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Dilution leading to viscosity increase based on the cononsolvency effect of temperature-sensitive microgel suspensions

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HIGHLIGHTS

- The relative zero shear viscosity vs Φ_{eff} at different temperatures and methanol fraction superpose to a single mastercurve.
- Both η_0 and η_{rel} of microgel dispersions was found to increase when diluting microgel dispersions from $X_{MEOH} = 0.25$ to $X_{MEOH} = 0.2$ or $X_{MEOH} = 0.175$ at 10 °C and 15 °C.
- η_{rel} of the microgel dispersions can be calculated based on hard sphere model and showed pronounced increase by adding methanol to the microgel dispersions.

GRAPHICAL ABSTRACT
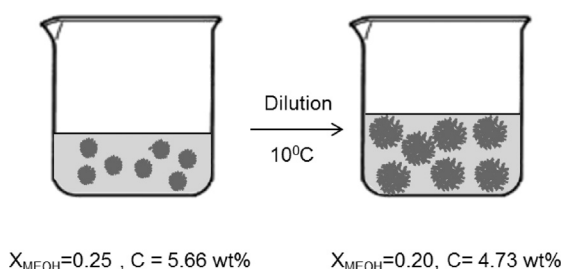
$X_{MEOH}=0.25$, C = 5.66 wt% $X_{MEOH}=0.20$, C= 4.73 wt%

ABSTRACT

An easy method was found to increase the viscosity of microgel suspensions just by diluting the suspensions at different temperatures and methanol fraction. Poly (N-isopropylacrylamide) (PNiPAm) based microgels coated with poly (ethylene glycol) methyl ether methacrylate (PEGMA) were synthesized and the flow behavior was investigated in water and methanol mixtures. Microgel suspensions shows cononsolvency effect in different methanol fraction and the hydrodynamic size varies with temperature, which leads to dramatic changes in effective volume fraction (Φ_{eff}). The relative zero shear viscosity (η_{rel}) at different temperatures and methanol fraction (X_{MEOH}) superpose to a single mastercurve when plotted vs the effective volume fraction, even microgels above the volume phase transition temperature (VPTT) at the collapse state. Both the zero shear viscosity and the relative zero shear viscosity of microgel dispersions was found to increase when diluting microgel dispersions from $X_{MEOH} = 0.25$ to $X_{MEOH} = 0.2$ or $X_{MEOH} = 0.175$ at 10 °C and 15 °C. Furthermore, the relative zero shear viscosity of the microgel dispersions are calculated at certain temperature and methanol fraction based on the mastercurve of hard sphere model, which showed pronounced increase by adding methanol to the microgel dispersions at a collapse state in various temperatures. This provides a new method to increase the viscosity through diluting method simply by preparing high swelling ratio microgel dispersions.

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1. Introduction

Flow properties of the sterically stabilized colloidal dispersion have been investigated for many years [1–7], because of the widely technical applications in various industries [8–12] and the close link to the processing of these materials. The viscosity is an important parameter that is used to investigate the structure of microgels and interaction among particles. Regarding to dilute solutions and concentrated solutions, microgels viscosify a solution by different mechanisms. Below the overlap concentration, the viscosity of microgels dispersions increase in proportion with the concentration, however, when the concentration of microgels reach a certain value, i.e. the overlap concentration, microgels tend to form close packed structure, and the viscosity increases more rapidly as concentration increases.

Apart from concentration effects, other factors (temperature, solvent and pH), which can affect the viscosity of the microgel suspensions. Microgels show multi-responsive behaviors, which can be triggered by different condition, such as temperature [13], solvent composition, and pH [14,15] by incorporated commoners into microgels. Multi-sensitive behavior of microgel dispersions has attracted massive applications in various fields [16–23]. In this way, the viscosity of the microgel suspensions changes with the variation of the environmental condition.

Generally, the viscosity of the microgels is a function of effective volume fraction. The effective volume fraction is defined as the concomitant rise of volume fraction of the uncovered latex particles. Due to the softness of colloidal particles, the determination of the effective volume fraction of concentrated soft particles is always a challenge for colloidal science. In dilute solution, the microgel particles are assumed as non-draining hard spheres and the effective volume fraction is the function of the mass fraction. Some studies about rheological properties of concentrated PNiPAm based microgel with various cross link densities and structures were reported [2,3,7]. Obviously, the viscosity of the microgel suspension will be changed by changing the size of the microgels and the concentration of the suspensions.

On the other hand, poly (N-isopropylacrylamide) (PNiPAm) based microgel is the most widely investigated polymer, which features a dramatic volume phase transition temperature (VPTT) at around $32\,^\circ$C in water. Heating over VPTT will lead to collapse of microgels. The microgels can also be controlled to swell and collapse by changing the composition of solvent mixtures. At room temperature, methanol and water are both good solvent for microgels, but at a certain mixtures of water and methanol, the microgels tend to collapse, which is called cononsolvency effect. Lots of reports and applications of this kind of behavior s have already published [24–30]. The coil-to-globule-to-coil transition of the microgel chains is mainly caused by the competitive hydrogen bonding by water and methanol molecules onto the polymer chain [26,31]. The various thermodynamic behaviors between PNIPAM and mixture solvents are related to different degrees of polymer–solvent interaction and structures of solvent used [32]. Scherziger and Richtering [33,34] investigated the cononsolvency effect and dynamics of microgels with different core–shell architectures, which the values of the apparent solvent viscosities inside the core of the microgels are higher than the bulk solvent.

PEGMA is a widely-use monomer stabilizer in microgel dispersions [35–38]. If incorporated into the particles during the polymerization, the steric interactions play a role in determining the stabilization of the microgel particles [39]. Coated PEGMA-PNiPAm microgels contribute more to the polymer/solvent interaction energy, which makes the particles more stable both in the synthesis process and the water/methanol mixtures [40].

PNiPAm based microgels copolymerized with PEGMA were successfully synthesized to investigate the viscosity of microgel dispersions at various temperatures and methanol fraction. Compared to hard spheres, microgels have the advantage of influencing the particle sizes through temperatures and methanol fraction changes. Both changes of temperature and solvent composition will lead to the changes of effective volume fraction, and then the viscosity changes. In this paper, we investigate the influence of the temperature and the methanol fraction on the viscosity of the microgel dispersions. To investigate the factors leading to the increase of viscosity, the microgel dispersions are diluted with water at a collapse state. Based on this experimental data, further calculations will be performed to verify and speculate the viscosity variation of the microgel dispersions at other methanol fraction and temperatures with the diluting method.

2. Experiments

2.1. Materials

Monomer N-isopropylacrylamide (NiPAm) was purchased from Acros. The stabilizer poly(ethylene glycol) methyl ether methacrylate (PEGMA), average $M_n = 2000$, 50 wt% dissolved in H_2O and the surfactant sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich (Germany). N,N′-methylenebisacrylamide (BIS) and the initiator potassium peroxodisulfate (KPS) were ordered from Merck. All the chemicals were used as received. Water for all purposes is double distilled.

2.2. Microgel synthesis

The microgel was synthesized by precipitation polymerization. In a 500 ml three necked round flask equipped with a stirrer, reflux condenser and a gas inlet and outlet. NiPAm (8.06 g), PEGMA (3.98 g, 50 wt.% dissolved in water) used as comonomer, cross-linker BIS (0.22 g) and SDS (0.11 g) dissolved in 400 ml water under stirring for 0.5 h. Then the oil bath was heated to $70\,^\circ$C and the initiator KPS (0.15 g) dissolved in water was added into the flask. The reaction is bubbled with nitrogen to expel oxygen for 30 min. After 6 h, the reaction was cool to room temperature and filtered with glass wool. Macroporous membrane ($M_W = 12,000$–14,000) was used for further purification.

2.3. Methods

The hydrodynamic size of the microgel particles was determined by Dynamic Light Scattering (DLS)on an ALV gonionmeter5000 at a wavelength of 647 nm, with a programmable cryostat to control the temperature [41]. The scattering angels were varied from 30° to 130°. The samples were highly diluted to avoid multiple scattering and the water filtered with 200 nm filter.

An automatic Schott Micro Ostwald or Ubbelohde viscometer was used to determine the kinematic viscosity (η_{kine}) of microgels in dilute solution. The dynamic viscosity (η_{dyn}) equals η_{kine} multiplied by density (ρ). The density is derived from the website (www.handymath.com).

Rheological properties of the concentrated microgel dispersions in water and methanol mixtures were investigated with a Malvern Kinexus pro rheometer with temperature-control system in cone/plate geometry using shear rate ramp procedure.

3. Results and discussion

3.1. The particle characterization of the microgels

The sterically stabilized microgel dispersions were synthesized by precipitation polymerization, using the water-soluble monomer