Thermal analysis of PNIPAAm-PAAm mixtures via photopyroelectric technique

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Abstract. Crosslinked poly (N-isopropylacrylamide) (PNIPAAm) is a temperature-sensitive hydrogel with approximately 32 °C lower critical solution temperature (LCST) in pure water. The PNIPAAm chains hydrate to form extended structures in water when the latter is below LCST. However, when heated to above LCST, they become compacted by dehydration. In this work, we have used the PNIPAAm- polyacrylamide (PAAm) mixtures with varying molar percentages of PNIPAAm and PAAm that were prepared by free radical crosslinking copolymerization. N’-N’methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and an initiator, respectively. A photopyroelectric technique was applied to test the universality of the sol- gel transition as a function of polymer concentration ratios and to determine thermal effusivity of PNIPAAm- PAAm mixtures. The effects of varying PAAm concentrations on the LCST were studied by determining the temperature dependence of the thermal effusivity, with emphasis is on the influence on the properties and formation on the LCST of PNIPAAm- PAAm mixtures of the acrylamide concentration.

1. Introduction

A polymer gel is a network formed by cross-linked long chain molecules [1]. The polymer gel under study is a weakly crosslinked thermostable network of polyacrylamide (PAAm), which is slightly impregnated with thermoreversible gel microparticles of poly(N-isopropylacrylamide). This weakly crosslinked PNIPAAm gel exhibits a temperature drive volume transition around 33.6 °C. The transition mechanism has been attributed to the change in the balance between hydrophilic and hydrophobic interactions [2].

Phase transitions and critical phenomena in polymer gels have attracted much attention due to their scientific interest and technological significance. The phenomena were theoretically described in terms of the Flory- Huggins mean- field equation of state consisting of four principal terms that represent the rubber elasticity, the interactions among polymer segments and solvents, the ionic osmotic pressure and the mixing entropy [3].
Most of the work on the phase transition and critical phenomena of PAAm and PNIPAAm have so far been limited to measurements on the macroscopic quantities such as volume [4], collective diffusion coefficient [5], and specific heat capacity [6].

In this article, we make use of a photopyroelectric (PPE) technique for measurements of thermal properties of polymers as a function of time and temperature. The photopyroelectric technique involves the direct detection of the temperature variations in a sample that are generated due to optical absorption of modulated light, using a pyroelectric transducer in intimate contact with the sample as a thermometer. The PPE signal in general depends on the optical and thermal properties of the sensor and the sample. A suitable selection of the experimental configuration allows to measure the thermal parameter of interest.

In the present work, we have used the so-called thermal effusivity configuration, where a thermally thick sample layer is in contact with a thermally thick PE sensor with light absorption taking place at the air-sensor interface [7, 8]. In this configuration the PPE signal depends only on the ratio of the thermal effusivities of sample and sensor. Given the thermal effusivity of the sensor accurately, it is possible to extract the thermal effusivity of the PNIPAAm- PAAm mixtures from the PPE signal amplitude and phase, and to study the mechanism of free radical crosslinking copolymerization in detail.

2. Theoretical Considerations

2.1. Critical Exponents for Gelation

Flory and Stockmayer developed a theory describing the sol-gel transition [3, 9]. An alternative to their chemical kinetic theory is the lattice percolation model [10, 11], where monomers are assumed to occupy the sites of a periodic lattice. Between two nearest neighbours of lattice sites a bond is formed randomly with probability \( p \). With increasing \( p \), in general a phase transition occurs at a critical point \( p = p_c \). At this so-called percolation threshold, the sol phase transforms into a gel phase, which is characterized by the appearance of an infinite cluster.

Both theories predict critical behaviour for \( p \) approaching \( p_c \). The gel fraction, \( G \), i.e. the fraction of the monomers that belong to the macroscopic network, is predicted to vary like \( G \sim \left( \frac{(p - p_c)}{p_c} \right)^\beta \) for \( p > p_c \). For \( p < p_c \), the weight averaged degree of polymerization \( DP_W \), is expected to diverge as \( DP_W \sim \left( \frac{(p - p_c)}{p_c} \right)^\gamma \).

Flory and Stockmayer predict \( \beta = \gamma = 1 \), whereas the percolation theory gives \( \beta = 0.45 \), and \( \gamma = 1.74 \) [10]. Gelation theories are expressed in terms of the conversion factor \( p \) to describe the behaviour of the gelation process. In practice, \( p \) may depend on temperature, on the concentration of monomers, on the concentration of cross-linking agents necessary for bond formation, and, most importantly, on the gel formation time \( t \) [10, 11]. Expectations are that in the critical region \( |p - p_c| \) should be linearly proportional to \( |t - t_c| \), with \( t_c \) the so-called gelation time [12, 13]. In this article, we start from the assumption that the thermal effusivity \( e \), i.e. the physical quantity experimentally accessible with the photopyroelectric technique, which is related to the structure-dependent thermal conductivity \( \kappa \) via the relation \( e = \sqrt{\rho C \kappa} \), with \( \rho \) the density and \( C \) the specific heat capacity, is also connected with the gel formation indicators \( DP_o \) (for \( t < t_c \)) and \( G \) (for \( t > t_c \)). As a result, above \( t_c \), the thermal effusivity is expected to reflect the critical behavior of \( G \), i.e. \( e = e_o + e_c \left| \left( t - t_c \right) / t_c \right|^{\beta} \).

3. Experiment

3.1. Sample Preparation

Mixtures were prepared with various molar percentages of PNIPAAm- PAAm in distilled water at room temperature. The monomers, NIPA and AA; a crosslinking reagent, N, N’- methylenebis (acrylamide) (BIS); an initiator, ammonium persulfate (APS); and an accelerator, N, N, N’, N’tetramethylenediamine
(TEMED) were used as reagents. The used materials were special grade (Merck®) and used without further purification. Before polymerization started, the mixtures were deoxygenated by bubbling with nitrogen for 5 minutes. They were then mixed, and 0.4ml of TEMED was added to the mixture.

3.2. Photopyroelectric Measurement

The time dependence of thermal effusivity of gels during the gel formation was investigated employing a photopyroelectric technique. A 260 micro thick PZT film, irradiated with a modulated IR LED light on the front side, and in contact with the gel mixture on the back side, was used as the PE sensor. The amplitude and phase of the PPE signal were determined by a lock-in amplifier, which was locked to the light modulation signal. The time evolution of the signal starting from adding the mixed components was recorded in steps of 30 seconds during several 3 hours. After the completion of gel formation a frequency scan was performed between 0.1 Hz and 1000Hz. The obtained spectrum was normalized with the frequency response of the sensor alone. The asymptotic effusivity \(e_\infty\), was determined by a least squares fit of the normalized spectrum, and used to determine the sensitivity factor of the detection system. Using the obtained value for \(e_\infty\), the time evolution of the thermal effusivity was determined by an iterative approach. Also the temperature dependence of the effusivity of a formed, wet pure NIPA gel was determined. The PPE signal amplitude and phase were recorded during heating and cooling cycles at a rate of ±0.1K/min.

4. Results and Discussion

4.1. Thermal effusivity results

Figure 1a depicts a typical experimental (circles) and fitted (line) PPE signal frequency dependence for a fully formed 10% NIPA gel. From the chi-square dependence \(\chi^2(e_\infty)\), we determined (Figure 1b) the statistical uncertainty on the fitted value of the thermal effusivity.

\[\chi^2(e_\infty)\]

\[\chi^2(f)\]

\[\chi^2\beta\]

\[\chi^2(\beta)\]

Fig.1. (a) Experimental result (circles) and best fit (line) for the frequency dependence of the normalized PPE amplitude and signal obtained for 10% PNIPAAm. (b) Least square analysis. (c) Time evolution of the effusivity during gel formation shown for 0% and 10% PNIPAAm.

Figure 2a reveals a weakly increasing value of the effusivity with PNIPAAm concentration, reflecting a slightly enhanced thermal conductivity due to increasingly rigid gel network. The value for \(e_\infty\), thus obtained was also used to determine the sensitivity factor of the system, and to extract the time evolution of thermal effusivity (Figure 1c). From the time derivative of the thermal effusivity curves, we obtained values for \(t_c\) that increase with increasing PNIPAAm concentration and which agree well with the literature values [14]. We have also fitted the time evolution of the thermal effusivity for \(t<t_c\), in order to determine the critical exponent \(\beta\). The least squares and most squares \(\chi^2(\beta)\) parabola [15] (Figure 2b) indicate that the fitting problem is well posed, with a best fit for \(\beta=0.41\pm0.06\) for 25 % PNIPAAm, in accordance with the value \(\beta=0.45\) predicted by percolation theory.
Fig. 2 (a) Composition dependence of thermal effusivity versus PNIPAAm concentration for two repeated experiments (circles and squares respectively). A dashed line is drawn as a guide to the eye. 
(b) Least (solid line) and most square (dotted line) parabola around the best fitting critical exponent $\beta$. 
(c) Temperature dependence of thermal effusivity of a wet 100% PNIPAAm gel. 

The temperature dependence of thermal effusivity of 100% PNIPAAm gel as shown in Figure 2c. At 32°C, the PNIPAAm gel undergoes a phase transition from a hydrophilic to a hydrophobic structure [2, 16].

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