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Research paper

Multi-stimuli responsive nanofluid with easy-to-visualize structural color patterns

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HIGHLIGHTS

- Multistimuli responsive nanofluid with easy-to-visualize structural color patterns is developed.
- A thermo-responsive polymer and superparamagnetic nanoparticles are used to realize it.
- In the temperature range of 5–30 °C, the interdroplet separation is reversibly tuned from 82 to 52 nm.
- Reversible swelling and collapse of polymer adsorbed at the O/W interface is manifested.
- Thermo-magneto responsive nanoemulsions offer exciting applications.

GRAPHICAL ABSTRACT

Schematics representation of PNIPAM stabilized emulsion and phase contrast optical microscopy images at different temperatures.
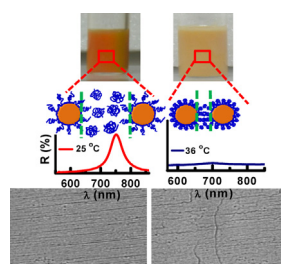
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ABSTRACT

We present the details of a multi- stimuli responsive nanofluid with easy-to-visualize structural color patterns. We have used a thermo-responsive polymer, *Poly (N-isopropylacrylamide)(PNIPAM)* and superparamagnetic nanoparticle to realize both thermal and magnetic actuation of the nanofluid. *PNIPAM* molecules adsorbed at the oil-water (O/W) interface acts as a stabilizer cum thermo-responsible moiety, while the superparamagnetic nanoparticles make the nanofluid magnetically responsive. Under a constant magnetic field and in the temperature range of 5–30 °C, the interdroplet separation is reversibly tuned from 82 to 52 nm. The reversible swelling and collapse of polymer adsorbed at the O/W interface is manifested from the Bragg peak shift at a constant magnetic force. Above the lower critical solution temperature (>35 °C), a strong attraction between adsorbed PNIPAM layers caused the bridging of PNIPAM covered droplets, which was evident from the disappearance of Bragg peak after the removal of magnetic stimulus and the presence of bridged long flexible chains of drops. It is observed that the incorporation of a small amount of anionic surfactant monomers dramatically increases the volume phase transition, the repulsive interaction forces and the interparticle tunability due to strong association of PNIPAM and sodium dodecyl suphate (SDS). Our results suggest that by using PNIPAM and an anionic surfactant, the interparticle interactions and optical properties of magnetically polarizable nanofluids can be reversibly tuned. Thermo-magneto responsive nanoemulsions offer exciting applications in optical devices (2D and 3D photonic crystals, optical gratings, body temperature sensor etc.), smart drug delivery systems and sensors. Besides, they are wonderful model system to probe temperature induced conformational changes under different physiological conditions.

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1. Introduction

Responsive stimuli materials have been an area of interest in recent years due to their potential applications [1–6]. For most of these applications, the response of the material to a particular stimulus is achieved using suitable organic moieties. By introducing molecules or materials which respond to more than one stimuli, it is possible to fine tune the behavior of the material with multiple stimuli. Magnetic nanoemulsions are one such response-stimulus materials that has shown to have several interesting applications [7,8]. Emulsions are thermodynamically unstable systems, but can be made kinetically stable by using suitable surface active species such as surfactants, polymers, polyelectrolyte or particle [9,10]. The repulsive forces that provides stability to such systems arises from electrostatic, steric, electro-steric or hard sphere forces [11–13].

The neutral polymers are widely used for the stabilization of dispersions as compared to charged molecules, due to its immunity to pH or ionic strength changes [14]. PNIPAM is one of the most widely studied systems, owing to its thermo responsive behavior close to human body temperature, insensitivity to physio-chemical condition (e.g. pH) and resemblance to biological phenomena, especially protein denaturation. Further, they have a wide range of applications in analayte sensors [15], protein sensor [16], drug delivery [17,18] and catalysis [19]. The ability of thermo-responsive polymer brushes to tune protein adsorption and cellular adhesion has been exploited in protein separations and tissue engineering [20].

Poly(N-isopropylacrylamide) (PNIPAM) is a water soluble temperature sensitive polymer with amphiphilic nature due to the hydrophilic amide group, the hydrophobic carbon backbone and *iso*-propyl group. It undergoes a coil to globule transition above a temperature called the lower critical solution temperature (LCST) between 32 and 34 °C due to large conformational changes [21–24]. Below LCST, the polymer coil is highly hydrated and swells due to repulsive interaction between the segments. However, above LCST polymer coils are dehydrated leading to a collapsed state due to inter and intra segmental attractive interactions [25]. The solvent quality can be described in terms of Flory free energy, $\chi_{eff}\varphi(1-\varphi)$, where φ is the monomer volume fraction and χ_{eff} is effective flory interaction parameter, related to second virial coefficient (ν) as $\nu = 1 - \chi_{eff}$, where $\nu > 0$ for a good solvent, $\nu = 0$ for a theta solvent and $\nu < 0$ for a bad solvent. Studies showed that as the solvency condition changes from good to poor, the polymer chain length is decreased from $N^{3/5}$ to $N^{1/3}$ [26]. A significantly reduced hydrogen bonding with the PNIPAM was observed above the LCST, resulting in a collapsed polymer conformation [27]. It has been shown that the thermo-responsive nature of PNIPAM can be tuned with salt [28], surfactant [29,30] and other biological molecules [31,32]. In general, surfactants increase LCST due to its favorable interactions with the PNIPAM that favors swelling of the polymers due to increased electrostatic repulsion and inhibit LCST of the polymer-SDS complex [33–35]. It is also observed that the incorporation of salts can lower the volume phase transition temperature.

Recently, multi-stimuli responsive polymers have been developed for biomedical applications. E.g., 4-vinylflavylium was copolymerized with PNIPAM to extend the response of PNIPAM to pH and light [36]. By incorporating tetraphenylethene as a cross linker in a PNIPAM matrix, fluorescence emission was achieved above the volume phase transition temperature, which was used for tracing and imaging of the biological processes such as cell transplantation, migration, fusion, and lysis [37]. Even though there are several studies on temperature induced transition of PNIPAM in aqueous solution using dynamic light scattering (DLS) [24,38], fluorescence spectroscopy [22,39] in solid/water interface, surface force apparatus (SFA) [40], atomic force microscopy (AFM) [41–43], to the best of our knowledge, no studies are reported on the behavior of PNIPAM at liquid-liquid interfaces upon application of temperature stimulus. As the conformation of macromolecules adsorbed at interfaces is altered under various environmental conditions that affect the product quality, an understanding the conformational changes is important from both the fundamental and practical point of view [44].

Although there are several molecular dynamics simulations studies exist, the experimental studies on the conformational changes of polymers adsorbed on to colloidal material are scarce. The aim of the present study is (1) to tailor a multi-stimuli emulsion that can respond to both temperature and magnetic stimulus (2) to probe the temperature and magnetic response of such multi-stimuli emulsion and (3) to study the conformational changes of adsorbed polymers at oil-water interfaces by looking at the Bragg peak changes under a constant magnetic force. Further, we demonstrate the manifestation of temperature induced conformational changes of adsorbed PNIPAM chains at oil-water interfaces through a simple spectroscopic experimental approach. We have successfully tuned the interdroplet interactions using both temperature and magnetic stimuli and obtained new insights into the conformational changes of adsorbed polymers.

2. Materials and methods

2.1. Materials

The polymer used in this study was a thermo-responsive polymer, PNIPAM, of average molecular weight 23,000 g/mol, obtained from Sigma Aldrich. The lower critical solution temperature (LCST) of the polymer was found to be 35 °C. The polymer is highly hydrophilic in nature below LCST and becomes more hydrophobic above the LCST.

Surfactant used in this study was SDS ($C_{12}H_{25}SO_4Na$), obtained from Sigma Aldrich. The purity of the surfactant and polymer are 99.9%, which were used without further purifications. Milli Q water, filtered with 0.22 μm Millipore filter, was used to make polymer and surfactant solutions.

2.2. Synthesis of oil-in-water nanoemulsion

The Fe_3O_4 nanoparticles were prepared using co-precipitation technique [45,46] where Fe^{2+} and Fe^{3+} ions in an alkaline medium were used [47]. 1:1 ratio of 0.2 M $FeCl_3 \cdot 6H_2O$ and 0.1 M $FeSO_4 \cdot 7H_2O$ were mixed under a contant stirring rate of 800 rpm at 60 °C for 5 min. Afterwards, 30% ammonium hydroxide was added rapidly under a stirring rate of 1200 rpm. Then oleic acid was added to the reaction mixtures and the pH was adjusted to ~9 and incubated for 30 min under a constant stirring rate of 1200 rpm. Then, particles were decanted, washed with water and acetone or ethanol and finally dried. The prepared nanoparticles were characterized by using X-ray Diffractometer (XRD), Vibrating Sample Magnetometer (VSM), Thermo gravimetric analyzer(TGA) and Fourier transform infrared (FTIR) spectrometer.

The room temperature XRD patterns of the as synthesized nanoparticles showed Bragg diffraction peaks, (220), (311), (400), (422), (511) & (440), which matched well with standard single-phase magnetite with cubic inverse-spinel type structure (JCPDS card no 88-0315). The average crystallite size calculated from the peak broadening of the most intense peak (311) was ~10 nm. The room temperature magnetization (M-H) curves of iron oxide nanoparticles showed superparamagnetic in nature at room temperature with insignificant hysteresis and remanence. Their saturation magnetization (M_s) value was 71.5 emu/g, after correcting the organic and moisture weight contributions from the TGA. The TGA of nanoparticles showed an initial weight loss of ~1.5% up to 100 °C due to the evaporation of moisture content. A large single