The BPA-model was refined by introducing more detailed representations of the spatial distributions of the macromolecular chains.5,6 Later, Haward7 recognized that finite extensibility might not be relevant for uncrosslinked thermoplastic polymers, and that the development of plastic strain in these materials can also be stabilized by simple neo-Hookean strain-hardening behavior without the restriction of finite extensibility. For a number of polymers it was indeed shown that an asymptotic upswing in stress during plastic deformation, associated with a finite extensible entanglement network was not observed experimentally.8,9

Nevertheless, all models seem to agree that the principal cause for strain-hardening in glassy
polymers is the rubber–elastic response of the entanglement network, although quantitative agreement seems to be lacking. One well-known feature of rubber-elasticity is that the modulus increases as a function of temperature. However, in the relatively few experimental studies of strain hardening in glassy polymers it has always been observed that the strain-hardening modulus decreases upon increasing temperature, which seems to be in conflict with the concept of an entropy-elastic network response. It has been proposed that the temperature dependence of the strain-hardening response originates from a change in chain density \(n\) (number of elastically active chains, which is equivalent to a change in the number of monomer units between entanglements \(N_e\)), because the total number of monomer units is conserved. Following Raha and Bowden, an empirical relation was proposed, to describe the evolving chain density with temperature.

It is well known that even the mechanical response of chemically crosslinked rubbers can be strongly influenced by stress relaxation, and that rubber elasticity strictly only holds for the equilibrium modulus. It, therefore, seems natural to relate the decreasing strain-hardening response with temperature to viscoelastic relaxation of the entanglement network. Because this relaxation process is known to be dependent on molar mass, it can be anticipated that strain hardening will also be dependent on molar mass. Furthermore, it is well known that the long relaxation times associated with relaxation of the entanglement network, allow for orientation of the network and strain hardening even for deformations applied above the glass transition temperature \(T_g\), which can be frozen-in (retained) upon quenching below \(T_g\). It is the objective of this study to characterize experimentally the strain-hardening response of poly-carbonate as a function of temperature and molecular weight, using, among others, a newly developed technique to ensure homogeneous deformation.

In this study, thermal and mechanical treatments will be used to ensure homogeneous deformation. In previous work it was shown that strain localization in polymer glasses is initiated by the nonlinear yield behavior. Strain hardening and intrinsic strain softening respectively stabilize and amplify nonhomogeneous behavior. Unfortunately, the stress dependence of the yield process is a material property and, therefore, it cannot be eliminated as a cause for inhomogeneous deformation behavior below the glass transition temperature.

However, by raising the temperature above the glass transition temperature, thermal agitation overwhelms stress-activated segmental flow, and the material will deform homogeneously like a rubber. Freezing in orientation applied above the glass transition temperature by quenching to room temperature, will result in anisotropic yield behavior, from which information about the strain-hardening behavior can be retrieved.

Another way to promote homogeneous behavior, is to eliminate intrinsic strain softening by means of mechanical conditioning. Large plastic deformations rejuvenate the material up to a saturation level that is maintained when the stress is released. As a result, subsequent testing will not lead to strain softening. In the next sections, these methods will be discussed in more detail.

**EXPERIMENTAL**

The most straightforward way to verify the strain-hardening response of polymer glasses experimentally, is to apply large homogeneous deformations. However, it is well known that most polymer systems, and especially polymer glasses, are prone to inhomogeneous deformation. To circumvent this, an experimental technique was developed in which locally a constant strain rate could be applied to an axis-symmetric hourglass-shaped sample, by means of video-controlled tensile testing (a digital closed loop system). It was also argued that the deformation in uniaxial and planar compression will remain homogeneous, because, contrary to a tensile test, there is no area reduction. This seems to be a rather strong assumption, because the development of shear bands in compression has been observed for a number of polymers. On the other hand, finite element calculations have shown that the effect of shear band formation on the global stress–strain behavior is not very large.

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Dumbbell-shaped specimen were cut from a 2 mm-thick extruded sheet of bisphenol A polycarbonate (Lexan 101, General Electric, number-average molar mass \( M_n \)/H11005 11,600 g/mol, and weight-average molar mass \( M_w \)/H11005 30,500 g/mol), according to ASTM D368 type III. To prevent degradation during predeformation at 160 °C, the material was dried at 80 °C for about 3 days. Before predeformation above the glass transition temperature, the samples were brought 15 °C above \( T_g \) for 15 min, to ensure the same testing conditions for all samples (\( T_g \) = 150 °C). Uniaxial predeformation was imposed using a FRANK 81565 tensile tester at a constant strain rate of 500 mm/min at 163 °C. In this way a range of predeformed samples were obtained up to a draw ratio of \( \lambda = 1.85 \), for which the deformation was visually homogeneous.

After predeformation, the oven was opened to enable rapid cooling to room temperature, to freeze-in the applied orientation. Because the yield stress, is strongly influenced by thermal history, an undeformed sample was given the same heat treatment.

To verify the amount of predeformation, markers were used on some of the samples. After determination of the amount of predeformation, these specimen were brought back to the oven at 180 °C for 15 min, to allow for shrinkage to measure the effective draw ratio. All samples showed complete recovery.

Planar predeformed sheets were generously provided by the university of Leeds (IRC of Polymer Science & Technology). On these sheets, the planar predeformation was imposed at a constant strain rate of 500 mm/min at 163 °C. From these sheets, small dumbbell-shaped samples were cut at different angles with the main principle–strain axis (see Fig. 1). To verify the homogeneity of the predeformation, an identifying grid was printed on the sample. After predeformation only the homogeneously deformed part of the sample was used. The grid lines shown in Figure 1, indicating the manner in which samples have been prepared from the predeformed sheet, are in scale with the real grid observed after pre-deformation.

To determine the anisotropic yield behavior, the uniaxially predeformed samples were tested on a FRANK 81565 tensile tester at four different strain rates, from \( 10^{-4} \) to \( 10^{-1} \) s\(^{-1} \). The dumbbell-shaped samples, cut in different orientations from the planar predeformed sheets, were tested on a Zwick 1432 tensile tester at three rates of strain: \( 10^{-4}, 10^{-3}, \) and \( 10^{-2} \) s\(^{-1} \). All tests were performed at room temperature (21 °C). True yield stresses were calculated assuming constant volume deformation.

The dynamic moduli of both polycarbonate grades were measured at a frequency of 1 Hz as a function of temperature on a Rheometrics RMS rheometer, using a plate–plate configuration.

**Predeformation Below the Glass Transition Temperature**

A way to enable large homogeneous deformations below the glass transition temperature, is to rejuvenate the material through mechanical conditioning at room temperature.

For this purpose, dogbone-shaped, axis-symmetrical tensile bars (see Fig. 2), manufactured from injection-molded bisphenol A polycarbonate rod, were subjected to large strain torsion at room temperature.

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![Figure 1. Schematic representation of the production of small dumbbell-shaped samples from a planar predeformed sheet (thickness: 2 mm). The grid lines were used to verify that the applied predeformation was homogeneous.](image1)

![Figure 2. Tensile bar used for mechanical conditioning below the glass transition temperature.](image2)
temperature. To evaluate the influence of molar mass, two polycarbonate grades were used: Lexan 101 \( (M_n = 11,600 \text{ g/mol}, \text{ and } M_w = 30,500 \text{ g/mol}) \) and Makrolon CD2000 \( (M_n = 9000 \text{ g/mol}, \text{ and } M_w = 18,000 \text{ g/mol}) \). The torsion was applied manually, by clamping the sample in a universal lathe and turning one side to and fro over 720 degrees, with a line on the sample as a reference. After predeformation some of the samples were heated to 180 °C, but no motion due to residual stress was observed. This indicates that, with respect to the strain-hardening response, the samples were returned to their isotropic state. A disadvantage of the method is that the predeformation is not homogeneously distributed and that the central fiber of the sample will not deform (and, therefore, not rejuvenate) at all.

Immediately after rejuvenation, the samples were tested uniaxially on a ZWICK Rel 1852 servo-hydraulic tensile tester \( (20 \text{ kN}) \). The relative accuracy in force and strain measurements was 1%. The tensile tests were performed at several temperatures between room temperature and the glass transition temperature, at constant strain rates. True stresses were calculated assuming constant volume deformation.

RESULTS AND DISCUSSIONS

Characterization of the Untreated Material

For polymer glasses, it is normally assumed that the strain hardening response and the yield behavior are two separate processes, which add up to the total stress–strain relation. Therefore, the nonlinear flow behavior (activation volume) should not be influenced by predeformation or strain hardening. To verify this assumption, first the yield behavior of the untreated material was determined. This untreated material was subjected to the same temperature history as the material predeformed above the glass transition temperature. An Eyring plot of the yield stress versus the logarithm of strain rate is depicted in Figure 3.

In the Eyring approach it is assumed that at the yield point, the material behaves as a generalized non-Newtonian fluid and that the plastic strain rate is approximately equal to the total applied strain rate. In generalized form, the Eyring equation reads:

\[
\dot{\gamma}_{eq} = \frac{1}{A} \sinh \left( \frac{\tau_{eq}}{\tau_0} \right) \tag{1}
\]

Here, \( \dot{\gamma}_{eq} \) is the equivalent shear rate, \( \tau_{eq} \) is the equivalent shear stress, and \( A \) and \( \tau_0 \) are fitting parameters. Here it should be noted that the parameter \( A \) depends on thermal history, but the parameter \( \tau_0 \) not. In case that \( \tau_{eq} \gg \tau_0 \), the equation above can be simplified to:

\[
\tau_{eq} = \tau_0 \left( \ln(2A) + \ln(\dot{\gamma}_{eq}) \right) = \tau_{eq,0} + \tau_0 \ln(\dot{\gamma}_{eq}) \tag{2}
\]

In the case of uniaxial deformation, \( \tau_{eq} = \sigma / \sqrt{3} \) and \( \dot{\gamma}_{eq} = \sqrt{3} \dot{\varepsilon} \). The best fit of the yield data in Figure 3 results in a value for the Eyring parameter \( \tau_0 = 0.73 \text{ MPa} \).

Predeformation Above the Glass Transition Temperature

By deforming the sample above the glass transition temperature it is possible to separate the nonlinear viscoelastic response and the elastic strain-hardening behavior, because the temperature treatment erases residual viscoelastic (memory) effects. Samples, predeformed above the glass transition, should have the same activation volume as untreated material. This was verified for a series of tensile bars, predeformed uniaxially above the glass transition temperature at five different levels of extension. Eyring plots of the yield stress as a function of logarithmic strain rate for untreated polycarbonate. The solid line is a best fit using eq 2.
activation volume is indeed independent of the strain-hardening response.

A disadvantage of predeformation above the glass transition temperature, is that large homogeneous deformations below the glass transition temperature cannot be obtained, because the heat treatment will restore the intrinsic strain-softening behavior together with the associated inhomogeneous deformation behavior. Therefore, information about the strain-hardening behavior can only be obtained indirectly from the anisotropic yield behavior. In principle, using a three-dimensional constitutive equation with one of the network models from the previous section to describe the strain-hardening behavior, the development of this anisotropy, as well as the effect on the stress-strain curve upon reloading, can be calculated numerically.\(^2\)

A useful approximation to determine the effect of orientational hardening on the yield point alone, is to assume that, at the yield point, the initial elastic strain rate is zero, and that the material response is adequately described by a Kelvin-Voigt model (see Fig. 5).

At low stress and at low temperature, the viscosity in the dashpot (Fig. 5) is very high. At high stress and/or at high temperature, the viscosity can be low enough to facilitate homogeneous deformation of the entanglement network, characterized by the rubbery modulus \(G_r\). If the material is homogeneously deformed above the glass transition temperature, quenching to room temperature will freeze-in the predeformed situation. After releasing the sample, the deviatoric network stress will be balanced by the deviatoric viscous stress. In other words, the high viscosity at room temperature and low stress, prevents the material from returning to its original state.

The representation by a Kelvin-Voigt model implies that the total deviatoric stress is decomposed in a network stress and a viscous stress:

\[
T^d = G_r \tilde{B}_p^d + 2\eta(V)\tilde{D}_p
\]

Here, \(G_r\) is the rubbery strain-hardening modulus, \(\tilde{B}_p\) is the “plastic” predeformation applied above the glass transition temperature, and \(T^d\) is the deviatoric stress acting over the dashpot. The “yield point” of this Kelvin-Voigt model is determined by a critical value of the second invariant of \(T^d\) (Von Mises yield criterion). The critical value of \(\Pi^d\), therefore, equals \(1/3\sigma_0\) with \(\sigma_0\) the uniaxial yield stress of the untreated isotropic material (\(\tilde{B}_p^d = 0\)).

**Uniaxial Predeformation**

In case of uniaxial predeformation, the frozen-in deformation is described by:
\[
\tilde{B}_p = \begin{pmatrix}
\lambda_p^2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & \frac{1}{\lambda_p}
\end{pmatrix}
\]  
(4)

\[
T_v^d = T^d - G_r \tilde{B}_p^d
\]

\[
= \begin{pmatrix}
\frac{2}{3} \left( \sigma - G_r \left( \lambda_p^2 - \frac{1}{\lambda_p} \right) \right) & 0 & 0 \\
0 & 0 & - \left( \sigma - G_r \left( \lambda_p^2 - \frac{1}{\lambda_p} \right) \right) \\
0 & 0 & 0
\end{pmatrix}
\]  
(5)

A relation between the yield stress of the predeformed material and the untreated isotropic material, respectively \(\sigma_y\) and \(\sigma_o\), can now be obtained from the critical condition for yield:

\[
II_{T_v} = \frac{1}{3} \sigma_o
\]  
(6)

This quadratic equation in \(\sigma_y\) has two solutions—one for the case of yielding in tension, and one for yielding in compression:

\[
\sigma_y = \sigma_o + G_r \left( \lambda_p^2 - \frac{1}{\lambda_p} \right)
\]  
(7a)

\[
\sigma_y = - \sigma_o + G_r \left( \lambda_p^2 - \frac{1}{\lambda_p} \right)
\]  
(7b)

According to eq. 7, the strain-hardening modulus \(G_r\) can be obtained from a plot of the yield stress as a function of predeformation. This is depicted in Figure 6, where it is shown that the true yield stress as a function of \((\lambda_p^2 - 1/\lambda_p)\) reveals a straight line, indicative of neo-Hookean behavior with a constant shear modulus \(G_r = 3\) MPa. Apparently, there is no effect of finite, extensibility up to a draw ratio of \(\lambda_p = 1.85\) (applied above the glass transition temperature).

**Planar Predeformation**

As in the case of uniaxial predeformation, samples, subjected to planar predeformation above the glass transition temperature, should have the same activation volume as the untreated material. This was verified for a series of tensile bars, cut at four different directions from a sheet, planarly predeformed above the glass transition temperature at two different levels of extension (see Fig. 1). Eyring plots of the yield stress as a function of logarithmic strain rate, at various levels of predeformation and at different levels of orientation are depicted in Figures 7 and 8. The solid lines in this figure are a fit using the same value of the Eyring parameter \(\tau_0\) as the untreated material. A good agreement is obtained, indicating that the activation volume is indeed independent of the strain-hardening response.

In the case of planar predeformation, the frozen-in deformation is described by:

\[
\tilde{B}_p = \begin{pmatrix}
\lambda_p^2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & \frac{1}{\lambda_p}
\end{pmatrix}
\]  
(8)

Figure 7. Yield stress versus strain rate for planarly predeformed samples (\(\lambda_p = 1.23\)), at different orientations with respect to the predrawing direction.
where \( \lambda_p \) is the planar draw ratio (see Fig. 1).

To examine the anisotropy in yield behavior introduced by planar predeformation, samples, cut in different orientations with respect to the drawing direction (see Fig. 1), were subjected to uniaxial tensile experiments at room temperature. During these uniaxial tensile experiments, the deviatoric “viscous” stress equals:

\[
T_v^d = T^d - G_s R \cdot B_p^d \cdot R^T
\]  
(9)

with the rotation tensor \( R \):

\[
R = \begin{pmatrix}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\]  
(10)

The uniaxial “yield stress” \( \sigma_y \) of a tensile bar, cut at an angle \( \theta \) with respect to the planar draw direction, is again determined by the critical value of the second invariant of the deviatoric “viscous-stress tensor,” eq. 6. Like in the case of uniaxial predeformation, this criterion results in a relation between \( \sigma_y \) and the isotropic yield stress \( \sigma_0 \), which is quadratic in \( \sigma_y \) and has two solutions, one in tension and one in compression:

\[
\sigma_y = \frac{1}{2\lambda^4} \left[ \frac{1}{2} G_s \lambda^2 (\lambda^2 - 1)(\lambda^2 + 3\lambda^2\cos(2\alpha) + 2) \\
\right. \\
+ \left. \left( 4\lambda^4( - G_s^2 \lambda^2 + G_s^2 \lambda^2 + G_s^2 \lambda^2 - G_s^2 \lambda^2 + \lambda^4\sigma_0^2) \\
+ \frac{1}{4} G_s^2 \lambda^4(1 - \lambda^2)^2(2 + \lambda^2 + 3\lambda^2\cos(2\alpha))^2 \right)^{1/2} \right]
\]  
(11a)

The yield stress data at different orientations and at two levels of predeformation (Fig. 7 and 8), were used to verify eq. 11a. This is depicted in Figure 9, which shows the yield stress as a function of orientation at two levels of predeformation and at a given strain rate. The solid line is the prediction of eq. 11a using the value of the strain-hardening modulus from the uniaxial predeformation experiments \( G_s = 3 \) MPa (see earlier).

Unfortunately, the value of the isotropic yield stress \( \sigma_0 \) was not known, because the exact temperature history of the predeformed samples (large sheets) was unknown. Therefore, one yield point at a given level of predeformation, orientation, and strain rate, was needed to determine \( \sigma_0 \), using eq. 11a.

From Figure 9 it is clear that, like in the case of uniaxial predeformation, simple neo-Hookean behavior with a constant modulus is able to capture the strain-hardening response accurately.

The good agreement between experiment and predictions observed in Figures 6 and 9 suggest that simple neo-Hookean behavior employing a constant shear modulus \( G_s = 3 \) MPa, is able to give a quantitative description of the state of de-
formation dependence of the strain-hardening response at a temperature of 163 °C up to a draw ratio of $\lambda^p = 1.85$. In particular, no effect of finite extensibility could be observed.

**Temperature Dependence of the Strain-Hardening Response**

Rejuvenated tensile bars of both polycarbonate grades were used to perform tensile tests at various temperatures above room temperature at a strain rate of $10^{-2}$ s$^{-1}$. The results are depicted in Figure 10. Strain-rate effects were small, and at all temperatures the strain-hardening response was essentially elastic until fracture occurred. From Figure 10, it is clear that neo-Hookean strain-hardening behavior is observed over the whole temperature range. The strain-hardening moduli as a function of temperature, determined from Figure 10, are summarized in Table 1. Although there is virtually no effect of strain rate on the hardening response, the strain-hardening modulus clearly decreases as a function of temperature.

**DISCUSSION AND CONCLUSIONS**

The main features of linear viscoelastic behavior of glassy polymers are determined by two characteristic relaxation mechanisms, the glass transition, governed by configurational rearrangements of molecular segments, and the relaxation of the entanglement network (reptation process), dominated by the steric hinderance between the polymeric chains. This is schematically shown in Figure 11, which depicts the dynamic modulus of polycarbonate as a function of temperature at a frequency of 1 Hz. The linear viscoelastic behavior is relevant for large deformations as well. The yield behavior can be described as a stress-induced glass transition,$^{17}$ and it seems logical to assume that the strain-hardening response is related to the plateau and terminal zone of the linear viscoelastic response. More specifically, it could be assumed that the strain-hardening acts parallel to the viscous segmental response. This is depicted graphically in Figure 11, where the values of strain-hardening modulus of Lexan 101 as a function of temperature (see Table 1) have been added to the dynamic moduli data. In this way, Figure 11 is a graphical representation of the premises that the strain-hardening response of a glassy polymer is “masked” by the viscous segmental contribution, and only manifests itself at high temperature ($>T_g$) or at high stress ($>\sigma_y$).

The temperature dependence of the strain-hardening modulus, as measured in uniaxial ten-

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**Table 1.** Strain-Hardening Modulus $G_e$ as a Function of Temperature Determined from Figure 10 for the Two Polycarbonate Grades Lexan 101 and Makrolon

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lexan 101 $G_e$ (MPa)</th>
<th>Makrolon $G_e$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>23.7</td>
<td>23</td>
</tr>
<tr>
<td>50</td>
<td>21.3</td>
<td>20.6</td>
</tr>
<tr>
<td>75</td>
<td>18.7</td>
<td>17</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>13.5</td>
</tr>
<tr>
<td>125</td>
<td>10.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>
sile deformation on mechanically conditioned samples and the dynamic modulus measured at 1 Hz, are depicted in more detail in Figure 12. To combine these two seemingly different quantities is allowed, because the strain-hardening response is independent of strain rate to a good approximation and, therefore, also valid at a frequency of 1 Hz. The two extra data points of the strain-hardening modulus for Lexan 101 in Figure 12, are the value of \( G_r = 3 \) MPa determined in text, and the strain-hardening modulus directly measured in a tensile test at 150 °C, where the samples deform homogeneously. The solid lines are a guides to the eye.

![Figure 12. Strain-hardening modulus \( G_r \) of polycarbonate as a function of temperature (from Fig. 10, together with the dynamic modulus data measured above \( T_g \) at a frequency of 1 Hz. The two extra data points for Lexan 101 are the value of \( G_r = 3 \) MPa determined in text, and the strain-hardening modulus directly measured in a tensile test at 150 °C, where the samples deform homogeneously. The solid lines are guides to the eye.](image)

The authors are indebted to I.M. Ward, R.A. Duckett and J. Sweeney at the University of Leeds (IRC of Polymer Science Technology) for stimulating discussions and experimental support.

### REFERENCES AND NOTES