



Thermally tunable grating using thermo-responsive magnetic fluid



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ABSTRACT

We report a thermally tunable grating prepared using poly(N-isopropylacrylamide) and super paramagnetic iron oxide nanoparticles. The array spacing is reversibly tuned by varying the temperature between 5 and 38 °C. Here, the ability of thermo-responsive polymer brushes to alter their conformation at an interface is exploited to control the grating spacing in nanoscale. The underlying mechanism for the temperature dependent conformational changes are studied by measuring the subtle intermolecular forces between the polymer covered interfaces. It is observed that the interparticle forces are repulsive and exponentially decaying with distance. The thermo-responsive grating is simple to use and offers a wide range of applications.

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1. Introduction

Ferrofluids [1–5], ferroemulsions [6,7] and magneto-rheological (MR) fluids [8] are magnetic response stimuli materials with fascinating physical properties. They respond to a magnetic field and change their functional properties significantly and hence come under the category of smart materials or response stimuli materials [9–11]. Ferrofluids are shown to have many technological applications in optical devices [12–22] and biomedicines [23]. Magnetic nanoemulsions are oil-in-water or water-in-oil emulsions of ~100 nm radius, stabilized with a surfactant or polymeric molecule. They are magnetically polarizable because of the superparamagnetic iron oxide particles (diameter ~10 nm) inside the droplets. Nanoemulsions exhibit interesting optical properties and have potential applications [7]. Recently, thermosensitive poly(N-isopropylacrylamide) (hereafter mentioned as PNIPAM) hydrogel with contraction capability suitable for drug release application was developed using magnetite nanoparticles [24]. PNIPAM is a water soluble thermo responsive polymer with amphiphilic nature due to the hydrophilic amide group and the hydrophobic carbon backbone and iso-propyl group. Due to large conformational changes, PNIPAM undergoes a coil to globule transition above a temperature called the lower critical solution temperature (LCST)

[25]. Below LCST, the polymer coil is highly hydrated and swells because of the repulsive interaction between the segments. Above LCST, polymer coils are in a collapsed state due to inter and intra segmental attractive interactions [26]. Here, we demonstrate a thermally tunable grating using thermo responsive nanoemulsion.

2. Materials & methods

We use PNIPAM, of average molecular weight 23,000 g/mol (Sigma Aldrich), with a LCST of 35 °C. To tune the LCST, we use an anionic surfactant of sodium dodecyl sulphate ($C_{12}H_{25}SO_4Na$), (hereafter mentioned as SDS) obtained from Sigma Aldrich (99.9% purity). Nanoemulsions were prepared by the classical inversion method using water containing an anionic surfactant and octane containing iron oxide nanoparticles of diameter ~10 nm, which were prepared using the co-precipitation technique [27]. From the initial polydisperse emulsion, highly monodisperse emulsion with polydispersity less than 0.07 is obtained by using the fractionation approach combined with magnetic separation [28]. The hydrodynamic size distribution was obtained using a Malvern Nanosizer (Zetasizer Nano-S) at a backscattering angle of 173°. The transmittance study was carried out using a fiber optic based spectrometer (Avaspec, Netherlands) with a white light source. The temperature was varied using a temperature controlled sample compartment (qpod TC 125, Quantum technologies) with a peltier base. A custom made solenoid with a programmable power supply (Agilent Technologies – N5770A) was used in the present study.

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The master emulsion was washed four times with PNIPAM solutions. The magnetic separation was used to separate the droplets. After every wash, the supernatant solution was removed and the emulsion was topped up with PNIPAM solution. After washing, the emulsion was left for 3 days to equilibrate.

3. Results and discussion

Fig. 1a shows the hydrodynamic size distribution of emulsion stabilized with 1 wt % of PNIPAM. The average hydrodynamic diameter and the polydispersity index were found to be 250 nm and 0.07, respectively. The polydispersity index is defined as $PDI = \frac{\sigma^2}{Z_D^2}$, where σ is the standard deviation and Z_D is the mean average size. The inset of Fig. 1 shows the molecular structure of the PNIPAM molecule. Fig. 1b shows the schematic representation of an emulsion droplet in the presence of magnetic field at a temperature below the LCST, when the magnetic field is ON. The magnetic particles inside the droplets orient in the direction of the magnetic field when the magnetic energy exceeds the thermal energy.

Below the LCST, the hydrated PNIPAM polymer, adsorbed at the liquid interface, extends out because of the repulsive interaction between the segments (Fig. 1b). The transmittance of pure PNIPAM solution at 550 nm as a function of temperature for various concentration of SDS, is shown in Fig. 1c. The temperature at which transmittance commences to decrease drastically is termed as LCST

or volume phase transition temperature. For pure PNIPAM solution, the LCST is found to be 35 °C and increases to higher value with increase in SDS concentration. Below LCST, PNIPAM solution shows nearly 100% transmittance, whereas above the LCST the polymer starts to aggregate and becomes a globular structure, due to the dehydration which followed by the formation of new bonding between carbonyl group and water. The M-H curve of the Fe₃O₄ nanoparticle is shown in Fig. 1d, shows the super-paramagnetic behavior of the ferrite nanoparticle.

Fig. 2a shows the Bragg spectra of PNIPAM stabilized emulsion containing 2 mM SDS. The Bragg peak is blue shifted from 756 nm to 640 nm as the temperature is increased from 5 to 32 °C. From 32 to 38 °C, a slight increase in the Bragg peak (~45 nm) wavelength is noticed probably due to densification of polymer at an interface. Above 38 °C, Bragg spectra is fully collapsed. Interestingly, the collapse was reversible with temperature. The corresponding Bragg peak wavelength as a function of temperature during heating and cooling is shown in Fig. 2b, where a Bragg peak wavelength change of 116 nm is found in a temperature range between 5 and 32 °C, followed by a complete collapse of Bragg peak at 38 °C. Fig. 2c and d shows the force-distance profile and the corresponding first interaction distance for PNIPAM stabilized emulsion with 2 mM SDS as a function of temperature. Fig. 2e and f shows the photographs of PNIPAM stabilized emulsion with 2 mM SDS at a temperature below (36 °C) and above the LCST (38 °C). The oil droplets

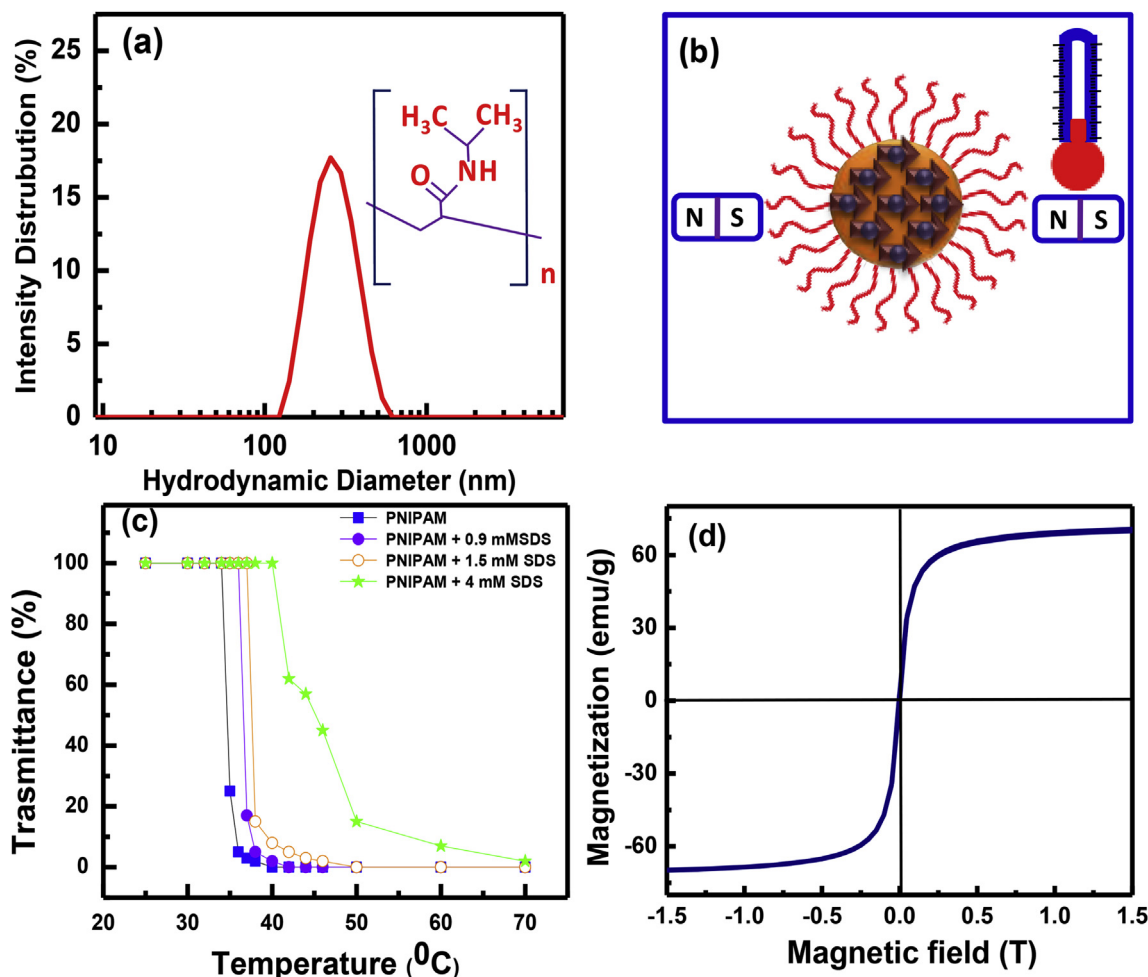


Fig. 1. (a) Hydrodynamic diameter of PNIPAM stabilized emulsion (Inset shows the molecular structure of PNIPAM) (b) Schematic representation of an emulsion at temperature below LCST under a magnetic stimulus. (c) transmittance at 550 nm from PNIPAM of 1 wt % at different SDS concentrations (d) M-H curve of Fe₃O₄ nanoparticles.

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