

Fabrication of Poly(N-isopropylacrylamide-co-Glycidyl Methacrylate) Electrospun Hydrogel Fibers

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Introduction

The synthesis of thermoresponsive smart polymers has been the main focus of recent researches due to their importance to various fields of bio-nanotechnology. Amongst the well-known thermal-stimulus responsive materials, poly(N-isopropylacrylamide) (PNIPAAm) has received considerable attention as the lower critical solution temperature (LCST) of this polymer causes a volume phase transition (VPT) depending on the temperature.

Demand for fibrous heterogeneous hydrogels

Water molecules should rapidly access the whole material for PNIPAAm hydrogels to have fast thermo-responsive characteristics. However, the ordinary isotropic hydrogels of this polymer, produced from bulk polymerization, suffer from slow stimuli responsivity and have poor mechanical properties.

Hydrophilic nanostructures are an ideal substitute for conventional hydrogels and have structural robustness at molecular and macroscopic levels. Suppose the hydrophilic polymer content of the nanostructure would be cross-linkable. In that case, the resultant reaches a fast hydration/dehydration response due to the easy accessibility of water molecules to the material's surface. However, nanofibers (e.g., nanofibrous membranes) of pure PNIPAAm are extremely difficult to crosslink, unstable, and unable to maintain their structural integrity in water. Furthermore, the pre-crosslinked form of PNIPAAm cannot be made into the desired nanoshapes. Therefore, the formulation of a new class of cross-linkable PNIPAAm copolymers is highly on demand. These copolymers can be further processed into nanofibrous membranes to form anisotropic heterogeneous hydrogels upon hydration.

Project Goal

In this work, for the first time, an innovative method was developed and validated to synthesize poly (NIPAAm-co-glycidyl methacrylate(GMA)) (P(NIPAAm-co-GMA)) block copolymers possessing high molecular weight and excellent electrospinnability.

Synthesis of cross-linkable block copolymers

The synthesis of thermoresponsive P(NIPAAm-co-GMA) with different monomer feed ratios was performed via free-radical copolymerization in an aqueous solution. After 5 hours of polymerization, high molecular weight copolymers ($118000 < Mw < 230000$) with narrow molecular weight distribution ($1.14 < PDI < 1.23$) were achieved. The FTIR spectra of the dialysed copolymers are demonstrated in figure 1. As the percentage of NIPAAm monomers in the initial feed decreases (from NGd97, in which NIPAAm/GMA feed ratio is 97/3, to NGd70, where mentioned ratio is 70/30), the GMA characteristic peaks at 1720, 1240, and 910 cm^{-1} , progressively increases (The peaks are corresponded to O-C=O stretching of GMA's ester configuration, and C-O-C stretching of epoxide groups, respectively).

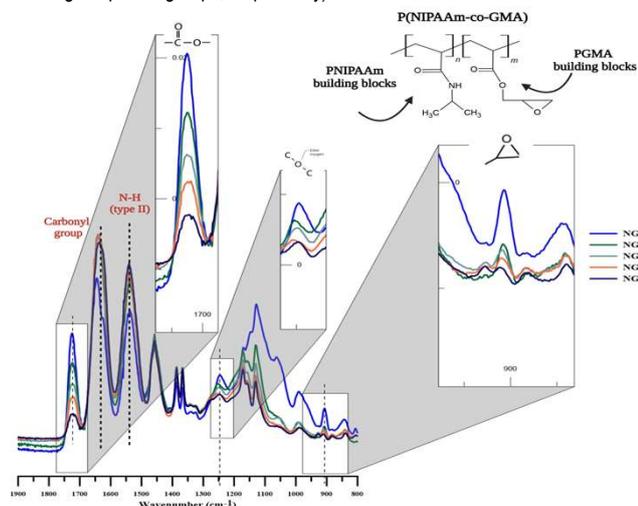


Figure 1. FTIR spectra of the synthesized crosslinkable P(NIPAAm-co-GMA) polymers.

CONCLUSIONS

An innovative method for fabricating fibrous hydrogels derived from P(NIPAAm-co-GMA) copolymers has been demonstrated in this work. The post electrospinning heat treatment led to the formation of highly crosslinked nanofibers. The fabricated membrane can tolerate several hydration/dehydration cycles. The results of this work can open the doors for these smart nanostructure hydrogels in applications such as drug delivery and tissue engineering.

ACKNOWLEDGMENTS

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Electrospun cross-linkable fibers

The anisotropic structures produced by electrospinning have exceptionally higher porosity and specific surface area, lower thickness, and better mechanical properties. Alas, this fabrication technique cannot be used to electrospin hydrogels. As an alternative route, electrospinning of hydrophilic cross-linkable copolymers, followed by post electrospinning heat treatments, has been developed in this study. This innovative method has been fine-tuned by adjusting the length and concentration of crosslinking moieties as well as the copolymer building blocks ratio. The formation of Adduct 1:1 resulted from the click chemistry reaction between GMA's building blocks, and crosslinker led to the disappearance of characteristic epoxide peak. The blue arrow indicates the shift of the peak at 1550 cm^{-1} , assigned to the N-H stretching of the amide group, to higher frequencies in as-spun and heat-treated samples. This occurrence can be explained by an overlap between the characteristic peak of the crosslinker functional groups with that of type 2 amide of P(NIPAAm). Moreover, the red arrow shows a shift of the GMA's ester configuration peak to lower frequencies due to the formation of hydrogen bonding between carboxyl groups and the hydroxyl group of the copolymeric chains.

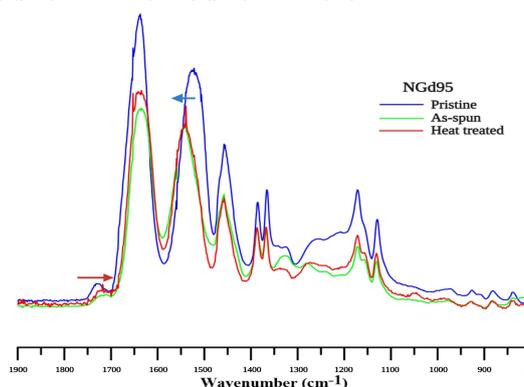


Figure 2. FTIR spectra of the pristine, as-spun, and heat treated P(NIPAAm-co-GMA).

The morphology of crosslinked fibrous membrane has been studied by SEM (dry state) and light microscope (wet state). Heat treatment causes the fibers to shrink, and as a result the average fiber diameter (AFD) decreases (Figure 3B). Hydrogel formation is repeatable for several hydration/dehydration cycles, although it has an irreversible effect on fiber diameter (Figure 3C).

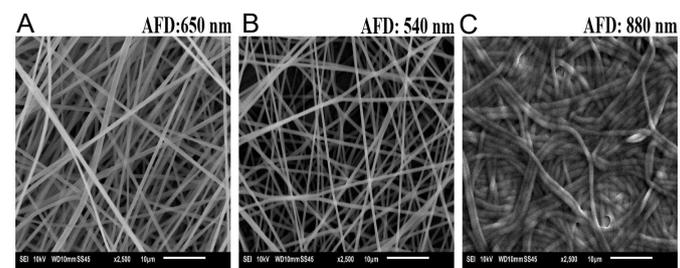


Figure 3. SEM images of nanofibrous membrane: (a) as-spun, (b) heat-treated, and (c) swelled in 20°C water and then dried at the same temperature.

As the water impregnates the membrane, the porosity and fiber diameter increase substantially (Figure 4).

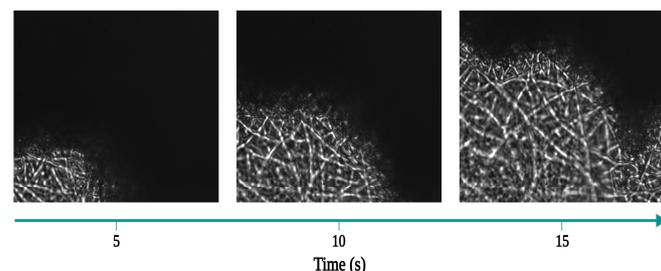


Figure 4. Time evolution of crosslinked fibrous membrane into its hydrogel state recorded by light microscope.