Stability and thermosensitive properties of various poly(N-vinylcaprolactam) microgels

Abstract  Thermally responsive microgels have been synthesised by polymerising N-vinylcaprolactam under various conditions. Stabilisation of the latices was of special interest and, thus, electrostatically, sterically, and electrosterically stabilised particles were prepared. Electrostatic stabilisation was achieved by the use of an ionic initiator and/or an ionic detergent. Steric stabilisation was realised through a macromonomer technique, where polymerisable poly(ethylene oxide)-containing macromonomers were utilised as a detergent. Capillary electrophoresis was used to compare the electrophoretic properties of the polymer particles. All the product particles show thermal behaviour typical of poly(vinylcaprolactam), but sterically stabilised ones are superior in the stability against added electrolytes.

Keywords  Poly(N-vinylcaprolactam) · Macromonomer technique · Microgel particles · Capillary electrophoresis · Colloidal stability

Introduction

Poly(N-vinylcaprolactam) (PVCL) is a polymer with amphiphilic and responsive character. It dissolves in cold water but undergoes a sudden conformational change, collapses and precipitates, upon heating. In this sense, PVCL closely resembles a well-known thermally responsive polymer, poly(N-isopropylacrylamide) (PNIPAM). Both polymers have a lower critical solution temperature (LCST) in water around 32 °C. Several potential applications have been suggested for both polymers; however, PVCL is expected to be more biocompatible than PNIPAM and, thus, to have a wider range of applicability [1, 2].

The syntheses of responsive polymers with different topological structures, like macroscopic, micro, or nanoscaled networks, is interesting not only for fundamental understanding of the properties of these materials but also for practical applications. Recently, microgels have attracted noticeable attention owing to the possibility of utilising them in constructing intelligent drug release systems [3, 4]. For demanding biotechnological applications or for those where polymer particles are used to bind metal ions, responsive polymer particles stable in various electrolyte solutions are needed. The stability of responsive microgels in electrolyte solutions has recently been studied using PNIPAM [5] and poly(N-isopropyl methacrylamide) (PNIPMAM) [6]. Methods of synthesising cross-linked PVCL particles stable against addition of electrolytes have not been studied so far.

The stability of aqueous polymer dispersions can be enhanced in several ways. In general, three methods are used: electrostatic, steric, or electrosteric stabilisation.
Of these, the first, based on the repulsion of surface charges of the particles, is most common. Electrostatic stabilisation is typically realised by using either ionic initiators or ionic surfactants in the polymer syntheses conducted in emulsions. Particles are obtained which repel each other owing to their electric charges. The strength of the repulsion force between the particles and the thickness of the electric double layer may be altered by changing the ionic strength of the aqueous medium [7]. At high electrolyte concentrations the repulsion between the particles vanishes and the coagulation out of the aqueous phase is fully diffusion controlled [8, 9]. Steric stabilisation may be achieved by grafting the particles with, for example, poly(ethylene oxide) (PEO) or with some other water-soluble polymer. The use of PEO is often considered advantageous because PEO considerably prevents the adsorption of proteins onto polymer surfaces and, thus, increases the biocompatibility of the polymer [10].

Steric stabilisation by nonionic hydrophilic polymers is independent of ionic strength, assuming that the added electrolyte does not change the thermodynamic quality of the aqueous solvent. PEO has been shown to be an effective steric stabiliser even at high electrolyte concentrations as long as the molecular mass of PEO is high [11]. Electrosteric stabilisation is a combination of electrostatic and steric stabilisation.

In this work, PVCL particles with varying surface charges and with different surface structures were synthesised. Thus, it was possible to compare the effectiveness of the stabilisation in each case and further to study the effects of electric charges and nonionic polymeric grafts on the thermal properties of the polymers. Particles stabilised electrostatically, sterically, and electrosterically, were prepared. Negatively charged particles were obtained by using potassium persulphate (KPS) ionic initiator, which upon decomposition forms sulphate anion radicals that covalently bind to the growing polymer. Ionic surfactants, like sodium dodecyl sulphate (SDS) can bind to the polymers and, in spite of a thorough purification of the product, introduce an electric charge [12]. Nonionic microgel particles were prepared in emulsions where both the initiator and the surfactant are electrically neutral. Stable microgels were obtained by the use of amphiphilic PEO-containing macromonomers.

Four samples of stabilised PVCL microgels were synthesised using both ionic and nonionic initiators and surfactants. The initiators and surfactants are shown in Fig. 1. Thermal and electrokinetic properties of the polymers are compared. The stability of the particles at temperatures above and below the LCST were studied by comparing the neutral grafted particles with the charged ones in aqueous solutions with varying concentrations of barium chloride.

**Experimental**

**Materials**

N-Vinylcaprolactam, purchased from Polysciences, was purified by distillation in vacuum. N,N'-Methylenbisacrylamide (BA, Electran), KPS (Merck, p.a.), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, Wako) and SDS (Fluka) were used without further purification. The amphiphilic PEO macromonomer (PEO-R-MA) was synthesised as reported previously [13]. Water used as a solvent was purified with an Elgastat UHQ-PS purification system.

**Preparation of the microgels**

All PVCL microgels were prepared by batch emulsion polymerisation in a 500 cm³ thermostated double-walled reactor fitted with a mechanical Teflon stirrer. Vinylcaprolactam monomer, the crosslinker, surfactant (either SDS or PEO-R-MA), and 240 cm³ water were transferred to the reactor. The amount of the cross-linker BA was 2 mol% of the monomer feed, except in the case of E1, where 3 mol% of BA was needed to retain the stability of the emulsion. The details of the polymerisation reactions are collected in Table 1. The solution was purged with nitrogen for 60 min to remove dissolved oxygen. At the same time the mixture was emulsified by stirring at 400 rpm. The initiator, either KPS or VA-086, was added through the septum to start the reaction. The polymerisation was carried out at 70 or 75 °C for 20 h. After the reaction the resulting microgels were purified by two different methods. One part of the microgel dispersion was dialysed for 1 week and the other was purged of unreacted monomers and surfactants using successive three-cycle centrifugation (Sigma 2K15C) at 15,300 rpm and 40 °C, decantation, and redispersion in water. Two methods of

![Diagram](attachment:image.png)

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Fig. 1 Structure of the initiators and the surfactants. Water-soluble initiator 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086) and the amphiphilic poly(ethylene oxide) macromonomer (PEO-R-MA) are both nonionic. Sodium dodecyl sulphate (SDS) and potassium persulphate (KPS) are ionic.