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In situ monitoring of energy release in real time during gelation of acrylamide (AAm)

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Abstract

Temperature variation and optical transmission was monitored in real time during the free radical crosslinking copolymerization (FCC) of acrylamide (AAm) and *N*,*N'*-methylenebis(acrylamide) (Bis). Gelation experiments were initiated at various onset temperatures (T_{on}). During gelation the temperature rose then decreased to its initial value as the gelation time increased. That is explained with the energy release (Gelation activation energy) during the polymerization process. Gelation activation energies, ΔE_G were measured and found to be increased as the onset temperature, T_{on} was increased. It was observed that transmitted photon intensities, I_{tr}, decreased dramatically at the reaction time, which were attributed to the increase in scattered light intensity, I_{sc}, during the formation of interconnected microgels in the system. Increase in I_{sc} was modeled using Rayleigh's equation where reaction time was found to be proportional to the volume of the microgels. It was observed that a number of microgels increased as the onset temperature, T_{on} was increased. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gelation activation energy; Microgels

1. Introduction

Extensive work has been reported in the literature for the physical properties of PAAm gels, however very few of them are concerned with the formation mechanism by free-radical crosslinking copolymerization (FCC). FCC of AAm and Bis monomers in water solution was studied extensively [1,2] and inhomogeneous crosslinking in PAAm gel was attributed to the difference in the vinyl group reactivity. Recently AAm and Bis copolymerization was investigated in water at a monomer concentration of 1.8 w/v % [3]. Experiments indicate that 80% of pendant vinyl groups are consumed by cyclization reactions and it was observed that the equilibrium degree of swelling of the PAAm gel is independent of their crosslinker content. These results suggested the formation of microgels prior to the onset of macrogelation, and as the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends. The microgels seem to act as the junction points of the final heterogeneous network.

Polyacrylamide (PAAm) gels are usually obtained by free-radical crosslinking copolymerization of acrylamide (AAm) and *N*,*N'*-methylenebis(acrylamide) (Bis) monomers [4]. Since AAm is solid at room temperature where the polymerization is usually performed, it is necessary to carry out the reaction in an aqueous environment. PAAm gels are hydrophilic gels which are called 'hydrogels'. Several studies showed that the hydrogel structure and thus the hydrogel properties, strongly depend on the initial degree of dilution of AAm [5–7]. As the amount of water increases during polymerization, the network structure becomes increasingly loose and it is unable to form a continuous network above a critical amount of water [8]. The same critical behavior can be expected when one decreases the Bis concentration in AAm polymerization is decreased, i.e. no continuous network can be formed below a critical amount of Bis content. It was also reported that acrylamide based hydrogels present heterogeneous crosslinking distribution [9,10]. The formation of the heterogeneities of crosslinked polymer gels has been the subject of great interest for many years. These structural inhomogeneities of a gel affect its physical properties such as optical and phase properties [10]. The effect of heterogeneities of the network on swelling equilibrium of PAAm gel during water absorption were studied by Hsu et al. [9]. Recently FCC of AAm and Bis were studied using optical transmission technique in our laboratory, where it was observed that transmitted light

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intensity, I_{tr}, decreased dramatically as AAm is copolymerized with Bis, indicating the formation of microgels [17,18]. Gel swelling and drying processes of PAAm gels are also reported using the same technique [19]. Here decrease in I_{tr} is attributed to the increase in scattering intensity which originated from the contrast between frozen blob clusters and holes in the swollen gel. In drying, increase in I_{tr} is observed due to homogenization of the gel.

The aim of this work is to monitor temperature variation and optical transmission simultaneously in real time during the copolymerization of AAm with Bis. In situ polymerization processes were carried out at six different onset temperatures (T_{on}) for a given Bis content. It was observed that transmitted photon intensity, I_{tr}, decreased dramatically while the temperature increased during gelation processes. Increase in temperature was explained with the exothermic reaction during polymerization which produced gelation activation energies ΔE_G. Decrease in I_{tr} was attributed to the increase in scattered light intensity, I_{sc}, from the gel due to spatial phase separation, which appeared during copolymerization of AAm with Bis. The increase in I_{sc} against time was modeled using Rayleigh's equation and it was observed that volume, v of PAAm particles grows linear with time.

2. Light scattering

Light scattering is caused by density and concentration fluctuations. Light is scattered only when a light wavelength, λ, is greater than the size of a particle of the dispersed phase. If λ is much smaller than the particle diameter, light is reflected. If the intensity of incident light is I_o and on passage of the light through a dispersed medium, the incident intensity is reduced to I_{tr} as a result of scattering. Rayleigh derived an equation by excluding the absorption of light by the medium, which connects I_o with I_{sc}. The intensity of light scattered per unit volume of a dilute system at unit distance as follows:

$$I_{sc} = I_o k c v^2 \lambda^{-\eta} \tag{1}$$

This equation is valid for spherical particles which do not conduct electric current and are small compared with the wavelength, λ, of the incident light. In Eq. (1) k is given by

$$k = 24\pi^3 \left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right) \tag{2}$$

where n_1 and n_0 are the indices of refraction of the dispersed phase and the dispersion medium respectively. The volume of a single particle is represented by v and c is the numerical concentration, i.e. the number of particles in 1 cc of the system in Eq. (1). Rayleigh's equation determines the opalescence of the medium and can be used for particles where the size is not more than 0.1 of the wavelength of light i.e. for particles of diameters from 40 to 70 nm. In this case I_{sc} changes in inverse proportion to the fourth power of λ ($\eta = 4$) [11]. When the size of particles in the dispersed medium becomes much greater than λ, light is no more scattered but reflected, regardless of the wavelength of the incident light. If the particles are too large in size, reflection of light from them increases which causes the reduction of the intensity of scattered light, however in the mean time the intensity of light scattering decreases as the particle size decreases. Therefore dispersed medium scatters light to the greatest extent. In conclusion Rayleigh's equation provides the following important informations to be used: For particles of a given size, the intensity of scattered light is directly proportional to the numerical concentration. This principle can be used to determine the concentration of the dispersed phase by measuring I_{sc} in the system.

3. Microgels

A microgel is an intramolecularly crosslinked macromolecule which is dispersed in normal or colloidal solutions, depending on the degree of crosslinking and on the nature of the solvent [12,13]. Microgels are molecular species on the border between normal molecules and particles [14,15]. Contrary to linear and branched macromolecules, the surface of microgels is rather fixed, thus approaching the characteristics of solid particles. As to their size, it is difficult to define a limit because the transition from a microgel to a larger polymer particle, e.g. in coarser polymer dispersions, it is gradual. Nonetheless, optical criteria related to solubility may be applied to distinguish microgels from larger polymer particles as, contrary to normal polymer dispersions, microgels form colloidal, opalescent or even clear solutions. For a long time, microgels were rather a nuisance to the science and technology of polymers because they interfered with the characterization of macromolecules by light scattering.

4. Experimental

Gels were prepared by using 2.0 g of AAm and 40 mg of ammonium persulfate (APS) as an initiator by dissolving them in 30 cc of water in which 20 μl of tetramethyl ethylenediamin was added as an accelerator [17,18]. Six different gelation processes were made at 25, 30, 35, 40, 45 and 50°C onset temperatures by adding 175 mg Bis into each sample. Gelations were performed in 1.0 × 1.0 cm quartz cells equipped with a heat reservoir. Temperature was monitored in real time and in situ, photon transmission measurements were performed simultaneously using Perkin Elmer UV Visible (UVV) spectrometer at 450 nm wavelength [17,18]. Photon transmission intensities, I_{tr}, were also monitored in real time by using the time drive mode of the spectrometer during copolymerization of AAm with Bis at six different onset temperatures.

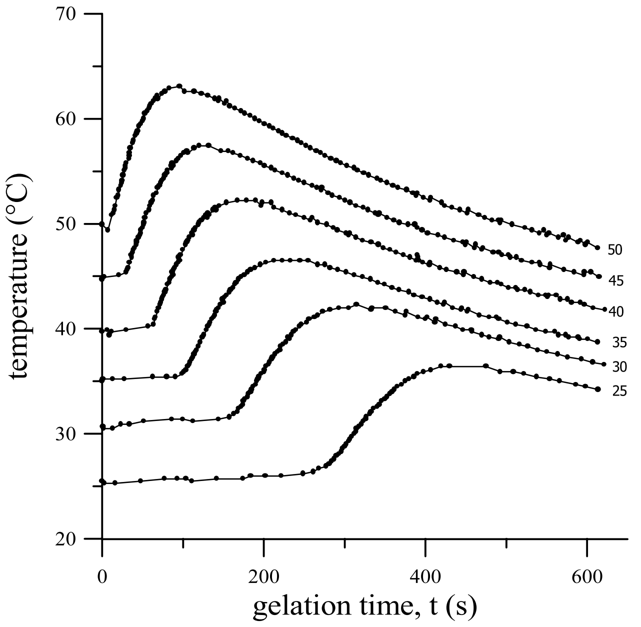

Fig. 1. In situ measured reaction temperatures vs. gelation time. Numbers on each curve present the onset temperatures, T_{on} in °C.

5. Results and discussion

5.1. Energy release during gelation

Increase in temperature against time during gelations at each onset temperature, T_{on}, are given in Fig. 1. Typical I_{tr} curves against reaction time for six different onset temperatures, T_{on}, are given in Fig. 2. In Figs. 1 and 2 it can be seen that as the temperature increased I_{tr} intensity decreased dramatically after a certain time. Thus indicated that as energy is released strong opalescence occurs during gelation for all samples. Here we have to state that 'increasing the onset temperature, T_{on}, decreases the onset of gelation time, t_o'. Fig. 3(a) and (b) compared temperature increase with I_{tr} in time for the samples gelled at 25 and 45°C onset temperatures respectively.

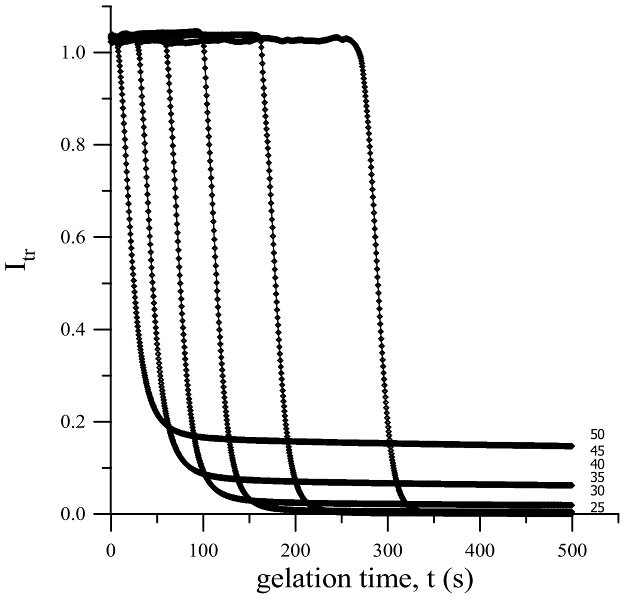

Fig. 2. Variation in transmitted photon intensities, I_{tr} vs. gelation time, t during in situ FCC for six different onset temperatures, T_{on} at 450 nm wavelength. Numbers on each curve present the onset temperatures, T_{on} in °C.

To interpret the above results the following naive kinetic model was proposed. The first step in free-radical polymerization is the decomposition of the initiator molecule with the rate constant, k_i, into two species carrying unpaired electrons called free radicals. A free radical can then react to open the double bond of a vinyl monomer and add to it, with one electron remaining unpaired. In a few seconds or

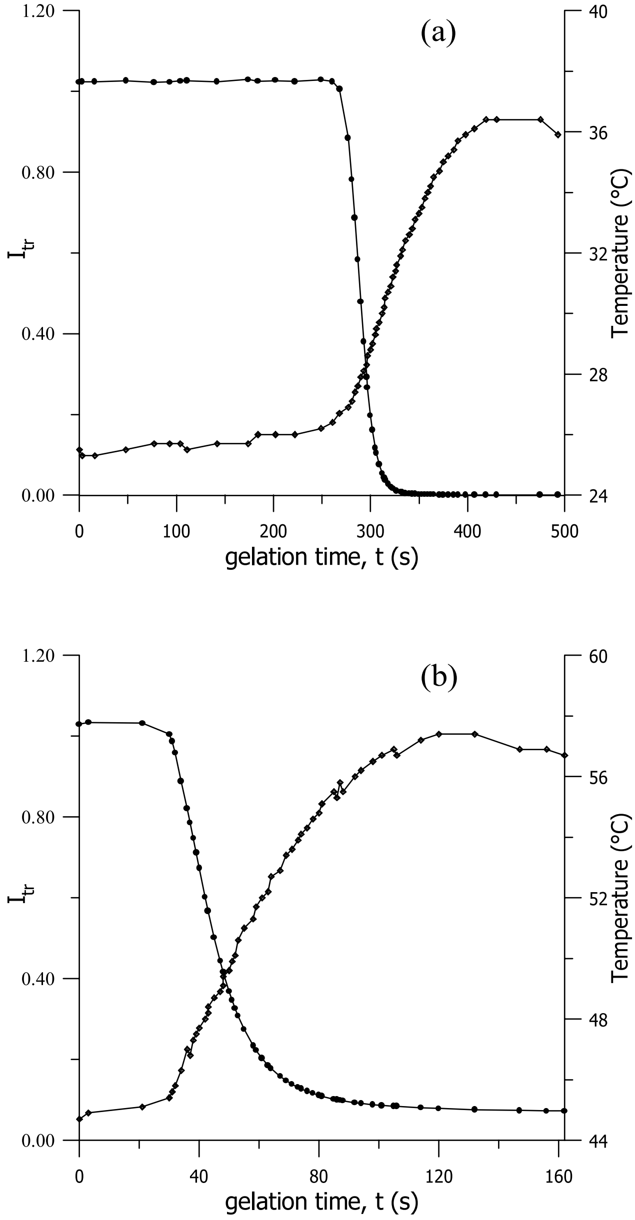

Fig. 3. Comparing of temperature vs. I_{tr} behavior for the samples of (a) 25 and (b) 45°C onset temperatures.

less, many more monomers add successively to the growing chain with the propagation rate constant, k_p. Finally two radicals react to end each other's growth activity and form one or more polymer molecules [16]. This bimolecular process is called termination and is identified with the rate constant k_t. During the free-radical crosslinking copolymerization (FCC), addition of divinyl monomers to the growing chain results in the formation of polymer molecules with reactive sites ('pendant vinyl groups'). These reactive sites on polymer chains offer the possibility of forming chemical structures of macroscopic dimensions called polymer gels. The rate of consumption of monomer is usually called the rate of polymerization and is given by the following equation

$$\frac{d[M]}{dt} = -\frac{k_p k_i^{1/2}}{k_t^{1/2}}[M][I]^{1/2} \tag{3}$$

which is applied only under steady-state conditions. Here $[M]$ and $[I]$ are the concentration of monomer and initiator. Often the rate constant for initiation, k_i, is large and only a small propagation of the initiator breaks down into radicals, which means that $[I]$ stays constant during the polymerization process and Eq. (3)

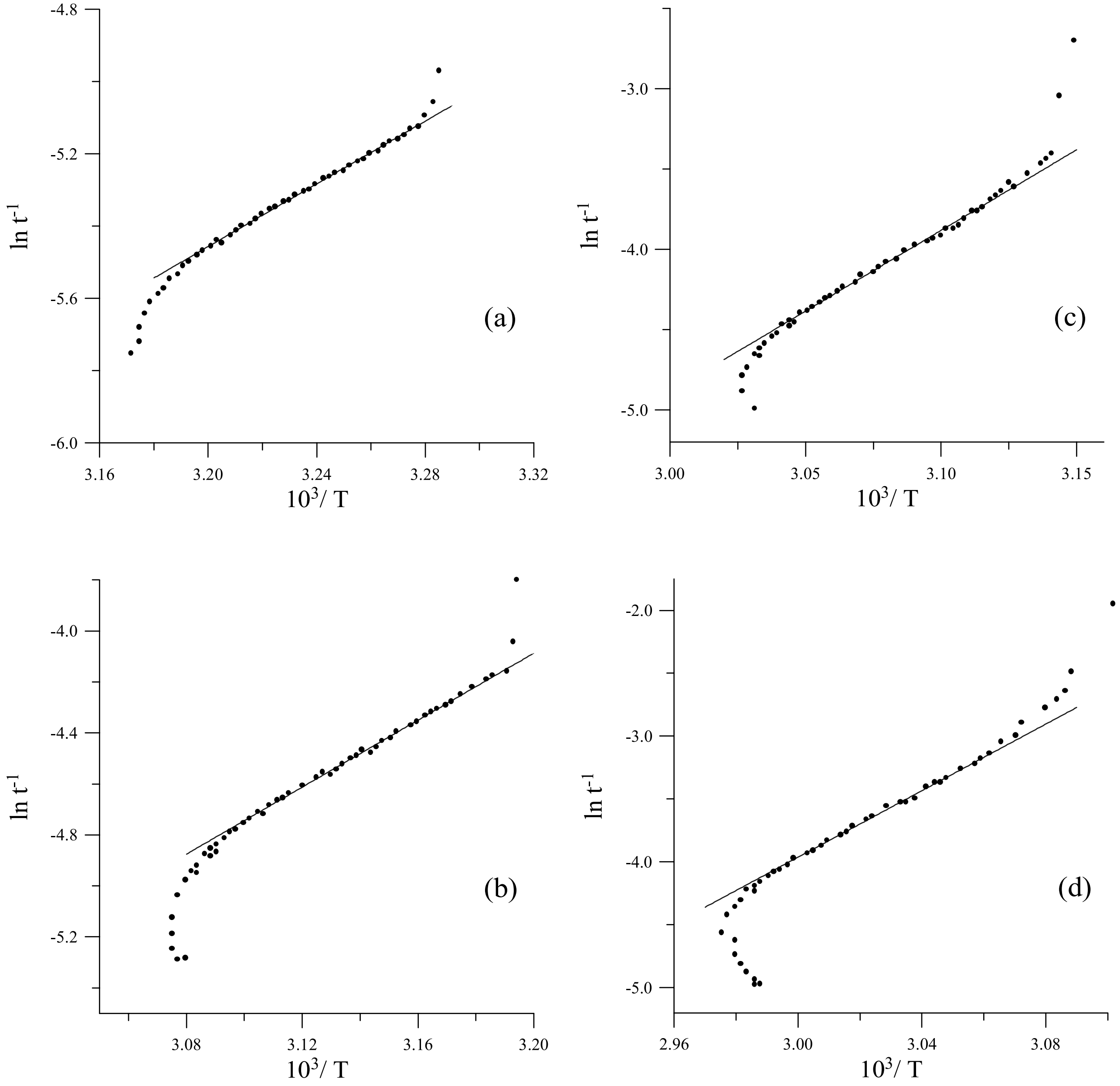

Fig. 4. The plots of $\ln t^{-1}$ vs. T^{-1} in Eq. (6) for the samples of (a) 30, (b) 40, (c) 45 and (d) 50°C onset temperatures. The slopes of the curves produce the gelation activation energies, ΔE_G.

can be written as

$$\frac{d[M]}{dt} = -k_r[M] \tag{4}$$

where k_r is the composite rate constant. The solution of the Eq. (4) produces the relation for the monomer consumption as follows

$$[M] = [M_o]\exp(-k_r t) \tag{5}$$

where $[M_o]$ is the concentration of monomer at $t = 0$.

A simple Arrhenius treatment to the data in Fig. 1 may produce the gelation activation energy, ΔE_G, for a given temperature range, where the following relation for $k_r = t^{-1}$ can be written

$$k_r = k_{ro}\exp(-\Delta E_G/kT) \tag{6}$$

where k_{ro} is the composite rate constant at infinite temperature and k is the Boltzman constant. The plots of $\ln t^{-1}$ vs. T^{-1} for various samples polymerized at different onset temperatures are given in Fig. 4. The slopes of linear relations in Fig. 4 produced the gelation activation energy i.e. the energy released during gelation which are plotted in Fig. 5 vs. onset temperatures, T_{on}. It is seen that as the onset temperature is increased, ΔE_G increased, indicating that energy release during gelation is strongly dependent on the temperature input to the polymerization process.

Similar Arrhenius treatment can also be performed for the onset of gelation time t_o, defined as the onset time for a decrease in I_{tr} shown in Fig. 2 as

$$t_o^{-1} = t_{oo}^{-1}\exp(-\Delta E'_G/kT) \tag{7}$$

where t_{oo} is the t_o at infinite temperature and $\Delta E'_G$ is the average gelation activation energy. In Fig. 6, the logarithmic plot of t_o^{-1} vs. inverse onset temperature, T_{on}^{-1}, is presented where the slope of the linear relation produced the $\Delta E'_G$ value as 22.4 kcal/mol. Here it can be seen that real gelation activation energies are obtained by in situ monitoring of temperature variation during FCC reactions which are plotted in Fig. 5. The relation in Eq. (7) however produces a type of average gelation activation energy.

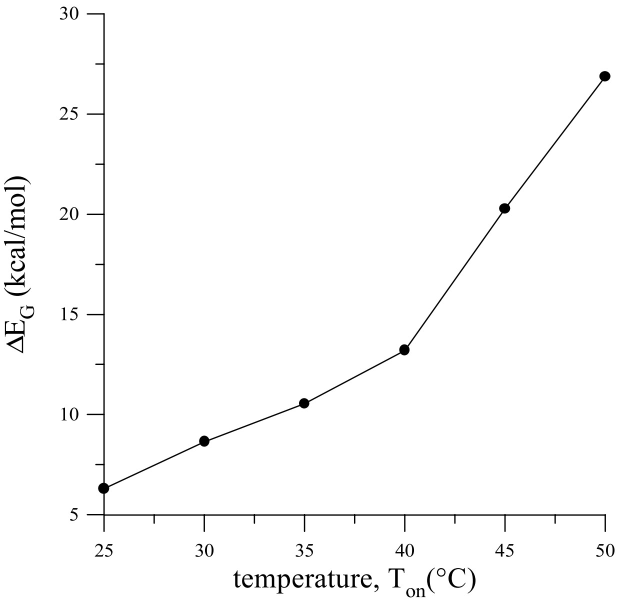

Fig. 5. The produce gelation activation energies, ΔE_G vs. onset temperatures, T_{on}.

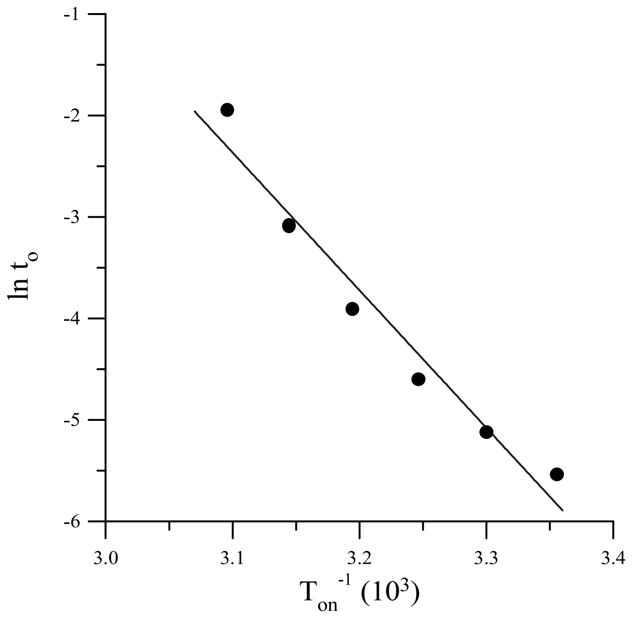

Fig. 6. Logarithmic plot of onset of gelation time, t_o vs. T^{-1}. Slope of the curve produces the average gelation activation energy, $\Delta E'_G$.

5.2. Microgel formation

Fig. 2 shows that I_{tr} intensities decreased dramatically above a certain gelation time by indicating that opalescence occurs during gelation. To interpret the results in Fig. 2, Eq. (1) is employed where it can be assumed that the decrease in I_{tr} during gelation solely originates from the increase in scattering intensity, I_{sc}. In Fig. 7 normalized $I_{sc} = (1 - I_{tr})$ intensities are plotted vs. t^2 in the experiments for the onset temperature of 25, 30, 35, 40, 45 and 50°C. Fig. 7 shows that I_{sc} present an increase above a certain time by indicating that hydrogel system scatters light dramatically by presenting a strong opalescence above this critical time. These results can be modeled in the knowledge that formation of PAAm microgels occurs prior to the onset of macrogelation [3]. As the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends due to the high extent of cyclization reactions. At this stage highly intramolecularly crosslinked microgel particles formed in the pre-gel period act as junction points. The microgels are presented as the junction points of the final inhomogeneous network structure.

If the microgel particles are assumed to be spherical with the volume v which grows linear in time, t, during gelation,

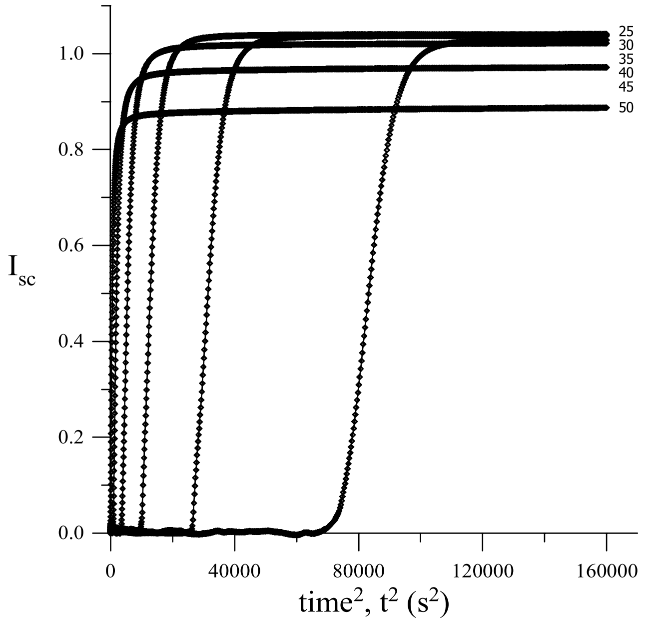

Fig. 7. The plot of I_{sc} vs. t^2. The slope of the linear relations produce $a = kc\lambda^{-\eta}$ values.

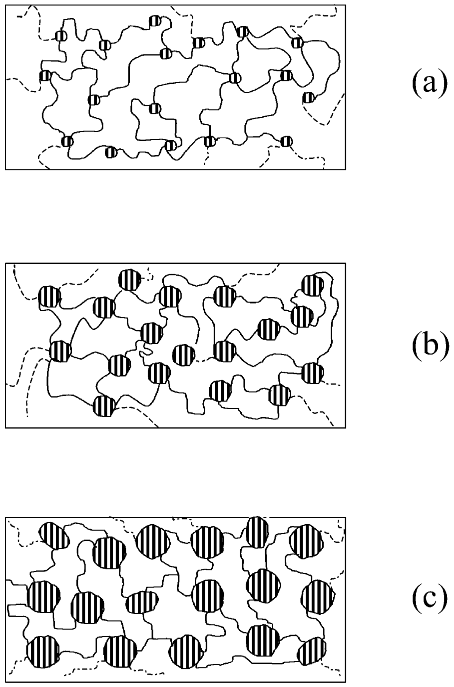

Fig. 9. Cartoon representation of the growing of microgel particles from *a* to *c* as the gelation time increase.

then the linear portions of I_{sc} data in Fig. 7 are fitted to Eq. (1). $I_{sc} - t^2$ curves in Fig. 7 produce the slopes which provide the values of $a = kc\lambda^{-\eta}b^2$, where b is the proportionality constant between v and t. The measured a values are plotted vs. onset temperatures in Fig. 8, where a values increased as T_{on} is increased. This behavior indicates that increasing T_{on} increases the number, c, of microgel particles. It should be noted that the increase in c follows the increase in ΔE_G in Fig. 5, indicating that forming more microgel particles needs more energy or higher onset temperature for the FCC reaction. For all samples initiated at different T_{on}, volume ν, of the microgel particle grows linear in time, t. Fig. 9 shows the growing of microgel particle for a given T_{on} as the gelation time is increased, i.e. gelation causes more scattering of light as the system goes from *a* to *c*. Fig. 7 shows that the saturation intensities of the scattering light, $I_{sc}(\infty)$ varies with the onset temperature, T_{on}. The results are plotted in Fig. 10, where as T_{on} is increased, $I_{sc}(\infty)$ decreased. This behavior predicts that gelation at high T_{on} causes smaller microgel volumes than at low T_{on}, which can be expected, i.e. gelation at high temperature forms small microgel volumes due to higher reaction rates.

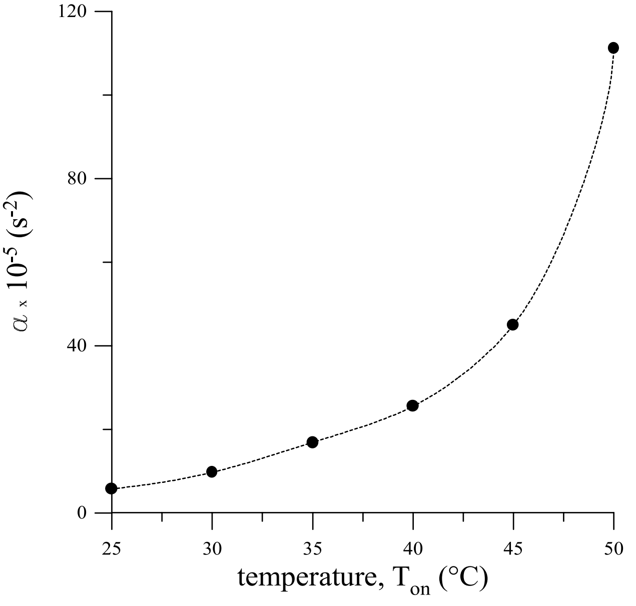

Fig. 8. The plot of a vs. onset temperature T_{on}.

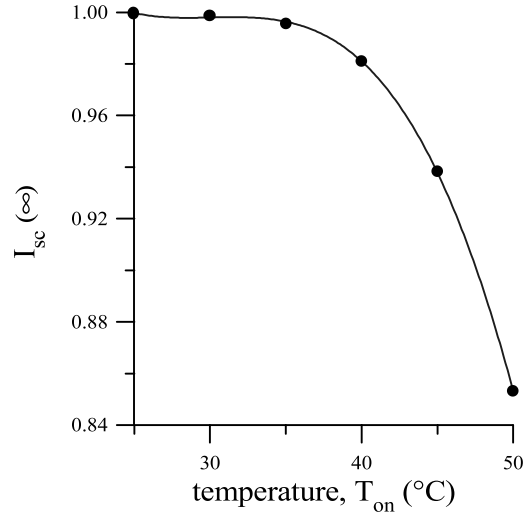

Fig. 10. The saturation intensities of the scattering light, $I_{sc}(\infty)$ vs. onset temperatures, T_{on}.

6. Conclusions

This work has shown that in situ monitoring of temperature and transmitted light intensities during FCC produce gelation activation energies, ΔE_G, and number of microgel particles, c at a given onset temperature, T_{on}. Both ΔE_G and c, were found to be increased as T_{on} is increased, indicating that in order to produce a large number of particles, FCC process needs higher energy. It is also observed that at high T_{on} temperatures a large number of smaller particles are produced compared to a smaller number of larger particles at low T_{on} temperatures.

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