A Study on Thermal Behavior and Degradation kinetic of Microgels Based on PEG/Poly (NIPAM-co-AMPS)

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ABSTRACT

Temperature-responsive copolymeric microgels were synthesized via free radical polymerization of N-isopropylacrylamide (NIPAM) and acrylamido-2-methylpropyl sulphonic acid (AMPS) in presence of PEG as microinitiator under emulsifier free conditions. The thermal behavior of microgels in water was studied by dynamic light scattering (DLS) at different temperature. The temperature-dependent equilibrium constant derived from swelling data obtained from DLS and thermodynamic quantities are measured by Van't Hoff analysis. The thermogravimetric analysis was used for the evaluation of thermal stability and degradation kinetics of different microgel samples. The integral procedure decomposition temperature (IPDT) used to estimate the inherent thermal stability of microgels including volatile parts. The IPDT of microgel sample without AMPS was 368.99°C and the IPDT increased with increasing AMPS concentration in the feed composition. Thus, the thermal stability increased with increasing the AMPS concentration in the samples. The activation energy (Ea) of different microgel samples were calculated by using Broido and Horowitz & Metzger methods. The activation energy was found to be increases from 27.36 KJ/mol to 53.66 KJ/mol depending upon AMPS concentration in the feed composition. The glass transition temperature (T_g) of the microgel samples were examined by differential scanning calorimetric analysis. The stability and thermal degradation kinetics are important for designing copolymer blends in different area of applications.

Key words: Microgels, Thermal degradation, Kinetic parameters, Integral procedure, Decomposition temperature, Activation energy.

1. INTRODUCTION

Microgel particles are three-dimensional cross-linked polymeric network structures in the range of 50 nm to 5 μm that swell in good solvents depending on the functional groups and cross-linking density. The swelling behavior of microgel particles is affected by many stimuli, including forces [1], temperature [2,3], pH [4,5] ionic concentration [6,7], and electric field [8,9].

Temperature responsive microgels are the most widely studied microgel particles among all stimuli. These microgels are being developed for diverse applications, such as drug delivery [10-20], biosensors [21-23], chemo-mechanical devices [24], separation/purification technologies [25], formation of responsive interfaces [26-29]. Textile [30], thin film and coating [31]. One of the most striking properties of temperature-sensitive poly (N-isopropylacrylamide) (PNIPAM) microgels is that they have the ability to undergo a reversible volume phase transitions temperature at ~34.5°C [32,33]. Below this temperature, the microgel particles are in a highly swollen state in the aqueous environment. However, when the temperature is raised above the VPTT, the polymer network collapses and expelling most of its water content along with any potentially dissolved molecule from the gel structure. The change in this phase transition is controlled by competing elastic, solvency, and ionic contributions.

The swelling properties of microgel particles are related to internal structure of individual particle. Wu *et al*., [34] investigated the kinetics of particle formation and internal structure of PNIPAM particles. They found that during the particle formation the cross-linker monomer (NMBA) was incorporated into the microgel structure faster than the N-isopropylacrylanide (NIPAM) monomer. This result implies that the different polymerization rates of the monomers lead to the formation of inhomogeneously cross-linked microgel particles. Hoare and Pelton [35] have also investigated how the functional group distribution (-COOH) affects the swelling of microgel particles. They found that microgel particles do not have a uniform distribution of comonomers within the particles, which in turn have an effect on the particle size distribution, swelling, stability, optical properties of microgels. It is well known that heat treatment of polymeric materials changes their morphological structure at temperatures higher than their glass transition temperature (Tg) which may lead to alter their electrical, optical, and thermal properties etc.

Thermal analysis is a very powerful technique to study the polymers structure [36]. To date, only differential scanning calorimetric (DSC) analysis was used to study the phase transition of PNIPAM hydrogels [37-39].

In this article, we are studying the phase transition using the Van't Hoff equation and thermal analysis study of copolymer microgels. Thermal

gravimetric analysis (TGA) and DSC analysis were used for this study. The Broido and Horowitz-Metzger approximate methods are used to calculate the activation energies for comparison.

2. EXPERIMENTAL

2.1. Materials

The monomer NIPAM, acrylamido-2-methylpropyl sulphonic acid (AMPS) was purchased from Sigma-Aldrich and were used as received, PEG-6000 Merck Specilities Pvt. Ltd., Mumbai, N,N'-methylenebisacrylamide (MBA), ammonium ceric (IV) nitrate, 99.99% Sigma-Aldrich was dried in oven at 105°C for 1h prior to use, reagent grade nitric acid.

2.2. Preparation of Microgels

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 to this solution 4 ml of 0.1 M $(NH_4)_2Ce(NO_3)_6$ solution prepared in 1N nitric acid was added and stirred for 5 min. Then the measured amount of NIPAM, acrylamido-2-methylpropyl sulphonic acid (AMPS) and MBA as cross-linker were added. Nitrogen was purged through the solution for 1 h to remove oxygen prior to polymerization. The polymerization was carried out at 50°C for 4 h under nitrogen atmosphere. The solution was then cooled to room temperature and then centrifuged 0.5 h (10.000 rpm, Eppendrof 5810R) at 40°C and then redispersed in distilled water. This process was repeated 3 times and then the samples were dried to a constant weight.

2.3. Characterization of Microgels

The hydrodynamic particle size and size distribution of microgel particles were measured at different temperature ranging from 25 to 50°C at constant copolymer concentrations in pure water by dynamic light scattering (DLS), Zetasizer Nano-S Malvern Instrument. The measurement was made at the scattering angle θ =173°, wavelength (λ) = 633 nm. The time average scattering intensity correlation functions were obtained with an acquisition time of 30 S for each run. The results of size distribution were analyzed with a Laplace inversion program (CONTIN). Thermal degradation of gels was investigated by a thermogravimetric analyzer (Model Perkin Elmer, Pyris, Dimond TGA/DTA) from room temperature to 750°C with heating rate 10°C/min. under nitrogen atmosphere.

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°C/min.

3. RESULTS AND DISCUSSION

3.1. Thermal Behavior in Water

Thermo-responsive microrogels were prepared by free-radical copolymerization of NIPAM and AMPS using PEG as macroinitiator in presence of MBA as cross-linking agent in water at 50°C. During the reaction PEG macroradicals were formed upon redox reaction of the –CH_2OH end groups with Ce(IV) ([Ce(IV)]/[OH end group] 1.2/1) in acidic medium [30]. Macroradical initiates water-soluble AMPS, MBA, and NIPAM monomers which then grow in solution until they reach a critical chain length to become colloidal precursor particles. Either the precursor particles deposit onto an existing polymer particle or aggregate with other precursor particles until they form a particle sufficiently large to be colloidally stable. PEG also helps to increase the colloidal stability of precursor particle. These stable particles create nuclei for growing polymer chains, indicated by turning of clear reaction mixture into milky. The formation of particles through precipitation polymerization mechanism is called soap-free emulsion polymerization. Due to the presence of negatively charged AMPS comonomer in the polymerization system, there is strong electrostatic repulsion among the sulfonate anion (-SO_3^-) which results in the expansion of network structure of microgels and have high water absorption properties.

The characterizations of particles size and particles size distribution of temperature-responsive microgels were investigated by means of DLS at different temperatures was reported in our previous article [40]. The swelling curves obtained show two-step process, where gel particles shift from swollen to collapsed state at temperature range 30–40°C as shown in Figure 1. The phase transition is an equilibrium process of the competing swollen and collapsed state. The equilibrium constant K_{eq}, which is equal to the ratio of (Collapsed)/(Swollen) [41] and determined from the swelling data of microgels. The cloud point measurement or DSC measurement done extensively used for the determination of phase transition of temperature of microgels [37-39]. Here, van't Hoff equation is used to measure ΔH, ΔS, ΔG of microgels sample from van't Hoff plot obtained by plotting lnK_{eq} versus 1/T, which show two-stage process with different enthalpy, entropy component. The slope and intercept of the straight line give ΔH and ΔS, respectively, as shown in Figure 2.

The enthalpy for stage I is endothermic i.e 6.29 and 2.13 kJ/mol; entropy –6.53 and –5.32 J/mol K for MG-100 and MG-102 respectively. In stage I microgels show water swelling properties due to the formation of hydrogen bond between water molecules and amide groups of PNIPAM, PAMPS, and ionization of sulfonic acid group in PAMPS. At the transition temperature hydrogen bonding between the polymer and water molecules disrupted, result dehydration of the system, and water is released out of the polymer network with a large gain in entropy. The enthalpy for the Stage II is also endothermic, i.e., 12.18 and 26.01 kJ/mol; entropy value 4.26 and 5.45 J/mol K for MG-100 & MG-102, respectively. The enthalpy obtained in Stage II is comparable to water hydrogen bond ΔH≈ 10 kJ/mol [42], thus; it assigned the loss of hydrogen bond above the transition temperature of polymer.

3.2. Thermal Stability

Thermogravimetric analysis is one of the common techniques to investigate the thermal stability and decomposition of different polymeric materials as a function of temperature or time [43]. Figure 3 shows the TGA thermograms of microgels with different concentrations
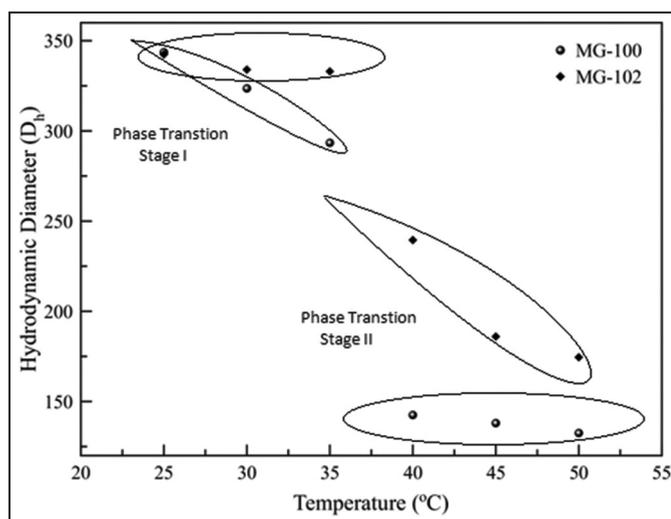
Figure 1: Hydrodynamic diameter of microgels at different temperature.
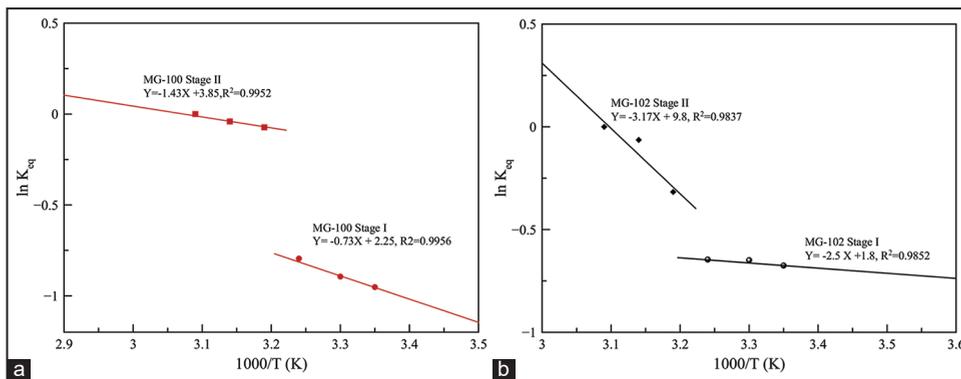
Figure 2: The van't Hoff plot for (a) MG-100, (b) MG-102.
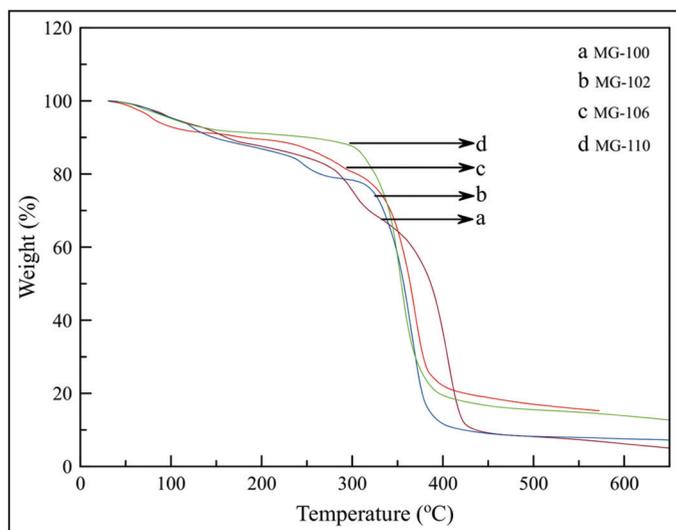
Figure 3: TGA thermograms of microgel samples with different AMPS content.
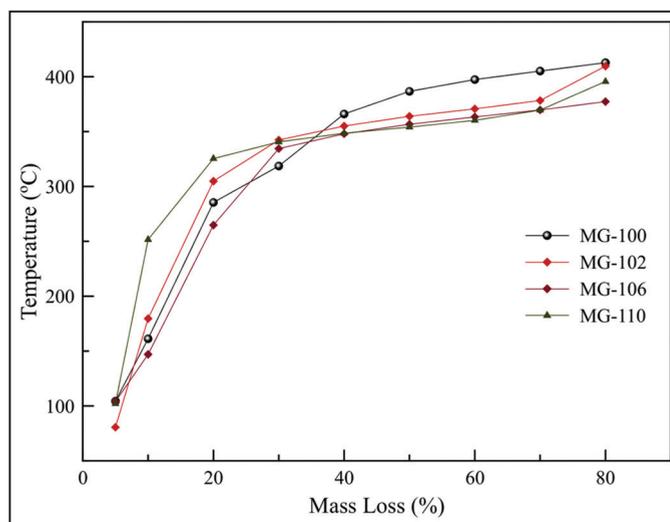
Figure 4: The weight loss temperature versus weight loss for microgel samples with different AMPS content.

of AMPS, from room temperature to 750°C in nitrogen atmosphere at heating rate 10°C/min and it observed that the rate of degradation of microgels slowed down with increasing AMPS concentration in the feed composition. Table 1 shows the characteristic temperature of thermal degradation of different microgels evaluated from TGA thermograms. It was observed that the microgels decomposed in two steps. The initial decomposition temperature of microgels samples increases from 39°C to 59°C whereas final decomposition temperature remains same for the sample MG-106 and MG-110. The weight loss involved in the first decomposition varied from 7 to 11% and in the second step of decomposition in ranged from 64 to 73%. All the microgel samples decomposed in the temperature range of 40–47°C. Figure 4 shows the weight loss temperature versus weight loss of microgel samples with different concentrations of AMPS. The thermal stability of sample MG-100 and MG-102 was lower than MG-106 and MG-110 and the weight loss % decreases with increasing AMPS concentration in the feed composition.

The integral procedure decomposition temperature (IPDT) which included the volatile parts of polymeric materials proposed by Doyle [44] and used to measure the inherent thermal stability of polymeric materials [45,46]. IPDT was calculated as per Doyle's method using the relation:

$$IPDT(°C) = A^* K^* (T_f – T_i) + T_i \qquad (1)$$

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \qquad (2)$$

$$K^* = \frac{S_1 + S_2}{S_1} \qquad (3)$$

Where A* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, T_f is the final experimental temperature. Figure 5 shows the representation of S_1, S_2, and S_3 for calculating A* and K*. The calculated results are given in Table 2, the IPDT of microgel samples found to be increase from 368.99 to 482.43°C with increasing the content of AMPS concentration. The incorporation of AMPS component improved the thermal stability of microgels by increasing the physical cross-linking or intermolecular hydrogen bonds between ether oxygen atoms in PEG chain and amide groups in microgels network.

The glass transition temperature (T_g) of the microgels was measured by DSC. Figure 6 presents the DSC thermogram of different microgels. The microgels sample MG-100 show a T_g at 114.5°C (ΔH 1.052 J/g; C_p 1398.8 mJ/°Cg) and MG-106 show at T_g at 144.96°C (ΔH 2.5 J/g; C_p 2320.69 mJ/°Cg). The glass transition temperature of microgel samples increases with increasing AMPS content in the samples. Glass transition temperature (T_g), enthalpy of transition (ΔH), and heat capacity (C_p) value obtained from DSC scans for different microgels are given in Table 2. The glass transition temperature depends on chain flexibility or mobility and polarity of polymeric materials, as the flexibility decreases when the glass transition temperature increased [47]. The incorporation of sulfonic acid makes the microgel structure more polar and rigid due to the inter or intramolecular force of interactions.

Table 1: Characteristic temperature for thermal degradation evaluated from TGA.

Sample	Temperature Range for Step-I (°C)	Weight loss Step-I (%)	Temperature Range for Step-II (°C)	Weight loss Step-II (%)	Decomposition temperature Range (°C)	ΔT (°C)	IPDT[a] (°C)	IDT[b] (°C)
MG-100	39–104	7	267–437	64	39–411	372	368.99	39
MG-102	45–177	11	267–438	73	45–438	393	383.91	45
MG-106	55–152	10	278–468	67	55–406	351	387.27	55
MG-110	56–151	7	295–475	69	56–407	351	482.43	56

[a]Integral procedural decomposition temperature; [b]Initial decomposition temperature.

Table 2: Kinetic parameters for the decomposition of different Microgel samples.

Sample	Stage	Temperature (°C)[a]		T_g^b (°C)	ΔH^b (J/g)	C_p^b mJ/°Cg	Activation energy, E_a (KJ/mol)		R^2
		Temperature range	Maximum temperature				Broido	Horowitz-Metzger	
MG-100	I	39–104	104	114.5	1.052	1398.8	14.56	27.36	0.8779
	II	267–437	437						
MG-102	I	45–177	177	130.1	1.671	1594.2	16.66	46.06	0.9296
	II	267–438	438						
MG-106	I	55–152	152	144.9	2.5	2320.6	19.37	50.3	0.9566
	II	278–468	468						
MG-110	I	56–151	151	156.4	9.43	1749.6	24.65	53.66	0.8725
	II	295–475	475						

[a]From TGA thermograms, [b]From DSC thermograms.
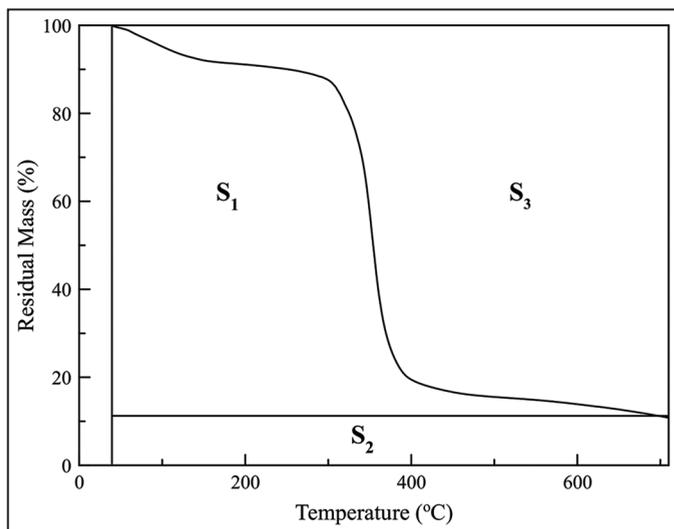
Figure 5: Schematic representation of S₁, S₂ and S₃ for A* and K*.

Figure 6: The DSC thermograms of different microgel samples.

3.3. Kinetics of Thermal Degradation in Nitrogen Atmosphere

The degree of conversion (α) is defined as the ratio of the actual weight loss to the total weight loss.

$$\alpha = \frac{M_o - M}{M_o - M_\infty} \quad (4)$$

Where M is the actual weight at temperature T; M_o is the initial weight and M_∞ is the weight at the end of non-isothermal experiments. The rate of degradation dα/dt, depends on the temperature and the weight of samples as given by equation-(1) [36].

$$\frac{d_\alpha}{d_t} = k(T)f(\alpha) \quad (5)$$

Where k(T) is the rate constant and f(α) is a function of conversion.

If $k(T) = A \exp^{(-Ea/RT)}$ and $f(\alpha) = (1-\alpha)^n$ then equation-(1) can be expressed as:

$$\frac{d_\alpha}{d_t} = A \exp^{(-Ea/RT)} (1-\alpha)^n \quad (6)$$

Where A represents the pre-exponential factor; E_a is the activation energy; R is the gas constant; T is the absolute temperature and n is the reaction order.

$$\frac{d_\alpha}{(1-\alpha)^n} = \left[\frac{A \exp^{(-Ea/RT)}}{\beta}\right]dT \qquad (7)$$

Where β is the rate of heating, A large number of pyrolysis process is represented with as first-order reaction [48]. Therefore, we assume n = 1 for further calculation. Integrating the equation-(4), we get

$$\ln(1-\alpha) = -\frac{A}{\beta}\int_{T_o}^{T_l} \exp^{(-Ea/RT)}dT \qquad (8)$$

The integration of equation-(8) is used to calculate the Horowitz and Metzger approximate.

$$\ln(1-\alpha) = -\frac{ART_m^2}{\beta E_a}\exp\left[\frac{-E_a^{(1-\theta/T_m)}}{RT_m}\right] \qquad (9)$$

Where $\theta = T - T_m$, T_m is the temperature of maximum degradation rates, when $T = T_m$, $\theta = 0$ and $\ln(1-\alpha) = -1$, the equation-(6) becomes

$$-1 = -\frac{ART_m^2}{\beta E_a}\exp\left[-E_a/RT_m\right] \qquad (10)$$

The substitution of this equation in equation-(9), we get

$$\ln(1-\alpha) = -\exp\left(\frac{E_a\theta}{RT_m^2}\right) \text{ or}$$

$$\ln(-\ln(1-\alpha)) = \frac{E_a\theta}{RT_m^2}$$

Thus, the plot of $\ln(-\ln(1-\alpha))$ versus θ gives a straight line whose slope is E_a/RT_m^2, and this procedure to calculate the activation energy is called the Horowitz-Metzger method [49].

In the Broido method, $\exp\left(-E_a/RT\right) \cong \left(T_m/T\right)^n \exp\left(-E_a/RT\right)$, The temperature range of analysis is close to T_m [48][36]. The equation-(5) may be written as

$$\ln(1-\alpha) = -\frac{ART_m^2}{\beta E_a}\exp\left(-E_a/RT\right)$$

Or

$$\ln(-\ln(1-\alpha)) = -\frac{E_a}{RT} + \text{constant}$$

By plotting $\ln(-\ln(1-\alpha))$ versus $1/T$ gives the straight line with slope $-E_a/R$, the activation energy is calculated from the slope. Figures 7 and 8 show the application of Broido and Horowitz-Metzger method for different samples. The activation energy obtained by both the Broido and Horowitz-Metzger methods are presented in Table 2. The difference in the values of the activation energy observed when it compared for the same composition of the samples. The different values of activation energy obtained are due to calculation method for a particular composition of microgel samples, i.e., activation energy calculated by Horowitz & Metzger method gives higher values. The activation energy calculated by both methods increased with increasing the AMPS content in the feed composition. This indicates that when
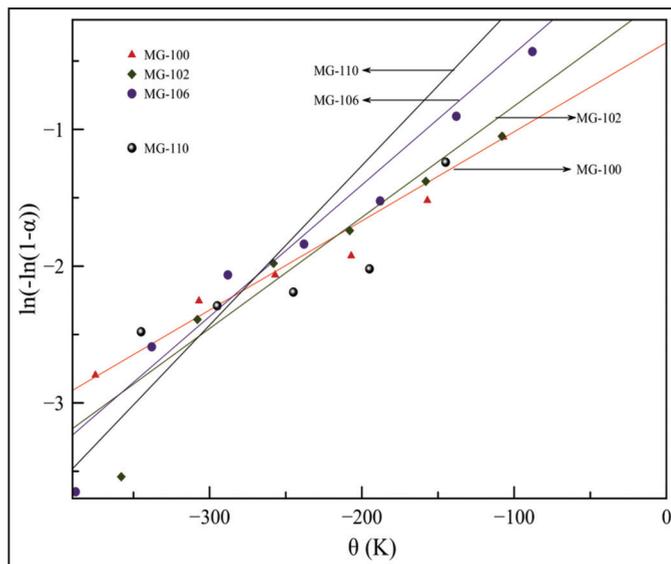
Figure 7: $\ln[-\ln(1-\alpha)]$ versus θ plots using Horowiz-Metzer method for the Microgel samples.
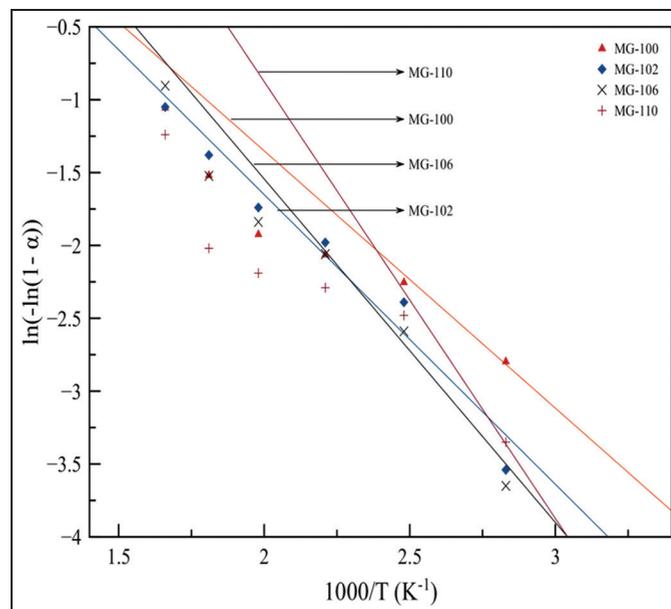
Figure 8: $\ln[-\ln(1-\alpha)]$ versus $1/T$ plots using Broido method for the Microgel samples.

energy barrier increases the weight loss process becomes more stable at higher temperature in respect to the composition of AMPS. The degradation of microgel samples depends on AMPS concentration with distinct activation energies from 27.36 KJ/mol to 53.66 KJ/mol.

4. CONCLUSION

Temperature-sensitive microgels with different compositions were prepared by soap-free emulsion polymerization. The composition of the microgels was controlled by adjusting the monomer feed composition and investigated the influence of the AMPS monomer concentration on phase transition behavior, thermal stability, and kinetics of thermal degradation for the different microgel samples. The thermal stability of microgel samples was improved by incorporation of AMPS monomer, thus it reduce the possibilities of physical changes during the processing and service condition. The activation energies (E_a) for all

the microgel samples increase with increasing AMPS concentration in the feed composition which is an indication of relative thermal stability of the microgels. Both Broido and Horowitz-Metzger methods give the different calculation results of activation energies. The variations of the calculated values may be due to the approximation used to evaluate the respective kinetic equations.

5. ACKNOWLEDGMENT

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