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Preparation and characterization of microgels sensitive toward copper II ions

Marat Muratalin [1], Paul F. Luckham *

Department of Chemical Engineering and Chemical Technology, Imperial College London, Prince Consort Road, London SW7 2AZ, UK

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ABSTRACT

An emulsion polymerization technique has been used to prepare chemically crosslinked microgels in aqueous suspension that are sensitive to the presence of copper ions. Poly(N-isopropylacrylamide) (PNIPAM) was copolymerized with different amounts of 1-vinylimidazole (VI), and the resultant microgels exhibited multi-responsive behavior being sensitive to changes in temperature, pH and to the presence of metal ions, particularly copper. These swelling properties of the microgel particles were characterized using dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The effect of temperature showed that the microgel particles shrunk continuously as the temperature was raised, up to a temperature of 50 °C, and the volume phase transition temperature, VPTT, has been shifted to higher temperatures (in the range of 35–45 °C) compared to pure PNIPAM microgels where the VPTT ≈ 30–35 °C. The particle size of these microgels was also investigated as a function of pH; the microgel particles became swollen at low pH and collapsed at high pH, due to the ionization of the VI component of the microgels. Most interesting, however, was the effect of the copper ion concentration in solution. The PNIPAM-co-VI microgels were found to swell with increasing concentration of Cu^{2+} up to 0.3 g/l of Cu^{2+} due to adsorption of the cations inside the particle, which leads to charging up the internal phase of the microgel. However, at higher concentrations of added copper (II) ions, the binding forces of complexation lead to conformational changes to the microgel resulting in weaker polymer–solvent interaction and consequential shrinkage again of the polymer. In addition, the copper (II) uptake was calculated, and the uptake was found to be well described by the Langmuir adsorption isotherm, with up to 2 g of copper II being taken up by 1 g of microgel.

1. Introduction

The preparation of colloidal microgels has been well documented [1–3]. Stimuli-responsive microgels undergo a large magnitude volume phase transition upon changes in surrounding media, namely changes in temperature [4–6], pH [7,8], and ionic strength [9]. Therefore, such "smart" materials offer a wide range of potential applications, including controlled drug release [10–18], catalysis [17–19], chemical separations [20–22], and enhanced oil recovery [23,24].

Arguably, the most studied microgels are those consisting of poly(N-isopropylacrylamide) (PNIPAM). These microgel particles undergo reversible volume phase transition induced by temperature changes, VPTT, that is, swell below the lower critical solution temperature (LCST) and shrink above it. The LCST for PNIPAM is reported to be 32 °C [25]. The microgel is swollen below the LCST due to hydrogen bonding between water and hydrophilic amide group of PNIPAM, while heating the solution above the LCST disrupts polymer–water hydrogen bonding, making the polymer less water soluble, causing hydrophobic interactions to dominate.

The monomer, 1-vinylimidazole, has been reported to exhibit metal- and pH-sensitive properties [21,26–31]; hence, copolymerizing this monomer with NIPAM could produce colloidal microgels with multi-responsive features. For macroscopic hydrogels, it has been shown by many authors [32–35] that copolymerization of poly(N-isopropylacrylamide) (PNIPAM) with other monomers, which have different degrees of hydrophilicity/hydrophobicity, can shift the lower critical solution temperature (LCST) and also make hydrogels responsive to pH and the presence of copper ions [29,36,37]. Microgels containing both isopropylacrylamide and vinyl imidazole have been prepared previously by Snowden and coworkers [38] and Kokufuta [39–44]. It is likely that copolymers of N-isopropylacrylamide and 1-vinylimidazole (PNIPAM-co-VI) will be responsive to both temperature and pH changes and also to the presence of metal ions, copper in particular [34,45,46]. It is thought that metal ions coordinate with several imidazole groups [47,48], so the addition of copper ions might cause swelling of the gel due to charging of the gel or deswelling due to the ions making complexes with the polymer. Ali et al. investigated the behavior of poly(vinylpyrrolidone) hydrogels, in which vinylpyrrolidone has rather similar structure to 1-vinylimidazole, and found

* Corresponding author.
E-mail addresses: marat.muratalin@googlemail.com (M. Muratalin), p.luckham01@imperial.ac.uk (P.F. Luckham).
[1] Current address: TCOV B5, Karaton-1, Tengiz Atyrau, Kazakhstan.

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that presence of electron donor atoms such as nitrogen leads to a high possibility of forming coordinate bonds with metals [35]. Hence, there is a high probability that microgels containing such electron donor atoms (Lewis base) would act in the same manner as the corresponding hydrogels.

Microgels containing poly NIPAM and vinyl imidazole have been prepared before in the work described here, and PNIPAM-co-VI microgel particles have been synthesized via emulsion polymerization technique. The resultant microgels were investigated as a function of temperature, pH and concentration of copper (II) salt added.

2. Experimental

2.1. Materials

NIPAM (99%) was obtained from Acros Organics, BIS (99%), VI (99%), a cationic initiator 2,2′-azobis[2-methylpropionamidine] dihydrochloride, also known as V50 (97%), copper (II) nitrate trihydrate (99%) were all supplied by Sigma–Aldrich and CTAB (99%) was obtained from BDH Chemicals. Analytical grade deionized water (Purite "Milli-Q" grade) was used in throughout this study.

2.2. Microgel synthesis

Colloidal microgel particles of PNIPAM-co-1-vinylimidazole were prepared using the emulsion polymerization method. Four microgel dispersions with 0%, 10%, 20%, and 30% w/w of 1-vinylimidazole monomer were prepared, and higher 1-vinylimidazole concentrations were attempted but did not produce stable microgels.

Microgel synthesis was carried out in a three-necked round bottom flask, which was immersed in a water bath, and the reaction temperature was set to 70 ± 1 °C. The flask was purged with nitrogen. The required amount of the monomers (the amount of NIPAM and 1-vinylimidazole presented in Table 1), the surfactant (cetyltrimethylammonium bromide [CTAB] 0.02 g) and the crosslinker (N,N′-methylenebisacrylamide [BIS] 0.5 g) were dissolved in 350 ml of water and stirred for 30 min. The surfactant was used in order to stabilize latex particles during the polymerization. To initiate the polymerization 0.2 g of V50 initiator, dissolved in 10 ml of water, was added to the mixture. A positively charged initiator was used in order to initiate the polymerization as 1-vinylimidazole is positively charged at most pHs, and so, a cationic initiator was chosen to ensure the microgels were stable by having a high positive charge. After 10 min, the solution had turned milky white. The reaction proceeded for 6 h under a nitrogen atmosphere and constant stirring. The pH of the resultant microgel dispersions was in the range of 6.0–6.5. The procedure for the synthesis of all microgel dispersions was the same, and only the NIPAM and 1-vinylimidazole monomers ratio varied.

Dialysis was employed for purification of all the colloidal dispersion of microgels. The resultant dispersions were put into dialysis tubing with molecular weight cut-off 12–14,000 Daltons; the tubing was obtained from Medicell International Ltd. The dialysis tubes were immersed in deionized water, and the process took 2 weeks with daily exchange of deionized water.

Table 1
The amounts of the monomer used for the preparation of the microgel dispersions with different concentrations of 1-vinylimidazole.

1-Vinylimidazole ratio in the copolymer	0%	10%	20%	30%
NIPAM (g)	5	4.5	4	3.5
1-Vinylimidazole (g)	0	0.50	1.00	1.50

3. Results and discussion

3.1. Response of the microgels to temperature

The particle sizes of the resultant microgel dispersions were investigated as a function of temperature at pH 6.0–6.5. A ZetaPALS (Brookhaven Instruments Corporation) instrument was employed to determine the diameter of the microgels at different temperatures. The results are presented in Fig. 1.

Analyzing the response of the microgel without any incorporated 1-vinylimidazole (VI) monomer, that is, pure PNIPAM, shows that the size of the swollen particle, which is approximately 300 ± 20 nm at 25 °C, has shrunk gradually to approximately 170 ± 20 nm at 55 °C. The majority of shrinkage occurring between 25 and 35 °C, whereas in the range of temperature changes between 35 and 55 °C, the particle size remains almost constant. Such behavior of pure PNIPAM microgels is consistent with previous studies [1].

Fig. 1 also illustrates that addition of 1-vinylimidazole (VI) has an impact on the diameter of the particles. This can be seen both in the collapsed, but more obviously in the swollen state, that is, at 55 °C and 25 °C, respectively. For example, the diameter of the pure PNIPAM microgel particles is about 300 ± 20 nm and 125 ± 20 nm at 25 °C and 55 °C, respectively, whereas the diameter of the microgels containing 30% 1-vinylimidazole (VI) is approximately 1025 ± 50 nm and 350 ± 50 nm at the same temperatures of 25 °C and 55 °C. The fact that the 1-vinylimidazole containing microgels are larger in size in the swollen state is due to the presence of electronegative nitrogen atoms in their structure that makes the molecule electron deficient and hence become protonated, that is, become positively charged, which repel each other causing the microgel to swell (as illustrated schematically in Fig. 2).

It is also worth of noting that microgels without any added 1-vinylimidazole have the greatest swelling in the range of temperature changes between 25 and 35 °C, while for those with 1-vinylimidazole, the largest change in the extent of swelling is observed between 35 and 45 °C. This behavior is similar to that shown by the microgels containing acrylic acid, which were described by Kratz et al. [49], and suggesting that addition of 1-vinylimidazole (which is relatively hydrophilic) makes the polymer more water soluble in the same way as addition of acrylic acid.

Additionally, the measurements of the diameter of the microgel particles in the swollen state obtained from DLS on a ZetaPALS (Brookhaven Instruments Corporation) instrument were confirmed by SEM imaging of freeze-dried samples of the corresponding

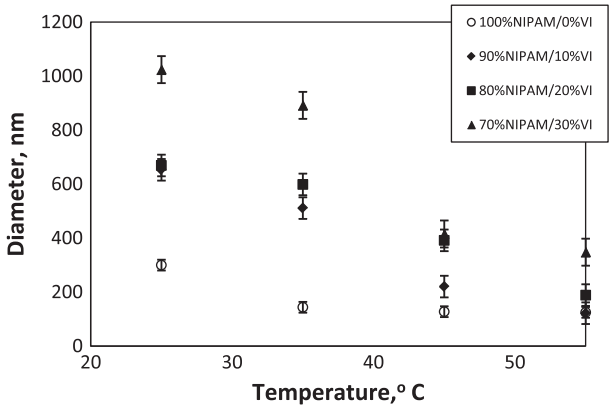

Fig. 1. The hydrodynamic diameter of the microgel particles with different concentration of 1-vinylimidazole as a function of temperature at pH 6.0 (electrolyte concentration 2×10^{-5} mol/l).