

Thermo-Responsive PNIPAM Hydrogel Nanofibres Photocrosslinked by Azido-POSS

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ABSTRACT

Photocrosslinkable thermo-responsive nanofibres were prepared by electrospinning poly(N-isopropylacrylamide) (PNIPAM) in the presence of an Azido-polyhedral oligomeric silsesquioxane (Azido-POSS). ultraviolet light (UV) irradiation yielded a highly-crosslinked hydrogel network within 2 min. The treated nanofibres showed outstanding stability in water, excellent hydrogel characteristics, fast response to temperature changes with fast swelling and de-swelling .

INTRODUCTION

Hydrogels capable of responding to surrounding temperature variations by swelling and de-swelling, also called thermo-responsive hydrogels¹, are some of the most studied “smart” polymeric gels. In this field, arguably the most significant challenge is to achieve both fast response and structural hydrogel integrity during the repeated volume changes². Nanomaterials have been shown promising results in these regards. For example, Wang et al.³ have recently reported a simple method to obtain electrospun PNIPAM nanofibres via thermal treatment, using OpePOSS as a crosslinker. However, heat-treatment has many disadvantages, such as fibre shrinkage during processing⁴. Heat treatments also become a major limitation in some areas of application (such as tissue engineering) where potential cargoes (proteins, or other biomolecules of interest, for instance) could deteriorate during heat curing⁵. A different way to crosslink PNIPAM is thus sought, ideally allowing room temperature treatments and minor morphological variations.

In this study, a new photocrosslinkable PNIPAM-based formulation was used to produce nanofibres: linear PNIPAM was electrospun in the presence of an Azido-POSS as a photocrosslinker, followed by a UV treatment at room temperature. The as-prepared hydrogel nanofibres showed fast swelling/de-swelling responses triggered by temperature changes.

EXPERIMENTAL

The polymer solution for electrospinning was prepared by dissolving PNIPAM and Azido-POSS (synthesized in our lab) in a DMF/THF (1:1, vol/vol) solution at room temperature. The solutions were electrospun using a conventional electrospinning setup⁶ to yield nanofibre mats. During electrospinning, the solution flow rate, the applied voltage and the electrospinning distance were set at 0.8 mL/hr, 12 kV and 17 cm, respectively.

To obtain a highly-crosslinked PNIPAM network, the as-electrospun nanofibres were subjected to UV irradiation

(Hg medium pressure, 450 W, 6 cm lamp-sample distance) at room temperature for 2 min, 5 min, 10 min, 15 min, and 20 min, respectively.

RESULTS AND DISCUSSION

Synthesis and structure of photocrosslinker Azido-POSS.

Fig. 1 shows the synthetic path to Azido-POSS, which has eight photo-active azido groups.

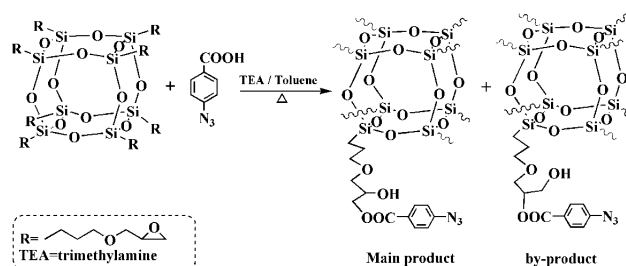


Fig. 1 Synthetic route of Azido-POSS via esterification between azidobenzoic acid and OpePOSS.

Photocrosslinking mechanism.

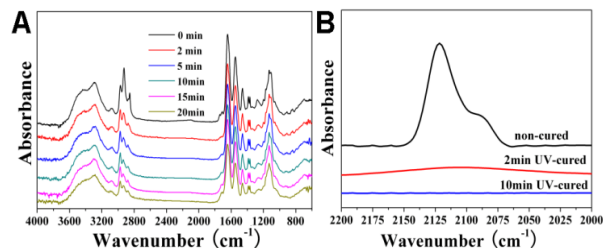


Fig. 2 (A) FT-IR spectra of UV-treated Azido-POSS/PNIPAM nanofibres at different treating time. (B) FT-IR spectra of selected UV-treated samples at wavenumber between 2000~2200 cm⁻¹.

FTIR analysis. The pre-prepared PNIPAM nanofibres were UV-cured for 2 min, 5 min, 10 min, 15 min, and 20 min, respectively. The FTIR spectra of non-cured PNIPAM/Azido-POSS and UV photo-crosslinked PNIPAM/Azido-POSS nanofibres at different UV-exposure time are presented in Fig. 2A. The FTIR bands were assigned as follows: 1366-1386 cm⁻¹ deformation of the two methyls in -C(CH₃)₂; 1458 cm⁻¹ -CH₃ and -CH₂(deformation); 1545-1645 cm⁻¹ amide II band (stretching); 1710-1735 cm⁻¹ -O=C=O stretching; ~2125 cm⁻¹ -N₃ asymmetric stretching; 2854 cm⁻¹ -CH₂ symmetric stretching; 2873 cm⁻¹ -CH₃ symmetric stretching; 2925 cm⁻¹ -CH₂ asymmetric stretching; 2970 cm⁻¹ -CH₃ asymmetric stretching; 3070 cm⁻¹ amide II overtone; wide band around 3300 cm⁻¹ secondary amide -NH stretching. A peak ascribed to the azide group is

visible in the untreated sample as a shoulder at about $\sim 2125 \text{ cm}^{-1}$. The intensity of the aryl-azide peak was observed to decrease as a function of time. Importantly, after just two minutes of treatment, the peak was barely measurable, as shown in Fig. 2B, suggesting that the crosslinking reaction was nearly complete after 2 min.

DSC analysis. DSC curves for photo-crosslinked PNIPAM/Azido-POSS nanofibres are shown in Fig. 3. For the non-cured nanofibres, the DSC curve showed a strong and exothermic peak at around 210°C . This peak has been related to the decomposition of the azido-group, $-\text{N}_3$, in arylazide-containing molecules⁷. However, no similar peak was found for the UV-treated samples, inferring that such decomposition could not take place after the photo-crosslinking treatment. All samples showed a glass transition (T_g) peak at around $120\sim 140^\circ\text{C}$. These results also suggest that the activation and decomposition of the azide upon exposure to UV light had high yield and rate.

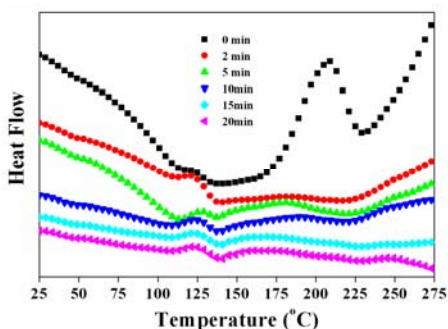


Fig. 3 DSC curves for the non-treated and UV-treated PNIPAM/AzidoPOSS nanofibres.

Thermo-responsive properties of photocrosslinked PNIPAM nanofibres.

When untreated nanofibre mats were immersed in water at 20°C , the fibre mats gradually dissolved (Fig. 4A1). Even one single drop of water was enough to dissolve the 2 cm^2 non-cured mat, as shown in Fig. 4C1~3. When the water in which the first mat was dissolved (Fig. 4A1) was heated to 40°C , no fibrous structure was recovered and the solution became cloudy (Fig. 4A2). In contrast, the nanofibre mat treated for 2 min under UV light became swollen and transparent upon immersion in water at 20°C (Fig. 4B1), showing no sign of dissolution, degradation or weight change after several weeks' immersing in water. It was observed that the projected size of the photo-crosslinked nanofibre mats (Fig. 4D1) decreased upon wetting with cold water (Fig. 4D2), while the thickness of the mat increased (Fig. 4E2). This phenomenon, commonly observed in nanofibre swelling, was not observed when using thermally crosslinked nanofibre mats,³ and can be ascribed to molecular relaxation taking place in presence of solvent. When the swollen nanofibre mats were immersed into hot water, both projected size (Fig. 4D3) and thickness (Fig. 4E3) decreased due to the de-swelling process characteristic of PNIPAM, taking place above LCST.

The macroscopic shrinking was quantified by measuring the area of a nanofibre mat above and below LCST. Based on Fig. 4D1~D3 and Fig. 4E1~E3 the volumetric values of dry, swollen (below LCST) and de-swollen (above LCST) samples were calculated as 46.3 , 106.7 and 14.7 mm^3 , respectively, indicating that the increased volume of the nanofibre mat can be related to the absorption of water. Additionally, the nanofibre mat above LCST (de-swollen state) showed a reduced volume, when compared to the same sample below LCST. This suggests that the volume transition of PNIPAM affects the size of the nanofibre mat in the three dimensions.

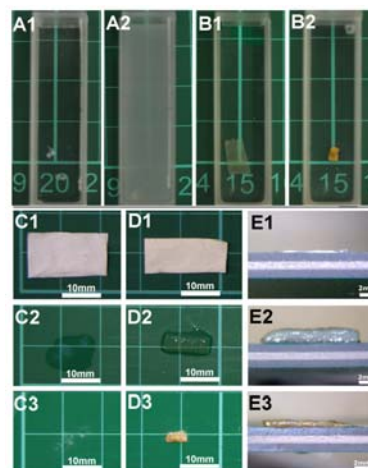


Fig. 4 Digital images of: (A1) non-cured nanofibre mat dissolving in cold water (20°C) and (A2) followed by hot water (40°C); (B1) UV-cured Azido-POSS/PNIPAM nanofibres in cold water (20°C) and (B2) followed by hot water (40°C); Non-cured and UV-cured PNIPAM nanofibres in: (C1, D1) dry state, (C2, D2) cold water and (C3, D3) hot water; Thickness changes of UV-cured PNIPAM nanofibre mats: (E1) dry sample, (E2) swollen state below LCST and (E3) shrunk state above LCST.

CONCLUSIONS

A novel strategy was used to produce stable and re-usable thermo-responsive PNIPAM hydrogel nanofibres by photo-crosslinking PNIPAM with Azido-POSS. Insoluble nanofibres composed of a highly-crosslinked PNIPAM polymer network were produced after electrospinning and subsequent UV photo-crosslinking. The UV-crosslinker Azido-POSS played a crucial role in the formation of a highly-crosslinked polymer network. The UV-cured nanofibre mats quickly became swollen and transparent upon contact with water at a temperature below their lower critical solution temperature (LCST) and showed fast and repeatable response to temperature.

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