



TEMPERATURE INDUCED VOLUME PHASE TRANSITIONS OF CROSS-LINKED PEG/POLY (NIPAM-CO-AMPS) GELS IN WATER

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ABSTRACT

The temperature sensitive copolymer of microsize hydrogels consist of N-isopropylacrylamide (NIPAM) and 2-acrylamido-2 methylpropanesulphonic acid (AMPS) have been synthesized by soap free emulsion polymerization method in presence of polyethylene glycol (PEG) as macroinitiator and N, N'-methylenebisacrylamide (NMBA) as cross-linker. In this work, Dynamic Light Scattering (DLS), Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM) technique were used to characterize copolymer microgels. The particle sizes observed by TEM were spherical with diameter around 103nm to 133.1nm. While DLS measurement shows narrow particle size distribution with hydrodynamic diameter from 343.6nm to 528 nm at temperature 25°C and 132.5nm to 414.4nm at temperature 50°C depending on AMPS content in microgels samples. The swelling ratio (α) and temperature sensitive properties of microgels were decreased with increasing AMPS content in feed composition. The volume phase transition of microgels in aqueous solution was investigated by mean of DLS. The transition temperature was determined from the first derivative curve of the hydrodynamic diameter with respect to temperature and practically found to be continuous. The volume change in the particles associated with temperature dependent hydrodynamic diameter of microgel particles. Further, the swelling data obtained from DLS measurements are analyzed using theoretical model Flory and Rehner. The description of volume fraction (ϕ) as a function of temperature by the Flory- Rehner is applicable to 2mol% AMPS content microgel sample only.

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INTRODUCTION

Microrogels are three-dimensional, water-swollen structures composed of mainly hydrophilic homopolymers or copolymers with characteristic dimensions of 50nm to 5 μ m. [1,2]. These particles are rendered insoluble in biological fluids due to the presence of chemical or physical cross-links. Recently environmentally sensitive microrogels have attracted much attention because they have many potential applications in advance biomedical technologies including “on-off” switching materials, [3]controlled drug release,[4] bioseparation [5] etc. These materials can change their behavior in response to changes in temperature [6], ionic strength, [6,7] solvent composition, [8] pH, [9] Selective reaction, [10] electric field [11]. The change in the volume of environmental sensitive microgels usually arises due to changes in osmotic pressure or charge density (i.e. pH-responsive hydrogels), solvent affinity

of the polymer backbone (i.e., temperature-sensitive hydrogels); or changes in the polymer crosslink density [12]. In contrast to the conventional colloids, the temperature sensitive microgel particles have different thermodynamic phase behavior from those for ordinary colloids. The Phase transitions in colloidal systems have been studied over past decades theoretically as well as experimentally by different for the fabrication of nano structured materials [13].

Volume transition of macroscopic hydrogels has been studied by different authors using different models theoretically as well as experimentally [14,15]. Flory studied the volume transition by balancing between osmotic pressure due to polymer solvent mixing and osmotic pressure due to elasticity of hydrogels [16]. While Tanaka et-al reported that the volume transition temperature of polyacrylamide hydrogel change from discontinuous to continuous by addition of ionic monomer [17]. This volume transition temperature was easily explained in Flory theory by considering change in interaction parameter. Most of these previous studies have been focused on

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macroscopic hydrogels, only few literatures are available for micro size hydrogels that is also restricted to neutral microgels [18]. The model is also applicable to micro or nanogels, as the physics of polymer solution are independent of their size.

Among various synthetic thermosensitive hydrogels, poly (N-isopropylacrylamide) (PNIPAM) is the most widely investigated example with a discontinuous volume phase transition temperature at $\sim 34.5^\circ\text{C}$ [19, 20]. However, continuous volume phase transition temperature observed for PNIPAM hydrogels, which can be modified according to specific needs by reducing cross-linking density or adding ionic monomer [21,22]. During the heating process of the microgel sample above volume transition temperature causes microgel to deswell by expel water molecules due to hydrophobic interactions and breakage of hydrogen bond between the carbonyl oxygen ($\text{R}-\text{C}=\text{O}\cdots\text{H}-\text{O}-\text{H}$) and protic hydrogen with water molecules ($\text{R}'-\text{N}-\text{H}\cdots\text{OH}_2$). The transition is reversible and microgels return to their original size by absorbing water if the solution temperature is lowered below volume transition temperature.

The measurement of microgels or nanogels particle size is the important parameter which can be analysed through several techniques. So, the size comparison between techniques is important and useful for research. Among the techniques employed in particle characterization are dynamic light scattering (DLS), atomic force microscope (AFM), transmission electron microscope (TEM) and scanning electron microscope (SEM). DLS technique could measure macromolecules colloids in solution [23]. AFM, TEM and SEM could measure particle size in dry condition [24]. AFM is ideally suited for characterizing nano or micro particles because it offers the capability of 3D visualization and both qualitative and quantitative information of the sample topology including morphology, surface texture and roughness and more important in this case the size of the particles [25]. Image analysis offers the possibility to measure both the size and the shape of particles using their two-dimensional projections. This approach is often considered as an ideal reference technique to validate other particle size distribution characterization methods.

The aim of this work was to characterize and quantitatively analyze the swelling/deswelling by Flory-Rehner theory for thermosensitive phase transition behavior.

Experimental

Materials

The monomer N-isopropylacrylamide (NIPAM), 2-acrylamido-2-methylpropane sulphonic acid (AMPS) from Sigma-Aldrich, and PEG-6000 from Merck Specialties Pvt. Ltd, India were used as received. An extra pure N, N-methylenebisacrylamide (NMBA) from SRL (India) was used as cross linker. Ammonia ceric (IV) nitrate, 99.99% pure from Sigma-Aldrich was dried in oven at 105°C for 1h prior to use. Double-distilled water drawn from a Millipore purification system was used as solvent. Reagent grade nitric acid was used for experiments.

Preparation of microgels

The copolymer microgels are synthesized via free radical precipitation polymerization in water according to procedures reported in our previous paper [26]. Polymerization was carried

out in a round bottom flask connected to a water condenser, 1 g PEG was dissolved in 10 ml of distilled water, and to this solution 4 ml of 0.1 M $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution prepared in 1N nitric acid was added and stirred for 5 minutes. Then the measured amount of N-isopropylacrylamide (NIPAM), Acrylamido-2-methylpropane sulphonic acid (AMPS), MBA as cross-linker were added and make the total volume of the solution to 50 ml. Nitrogen was purged through the solution for 1 hour to remove oxygen prior to polymerization. The polymerization was carried out at 50°C for 4 hours under nitrogen atmosphere. The solution was then cooled to room temperature and centrifuged for half an hour (10,000 rpm, Eppendorf 5810R) at 40°C and then redispersed in distilled water. This process was repeated three times and then the samples were dried in a vacuum to a constant weight.

Characterization of microgels

The structural characterization of the Microgels sample was carried out on Fourier-transform infrared spectrophotometer model FTIR-8700 SHIMADZU Japan in the range of $4400-400\text{ cm}^{-1}$. The glass transition temperatures of the microgels sample were determined using differential scanning calorimetric (DSC). Measurements were performed on a TA instruments DSC Model 2010 in nitrogen atmosphere with 2–5 mg of polymer samples weighed in aluminum pans at a heating rate of $10^\circ\text{C}/\text{min}$.

The hydrodynamic particle size and size distribution of microgel particles were measured at different temperature ranging from 25°C to 50°C at constant copolymer concentration in pure water by dynamic light scattering (DLS), Zeta-sizer Nano-S Malvern Instrument. The measurements were made at the scattering angle $\theta = 173^\circ$ and wavelength (λ) = 633nm.

The swelling ratio (SR) is widely used to characterize the volume phase transition of microgels and defined as:

$$\text{SR} = \frac{V_S}{V_C} = \left(\frac{R_S}{R_C}\right)^3 \quad (1)$$

$$\frac{V_S}{V_C} = \frac{1}{\phi} \quad (2)$$

Where R_s is the hydrodynamic radius at 25°C and R_c is the hydrodynamic radius at 50°C , V_S , V_C are the volume of swollen and collapse gels respectively, ϕ is the volume fraction of polymer.

The particle size, shape were determined by transmission electron microscope (TEM), Morgagni-268D, FEI Company. TEM images were analysed in ImageJ 1.43 q (NIH, Bethesda, MD, USA).

Theory of Swelling Equilibrium

Swelling equilibrium is attained when the total change in the free energy (ΔF_{total}) reaches to a minimum, when chemical potentials of all the mobile components in the coexisting phases are same. For the nonionic hydrogels swollen in water, the total free energy (ΔF_{total}) is the sum of the free energy of mixing (ΔF_{mix}) of the hydrogel chains and water molecules and the free energy of elastic deformation of the hydrogel (ΔF_{el}) but in the case of ionic hydrogels there is an additional term due to the presence of the counterions (ΔF_{ion}), therefore, total free energy as:

$$\Delta F_{\text{total}} = \Delta F_{\text{mix}} + \Delta F_{\text{el}} + \Delta F_{\text{ion}} \quad (3)$$

The osmotic pressure of a microgel particle determines whether the size of microgel particle tends to expand or to shrink. At the state of equilibrium swelling total osmotic pressure equal to zero, this involved derivatives of the free energy. The temperature sensitive swelling behavior of microgels was analyzed by using Flory-Rehner theory of swelling equilibrium [16].

$$\Pi_{\text{total}} = -\left(\frac{\partial \Delta F_{\text{total}}}{\partial n_1}\right) = \Pi_{\text{mix}} + \Pi_{\text{el}} + \Pi_{\text{ion}} \quad (4)$$

Where Π_{total} is the swelling pressure of the microgel particle, Π_{mix} , Π_{el} , and Π_{ion} are the mixing, elastic and ionic contributions of Π_{total} respectively, V_1 is the molar volume of the solvent and n_1 is the number of moles of solvent.

According to the Flory-Huggins theory, Π_{mix} is given by

$$\Pi_{\text{mix}} = -\frac{RT}{V_1}(\ln(1-\phi) + \phi + \chi\phi^2) \quad (5)$$

Where V_1 is the molar volume of the solvent, ϕ is the polymer volume fraction and χ is the Flory polymer-solvent interaction parameter.

In the slightly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the affine network model. If the polymer is prepared in solution, where the chains are in relaxed conformation then the elastic contribution (Π_{el}) to the swelling pressure described as:

$$\Pi_{\text{el}} = -\frac{RT\rho}{V_1\bar{M}_c}\left(\phi^{1/3}\phi_0^{2/3} - \frac{\phi}{2}\right) \quad (6)$$

Where ϕ_0 is the polymer volume fraction in the relaxed state, in the case when polymer is not polymerized in presence of solvent $\phi_0=1$, ρ is the density of the polymer; V_1 is the molar volume of the solvent and \bar{M}_c is the average molecular weight between consecutive cross-links.

The ionic contribution (Π_{ion}) to the swelling pressure is caused by concentration difference between counter ions inside the microgel particle and the outer solution and described by the Donnan theory.

$$\Pi_{\text{ion}} = RT \sum_{j=1}^N (C_j^{\text{gel}} - C_j^{\text{sol}}) \quad (7)$$

Where C_j^{gel} and C_j^{sol} are the concentration of the ions in the microgel particle and the equilibrium solution respectively, N is the number of mobile ions in the system.

For equilibrium swelling of microgels in water, equations (6) to (9) and putting $\Pi_{\text{total}} = 0$, equation-(5) becomes

$$(\ln(1-\phi) + \phi + \chi\phi^2) + \frac{\rho}{\bar{M}_c}\left(\phi^{1/3}\phi_0^{2/3} - \frac{\phi}{2}\right) - \frac{V_1 f_i}{V_r} = 0 \quad (8)$$

For the temperature dependent swelling/shrinkage polymer interaction parameter χ depends on the temperature and polymer concentration and expressed as a series expansion in powers of the cross-linked polymer volume fraction ϕ , [27]

$$\chi(T, \phi) = \chi_1(T) + \chi_2\phi + \chi_3\phi^2 + \dots \quad (9)$$

where, the coefficient χ_1 , χ_2 , and χ_3 are the functions of temperature and molecular characteristic of polymer solvent system. χ_1 is given by

$$\chi_1 = \frac{\Delta F}{K_b T} = \frac{\Delta H - T\Delta S}{K_b T} = \frac{1}{2} - A\left(1 - \frac{\Theta}{T}\right) \quad (10)$$

where $A = (2\Delta S + K_b)/2K_b$ and $\Theta = 2\Delta H/(2\Delta S + K_b)$, ΔS and ΔH are the change of entropy and enthalpy of the process respectively.

Using the value of χ_1 in equation-(10) for first order volume expansion, the expression of interaction parameter as

$$\chi = \frac{1}{2} - A\left(1 - \frac{\Theta}{T}\right) + \chi_2\phi \quad (11)$$

By introducing the value of χ in equation-(9) to obtained the equation related to temperature with the polymer volume fraction at $\Pi_{\text{total}} = 0$,

$$T_{\Pi=0} = \frac{\Theta A \phi^2}{\frac{V_1 f_i}{V_r} - \ln(1-\phi) + \phi - \frac{\rho}{\bar{M}_c}\left[\phi^{1/3}\phi_0^{2/3} - \frac{\phi}{2}\right] - \left(\frac{1}{2} - A\right)\phi^2 - \chi_2\phi^3} \quad (12)$$

This equation is used to fit our swelling data using equations-(1) & (2), since the volume fraction in relaxed state i.e in deswelling state is unknown, we performed the fit curve by assuming $\phi_0 = 0.8$.

RESULTS AND DISCUSSIONS

Particles size analysis

The microgels particles characterized by DLS were reported previously [26]. The hydrodynamic diameter was determined by Stokes-Einstein relations and the hydrodynamic diameters of microgels increases from 343.4 nm to 538 nm at 25°C and 132.5 nm to 414.8 nm at 50°C with increasing AMPS concentration in the feed recipe but its diameters reduces with increasing temperature. At 25°C, the bimodal peak with broad size distribution was observed for the microgels sample with low mole% of AMPS i.e. MG-100, MG-102 and MG-106. Only monomodal peak with narrow size distribution observed for all microgels at 50°C, which means that the process of aggregation of microgel particles was already completed. At the temperature of 50°C, which is well above the LCST of PNIPAM, the PNIPAM chains shrink and all individual particles aggregate because of attractive forces i.e. intra/intermolecular and hydrophobic interaction, which dominate over interaction between polymers with water molecules. At low temperature, the aggregates will dissociate in individual swollen particles which show broad size distribution. The intensity of microgel particles is found to be increased with increasing AMPS content, which may be due to high particle density. The polydispersity of microgels is strongly influenced by the temperature, as it decreasing with an increase in temperature. The trends of increasing hydrodynamic diameter and increase in polydispersity are consistent with TEM measurements.

Table I The characteristics of microgel particles with 0 mol%, 2 mol%, 6 mol%, 10 mol% AMPS, hydrodynamic diameter at 25°C, 50°C, swelling ratio and transition temperature

Sample Designation	AMPS Mole Fraction	Hydrodynamic Diameter (nm)		PDI		TEM (g/g)	SR	VPTT (°C)
		25°C	50°C	25°C	50°C			
MG-100	0	343.6	132.5	0.436	0.197	103	17.41	37.13
MG-102	0.0002	342.4	174.6	0.574	0.268	109.6	7.6	39.4
MG-106	0.0006	487.1	359.9	0.417	0.296	123.4	2.5	46.5
MG-110	0.001	538.1	414.4	0.290	0.305	133.1	2.1	-

Thermodynamics of phase transition behavior

The average hydrodynamic diameter, polydispersity index (PDI), swelling ratio (SR) and transition temperature (VPTT) of microgel particles with different AMPS content are listed in Table I. The sizes of the microgel particles are in the range of 133-538 nm and PDIs are in the range 0.197-0.436 depending on AMPS content and temperature. The size and PDI of microgel particles is decreasing with increased temperature.

The Figure 1 shows the temperature dependent swelling behavior of the microgels dispersion at concentration 3.0×10^{-4} g/ mL with different AMPS content in water. The hydrodynamic diameters (D_h) are measured when temperature is increased from 25°C to 50°C. The results show that the swelling and collapse behavior depend on the amount of AMPS present in the microgels and temperature of microgels dispersion. The swelling ratio (SR) of microgel particles was also decreased from 17.41 to 2.2 with increasing AMPS content from 0 to 10 mol% but it is expected that the swelling ratio should be increased with increase in hydrophilic content. This shows the inhomogeneity in network structure due to high consumptions of MBA at polymerization temperature and physical interactions. There by, strong difference in the local network motion. Microgels with 10 mol% of AMPS monomer shows less sensitive to temperature variation. The polymer-solvent interaction, cross-linking density and the dissociation degree of sulphonic acid group as a function of temperature are the important parameters for these swelling characteristics.

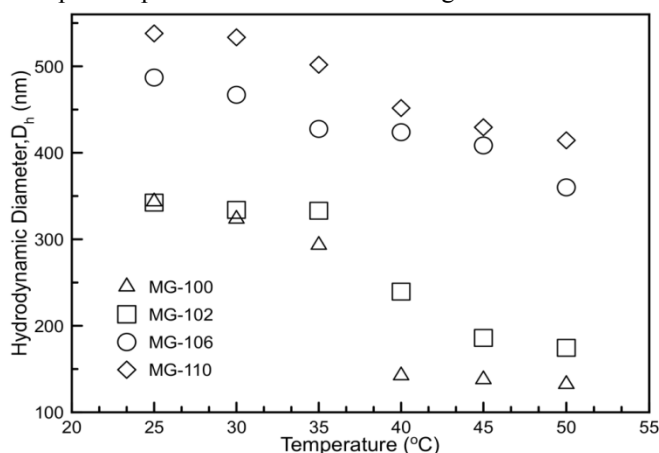


Figure 1 Hydrodynamic diameter of microgels at different temperature.

The temperature induced phase transition of hydrogels was identified by changing their volume with small change in temperature. This may be continuous or discontinuous depending on their composition and network structure [14]. The exact value of volume phase transition temperature (VPTT) determined from minimum of first derivative curve of hydrodynamic diameter at various temperature. The volume phase transition temperature of microgels is increased from 37.13°C to 46.5°C up to 6mol% AMPS concentration. An increase in the AMPS content in the network i.e increasing the degree of ionization, increase the swelled volume of the microgels and shift the transition temperature to broader range. Higher the ionic groups content inside the microgels, the higher the osmotic pressure of the counter ions inside the gel particles, so that a high temperature is required to balance this swelling pressure by hydrophobic interaction of PNIPAM chains and induce a volume phase transition to the collapsed state by expelling water molecules. Generally, the

incorporation of small amounts of ionic monomer in the PNIPAM chains increase the LCST or it disappears [28].

The Flory–Rehner theory had been used to fit the swelling data of thermosensitive non-ionic microgels with reasonable agreement [18]. The volume fraction of polymer (ϕ) has been calculated by using equation (2) are fitted in Flory–Rehner theory equation (12) to obtained temperature at $\Pi=0$. The volume fraction of polymer (ϕ) values of sample with 6 mol% and 10 mol% AMPS content could not fitted in Flory–Rehner theory equation (12). Figure 2 shows the temperature (T)-volume fraction (ϕ) phase diagram with Flory–Rehner fits of microgels. The resulting fitting parameters are listed in **Table II**. As the literature is concern PNIPAM microgel particles contain 20 wt% water at totally collapsed state therefore, we are used polymer volume fraction (ϕ_0) in the collapsed state 0.8 for calculation equation (12) [18]. For the present system, the polymer volume fraction (ϕ_0) in the collapsed state was obtained from the vertical line in Figure 3 as 0.89 and 0.82 for sample MG-100 and MG-102 respectively. The polymer volume fraction (ϕ) increases gradually withincreasing temperature until a sharp volume transition from swollen to collapsed state takes place. The volume transition of microgels was controlled by χ parameter [29]. A continuous volume transition of Microgels was observed experimentally dependence on the Flory interaction parameter.

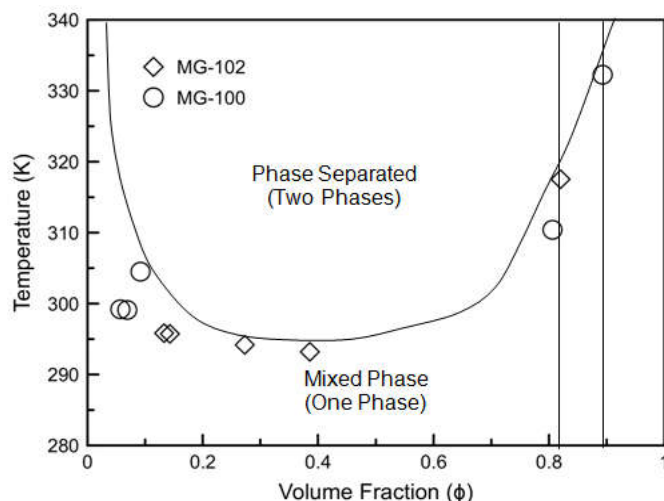


Figure 2 Flory–Rehner fitted curve for of microgels with AMPS content of 0 mol% and 2 mol%.

Table II The results of the Flory-Rehner analysis of microgels

Sample Designation	AMPS Mole Fraction	ϕ_0	χ_2	N	ΔH (J/mol)	ΔS (J/mol K)	A	Θ (K)
MG-100	0	0.8	0.519	572	-12037.16	-34.79	-4.67	309.03
MG-102	0.0002	0.8	0.544	28	-9265.60	-26.18	-3.64	305.31

The temperature dependent polymer-solvent interaction parameter (χ_2) is one of the basic structural parameter of microgels fit in the equation (10), which is related to polymer volume fraction (ϕ) by equation (11) and its value increasing with increased AMPS content. At low temperature that is for high swelling ratio χ is reduce to χ_1 [30].The variation of χ parameter as a function of $1/T$ for microgel MG-100 and MG-102 is shown in Figure 3. The χ values of microgels at low temperature are located around 0.5. This assumes that the hydration of microgels depends on the hydrogen bonding

interaction between water molecules and amide groups, thus the enthalpy and entropy contribution to χ parameter is constant.

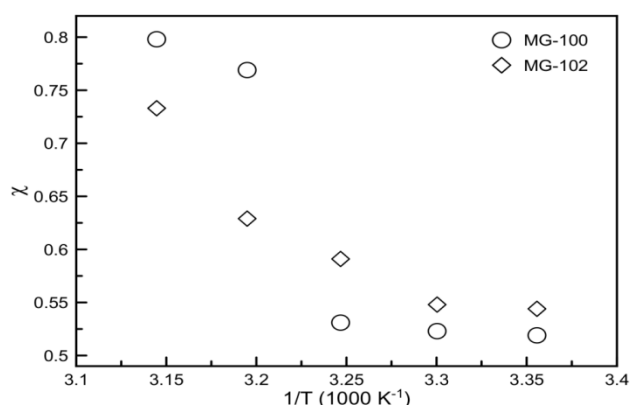


Figure 3 χ parameter as a function of inverse temperature ($1/T$).

The values of ΔH and ΔS appearing in the χ_1 parameter in equation (10) were calculated from the slope and intercept of straight line obtained between χ vs $1/T$ at low temperature for microgel MG-100 and MG-102. The values of ΔH and ΔS are given in Table II. The negative values of enthalpy and entropy of hydrogels characterized that the polymer solvent system possesses the lower critical solution temperature (LCST)[31]. The value of enthalpy decreasing with increased AMPS content in the feed composition where as entropy values slightly decreased.

The number of segments between the crosslinked points (N) was found to be 572 and 28 for sample MG-100, MG-102 respectively. A high value of N give the weakly crosslinked polymer network structure, where as low N values gives highly crosslinked polymer structure. In our system crosslinker N , N -methylene bisacrylamide (NMBA) amount was constant for all microgel samples and expected to have constant crosslink density. The increased in crosslink density can be explained as ion pairs attract each other due to dipole-dipole interaction and physical cross-links in the hydrogels thus, cross-link density increases. The behavior is similar to results reported elsewhere by different authors [10,32].

The Θ - temperature value observed decreased with increase AMPS content in microgels where as VPTT value increased with increase in AMPS content in the same composition and its value disappearance when AMPS content exceed 6 mol%.

The microgel particles swell or de-swell depending on the sign of the osmotic pressure. The mixing, elastic and ionic in equation (4) are the different osmotic components that contribution to the total osmotic pressure of microgels. Figure 4 shows the variation of the osmotic pressure as a function of the polymer volume fraction for microgels MG-100 and MG-102. The osmotic pressure of microgels were calculated from equation (4) and plot as a function of polymer volume fraction which gives a continuous curves. An osmotic pressure basically expands the microgel particles and an elastic pressure that resist its expansion. It has been observed that during the heating processes of microgels, the osmotic pressure is increasing with increases of polymer volume fraction and temperature. The vertical line in Figure 4 shows the increase in osmotic pressure at $T = 45^\circ\text{C}$ and at $\phi = 0.89$ for MG-100 i.e MPa which is higher than MG-102. In practice microgels with AMPS should have high osmotic pressure and high swelling

pressure due to its high hydrophilicity/high ionizability. This can be probably caused by the high cross-link density of MG-102 due to physical cross-linking of $-\text{NH}$, $-\text{OH}$ and $-\text{SO}_3\text{H}$ or high consumption of cross-link agent N , N -methylenebisacrylamide (NMBA) during polymerization processes.

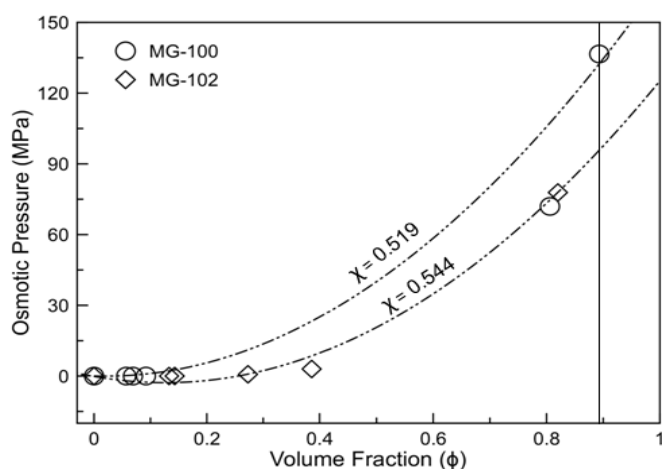


Figure 4 Plot of the osmotic pressure with polymer volume fraction for microgels MG-100 and MG-102

CONCLUSIONS

Temperature sensitive copolymer microgels with different molar composition were prepared through soap free emulsion polymerization and shows decreasing in swelling ration with increase in AMPS concentration. We investigate the influence of the AMPS monomer concentration on particle size, distribution and shape were measured by DLS, TEM. The particle size of microgels was found to be larger size in DLS measurements and comparable size between TEM measurements. The volume phase transition temperature (VPTT) of microgels was increased with increasing AMPS content and disappearance when AMPS content more than 6mol%. The swelling behavior of the microgel particles could be described using the Flory–Rehner theory only to 2 mol% of AMPS content. Thus, the Flory–Rehner theory partially satisfies to describe the swelling behavior of microgels for low contents of an ionic comonomer.

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