ELSEVIER

Polymer 41 (2000) 5729–5735

polymer

Phase separation during the formation of poly(acrylamide) hydrogels

S. Durmaz[a,b], O. Okay[a,b,*]

[a]Department of Chemistry, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey
[b]Department of Chemistry, TUBITAK Marmara Research Center, Gebze, Kocaeli, Turkey

Received 1 March 1999; received in revised form 9 July 1999; accepted 28 October 1999

Abstract

The crosslinking polymerization of acrylamide (AAm) was investigated at a monomer concentration of 5 w/v% in water with *N*,*N*′-methylenebis(acrylamide) (BAAm) as the crosslinker. The crosslinker ratio (mole ratio of BAAm to AAm) was set to 1/82. The fractional monomer conversion x, the weight fraction of gel W_g, and the equilibrium weight swelling ratio q_w of the hydrogels were measured as a function of the reaction time. Experimental results indicate that the first gel molecule in the reaction system appears after a reaction time $t_c = 4 \pm 1$ min or after a monomer conversion of $x_c = 0.07 \pm 0.02$. At this critical point the homogeneous reaction system turned into a heterogeneous one consisting of gel and separated solution phases. The network formation process took place in this heterogeneous system within the first 60 min of the reaction time. Experimental x, W_g, and q_w data indicate that, during the gel growth process, the growing hydrogel molecule cannot occupy the entire polymerization system, which is responsible for the observed phase separation. It was shown that the volume of the separated liquid phase decreases as the polymerization and crosslinking reactions proceed and finally, the reaction system becomes homogeneous again due to the decreasing dilution degree of the hydrogel. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinking polymerization; Acrylamide; Poly(acrylamide)

1. Introduction

Acrylamide (AAm)-based hydrogels are important materials of both fundamental and technological interests. These hydrogels are mainly obtained by FCC of AAm in the presence of *N*,*N*′-methylenebis(acrylamide) (BAAm) as the crosslinker. Since the monomers are solid at the polymerization temperature, the reactions are necessarily carried out in an aqueous solution of the monomers. Investigations of the swelling behavior of hydrogels derived from AAm have been reported repeatedly in the last four decades. However, theories are still unable to predict their physical properties from the synthesis conditions. This is due to the several non-idealities of the polymerization system such as the different and conversion-dependent reactivities of the vinyl groups [1,2], cyclization [2–5], multiple crosslinking [3], inhomogeneities [6–9], microgel formation [10], and diffusion-controlled reactions [3,11]. The hydrogels formed in such a non-ideal picture include defects, which influence their physical properties and lead to the observed deviations from the prediction of gelation and swelling theories [12–16].

Heterogeneity in polymer gels is another non-ideality directly affecting their physical properties such as swelling, permeability, turbidity, and elasticity [17,18]. Heterogeneity appears as a result of a phase separation during the formation of polymer gels. Phase separation may occur in the form of microsyneresis (separation of solution droplets from the continuous gel phase) or macrosyneresis (deswelling of the gel phase) [19–22]. In both cases, after complete conversion of monomers to polymer heterogeneous gels consisting of gel and solution phases are obtained. Recently, we proposed a kinetic-thermodynamic model to predict the extent of phase separation and the resulting heterogeneities during the free-radical crosslinking copolymerization (FCC) of vinyl–divinyl monomers [23]. The FCC system separates into two phases depending on the degree of dilution of the growing gel and on its swelling capacity. We have shown that the degree of heterogeneity in the gel depends on the amounts of the crosslinker and the solvent present in the reaction system as well as on the polymer–solvent interaction parameter [23].

The extent of phase separation during the crosslinking copolymerization of styrene–divinylbenzene as well as of 2-hydroxyethyl methacrylate–ethyleneglycol dimethacrylate comonomer systems have been the subject of a large number of studies during the last four decades [24–31]. However, in spite of the extensive works on the characterization of poly(AAm) hydrogels, the degree of

---

* Corresponding author. Fax: +90-262-6412300.
E-mail address: oguz@mam.gov.tr (O. Okay).

PII: S0032-3861(99)00809-5

heterogeneity in these hydrogels has not been studied previously. Bansil and Gupta showed formation of opaque poly(AAm) hydrogels above 2 mol% crosslinker concentration [18]. Tobita and Hamielec pointed out that, during the formation of poly(AAm) hydrogels, gel molecules start to form in the lower part of the polymerization reactor [3]. No further details or experimental data were given by these authors. Our preliminary experiments also showed that during the crosslinking polymerization of AAm under the classical reaction condition, i.e. at 5 w/v% initial monomer concentration and with peroxide initiators, a solution phase separates out of the gel phase.

Our purpose of the present study was to investigate the extent of phase separation during the formation of AAm-based hydrogels. The hydrogels were prepared by FCC of AAm and BAAm at 40°C in the presence of potassium persulfate as the initiator. The crosslinker ratio (mole ratio of the crosslinker BAAm to monomer AAm) and the initial monomer concentration were set to 1/82 and 0.700 M, respectively. As expected [18], under this reaction condition transparent gels were obtained. However, as will be seen below, although the polymerization system was clear, it was heterogeneous consisting of gel and separated liquid phases. Since the measurement of the volume of the phases during FCC could not be carried out directly, we measured the dilution degree of the growing gel and its swelling capacity as a function of the reaction time. These two quantities allowed calculation of the extent of phase separation during the formation of poly(AAm) hydrogels.

2. Experimental

2.1. Materials

Acrylamide (AAm, Merck) was crystallized from acetone/ethanol mixture (70/30 by volume) below 30°C. *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck) and potassium persulfate (KPS, Merck) were used as received. KPS stock solution was prepared by dissolving 0.040 g of KPS in 10 ml of distilled water. Distilled and deionized water was used for the swelling experiments. For the preparation of the hydrogels, distilled and deionized water was distilled again prior to use and cooled under bubbling nitrogen.

2.2. Synthesis of hydrogels

AAm crosslinking polymerization was carried out in water, as the polymerization solvent, at 40°C in the presence of 0.474 mM KPS as the initiator. Both the crosslinker ratio (mole ratio of the crosslinker BAAm to the monomer AAm) and the initial monomer concentration were fixed at 1/82 and 0.700 M, respectively. To illustrate the synthetic procedure, we give details for the preparation of the hydrogels: AAm (4.97 g) and KPS stock solution (3.2 ml) were dissolved in 96.8 ml of distilled water. After bubbling nitrogen for 20 min, the solution was poured into several glass tubes of 11 mm internal diameter and about 250 mm long. Thereafter, 10 min of nitrogen bubbling was required through each solution to obtain reproducible results. The glass tubes were sealed, immersed in a thermostated water bath at 40°C and the polymerization was conducted for predetermined reaction times. Temperature measurements showed a temperature rise inside the reaction solution less than 1°C, indicating that the dilute reaction condition provides a nearly isothermal condition.

For the dilatometric studies, dilatometers consisting of a blown glass bulb connected to a 30 cm length of 0.918 mm precision-bore capillary tubing with a ground-glass joint were used. The polymerization technique used was described in detail elsewhere [32].

2.3. Gel points

Gel point measurements were carried out using two different methods. First, the gravimetric technique was used to follow the gelation process. The gel point was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in water. For ascertaining the insoluble gel component of samples, the latter were treated with an approximately 50-fold excess of water at room temperature. The formation of insoluble polymer was detected visually from the appearance of gel particles in water. Second, dilatometers containing a teflon-covered steel sphere of 5 mm diameter was used for the gel point measurements. The midpoint between the last time at which the sphere moves magnetically and that at which it stops moving is taken as the gel point.

2.4. Gel fraction

Water was chosen as the extraction solvent for the crude hydrogels and employed at room temperature. After the predetermined polymerization times, the reaction was stopped by cooling the reaction mixture in an ice–water bath. The crude hydrogels, 11 mm in diameter, were freed from the glass tubes and they were cut into samples of about 10 mm length. Each sample was placed in an excess of water containing a small amount of hydroquinone as an inhibitor, and the solvent was replaced every other day over a period of at least one-week until no further extractable polymer could be detected. The hydrogels after extraction were carefully deswollen in a series of water–acetone mixtures with increasing acetone contents. This solvent exchange process facilitated final drying of the hydrogel samples. They were then washed several times with acetone and dried at 70°C under vacuum to constant weight. The amount of soluble polymer in water solution was determined gravimetrically after evaporation and precipitation in acetone. The weight fraction of gel W_g was calculated as

$$W_g = \frac{m_{gel}}{m_{gel} + m_{sol}} \tag{1}$$

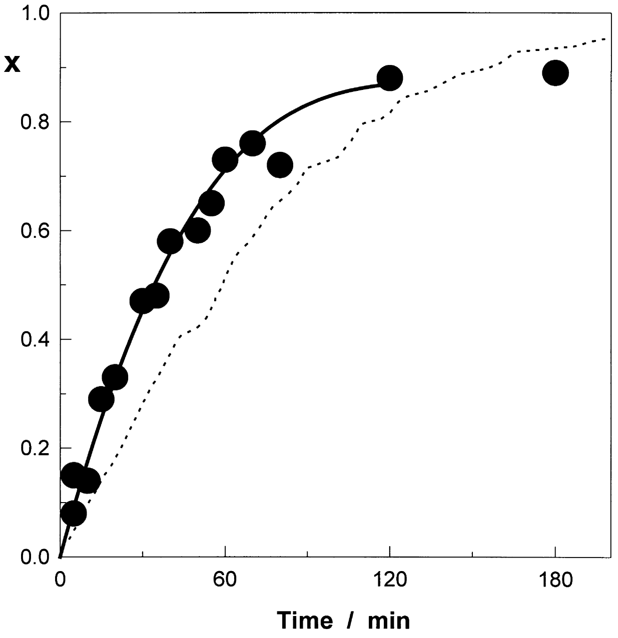

Fig. 1. Variation of the monomer conversion *x* with the reaction time *t* in crosslinking polymerization of AAm. The filled circles are the results of the gravimetric measurements. The solid curve is a polynomial best fit to the experimental data points. The dotted curve was obtained by the dilatometric technique.

where m_{gel} and m_{sol} are the weights of extracted dry hydrogel and of the soluble polymer, respectively.

2.5. Swelling measurements

The swelling measurements were carried out in water at room temperature (19 ± 1°C). In order to reach the equilibrium degree of swelling, the hydrogels were immersed in water for at least two weeks; the swelling equilibrium was tested by weighing the samples. To achieve good precision, three measurements were carried out on samples of different weight taken from the same gel. The networks were then weighed in the swollen state and dried, after a solvent exchange with acetone as described above, under vacuum to constant weight. The equilibrium weight swelling ratio was characterized by q_w, which was calculated as

$$q_w = \frac{m_s}{m_d} \tag{2}$$

where m_s and m_d and the weights of the hydrogels in the swollen state and the dry state, respectively. Both q_w and W_g data reported in this work are average of seven separate experiments.

3. Results and discussion

3.1. Hydrogel properties versus reaction time

The fractional monomer conversion *x* versus time *t* history in crosslinking polymerization of AAm was measured by both gravimetric and dilatometric techniques. In Fig. 1, the symbols represent the results of the gravimetric measurements. Each symbol in the figure is an average of four to seven separate experiments; standard deviations are smaller than the symbols themselves. The dotted curve in Fig. 1 was obtained by the dilatometric technique. It is seen that the dilatometric technique gives lower reaction rates than the gravimetric technique; this is due to the formation of gel particles in the reaction system (after about 4 min) which limits the contraction of the reaction solution in the capillary. The solid curve in Fig. 1 that is a polynomial best fit to all experimental data yields:

$$x = 1.9 \times 10^{-2} t - 1.4 \times 10^{-4} t^2 + 3.5 \times 10^{-7} t^3 \text{ min} \tag{3}$$

for $t < 120$ min. For longer reaction times up to 3 h the monomer conversion *x* remained at the limiting value of about 0.9. According to Eq. (3), the initial rate of polymerization is 1.9×10^{-2} min^{-1}, about five times higher than that of linear AAm polymerization under the same reaction condition [11,33,34]. This is due to the higher reactivity of BAAm compared to AAm, which increases the polymerization rate even in the pregelation period [3,4].

The first insoluble polymer in the reaction system appeared after a reaction time $t_c = 4 \pm 1$ min or after a monomer conversion of $x_c = 0.07 \pm 0.02$. Thus, this reaction time or monomer conversion is a critical point at which an infinite cluster starts to appear in the reaction system. However, by use of the dilatometric technique, we observed that this critical point does not correspond to the classical gel point, at which the system changes from liquid to solid-like state. It rather corresponds to a point at which gel particles start to form in the reaction mixture. At this critical point, the microsphere inside the dilatometer stopped moving only in the lower part of the solution. Repeated measurements indicated formation of gel regions distributed inside the solution phase. This means that the volume of the first formed gel is not equal to the reaction volume so that the reaction mixture separates into two phases at t_c. Because the refractive indices of both phases did not differ much from each other, the reaction mixture remained transparent during the polymerization. As reported earlier [18], at higher BAAm concentrations, the reaction system becomes turbid due to the increase in the concentration difference between the phases.

The weight fraction of the poly(AAm) hydrogels W_g (mass of dry gel/mass of total polymer) is shown in Fig. 2 as a function of the reaction time t and the monomer conversion *x*. The error bars indicate standard deviations of the results of seven separate experiments. W_g which is zero at t_c or x_c rapidly increases with increasing reaction time or monomer conversion, reaches a value of 0.8 after 60 min or after 70% monomer conversion and then levels off. The growing gel isolated at various reaction times was immersed in an excess of water and subjected to swelling measurements. Fig. 3 illustrates how the equilibrium weight

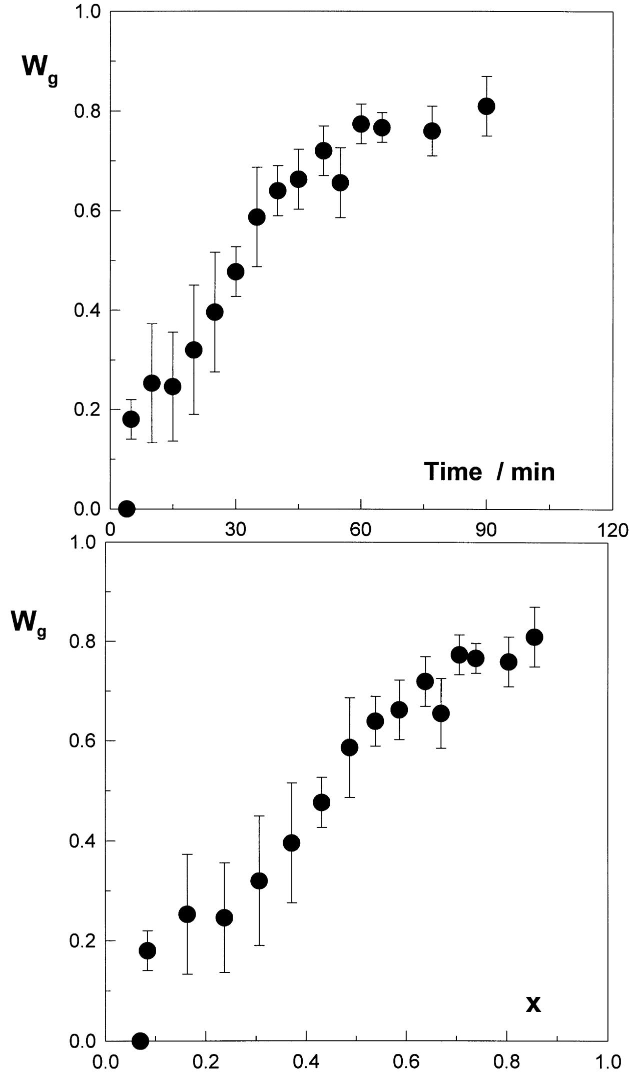

Fig. 2. Variation of the gel fraction W_g with the reaction time t and the monomer conversion x in crosslinking polymerization of AAm. The error bars indicate standard deviations of the results of seven separate experiments.

swelling ratio q_w varies with the reaction time. The equilibrium swelling ratio q_w decreases abruptly in the first 60 min of the reaction time, and then q_w begins to drop to an equilibrium value. From Figs. 2 and 3, it is seen that the structure formation process of poly(AAm) hydrogels takes place in the first hour of the reaction time.

3.2. Extent of phase separation during the crosslinking polymerization

As pointed out in Section 3.1, the onset of gelation in crosslinking polymerization of AAm simultaneously resulted in a phase separation of the reaction system. Visual observation showed separation of a liquid phase out of the gel phase and formation of gel particles in the reaction mixture. This occurs because the gel formed cannot absorb all the available reaction solution; in other words, the swelling capacity of the gel is less than the amount of solution present in the system [23].

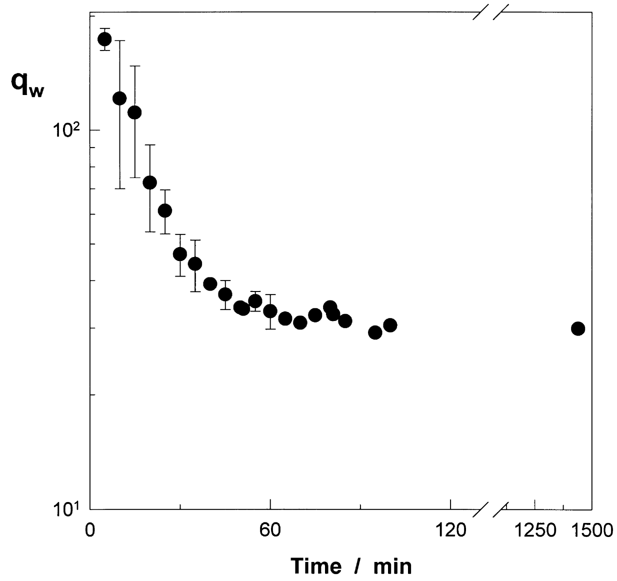

Fig. 3. Variation of the equilibrium swelling ratio of the gel in water q_w with the reaction time t in crosslinking polymerization of AAm. The error bars indicate standard deviations of the results of seven separate experiments. Standard deviations are smaller than the symbols themselves for those without an error bar.

Let $q_{v,t}$ be the equilibrium volume swelling ratio of the network formed at time t, and $q_{v,t}^0$ be its degree of dilution in the reaction system, i.e. the volume of the reaction mixture available to 1 ml of dry hydrogel. If $q_{v,t} > q_{v,t}^0$, only one phase exists because the growing gel absorbs all the reaction solution available. A phase separation during FCC requires the condition:

$$q_{v,t} \le q_{v,t}^0 \tag{4}$$

The degree of dilution of the network at a reaction time t, $q_{v,t}^0$, can be calculated as

$$q_{v,t}^0 = \frac{100\rho}{cxW_g} \tag{5}$$

where ρ is the polymer density, and c is the initial monomer concentration in w/v%. Using the experimental x and W_g data (Figs. 1 and 2) together with the values $\rho = 1.35\ \rho/\mathrm{cm}^3$ [35] and $c = 4.97$ g/100 ml, we estimated the degree of dilution of the network $q_{v,t}^0$ using Eq. (5) as a function of the reaction time. The results are shown in Fig. 4 as filled symbols plotted as a function of the monomer conversion and the reaction time. It is seen that the poly(AAm) hydrogel formed just beyond the gel point is highly diluted in the reaction system. After 1 min of the gel point, $q_{v,t}^0$ is equal to 2000, indicating that 2000 ml reaction solution are available for 1 ml of dry hydrogel. This value decreases rapidly in the first 60 min of the reaction due to the increasing amount of the network (xW_g).

The equilibrium volume-swelling ratio of the network

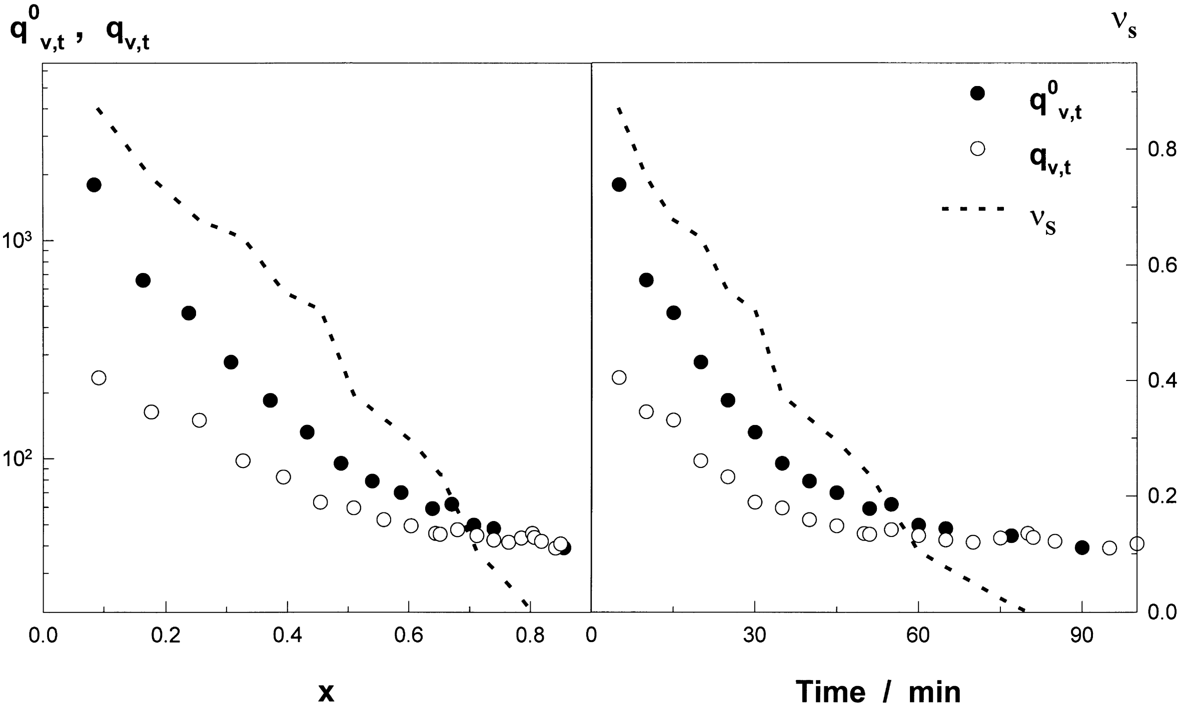

Fig. 4. The degree of dilution of the network $q^0_{v,t}$ (●), its equilibrium volume swelling ratio $q_{v,t}$ (○) and the volume fraction of the separated solution phase ν_s (- -) shown as a function of the monomer conversion x and the reaction time t in crosslinking polymerization of AAm.

formed at time t (volume of swollen hydrogel/volume of dry hydrogel) can be calculated from its corresponding weight swelling ratio q_w as:

$$q_{v,t} = 1 + \frac{(q_w - 1)\rho}{d_1} \tag{6}$$

where d_1 is the density of water (1 g/cm^3). The values $q_{v,t}$ calculated from the experimental weight swelling ratios q_w of hydrogels (Fig. 3) and using Eq. (6) are also shown in Fig. 4 as empty symbols. The degree of dilution of the network $q^0_{v,t}$ is larger than its equilibrium swelling ratio $q_{v,t}$ in the first 75 min of the reaction time or, up to about 80% monomer conversion. This indicates that during the formation process of poly(AAm) hydrogels, the infinite network cannot occupy the whole available volume. As a result, $q^0_{v,t} - q_{v,t}$ ml of solution will separate out of $q_{v,t}$ ml of swollen gel. The volume fraction of the separated solution phase, ν_S, calculated as

$$\nu_S = 1 - q_{v,t}/q^0_{v,t} \tag{7}$$

are also shown in Fig. 4 as the dotted curves. An interesting aspect of ν_S versus time curve in Fig. 4 is that ν_S is close to unity at the early stage of the gel growth process, indicating that this critical point corresponds to microgelation rather than the macrogelation point. ν_S is a decreasing function of the monomer conversion or the reaction time due to the fact that, the degree of dilution of the network decreases much more rapidly than its equilibrium degree of swelling; after about 75 min $q_{v,t}$ becomes equal to $q^0_{v,t}$, which indicates re-homogenization of the reaction system. Note that in the above calculations the swelling capacity of the network in the reaction solution at 40°C was assumed to be equal to that in pure water at room temperature. Our previous work showed that the swelling ratio of poly(AAm) hydrogels does not depend much on the swelling temperature [36]. However, the swelling ratio of the hydrogel in the reaction solution must be lower than in pure water due to the existence of soluble chains (sol) in the solution, which creates an osmotic pressure compressing the hydrogel [37]. Thus, the value of $q_{v,t}$ in the reaction solution must be lower than that measured in pure water so that the extent of phase separation is expected to be higher than that shown in Fig. 4.

From the equilibrium swelling ratio of hydrogels isolated at various reaction times, their crosslink densities were evaluated using the Flory–Rehner (FR) theory of swelling equilibrium for tetrafunctional networks [38]:

$$\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2 + N^{-1}(\nu_2^{1/3}\nu_2^{0^{2/3}} - \nu_2/2) = 0 \tag{8}$$

where ν_2 is the volume fraction of the network in the equilibrium swollen gel, i.e. $\nu_2 = 1/q_{v,t}$, χ is the polymer–solvent interaction parameter, N is the average number of segments in the network chain and ν_2^0 is the volume fraction of polymer network at preparation. The χ parameter value for poly(AAm)–water system has been evaluated from the swelling data for uncharged poly(AAm) hydrogels swollen in water [39]. A best-fit value for χ of 0.48 was obtained [15]. In the following calculations, χ was held constant at this value. The solution of Eq. (8) for the crosslink density

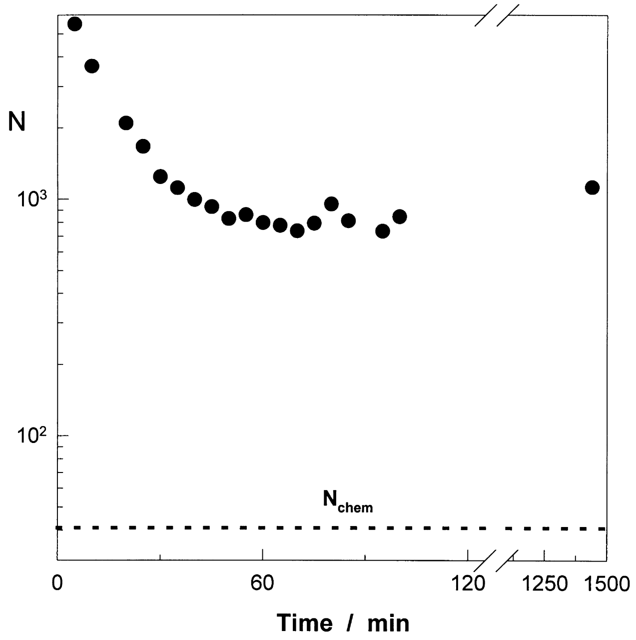

Fig. 5. Variation of crosslink density of poly(AAm) hydrogels, in terms of the average number of segments in the network chain *N*, with the reaction time *t* in crosslinking polymerization of AAm. The dashed horizontal line represents the chemical value of $N(N_{\text{chem}} = 41)$, expected from the crosslinker ratio 1/82 used in the hydrogel synthesis.

of hydrogels *N* requires the value of v_2^0 during the crosslinking copolymerization. For a homogeneous reaction system, v_2^0 remains equal to $1/q_{v,t}^0$ throughout the reaction since all the reaction system is absorbed by the gel. However, for the present heterogeneous gelling system, the following relations hold:

$$v_2^0 = 1/q_{v,t} \qquad \text{for } q_{v,t} < q_{v,t}^0 \tag{9}$$

$$v_2^0 = 1/q_{v,t}^0 \qquad \text{for } q_{v,t} > q_{v,t}^0 \tag{10}$$

Calculated values of *N* using Eq. (8) are shown in Fig. 5 as a function of the reaction time of AAm polymerization. The dashed horizontal line in the figure represents the chemical value of *N*, expected from the crosslinker ratio 1/82 used in the hydrogel synthesis. It is seen that *N* decreases rapidly in the first 60 min of the reaction and finally reaches the limiting value of 800. This means that about 1600 AAm units are connected by one effective BAAm crosslinkage, i.e. the effective crosslinker ratio in the hydrogel is 1/1600 compared to its chemical value of 1/82. Thus, only 5% of the crosslinker BAAm used in the hydrogel synthesis form elastically effective crosslinks in the final network, while the remaining 95% of BAAm is missing. BAAm units involved in cycles, in multiple crosslinks as well as those bearing pendant vinyl groups may be responsible for the wasted fraction of BAAm in the final hydrogels. Indeed, previous works indicate that, during the crosslinking polymerization of AAm, about 80% of BAAm are used in cyclization reactions [2,3]. The multiple crosslinking reactions are also important in AAm–BAAm system [3]; these reactions are responsible for the formation of highly crosslinked regions in the final hydrogel, acting as single crosslink points and contributing to the number of ineffective BAAm units in the hydrogels [2].

4. Conclusions

The crosslinking polymerization of AAm was investigated at a monomer concentration of 5 w/v% in water with BAAm as the crosslinker. Experimental results indicate that the first gel molecule in the reaction system appears after a reaction time $t_c = 4 \pm 1$ min or after a monomer conversion of $x_c = 0.07 \pm 0.02$. At this critical point the homogeneous reaction system turned into a heterogeneous one consisting of gel and separated solution phases. The network formation process took place in this heterogeneous system within the first 60 min of the reaction time. Experimental x, W_g, and q_w data indicate that the gel molecule cannot occupy the entire polymerization system, which is responsible for the observed phase separation. The volume of the separated liquid phase decreased as the polymerization and crosslinking reactions proceed and finally, the reaction system became homogeneous again due to the decreasing dilution degree of the hydrogels.

In light of the findings of this study, the crosslinking polymerization of AAm is seen to be heterogeneous even in the presence of a small quantity of the crosslinker BAAm (82 mol AAm per mol BAAm in the initial monomer mixture). However, kinetic gelation theories previously proposed all assume that the entire reaction system is occupied by the gel molecule uniformly [40–42]. A realistic model for hydrogel formation must account for the polymerization and crosslinking reactions occurring simultaneously both in the gel and separated solution phases. This requires the concentration of the reacting species in both phases, which can be obtained from the thermodynamic treatment of the gel formation system [23].

Acknowledgements

Work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK), TBAG-1561 and by the Istanbul Technical University Research Found, ITU-1054.

References

[1] Baselga J, Llorente MA, Hernandez-Fuentes I, Pierola IF. Eur Polym J 1989;25:471.
[2] Naghash HJ, Okay O. J Appl Polym Sci 1996;60:971.
[3] Tobita H, Hamielec AE. Polymer 1990;31:1546.
[4] Keskinel M, Okay O. Polym Bull 1998;40:491.
[5] Okay O, Balimtas NK, Naghash HJ. Polym Bull 1997;39:233.

[6] Weiss N, van Vliet T, Silberberg AJ. Polym Sci: Polym Phys Ed 1974;17:2229.
[7] Hsu TP, Ma DS, Cohen C. Polymer 1983;24:1273.
[8] Hecht AM, Duplessix R, Geissler E. Macromolecules 1985;18:2167.
[9] Matsuo ES, Orkisz M, Sun ST, Li Y, Tanaka T. Macromolecules 1994;27:6791.
[10] Funke W, Okay O, Joos-Muller B. Adv Polym Sci 1998;136:139.
[11] Kim CJ, Hamielec AE. Polymer 1984;25:845.
[12] Hino T, Prausnitz JM. J Appl Polym Sci 1996;62:1635.
[13] Bromberg L, Grosberg AY, Matsuo ES, Suzuki Y, Tanaka T. J Chem Phys 1997;106:2906.
[14] Skouri R, Schosseler F, Munch JP, Candau SJ. Macromolecules 1995;28:197.
[15] Baker JP, Hong LH, Blanch HW, Prausnitz JM. Macromolecules 1994;27:1446.
[16] Nossal R. Macromolecules 1985;18:49.
[17] Richards EG, Temple C. J Nat Phys Sci 1971;230:92.
[18] Bansil R, Gupta MK. Ferroelectrics 1980;30:64.
[19] Dusek K. J Polym Sci: Polym Lett 1965;3:209.
[20] Dusek K. J Polym Sci C 1967;16:1289.
[21] Dusek K, Prins W. Adv Polym Sci 1969;6:1.
[22] Dusek K. In: Chompff AJ, Newman S, editors. Polymer networks: structural and mechanical properties, NY: Plenum, 1971 p. 245.
[23] Okay O. Polymer 1999;40:4117.
[24] Okay O. J Appl Polym Sci 1986;32:5533.
[25] Dusek K. In: Haward RN, editor. Developments in polymerization 3, London: Applied Science, 1982. p. 143.
[26] Janacek J. J Macromol Sci Rev Macromol Chem 1973;C9:1.
[27] Sedlacek B, Konak C. J Colloid Interface Sci 1982;90:60.
[28] Huglin MB, Yip DCF. Makromol Chem Rapid Commun 1987;8:237.
[29] Okay O, Gurun C. J Appl Polym Sci 1992;46:401.
[30] Huglin MB, Yip DCF. Macromolecules 1992;25:1333.
[31] Horak D, Lednicky F, Bleha M. Polymer 1996;37:4243.
[32] Okay O, Naghash HJ, Capek I. Polymer 1995;36:2413.
[33] Riggs JP, Rodrigues F. J Polym Sci A 1967;1(5):3151.
[34] Shawki S, Hamielec AE. J Appl Polym Sci 1979;23:3323.
[35] Ilavsky M. Polymer 1981;22:1687.
[36] Kayaman N, Okay O, Baysal BM. J Polym Sci: Polym Phys Ed 1998;36:1313.
[37] Kayaman N, Okay O, Baysal BM. Polym Gels Networks 1997;5:167.
[38] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[39] Hooper HH, Baker JP, Blanch HW, Prausnitz JM. Macromolecules 1990;23:1096.
[40] Tobita H, Hamielec AE. Macromolecules 1989;22:3098.
[41] Zhu S, Hamielec AE. Macromolecules 1992;25:5457.
[42] Okay O. Polymer 1994;35:796.