



Interplay of molecular and specimen length scales in the large deformation mechanical behavior of polystyrene nanofibers



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ABSTRACT

Bulk polystyrene (PS) undergoes craze-assisted brittle failure at room temperature. In this work it is shown that the synergistic coupling of the material length scale as defined by macromolecular size, and the specimen size as defined by the nanofiber diameter, can result in extreme ductility and simultaneous strengthening and toughening for fiber diameters at the submicron scale. Combinations of PS fiber diameters between 150 nm and 5000 nm, and molecular weights between 13,000 g/mol and 9,000,000 g/mol provided a spectrum of degrees of molecular confinement, which, for particular pairs of molecular weight and fiber diameter, allowed for large fiber extensions through the process of necking followed by large homogenous deformation controlled by strain hardening. Compared to bulk PS, the combined necking and post-neck strain hardening increased the fiber strength by 350% and the fiber ductility by as much as 4000%. This mechanical response was shown to scale well with the confining parameter D_{norm} , defined as the ratio of the initial fiber diameter (D_0) to the root-mean-square end-to-end distance (R_{ee}), with $D_{\text{norm}} \sim 18$ identified as the threshold for the transition from necking to crazing of PS nanofibers. The large deformation response of PS nanofibers with molecular weights above a threshold value is shown to obey a master true stress vs. normalized strain curve that is independent of molecular weight.

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1. Introduction

A defining characteristic of nanoscale polymeric structures is the increased fraction of surface macromolecules that contribute significantly to the effective physical and mechanical behavior. The deviation in mobility and relaxation spectra of surface chain segments compared to those in the interior/bulk has been documented by many experimental studies on structural relaxations as a function of the glass transition temperature (T_g) [1–4]. However, due to challenges in performing direct mechanical experiments with very small polymer volumes, the effects of specimen and molecular size on the small and, more importantly, the large mechanical deformation of polymeric nanostructures such as nanofibers still remain elusive. Quite often, the role of molecular confinement in the mechanical behavior of submicron scale polymeric structures is deduced from trends in T_g [5] on the basis of a direct correlation between T_g and the material free volume. Since T_g is associated with changes in small scale segmental motions of macromolecular

chains, any inferences about the mechanical response are limited to the small strain regime. Recent studies on thin films of polymer glasses have shown that such a correlation is weak, thus establishing the need for direct experiments to probe the mechanical properties of ultra-small polymer volumes [6,7]. To date, there are limited experiments on the large elasto-plastic mechanical response of amorphous polymeric nanostructures: recent nano-indentation studies on ultra-thin polystyrene (PS) films attached to a silicon substrate have shown accelerated plastic deformation as a function of molecular weight under conditions of molecular confinement [8]. In other works, the macromolecular confinement dependent mechanical response has been deduced from macroscale composite structures [9–11]. Such studies have indicated a specimen size dependent brittle-to-ductile transition with [10] or without [9] the loss of strength. More recently, experiments with ultrathin PS films of high molecular weight noted the potential of PS to undergo necking [12]: based on the assumption of isochoric deformation, the neck ratio was used to infer the elongation of PS molecules under spatial confinement and relate it to the contribution of inter-chain and self-entanglements.

This study presents a direct investigation of the effects of molecular confinement on the large deformation behavior of

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individual PS nanofibers in their glassy state, which are subjected to uniaxial tension. It establishes that individual PS fibers at the submicron scale can have pronounced ductile behavior followed by significant strengthening. Experiments with individual PS nanofibers with initial diameters (D_0) that are 1–10 times the macromolecular root-mean-square end-to-end distance (R_{ee}), are employed to study the fiber strength, ductility and mode of deformation by modifying the ratio D_0/R_{ee} . Such an ability to simultaneously control the ductility and the tensile strength of PS at temperatures corresponding to its macroscopically glassy state could dramatically expand the technological utility of common polymer glasses as macroscopically functional materials and structures, such as tissue scaffolds [13], body armor fabrics [14] and energy devices [15,16].

2. Materials and methods

2.1. Fabrication of polystyrene (PS) nanofibers

The spatial confinement of macromolecules in nanofibers is influenced by two competing length scales: (a) the initial fiber diameter, D_0 , and (b) the molecular length scale as described by the root-mean-square end-to-end distance, $R_{ee} \propto MW^{3/5}$ of individual polymer chains, which depends on the molecular weight, MW . Control of these two length scales was achieved by electrospinning solutions of linear atactic monodisperse PS with MW between 13,000 and 9,000,000 g/mol, resulting in fibers with diameters between 150 nm and 5 μm . 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). PS solutions of different concentrations were prepared in *N,N*-dimethylformamide (DMF) and subsequently electrospun under an applied voltage of 25 kV and a source-to-collector distance of 25 cm, at the temperature of 22 ± 3 °C and $19 \pm 2\%$ relative humidity. Nanofibers formed in freestanding configuration across the gaps of the metal wires of a stationary wireframe collector. Fabrication of submicron diameter fibers from PS with low MW (13,000 and 50,000 g/mol) was not feasible due to a minimum chain entanglement density requirement for electrospinning [17,18]. Table 1 provides an account of the polydispersity index (PDI) of the PS powders and the concentration of the solutions used to fabricate fibers with particular diameter ranges and MW .

Table 1
Electrospinning and annealing parameters for the preparation of PS fibers.

Molecular weight (g/mol)	PDI	Solution concentration (weight %)	Annealing conditions		Fiber diameter (nm)
			Temperature (°C)	Time ($\times \tau_{d\text{-bulk}}$)	
13,000	1.06	60	110	–	5000–6000
50,000	1.06	45	110	134	2000–3500
123,000	1.06	30 ^a	110	6.3	200–500
		30	110	6.3	700–900
		50	110	6.3	>1000
400,000	1.06	15	120	8.3	150–250
		20	120	8.3	300–600
900,000	1.10	7.5	125	2.5	150–250
		10	125	2.5	300–500
		15	125	2.5	650–900
2,000,000	1.30	2.0	125	0.2	150–250
		4.5	125	0.2	300–800
		20	125	0.2	1000–2500
9,000,000	1.25	0.1	125	0.001	150–700

^a Solution contained 1 wt% tetrabutyl ammonium chloride (TBAC) to reduce the fiber diameter.

As-spun PS fibers were annealed prior to mechanical testing, to avoid them of the molecular orientation and an undesirable axially corrugated morphology arising from electrospinning, as shown in Fig. 1(a,b). All fibers were annealed for 100 min in their freestanding configuration, at temperatures of 10–25 °C above the T_g of bulk PS (100 °C), and were cooled to room temperature at a rate of 0.50 K/min. The annealing temperatures varied with MW so that fibers with higher MW were annealed at higher temperatures. All fibers, with the exception of those with the two highest MW s, were annealed for 2–8 times the reptation time for bulk PS chains ($\tau_{d\text{-bulk}}$) of the corresponding MW , which was calculated as the time intercept of the intersection between linear extrapolations of the rubbery plateau and the flow regimes using the creep compliance data and shift factors for monodisperse PS with $MW = 600,000$ g/mol [19,20].

In order to overcome the initial molecular orientation stemming from electrospinning, all PS fibers were heated much longer than the time scale for relaxation of the entanglement network, τ_e , and the Rouse times, τ_R , (with the exception of $MW = 9,000,000$ g/mol) which are related to strain hardening and long range orientation of polymer chains [21]. The temperatures and the duration of annealing were sufficient to completely eliminate the severe initial corrugated fiber morphology due to electrospinning [22]. The annealing times for fibers with MW above the entanglement threshold are expressed in Table 1 as multiples of the bulk reptation time, $\tau_{d\text{-bulk}}$.

2.2. Mechanical experiments with individual PS nanofibers

Measurements of the elasto-plastic mechanical response of individual PS nanofibers subjected to uniaxial tension were made possible by a microelectromechanical systems (MEMS) device designed for nanomechanical testing in ambient conditions. This experimental method provides independent measurement of the applied force (engineering stress) and elongation (stretch ratio) with resolution of 50 nN and 25 nm, respectively [23]. The experiments were conducted in ambient conditions under an optical microscope (23 °C and 20–30% relative humidity) in order to collect high magnification optical images during testing. 150 μm long individual PS fibers were isolated and mounted across a 30 μm gage section between the cross-heads of the MEMS device, using a two-part epoxy. All experiments were conducted at cross-head strain rates of 10^{-2} s⁻¹. High magnification SEM micrographs of the undeformed fiber segments that were outside the gage section as well as the gage section itself were obtained after the completion of mechanical testing to measure the corresponding fiber diameters. In the case of experiments that were interrupted at different stages of fiber extension before failure, the fibers were completely unloaded and then imaged by an SEM. A thin (~5 nm) Au–Pd layer was sputtered onto the fibers prior to SEM imaging.

3. Results and discussion

Qualitatively, all PS fibers subjected to uniaxial extension demonstrated a mechanical response that partially or entirely followed the engineering stress (σ) vs. stretch ratio (λ) curve shown in Fig. 2, consisting of (i) an initial viscoelastic regime (shaded region), (ii) a long plateau flow stress regime due to the formation and propagation of a stable neck, and (iii) a pronounced strain hardening regime after completion of neck propagation along the fiber. Unlike bulk PS, the mechanical behavior of PS nanofibers is characterized by large deformation followed by major strengthening and significant homogenous extension that is controlled by strain hardening.

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