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Thermo-, and pH dual-responsive poly(*N*-vinylimidazole): Preparation, characterization and its switchable catalytic activity

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ABSTRACT

A monomer, 2-(isobutyramido)-3-methylbutyl methacrylate (IMMA) was synthesized through a two-step reaction. When a few of IMMA (less than 4 mol%) was copolymerized with *N*-vinylimidazole (VIm) under free radical polymerization condition, water-soluble P(VIm-*co*-IMMA) copolymers were obtained. Their structural information was verified and interpreted from ^{1}H NMR, FTIR and GPC. Kinetic analyses from ^{1}H NMR demonstrated that one-batch addition of IMMA into the polymerization system led to an inhomogeneous distribution of IMMA units in the copolymers, whereas homogeneous distribution of IMMA units in the copolymers could be obtained through the portion-wise addition of IMMA monomer. The thermal properties of such copolymers were measured by DSC. Compared with PVIm homopolymer, the few IMMA units in the P(VIm-*co*-IMMA) copolymer had little influence on the T_g values. The obtained P(VIm-*co*-IMMA) copolymers were thermoresponsive in water, and their phase transition temperatures could be efficiently raised through reducing the IMMA content in the copolymers, raising the addition times of IMMA monomers or lowering the pH of media. Dynamic light scattering analysis showed that unlike the traditional thermoresponsive linear polymers, obvious size shrinkage around the phase transition temperature could not be observed in such P(VIm-*co*-IMMA) copolymers. Such copolymers could be used as smart organocatalysts in the hydrolysis of *p*-nitrophenyl acetate. Below the phase transition temperature the reaction rate followed the Arrhenius law, but above the phase transition temperature the reaction rate increased much slower than the prediction from the Arrhenius law. Moreover, the catalytic transition temperature could be tuned through utilizing the P(VIm-*co*-IMMA) copolymers with different phase transition temperature. The mechanism was discussed accordingly.

1. Introduction

During the past decade polymer with stimuli-responsive properties, such as reversible and fast conformational or phase changes in response to variations in temperatures, light, pH or ion strength have attracted plenty of interest in many aspects [1–4]. One of the most appealing stimuli-responsive species is the thermoresponsive polymer with a lower critical solution temperature (LCST) in aqueous solution, which show a large decrease in solubility in water above a specific temperature [5].

Imidazole is one of the most important heterocyclic aromatic compounds. It plays a crucial role in primary biomacromolecules, such as amino acids, nucleic acids and proteins, and also in many pharmaceutical and agrochemical compounds. *N*-vinylimidazole (VIm) was frequently used to prepare synthetic macromolecules with imidazole group [6–9]. Its homo- or copolymers had many potential applications, such as fuel cells [10–13], membranes for metal ion complexing and removal [14,15], gene delivery vectors [16–20], ionic liquid [21,22], and catalysts [23,24]. Poly(*N*-vinylimidazole) (PVIm) is water-soluble, but not thermoresponsive. For endowing thermoresponsive properties to PVIm, the frequently-adopted methods were to incorporate a big quantity of well-known thermoresponsive units, such as *N*-vinylcaprolactam (NVCL) and *N*-isopropylacrylamide (NIPAm), into the PVIm chains [23–31]. In such thermoresponsive copolymers, the amount of VIm units were usually less than 50 mol% and one of VIm units' roles was to modulate the LCSTs of the well-known thermoresponsive polymers. Therefore, the properties of such copolymers were deviated pronouncedly from PVIm homopolymer. In this study, we prepared PVIm copolymers through the copolymerization of VIm

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with a few of functional monomer (less than 4 mol%). Thus, it was possible for the obtained PVIm copolymers to inherit the properties of PVIm homopolymer to a maximum extent. Such PVIm copolymers in aqueous media were thermo- and pH- dual stimuli-responsive. Moreover, such thermoresponsive PVIm copolymers could be used as smart catalyst and their catalytic activities became less than the predicted ones above the phase transition temperature, which was different from the ever-reported thermoresponsive copolymers containing VIm units whose catalytic activities were higher than the predicted ones above the phase transition temperature [23,24].

2. Experimental

2.1. Materials

N-Vinylimidazol (VIm, 99%) was purchased from Aldrich and purified by vacuum distillation before use. Azoisobisbutyronitrile (AIBN, 98%) was purchased from Fluka and recrystallized from methanol solution. Triethylamine (TEA, 99%) was purchased from Tianjin Kewei Chemical Company and purified by distillation before use. Isobutyryl chloride (98%) was purchased from Alfa Aesar and used directly. *L*-Valinol (98%) was purchased from Beijing Ouhe Technology Company and used as received. Methacryloyl chloride (98%) was purchased from HEOWNS and used directly. *p*-Nitrophenyl acetate (NPA, 98%) was purchased from TCI and used as received. Benzoylated cellulose membrane (MWCO 1000 g/mol) was purchased from Sigma and used as received. De-ionized water was double-distilled before use.

2.2. Synthesis of N-(1-hydroxy-3-methylbutan-2-yl)isobutyramide

To an ice-cooled solution of *L*-valinol (4.82 g, 46.8 mmol) in dry CH_2Cl_2 (100 mL), fresh TEA (14.0 mL, 100 mmol) was added, and then isoburyryl chloride (4.18 g, 39.5 mmol) was added dropwise over a period of 2 h. The reaction mixture was warmed to room temperature and stirred overnight. After diluting with CH_2Cl_2 (300 mL), the organic layer was washed once with 100 mL of HCl aq (1 M), once with 100 mL of saturated $NaHCO_3$ aq and twice with 100 mL of saturated brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford the desired compound as white solid (3.8 g, yield 50%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.94 (m, 6H), 1.17 (m, 6H), 1.87 (m, 1H), 2.39 (m, 1H), 3.61–3.72 (br, 3H).

2.3. Synthesis of 2-(isobutyramido)-3-methylbutyl methacrylate (IMMA)

Fresh TEA (1 mL, 7.5 mmol) and *N*-(1-hydroxy-3-methylbutan-2-yl)isobutyramide (0.87 g, 5.0 mmol) were added to dry CH_2Cl_2 (20 mL), and the solution was cooled to 0 °C by an ice bath. Methacryloyl chloride (0.55 g, 5.3 mmol) was added dropwise to the above mixture over a period of 30 min. The reaction mixture was warmed to room temperature and stirred overnight. After being diluted with CH_2Cl_2 (60 mL), the organic layer was washed once with 30 mL of HCl aq (1 M), once with 30 mL of saturated $NaHCO_3$ aq, and twice with 40 mL of saturated brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford a crude product IMMA (1.0 g, yield: 83%). The product was further purified by a silica column to give a white solid (0.81 g, yield: 67%). $T_m = 43–47$ °C. FT-IR: 3426 and 3277 cm^{-1} (υ-N-H), 3097 cm^{-1} (υ-C-H in vinyl bond), 2967 cm^{-1} (υ-C-H), 1720 cm^{-1} (υ-C=O in ester group), 1644 and 1557 cm^{-1} (υ-C=O, in amide gorup); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.97 (t, 6H), 1.15 (t, 6H), 1.86 (m, 1H), 1.96 (s, 3H), 2.36 (m, 1H), 4.05–4.20 (br, 2H), 4.25–4.35 (br, 1H), 5.59 (s, 1H), 6.11 (s, 1H). MS (ESI) *m/z*: $[M+H]^+$, 242.3 (Calcd. 242.33), $[2M + H]^+$, 483.2 (Calcd. 483.66).

2.4. Nomenclature

S-PVIm-IMMA$_x$ (abbreviated as S-I$_x$) represents the copolymer of VIm and IMMA, S means that IMMA was added in one batch, and x denotes the mole percentage of IMMA units in the copolymer. MY-PVIm-IMMA$_x$ (abbreviated as MY-I$_x$) represents the copolymer of VIm and IMMA, M means that IMMA was added in multiple batches, and Y means the addition times of IMMA monomer to the polymerization system.

2.5. Copolymerization of VIm and IMMA

A typical procedure for one batch copolymerization was as follows (for S-I$_{3.3}$): IMMA (0.14 g, 0.58 mM), VIm (1.82 g, 19.36 mM) and AIBN (12 mg) were dissolved in 12 mL of methanol, and the mixture was degassed through three cycles of vacuum-nitrogen purge and then immersed in an oil bath thermostated at 70 °C for 12 h. Samples were taken before the purification to identify the conversion of the monomers. Then the reaction solution was dialyzed in methanol for 48 h and in water for 24 h to remove the low molecular weight impurities, and the dialysis solvent was exchanged every 12 h. After dialysis, polymer solutions were freeze-dried for 20 h.

A typical procedure for the copolymerization using the portion-wise addition of IMMA monomers was as follows (For M3-I$_{3.3}$): IMMA (70.0 mg, 0.29 mM) was divided into three portions. The first portion of IMMA (23.3 mg, 0.097 mM), VIm (0.91 g, 9.68 mM), AIBN (10 mg) were dissolved in 3 mL of methanol and placed in a three-neck flask that was equipped with a constant pressure dropping funnel and a condenser. The other two portions of IMMA (46.7 mg, 0.194 mM) were dissolved in 3 mL of methanol and placed in the dropping funnel. The mixture was degassed through three cycles of vacuum-nitrogen purge and then immersed in an oil bath thermostated at 70 °C. Each portion of IMMA in the dropping funnel was dropped into the flask after 3-h interval. The product was purified by dialysis. M4-I$_{3.3}$ and M8-I$_{3.3}$ were produced by a similar way, but IMMA was divided into 4 and 8 portions, and the dropping interval was 2 and 1 h, respectively.

2.6. Kinetics of catalytic reaction

The kinetic study of the hydrolysis of NPA was conducted in a quartz cuvette using a UV/vis spectrophotometer equipped with a temperature controller. The polymer solutions with a concentration of 2 mg/mL were prepared in 10 mM PBS (NaH_2PO_4/Na_2HPO_4) with pH = 7.4. NPA was dissolved in acetonitrile with a concentration of 0.4 M. The progress of catalytic reaction was monitored by tracing the rate of optical density increase at 402 nm due to the release of p-nitrophenol in a deprotonated form. A typical procedure for the NPA hydrolysis experiment is described below: Two milliliters of the polymer buffer solution was kept in quartz cuvette at a fixed temperature for 20 min, and then 10 μL of NPA solution was promptly injected into the cuvette with an injector. The reaction mixture was immediately agitated with a glass pipette for 5 s, and the optical density at 402 nm of the solution was detected by the UV-vis spectrometer.

2.7. Characterization

^{1}H NMR spectra were recorder using Bruker AVANCE III 400M spectrometer operated at 400 MHz. The chemical shifts are given in parts per million (ppm). Electrospray ionization/mass spectrometry