5916 *Macromolecules* **2009**, *42*, 5916–5918
DOI: 10.1021/ma9014356

Macromolecules
COMMUNICATION TO THE EDITOR

Thermo-Responsive Nanofiber Mats

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Received July 2, 2009
Revised Manuscript Received July 22, 2009

Polymer gels that undergo volume changes in response to various environmental stimuli such as temperature, solvent composition, pH, electric field, and light irradiation are capable of transducing chemical or physical energy directly into mechanical work.[1−3] Poly(*N*-isopropylacrylamide) (poly(NIPA)), a typical thermo-responsive polymer with a lower critical solution temperature (LCST) in water at 32 °C, has been paid considerable attention not only from the fundamental viewpoint of thermodynamics and kinetics of phase transition but also for the promising applications in sensors, actuators, drug delivery systems, and cell cultures,[4−6] where rapid volume changes of gels are crucially important for the practical use. Since swelling−deswelling of gels is caused by collective diffusion of polymer networks in a fluid, the relaxation time (τ) of volume change can be expressed as $\tau = R^2/\pi^2 D$, where R and D are characteristic length of a gel and collective diffusion coefficient of a polymer network, respectively.[7] The equation describes the relaxation time is proportional to the square of the characteristic length of a gel, which clearly demonstrates that downsizing of gels would significantly enhance the rate of volume changes.

Electrospinning, a facile, inexpensive, and template-free method, which enables fabrication of nanometer-scaled fibers, has been applied to various polymer solutions and melts,[8−10] where electrospun nanofibers are directly deposited on a grounded target as a randomly oriented mat. If poly(NIPA) could be electrospun into nanofiber mats, rapid macroscopic volume changes to a stimulus of temperature might be achieved both due to the small diameter of nanofibers and large specific surface area of the mat. Although poly(NIPA) can be electrospun from various solvents,[11,12] the resulting mats dissolve in water below the LCST, while above the LCST nanofibers come apart and disperse in water, which is ascribed to lacks of interpolymer and interfiber cross-links to keep its shape in the swollen state. Therefore, it is considerable that long alkyl side-chains incorporated into poly(NIPA) aimed at aggregating in water via hydrophobic interactions,[13] can lead to the formation of interpolymer and interfiber physical cross-links. Herein, we report on a successful one-step fabrication of fast thermo-responsive poly(NIPA)-based nanofiber mats which were cross-linked via hydrophobic interactions of stearyl side-chains by using an electrospinning technique. We also demonstrate for the first time kinetics of volume changes of a single nanofiber.

Poly(NIPA-*co*-SA) was synthesized by free radical copolymerization of *N*-isopropylacrylamide (NIPA) with stearyl acrylate (SA) used as a hydrophobic monomer bearing a long alkyl chain (see Supporting Information). The molar ratio of SA incorporated into the copolymer evaluated by ^{1}H NMR (Unity plus-400, Varian) was 3.9 mol % (monomer feed ratio was 3.0 mol %). The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (M_w/M_n) measured by GPC (UFLC, Shimadzu) were 35 200 g mol^{-1}, 18 200 g mol^{-1}, and 1.93, respectively. The electrospinning was performed on 25 wt % methanol solution of the poly(NIPA-*co*-SA) at a voltage of 30 kV for 5 h and results are shown in Figure 1. The poly(NIPA-*co*-SA) was successfully electrospun into nanofibers having an average diameter of d_{dry} = 207 nm (c, d) and deposited on a glass substrate as a mat with a thickness of *ca.* 20 μm (a). It is noted that the poly(NIPA-*co*-SA) nanofiber mat does not dissolve in water at 25 °C but spontaneously peels off the substrate and shrinks in water by *ca.* 35% (b) due to relaxation of inner stress and/or surface tension to minimize the surface area.

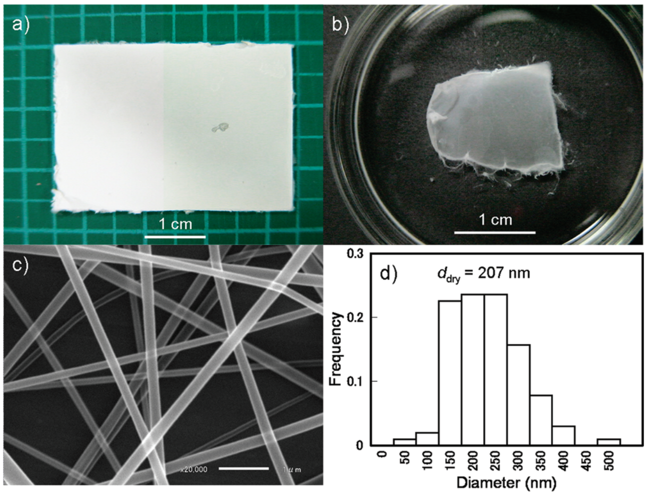

Figure 1. Optical images of poly(NIPA-*co*-SA) nanofiber mat deposited on glass substrate (a) and shrunk in pure water at 25 °C (b). (c) SEM micrograph and (d) distribution of fiber diameter of poly(NIPA-*co*-SA) nanofibers. The electrospinning was performed on 25 wt % methanol solution of poly(NIPA-*co*-SA) at 30 kV for 5 h.

A typical volume change of the nanofiber mat as temperature increases is demonstrated in Figure 2a. One can see the nanofiber mat deswells linearly with increasing the temperature from 25 °C and reaches *ca.* 70% of its initial length at temperatures higher than 32 °C. Assuming that the mat shrinks isotropically, the volume change in this temperature range is calculated to be 66%. To clarify the mechanism of thermo-responsive volume change, temperature dependence of transmittance was evaluated with a UV−vis−NIR spectrometer (V-670, Jasco) for aqueous solutions of poly(NIPA) and poly(NIPA-*co*-SA) and results are shown in the inset of Figure 2a. The transmittance of the poly(NIPA) solution drops in a narrow temperature range around 32 °C, corresponding to a LCST, which represents a coil−globule transition of polymer chains and subsequent aggregation of hydrophobic globules is responsible for the scattering of visible light.[14] The incorporation of hydrophobic SA monomer not only shifts the LCST from 32 °C to around 23 °C but also decreases the sharpness of the temperature-dependent transmittance change. Moreover, the poly(NIPA-*co*-SA) solution remains turbid even at 10 °C with a transmittance of 80%, suggesting a formation of micelle-like aggregates of hydrophobic stearyl groups in water that can not be dissociated entirely below the LCST.[15] Therefore, the poly(NIPA-*co*-SA) nanofiber mat is insoluble but swells in water at 25 °C because long alkyl side-chains form physical cross-links between polymer chains and nanofibers through

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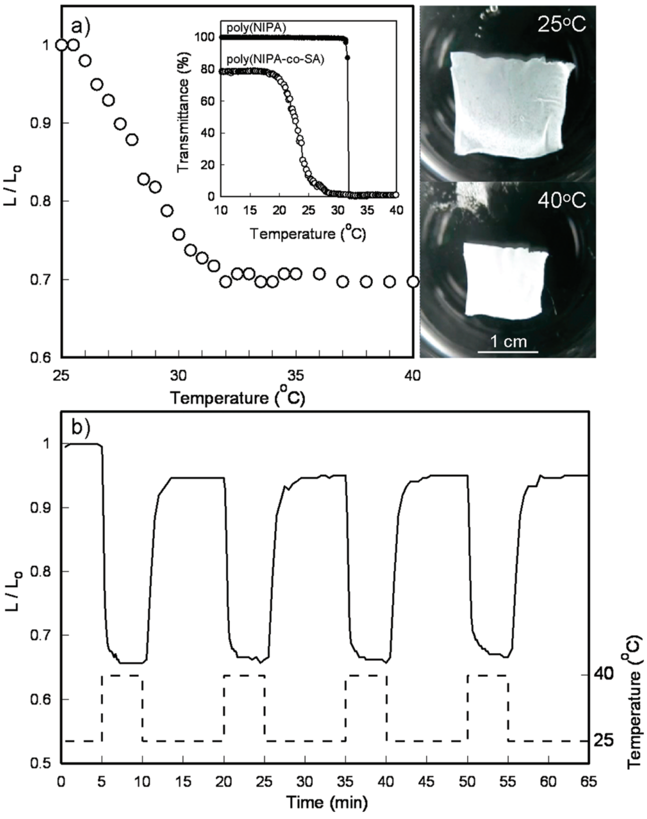

Figure 2. (a) Temperature-dependent relative length change of poly(NIPA-*co*-SA) nanofiber mat (2 cm × 2 cm × 20 μm) in pure water measured at a heating rate of 0.1 °C min^{-1} and optical images at 25 and 40 °C. The inset shows temperature dependence of transmittance for poly(NIPA) and poly(NIPA-*co*-SA) aqueous solutions with concentrations of 1 wt %. (b) Reversibility and reproducibility of time-dependent deswelling and swelling of poly(NIPA-*co*-SA) nanofiber mat (2 cm × 2 cm × 20 μm) in pure water between 25 and 40 °C.

hydrophobic interactions.[13] In order to evaluate dynamics of thermo-responsive behavior, time-dependent deswelling-swelling of poly(NIPA-*co*-SA) nanofiber mat is measured and the result is demonstrated in Figure 2b. It is well-known that deswelling of poly(NIPA) bulk gel becomes very slow after a certain period and it requires a few days to reach the equilibrium state, which is ascribed to the formation of a dense skin layer on the gel surface which strongly hinders diffusion of water.[5] Interestingly, poly(NIPA-*co*-SA) nanofiber mat exhibits rapid and significant shrinkage by 34% of its initial length within 2 min after a jump in temperature from 25 to 40 °C, which suggests no skin layer forms on the surface of the nanofiber and will be discussed later. On the other hand, decreasing the temperature from 40 to 25 °C brings about rapid swelling up to 95% of the initial length within 4 min and reversible swelling−deswelling was repeated at least 4 times. It is important to note that swelling rate of the nanofiber mat is more than 1 order of magnitude faster than bulk gels[16] because swelling rate of gels is controlled by diffusion of polymer networks and characteristic size of the gel. In other words, the rapid swelling of the nanofiber mat might be associated with a larger specific surface area of the mat and small diameters of nanometer-scaled fibers fabricated by electrospinning.

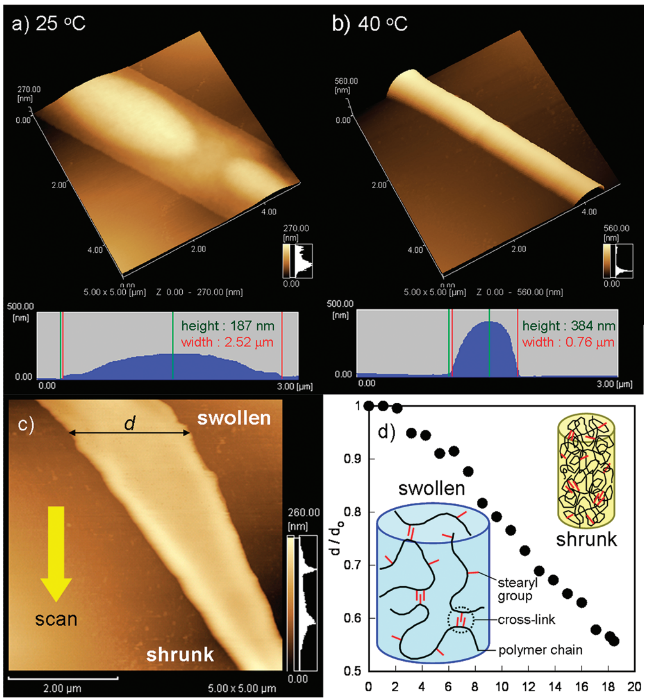

Figure 3. AFM images of a single poly(NIPA-*co*-SA) nanofiber measured at 25 °C (a) and 40 °C (b) with a thermostatic solution-cell by a tapping mode at a frequency of 0.2 Hz. Note that AFM images of parts a and b represent the same area. (c) Temperature-modulated AFM image and (d) time-dependent deswelling of a single poly(NIPA-*co*-SA) nanofiber measured by a tapping mode at a frequency of 0.2 Hz where the solution−cell is heated from 25 to 40 °C when scanning starts.

To clarify the mechanism of rapid swelling−deswelling of the nanofiber mat in more detail, AFM measurements were performed on a single poly(NIPA-*co*-SA) nanofiber with a SPM (SPM-9600, Shimadzu) and results are shown in Figure 3. Since the average diameter of nanofibers in a dry state (d_{dry}) is 207 nm (Figure 1d), the nanofiber with height and width of 187 and 2520 nm, respectively, in water at 25 °C (a) appears to be in a swollen state, the flat shape of which may result from depression by a cantilever probably due to the low elastic modulus of the swollen nanofiber. It is noted that a rise in the temperature to 40 °C (b) causes significant decrease of width (760 nm) but increase of height (384 nm), indicating the nanofiber is shrunk into more stiff original cylindrical shape due to deswelling. The volume change of the nanofiber estimated from cross-sectional areas at 25 and 40 °C is *ca.* 37% which is nearly half that of the mat (66%) as shown in Figure 2a. The fact demonstrates that not only swelling−deswelling but also dissociation-association of nanofibers are crucially important for the macroscopic volume changes of the nanofiber mat. Furthermore, we have successfully measured for the first time shrinking process of a single nanofiber by means of a temperature-modulated AFM technique where solution-cell is heated from 25 to 40 °C when scanning starts. It is seen from Figure 3c that a nanofiber becomes finer as the scan proceeds (from top to bottom), which reveals deswelling of the nanofiber where formation of bumps around the edges during the deswelling is probably due to the slow heat conduction from the surface to the core of the nanofiber. Figure 3d shows the time dependence of deswelling evaluated from a scanning frequency (0.2 Hz). Relatively slow deswelling of the nanofiber is ascribed to sluggish heat conduction through water in the thermostatic solution−cell because stirring of water is not allowed during the AFM measurement. It should be emphasized that deswelling of the nanofiber takes place linearly with elapse of time, which strongly suggests no skin layer forms on the surface of the nanofiber. Shibayama and co-workers[17] investigated shrinking kinetics of poly(NIPA) gels by means of small-angle neutron scattering coupled with static/dynamic light scattering. They found that skin formation plays a major role in slow shrinking kinetics and evaluated the thickness of skin layer to be *ca.* 3 μm. By comparison with the thickness of the skin layer, the diameters of poly(NIPA-*co*-SA) nanofibers in the swollen state are smaller, which evidently indicates that nanofiber transforms directly from a swollen state to a shrunk state without formation of a skin layer that significantly slows down the rate of deswelling.

In conclusion, the fast thermo-responsive volume changes of poly(NIPA-*co*-SA) nanofiber mat lie in the rapid swelling–deswelling of the nanofibers and their dissociation-association through hydrophobic interactions where the large specific surface area is favorable for free diffusion of water in the mat. It is worthy to note that (i) the LCST of polymers can be tuned by choosing alkyl chain-length of hydrophobic monomer and its composition and (ii) not only the morphology of the mat but also the fiber diameter can be controlled by electrospinning conditions, which will open up a new field of applications to fast thermo-responsive actuators or drug delivery systems.

Acknowledgment. This work was supported in part by Tokyo Electron Ltd. for funding the Laboratory of Organic Robotics. The authors gratefully acknowledge Dr. Shi-Jian Su and Mr. Akinori Kogure (Shimadzu Co.) for the NMR and AFM measurements.

Supporting Information Available: Scheme showing the synthesis of poly(NIPA-*co*-SA). This material is available free of charge via the Internet at http://pubs.acs.org.

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