THE ROLE OF MOLECULAR LENGTH SCALE ON THE VISCOPLASTIC RESPONSE OF AMORPHOUS POLYMER NANOFIBERS IN THE GLASSY STATE

BY

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DISSERTATION

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ABSTRACT

Polymeric nanostructures are quite distinct because of the large ratio of surface-to-volume macromolecules which result in very different physical and mechanical behavior compared to bulk. Of special interest are nanostructures in which the constituent polymer is in its glassy state to provide structural and dimensional stability against surface forces that are particularly strong at the micron and submicron scales. The majority of existing literature on the mechanical properties of ultra-small volumes of polymers in their glassy state focuses on ultra-thin films and is limited to small deformations and the viscoelastic regime. Experiments with composite materials encapsulating polystyrene (PS) thin films and in their glassy state at room temperature have demonstrated shear yielding and large deformations that are not possible at the macroscale where PS fails at small strains due to crazing. This dissertation research focused on direct experiments with atactic PS nanofibers to elucidate and quantify the unusual viscoplastic response of ultra-small volumes of PS as a function of the underlying molecular and structural length scales. PS is an ideal polymer for this study because it is amorphous and its glass transition temperature, $T_g$, is much higher ($100^\circ$C) than room temperature.

The objective of this research was to understand the synergistic coupling between the material length scale as defined by macromolecular size, and the specimen size as defined by the fiber diameter, which can result in extreme ductility and simultaneous strengthening and toughening for fiber diameters at the submicron scale. To this goal, PS fibers with diameters 150–5,000 nm were electrospun from monodisperse PS powders with molecular weights, MW, in the range 13,000–9,000,000 g/mol. Individual nanofibers were tested using a surface micromachined device for nanofiber testing at the quasi-static strain rate of $10^{-2}$ s$^{-1}$. Unlike the brittle behavior of bulk PS, the engineering stress vs. stretch ratio of individual nanofibers with several combinations of MW and diameter displayed very repeatable post-yield behavior including necking and pronounced strain-hardening. Specifically, the ratio of the structural length scale (fiber diameter) to the intrinsic macromolecular length scale (root-mean-square end-to-end
chain distance), $D_{\text{norm}}$, was shown be an excellent scaling parameter to determine the occurrence and evolution of necking and strain hardening in submicron scale PS fibers. This interplay between molecular and structural length scales in glassy PS fibers was favorably exploited to harness a ~3,000% increase in toughness along with simultaneous increase in tensile strength: the highest fiber strength was achieved for $D_{\text{norm}} = 3–5$, whereas increasing $D_{\text{norm}}$ resulted in gradual decline in strength. Bulk-like brittle behavior took place for $D_{\text{norm}} > 18$. It was shown that the effects of molecular and structural lengths scales on large deformation behavior of fibers could be collapsed onto a single master curve as long as the MW was larger than the critical value for constant inter-chain entanglement length. Furthermore, it was shown that the pronounced hardening in PS nanofibers is not a result of post yield necking, but part of the material constitutive response: experiments on individual poly(lactide-co-glycolic acid) (PLGA) nanofibers showed that unlike in bulk specimens, nanoscale imperfections and specimen irregularities are rather benign and strong post-yield strain hardening occurs even when necking is suppressed.

The viscous component of the large deformation response in PS nanofibers was assessed by tensile experiments with PS nanofibers with $\text{MW} = 123,000 – 2,000,000$ g/mol and diameters of $200 – 750$ nm in the range of strain rates $10^{-4} - 10^{2}$ s$^{-1}$. For fibers with $D_{\text{norm}} < 8$, it was shown that increasing strain rate resulted in monotonic increase of the stress amplitude without affecting the large fiber stretch ratios. In contrast, the strain rate influenced both the stress and the stretch ratio of fibers with $D_{\text{norm}} > 10$, i.e. fibers without significant post-neck hardening. For all PS fibers, the rate dependent stress vs. stretch ratio curves scaled with yield stress. Therefore, a normalized stress vs. strain curve could be generated to combine size effects and temporal effects on the mechanical behavior of PS nanofibers at room temperature.
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CHAPTER 1

INTRODUCTION

In their simplest form, polymer molecules are linear chains, which in the melt state configure into a statistically probable random coil, often described by the root-mean-square end-to-end distance, $R_{ee}$, as schematically illustrated in Figure 1.1(a) [1]. For amorphous and unoriented polymers, the characteristic length scales range from the size of the monomer (< 1 nm) to the $R_{ee}$ which can be several tens of nanometers depending on the number of monomers comprising the polymer macromolecule. In a polymeric structure composed of many macromolecules, additional length scales arise from inter-chain interactions. The reduction of the volume of polymeric structures to the submicron and the nanometer regimes leads to an increase in the ratio of surface to interior (bulk-like) molecules. The physical properties of surface and interface molecules are known to deviate from those in the bulk due to reduced intermolecular constraints [2] and new molecular interactions arising at interfaces. In the vicinity of an interface or within ultra-small material volumes that are comparable to $R_{ee}$, surface forces orient polymer molecules to conform to the given spatial confinement, as illustrated in Figure 1.1(b) [3,4], which contributes to the distinctly different properties of ultra-small polymer volumes and free surfaces.
Figure 1.1. (a) Schematic representation of the root-mean-square end-to-end distance of a polymer chain, $R_{ee}$, with an enlarged view of a small segment of the chain consisting of a few monomers. (b) Schematic illustration of the role of spatial constraints near the free surface and in the vicinity of rigid substrate in the reconfiguration of polymer chains.

The departure of molecular conformation and properties from the bulk under spatial confinement has been extensively studied in terms of spatial variations in glass transition temperature ($T_g$) of polymer films. Quite often, these results have been used to infer local variations in mechanical properties [5]. This Chapter discusses the current understanding in the physical properties of common polymers under spatial confinement and presents the motivation for this dissertation research to study the large deformation mechanical behavior of polymer nanofibers vis-à-vis the macromolecular scale described by $R_{ee}$. 
1.1 Physical Properties of Amorphous Polymeric Nanostructures

Experimentally, current understanding of the physical properties of polymeric nanostructures originates in extensive studies of their glass transition behavior. When a polymer melt is cooled, it undergoes a transition from a rubbery state to an amorphous glassy state that lacks long range order. This transition, known as the glass transition, is characterized by many orders of magnitude decrease in molecular mobility over a small temperature window, wherein polymer molecules lose their ability to reach equilibrium configurations within the experimental time scales. Polymers confined in nanoscale pores [6,7] and ultra-thin films [8,9] exhibit significant variations in their glass transition temperature ($T_g$), relative to the bulk. Changes in $T_g$ at small scales have been found to depend on the nature/configuration of the confining interface (free surface or a substrate) which defines local molecular interactions, the chemistry of the polymer and the extent of confinement (film thickness, distance from an interface, etc.) [10]. Due to the association of $T_g$ with cooperative segmental mobility of macromolecular chains (i.e., mobility of groups of a few tens of monomers), changes in $T_g$ are interpreted as changes in segmental mobility of polymers confined to small volumes [2,11]. For instance, the significant decrease in $T_g$ at the free surface of polystyrene (PS) thin films has been explained in terms of increased segmental mobility near the free surface [9]. While changes in $T_g$ are associated with relatively small segmental length scales at the macromolecular level, $T_g$ changes in freestanding thin films of PS and poly(methyl methacrylate) (PMMA) have been found to span distances of 50 – 60 nm and follow a systematic molecular weight dependence [12-15]. Specifically, PS thin films of molecular weight ($MW$) larger than 350,000 g/mol demonstrated a depression in $T_g$ relative to the value for bulk when film
thicknesses approached $R_{ee}$ [13,14]. Additionally for film thicknesses less than $R_{ee}$ and $MW > 350,000$ g/mol, the slope of $T_g$ vs. film thickness plots increased with $MW$, i.e., thin films with higher $MW$ experienced a steeper reduction in $T_g$ with film thickness. Intermolecular interactions also affect the change in $T_g$: For instance, the reduction in $T_g$ for PMMA was much smaller than for PS [14,15]. More recently, local $T_g$ measurements using fluorescent dyes showed that both supported and freestanding PS films have a $T_g$ depression of 35 °C in a 14-nm thin region near the free surface [16,17]. Additionally, freestanding PS films with thicknesses larger than 60 nm demonstrated a gradient in $T_g$ between the free surface and the interior [17]. The bulk value of $T_g$ was attained at ~250 nm from the free surface [16].

Several relaxation processes occur at or near $T_g$: Relaxations at $T_g$ are termed primary relaxations or $\alpha$ relaxations, while secondary relaxations occur below $T_g$ and are labeled as $\beta$, $\gamma$ or $\delta$ transitions in decreasing order of temperature [18]. Understanding the nature and physics of each relaxation process, could shed light into the time and rate sensitivity of the mechanical behavior of polymers [19] and provide insights into the relevant molecular mechanisms [20]. For instance, the $\alpha$-transition is related to segmental mobility of chains where a small group of 5–10 monomers undergoes collective motion. On the other hand the $\beta$-relaxation is often linked to rotations of specific groups such as phenyl rings that are either side-groups or located within the chain backbone [19,20].

Direct measurements of relaxation times are difficult for ultra-small volumes of confined polymers, and hence only few such studies exist that are focused on the $\alpha$-relaxation process. The majority of such studies have described a broadening of the $\alpha$-
relaxation peak with decreasing film thickness [10,21-23], which can be attributed to either through-thickness gradients in $T_g$ or changes in the relaxation times in the entire sample. However, coupled with observations of the lack of a $T_g$ gradient in films with thicknesses less than 60 nm [17], broadening of the $\alpha$-relaxation peak indicates that the relaxation times in the lower temperature portion of the original peak have shifted to even lower temperatures. In other words, faster relaxation mechanisms are active in polymer thin films. To this effect, recent photobleaching studies have shown that faster relaxations are indeed likely in freestanding PS films [24]. Although these faster relaxations should be independent of $MW$ [24], $T_g$ measurements suggest otherwise [14]. Measurements of $\beta$-relaxations in thin PMMA films have also shown that the changes in this process are likely coupled to changes in $\alpha$-relaxation and that a decreasing film thickness results in accelerated $\beta$-relaxations [25,26].

Unlike changes in short range motions and segmental mobility that are well documented for model polymer glasses such as PS, the effects of volumetric confinement on large range chain motions are less understood. The most common approach to study such phenomena is via dewetting of thin films [27-32]. At temperatures above $T_g$, the onset of large range chain motions leads to film dewetting or hole-growth. Experiments with freestanding ultra-thin films or films bonded to substrates have identified that dewetting or hole-growth only occurs at temperatures higher than $T_{g\text{-bulk}}$ [31], thus suggesting that large range chain motions may not be affected by molecular confinement. In terms of data analysis, diffusion experiments are relatively straightforward compared to dewetting experiments, and provide the flexibility to measure the diffusion constants in...
directions parallel and perpendicular to the confining dimension, e.g. the film thickness. Reports based on such experiments provided conflicting conclusions, showing that the mobility of entire polymer chains in the confining direction is either reduced for films that are less than 150 nm thick [27,28], or is comparable to bulk specimens [29,30].

Accelerated relaxations in polymers confined to small volumes could have important implications in their physical aging, which refers to the process of gradual transition of non-equilibrium polymer chain configurations in the glassy state to equilibrium configurations. Much like the $T_g$ behavior, aging in spatially confined polymers can be affected by variables such as the confining interface and the distance from it, the chemistry of the polymer, etc. [33]. Furthermore, aging occurs below $T_g$, and the extent of physical aging with spatial confinement is also related to the aging temperature differential. Local fluorescent measurements on PMMA films have identified significant deceleration of aging at 200 nm from the free surface near room temperature [34] while PS films either showed enhanced aging with decreasing thickness [35] or no appreciable change in the aging response for films as thin as 400 nm [36]. However, unlike the changes in $T_g$ that typically occur for film thicknesses of 100 nm or less, changes in physical aging span micron or submicron length scales. Finally, other physical properties of amorphous polymers such as the entanglement density also change in the vicinity of the confining interfaces and free surfaces [32,37-40].
1.2 Motivation and Relevance

The increasing use of microscale polymeric structures, such as thin films and nanofibers in microelectronics [41], energy conversion and storage [42,43], structural nanocomposites [44], advanced textiles [45] and regenerative medicine [46], requires a better understanding of the changes in the mechanical response with decreasing specimen size. The mechanical response of amorphous polymers is intricately linked to their physical properties such as $T_g$, aging and entanglement structure [5], all of which are likely to change at the nanometer scale. Due to challenges in performing direct mechanical experiments with very small volumes of polymers, few studies have explored the mechanical behavior of polymeric nanostructures through direct measurements. Quite often, the effect of molecular confinement on the mechanical behavior of submicron scale polymeric structures has been deduced from trends in $T_g$ on the basis of a direct correlation between $T_g$ and the material free volume [47]. However, recent studies have shown that the basis for such inferences is rather weak [48-51]. For instance, biaxial creep compliance measurements on ultra-thin PS and polyvinyl acetate (PVAc) films [50] have shown that the viscoelastic creep compliance does not follow the corresponding trends in $T_g$: Although 20 nm thick PS films displayed a $30 – 40 \, ^\circ\text{C}$ depression in $T_g$ compared to bulk, their creep compliance was 2 – 3 times lower than bulk-like specimens in the glassy state and 50 times lower than bulk-like specimens in the rubbery regime. Ultra-thin PVAc films also showed a similarly dramatic reduction in creep compliance despite the invariance of $T_g$ for thicknesses as small 20 nm. Moreover, changes in creep compliance occur for film thicknesses of 100 – 1000 nm for both PS and PVAc, while the $T_g$ of PS thin films reaches bulk-like values for thicknesses of 100 nm or less.
Interestingly, the corresponding creep compliance curves also follow the principle of time-temperature superposition for film thicknesses as small as 20 nm, unlike indications from $T_g$ and hole-growth measurements. These observations clearly show a lack of correlation between changes in $T_g$ and the mechanical behavior of thin polymer films, thus highlighting the need for direct mechanical experiments to quantify the role of spatial confinement. Notably, almost all existing mechanical testing methods are limited in their ability to study (a) the large deformation behavior of freestanding polymeric specimens, and (b) the strain rate dependence of small and large deformation.

In the past, indirect experiments with glassy PS films have deduced a size dependent brittle-to-ductile transition [52] and alluded to confinement controlled ductile behavior [39]. Specifically, the tensile stress-strain response of laminated composites comprised of alternating layers of polyethylene (PE) and PS was used to infer a size dependent brittle-to-ductile transition for submicron scale PS layers [52]. Recently, tensile experiments with ultra-thin PS films of high $MW$ noted the potential of these films to undergo necking, contrary to bulk PS: Based on an assumption for isochoric deformation, the authors in [39] used the neck ratio to infer elongations of PS molecules under spatial confinement and relate those through a model to changes in inter-chain and self-entanglements in confined PS. However, the experimentally measured neck ratios and the corresponding inferred elongations were much larger than the estimated theoretical extensibility of the entangled PS network, indicating the likelihood of crazing in these thin films [53], which, in turn, invalidates the assumption of isochoric deformation. Even so, the idea of achieving significant increases in ductility and
toughness at a structurally useful length scale by confining glassy polymers to ultra-small spatial volumes is very appealing. To this effect, microscale tensile tests on electrospun polyacrylonitrile (PAN) nanofibers have shown an unusual viscoplastic response compared to bulk [54-56]. However, despite the well-documented physical property changes of amorphous polymers at the nanoscale, and indications that the unique improvements in mechanical behavior of semi-crystalline polymer nanostructures are likely to be influenced by their amorphous regions [57-59], our knowledge of the viscoplastic behavior of amorphous polymers at the nanoscale is still very limited.

1.3 Objectives and Approach of this Dissertation Research

The objective of this Ph.D. dissertation research is to elucidate the effect of spatial confinement on the large deformation mechanical behavior of polymer macromolecules confined within ultra-small volumes that are defined by the cross-section of nanofiber specimens. This objective is accomplished by:

(a) A study of the interplay between the specimen diameter and the intrinsic/material length scale $R_{ee}$ on the elasto-plastic response of PS, which is used as a model polymer at its glassy state. The material length scale, defined by $MW$, and the specimen diameter offer control of the fraction of surface molecules and the extent of spatial confinement of individual macromolecules.

(b) A parallel study of the viscous nature of the plastic deformation as described by strain rate dependent yielding and strain-hardening for nanofibers with different diameters and $MW$. 

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Specifically, PS nanofibers with diameters in the range 150 – 5,000 nm and monodisperse $MW = 13,000 – 9,000,000$ g/mol are fabricated by the method of electrospinning. The details of nanofiber fabrication and the microscale tension testing method used to obtain the mechanical response of individual nanofibers are presented in Chapter 2. The molecular and structural length scale effects on the mechanical behavior are evaluated in Chapter 3 based on the stress-strain response of individual PS nanofibers of different diameters and $MW$. Post-mortem analysis of the test specimens is used to identify the underlying deformation mechanisms at the submicron scale. Chapter 4 discusses microscale tension experiments with individual PS nanofibers, performed across a wide range of strain rates ($10^{-4} – 10^{2}$ s$^{-1}$) to study the viscous character of plastic deformation in PS nanofibers. The role of geometric factors arising from submicron scale surface roughness and non-uniformities on the plastic deformation of submicron volumes of polymer nanofibers are studied in Chapter 5 using electrospun PLGA (poly(lactic-co-glycolic acid)) nanofibers. Finally, Chapter 6 presents an account of the main conclusions of this Ph.D. dissertation and a discussion of future research prospects.
CHAPTER 2

EXPERIMENTAL METHODS

An increasing emphasis to understand the mechanical behavior of soft nanostructures has led to the development of novel experimental methods to evaluate the mechanical behavior of ultra-small specimens. In this Chapter, a brief background of experimental methods for mechanical testing of small-scale polymer specimens and their limitations are discussed, followed by a description of the experimental method used in this dissertation research to study the large deformation mechanical behavior of PS and PLGA nanofibers and a description of the specimen fabrication procedures.

2.1 Experimental Methods for Small-scale Polymer Specimens

Most experimental studies of polymeric micro and nanostructures have relied on instrumented nanoindentation or scanning probe microscopes (SPM) to readily provide fine displacement control and high resolution images [60]. For instance, instrumented nanoindentation has been applied to probe the effects of spatial confinement on the thermo-mechanical response of ultra-thin polymer films [61], although the complex loading profile under the indenter tip and the spatial confinement induced by the indenter
tip have led to convoluted effects [62]. In a different approach, buckling instabilities in thin polymer films subjected to compressive loading have been harnessed to study the small-strain mechanical response of ultra-thin polymer films, while an SPM was used to measure the dimensions of the surface wrinkles [51,63]. This indirect method is quite limited as it requires knowledge of the material properties of the substrate, and the elastic constants of the thin films are extracted from fits to analytically derived expressions. A major limitation arises from the need to bond the polymer films onto a rigid substrate, thereby precluding the study of freestanding films or the application of large material deformations. This is of particular concern since the physical properties, such as $T_g$ and aging, are controlled by interactions between the polymer molecules and the substrate typically for distances of 10-250 nm [16,34].

In general, application of tension to freestanding polymer microscale and nanoscale structures is more difficult than normal compression of films bonded to a substrate. Among the few exceptions, the bubble inflation technique has been successfully adapted to study freestanding ultra-thin polymer films by subjecting them to biaxial tension [64,65]. This method has been used to study the thermo-viscoelastic response of polymer films as thin as $\sim$10 nm [66], although films thicker than 150 – 200 nm could not be reliably evaluated with this method because they could no longer be described by a simplified membrane analysis [50,64]: even at temperatures as high as 90 °C, the pressure required to inflate a bubble specimen was high enough to burst films thicker than 100 nm at their support [50]. The particular application of this method in ultra-thin polymer films was also subject to practical limitations stemming from the use
of atomic force microscopy (AFM) that is inherently a slow metrology method, allowing for measurements at the time scale of minutes [66]. Thin film specimens, although popular due to the ease in preparing and handling on rigid substrates, are not suited for the study of the large deformation behavior of polymers due to lateral film buckling at large extensions. By contrast, the one-dimensional (1D) geometry of nanofibers permits the application of large extensions and for this reason was selected for this research. Moreover, for similar values of fiber diameter and film thickness, fibers result in larger surface-to-volume ratios, which will accentuate the effect of molecular confinement.

Although quite a few methods have been developed to study the mechanical behavior of 1D nanostructures, such as nanowires and nanotubes [67-73], a very limited number of efforts have been focused on mechanical testing of polymeric nanofibers using microscale tools [74-76]. Experiments with carbon nanotubes and metallic nanowires can be performed inside an electron microscope to achieve high resolution imaging, contrary to polymers, which are extremely sensitive to electron beam radiation and vacuum environments [77]. Moreover, the electrically insulating nature of most polymers requires a conductive surface coating which would preclude direct testing. On the other hand, most methods developed in the past to study the mechanical behavior of polymeric nanostructures in ambient conditions allow for a limited range of strain and strain rates [74-76]. In contrast, surface micromachined tools based on technologies for Microelectromechanical Systems (MEMS), are well suited for microscale specimen handling and testing of small-scale specimens. Special emphasis in this field has been placed on MEMS devices for on-chip mechanical testing using integrated electrical or
thermal actuation [69,70, 72,73], on-chip actuation for testing polymer nanofibers has two main limitations:

(a) The actuation range is limited to a few microns which is adequate for brittle nanowires of short gage lengths but not for ductile polymer nanofibers. An alternative approach to overcome displacement limitations imposed by on-chip actuation is to use an inchworm type actuator [78], also called the “nanotractor”, which is capable of achieving displacements of up to 100 µm.

(b) The range of actuation rates is quite restricted, thus limiting strain rate studies with polymeric nanostructures.

A MEMS based method developed by this group in the past [79-81] addresses the shortcomings of previous experimental methods. This experimental method was employed in this study and is described in the following Section.

2.2 Microscale Tension Experiments with Polymeric Nanofibers

In the MEMS-based method [79-81] employed in this research, actuation is accomplished by an off-chip actuator while strain and force measurements are obtained from optical images. Off-chip actuation allows for practically unlimited specimen extensions and strain rates, while also reducing the number of unsuccessful experiments due to the poor yield of functional on-chip actuators. All experiments were performed in ambient conditions to avoid electron beam damage to the polymer specimens, while high resolution optical images were acquired by a CCD camera. An example of the test of a
PS nanofiber with 250 nm diameter is shown in Figure 2.1. The nanofiber is in the undeformed state in Figure 2.1(a), while Figure 2.1(b) shows the loaded fiber and the labeled functional components of the MEMS device. Specifically, component #1 is bonded to the underlying silicon wafer which, in turn, is attached to a translation stage driven by a piezoelectric actuator with a displacement resolution of ~15 nm. The components #2 and #3 are freestanding and connected to each other by 4 pairs of compliant beams whose stiffness was defined in the design phase [80,81] and was experimentally measured [80] as shown in Figure 2.2. During an experiment component #3 is held stationary by an external probe while component #1 is actuated to the left. The rigid body displacements $u_{xx}^1$, $u_{xx}^2$ and $u_{xx}^3$, are obtained for components #1, #2 and #3, respectively, using the average values of the full-field displacements computed for each image via digital image correlation (DIC), as shown in Figure 2.1(b). $u_{xx}^1$, $u_{xx}^2$ and $u_{xx}^3$ allow for the independent calculation of the engineering stress, $\sigma_{xx}$, and engineering strain, $\varepsilon_{xx}$, as:

$$
\varepsilon_{xx} = \frac{u_{xx}^1 - u_{xx}^2}{l} ; \quad \sigma_{xx} = \frac{(u_{xx}^2 - u_{xx}^3) \cdot k}{\left(\pi d^2 / 4\right)}
$$

(2.1)

where $l$ is the undeformed fiber gage length, $k$ is the stiffness of the beams connecting components #2 and #3, and $d$ is the undeformed fiber diameter.
Figure 2.1. Snapshots from a mechanical test of a PS fiber with 250 nm diameter. (a) Unloaded fiber mounted on a MEMS testing device. (b) Calculations of rigid body motion with the aid of DIC, superposed on the components of the MEMS device.
The mechanical stiffness of the loadcell was obtained by attaching glass beads of known mass at its end and measuring the opening \( \Delta u = (u_{x_1}^2 - u_{x_1}^3) \) for the range of opening displacements expected in the experiments. Figure 2.2 shows an example calibration of a loadcell whose design stiffness was 1.2 N/m. The linearity between the loadcell opening and the applied force was maintained for openings up to 18 \( \mu \text{m} \), corresponding to 20 \( \mu \text{N} \).
for the loadcell in Figure 2.2. This force range corresponds to 80 MPa engineering stress in a fiber with 500 nm diameter. Previous calibrations of similar loadcells have shown that force linearity can be maintained for openings as large as 30 µm [80]. For fiber diameters larger than 500 nm, loadcells with stiffness in the range of 3.5 – 7 N/m were employed.

2.2.1 Uncertainties in Stress and Strain Measurements

The uncertainty in strain calculation using Equation 2.1 is directly proportional to the uncertainty in displacements, $u_{xx}$, resolved by DIC. The latter was quantified by rigid body translation of a patterned surface using a PZT actuator with step size of 12 nm in a total distance of 1,200 nm [82]. A comparison with the cumulative displacement computed by DIC showed that the uncertainty is of the order of 25 nm (0.15 pixels) [79,82] and is not cumulative, i.e. remains the same regardless of the total displacement. For instance, the uncertainty in measuring engineering strain in a 30 µm long fiber, as shown in Figure 2.1, is always less than 0.1–0.2% strain. The uncertainty in stress is affected by uncertainties in measuring the stiffness of the loadcell and the fiber diameter. The uncertainty in the measurement of the fiber diameter using an SEM, which is fairly size independent, dominates the uncertainties stemming from DIC calculations due to the higher power of the diameter term in Equation (2.1): assuming an uncertainty
Figure 2.3. Motion ($u_x^i$) of components (a) #1, (b) #2 and (c) #3 designated in Figure 2.2 in the direction of the fiber, as resolved via DIC. An artificial pattern was created on the device surface by FIB to enhance displacement resolution.
of ±5 nm in the fiber diameter, a 3% uncertainty in the measurement of the loadcell stiffness [80] and 25 nm resolution in rigid body displacement calculations, the maximum uncertainty in measuring 50 MPa stress (which is close to the yield strength of many amorphous polymers) in a fiber of 200 nm diameter is ~5.0 MPa. Similarly, the uncertainty in measuring a 50 MPa stress in a fiber of 400 nm diameter is reduced to ~3.5 MPa.

An important consideration in minimizing the sub-pixel uncertainty in the displacements calculated by DIC is to ensure a good speckle pattern with smooth grey scale gradients. The natural roughness of the top surface of the polysilicon films comprising the MEMS devices resulted in a fine grey scale pattern when imaged by an optical microscope in dark field conditions, e.g. Figure 2.1. This natural pattern was proven highly effective at imaging rates up to 15 fps. The camera sensor noise for optical imaging at 5,000 fps or higher precluded the use of the natural speckle pattern unless a high intensity light was employed, which, however, could overheat the polymer fibers. In these cases, an artificial random pattern was generated by surface milling using a Focused Ion Beam (FIB). Closely spaced circular regions with diameters of 200–2500 nm were milled to depths of 200 nm. The resulting patterns provided good convergence of DIC with the rigid body displacements being as accurate as ~1/20th of a pixel, as shown in Figure 2.3. For the particular image pixel size of 800×350 nm², the sub-pixel displacement resolution provided by this pattern translated to an uncertainty of only ±20 nm.
2.2.2 Experimental Procedures

The experiments presented in Chapter 3 and Chapter 5 were carried out at actuator velocities $\dot{\delta}_{\text{app}} = 400 \text{ – } 500 \text{ nm/s}$ and specimen gage lengths $l = 25 \text{ – } 30 \mu\text{m}$, which resulted in cross-head strain rates of $\sim 10^{-3} \text{ s}^{-1}$ in the elastic regime and $\sim 10^{-2} \text{ s}^{-1}$ during plastic deformation (see Appendix I for details). In these experiments optical images of $1280\times960$ pixels were collected at 5 fps using a Sony DFW-SX910 camera. For the experiments at multiple strain rates described in Chapter 4, fibers with $30 \text{ – } 35 \mu\text{m}$ gage lengths were stretched at actuation velocities $12 \text{ nm/s} \text{ – } 6 \text{ mm/s}$ which corresponded to plastic strain rates of $10^{-4} \text{ – } 200 \text{ s}^{-1}$. For the slowest strain rates of $10^{-4} \text{ s}^{-1}$ and $10^{-2} \text{ s}^{-1}$, optical images of $1280\times960$ pixels were collected with the Sony XCD-SX90 camera at 1 and 15 fps, while for two fastest strain rates of $10^0 \text{ s}^{-1}$ and $10^2 \text{ s}^{-1}$ optical images of $512\times512$ pixels were collected with a Red Lake Motion Pro X camera at 5,000 – 40,000 fps. The statistical variability in the mechanical behavior of PS nanofibers subjected to different strain rates as described in Chapter 4, was minimized by isolating a single PS nanofiber of a particular $MW$ and diameter, which was then cut into multiple segments, each tested at a different cross-head strain rate.

2.3 Preparation of PS Nanofiber Specimens

Linear atactic PS was selected for the purposes of this study because its physical properties under confinement have been studied extensively in the past. The spatial confinement of macromolecules in nanofibers is governed by the competition between the fiber diameter, $D$, and the molecular length scale that most closely relates to $D$. The
molecular length scale can be described by the root-mean-square end-to-end distance, $R_{ee}$, of individual polymer chains, which, in turn, depends on $MW$. Control over the two length scales was achieved by electrospinning solutions of monodisperse PS with $MW = 13,000$ and $9,000,000$ g/mol, which resulted in fibers with diameters between 150 nm and 5 µm, as listed in Table 2.1. Monodisperse PS powders were purchased from Pressure Chemicals Inc. (13,000 – 2,000,000 g/mol) and Polymer Source Inc. (9,000,000 g/mol), and were used as-received. The powders with the two highest $MW$ had slightly higher polydispersity indices than the rest, as shown in Table 2.1. PDI $\rightarrow$ 1 is preferred because it implies that all polymer chains in a fiber have the same length, thus enabling the use of a single molecular length scale ($R_{ee}$) to describe the material comprising a nanofiber.

PS solutions of different concentrations were prepared by dissolving the powders in $N,N$-dimethylformamide (DMF) and electrospun under an applied voltage of 25 kV and a source-to-collector distance of 25 cm. All fibers were electrospun at 22±3 °C and 19±2 % relative humidity. The electrospinning voltage and distance are known to affect the initial state of the fibers [55], and therefore were kept constant. The selected voltage and distance to the collector provided the widest range of fiber diameters for the range of $MW$ used in this study. Fabrication of submicron diameter fibers from PS of low $MW$ of 13,000 and 50,000 g/mol was not feasible due to a minimum chain entanglement density requirement for successful electrospinning [83,84]. Similarly, extremely thick, micron sized fibers of higher $MW = 400,000 – 2,000,000$ g/mol could not be electrospun due to the rapidly increasing viscosity of the solutions above a critical concentration, e.g. 25% for $MW = 2,000,000$ g/mol.

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Table 2.1. Electrospinning and annealing parameters for the preparation of PS fibers.

<table>
<thead>
<tr>
<th>Molecular Weight (g/mol)</th>
<th>PDI</th>
<th>Solution Concentration (weight %)</th>
<th>Annealing Conditions</th>
<th>Fiber Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td>Time (×τ_d-bulk)</td>
</tr>
<tr>
<td>13,000</td>
<td>1.06</td>
<td>60</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>50,000</td>
<td>1.06</td>
<td>45</td>
<td>110</td>
<td>134</td>
</tr>
<tr>
<td>123,000</td>
<td>1.06</td>
<td>30*</td>
<td>110</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>110</td>
<td>6.3</td>
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<tr>
<td></td>
<td></td>
<td>50</td>
<td>110</td>
<td>6.3</td>
</tr>
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<td>120</td>
<td>8.3</td>
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<tr>
<td></td>
<td></td>
<td>20</td>
<td>120</td>
<td>8.3</td>
</tr>
<tr>
<td>900,000</td>
<td>1.10</td>
<td>7.5</td>
<td>125</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>125</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>125</td>
<td>2.5</td>
</tr>
<tr>
<td>2,000,000</td>
<td>1.30</td>
<td>2.0</td>
<td>125</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5</td>
<td>125</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>125</td>
<td>0.2</td>
</tr>
<tr>
<td>9,000,000</td>
<td>1.25</td>
<td>0.1</td>
<td>125</td>
<td>0.001</td>
</tr>
</tbody>
</table>

As-spun PS fibers were annealed in their freestanding configuration prior to mechanical testing, to devoid them of molecular orientation and the undesirable axially corrugated morphology arising from electrospinning as shown in Figure 2.4. The annealing cycle was comprised of a heating ramp at 2 K/min to peak temperatures that were 10 – 25 °C above the $T_g$ of bulk PS, namely 100 °C [23], followed by a dwell-period of 100 min at the peak temperature and finally cooling down to room temperature.

* Solution contained 1 wt% tetrabutyl ammonium chloride (TBAC) to reduce the fiber diameter.
at 0.50 – 0.25 K/min. The annealing temperatures varied with $MW$ as noted in Table 2.1. Fibers of lower $MW$ underwent severe disintegration beyond the listed temperatures. With the exception of $MW = 9,000,000$ g/mol, all PS fibers were heated well beyond the time required for relaxation of the entanglement network ($\tau_e$) and the Rouse times ($\tau_R$), in order to eliminate any initial molecular orientation induced by electrospinning [85]. With the exception of fibers of the two highest $MW$, the annealing conditions presented in Table 2.1 were estimated to correspond to 2–8 times the reptation time for bulk PS chains ($\tau_{d,bulk}$). $\tau_{d,bulk}$ was calculated as the time intercept of the intersection between linear extrapolations of the rubbery plateau and flow regimes using the creep compliance data and shift factors for the reference molecular weight of $MW_{ref} = 600,000$ g/mol [86,87]. Figure 2.5 shows the creep compliance as function of time for 110, 120 and 125 °C and a calculation of the reptation time at 120 °C. The reptation times for other molecular weights were then estimated by

$$\left(\tau_{d,bulk}\right)_{MW} = \left(\tau_{d,bulk}\right)_{MW_{ref}} \cdot \left(\frac{MW}{MW_{ref}}\right)^{3.4}$$

An earlier study established that in addition to overcoming the initial corrugated fiber morphology, the temperatures and the duration of annealing applied in this study are sufficient to eliminate any internal defects generated during electrospinning, even for $MW = 2,000,000$ g/mol [88].
Figure 2.4. SEM micrographs of PS nanofibers of four different \( MW \): (a) before and (b) after thermal annealing above the bulk \( T_g \). The initial axially corrugated surface morphology in the as-spun state was replaced by a uniform and smooth surface morphology after annealing.
Figure 2.5. Log-log plots of creep compliance, \( J(t) \), as a function of time, \( t \), at three different temperatures for the reference \( MW = 600,000 \text{ g/mol} \), showing the determination of reptation time (\( \tau_{d-bulk} \approx 2,875 \text{ s} \)) at \( T = 120 \degree \text{C} \). Solid lines are linear fits to the data in the rubbery and flow regimes.

2.4 Summary

The experimental methods and specimen fabrication processes employed in this dissertation research to achieve the objectives set forth in Chapter 1 were discussed. A surface micromachined platform for microscale tensile testing of extremely ductile nanofibers over the wide range of strain rates \( 10^{-4} \text{ – } 10^{2} \text{ s}^{-1} \) was employed to study the viscoplastic response of PS which is a model amorphous polymer. The experimental method relies on the use of DIC to achieve displacement resolution of \( \approx 20 \text{ nm} \) by only using optical microscopy in ambient conditions. A surface pattern created by a FIB
allowed maintaining the high displacement resolution under low light conditions that were encountered at fast imaging rates. PS fibers spanning an extremely wide range of monodisperse molecular weights of 13,000 – 9,000,000 g/mol and fiber diameters between 150 – 5,000 nm were fabricated using electrospinning, in order to study the effects of molecular and structural length scales on the mechanical behavior of nanoscale PS specimens. The fibers were subsequently annealed above their $T_g$ to overcome the initial processing effects, which resulted in specimens with very smooth surfaces.
CHAPTER 3

LARGE TENSILE DEFORMATION OF PS NANOFIBERS

Amorphous polymers exhibit two distinct modes of deformation when subjected to tensile loads in the glassy state: (i) immediate failure after yielding due to severe localization of plastic deformation, e.g. PS or PMMA, or (ii) sustained large deformation due to stabilization of strain localization, e.g. polycarbonate (PC) [5]. It should be noted that the former class of polymers is intrinsically ductile and undergoes large deformations along with post-yield strain hardening when subjected to compressive loads. Harnessing this intrinsic ductility of the former class of polymers at the bulk-scale and under tensile loading has been a topic of extensive research. Different approaches to this goal have included the addition of cavitating rubber particles, creation of a rubbery second phase via the addition of polymers such as polybutadiene, [89-92], reduction of the softening behavior via mechanical rejuvenation [93] or orientation of the polymer molecules by melt stretching [94]. Most of these methods produce a modest increase in ductility (< 50%) but compromise the strength and the stiffness of the original polymer.
Prior studies have alluded to a size dependent brittle-to-ductile transition at the submicron scale where a modest increase in ductility can be achieved while maintaining the strength [52]. However, there are no direct experiments to demonstrate large extensional deformations of ultra-small volumes of amorphous polymers, including a recent study of melt stretched PS, PMMA and PC, which, although acknowledged the importance of a brittle-to-ductile transition, did not study the role of size effects [94].

The focus of this Chapter is to understand the tensile response of individual PS nanofibers as a function of two length scales: the molecular length scale that is controlled by varying the $MW$, and the confining structural length scale defined by the fiber diameter, $D$. The combined effect of $MW$ and fiber diameter on the brittle-to-ductile transition of PS nanofibers is presented in Section 3.1, followed a study of the post-yield behavior as a function of a spatial confinement parameter in Sections 3.2 and 3.3. Experimental results for the large deformation behavior at low and high values of the confinement parameter are presented in Section 3.4. The implications of these results in terms of in expanding the structural capabilities of amorphous polymers and understanding the underlying molecular mechanisms are critically discussed (section 3.5).

3.1 Transition from Crazing to Necking in Submicron Scale PS Fibers

The uniaxial stress vs. stretch ratio response of PS nanofibers in Figure 3.1(a,b) show a transition from the macroscale brittle behavior for large fiber diameters (bottom panels) to a ductile behavior for submicron scale fiber diameters (top panels), for $MW =$
123,000 in Figure 3.1(a) and \( MW = 2,000,000 \) g/mol in Figure 3.1(b). The corresponding post-mortem SEM images in Figure 3.2 provide proof that this transition in mechanical behavior is associated with a change in the deformation mechanism, namely the large extension of submicron PS fibers is facilitated by stable necking, Figure 3.2(a), while localized fibrillation without necking significantly limits the overall fiber extension, as illustrated by the matching fracture surfaces of a PS nanofiber with \( MW = 123,000 \) g/mol in Figures 3.2(b,c). Further examination of the range of fiber diameters shown in the top and bottom panels of Figure 3.1(a,b) reveals that the transition from brittle to ductile response depends on the fiber diameter and the \( MW \). PS fibers of \( MW = 123,000 \) g/mol and diameters between 800 – 1000 nm, Figure 3.1(a), demonstrated bulk-like brittle response, while fibers in the same range of diameters but \( MW = 2,000,000 \) g/mol, Figure 3.1(b), were very ductile. Therefore, the brittle-to-ductile transition in PS nanofibers is driven by the degree of spatial confinement, which controls the interaction between molecular and specimen length scales. According to the plots in Figures 3.1(a,b), this brittle-to-ductile transition results in simultaneous increase in strength (\( \sim 50\% \)), ductility (\( \sim 4,000\% \)) and toughness (\( \sim 3,000\% \), as measured by the area under the engineering stress vs. stretch ratio curve). It is noteworthy that the fibrillation observed in Figure 3.2(b,c) is not the conventionally observed surface crazing, also shown later in Figure 3.12(c); rather it is initiated in the interior of the fiber as indicated by the two matching failure surfaces. The fibrils in Figure 3.2(c) are clearly drawn from the central hollow region in Figure 3.2(b), thus causing fibrillation and voiding. This intrinsic form of crazing, where cavitation and subsequent fibrillation originate in the interior of the specimen, is similar to crazing of bulk PS specimens with exceptionally smooth surfaces and no sub-surface defects.
Accordingly, the measured yield strength of the fibers in the lower panels of Figure 3.1(a,b) agrees well with the intrinsic uniaxial tensile craze yield strength of 55 MPa reported for isotropic bulk PS [96]. The transition to shear yielding occurred at very similar yield stresses and the elongation of the ductile fibers in Figure 3.1(a,b) is in agreement with that observed in shear deformation zones of bulk PS [97].

![Figure 3.1](image)

**Figure 3.1.** Engineering stress vs. stretch ratio curves of PS fibers showing a transition from bulk-like tensile brittle failure (lower panels) to extremely ductile tensile failure (top panels) for (a) $MW = 123,000$ g/mol and (b) $MW = 2,000,000$ g/mol.
Figure 3.2. High resolution SEM micrographs showing (a) the formation of a neck in a ductile PS nanofiber with $MW = 2,000,000$ g/mol, and (b,c) the matching failure surfaces of a macroscopically brittle fiber with $MW = 123,000$ g/mol that failed catastrophically due to fibrillation.
Qualitatively speaking, all PS fibers subjected to uniaxial extension demonstrated a mechanical response that followed the engineering stress, $\sigma$ vs. stretch ratio, $\lambda$, curve in Figure 3.3 consisting of (i) an initial viscoelastic regime (shaded region), (ii) a long flow stress plateau regime due to the formation and propagation of a stable neck, and (iii) a pronounced post-neck strain hardening regime, the onset of which is denoted by the stretch ratio $\lambda_h$. The shaded region in Figure 3.3 identifies the portion of the curve that applies to bulk PS. The ductile response of PS nanofibers is similar to that of amorphous polymers such as PC, although the latter has ultimate engineering tensile strength of $\sim$15% higher than the yield strength [94,97-100].

**Figure 3.3.** Representative engineering stress vs. stretch ratio curve for ductile PS nanofibers with a schematic description of the relevant deformation mechanisms. The grey-shaded region identifies the portion of the curve that applies to bulk PS.
3.2 Scaling of Large Deformation with Spatial Confinement

The ductility and strength of PS nanofibers are controlled by yielding and strain hardening, which, in turn, are influenced by the spatial confinement of PS molecules, namely, the interplay between $MW$ and fiber diameter. To this effect, the experimental results for PS nanofibers with different diameters and $MW = 400,000 – 2,000,000$ g/mol are presented in Figures 3.4(a-i). For each $MW$, the experimental plots are grouped according to the amount of fiber elongation exhibited during necking. A comparison of the plots for each $MW$, e.g. Figures 3.4(a-c), illustrates the effect of fiber diameter on the mechanical response: a reduction in fiber diameter resulted in lower stretch ratio at the onset of post-neck hardening, $\lambda_h$. For thinner fibers, the reduction in $\lambda_h$ was offset by increased strain hardening, as quantified by the post-neck hardening modulus, namely the slope of the post-neck strain hardening regime shown Figure 3.3. Consequently, thinner fibers exhibited increased tensile strength. In fact, fibers with initial diameters smaller than 500 nm displayed major post-neck strain hardening leading to 65 – 100% increase in tensile strength compared to the plateau/flow stress, and an additional 25 – 100% elongation after necking. On the contrary, PS fibers with initial diameters larger than 500 nm did not show explicit strain hardening, although they exhibited significant elongation during necking. These opposing trends in strain hardening and the fiber stretch ratio resulted in fairly constant toughness for all fibers that demonstrated the general mechanical behavior in Figure 3.3.

On the other hand, each row of plots in Figure 3.4 presents the stress-stretch ratio response of PS nanofibers grouped in comparable diameter ranges. The differences in the
mechanical response shown in each row are indicative of the influence of molecular length scale. As shown in Figures 3.4(b,e,h), increasing $MW$ (i.e., molecular chain length) increases the strain hardening modulus and fiber strength but decreases the elongation due to necking, $\lambda_h$. Clearly, the molecular scale and the fiber diameter scale have opposing effects on the evolution of large deformation. The combined effect of the two length scales could be described simultaneously by the single metric of the ratio of the fiber diameter, $D$, to the root-mean-square end-to-end distance of an individual polymer chain, $R_{ee}$, in the glassy state, namely the normalized fiber diameter, that hereafter is referred to as $D_{\text{norm}}$. Note that $D_{\text{norm}}$ is just a construct to describe the extent of molecular confinement in a nanofiber diameter as a multiple of $R_{ee}$, which has been used in the past for thin polymer films [39] and nanofibers [101]. Decreasing values of $D_{\text{norm}}$ imply increasing spatial confinement that arises from the need to conform the polymer chains in a smaller fiber cross-section. The mechanical properties of fibers with smaller $D_{\text{norm}}$ values are dominated by a larger fraction of polymer chain segments in the vicinity of the free surface. For example, for $D_{\text{norm}} = 3$, 85% of the polymer chain segments could be within a distance of one $R_{ee}$ from the fiber surface. It should be noted that the confining geometry of a nanofiber influences the true spatial arrangement of macromolecules to deviate from their bulk-like conformations [102].

A clear picture of the role of molecular confinement on the large deformation behavior of PS fibers emerges upon plotting the engineering stress vs. stretch ratio data in Figures 3.4(a-i) according to $D_{\text{norm}}$, as shown in Figure 3.5(b). Three regimes of $D_{\text{norm}}$ arise, each including stress vs. stretch ratio plots with comparable elongation during
Figure 3.4. Molecular weight and specimen size effects on uniaxial tension engineering stress vs. stretch ratio curves of PS nanofibers with (a-c) $MW = 400,000 \text{ g/mol}$, (d-f) $MW = 900,000 \text{ g/mol}$, and (g-i) $MW = 2,000,000 \text{ g/mol}$, grouped according to common values of $\lambda_h$. The data in panel (e) come from fibers fabricated using THF for electrospinning.
necking, strain hardening modulus and failure strength, for a large variety of MW values and fibers diameters. Nanofibers comprised of 65 – 85% surface chain segments (3 ≤ D_{norm} ≤ 5) demonstrated significant hardening and a threefold increase in engineering strength compared to bulk PS. Actually, the true strength, ranging between 200 – 240 MPa, was 4 – 5 times that of bulk PS. On the other hand, fibers in which 40 – 50% surface chain segments were in the vicinity of the free surface (7 ≤ D_{norm} ≤ 9) demonstrated moderate engineering strength of 100 MPa due to limited strain hardening. Fibers consisting of 30% surface chain segments (11 ≤ D_{norm} ≤ 13) exhibited no final strain hardening and lower strength of 50 – 100 MPa, i.e. 1 – 2 times that of bulk PS. Finally, a transition to bulk-like brittle response occurred for D_{norm} ≥ 18 that was characterized by fibrillar failure, as shown in Figure 3.2(a,b), and engineering strength values similar to unoriented bulk PS. The values of λ_{h} converge to a common value for D_{norm} > 7 in Figure 3.5(b) which corresponds to less than 50% of molecules near the fiber surface. There is more dispersion in the values of λ_{h} for D_{norm} < 5 which may be attributed to the rapidly increasing fraction of surface molecules for low values of D_{norm}. This is evident in Figure 3.6 where both λ_{h} and the stretch ratio at fiber failure, λ_{failure}, are shown to scale fairly linearly with D_{norm}, thereby confirming that λ_{h} is indeed proportional to D_{norm}. Interestingly, the normalized hardening strain, ε_{norm,h} = (λ_{h}-1)/(λ_{failure}-1), was independent of D_{norm}, Figure 3.6, which indicates that λ_{h} and λ_{failure} are not independent. Actually, ~60% of the overall elongation occurred by way of necking at a constant drawing stress, while the post-neck strain hardening regime accounted for ~40% of the total elongation. It is also noted that the value of ε_{norm,h} ≈ 0.61 for the PS nanofibers agrees very well with simulations (0.60±0.03) for isotropic amorphous polymers [103].
$D_{\text{norm}} = (D/R_{ee})$

Figure 3.5. (a) Schematic of a fiber cross-sectional view that illustrates the physical significance of $D_{\text{norm}}$ in terms of $R_{ee}$ and $D$. (b) Engineering stress vs. stretch ratio curves for PS fibers grouped according to $D_{\text{norm}}$. Solid, dashed and dashed-dotted lines represent data from fibers with $MW = 400,000, 900,000$ and $2,000,000$ g/mol, respectively.
Figure 3.6. Stretch ratio at failure, $\lambda_{\text{failure}}$, stretch ratio at the onset of hardening, $\lambda_h$, and normalized strain, $(\lambda_h-1)/(\lambda_{\text{failure}}-1)$, as a function of $D_{\text{norm}}$ for PS nanofibers with $MW = 400,000 – 2,000,000$ g/mol. The dashed lines in the top two panels represent linear fits to the data. All error bars represent the standard error of the mean.

3.3 Evolution of Flow and Hardening in PS Nanofibers

Further insight into the evolution of the large deformation response of PS nanofibers and its scaling with $D_{\text{norm}}$ requires knowledge of the evolution of true stress after completion of necking, which was obtained via interrupted tensile experiments. The onset of necking in PS nanofibers signified a locally smooth reduction in the fiber
diameter from $D_0$ to $D_{\text{neck}}$. After neck propagation, the entire fiber had a new diameter $D_{\text{neck}}$, which was verified by tensile experiments with multiple segments of the same fiber whose stress vs. stretch ratio curves are shown in Figures 3.7(a,b). Similarly, it was found that only a small change of less than 10 nm in the fiber diameter took place during the final strain hardening regime.

The measured $D_{\text{neck}}$ and the fiber diameter at failure, $D_{\text{failure}}$, the true stress at the onset of hardening, $\sigma_{\text{flow}}$, and failure, $\sigma_{\text{failure}}$, were obtained as shown for instance in Figure 3.7(c). The measured values for $D_{\text{neck}}$ and $D_{\text{failure}}$ together with $\lambda_h$ and $\lambda_{\text{failure}}$ were used to evaluate changes in volume, $\Delta V$, as shown for instance in Figure 3.7(c). Using several interrupted experiments with PS nanofibers of different $MW$, the ratio of the original fiber diameter, $D_0$, to $D_{\text{neck}}$ was estimated and is included in the SEM images in Figure 3.8. The ratio of the fiber volume before and after necking is estimated as

$$\frac{V_{\text{neck}}}{V_{\text{initial}}} = \frac{L_{\text{neck}} \cdot D_{\text{neck}}^2}{L_{\text{initial}} \cdot D_0^2} = \frac{\lambda_h}{\left(\frac{D_0}{D_{\text{neck}}}\right)^2}$$

(3.1)

Similarly,

$$\frac{V_{\text{failure}}}{V_{\text{initial}}} = \frac{\lambda_{\text{failure}}}{\left(\frac{D_0}{D_{\text{failure}}}\right)^2}$$

For PS nanofibers with $D_0 < 400$ nm, the quick emergence and propagation of multiple, closely spaced necks (which is likely the result of local molecular inhomogeneities for small values of $D_{\text{norm}}$) precluded the precise identification of a stable $D_{\text{neck}}$. In such cases, the ratio of $D_0/D_{\text{neck}}$ was estimated from measurements of $D_{\text{failure}}$, and was noted to have decreased slightly.
Figure 3.7. (a) SEM image from an interrupted tensile experiment with a PS fiber of $MW = 400,000$ g/mol showing constant neck diameter. (b) Engineering stress vs. stretch ratio response from tests on two segments of the same fiber ($MW = 400,000$ g/mol), interrupted right after the onset of necking (red), and just before the end of necking (blue). The red and blue bordered insets show corresponding post-mortem images. A 22% increase in volume during necking was calculated using Equation 3.1. (c) Estimated true flow and failure stress (dashed curves) from the solid curve in black using the fiber radii measured by interrupted experiments on a PS nanofiber of $MW = 2,000,000$ g/mol.
Figure 3.8. SEM images from interrupted tensile experiments showing the neck ratio of PS nanofibers with $MW$: (a) 400,000 g/mol, (b) 900,000 g/mol and (c) 2,000,000 g/mol.
It is important to mention that the large plastic deformation taking place during necking of submicron scale PS fibers was accompanied by a volume increase of 10 – 15% and in some cases 25%, which may be attributed to increasing free volume.

Unlike the $D_{\text{norm}}$ dependence of fiber elongation during necking, Figure 3.6, the tensile flow stress, $\sigma_{\text{flow}}$, calculated using the final neck diameter was quite independent of $D_{\text{norm}}$, averaging 98±11 MPa, Figure 3.9(a). Actually, $\sigma_{\text{flow}}$ represents the stress at the onset of post-neck hardening. As such, is similar to cold drawing stress experienced by individual craze fibrils in isotropic bulk PS, subjected to uniaxial tension [104]. The post-neck hardening of PS nanofibers was quantified by the hardening modulus, namely the slope of the stress vs. stretch ratio curve in this region. In doing so, the engineering stress in this regime was multiplied by a factor of $(D_0/D_{\text{neck}})^2$ to reflect the true stress at the onset of hardening. The hardening modulus, $E_h$, was estimated by

$$\sigma_{\text{hardening}} \approx \left(\frac{D_0}{D_{\text{neck}}}\right)^2 \cdot \sigma_{\text{eng-hardening}} = E_h \cdot \lambda$$ \hspace{1cm} (3.2)$$

and is plotted in Figure 3.9(b) as a function of $D_{\text{norm}}$. It is evident that the hardening modulus scales with $D_{\text{norm}}$, unlike $\sigma_{\text{flow}}$ that remained constant. For $D_{\text{norm}} \approx 3$, $E_h$ was 5 – 7 times the $E_h$ of an individual craze fibril in bulk PS, calculated in the same way as described above using the data in [104], which explains the significantly increased strength of submicron PS fibers. While $\sigma_{\text{flow}}$ was found to be constant for PS nanofibers, the value of $E_h$ was inversely proportional to $D_{\text{norm}}$, Figure 3.9(a,b), counteracting the post-yielding softening response and, hence leading to stable necking.

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Figure 3.9. (a) Flow stress $\sigma_{\text{flow}}$, and (b) hardening modulus, $E_h$, as a function of $D_{\text{norm}}$. A comparative estimate of the strain-hardening modulus for a PS craze fibril using the data in [104] is also shown. The black dashed line is provided only as a visual aid.
The large deformation of PS nanofibers was enabled by stable necking with $\sigma_{\text{flow}} = 98 \pm 11$ MPa, which was $D_{\text{norm}}$ independent and in good agreement with the drawing stress of individual craze fibrils in bulk PS. Thus, although the process of neck localization is macroscopically different from crazing, the molecular mechanism of chain uncoiling in the neck transition region takes place at similar stresses as in the active zone in bulk PS [97]. However, $E_h$ decreased with increasing $D_{\text{norm}}$, eventually leading to brittle failure.

The molecular origins of the post-yield deformation of PS nanofibers can be better understood by invoking the physically entangled network model for polymer glasses which suggests that the large deformation of amorphous polymers during necking arises from the elongation of polymer chains between successive inter-chain entanglements [97]. The distance between successive inter-chain entanglement points is considered to be a material property above the critical molecular weight, $M W_{\text{critical,PS}} \approx 200,000$ g/mol, i.e. \( \approx 10 \) times the entanglement molecular weight for PS [105]. Furthermore, the theoretical limit for chain extensibility associated with the distance between inter-chain entanglements is $\lambda_{\text{limit}} \approx 4.2$ [97]. However, the extensions undergone by PS fibers with $M W > M W_{\text{critical,PS}}$ were less than $\lambda_{\text{limit}}$, e.g. Figure 3.6, suggesting that the inter-chain entanglement network is not disrupted significantly during necking. In fact, recent coarse grain molecular simulations [106], experiments on bulk PC [107], and the preliminary experiments with PS nanofibers in Section 6.2 also indicate that the large deformation of amorphous polymers during neck propagation is associated with molecular uncoiling between inter-chain entanglements, wherein, the inter-chain entangled network structure is preserved and neck deformation can be reversed by
heating the specimens at $T_g$. Therefore, the gradual decrease of $\lambda_h$ at small values of $D_{\text{norm}}$, in Figure 3.6, should be related to the reduced ability of chain segments between inter-chain entanglements to extend or uncoil. The shear stresses in the neck region support efficient molecular uncoiling between inter-chain entanglement sites. Following the physical construct of $D_{\text{norm}}$ in Figure 3.5(a), the core PS molecules that are fully confined by surrounding molecules have a higher number of inter-chain entanglements, as opposed to the molecules near the free-surface. Thus, small values of $D_{\text{norm}}$ reduce the fraction of internal molecules with the maximum number inter-chain entanglement points ($MW > MW_{\text{critical,PS}}$) that promote molecular uncoiling. As a consequence of this heterogeneous distribution of intermolecular interactions across the fiber cross-section, fibers of smaller $D_{\text{norm}}$ effectively undergo lesser molecular uncoiling, leading to reduced $\lambda_h$, as supported by the data in Figure 3.6.

This explanation for the dependence of $\lambda_h$ on $D_{\text{norm}}$ provides the basis to understand the corresponding trends in $E_h$ and $\sigma_{\text{flow}}$ in Figures 3.9(a,b). Physically speaking, the molecular extension between two inter-chain entanglements is viewed as a process of overcoming a series of intra-chain energy barriers (i.e., intra-chain interactions/entanglements) leading to uncoiling and extension of chain segments between successive inter-chain entanglements. Propagation of a stable neck along the length of a fiber provides significant fiber extension at constant flow stress leading to a uniformly new material state with increased alignment of the polymer chains with respect to the fiber axis. Additional fiber extension by further chain disentanglement can occur at higher stresses in the post-neck hardening portion of the stress vs. stretch ratio curves,
e.g. Figure 3.3. For the reasons stated above, the increased fraction of surface chain segments for smaller $D_{\text{norm}}$ values would require larger stresses to achieve further post-necking plastic deformation, which manifests itself by an inversely proportional dependence of $E_h$ on $D_{\text{norm}}$.

Figure 3.10. True stress vs. normalized strain for PS nanofibers of four $MW$. The error bars (shown only for the post-yield response) represent the standard error of the mean within each binned normalized strain increment of 1%. The dashed line marks the end of necking at constant $(\dot{\lambda}_{\text{h}}^{-1})/(\dot{\lambda}_{\text{failure}}^{-1})$.

The stress vs. stretch ratio curves for fibers with different values of $D_{\text{norm}}$, and as a result $\lambda_{\text{max}}$, can be unified by employing the normalized strain, $\varepsilon_{\text{norm}} = (\lambda^{-1})/(\lambda_{\text{max}}^{-1})$. Correspondingly, the spectrum of $D_{\text{norm}}$ dependent large deformation responses by PS
nanofibers of $MW = 400,000 - 2,000,000$ g/mol (shown in Figure 3.4) collapses to a “universal” true stress vs. normalized strain response that is independent of $D_{\text{norm}}$, as shown in Figure 3.10. Notably, the normalized strain at the end of necking occurs at the constant value of $\epsilon_{\text{norm},h} = (\lambda_h-1)/(\lambda_{\text{max}}-1) \approx 0.6$. PS nanofibers with $MW = 123,000$ g/mol exhibited a qualitatively similar response, but with reduced yield strength and hardening modulus, because this molecular weight is below $MW_{\text{critical,PS}} \approx 200,000$ g/mol [105,106].

### 3.4 Mechanical Behavior of PS Fibers for Extreme Values of $D_{\text{norm}}$

In the preceding section the geometrical construct of $D_{\text{norm}}$ was shown to provide a good interpretation for the scaling of $\lambda_h$ and $E_h$ with $D_{\text{norm}}$. A question remains, however, about the utility and the meaning of $D_{\text{norm}}$ for near unit values and for very large values that correspond to bulk PS. For instance, the minimum value of $D_{\text{norm}} = 18$, beyond which large fiber extensions transition to brittle fracture, can be calculated by using Figure 3.1(a,b). This transition in the mechanical behavior takes place at the fiber level, while locally, large deformation still occurs in the form of heavily elongated fibrils, as shown in Figure 3.2(b,c). Increasing $D_{\text{norm}}$ provides a measure for effective uncoiling of polymer chain segments between inter-chain entanglements, as manifested by the macroscopic value of $\lambda_h$. At a critical $D_{\text{norm}}$, a polymer chain uncoiling between entanglements reaches a limit and further deformation can only occur through disruption of the local entanglement network via chain scission [105] that results in local microscopic void nucleation followed by fibrillation/crazing [108]. Once formed, individual craze fibrils, e.g. Figure 3.2(c), could locally undergo extensions greater than
\( \lambda_{\text{limit}} \) [97,104], although the overall fiber extension is small, exhibiting macroscopically brittle failure.

This molecular view of craze-to-shear transition is supported by the present data: an extrapolation of the linear fit for \( \lambda_h \) vs. \( D_{\text{norm}} \), Figure 3.6, to the experimentally determined limiting value of \( D_{\text{norm}} \approx 18 \), provides an estimate for the maximum extension via stable necking \( \lambda_{h\text{-max}} \approx 3.1 \). In fact, \( \lambda_{h\text{-max}} \approx 0.75 \times \lambda_{\text{limit}} \) is in good agreement with previous studies which have identified that the shear-to-craze transition in PS occurs between \((0.6 – 0.8) \lambda_{\text{limit}} \), when heavily stressed individual PS chain segments undergo scission to form craze fibrils [97]. A similar extrapolation of \( \lambda_{\text{failure}} \) in Figure 3.6 to \( D_{\text{norm}} \approx 18 \) estimates that the maximum extension of PS at failure is \( \lambda_{\text{failure\text{-max}}} \approx 4.1 \), which is in excellent agreement with the theoretical estimate of \( \lambda_{\text{limit}} = 4.2 \) [97].

It is noteworthy that the PS fibers with \( D_{\text{norm}} = 11–13 \) in Figure 3.4(c) exhibited \~25\% increase in volume during stable necking and failed without further hardening which could have prevented them from attaining the estimated \( \lambda_{\text{failure\text{-max}}} \). These fibers underwent extensions of \( \lambda_h = \lambda_{\text{failure}} \approx 2.45 \), in agreement with the lower bound of \( 0.6 \times \lambda_{\text{limit}} \) for shear-to-craze transition [97]. By contrast, PS fibers with \( D_{\text{norm}} = 4 – 5 \) displayed only 5-10\% increase in volume during necking, Figure 3.7(b), and significant post-neck hardening with an additional 10 – 15\% volume increase prior to failure so that the total volume dilatation was still of the order of 25\%.

The geometrical construct in Figure 3.5(a) implies a significant loss of the average density of inter-chain entanglements for \( D_{\text{norm}} < 3 \) [109]. The large fraction of surface chain segments is unlikely to support significant shear stresses [110], and
therefore, is less likely to sustain necking. Tensile tests with PS fibers of $MW = 9,000,000$ g/mol ($R_{ee} \approx 250$ nm) and diameters $440$ nm $< D < 660$ nm (namely $1 < D_{\text{norm}} < 3$), showed complete suppression of necking due to craze-assisted brittle failure, as shown in Figures 3.11 and 3.12(c). The crazing behavior for $1 < D_{\text{norm}} < 3$ shown in Figure 3.12(c) is surface controlled, as opposed to intrinsic crazing for $D_{\text{norm}} = 18$ shown in Figures 3.2(b,c). Furthermore, fibers with $1 < D_{\text{norm}} < 3$ had lower tensile strength of $30 – 35$ MPa, as opposed to $\sim 50$ MPa for intrinsic crazing recorded for fibers with $D_{\text{norm}} > 18$, despite the much larger $MW$ of the former and the similar surface finish. In light of these observations, it is worth noting that for $D \sim (1 – 2) \times R_{ee}$, a reduction in $T_g$ across most of the fiber diameter could have enhanced segmental mobility [14], and thus, the propensity for surface crazing as also described by a recent model for crazing [111].

On the other hand, fibers with $MW = 9,000,000$ g/mol and $D < 250$ nm (i.e., $D_{\text{norm}} \sim 1$) demonstrated a ductile response via uniform extension, Figure 3.12(d), resulting in increased mechanical strength, Figure 3.11, therefore, the plots in the third panel of Figure 3.11 provide an approximation for the average constitutive behavior for this particular fiber. Interestingly, an extrapolation of the linear fit of $\lambda_h$ vs. $D_{\text{norm}}$ in Figure 3.6 to $D_{\text{norm}} = 1$, predicts $\lambda_h \approx 1.2$ which is in agreement with the experimental stretch ratio shown in the third panel of Figure 3.11.

Thus, even for $MW = 9,000,000$ g/mol, the reduction of $D_{\text{norm}}$ from 3 to $\sim 1$ provided a concurrent increase in strength (150%), ductility (400%) and toughness (2,000%), which is consistent with the results for $MW = 123,000 – 2,000,000$ g/mol. The fractographic evidence of crazing for PS fibers with diameters of $440$ nm $< D < 660$ nm...
is additional proof that the craze-to-shear transition in PS is affected by molecular confinement [112].

Figure 3.11. Stress vs. stretch ratio curves for PS fibers of $MW = 13,000$ g/mol, 50,000 g/mol, and 9,000,000 g/mol.
Figure 3.12. SEM images of fibers with (a) $MW = 13,000$ g/mol and smooth, glass-like failure surface, (b) $MW = 50,000$ g/mol and rough but relatively flat failure surface, (c) $MW = 9,000,000$ g/mol and $D > R_{ee}$ demonstrating crazing, and (d) $MW = 9,000,000$ g/mol $D \sim R_{ee}$ which failed after homogenous deformation without crazing.

The critical role of the chain entanglement network in neck stabilization and sustained large fiber extensions is further supported by experiments with PS fibers with the low $MW = 13,000$ g/mol and 50,000 g/mol. Given that the entanglement molecular weight ($M_e$) of PS is 17,000 g/mol [113], PS fibers of $MW = 13,000$ g/mol are comprised of short, unentangled chains. Consequently, the lack of entanglements leads to smooth,
glass-like brittle failure surfaces as shown in Figure 3.12(a) that are associated with the brittle stress-stretch ratio response in the first panel of Figure 3.11. For $MW = 50,000$ g/mol, the PS chains began to form an entangled network and the corresponding fracture surfaces became fibrillar, Figure 3.12(b), while the fibers failed in a brittle manner, as shown in the central panel of Figure 3.11. This mechanical behavior is consistent with the construct of $D_{\text{norm}}$: PS fibers of $MW = 50,000$ g/mol and large diameters of $2 – 3 \ \mu m$ result in $D_{\text{norm}} = 200 – 270$, therefore are macroscopically brittle. The highly ductile individual fibrils on the failure surface in Figure 3.12(b), are a few tens of nanometers in diameter and correspond more closely to $D_{\text{norm}} < 18$.

3.5 Discussion

The large deformation behavior of submicron PS nanofibers has common features with bulk-scale strategies for toughening of neat PS, namely pre-conditioning and melt-stretching. Unlike mechanically pre-conditioned specimens [114], the toughness of submicron PS fibers is permanent: annealed specimens stored for 2 – 3 years at room temperature exhibited similar mechanical response as those tested soon after annealing. Similarly, melt-stretched PS specimens have lasting increase in strength and toughness by way of necking [94]. However, the strength and toughness improvements in PS nanofibers by way of spatial confinement are nearly 50 – 100% greater than those achieved by melt stretched PS fibers [94]. More importantly, unlike melt-stretched PS, the mechanical behavior of PS nanofibers undergoing necking still retained some of the properties of unoriented bulk PS:
The yield strength of ductile PS nanofibers has been shown to be fairly constant, 50 – 60 MPa, while comparable changes in failure strength and ductility in melt-stretched samples are accompanied by a twofold increase in yield strength.

Although all PS nanofibers with $D_{\text{norm}} = 3 – 13$ exhibited different failure strain, 60% of the fiber extension was due to necking and the remaining 40% occurred during post-neck hardening.

These aspects PS nanofibers reinforce our view that their dramatic strengthening and toughening response are not due to fabrication induced orientation effects, rather due to the confining effect of the fiber specimen geometry. Other factors related to the effects of specimen fabrication have also been considered but could not explain the observed large deformation behavior. For instance, it has been widely reported that thin films are typically annealed for up to 12 hr to remove the effects of molecular orientation arising from spin casting. However, experiments with $MW = 2,000,000$ g/mol fibers annealed for 17 hr (a tenfold increase in the annealing time in earlier reports and 2 times the $\tau_{d-bulk}$ based on the calculations in Section 2.2) did not show significant differences in the dependence of large deformation behavior on fiber diameter, as shown in Figure 3.13. Similarly, residual solvent effects and polymer density variations across the fiber diameter that often result from electrospinning [115] were also ruled out since all fibers produced from different solution concentrations and solvents (e.g. data corresponding to $MW = 900,000$ g/mol in Figure 3.4(e) and $D_{\text{norm}} \approx 5$ in Figure 3.6) displayed the same scaling with $D_{\text{norm}}$ in their mechanical behavior.
Figure 3.13. Stress-strain curves from nanofibers with $MW = 2,000,000$ g/mol fabricated from a solution of 4.5 wt% PS in DMF solvent and annealed for 17 hr at $(T_g+25)$ °C.

Finally, it is noted that the decreasing hardening and flow strain with $D_{norm}$ exhibited by the PS nanofibers are analogous to the dramatic stiffening observed in ultrathin PS films subjected to biaxial tension in the viscoelastic regime [50,64-66]. The origin of the dramatic stiffening in the biaxial tension experiments was posited to arise from pinning of surface chain segments close to the free surface, although the origins and details of such process were noted to be unclear. It is also important to note that biaxial tension experiments with thin films could only be carried out close to their $T_g$, and hence thinner films were studied at lower absolute temperatures than thicker films, a factor that
is likely to contribute to the observed stiffening of thinner films. In contrast, the uniaxial tension experiments with PS nanofibers in this study were performed at room temperature, i.e., deep in the glassy state, thus ruling out temperature as the contributing factor. It is therefore likely that modifications in molecular conformations near the free fiber surface [102,109] along with additional molecular constraints [116], are responsible for the enhanced hardening behavior and the reduction in the overall nanofiber ductility for small values of $D_{\text{norm}}$.

### 3.6 Conclusions

The interplay between molecular and specimen length scales in glassy amorphous PS fibers was shown to allow for 3,000 – 4,000 % increase in toughness with simultaneous increase in failure strength by ~350%, compared to brittle bulk PS. The ratio of the characteristic specimen length scale (fiber diameter) to the intrinsic macromolecular length scale (end-to-end chain distance), $D_{\text{norm}}$, was shown to be serve as an excellent scaling parameter to predict the evolution of necking and strain hardening in submicron scale PS fibers. The outstanding toughness of PS nanofibers was fairly constant over a broad range of monodisperse $MW = 123,000 – 2,000,000$ g/mol and $D_{\text{norm}} = 3 – 18$, while strength and ductility varied: increasing fraction of surface to interior molecules increased the tensile fiber strength at the expense of ductility. The strength was achieved for $D_{\text{norm}} = 3 – 5$. For $3 > D_{\text{norm}} > 13$, stable neck propagation consistently produced ~60% of post-yield elongation, while subsequent homogenous hardening resulted in an additional ~40% elongation, with the area under the engineering stress vs.
stretch ratio curves remaining fairly constant. An analysis based on the scaling of the fiber stretch ratio with $D_{\text{norm}}$ helped to explain the different fiber extension modes ranging from craze-assisted brittle failure ($D_{\text{norm}} > 18$), to necking ($3 < D_{\text{norm}} < 18$), to homogenous deformation ($D_{\text{norm}} \sim 1$), which are summarized graphically in Figure 3.14.

Figure 3.14. Representative engineering stress vs. stretch ratio curves for increasing $D_{\text{norm}}$ (top abscissa) going from top left to bottom right. SEM images depict the different deformation modes possible in ductile ($D_{\text{norm}} < 18$) and brittle ($D_{\text{norm}} > 18$) regimes.
CHAPTER 4

EFFECT OF STRAIN RATE ON THE
DEFORMATION OF PS NANOFIBERS

The mechanical behavior of polymers depends on the rate of deformation even at temperatures well below $T_g$. The viscous component of the mechanical behavior of glassy polymers encompasses several structural relaxation mechanisms, ranging from the relatively fast segmental relaxations such as side-group rotation, to the slower and larger scale cooperative molecular motions [20,117]. Their relative contribution to the overall mechanical response is dictated by the amplitude of the mechanical load and the rate of loading. For instance, yielding and the subsequent deformation of amorphous polymers can be understood as the result of the competition between material softening and hardening, each having a different strain rate dependence according to the contribution of $\alpha$- and $\beta$-relaxations [19,118]. Only the $\alpha$-relaxation affects polymer yielding at slow strain rates, while the influence of both relaxation processes on yielding can be observed at higher strain rates [19,118]. As discussed in Section 1.1, amorphous polymeric nanostructures can experience significant differences in the spectrum of relaxation
processes with a likely broadening and/or shift of the \( \alpha \)-regime [10,17,21-26], which, in turn, can affect their viscoplastic behavior.

Although numerous experimental and modeling studies have been devoted to the study of the viscous character of elasto-plastic deformation processes and the failure mechanisms of amorphous polymers at the bulk-scale [19,100,118-122], very few relevant experimental studies exist at the submicron scale [50,123,124]. Almost all experimental reports at the submicron scale focus on relatively long time scales that can be probed by raising the temperature. Interestingly, direct nanoscale experiments [50,65] of the thermo-viscoelastic behavior of ultrathin amorphous PS and poly(vinyl acetate) (PVAc) thin films have identified that, contrary to expectations for increased mobility of polymer chain segments at the free surface, many relaxation modes (especially the slower relaxation modes) are suppressed at their free surfaces. Similarly, it has been shown that the slowest characteristic relaxation times of as-spun, semi-crystalline PAN nanofibers display further retardation with decreasing fiber diameter (i.e. fibers with a larger fraction of surface molecules) [56]. These experiments [56] captured the viscoplastic response of polymer nanofibers over a wide range of strain rates, which is needed to understand the factors governing the unique strain hardening behavior of the amorphous PS nanofibers discussed in Chapter 3.

In this Chapter, the strain rate dependent tensile response of PS nanofibers with \( MW = 123,000 \) g/mol, 400,000 g/mol and 2,000,000 g/mol was studied for six orders of applied strain rate \( (10^{-4} - 10^{2}) \) by the methodology described in Section 2.2. The choice of \( MW \) was motivated by the observation of an overarching effect of \( MW \) on the large
The deformation of PS nanofibers in Section 3.3: \( MW = 123,000 \) g/mol is below the \( MW_{\text{critical,PS}} \), while \( MW = 400,000 \) and \( 2,000,000 \) g/mol are above \( MW > MW_{\text{critical,PS}} \). The latter also represent the extremes for which the true stress vs. normalized strain curves collapsed onto a master curve as shown in Figure 3.10. The interplay between time and length scales was studied via experiments on fibers of two distinctly different diameters for each \( MW \), thereby covering a wide range of \( D_{\text{norm}} \) values.

In the subsequent sections of this dissertation the use of the term strain rate refers to the cross-head strain rate. The cross-head strain rates were measured via linear fitting of the cross-head strain vs. time data from each experiment, as illustrated in Figure 4.1. Due to the compliance of the MEMS loadcell which is in line with the fiber specimen, and the post-yield strain localization in PS nanofibers, the cross-head strain rates measured during the elastic and post-yield plastic regimes are different in Figure 4.1. Appendix I provides further details. The value of \( \dot{\varepsilon}_{\text{plastic}} \) used in this Chapter refers to the slope of a single linear regression fit line across the entire post-yield regime that includes necking and strain hardening, as the slopes of these two regimes are quite similar. Where specifically noted, the elastic strain rate, \( \dot{\varepsilon}_{\text{elastic}} \), is the cross-head strain rate in the pre-yield, elastic regime.

This Chapter is organized as follows: the viscoplastic response of PS nanofibers with \( MW = 123,000 \) g/mol is discussed in Section 4.1, followed by the viscoplastic response of fibers with \( MW = 400,000 \) and \( 2,000,000 \) g/mol in Section 4.2. Sections 4.3 and 4.4, respectively discuss the strain rate sensitivity, and the scaling of the large deformation response of PS nanofibers as a function of \( D_{\text{norm}} \).
Figure 4.1. Representative calculations of strain rate obtained from linear regression to the engineering strain vs. time data. The linear correlation coefficient (R^2) is also shown. Inset provides an enlarged view of the elastic regime.

4.1 Viscoplastic Behavior of PS Nanofibers with $MW = 123,000$ g/mol

Representative engineering stress vs. stretch ratio curves for PS nanofibers of $MW = 123,000$ g/mol tested at different cross-head strain rates are shown in Figure 4.2. The test specimens were four segments of the same nanofiber with an initial diameter of 190 nm ($D_{\text{norm}} \approx 8$) in Figure 4.2(a), and 420 nm ($D_{\text{norm}} \approx 18$) in Figure 4.2(b). In both cases, the engineering stress increased with the strain rate which is consistent with the notion that increasing strain rate diminishes the time available for some relaxation processes to occur. For fibers of $D_{\text{norm}} \approx 8$ in Figure 4.2(a), all the fiber segments exhibited nearly similar values for $\lambda_h$ and $\lambda_{\text{failure}}$. All fiber segments exhibited stable necking and
pronounced post-neck hardening for strain rates $10^{-4} - 10^2 \text{ s}^{-1}$. By contrast, increasing the strain rate led to non-monotonic changes in $\lambda_h$ for fibers with $D_{\text{norm}} = 18$, in Figure 4.2(b): increasing the strain rate from $10^{-4}$ to $1 \text{ s}^{-1}$ increased the stretch ratio from 20% to 90%, while additional increase in the elastic strain rate to $30 \text{ s}^{-1}$ resulted in a ductile-to-brittle transition. Bulk PS specimens that exhibited ductility under uniaxial tension at elevated temperatures of $65 - 85 \degree \text{C}$ displayed a similar rate dependent ductile-to-brittle transition, although the corresponding strain rate was already low and decreased further with temperature. Specifically, the ductile-to-brittle transition at $85 \degree \text{C}$ occurred at $10^{-2} \text{ s}^{-1}$, while at $65 \degree \text{C}$ this transition occurred at $10^{-3} \text{ s}^{-1}$ [125]. However, PS nanofibers of $D_{\text{norm}} \approx 18$ demonstrated this ductile-to-brittle transition at $\sim 10 \text{ s}^{-1}$ at room temperature, while fibers of $D_{\text{norm}} \approx 8$ sustained their strength and toughness until cross-head strain rates of $150 \text{ s}^{-1}$.

The deformation pathways leading to the stress-stretch ratio curves in Figure 4.2 were evaluated based on the corresponding post-mortem SEM images in Figure 4.3. Figures 4.3(a,b), corresponding to a fiber with $D_{\text{norm}} \approx 18$, show the matching failure surfaces for a segment that failed catastrophically when tested at the highest strain rate ($\dot{\varepsilon}_{\text{elastic}} = 30 \text{ s}^{-1}$). There is no evidence of defects in the vicinity of the failure site that could have resulted in premature failure. Instead, failure occurred when localized deformation did not stabilize into a neck, instead leading to local voiding and fibril formation. Representative matching failure surfaces for fibers with $D_{\text{norm}} = 18$ that elongated until failure at lower strain rates ($10^{-4} - 1 \text{ s}^{-1}$), Figure 4.3(c), displayed similar
Figure 4.2. Engineering stress-stretch ratio plots for PS nanofibers of $MW = 123,000$ g/mol, and (a) $D = 190$ nm ($D_{\text{norm}} \approx 8$), (b) $D = 420$ nm ($D_{\text{norm}} \approx 18$) for four different strain rates. The legend shows ($\dot{\varepsilon}_{\text{elastic}}$; $\dot{\varepsilon}_{\text{plastic}}$) where applicable. The arrows (↓) in (a) indicate the value of $\lambda_h$. 
Figure 4.3. SEM images of segments of a fiber with $D_{\text{norm}} \approx 18$ corresponding to the stress vs. stretch ratio responses in Figure 4.1(b). (a,b) Matching fracture surfaces for $\dot{\varepsilon}_{\text{elastic}} = 29 \text{ s}^{-1}$, (c) representative matching fracture surfaces for $\dot{\varepsilon}_{\text{plastic}} = 1.4 \text{ s}^{-1}$, (d) gage section after failure showing remnant unnecked region. (e,f) Representative fracture surfaces for fibers with $D_{\text{norm}} \approx 8$, ($\sigma - \lambda$ response given in Figure 4.1(a).
fibrillation. However, gage section regions that did not undergo necking were also present along the fiber length as shown in Figure 4.3(d). By contrast, Figures 4.3(e,f) show fracture surfaces from thinner nanofibers ($D_{\text{norm}} = 8$) with no hints of fibrillation or void formation on the fracture surface, thus, suggesting that these fibers did undergo shear yielding. Thus, the absence of fibrillation in thinner fibers allowed for stable necking at all strain rates resulting in increased fiber strength and toughness. On the contrary, thick fibers attained maximum elongation and toughness at the strain rate of $\sim 1$ s$^{-1}$, as shown in Figure 4.2(b).

4.2 Viscoplastic Behavior of PS Nanofibers with High Molecular Weights

Engineering stress vs. stretch ratio curves for $MW = 400,000$ g/mol are shown in Figure 4.4 for fiber diameters of $D = 350$ nm ($D_{\text{norm}} \approx 8$) and $D = 475$ nm ($D_{\text{norm}} \approx 11$). Similarly, Figure 4.5 shows the engineering stress vs. stretch curves for $MW = 2,000,000$ g/mol and fiber diameters of $360$ nm ($D_{\text{norm}} \approx 3$) and $750$ nm ($D_{\text{norm}} \approx 6$). Qualitatively, the mechanical response of fibers with $MW = 400,000$ g/mol illustrated in Figure 4.4 is similar to that for fibers with $MW = 123,000$ g/mol: the fibers with relatively low $D_{\text{norm}} \approx 8$ in Figure 4.4(a) sustained stable necking and subsequent hardening over the entire strain rate range with no significant changes in ductility, while fibers with larger $D_{\text{norm}} \approx 11$ demonstrated very consistent $\lambda_{\text{failure}}$, Figure 4.4(b). At the slowest plastic strain rate of $\sim 10^{-4}$ s$^{-1}$ these fibers failed prematurely before the completion of neck propagation, a feature that is qualitatively similar to fibers with $MW = 123,000$ g/mol and $D_{\text{norm}} \approx 18$. 
Figure 4.4. Engineering stress vs. stretch ratio plots for PS nanofibers with $MW = 400,000$ g/mol, and (a) $D = 350$ nm ($D_{\text{norm}} \approx 8$) and (b) $D = 475$ nm ($D_{\text{norm}} \approx 11$) for different strain rates (legend shows $\dot{\varepsilon}_{\text{elastic}}$; $\dot{\varepsilon}_{\text{plastic}}$). The arrows (↓) in (a) and (b) indicate the $\lambda_h$. 

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Figure 4.5. Engineering stress vs. stretch ratio plots for PS nanofibers with $MW = 2,000,000$ g/mol, and (a) $D = 360$ nm ($D_{\text{norm}} \approx 3$), (b) $D = 750$ nm ($D_{\text{norm}} \approx 6$) for different strain rates (legend shows $\dot{\varepsilon}_{\text{elastic}} ; \dot{\varepsilon}_{\text{plastic}}$). The arrows (↓) in (a) and (b) indicate the $\lambda_h$. 
Notably, fibers with $MW = 2,000,000$ g/mol shown in Figure 4.5 sustained stable necking followed by strain hardening at all strain rates in the diameter range of 360 – 750 nm which corresponds to $D_{\text{norm}} = 3 – 6$. These data clearly suggest that the effect of strain rate is coupled with the fiber diameter and $MW$, namely $D_{\text{norm}}$. Fibers with $D_{\text{norm}} > 10$ are likely to show unstable necking, whereas fibers with $D_{\text{norm}} < 8$ are likely to sustain stable necking followed by hardening over a wide range of strain rates.

4.3 Strain Rate Sensitivity of PS Nanofibers

The strain rate sensitivity of the applied stress in glassy amorphous polymers is typically estimated by the Eyring equation [126]:

$$\sigma = \frac{\Delta H}{V^*} + k \cdot T \cdot \frac{V^*}{V^*} \cdot \ln \left( \frac{\dot{\lambda}}{\dot{\lambda}_0} \right)$$

(4.1)

where the activation energy, $\Delta H$, the activation volume, $V^*$, and the reference strain rate, $\dot{\lambda}_0$, are fitting parameters. For PS nanofibers with $D_{\text{norm}} < 8$, (e.g., Figures 4.5) the deformation regimes of necking and subsequent hardening began and ended at similar stretch ratios across a wide range of strain rates. Hence, Equation 4.1 re-written as

$$\sigma(\lambda) = H(\lambda) + S(\lambda) \cdot \ln(\dot{\lambda})$$

(4.2)

can be applied to the entire stress-stretch curve, by considering the fitting parameters as functions of $\lambda$ [127,128]. In other words, attaining a particular value of $\lambda$, implies overcoming a particular energy barrier, $\Delta H(\lambda)$ and involves an activation volume $V^*(\lambda)$.
The slopes, $S(\lambda)$, and intercepts, $H(\lambda)$, obtained from linear fitting between $\sigma_{\text{eng}}(\dot{\lambda})$ and $\ln(\dot{\lambda})$ in Figures 4.2(a), 4.4(a) and 4.5(a) are shown in Figures 4.6. The calculation procedure is described in Appendix II. The linear correlation coefficients, $R^2$, in Figure 4.6(a) indicate the goodness-of-fit to Equation 4.2. The high values of the $R^2$, mostly > 0.90, indicate that the entire post-yield deformation is strain rate sensitive. In Figure 4.6(b), the values of the slope $S(\dot{\lambda}) = \frac{k \cdot T}{V^*(\lambda)}$ were found to increase with $\lambda$, thus indicating that the latter stages of deformation are more strain rate sensitive.

The corresponding best fit values for the intercept $H(\dot{\lambda}) = \frac{1}{V^*(\lambda)} \left[ \Delta H(\dot{\lambda}) - k \cdot T \ln(\dot{\lambda}_o(\lambda)) \right]$ in Figures 4.7(a) displayed similar trends as in Figures 4.6(b). However, these trends are a reflection of the trends in the pre-factor term of $\left( \frac{1}{V^*(\lambda)} \right)$. This was verified in Figure 4.7(b) wherein the term $\left[ \frac{\Delta H}{k \cdot T} - \ln(\dot{\lambda}_o) \right]$, calculated as $\frac{H(\dot{\lambda})}{S(\lambda)}$, was not found to vary with $\lambda$ in the entire post-yield regime. Additional experiments at different temperatures could help to decouple the individual trends of the two fitting parameters $\Delta H$ and $\ln(\dot{\lambda}_o)$ with $\lambda$. Similar conclusions can be drawn if $\sigma_{\text{true}}(\lambda)$ were to be used in the above calculations instead of $\sigma_{\text{eng}}(\lambda)$, as shown in Figure 4.8.
Figure 4.6. Trends in (a) slope, $S(\lambda)$, obtained by fitting engineering stress, $\sigma_{\text{eng}}(\dot{\lambda})$, using the data in Figures 4.1(a) [squares], 4.4(a) [diamonds] and 4.5(a,b) [triangles], to the corresponding values of $\ln(\dot{\lambda})$ according to Equation 4.2. (b) Linear correlation coefficients $R^2$ for the fits.
Figure 4.7. Trends in (a) intercepts, $H(\lambda)$, and (b) $\left(\frac{\Delta H}{kT}\right) - \ln(\dot{\lambda}_0)$ obtained by fitting the engineering stress, $\sigma_{\text{eng}}(\lambda)$, using the data in Figures 4.1(a) [squares], 4.4(a) [diamonds] and 4.5(a,b) [triangles], to the corresponding values of $\ln(\dot{\lambda})$ per Equation 4.2.
Figure 4.8. Trends in (a) slopes, $S(\lambda)$, (c) intercepts, $H(\lambda)$, and (d) $\left[\frac{\Delta H}{kT} - \ln(\dot{\lambda}_o)\right]$ obtained by fitting true stress, $\sigma_{true}(\lambda)$, using the data in Figures 4.1(a) [squares], 4.4(a) [diamonds] and 4.5(a,b) [triangles], to the corresponding values of $\ln (\dot{\lambda})$ according to Equation 4.2. The linear correlation coefficients $R^2$ for these fits are shown in (b).
The value of $S(\lambda)$ for ductile PS nanofibers with 350 nm diameter and $MW = 400,000$ g/mol, ($D_{\text{norm}} \approx 8$) is compared in Figure 4.9 with that of uniaxial compression of bulk PS specimens and comparable $MW = 483,000$ g/mol reported in [127]. The results are expressed in terms of true strain, $\varepsilon_t = \ln(\lambda)$ and true strain rate, $\dot{\varepsilon}_t$, as also reported in [127]. There is no significant deviation in $S(\varepsilon_t)$ between nanofibers and bulk PS until the onset of post-neck hardening of the nanofibers, as indicated by the dashed lines in Figure 4.8. In light of previous studies on bulk-scale glassy PC specimens [128] that have shown significant changes in $S(\varepsilon_t)$ with increasing specimen pre-orientation, the results in Figure 4.9(a) could be used to preclude the role of chain orientation arising from electrospinning of nanofibers as the origin of their large deformation behavior.
Figure 4.9. (a) Strain rate sensitivity of PS nanofibers (diamonds) and bulk specimens (stars) [127] of comparable $MW$ (but different applied stress). Solid, open and half-filled diamonds depict the pre-yield, necking and post-neck hardening regimes, respectively. Dashed lines depict the bounds of $S(\dot{\varepsilon})$ during nanofiber necking. (b) Linear correlation coefficient, $R^2$, for the nanofiber data.
4.4 Scaling of Strain Rate Dependent Response of PS Nanofibers

As shown in Sections 4.1 and 4.2, ductile PS nanofibers exhibited stable necking and significant post-neck hardening with very similar stretch ratios marking the beginning and the end of major deformation regimes, although the amplitude of stress scaled with the applied strain rate. This vertical shifting of the engineering stress vs. stretch ratio response provided the basis to explore its scaling with the corresponding yield or flow stress. Specifically, the engineering stress vs. stretch ratio curves at different strain rates in Figure 4.5(a) are shown to collapse onto a single curve in Figure 4.10(a) when the engineering stress was normalized by the flow stress corresponding to each plot. Small deviations in the post-neck strain hardening regime are clearly due to the vertical ordering of the curves arising from minor differences in $\lambda_h$. These differences are further reduced when the data are scaled with the yield stress, Figure 4.10(b), which is more appropriate for the data in Figure 4.2(a), where there is no clear engineering stress plateau. The engineering stress vs. stretch ratio responses normalized by the yield stress for fibers with $MW = 123,000 – 2,000,000$ g/mol in Figures 4.1(a), 4.4 (a) and 4.5(b), are given in Figure 4.11.

Recent molecular simulations [106] and theoretical studies [129] have identified similar scaling of the rate dependent stress vs. stretch response of amorphous polymers with the yield or flow stresses, thus signifying a multiplicative decomposition of stress into shape and rate components given by

$$\sigma (\lambda, \dot{\lambda}) = f(\lambda) \cdot \sigma_{yield/flow} (\dot{\lambda})$$  \hspace{1cm} (4.3)

where $f(\dot{\lambda})$ is the shape factor, as plotted in Figures 4.9 and 4.10 for different PS fibers.
Figure 4.10. Engineering stress vs. stretch ratio curves in Figure 4.5(a) normalized by (a) flow stress and (b) yield stress.
Figure 4.11. Engineering stress vs. stretch ratio responses in (a) Figure 4.1(a), (b) Figure 4.4(a) and (c) Figure 4.5(b), normalized by the yield stress.
Experimentally, similar scaling of stress has also been shown for bulk PS subjected to uniaxial compression [130], albeit, over the very small strain rate range of $10^{-4} - 10^{-3}$ s$^{-1}$ and a smaller range of stretch ratio, $\lambda < 1.5$. However, slight yet systematic differences between the scaled curves at increasing strain rate have been reported for $\lambda > 1.5$ [130], thus suggesting that Equation 4.3 may not hold at low strain rates, although it may hold at the time scales of molecular simulations [106,131] corresponding to $\dot{\varepsilon} > 1,000$ s$^{-1}$. By contrast, Equation 4.3 is applicable for the experimental stress vs. stretch ratio data in Figures 4.10 and 4.11 that span a much wider range of strain rates between $10^{-4}$ and $10^{2}$ s$^{-1}$ (yet lower than the rates in molecular simulations). These data also show that Equation 4.3 is applicable over a much wider range of stretch ratios ($\lambda \approx 2 - 2.5$). Unlike bulk PS [130], $f(\lambda)$ for PS nanofibers did not exhibit any systematic trends with strain rate in the post-neck hardening regime.

Scaling of the strain hardening response with yield or flow stress implies that the origin of strain hardening arises from the dominant influence of dissipative/viscous forces at a segmental chain length scale [106,129-131]. Theoretically speaking, the strain hardening behavior is an outcome of anisotropic chain conformations developed during large deformation which modified inter-chain packing, increased dynamic constraints and prolonged segmental relaxations, thereby making it difficult to overcome the energy barrier for activated hopping mechanisms to occur in this regime [129]. Similarly, molecular simulations suggested that strain hardening arises from increasing dynamical constraints when more energy is dissipated to permanently rearrange chain segments.
between entanglements in the direction of the applied stress while maintaining interconnectivity of the polymer chain network [132].

It is important to note that the segments of each fiber tested at different strain rates exhibited fairly repeatable $\lambda_h$, which indicates a consistent neck ratio as a function of strain rate. This outcome was verified via interrupted experiments with segments of the same fiber corresponding to the plots in Figure 4.5(a), where neck diameter was consistently 300 nm at all strain rates. Thus, although the values of $f(\lambda)$ in Figures 4.9(b) and 4.10 are based on engineering stresses, they are likely to be valid for true stresses too. In fact, the theoretical treatment in [129] does not require a distinction in the stress state and is expected to work for uniaxial tension and complex states of stress.

It can be recalled from the discussion in Chapter 3 that the engineering stress vs. stretch ratio curves for different values of $D_{\text{norm}}$ could be collapsed onto the master curve in Figure 3.10. This result can be combined with the results of this Chapter where the stress vs. stretch ratio curves for different strain rates can be normalized with respect to stress: The plots in Figures 4.1(a), 4.4(a) and 4.5(a) can be re-plotted in normalized stress and normalized strain axes, as shown in Figure 4.12. As shown, the resulting master curve captures temporal and size effects until the completion of necking. However, the post-neck hardening response exhibited $D_{\text{norm}}$ dependence: decreasing $D_{\text{norm}}$ led to an increase in the slope of the post-neck hardening response in the normalized stress-strain space. Notably, the normalized strain at the completion of necking in Figure 4.12 ($\varepsilon_{\text{norm},h} \approx 0.57$) is in reasonable agreement with that in Figure 3.10 ($\varepsilon_{\text{norm},h} \approx 0.61$).
Figure 4.12. Normalized true stress vs. normalized strain combining the plots in Figures 4.1(a) \([MW = 123,000 \text{ g/mol}, D_{\text{norm}} = 8]\), 4.4(a) \([MW = 400,000 \text{ g/mol}, D_{\text{norm}} = 8]\), 4.5(a) \([MW = 2,000,000 \text{ g/mol}, D_{\text{norm}} = 6]\) and 4.5(b) \([MW = 2,000,000 \text{ g/mol}, D_{\text{norm}} = 3]\).

The origin of the \(D_{\text{norm}}\) dependence of post-necking hardening in the normalized true stress vs. normalized strain curves in Figure 4.12 is not readily evident. While molecular simulations have suggested that the increasing slope of the strain hardening response with increasing strain rate is related to the decreasing rate of plastic rearrangement of stressed polymer chain segments \([132]\), such an argument cannot be readily used to explain the results in Figure 4.12 as it has been well established by the large number of \(T_g\) experiments on thin PS films described in Chapter 1 that the increasing proportion of free surface chain segments in fibers of small \(D_{\text{norm}}\) are expected to have fewer constraints and consequently lesser restrictions for their spatial rearrangement.
4.5 Conclusions

The strain rate dependent large deformation of individual PS nanofibers with $MW = 123,000 – 2,000,000$ g/mol and diameters of 200 – 750 nm was studied under the conditions of uniaxial tension, across a wide range of strain rates ($10^{-4} – 10^{2}$ s$^{-1}$). The viscoplastic response of PS nanofibers was found to be length scale dependent. Specifically, fibers with $D_{\text{norm}} \leq 8$ displayed consistently stable necking and subsequent post-neck hardening with little change in $\lambda_h$, but with significant increases in stresses, thus resulting in significant strengthening and toughening of the fibers. Nanofibers with $D_{\text{norm}} > 10$ displayed unstable necking and strain rate dependent elongation although the stresses continued to increase with strain rate. In fact, nanofibers with $MW = 123,000$ g/mol and $D_{\text{norm}} \approx 18$, demonstrated a ductile-to-brittle transition upon increasing the strain rate from 1 s$^{-1}$ to 100 s$^{-1}$. Importantly, the strain rate dependent engineering stress vs. stretch ratio response of each PS nanofiber was shown to scale with the yield stress over the wide range of strain rates used in this study, thus indicating that the post-yield deformation is dominated by changes in intermolecular interactions at the segmental length scale. A master curve composed of normalized stress and strain axes was shown to capture temporal and length scale effects until the completion of necking. The post-neck hardening response was shown to be $D_{\text{norm}}$ dependent and therefore length scale dependent.
CHAPTER 5

THE ROLE OF NANOFIBER GEOMETRY ON DEFORMATION EVOLUTION

Electrospinning is a rapid, economical and easy to implement approach to produce polymer nanofibers and non-woven fiber mats for a wide range of applications. A prominent application is the fabrication of synthetic tissue engineering scaffolds that can mimic the fibrous surroundings of tissues with appropriate gradation in mechanical properties [133]. As-spun nanofibers assume many different morphological shapes, textures and non-uniformities depending on many process parameters such as the electric field, spinning distance, solvent and humidity [83,84,88,134-137]. However, despite the large variation in morphologies, little is known about their impact on the mechanical behavior of polymers. Understanding the effects of fiber morphology on the mechanical response of individual nanofibers is crucial for the design and fabrication of appropriate scaffolds. In this Chapter the mechanical behavior of a biocompatible polymer, poly(lactic-co-glycolic acid) (PLGA), used in tissue engineering applications of the tendon-to-bone insertion site is studied. PLGA is also an amorphous polymer similar to PS, although it has much lower $T_g$ (40–60 °C) compared to PS.
5.1 Specimen Preparation

PLGA powder ($MW = 50,000 - 75,000$ g/mol, with 85:15 lactide/glycolide ratio) was dissolved in an 80/20 mix of dichloromethane (DCM) and $N,N$-dimethylformamide (DMF) to result in a concentration of 25% weight-in-volume (w/v). This solution was electrospun at 15 kV onto a flat sheet of aluminum foil placed at 15 cm distance. The solution was pumped at 0.5 mL/h. After the fiber deposition stabilized, either an aluminum wire mesh, or Cu TEM grids attached with carbon tape to the surface of a glass slide, were briefly (< 10 s) positioned between the needle tip and the collector to collect sparsely spaced nanofibers. All specimens were treated with a plasma cleaner (Harrick Plasma PDC-001) for 8 min at 10.5 W to increase the hydrophilicity of the nanofiber surfaces and enhance the deposition of calcium phosphate during subsequent mineralization [138]. The resulting PLGA nanofibers had one of three morphologies: (a) uniform circular cross-section with sparsely spaced surface irregularities, (b) non-uniform/irregular cross-section along the entire nanofiber, and (c) uniform ellipsoidal cross-section, as shown in Figure 5.1.
Figure 5.1. SEM images of undeformed PLGA fibers with (a) uniform circular cross-section and few sharp surface protrusions pointed by arrows, (b) non-uniform (irregular) cross-section, and (c) uniform ellipsoidal cross-section.
5.2 Mechanical Behavior of PLGA Nanofibers

The engineering stress vs. strain curves of as-spun PLGA nanofibers in Figures 5.2(a-c) clearly display a dependence on the cross-sectional morphology. The advantageous strain hardening component of the engineering stress vs. strain curves, which provides outstanding mechanical strengthening and toughening while preventing catastrophic failure, gradually changes with fiber geometry, and is accompanied by opposite changes in fiber ductility.

Representative engineering stress vs. strain curves of nanofibers with uniform circular cross-sections in Figure 5.2(a) displayed large elongations at a constant plateau stress with no subsequent hardening response, thus resulting in bulk-like tensile strength. Compared to nanofibers with uniform circular cross-sections, the nanofibers with non-uniform/wavy cross-sections, e.g. Figure 5.1(b), supported significant post-plateau hardening, which increased the nanofiber strength by ~50%. Nanofibers with uniform ellipsoidal cross-sections yielded at stress values comparable to those with the other two morphologies, but displayed a relatively short stress plateau, followed by extraordinary strain hardening. Clearly, the correspondence between cross-sectional morphology and mechanical response could be exploited to activate distinct deformation mechanisms and tune the nanofiber mechanical response, especially in light of the consistency of the experimental measurements for each fiber. The mechanical response of individual fibers from the same scaffold was highly repeatable. For instance, Figure 5.2(a) shows the highly consistent engineering stress vs. strain behavior of four segments of a representative PLGA nanofiber with uniform circular cross-section. Two of the nanofiber
segments were extended to failure at 150% engineering strain, and the other two segments were extended to 30% and 65% engineering strain before unloading, following very closely the behavior of the first two segments. Similarly, the engineering stress vs. strain responses of several segments of nanofibers with the other two morphologies were also highly consistent, as shown in Figures 5.2(b,c). The elastic modulus, yield stress, failure strain and strength for electrospun PLGA nanofibers of different cross-sectional morphologies are given in Table 5.1.

In general, electrospun PLGA nanofibers exhibited improved mechanical strength and toughness as compared to bulk PLGA [139,140]. In addition, all electrospun PLGA nanofibers studied here exhibited significantly greater elongations compared to the bulk specimens. Specifically, the elastic modulus and yield strength were comparable to the highest values reported for bulk PLGA specimens that were prepared with special drawing processes [139,140]. Bulk PLGA fibers are often brittle and fail at ~50 MPa with elongations smaller than 5%, and without strain hardening [139]. It has also been reported that micron-sized PLGA fibers fabricated by a two-stage, high temperature drawing process displayed modest improvements in extensibility, reaching failure strains of ~10–15% while the tensile strength reached ~65 MPa, although their yield strength was only ~35 MPa [140]. The increase in failure strength and ductility of drawn micron-sized fibers was attributed to improvements in molecular orientation and increased crystallite size arising from the high temperature drawing process. In comparison, nanofibers with uniformly circular cross-sections could reach very high elongations of
150% while still achieving a yield stress of 55 MPa, thereby increasing the toughness by almost 1,500% compared to the fibers reported in [139,140].

**Figure 5.2.** Engineering stress vs. strain curves for PLGA nanofibers with (a) uniform circular, (b) non-uniform (irregular) and (c) uniform ellipsoidal cross-sections. The entire loading–unloading curves are shown for tests that were interrupted before fiber failure. The fiber with 910 nm diameter shown with a solid black line in panel (b) represents an interrupted experiment, where unloading data could not be collected. Fibers with identical diameter were segments of the same long fiber.
Table 5.1. Mechanical properties (± standard error) for PLGA nanofibers with different cross-sectional morphologies determined from engineering stress vs. strain curves.

<table>
<thead>
<tr>
<th></th>
<th>Uniform Circular</th>
<th>Non-uniform</th>
<th>Uniform Ellipsoidal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elastic Modulus (GPa)</strong></td>
<td>1.65±0.15</td>
<td>1.39±0.10</td>
<td>2.25±0.25</td>
</tr>
<tr>
<td><strong>Yield Stress (MPa)</strong></td>
<td>55±5</td>
<td>40±7</td>
<td>65±2</td>
</tr>
<tr>
<td><strong>Tensile Strength (MPa)</strong></td>
<td>56±3</td>
<td>89±7</td>
<td>145±12</td>
</tr>
<tr>
<td><strong>Tensile Strain (%)</strong></td>
<td>150±25</td>
<td>122±7</td>
<td>81±7</td>
</tr>
<tr>
<td><strong>Number of fibers tested (total number of segments from all fibers)</strong></td>
<td>3 (10)</td>
<td>2 (3)</td>
<td>5 (6)</td>
</tr>
</tbody>
</table>

At the other extreme, nanofibers with uniform ellipsoidal cross-sections exhibited a three-fold increase in tensile strength, while the tensile strain (~80%) was reduced by ~45% compared to fibers with circular cross-sections. PLGA nanofibers with non-uniform cross-sections yielded at lower stresses (30–50 MPa) than nanofibers with uniform circular or ellipsoidal cross-sections (50–60 MPa). However, the tensile strength was greater than that experienced by fibers of uniform circular cross-sections, achieved due to the distinct strain hardening regime following the plateau stress. Non-uniform fibers underwent ~100% elongation that was nearly 35% lower than tensile strain of fibers with circular cross-sections, Table 5.1. However, the combination of strength and ductility of non-uniform and uniform ellipsoidal PLGA nanofibers resulted in increase of energy dissipation by 1,250 – 1,500% compared to bulk PLGA, which is comparable to that of uniform circular fibers.
5.3 Deformation Mechanisms in PLGA Nanofibers

In addition to nanofiber segments tested to failure, interrupted tensile experiments were performed with segments of the same fiber, which were partially stretched and then unloaded. The deformation mechanisms resulting in the intriguing stress-strain curves in Figures 5.2(a-c) were then evaluated via subsequent post-test SEM imaging. These experiments revealed that the trends in the engineering stress vs. strain curves in Figures 5.2(a-c) were not due to differences in the constitutive material behavior; rather, arising from effects of fiber surface morphology and cross-sectional geometry on the evolution of mechanical extension and material deformation.

5.3.1 Nanofibers with Uniform Circular Cross-sections

Post-mortem SEM micrographs of PLGA nanofibers with uniform circular cross-sections, corresponding to the stress vs. strain curves shown in Figure 5.2(a), are presented in Figure 5.3. These SEM images revealed that the large ductility of PLGA nanofibers with uniform circular cross-sections was due to neck formation and propagation at a plateau threshold stress of ~55 MPa, as shown in Figure 5.2(a). Neck initiation is a structural instability, but neck propagation depends on the intrinsic material behavior of PLGA. During this instability, deformation localizes at a small defect in the fiber and the cross-section is reduced while molecular uncoiling takes place. When this process is completed, a stable neck forms, which then propagates along the fiber, thus reducing its diameter and increasing the true stress throughout the fiber. Thus, the stable neck propagation observed in PLGA nanofibers with uniform circular cross-sections
required sufficient strain hardening within the neck transition region to stabilize the instability by counteracting molecular flow.

Figure 5.3. Post-mortem SEM images of PLGA fibers with uniform circular cross-sections shown (a) after $\varepsilon \approx 65\%$, and (b) $\varepsilon \approx 165\%$. Remnant neck fronts in the fiber after its failure are marked in (b).
The absence of hardening process would otherwise result in premature failure of the fiber due to unrestricted local thinning at the weakest point while the rest of the fiber cross-section would remain largely intact. In fact, after accounting for the reduced cross-sectional area of the necked region that was 60 – 70% that of the intact region, Figure 5.3(a), the true failure strength of PLGA nanofibers with uniform circular cross-sections was calculated to be 130 – 165 MPa. This true failure strength is nearly 4 times that of the bulk values reported in [140]. One likely cause for the improved hardening behavior of electrospun PLGA nanofibers is molecular orientation arising from the electrospinning process [55], which limits additional macromolecular uncoiling and orientation during necking or strain localization, thus providing the necessary resistance to counteract post-yield molecular flow and prevent continued localized deformation and premature fiber failure.

Post-neck deformation, depends on the ability of the polymer to harden further and could either result in immediate failure, Figure 5.2(a), or lead to further elongation and strengthening via additional hardening, Figures 5.2(b,c). However, the post-mortem SEM images in Figure 5.3(b) show remnant necks across the length of the fiber, thus indicating that neck propagation was not always complete for PLGA fibers with uniform circular cross-sections. This is likely due to neck arrest and additional stress localization in the vicinity of sharp surface irregularities, as shown in the inset of Figure 5.3(b). The length of the fiber that underwent necking could be estimated by measuring the length of the fiber sections that did not undergo necking, after failure. When accounted together with the cross-head strain imparted to the fibers, it is estimated that an additional
elongation of ~200% could have been achieved had the entire initial length of the fiber completed the process of necking, thus resulting in ~2,000% increase in toughness compared to the bulk PLGA. This estimate of the actual toughness in uniformly circular PLGA nanofibers is 25 – 50% higher than the toughness of uniform ellipsoidal fibers.

5.3.2 Nanofibers with Irregular Cross-sections

The limiting effect of the stress plateau on the tensile strength of nanofibers with uniformly circular cross-sections could be overcome by modifying the nanofiber surface or cross-sectional symmetry: engineering stress vs. strain curves of fibers with irregular cross-sections, Figure 5.2(b), demonstrated an increase in tensile strength with the aid of distinct strain hardening. The deformation mechanisms underlying the stress vs. strain behaviors of fibers with irregular and ellipsoidal cross-sections were elucidated via SEM imaging of fibers stretched to different strain levels, as shown in Figure 5.4. A fiber with the initial undeformed fiber morphology in Figure 5.4(a) was stretched by 30% via strain localization in the initially thinner locations, Figure 5.4(b). The pronounced cross-sectional irregularity forced strain localization at multiple sites along the fiber. Interestingly, the fiber became relatively smooth by the time it was drawn to failure, as shown in Figure 5.4(c), without remnant necks as observed in fibers with uniformly circular cross-sections, Figure 5.3(b). These observations suggest that initially irregular fiber morphologies, e.g. Figure 5.4(a), are not catastrophic. Instead, the surface non-uniformity is gradually lost via large deformations occurring at a plateau engineering
Figure 5.4. PLGA nanofibers with non-uniform initial cross-sections (a) in the undeformed state, (b) after 30% elongation and (c) after failure at 130% elongation.
stress, thus allowing for a post-plateau hardening response after the fiber cross-section reaches relatively uniform cross-section, e.g. Figure 5.4(c). The absence of stable necking in fibers with irregular cross-section prevented extended macromolecular uncoiling that typically occurs during stable necking, which in turn led to an additional 50% post-neck extension at higher stresses. Post-neck hardening increased the engineering tensile strength by 100% as compared to fibers with uniformly circular cross-sections.

5.3.3 **Nanofibers with Uniform Ellipsoidal Cross-sections**

Nanofibers with uniform ellipsoidal cross-sections, Figure 5.2(c), also displayed a consistent strain hardening response. The post-yield engineering stress-strain response of these fibers consisted of a very brief strain softening response before the onset of hardening, unlike the other two fiber morphologies that exhibited fairly large post-yield extensions at a constant plateau stress. The mechanical response of nanofibers with uniform ellipsoidal cross-sections ruled out the possibility of necking [141]. Instead, large extensions were achieved by uniform, non-localized deformation which provided a measure for the constitutive material response of electrospun PLGA fibers. Evidence for the absence of strain localization was provided by comparison of the high resolution optical micrographs, Figure 5.5, collected during tensile testing of nanofibers with uniformly circular cross-section that demonstrated necking, and nanofibers with uniformly ellipsoidal cross-sections. While localized deformation due to necking could be discerned in uniform circular fibers as a sharp change in the fiber cross-section in Figures 5.5(b,c), no such change could be detected in fibers with uniform ellipsoidal
cross-section in Figures 5.5(e,f). This was further confirmed by interrupted tensile experiments which showed no hints of strain localization, as shown in Figure 5.6. The reduction in diameter of fibers with uniform ellipsoidal cross-section during the entire extension process was estimated by measuring in SEM images the diameter of fibers stretched until failure near their fracture point, e.g. Figure 5.6(c).

Since PLGA nanofibers with ellipsoidal cross-sections deformed homogenously, the corresponding stress vs. strain curves of these fibers shown in Figure 5.2(c) represent the constitutive response of electrospun PLGA nanofibers. These fibers exhibited nearly 500% increase in elongation and 200% increase in tensile strength compared to bulk PLGA. Interestingly, unlike the PS nanofibers studied in Chapters 3 and 4, the constitutive response of PLGA nanofibers did not display a measurable fiber size effect for fiber diameters between 300 – 900 nm. The lack of size effect is likely due to the low $MW = 50,000$ g/mol of PLGA nanofibers: the relatively small molecule size precluded significant macromolecular confinement effects in this range of diameters. In comparison, previous studies conducted with homogenously deforming semi-crystalline PAN nanofibers with $MW = 150,000$ g/mol demonstrated significant size effects across the same diameter range [54,55].
Figure 5.5. Optical micrographs of a $D = 650$ nm PLGA nanofiber with uniformly circular cross-section (a) just before and (b,c) after yield, in the stress plateau regime (arrows show necked regions). (d) Pre-yield and (e,f) stress plateau regime images of a $D = 870$ nm fiber with uniformly ellipsoidal cross-section that do not show localization.
Figure 5.6. PLGA nanofibers with uniformly ellipsoidal cross-sections (a) in the undeformed state, (b) after 55% elongation and (c) after failure at 70% elongation. Inset in (c) shows a failure cross-section.
5.4 Conclusions

It was shown that the mechanical response of individual PLGA nanofibers could be dramatically different from bulk PLGA, providing an optimal mechanical response in terms of tensile strength and ductility, namely a 500% increase in elongation and 200% increase in tensile strength compared to bulk PLGA. Control of nanofiber cross-sectional morphology resulted in a variety of deformation modes spanning necking, hardening and homogeneous fiber extension, which have not been shown before for micron or larger size fibers without modification of the polymer itself. It was also shown that, unlike macroscale fibers and materials, surface non-uniformity does not result in premature fiber failure: geometric imperfections in soft materials at the submicron scale are quite benign compared to the macroscale. In the case of sharp surface irregularities, plastic deformation by way of strain localization allowed for smoothing of surface depressions, leading up to 150% fiber elongation and major strain hardening. The insensitivity to surface defects is owed to the underlying macromolecular length scale which is comparable to the length scale of imperfections: molecular conformations and local chain orientation are influenced by surface imperfections during fabrication. The increased material strain hardening mitigates stress concentrations at surface non-uniformities and provides resistance to early localized failure.
CHAPTER 6

CONCLUSIONS

The objective of this Ph.D. dissertation research was to quantify the large mechanical deformation of a typical amorphous polymer subjected to spatial confinement at the submicron scale. This Chapter summarizes the research outcomes and provides an assessment of the extent to which the dissertation objectives were met.

6.1 Assessment of Dissertation Outcomes

Before this research, the large mechanical deformation behavior of PS at the submicron scale (100 – 1,000 nm) was largely unexplored and direct experimental data were lacking. The only literature data at this length scale were found in studies of individual craze fibrils in the vicinity of a crack or a notch in macroscale specimens [97]. This dissertation research is the first direct investigation of the large deformation behavior of ultra-small volumes of PS at the glassy state, accomplished via experiments on individual PS and PLGA nanofibers using a MEMS based method for tensile testing of nanofibers [54] and microscale fibers [81] in ambient conditions. The present experiments allowed us to capture in a clear and unequivocal manner the specimen size
and molecular scale dependent transition from ductile response to craze-assisted brittle failure. The experimental method provided the capability for mechanical studies over a broad range of strain rates, which resulted in new and interesting results about the behavior of PS in ultra-small volumes and at very short time scales.

6.1.1 Confinement Effects on Large Deformation Behavior of PS Nanofibers

The basic experimental challenge was obtaining high quality fiber specimens with a variety of $MW$ in order to control the degree of spatial molecular confinement. The two parameters of $MW$ and fiber diameter were represented by the confinement parameter, $D_{\text{norm}}$, which was defined as the ratio of nanofiber diameter to molecular length scale ($D/R_{\text{ee}}$). Experiments with PS nanofibers with $D_{\text{norm}} = 1 – 20$ were possible for various combinations of $MW$ and fiber diameter. The range of $MW$ and $D_{\text{norm}}$ values employed in this dissertation are the widest in literature about PS nanofibers.

It was shown that PS nanofibers with $3 < D_{\text{norm}} < 13$ display a fairly constant toughness, representing a $3,000 – 3,500\%$ increase compared to bulk PS. Strain hardening, fiber strength, and ductility were shown to scale with $D_{\text{norm}}$, namely the extent of macromolecular confinement, transitioning to bulk-like values at the limit of $D_{\text{norm}} \approx 18$. These results indicate that macromolecular confinement could serve as an efficient way to control the strength and ductility of amorphous polymers in order to demonstrate mechanical behaviors that have not been possible at the bulk-scale. Similarly, using PS nanofibers of extremely high $MW = 9,000,000$ g/mol, it was further shown that a brittle-
to-ductile transition occurs for $1 < D_{\text{norm}} < 3$, wherein fibers with $D_{\text{norm}} \sim 1$ demonstrated significant hardening and strengthening by way of homogeneous extension.

It was further shown that the trends in the mechanical response were qualitatively the same for $MW$ as low as 123,000 g/mol. Limitations in electrospinning sufficiently thin nanofibers from solutions of low $MW$ PS with reduced entanglement density and viscosity prohibited the study of fibers with nanoscale diameters. For the same reasons, the confinement range of $0.1 < D_{\text{norm}} < 1$, typically used to study $T_g$ and the rheological behavior of confined polymers, could not be evaluated. Additionally, the choice of isolating and testing nanofibers under an optical microscope led to a pragmatic lower limit of $\sim 100$ nm for the diameter of fibers that could be isolated and tested. Even though this issue was partially addressed by the use of high $MW$ to increase $R_{\text{cc}}$, it was not sufficient to generate fibers of $D_{\text{norm}} < 1$.

### 6.1.2 Strain Rate Dependent Deformation of PS Nanofibers

Given that the strength and ductility of polymers are intricately linked to time, the large deformation behavior of PS nanofibers was studied across a range of six orders of strain rate, namely $10^{-4} - 200 \text{ s}^{-1}$. The experiments revealed that the nanofiber elongation was independent of strain rate for $D_{\text{norm}} < 10$, thus leading to greater energy dissipation and strength at higher strain rates. For $D_{\text{norm}} > 10$, the large deformation behavior was less sustainable with increasing strain rate. More fundamentally, the post-neck hardening regime was strain rate dependent, with the entire post-yield stress response scaling with the yield strength. This scaling suggests that the entire post-yield stress response is
dominated by intermolecular interactions at the segmental length scale, a result that is corroborated with simulations [106] and theory [129] on the intrinsic response of glassy polymers. The results presented here cover a wide range of strain rates, up to just a decade below the lowest strain rate (10^3 s^{-1}) in molecular simulations [131].

Some limitations in the strain rate experiments arose from the localization of deformation in a neck, which resulted in sudden increase in the applied strain rate, \( \dot{\varepsilon} \), between the elastic and plastic regimes, Figure 4.1. This issue was due to the use of a compliant loadcell and the application of constant displacement rate to the specimen-loadcell assembly, as shown in Figure 2.1. An additional, albeit less significant change in strain rate, arose in the post-neck hardening regime when the loadcell began to open again. While changes in strain rate arising from loadcell opening can be accounted for, the effect of necking on sudden changes in strain rate cannot be counteracted in real time as done in macroscale experiments [142]. Necking did not allow plotting the evolution of true stress and strain during neck formation and propagation. Instead, the neck size and the post-neck fiber diameter were determined via interrupted experiments which provided us with the necessary data to compute the true stress in the post-neck hardening phase of fiber extension.

6.2 Future Directions

Experiments at elevated temperatures would complement the high strain rate mechanical experiments performed in this dissertation by accelerating the slow relaxation mechanisms and, thus, extend the ability to probe a wider range of time scales. When
combined with the data in Chapter 4, experiments at elevated temperatures would also provide the activation energies for yielding and strain hardening as function of $D_{\text{norm}}$, which, in turn, would result in a more definitive picture of the factors affecting the large deformation behavior at small-scales. Such elevated temperature experiments were proven challenging due to the lack of appropriate adhesives that retained their stiffness at higher temperatures, as shown in Figure 6.1.

With this experimental capability, it is of interest is to study the recovery of cold drawn necks using single fiber experiments at elevated temperatures, where the retraction stresses are smaller than $\sigma_y$. In recent works on bulk PC and PMMA, the recovery of cold-drawn necks was used to understand the likely role of inter- and intra-chain interactions under tension [107]. Preliminary experiments with PS nanofibers of $MW = 400,000\ \text{g/mol}$ and $D = 200 – 250\ \text{nm}$, Figure 6.2, showed that retraction stresses of $\sim 5\ \text{MPa}$ might still take place at $85\ ^\circ\text{C}$, even though fibers have already recovered substantially after $4,000\ \text{s}$ at $65 – 75\ ^\circ\text{C}$.

In Chapter 4, it was shown that a single linear fit could describe the strain rate sensitivity of the applied stress for the entire post-yield regime, across the wide range strain rates $10^{-4} – 10^2\ \text{s}^{-1}$. This indicates that a single process ($\alpha$-relaxation) controls the large deformation response of PS nanofibers at these rates, unlike bulk PS and PMMA for which the contribution of the $\beta$-relaxation begins at strain rates as low as $10^{-2} – 10^{-1}\ \text{s}^{-1}$ [19,118]. A likely possibility is that the onset of $\beta$-relaxation in PS nanofibers might occur at much higher strain rates of $10^3\ \text{s}^{-1}$ or more that are well into the dynamic regime. Exploring this possibility requires experiments which could be achieved by upgrading the
current apparatus with a faster actuator. Alternatively, a combination of dynamic mechanical analysis of individual nanofibers and tensile tests at elevated temperatures could be used to identify the onset of such relaxations at the nanoscale and their impact on the large deformation response, as has been shown before for bulk PC in [118]. Also, an extension of the current dissertation research to other amorphous polymers such as PMMA for which the $\alpha$ to $(\alpha+\beta)$ transition occurs at a lower strain rate compared to PS, could be instructive to understand the role of relaxation processes at the nanoscale.

**Figure 6.1.** Experiments at elevated temperatures with three PS nanofibers ($MW = 2,000,000$ g/mol and $D = 350 – 400$ nm). The shaded region points to fiber sliding through the temperature softened epoxy at the grips.
Figure 6.2. PS nanofiber with $MW = 400,000$ g/mol and diameter 200-250 nm subjected to (a,b) cold drawing until $\lambda < \lambda_h$ and (c,d) recovery at elevated temperatures. The dwell times and temperatures are shown. A stress of ~5 MPa is measured at 85 °C. The partial recovery in 1,850 s dwell time at ~70 °C is not shown. The scale bars are 50 µm.
A.1. Relationship between MEMS Actuation Velocity and Fiber Strain Rate

Based on the design of the compliant MEMS platform for nanofiber testing described in Section 2.1, an applied displacement $\delta_{app}$ contributes to nanofiber stretching, $\delta_{fib}$, and opening of the compliant loadcell, $\delta_{ld}$, which measures the force on the fiber

$$\delta_{app} = \delta_{fib} + \delta_{ld} \quad (A.1)$$

If the initial fiber gage length is $L_i$, and the stretched length is $L_f$, then

$$L_f = \delta_{fib} + L_i \quad (A.2)$$

The stiffness of the fiber in its extended state is

$$\delta_{fib} = \frac{F \cdot L_f}{A_f \cdot E} \quad (A.3)$$

where $F$ is the applied force, $A_f$ is the true cross-sectional area and $E$ is the Young’s modulus of the fiber. Assuming isochoric deformation in the initial viscoelastic regime, the initial cross-sectional area $A_i$ is

$$A_i = A_f \cdot \frac{(\delta_{fib} + L_f)}{L_f} \quad (A.4)$$

Based on the calibrated stiffness of the MEMS loadcell, $k$, the force experienced by the loadcell and the fiber can be written in terms of the loadcell opening, $\delta_{ld}$, as

$$F = k \cdot \delta_{ld} \quad (A.5)$$

Substituting Equations (A.4) and (A.2) into (A.3):
\[ \delta_{ld} = \frac{L_f \cdot \delta_{fib} \cdot A_i \cdot E}{k \cdot (L_f + \delta_{fib})^2} \]  \hspace{1cm} (A.6)

Substitution of Equation (A.6) in (A.1) provides a cubic equation relating \( \delta_{app} \) and \( \delta_{fib} \).

With the simplification \( \delta_{fib} << L_f \), in the elastic regime and derivatives we have:

\[ \dot{\delta}_{fib} = \left( \frac{k \cdot L_i}{(k \cdot L_i) + (A_i \cdot E)} \right) \cdot \dot{\delta}_{app} \]  \hspace{1cm} (A.7)

Based on Equation (A.6), it is possible to set an appropriate velocity ramp during actuation that gradually increases to account for \( \delta_{ld} \), so that a constant strain rate is maintained. However, the instantaneous localization of deformation during the necking instability precludes a real-time adjustment of strain rate. Upon the onset of strain localization, the fiber flows at the constant force, and hence, the loadcell does not open further. Thus, Equation (A.1) changes to \( \delta_{app} = \delta_{fib} \), and therefore, the rate of extension experienced by the fiber is the same as the applied actuation velocity, i.e., \( \dot{\delta}_{app} = \dot{\delta}_{fib} \).
A.2. Determination of Strain Rate Sensitivity

In Section 4.2, the strain rate sensitivity was obtained as a function of the stretch ratio by fitting the stress values at different strain rates and a fixed value for the stretch ratio to Equation 4.2, in order to determine $S(\lambda)$ and $H(\lambda)$. Since the raw engineering stress vs. stretch data at different strain rates were collected at different frequencies, the first step was to reduce the data to a common frequency. This was performed by binning the stress data along each stress-stretch curve in stretch ratio increments of 1%. The so obtained average stress vs. strain curves matched very well with the raw stress vs. stretch curves shown in Figure A.1(a) for the data in Figure 4.5(a). The average stretch ratio and average time increments for a 1% stretch increment were also evaluated within each bin to compute the average strain rate ($\frac{\Delta \lambda}{\Delta t}$) for that bin, as shown in Figure A.1(b). The average strain rate within each bin, although noisy, followed the strain rate measured from the raw data as described in Figure 4.1. Therefore, the manually fit strain rates were used in the fitting process. However, the use of noisy instantaneous strain rates or the smoother manually fit strain rates did not alter the results and conclusions in Section 4.2.

The true stress was computed as the product of the average engineering stress in each bin with the corresponding average stretch ratio of that bin. The true strain was determined as natural logarithm of the average stretch ratio of each bin. The true strain rate was however, determined from the raw time and true strain data following a procedure similar to that shown in Figure 4.1. Subsequently, the natural logarithm of the average strain rate in each bin and the average stress within each bin was fit to a strain line using MATLAB.
Figure A.1. (a) Raw values of stress vs. the binned average stress, and (b) instantaneous strain rates (dashed curves) computed for each bin vs. manually fit strain rates (solid lines) determined from the raw data as described in Figure 4.1.
REFERENCES


[81] K. Sahin, N.A. Fasanella, P.V. Kolluru and I. Chasiotis, “Mechanical property experiments with micrometer scale high strength fibers”, (submitted to *Experimental Mechanics*).


