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A novel method for preparation of cross-linked PEGDA microfibers by low-temperature photopolymerization

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ABSTRACT

The objective of this work is to demonstrate the feasibility of fabricating cross-linked poly(ethylene glycol) diacrylate (PEGDA) microfibers by low-temperature photopolymerization. The morphology and diameter, water absorption property, and thermal stability of the obtained fibers were characterized by scanning electron microscope (SEM), swelling test in water and thermogravimetry (TG), respectively. The results indicated that the diameter of obtained fibers lay in the submicro-/micro-scale within the range of 0.5–10 μm. The suitable PEGDA concentration for the fabrication of microfibers by low-temperature photopolymerization was less than 0.5 wt%. The fiber diameter and water absorption ratio became larger as the concentration of PEGDA increased, and thermal stability of the fibers was also enhanced as the increase of PEGDA concentration owing to the increased cross-linking density. This approach has the potential to be applied to a much wider range of monomers or crosslinkable biopolymers to satisfy the needs of different applications.

1. Introduction

Poly (ethylene glycol) (PEG) has good solubility in both polar and non-polar solvents (i.e., in water and many organic solvents) [1] and it is a biocompatible polymer [2] that has been suggested for use in a variety of biomedical applications [3]. Poly (ethylene glycol) (PEG) hydrogels can be modified by cross-linking a large number of bioactive moieties (peptides, glycosaminoglycans, growth factors) to achieve a high degree of specific bioactivity [4]. Indeed it is widely reported that peptides tethered to either the surface or bulk phase of PEG hydrogels made by crosslinking of poly(ethylene glycol) diacrylate (PEGDA) will retain their bioactivity after this modification [5].

Significant advancements in fiber production techniques have wide applications for fibrous materials in diverse fields such as optoelectronics, regenerative medicine, piezoelectrics, ceramic materials, etc. [6–8]. A number of approaches have been used for fabricating continuous polymeric micro/nano-fibers, including electrospinning [9], self-assembly [10], forcespinning [11] and freeze-drying [12,13]. However, all of the existed methods for fabrication of fibers have no feasibility to fabricate crosslinked micro/nano-fibers straightforwardly from the corresponding monomers or from pre-cross-linked polymers, owing to the low viscosity of monomers and insolubility of cross-linked polymers.

Hence, we described a novel concept for the preparation of cross-linked PEGDA micro/nano-fibers by low-temperature phase-separation photopolymerization. So far, to the best of our knowledge, its use in the synthesis of cross-linked polymer fiber has not been reported yet. In our previous study, macroporous crosslinked polymers with 2D or 3D shape from corresponding monomers with no template and no surfactant or other additives were fabricated by similar phase-separation photopolymerization method in low-temperature [14]. That method required a high monomer ratio (mainly higher than 10%) and the obtained structure could not achieve micro-/nano-fibers. In our present study, we successfully fabricate cross-linked PEGDA micro/nano-fibers by low-temperature phase-separation photopolymerization with low monomer concentration combined with freeze drying. We mainly focus on the fabrication of PEGDA-based micro/nano-fibers; however, we believe that this approach can be applied to a much wider range of monomers or crosslinkable biopolymers which could be polymerized by photo-induced free radical polymerization, thiol-ene reaction or [2+2] cycloaddition reaction.

2. Materials and method

2.1. Materials

Poly (ethylene glycol) diacrylate (PEGDA, molecular weight

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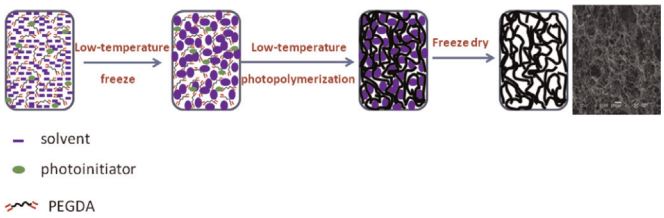

Fig. 1. Preparation process of cross-linked PEGDA microfibers by low-temperature photopolymerization.

750 g/mol) was purchased from Sigma-Aldrich. The photoinitiator 2-hydroxy-4- (2-hydroxyethoxy)-2-methyl propiophenone (2959) was purchased from BASF Schweiz AG (Switzerland).

2.2. Preparation of PEGDA fibers

The preparation process of PEGDA fibers is shown in Fig. 1. First, PEGDA monomer/ water solution with a certain weight ratio (0.1 wt%, 0.3 wt%, and 0.5 wt%, respectively) was treated at low-temperature (−20 °C) for 2 h to make it freezing. The photo-initiator 2959 was added initially, before being frozen with an amount of 1 wt% towards the mass of PEGDA. Next, for all of the samples, photo irradiation using a pointolite (Omni-Cure series 1000; wavelength range: 200–500 nm) was performed at −20 °C for 10 min. The irradiation intensity was 15 mW/cm^2. Finally, the remaining water was removed by freeze drying at −60 °C for 24 h.

2.3. Characterization

SEM was performed by a S-4700 (Hitachi) microscope. At least

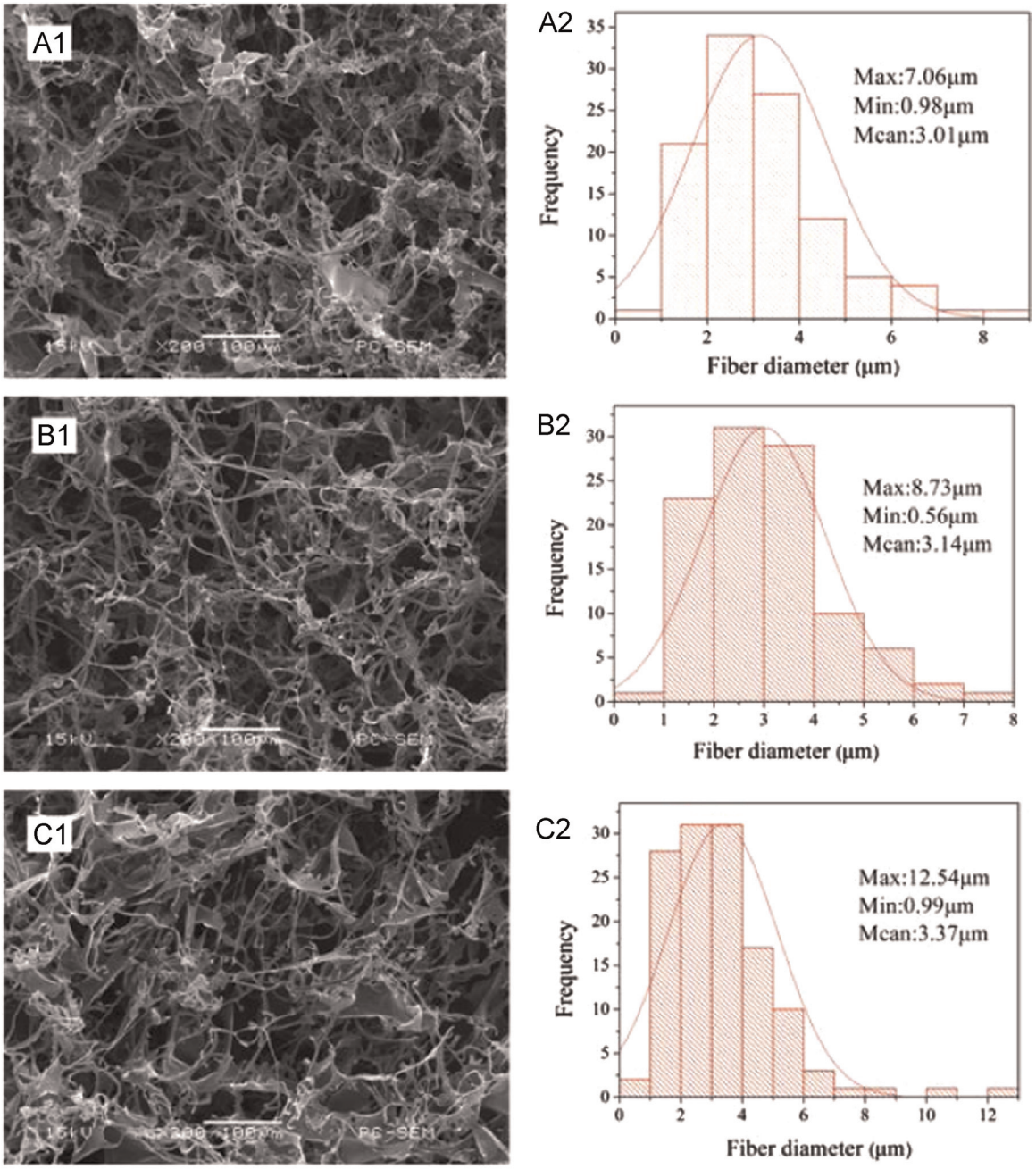

Fig. 2. SEM images and diameters distribution of crosslinked PEGDA fibers at different concentration: (A) 0.1 wt%, (B) 0.3 wt%, (C) 0.5 wt%.