Optical and rheological studies on weak gel-sol transition in aqueous solutions of poly(*N*-isopropylacrylamide)-block-polystyrene

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Abstract. The optical and rheological properties of aqueous solutions of block copolymer composed of low molecular weight poly(*N*-isopropylacrylamide)-*b*-polystyrene are studied as a function of temperature. From light scattering measurements the block copolymer solution is found to form micelles at very low concentrations and the critical micellar concentration is identified as 0.005 wt%. Apart from the concentration dependence, a unique temperature dependent micelle formation is noted at 34 °C. Further, temperature dependent refractive index measurements shows that the refractive index increases with temperature (beyond the lower critical solution temperature, 31.6 °C of the polymer), and is attributed to the stable rearrangement of the proximal hydrophobic isopropyl-polystyrene chains in the collapsed polymer so as to overcome the steric hindrance effects offered by the hydrophobic chains. In the polymer concentrations investigated for rheological studies, the solution flows, yet manifested solid like behavior with $G' > G''$ with the modulus being frequency dependent and the magnitude of G' two-fold higher than G'' implying a weak gel state. Weak gel states are in general noted at high temperatures in most of the polymer systems, contrary to this, in our studies weak gel state is observed at lower temperature. Further, a transition from weak gel to sol state is observed at slightly elevated temperatures. The reason for the existence of weak gel state below the lower critical solution temperature is due to the micellar entanglements of poly(*N*-isopropylacrylamide)-*b*-polystyrene with one another and whereas above the lower critical solution temperature disentanglement of the micelles makes the system behave like a viscoelastic liquid.

Keywords: rheology, block copolymer, PNIPAM, light scattering, micelles

1. Introduction

With the recent developments in synthesis strategies of novel macromolecules, it is now possible to tune the macromolecular size and shape by covalent and non-covalent interactions. The covalent interactions can be effectively tapped to form block copolymers (BCPs) which has numerous applications such as, an etch mask for nano/meso scale patterning, photovoltaic devices, drug delivery, etc [1–6]. Apart from

the cited applications, BCPs are also being explored for their applicability as photonic materials [7–12]. Among the numerous strategies of controlled/living free-radical polymerization for the synthesis of BCPs, reversible addition–fragmentation chain transfer (RAFT) polymerization process stays in the forefront. The advantage of RAFT polymerization is that, it results in polymers with controlled molecular weight and with narrow polydispersities and offers a wide

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range of monomer selection and reaction conditions. The mechanism of RAFT polymerization occurs through a reversible addition-fragmentation sequence in which the transfer agent exhibits very high transfer constants for a rapid rate of exchange between dormant and living chains. Some of the routinely employed RAFT chain transfer agents (CTA) are trithiocarbonates [13–15], dithiocarbamates [16–18], dithiobenzoates [19–22], etc.

Imparting responsive nature to the block copolymers enables to understand the behavior of the polymer (shape, permeability, or color) in response to a series of changes in external stimuli such as pH, temperature, salt concentration, charge, light, etc. Despite the synthesis challenges, responsive block copolymers can produce well-defined materials either by triggered or non-covalent associations of one or more blocks. This in turn imparts the tunability of the physical properties of the polymer such as colour, shape, Young's modulus of elasticity, tacticity, glass transition temperature, etc, subjected to changes in stimuli. Polymers based on poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*-vinylcaprolactam) (PVCL) exhibit thermo-sensitivity, and those based on poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAAc) exhibit pH sensitivity. By making use of amphiphilic diblock copolymers, it is possible to achieve self-assembly of the block copolymer segments into spherical micelles by selectively solubilizing only one block in a suitable solvent [23]. The micelles can be disrupted by applying stimulus such as pH, temperature, solvent/salt concentration. In a study by Tang *et al.* [24], the temperature, pH, and sugar induced micellization and dissociation transition of poly(3-acrylamidophenylboronic acid)-*b*-poly(*N*-isopropylacrylamide) (PAAPBA-*b*-PNIPAM) block copolymer was investigated by light scattering technique and the block copolymer self-assembles into micelles with the core made up of PAAPBA and shell of PNIPAM. An increase in temperature led the micelles to shrink at pH 6.2, whereas at an elevated pH of 10.0, due to the increase in hydrophilicity of the PAAPBA block, the micelles completely dissociated to unimers and proceeds through a step-by-step sequential expulsion of individual chains. Poggi *et al.* [25] showed that, the self-assembly properties of poly(vinyl alcohol)-block-poly(acrylic acid)-block-poly(4-vinylpyridine) triblock terpolymer (PVOH-*b*-PAA-*b*-P4VP) in water as a function of pH exhibited three different aggregation states and

the micellar disassembly can be achieved by changing the temperature. The aggregation number of the PVOH-*b*-PAA-*b*-P4VP micelles and their size in turn can be tailored by controlling the ionic strength of the solution prior to micellization. Further the charged PAA segments in the shell upon the addition of calcium ions collapses onto the P4VP core. Since our group has a long-standing interest in stimuli responsive polymers based on PNIPAM, which exhibits a lower critical solution temperature (LCST) at ~32 °C [26–30], we too synthesized low molecular weight hydrophilic-hydrophobic block copolymers of poly(*N*-isopropylacrylamide)-block-polystyrene (PNIPAM-*b*-PS) by RAFT polymerization using 2-(dodecylthiocarbonothioylthio)-2-methylpropion-cacid (DDMAT).

The PNIPAM-*b*-PS block copolymer upon selective solubilization of the PNIPAM segments can form micelles in water; and thus it will be of interest to investigate the effect of temperature on the micellar behaviour. The effect of temperature and concentration on aqueous solutions of the PNIPAM-*b*-PS block copolymer optical and rheological properties is reported in this paper. The micellar behaviour (size change) can be studied using dynamic light scattering technique. It is observed that micelle formation is not just concentration dependent but also depends on the temperature. The rheological studies on aqueous solutions of the block copolymer reveal a weak gel to sol transition across the LCST different from the existing reports [31–33]. In the polymer concentrations investigated, the solution flows, yet manifested solid like behavior with $G' > G''$ with the modulus being frequency dependent and the magnitude of G' is two-fold higher than G'' which implies a weak gel state. Weak gel states are in general noted at high temperatures in other polymer systems, contrary to this, in our studies weak gel state is observed at lower temperature. A plausible reason for the weak gel behavior is discussed. Apart from the concentration dependence, it is observed that temperature too plays a crucial role in the formation of micelles beyond the LCST of the block copolymer.

2. Experimental

2.1. Chemicals

N-isopropylacrylamide (NIPAM, 97%), styrene containing 4-tert-butylcatechol (99%), 2, 2-azobis (2-methylpropionitrile) (AIBN, 98%), 1, 4-dioxane (99.8%) and 2-(dodecylthiocarbonothioylthio)-2-

methylpropanoic acid (DDMAT) (98%) were purchased from Sigma Aldrich. NIPAM was recrystallized in hexane. Styrene was washed with NaOH to remove the stabilizer. All the chemicals used were of analytical grade and used as received. The glass wares were pre-cleaned and dried before use.

2.2. Synthesis of macro

poly(*N*-isopropylacrylamide)–chain transfer agent (macro PNIPAM-CTA)

NIPAM (0.8 mol), DDMAT (0.2 mmol) and AIBN (1.6 mmol), was added to 80 mL of 1, 4-dioxane in a round-bottom flask equipped with a stir bar. The reaction flask was sealed with a rubber septum and purged with nitrogen gas for 30 min in an ice bath. The solution was degassed by three freeze-pump-thaw cycles followed by quick vacuum sealing and placing it in a thermostatically controlled oil bath and the reaction was allowed to proceed at 70 °C for 60 hrs. After the polymerization the reaction mixture was cooled to room temperature and precipitated by adding cold ether. The resultant macro PNIPAM-CTA had a pale yellow tinge and the yield was quantified as 5.8 g.

2.3. Synthesis of

poly(*N*-isopropylacrylamide-*lock*-styrene) (PNIPAM-*b*-styrene)

For the synthesis of PNIPAM-*b*-styrene from macro PNIPAM-CTA, 2.50 g of macro PNIPAM-CTA, styrene (0.4 mol) and AIBN (1.54 mmol) was added to 50 mL of 1, 4-dioxane. After sealing the reaction flask, nitrogen gas was purged for 30 min and the solution was degassed by three freeze-pump-thaw cycles following which the reaction flask was vacuum sealed and reacted at 80 °C for 24 hrs. After the polymerization the reaction mixture was cooled and precipitated from cold ether, yielding 2.3 g of yellow solids. Figure 1 summarizes the synthetic route for obtaining the diblock copolymer PNIPAM-*b*-PS from its monomer and CTA.

3. Characterization techniques

3.1. FTIR, NMR and GPC

Macro PNIPAM-CTA and PNIPAM-*b*-PS block copolymers were characterized by Fourier-transform infrared spectroscopy (FTIR) and ¹H nuclear magnetic resonance spectrometry (NMR). FTIR spectra of the polymer was recorded on a Fourier Transform Infrared Spectrophotometer (IR Tracer-100 Shimadzu) using the KBr pellet technique. From the FTIR spectrum, the presence of PNIPAM-CTA is confirmed by the peaks at 1070–1246 cm^{−1} (stretching vibration of C=S and –C–S–C–), the peaks at 3292 cm^{−1} correspond to the secondary amide N–H stretching cm^{−1}, the peak at 1640 cm^{−1} shows secondary amide C=O and acid group (COOH) and the CH₃ asymmetric stretching vibration bands appear at 2970 cm^{−1}. PNIPAM-*b*-PS was identified by the peaks at 3076 cm^{−1} (C–H aromatic tension), 615–879 cm^{−1} (aromatic C–H bending), 1500–1700 cm^{−1} (aromatic C=C bending), CH₂ asymmetric and symmetric tension at 2875–2976 cm^{−1}. A Bruker 300 MHz ¹H NMR spectrometer was used with CDCl₃ as the solvent and tetramethylsilane as the internal reference. The macro PNIPAM-CTA showed chemical shifts in the ¹H NMR at 0.99–1.30 (m, 3H, –CH₃), 1.70–2.50 (m, –CH₂–CH–), 3.55 (–CH₂S), (m, –CH(CH₃)₂ and –CH₂–CH– on the polymer's main chain), 4.02 (s, –NHCH(CH₃)₂) and the chemical shifts for the PNIPAM-*b*-PS block copolymer is 1.16–2.64 (m, –CH(CH₃)₂ and –CH₂–CH– on the polymer's main chain), 4.02 (s, –NHCH(CH₃)₂), 5.67–7.0 (m, C₆H₅ of styrene and –NHCH(CH₃)₂). The molecular weights and the polydispersities index (PDI) of the macro PNIPAM-CTA, and the PNIPAM-*b*-PS block copolymers were determined by gel permeation chromatography (GPC), using an Auto system XL GC with Turbo mass from Perkin Elmer. GPC was performed with tetrahydrofuran as solvent at 45 °C at a flow rate of 1.0 mL/min, and the calibration was based on a set of monodisperse polystyrene standards. The GPC curve exhibits unimodal distribution,

Figure 1. Synthetic route for obtaining the diblock copolymer PNIPAM-*b*-PS

implying monodisperse sample and homopolymers being absent in the block copolymer. The molecular weight of macro PNIPAM-CTA and PNIPAM-*b*-PS block copolymer is found to be 6894 and 9695 g/mol with PDI of 1.25 and 1.27 respectively. The GPC measurements have been repeated and the results were reproduced with an accuracy of 0.1%. There are several reports on block copolymers synthesized by RAFT polymerization exhibiting unimodal and narrow molecular weight distribution [34–37]. From the molecular weight the number of PNIPAM and polystyrene segments is found to be 67 and 27 respectively and hence the short form PNIPAM₆₇-*b*-PS₂₇ is used in the entire text to denote the block copolymer. In arriving at the number of monomer segments the contribution of the chain transfer agent is neglected.

3.2. DLS, transmission spectroscopy, refractometry

The hydrodynamic diameter and effect of temperature on the hydrodynamic diameter of PNIPAM₆₇-*b*-PS₂₇ block copolymers was determined by Dynamic Light Scattering, using Malvern–UK, 4700 model. In DLS, the intensity-intensity auto correlation function $g^{(2)}(q, t)$, measured at a given scattering wave vector, q is given by Equations (1) and (2):

$$g^{(2)}(q, t) = \frac{I(q, 0)I(q, t)}{(I(q, 0))^2} \quad (1)$$

$$q = \frac{4\pi\mu_{\text{medium}}}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

where μ_{medium} is the refractive index of the medium, θ is the scattering angle and λ is the wavelength of the incident laser light. The normalized electric field autocorrelation function $f(q, t)$ is related to $g^{(2)}(q, t)$ by the Siegert-relation [27] (Equation (3)):

$$g^{(2)}(q, t) = 1 + \beta |f(q, t)|^2 \quad (3)$$

where β is the coherence factor. In a non-interacting system, $f(q, t)$ can be expressed by Equation (4):

$$f(q, t) = \exp(-D_0 q^2 t) \quad (4)$$

where D_0 is the free diffusion coefficient and is related to the hydrodynamic diameter, d_h by the Stokes-Einstein relation given by Equation (5):

$$d = \frac{k_B T}{3\pi\eta D_0} \quad (5)$$

where k_B , η and T are the Boltzmann constant, the solvent (water) viscosity and the absolute temperature, respectively. In the DLS measurements, the Z-average diameter given as the output of the measurements by the instrument refers to the mean hydrodynamic diameter, d_h and the polydispersity index estimates the width of the distribution.

Temperature dependent transmittance of the PNIPAM₆₇-*b*-PS₂₇ block copolymers was determined using a UV-Visible spectrophotometer (JASCO V-670, Japan). The refractive indices of the block copolymer solution were measured at various temperature (20–40 °C) using Rudolph Research Analytical, J457 Automatic Refractometer, USA.

3.3. Rheology

Rheological measurements on aqueous solutions for various concentrations of PNIPAM₆₇-*b*-PS₂₇ block copolymer have been carried out using a MCR 301 Rheometer (Anton Paar, Germany) in the double gap geometry. Frequency sweep-measurements have been performed in the range of 0.1 to 100 rad/s to measure G' (ω) and G'' (ω), the linear viscoelastic storage modulus and the loss modulus respectively.

4. Results and discussion

4.1. Effect of temperature on the optical properties

The critical micellar concentration (CMC) of the PNIPAM₆₇-*b*-PS₂₇ block copolymer has been determined by DLS technique, by preparing a series of aqueous solutions in the concentration range of 0.0001 to 0.05 wt% at 25 °C. The intensity of scattered light as a function of concentration is shown in Figure 2. The intercept of the two slopes is identified as the CMC of the polymer which is 0.005 wt%. Below the CMC almost constant scattering intensities is detected whereas beyond the CMC the scattered light intensity profile showed a linear increase with concentration.

Having established the CMC of the PNIPAM₆₇-*b*-PS₂₇ block copolymer solution as 0.005 wt%, the hydrodynamic size of the micelles and the effect of temperature on the size of the micelles is determined by DLS. At 25 °C, the hydrodynamic diameter of the

Figure 2. Scattered intensity as a function of concentration of PNIPAM₆₇-*b*-PS₂₇ at 25 °C

micelles is found to be 85.2 ± 5.66 nm. Figure 3 shows the plot of hydrodynamic diameter, d of the micelles as a function of temperature for the 0.005 wt% PNIPAM₆₇-*b*-PS₂₇ block copolymer solution. The temperature induced collapse of the PNIPAM₆₇-*b*-PS₂₇ aggregates is observed at 31.6 °C and the collapse can be explained as follows. Upon contact with water the amide side chains of PNIPAM block form intermolecular hydrogen bonding with the surrounding water molecules. It is also reported that there is also some structured water around the isopropyl groups of PNIPAM [38]. This results in strong polymer-water (solvent) interaction and as a consequence the polymer swells in the solvent. Beyond a certain temperature known as the lower critical solution temperature (LCST) the inter-molecular hydrogen bonds with the water molecules break. The characteristic LCST of the PNIPAM is ~ 32 – 33 °C at which the PNIPAM undergoes an entropically favored volume change (breaking of the hydrogen bonds) [26–28, 38–41], the LCST range is tunable by the addition of co-monomers leading to the deswelling of the polymer chains. Beyond the LCST of the polymer, the turbidity of the solution intensifies. This change in

Figure 3. Temperature dependence of hydrodynamic diameter (d_h) of PNIPAM₆₇-*b*-PS₂₇ 0.005 wt% aqueous solution

Figure 4. Transmittance change as a function of temperature for 0.001 wt% PNIPAM₆₇-*b*-PS₂₇ block copolymer solution at various wavelengths. Inset shows the change in scattered intensity as a function of temperature measured by DLS. Arrows represent the LCST and CMT.

turbidity is expected to change the optical properties of the polymer such as its transmittance and refractive index, due to the increased Rayleigh scattering arising from the larger refractive index contrast with the solvent. Further it has been reported that PNIPAM block can self-assemble into micellar aggregates in aqueous solution at elevated temperatures [42, 43]. The PNIPAM chains are easily solvated in water and thus the block copolymer can self-assemble into core-shell micelles. We also verified the influence of temperature on the micelle formation in a dilute solution (0.001 wt%) by monitoring the optical transmittance as a function of temperature for a series of wavelengths. From Figure 4, it can be seen that, apart from the dip in transmittance at the LCST a significant decrease in the transmittance is observed above 34 °C, which is identified as the critical micellization temperature (CMT). Similar increase in the scattered light intensity is noted in the 0.001 wt% solution in DLS as a function of temperature (inset in Figure 4). Zhou *et al.* [44] also observed that scattered light intensity of 0.2 g/L PNIPAM₆₇-*b*-PS₂₇ aqueous solution increases at 42 °C, whereas the CMT determined by optical transmittance was 38.5 °C and the difference was attributed to the polymer concentration effects. Since, we carried out scattered intensity and transmission measurements on the same polymer concentration, we could observe both the increase in scattered light intensity and decrease in optical transmittance at 34 °C. A look at the inset in Figure 4 reveals that at slightly elevated temperatures beyond the

CMT, the scattered intensity saturates. The saturation in micellar size is also noted in Figure 3. Saturation in micelle size implies that no more association of the micelles occurs and they are stable. Stable micelles are formed because the investigations are carried out at very low polymer concentrations and even at these concentrations, despite the small number of ionic end-groups, the charges in the PNIPAM chains of the micelles screens the inter-micellar interactions and thus the block copolymer solution gets charge stabilization even at temperatures beyond the LCST. The refractive index of 0.005 wt% PNIPAM₆₇-*b*-PS₂₇ solution increases from 1.336 to 1.352 when the temperature is varied from 20 to 40 °C (Figure 5). In Figure 5, two regions can be identified, region (a) where there is no significant change in refractive index with increase in temperature and in region (b) refractive index increases with temperature. The refractive index values are arrived based on the number density of electronic dipoles present in the solution. For solutions which undergo phase separation there will be significant changes in bond polarization [45]. In region (a) with increase in temperature, there is not much change in the refractive index; this is because the polymer-solvent exist as a homogeneous single phase. This may not be the case when the polymer undergoes LCST as the polymer starts to phase separate in the solvent (water). It is visible from the plot that with increase in temperature a change in slope is observed at 31.6 °C, this change correlates to the LCST of the polymer determined from DLS. The gradual proximity of the hydrophobic isopropyl groups of the PNIPAM chain coupled with the chains of polystyrene results in the increase in refractive index even after the collapse of the polymer which is the region (b). From the size information obtained from DLS, not much change in the diameter is noted beyond 34 °C, thus one assumes that almost all the bound/structured water is expelled from the polymer chain, however the observation of increase in refractive index implies that the proximal hydrophobic isopropyl and polystyrene chains in the collapsed (phase separated) polymer cycles to a stable rearrangement to overcome the steric hindrance effects offered by the hydrophobic chains.

In the PNIPAM₆₇-*b*-PS₂₇ micelles the hydrophilic PNIPAM chains extend into water and PS forms the micelle core. The interplay of steric hindrance offered by the collapsed PNIPAM shell and the unchanged

Figure 5. Refractive index as a function of temperature for 0.005 wt% PNIPAM₆₇-*b*-PS₂₇ blocks copolymer solution. Intercept of the slopes corresponds to the LCST.

PS core increases the density of the electron cloud leading to an increase in the refractive index.

4.2. Rheological characterization of PNIPAM₆₇-*b*-PS₂₇ solution

4.2.1. Effect of temperature on the rheological behavior

Oscillatory shear measurements on aqueous PNIPAM₆₇-*b*-PS₂₇ solution has been performed as a function of temperature for micelle pre-formed 0.05 and 2 wt% PNIPAM₆₇-*b*-PS₂₇ aqueous solution at a constant angular frequency of $\omega = 3 \text{ rad/s}$ and is shown in Figure 6. The PNIPAM₆₇-*b*-PS₂₇ readily forms viscoelastic solutions even at very low concentrations due to the associative nature of the hydrophilic PNIPAM segments (below LCST) and hydrophobic PS. Both the solutions follow the same trend and exhibits an apparent increase in both G' and G'' beyond 30 °C with the steepness of the slope increasing at the LCST of the polymer. Below 30 °C, $G' > G''$ implying the behavior of the polymer with dominant elastic response. For the 0.05 and 2 wt% polymer solution G' crossover G'' at 30.7 and 29.9 °C respectively (inset in Figure 6) beyond which $G'' > G'$. The temperature at which G' (elastic modulus) curve intersects that of G'' (viscous modulus) indicates the gel-sol transition point. The study proves that cross-over temperature is concentration dependent.

In general, a gel exhibits $G' > G''$ throughout the frequency range and behaves like solid, with frequency independent of the modulus. For very dilute solutions $G'' > G'$ at low frequencies. The relaxation times

Figure 6. Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of temperature for 0.05 and 2 wt% PNIPAM₆₇-*b*-PS₂₇ aqueous solution. Inset shows the shift in crossover temperature with increase in concentration.

exhibit concentration dependence in which the high concentration solutions can undergo entanglements and the entanglements persist during the oscillation with mechanical behavior resembling like a solid with $G' > G''$, whereas in the case of dilute solutions the entanglements can disentangle and flow during shear leading to $G'' > G'$. Then the solution behaves like a viscoelastic liquid. In the polymer concentrations explored in our study, the solution was flowing yet manifested solid like behavior with $G' > G''$ and the modulus was found to be frequency dependent, with magnitude of G' two-fold higher than G'' . This implies a weak gel behavior in the solutions explored. Weak gel behavior is previously reported in aqueous dispersion of κ -carrageenan helices [46, 47], ionic liquids [48], etc. Ikeda and Nishinari [46] observed the predominance of storage modulus G' over the loss modulus G'' in non-aggregated κ -carrageenan helices (polysaccharide) at 20 °C in the frequency range of 0.5–100 rad/s and $G''/G' > 0.1$, which is typical of weak gels. The weak gel-type behavior of the κ -carrageenan dispersions arises from the sufficiently long relaxation time of the topological entanglements among double-helical conformers. Thermoreversible viscoelastic to weak gel transition in ionic liquid is observed in a micellar solution of 1-butyl-3-methylimidazolium chloride (BmimCl) containing 4.45 wt% sodium dodecylsulfate (SDS) upon the addition of lithium chloride by Saravanakumar *et al.* [48]. Upon heating the ionic liquid mixture >80 °C weak gel behavior is noted, however upon cooling, the mixture exhibited a viscoelastic liquid state. Here, the authors attribute the weak gel behavior

Figure 7. Schematic of the PNIPAM₆₇-*b*-PS₂₇ micelles (a) entangled before and (b) disentangled after LCST

to arise from micellar network structures in the ionic liquid mixture.

In our investigations, we observed weak gel behavior at lower temperatures and viscoelastic liquid behavior upon heating the weak gel solution. This behavior can be explained as follows;

Below the LCST the shell of PNIPAM chains in the micelles are swollen in water and form inter-micellar entanglements and thereby the swollen micelles occupy more space in the given volume and hence the solution behaves like a gel and thus $G' > G''$, however upon crossing the LCST, the shell shrinks leading to disentanglement of the PNIPAM chains and the micelles have enough space to execute free motion as compared to their swollen state. In this state the polymer behaves like a liquid and hence $G'' > G'$. The difference in the crossover temperature for the 0.05 and 2 wt% polymer solution is attributed to the concentration effect. Schematic of the above explanation is shown in Figure 7.

4.2.2. Effect of polymer concentration on the rheological behavior

The effect of concentration of four different aqueous solutions (0.05, 0.5, 1 and 2 wt%) of PNIPAM₆₇-*b*-PS₂₇ has been carried out as a function of angular frequency at 25 °C and is shown in Figure 8. The plot shows $G' > G''$, for all the four concentrations with a concentration dependent behavior throughout the frequency range. Further the value of the moduli increased with increase in polymer content. The associative nature of the PNIPAM and PS segments leading to the formation of micelles causes the samples to exhibit viscoelastic properties even at a polymer concentration of 0.05 wt%. We observed power law dependence of the moduli on the frequency with $G' \approx \omega^2$ and $G'' \approx \omega^1$ and the power law holds true in solutions where inter-micellar entanglements are present. All the four concentrations explored in the study manifested weak-gel behavior at 25 °C.

Figure 8. Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of angular frequency for four different PNIPAM₆₇-*b*-PS₂₇ concentrations (0.05, 0.5, 1 and 2 wt %) performed at 25 °C. The graph has been split for visualization of the data points

Figure 9 shows the plots of G' and G'' as function of ω at four different temperatures for the 2 wt% solution. At 24 °C $G' > G''$ in the entire ω range, and the damping factor, δ ($\delta = G''/G'$) throughout the frequency sweep ranged between ~ 0.117 – 0.29 . A relatively large frequency dependence of the moduli, accompanied by a $\tan\delta$ value > 0.1 , is the signature of a weak gel [41]. The above observation thus, implies that the PNIPAM₆₇-*b*-PS₂₇ solution behaves like a weak gel at 24 °C. At 30 °C, crossover of the modulus is observed at $\omega = 7.36 \text{ s}^{-1}$. At 32 °C the crossover was found to be shifted to a higher $\omega = 25.1 \text{ s}^{-1}$. Beyond 36 °C G'' dominates G' throughout the frequency range swept. This implies that the entangled chains of PNIPAM in the micelle start to recede upon crossing the LCST and temperature disentangles the polymer chains and the solution behaves like a viscoelastic liquid.

Figure 9. Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of angular frequency in 2 wt% PNIPAM₆₇-*b*-PS₂₇ block copolymer solution with increasing temperature

5. Conclusions

Water dispersible block copolymer composed of low molecular weight poly(*N*-isopropylacrylamide)-*b*-polystyrene has been synthesized by RAFT polymerization. From GPC measurements the molecular weight of PNIPAM₆₇-*b*-PS₂₇ block copolymer is found to be 9695 g/mol with PDI of 1.27. The critical micelle concentration is identified as 0.005 wt%. The effect of temperature on the hydrodynamic diameter of the micelles formed in 0.005 wt% polymer solution is studied by means of DLS. From DLS, the hydrodynamic diameter of the micelles is found to be $85.2 \pm 5.66 \text{ nm}$ at 25 °C. A dilute solution (0.001 wt%) where micelles are absent at 25 °C formed micelles beyond the LCST of the polymer which indicates that micelle formation also depends on the temperature and the critical micelle temperature is identified as 34 °C by transmission spectroscopy. Rheological studies on the block copolymer solution showed that the solution exhibits weak gel-like behavior and transforms to liquid like behavior with changes in temperature, the transition point is found to be dependent on the block copolymer concentration. Unlike other reported works on sol-weak gel behaviour upon increasing the temperature in this study we observed weak gel behavior at lower temperatures and viscoelastic liquid behavior upon heating the weak gel solution. The observed weak gel to liquid behavior is due to the inter-micellar entanglement-disentanglements influenced by temperature.

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