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Synthesis and investigation of poly(N-isopropylacrylamide-co-N-vinylcarbazole) hydrogels morphological, fluorescence and electrical properties

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ABSTRACT

In this study, poly(N-isopropylacrylamide-co-N-vinylcarbazole) gels were prepared and characterized with Fourier Transform Infrared Spectroscopy, Photoluminescence Spectroscopy, Scanning Electron Microscopy, Differential Scanning Calorimetry and DC conductivity methods. The synthesis and characterization results showed that the presence of NVCz moieties affected the thermal characteristics, topological properties and conductivity of the gels. The obtained NIPA hydrogel was found to swell in aqueous media for up to 80%, while the 50% NVCz incorporated sample swells up to 40%. Here we report that the fluorescence emission and electrical conductivity results attest the opportunity to manufacture a tunable biomedical materials. Since, the maximum peak at 350 nm red shifted to 385 nm, whilst a second peak appeared at 425 nm by the presence of the conductive PNVCz moieties allowing the possibility to control the fluorescence character of the gel. For instance an in-vivo drug release system tracking in a Fluorescence Image-Guided Surgery (FIGS) in which resolution deepness is essential in the visible wavelength could be extended when excited by means of a fluorophore compound.

1. Introduction

Hydrogels are networks of linear hydrophilic polymers that can swell by taking up to thousands of times their dry weight in aqueous media [1]. They could be adjustable to a variety of stimuli such as changes in pH, temperature, ionic strength, light, electricity and magnetic field [2]. For instance, the hydrophilic (-NH and C=O) or hydrophobic (isopropyl) functional groups present on PNIPA hydrogel affects the interaction of the network surface with the water molecule via hydrogen bindings. A sharp transition, known as lower critical solution temperature (LCST), is observed around 32°C in aqueous solutions [3]. Below the LCST, the gel is hydrated and has a random coil-to-globule structure because of a stronger water–polymer interaction compared to the polymer–polymer interactions. Whereas the hydrogen bonds faded at higher temperature and the hydrophobic isopropyl groups became predominant. This property could be altered by the addition of hydrophilic or hydrophobic copolymers to the gel structure. N-isopropylacrylamide (NIPA) has been widely used to prepare stimuli-sensitive polymers by free radical solution polymerization with various monomers (such as poly(acrylic acid) [4], poly(N-dimethylacrylamide) [5], poly(methacrylic acid) [6] and poly(-methyl methacrylate) [7]). Conventional PNIPA hydrogels have been prepared with N, N-methylene bisacrylamide as a crosslinker and are widely used for various applications in biotechnology and medicine [4–9].

On the other hand, carbazole based compounds exhibit a great interest due to the hole-transportation, charge carrier ability and electroluminescence [10,11] properties. Latest advances in their use have established applications in polymeric light-emitting diodes [12], electrochromic displays [13,14], organic transistors, rechargeable batteries, modified electrodes [15,16] dye sensitized solar cells [17] and organic photo-refractive materials [18]. Poly (N-vinyl carbazole) (PNVCz) is characterized as a π – conjugated and electron-rich heteroaromatic rings containing polymer with photo luminescent properties [19,20]. Polymerization of N-Vinylcarbazole (NVCz) through vinyl group gives a white insulating product while the polymerization occurring through the aromatic ring gives a

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Table 1
Compositions of PNIPA-PNVC composite gels.

Sample code	NIPA (Mol/L)	NVC (Mol/L)	BIS (Mol/L)	AIBN (Mol/L)
S1	1	0	10^{-2}	5×10^{-3}
S2	0.8	0.2	10^{-2}	5×10^{-3}
S3	0.6	0.4	10^{-2}	5×10^{-3}
S4	0.5	0.5	10^{-2}	5×10^{-3}
S5	0.4	0.6	10^{-2}	5×10^{-3}
S6	0	1	10^{-2}	5×10^{-3}

green, cross-linked polymer, mostly insoluble due to π-π backbone interactions. NVCz is a well-known nitrogen-containing heterocyclic compound undergoing free radical, cationic and charge-transfer polymerization. Nevertheless, Mori et al. demonstrated that PNVCz could also be produced via controlled radical polymerization mediated by a xanthate derivative as a chain transfer agent [21,22]. While, a NIPA block copolymer with a pH sensitive Poly(2-(dimethylamino)ethyl acrylate) counterpart and fluorescent sensitive PNVCz graft has led to a multipurpose systems that respond to both temperature and pH stimuli, while exhibiting fluorescence properties [23,24]. Although, inter penetrating network structure of PNVCz containing PNIPA hydrogels were synthesized, no literature was found on the PNIPA-NVCz polymeric gels [25]. Although the addition of metal nanoparticles [26], and different carbon allotropes [27], are well-known methods to enhance the electrical properties, the resulting products are heterogeneously distributed and tend to aggregate. The purpose of this manuscript is the synthesis of a homogeneous stimuli-responsive PNIPA hydrogels with fluorescent sensitive PNVCz parts with electrical properties for a various range of technological applications [28], such as electrochemically [29] controlled drug release system.

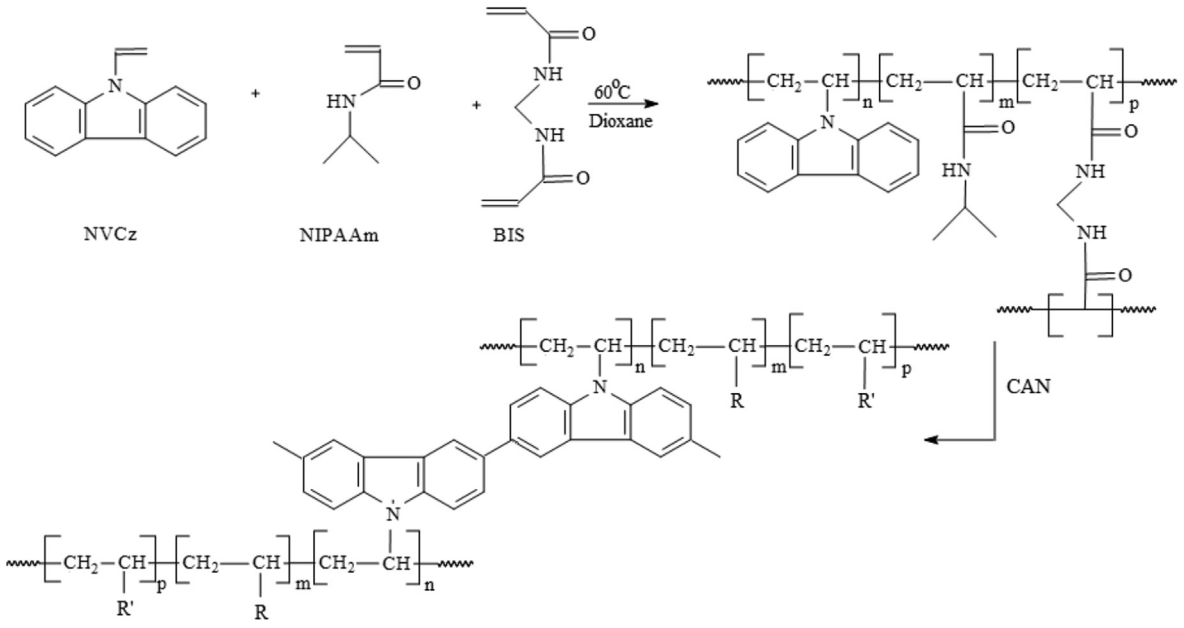
2. Experimental part

2.1. Materials and synthesis procedure

The composite gels were synthesized via free radical cross-linking copolymerization of N-isopropylacrylamide (NIPA) and N-vinylcarbazole (NVCz) in varying amount. N,N'-methylenebisacrylamide (BIS) was used as crosslinker and 2,2- Azobisisobutilonitrile (AIBN) was used as initiator. All the chemicals were purchased from Sigma–Aldrich and used as received. The compositions of samples and amounts of them were summarized in Table 1. A conventional gel synthesis method with dioxane as common solvent media was used for the P(NIPA-NVC) hydrogels [24]. After all the ingredients were solved and mixed in dioxane, the samples were deoxygenated by bubbling nitrogen during 10 min in capped cylindrical glass tubes and the gelation was performed at 60 °C in a heat bath during 48 h. Schematic representation of the reaction is given in Scheme 1. After the gelation was completed, gels were dried and cut in slice shapes to measured electrical conductivity. Conversely, some parts of the samples were released in 1 M Ceric (IV) ammonium nitrate (CAN) dissolved in dioxane solution to allow the ring polymerization process during 24 h at ambient room temperature. A green-black colour was observed at the first contact with CAN solution. After the first hour, no further physical and colour change were observed.

2.2. Characterization techniques

Electrical measurements were taken on Keithley Model 6487 Picoammeter/Voltage Source. Fluorescence measurements were carried out by using a Varian Cary Eclipse model spectrometer. SEM images were taken by using FEI Quanta FEG 250. FTIR spectra of the samples were recorded on Perkin Elmer Spectrum One (FTIR-reflectance, Universal ATR with diamond and ZnSe) spectrophotometer using the samples in powdered form. DSC was performed on a TA DSC-Q2000 under a continuous flow of nitrogen atmosphere, by heating from 10 °C to 200 °C with ±0.5 °C modulation mode every 60 s and the thermograms were recorded at a heating rate of 20°C/min. After cooling to 10 °C, heating procedure was repeated. Only second cycle values were collected. The glass transition temperatures (T_g) of the samples were determined by this method.



Scheme 1. Synthesis of P(NVC-co-NIPA) hydrogel.