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Synthesis, characterization and the rapid response property of the temperature responsive PVP-*g*-PNIPAM hydrogel

Shuping Jin [a,b], Mingzhu Liu [a,*], Shilan Chen [a], Chunmei Gao [a]

[a] Department of Chemistry and State Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China
[b] Department of Chemistry, Hexi University, Zhangye 734000, PR China

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ABSTRACT

In this study, a poly(*N*-vinylpyrrolidone)-*graft*-poly(*N*-isopropylacrylamide) hydrogel (PVP-*g*-PNIPAM) was synthesized through the "grafting from" process. Grafting of temperature responsive poly(*N*-isopropylacrylamide) (PNIPAM) brushes was carried out from the poly(*N*-vinylpyrrolidone) (PVP) synthesized with free radical polymerization and functionalized with ATRP initiator, PVP–Br, which was performed through a bromination reaction between pendant allylic groups of the PVP and *N*-bromosuccinimide (NBS). The structure of the initiator and PVP-*g*-PNIPAM was characterized by ultraviolet and visible (UV/Vis) absorption, nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) measurements. Scanning electron microscope (SEM) morphology measurement displayed some dendritic grafted chains dangling onto the pore wall of the hydrogel.
The characteristic in response to the change in environmental temperature was investigated by the fluorescence anisotropy and UV/Vis transmittance measurements. The results showed that the PVP-*g*-PNIPAM hydrogel exhibited rapid response to the change in environmental temperature due to free and mobile graft chains compared with the P(VP-*co*-NIPAM) hydrogel, which was prepared by free radical copolymerization in this work.

1. Introduction

It is well known that the ability to bind reversibly to various molecules (dyes, metals and some polymers) in solution, accompanying with excellent biocompatibility with living tissue and low cytotoxicity, enable poly(*N*-vinylpyrrolidone) (PVP) to act as a carrier of some hydrophilic or hydrophobic drugs [1,2]. Hence, it has been attracting more and more attention as a material for application in medicine and pharmaceutics. Recently, it has also been used for encapsulating DNA and protecting it from intracellular degradation [3]. However, PVP dissolved in pure water does not exhibit a phase transition at temperatures below the boiling point of water [4]. By introducing a component, which is thermo-responsive in a proper temperature range, into PVP, the advantages of using PVP in medical applications may be taken together with the thermo-responsive behavior.

In many applications, such as drug delivery and biosensor, the usefulness of conventional hydrogels is limited by their slow swelling and shrinking rates [5]. One approach, which has been investigated to enhance these swelling and shrinking rates, is to synthesize graft-type hydrogel. Lee et al. synthesized graft-type macroporous hydrogel by grafting temperature sensitive poly(*N*-isopropylacrylamide) (PNIPAM) onto the surface or bulk of the pH sensitive alginate [6–8]. Both the free graft chains and macroporous make the graft-type hydrogels reach its equilibrium swollen state within about 10 min.

In general, the synthesis of graft copolymer can be accomplished by one of three routes: "grafting from" reactions, "grafting through" and "grafting onto" processes. The "grafting from" method has been carried out in conjunction with ATRP. Temperature sensitive PNIPAM brushes were grafted from polystyrene particles synthesized with

* Corresponding author. Tel.: +86 931 8912387; fax: +86 931 8912582.
E-mail address: mzliu@lzu.edu.cn (M. Liu).

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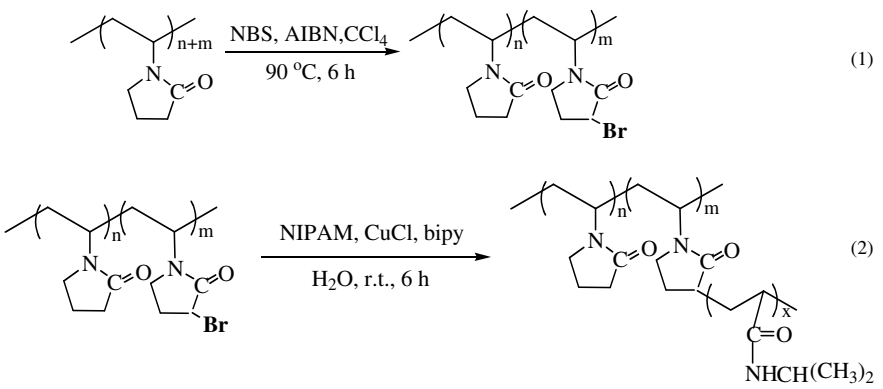

Scheme 1. The synthesis of ATRP initiator, PVP–Br, by bromination reaction (1), and PVP-*g*-PNIPAM hydrogel by ATRP of NIPAM using PVP–Br as a macroinitiator (2).

surfactant free emulsion polymerization and functionalized with a thin shell of ATRP initiator on the surface [9]. Wang et al. prepared the graft copolymers that have an ethylene–propylene–diene terpolymer (EPDM) rubber backbone and poly(methyl methacrylate) (PMMA) branches. The brominated EPDM (EPDM–Br) was produced by the reaction between the EPDM and *N*-bromosuccinimide (NBS). Then the EPDM-*g*-PMMA was created through the ATRP of MMA initiated by EPDM–Br in the presence of CuBr/bpy at 90 °C [10].

However, *N*-vinylpyrrolidone (NVP) does not form radicals stabilized by resonance and inductive effects. Therefore, the polymerization of the monomer has not yet performed efficiently by ATRP [11,12]. Several efforts have been made to overcome this limitation in order to prepare some well-defined structure copolymers by combining controlled/living radical polymerization with different polymerization methods. For example, through combination ATRP and conventional free radical polymerization, a block copolymer, poly(hydroxyethyl methacrylate-*b*-vinyl pyrrolidone) with well-controlled molecular weight and low polydispersity (<1.4), has been successfully prepared by Huang [13].

In this work, a novel PVP-*g*-PNIPAM hydrogel was prepared by a polymerization of NIPAM using an ATRP initiating species, PVP–Br, which was prepared by the bromination reaction between pendant allylic groups of PVP hydrogel and NBS (Scheme 1). Then fluorescence anisotropy (*r*), together with UV/Vis transmittance (*T*%) measurements, investigated the rapid response characteristic of the PVP-*g*-PNIPAM hydrogel by comparison with conventional P(VP-*co*-NIPAM) hydrogel.

2. Experimental

2.1. Materials

The PVP hydrogel (the equilibrium swelling degree, SW_{eq}, is around 34) and linear PVP (the viscosity average molecular weight, M_v, is about 38,000) were obtained in our laboratory during the previous works [14,15]. *N*-Vinylpyrrolidone (NVP, Fluka) was distilled under vacuum to eliminate the stabilizer just before use. 2,2′-Azobisisobutyronitrile (AIBN) and *N*,*N*′-methylenebisacrylamide (NNMBA) were recrystallized from 95% ethanol. Acenaphthylene (ACE, Fluka) was recrystallized from methanol. CuCl was prepared in our laboratory. *N*-Isopropylacrylamide (NIPAM, Aldrich), *N*-bromosuccinimide (NBS, Aldrich) and 2,2′-bipyridine (bipy) was used as received.

2.2. Synthesis of ATRP initiator (PVP–Br) by allylic bromination of PVP

After completely swelling (0.4 g zerogel) in deionized water, the PVP hydrogel (the diameter of swollen PVP hydrogel bead is about 2–4 mm) was immersed into CCl_4 (25 mL), then the bromination was carried out by adding a suitable amount of NBS (the molar ratio of NBS to monomer unit of PVP is 2:1) and AIBN (catalyst, the mass ratio of AIBN to NBS is 1:200) and reflux at 90 °C. After 6 h, the reaction system was cooled, and then was filtered. To obtain a pure PVP–Br hydrogel, the product was immersed in deionized water for 2 days at room temperature and the water was replaced four times daily. Then it was dried in vacuum at 40 °C for 48 h and used as an initiator for the polymerization of NIPAM to prepare the PVP-*g*-PNIPAM hydrogel. The linear PVP–Br polymer was synthesized from the linear PVP by the same procedure, and purified through dissolutions (2×) in distilled water followed by precipitation into acetone. It was used as an initiator to prepare the linear PVP-*g*-PNIPAM.

2.3. Synthesis of PVP-g-PNIPAM hydrogel by "grafting from" polymerization

The procedure of "grafting from" polymerization is given below: certain amounts of PVP–Br zerogel were immersed into deionized water (10 mL) containing suitable amounts of NIPAM and bipy (the feed compositions are described in Table 1). The system was left at room temperature for 24 h to allow the PVP–Br to swell completely (the diameter of swollen PVP–Br hydrogel bead is about 2–4 mm), and then the pressure of the system was reduced to remove oxygen. Subsequently, fresh CuCl (the molar ratio of CuCl to bipy is 1:2) was introduced into the above system to start the polymerization under vacuum at room