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Conducting semi-interpenetrating polymeric composites via the preparation of poly(aniline), poly(thiophene), and poly(pyrrole) polymers within superporous poly(acrylic acid) cryogels

Nurettin Sahiner *, Sahin Demirci

[a] Department of Chemistry, Faculty of Science & Arts, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey
[b] Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey

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ABSTRACT

In this study, a novel and special form of hydrogel known as cryogel with super and interconnected pore structures was synthesized as p(acrylic acid) (p(AAc)) cryogel by a cryopolymerization technique. Then, the superporous p(AAc) cryogels were used as template for the synthesis of conductive polymers such as poly(aniline) (p(An)), poly(thiophene) (p(Th)), and poly(pyrrole) (p(Py)). To the best of the authors' knowledge, this is the first study of its kind to report the synthesis of conductive polymers, p(An), p(Th), and p(Py), within the superporous network of cryogel. The synthesized p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) conducting semi-interpenetrating polymeric network (semi-IPN) cryogel composites were characterized by using Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), and conductivity measurements. The conductivities of p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) toward semi-IPN cryogels were measured as $2.2 \times 10^{-4} \pm 1 \times 10^{-5}$, $3.2 \times 10^{-4} \pm 0.9 \times 10^{-5}$, and $3.2 \times 10^{-3} \pm 5 \times 10^{-4}$ S cm^{-1}, whereas the conductivity of bare p(AAc) cryogels was calculated to be about $3.2 \times 10^{-9} \pm 2.1 \times 10^{-10}$ S cm^{-1}.

1. Introduction

Over the past decades, there has been significant investigation of various morphologies and sizes of hydrogels for interesting properties. A special form of hydrogel known as cryogel provides significant advantages and has been extensively examined due to inherently superior characteristics such as super and interconnected porosity, structural flexibility, higher mechanical strength, and fast responsiveness in comparison to conventional hydrogels [1–3]. The synthesis of cryogels is generally carried out under cryogenic conditions (below the freezing point of solvent) with a cryopolymerization technique [4,5]. Under cryogenic conditions, if the used solvent is water, the ice crystal dimensions are the template agents responsible for providing a superporous three-dimensional (3D) network for the cryogels. As the cross-linking and polymerization are carried out around the ice crystals, pore sizes ranging from few tens to few hundreds of micrometer are readily formed [6–8]. Because of the porous structure, cryogels have found potential uses in many applications such as template for in situ metal nanoparticle preparation [9], column filler material [10], cell scaffolds or tissue engineering [11], adsorbents for environmental applications [12] and bioseparation [13], and in the design of biosensing devices [14].

Electroconductive polymers are conjugated polymers with spatially extended π-bonding that confers unique electrical, electrochemical, and optical properties [15,16]. Inherently conductive polymers represent a group of conjugated organic polymers such as poly(acetylene), poly(paraphenylene), poly(aniline), poly(pyrrole), and poly(thiophene) offering high electronic conductivity [17–19]. Polyelectrolyte hydrogels such as p(AMPS), p(APTMACl), and p(AAc) also provide ionic conductivity because of their ionic functional groups [20–22]. During recent years, researchers have paid special attention to the synthesis or embedding of conductive polymers within polymeric hydrogels [23–26]. The synthesis of conductive polymer–polymeric hydrogel, semi-interpenetrating polymer network (semi-IPN) or IPN systems such as p(aniline) prepared in p(2-acrylamido-2-methyl propanesulfonic acid), and p(vinyl alcohol) hydrogels was investigated by Gangopadhyay et al. [26] IPNs are interpenetrations of a minimum of two polymers (absence or presence of mutual chemical interactions), at least one of which is synthesized and cross-linked in the presence of the other [27]. If one polymer is cross-linked and the other is linear or branched and entangled with strong interactions with the other polymer, the IPN systems are called semi-IPN systems [28]. Composite materials constructed by two or more constituent materials with significant different physical and chemical properties were also investigated by many researchers because of the synergistic effects of all the components providing interesting properties of the used materials [29].

* Corresponding author at: Department of Chemistry, Faculty of Science & Arts, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey.

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In this study, we report for the first time the synthesis of conductive polymers within superporous p(acrylic acid) (p(AAc)) cryogels as conducting semi-IPN p(acrylic acid)/p(aniline) (p(AAc)/p(An)), p(acrylic acid)/p(thiophene) (p(AAc)/p(Th)), and p(acrylic acid)/p(pyrrole) (p(AAc)/p(Py)) cryogel composites. The superporous p(AAc) cryogels were synthesized at cryogenic conditions (T < 0 °C) and used as template for in situ room-temperature oxidative polymerization of conductive p(An), p(Th), and p(Py) polymers. The synthesized semi-IPN conducting p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) superporous cryogel composites were characterized by Fourier transform infrared (FT-IR) spectroscopy for structural analysis, thermogravimetric analysis (TGA) for thermal characterization, and then conductivity measurements. The conductivities of synthesized p(AAc)/conductive polymer semi-IPN cryogels were compared.

2. Experimental

2.1. Materials

Acrylic acid (AAc, 99%, Sigma-Aldrich) was used as a monomer, *N,N′*-methylenebisacrylamide (MBA, 99%, Acros) as cross-linker, potassium persulfate (KPS, 99%, Sigma-Aldrich) as initiator, and sodium metabisulfide (SMS, 99%, Sigma-Aldrich) was used as an accelerator for the preparation of cryogels. Aniline (99%, Sigma-Aldrich), thiophene (99%, Aldrich), and pyrrole (98%, Aldrich) were used as monomers in the synthesis of the corresponding conductive polymers. Ammonium persulfate (APS, 98%, Sigma-Aldrich) solution in hydrochloric acid (HCl, 36.5–38%, Sigma-Aldrich) was used as an initiator system for the synthesis of poly(aniline) (p(An)). Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%, Acros) solution in chloroform (CH_3Cl, 99%, Riedel de Haen) and water were used as initiator systems for synthesis of poly(thiophene) (p(Th)), and poly(pyrrole) (p(Py)). Distilled water (DI) was used for washing cryogels and throughout experiments.

2.2. Synthesis of p(AAc) cryogels

P(AAc) cryogels were synthesized according to the procedure reported in ref. [1]. Briefly, certain amounts of AAc monomer (0.76 mL) and MBA (0.254 g) were dissolved in a vial with 4.24 mL of DI. Certain amounts of KPS (0.0291 g) and SMS (0.0411 g) were dissolved in 1 mL of DI in a separate vial as an initiator system. All the solutions in vials were cooled in a freezer at 0 °C for about 5 min. Then, the cooled initiator system was added to the monomer solution immediately and after rapid vortex mixing placed into plastic straws (~8 mm in diameter). Then, the plastic straws were placed in −18 °C for 24 h to complete cryopolymerization. The synthesized p(AAc) cryogels were cut into equal shapes of length approximately 1 cm and washed with DI several times and dried using a freeze dryer.

2.3. In situ synthesis of electroconductive polymers within p(AAc) cryogels

2.3.1. Synthesis of p(AAc)/p(An) semi-IPN cryogels

For the synthesis of p(An) within p(AAc) cryogels, the synthesized dried p(AAc) cryogels were weighed and placed into a beaker with 10-mL aniline for 30 min to load aniline into the cryogel network. The An-loaded p(AAc) cryogels were weighed again and the amount of An loaded in p(AAc) cryogels was calculated. Then, the aniline-absorbed cryogel was placed in APS solution in 1 M HCl with 1:1.25 mol ratio for aniline (1 = APS) [26]. The polymerization reaction of aniline continued for 3 h at room temperature at 300 rpm mixing rate. Then, the prepared p(AAc)/p(An) semi-IPN cryogels were washed at least thrice with ethanol–water mixture, dried in an oven at 50 °C, and stored in a closed container for further use.

2.3.2. Synthesis of p(AAc)/p(Th) semi-IPN cryogels

The cleaned and dried p(AAc) cryogels weighing 0.5 g were placed into 20 mL 0.3 M thiophene solution in DI and stirred for 2 h at a mixing rate of 250 rpm. Then, the thiophene-loaded p(AAc) cryogels were placed into a 100-mL flask containing 50 mL of 0.3 M $FeCl_3$ solution in chloroform, and stirred at 65 °C via a reflux system for 16 h at a mixing rate of 500 rpm [30]. Then, the synthesized p(AAc)/p(Th) semi-IPN cryogels were washed at least thrice with ethanol–water mixture (50:50 by volume) and dried in an oven at 50 °C. The dried p(AAc)/p(Th) semi-IPN cryogels were stored in a closed container for further characterization.

2.3.3. Synthesis of p(AAc)/p(Py) semi-IPN cryogels

The cleaned and dried p(AAc) cryogels weighing 0.5 g were put into 20 mL of 0.5 M pyrrole solution in DI to load the pyrrole monomer into p(AAc) cryogels under constant stirring at 250 rpm for 2 h. The pyrrole-absorbed p(AAc) cryogels were added into 0.5 M $FeCl_3$ solution in DI at room temperature under 500-rpm mixing rate for 16 h for the polymerization of pyrrole monomer in p(AAc) cryogels [17]. Then, the prepared p(AAc)/p(Py) semi-IPN cryogels were washed with ethanol–water mixture (50:50 by volume) at least thrice and dried in an oven at 50 °C. The dried p(AAc)/p(Py) semi-IPN cryogels were stored in a closed container for further use.

2.4. Characterization

The scanning electron microscopy (SEM) images of freeze-dried p(AAc)-based cryogels were obtained using an SEM (JEOL JSM-5600) with an operating voltage of 20 kV. The images were acquired after placing p(AAc)-based cryogels onto carbon tape-attached aluminum SEM stubs at room temperature after coating with gold to a few nanometer thicknesses under vacuum.

The FT-IR spectra of p(AAc), p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) semi-IPN cryogel systems were recorded in the 650–4000 cm^{-1} spectral range with 4 cm^{-1} resolutions via attenuated total reflectance attached FT-IR spectrometer (Thermo, Nicolet-iS10).

Thermal stabilities of p(AAc), p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) semi-IPN cryogel systems were investigated by using thermogravimetric analyzer (TGA, SII TG/DTA 6300, Exstar) under nitrogen atmosphere with a flow rate of 200 mL/min and heating rate of 10 °C/min to 900 °C.

The conductivities of p(AAc), p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) semi-IPN cryogel systems were calculated from current–voltage measurements using a computer-controlled electrometer (Keithley 2400 Source-Meter) at room temperature. Carbon tape was attached to the top and bottom of p(AAc), p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) semi-IPN cryogel systems to connect the electrodes, and the conductivity was measured at room temperature using the slope of the Ohmic region of the I—V curves.

3. Results and discussion

3.1. Synthesis and characterization of p(AAc), p(AAc)/p(An), p(AAc)/p(Th), and p(AAc)/p(Py) semi-IPN cryogels

The p(AAc) cryogels were synthesized by cryopolymerization technique [8,9,12,31]. AAc monomers were cross-linked with methylene bis acrylamide (15% of moles of AAc) under cryogenic conditions (−18 °C) in the presence of KPS and SMS. During the cryogelation process, a superporous network of p(AAc) was formed because of the existence ice crystals in the reaction media. These pores generated within p(AAc) cryogels provide spaces to be used for the synthesis of other polymers using the p(AAc) network as a template, such as synthesis of conductive polymers of p(An), p(Th), and p(Py). The preparation schema for conductive polymer preparation of p(An), p(Th), and p(Py) within p(AAc) cryogel networks are illustrated in Fig. 1(a), as (1), (2)