J Fluoresc (2011) 21:865–871
DOI 10.1007/s10895-009-0588-2

ORIGINAL PAPER

The Role of Pyranine in Characterization of PAAm-κC Composites by Using Fluorescence Technique

Gülşen Akin Evingur · Önder Pekcan

Received: 30 October 2009 / Accepted: 22 December 2009 / Published online: 19 January 2010

Abstract Polyacrylamide (PAAm) doped by κ-carrageenan (κC) gels were prepared with various amounts of κC varying in the range between 0 wt.% and 3 wt.%. Steady-state fluorescence (SSF) technique was employed for studying sol-gel transition and swelling of PAAm-κC composite gels which were prepared by free-radical cross-linking copolymerization. Pyranine was introduced as a fluorescence probe. Pyranine molecules start to bind to acrylamide polymer chains upon the initiation of the polymerization, thus the spectra of the bonded pyranines shift to the shorter wavelengths. Fluorescence spectra from the bonded pyranines allow one to monitor the sol-gel transition and to test the universality of the sol-gel transition as a function of some kinetic parameters like polymer concentration. Observations around the gel point, t_c for PAAm-κC composite gels showed that the gel fraction exponent β obeyed the percolation result for low κC (<2.0 wt. %) however classical results were produced at higher κC (>2.0 wt.%). On the other hand, fluorescence intensity of pyranine was measured during in situ swelling process at various amounts of κC and it was observed that fluorescence intensity values decreased as swelling is proceeded. Li-Tanaka equation was used to determine the swelling time constants, τ and cooperative diffusion coefficients, D.

G. A. Evingur (✉)
Faculty of Science and Letters, Physics Department,
Istanbul Technical University,
34469 Maslak- Istanbul, Turkey
e-mail: evingur@itu.edu.tr

Ö. Pekcan
Kadir Has University,
34320 Cibali- Istanbul, Turkey
e-mail: pekcan@khas.edu.tr

Keywords Steady state fluorescence · Pyranine · Polyacrylamide · κ- carragenan

Introduction

Polymer gels are unique soft materials in that they can retain a large amount of fluid and can exchange this fluid with their surrounding environment. Gel, made of weakly cross-linked networks of homopolymers, is known to exist in two distinct phases, swollen and collapsed, in a liquid [1]. A number of studies on weakly cross-linked polymer gels have revealed a discontinuous volume phase transition. It is well established that polyacrylamide is the chemically crosslinked gel which is a chemical intermediate used in the production and synthesis of polyacrylamide. These high molecular weight polymers can be modified to develop nonionic, anionic, or cationic properties for specific uses [2]. On the other hand, κ-carrageenan, industrially important sulphated galactan, is physically crosslinked gel. Kappa and iota are the common carrageenan groups and found in the gamet to phytic life phase of various seaweed species [3].

In order to understand the physical nature of polymerization processes underlying the transitions from sol to the gel state, one must follow the reaction kinetics, compare results with experiments directly measuring some physical properties in the course of the polymerization reaction. Experimental techniques used for monitoring this transition must be very sensitive to the structural changes, and should not disturb the system mechanically. Fluorescence technique is of particularly useful for elucidation of detailed structural aspects of the gels. This technique is based on the interpretation of the change in anisotropy, emission and/or excitation spectra,

emission intensity, and viewing the lifetimes of injected aromatic molecules to monitor the change in their microenvironment [4, 5]. Fluorescence probes can be used in two ways for the studies on polymerization and gelation. First, one can add a luminescent dye as a probe to the system (extrinsic fluoroprobe). By using this fluoroprobe it is possible to measure some physical parameters of the polymerizing system, like polarity [6, 7], viscosity [8, 9], and hydrophobicity 10]. In the second approach, the fluorophore is covalently attached to the polymer, and serves as a polymer-bond label (intrinsic fluoroprobe) [11], where the polymer fluoroprobe association depends on some factors including Coulombic interactions, the hydrophobicity of the polymer-fluorophore pair, etc. These techniques have been successfully used to perform the experiments on polymerization and chemical gel formation [12, 13] and swelling [14].

Pyranine has three functional groups that can be bonded to the polymeric network, branched, or linear polymers. The probability that pyranine is bonded to the system over more than one functional group may increase with increasing polymer concentration, and also with the reaction time. As the polymerization progresses pyranine can have a chance to bind the polymeric system over two or three functional groups [15].

In this work, we aimed to study the free-radical cross-linking polymerization and swelling processes of PAAm-κC gel composites by using steady state fluorescence technique. The pyranine, added to the pre-polymerization solution in very small amount, shows a spectral shift to the shorter wavelengths upon the initiation of polymerization. This spectral shift is due to the binding of pyranine to the polymer chains during the PAAm- κC gel polymerization.

The pyranine, thus, becomes an intrinsic fluoroprobe while it is extrinsic at the beginning of the reaction. The total fluorescence intensity of the pyranine bonded to the strands of the polymers allows one to measure directly the gel fraction near the sol-gel transition, and thus the corresponding critical exponent, β. On the other hand, Li-Tanaka equation was used to determine the swelling time constants, τ and cooperative diffusion coefficients, D for the swelling processes. It was observed that, τ and D decreased and increased respectively as the κC content in PAAm gel was increased.

Theoretical consideration

Gelation theory

Several theories have been developed in the past half century to describe gel formation, among which Flory-Stockmayer theory and percolation theory have provided the bases for modeling the sol-gel phase transition [16–22]. Statistical theories based on a tree-like structure (Bethe lattice) use mean field approximation, which originates from Flory [16] and Stockmayer [17], and assume equal reactivities of functional groups and the absence of cyclization reactions. Percolation offers a particularly simple and yet detailed picture through which one may seek to understand gelation [18–20, 22]. In the language of percolation, one may think of monomers as occupying the vertices of a periodic lattice, and the chemical bonds as corresponding to the edges joining these vertices, at any given moment, with some probability p. Then, the gel point can be identified with the percolation threshold p_c, where, in the thermodynamic limit, the incipient infinite cluster starts to form. Identifying the weight average degree of polymerization DP_W with the average cluster size S_{av} and the gel fraction G with the probability P_∞ of an occupied site belonging to the incipient infinite cluster, one can predict the scaling behavior of these and related quantities near the gel point, as a function of $|p - p_c|$,

$$DP_w \propto (p_c - p)^{-\gamma}, \quad p \to p_c^- \tag{1}$$

$$G \propto (p - p_c)^{\beta}, \quad p \to p_c^+ \tag{2}$$

If p approaches p_c from below it is denoted as $p \to p_c^-$; in contrast, $p \to p_c^+$ denotes when p approaches p_c from above. Here, β and γ are the critical exponents. The critical exponents in percolation theory, β=0.41 and γ=1.70, differ from those found in Flory-Stockmayer, β=1 and γ=1.

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 [18, 19]. 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 [23, 24]. In this article, we start from the assumption that the fluorescence intensity, I, is also connected with the gel formation indicators DP_w (for $t < t_c$) and G (for $t > t_c$). Therefore, below the gel point, i.e., for $t < t_c$ the maximum fluorescence intensity, I_{max}, measures the weight average degree of polymers (or average cluster size). Above t_c, if the intensity from finite clusters distributed through the infinite network I_{ct} is subtracted from the maximum fluorescence intensity, then, the corrected intensity I_{max}- I_{ct} measures solely the gel fraction G, the fraction of the monomers that belong to the macroscopic network.

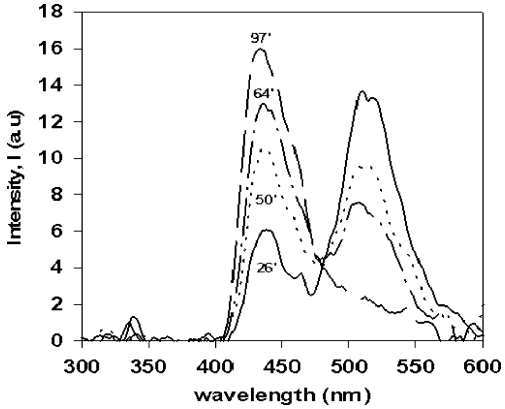

Fig. 1 Typical fluorescence spectra of pyranine at different stages during the AAm-κC-BIS polymerization. Numbers on the spectra show corresponding reaction times

Swelling theory

The equation for the kinetics of swelling of a polymer gel disk, as expressed by Li and Tanaka [25], is as follows

$$\frac{U(r,t)}{U(r,0)} = \sum_{n=1}^{\infty} B_n e^{\frac{-t}{\tau_n}} \tag{3}$$

where *U(r, 0)* is total change of radius, t is the time, *U(r, t)* is the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen and B_n is pre- exponential factor. Each component of the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen, decays exponentially with a time constant τ_n, which is independent of time t [25] and is inversely proportional to the cooperative diffusion coefficient D of a gel disk at the surface and given by the relation [25]

$$\tau_n = \frac{3a^2}{D\alpha_n^2} \tag{4}$$

Here a represents the half of the disc thickness in the final infinite equilibrium which can be experimentally determined.

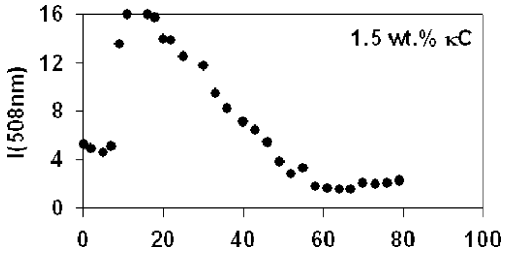

Fig. 2 Fluorescence intensity of the free pyranine at 508 nm, I_{508nm}, versus reaction time for 1.5 wt.% κC

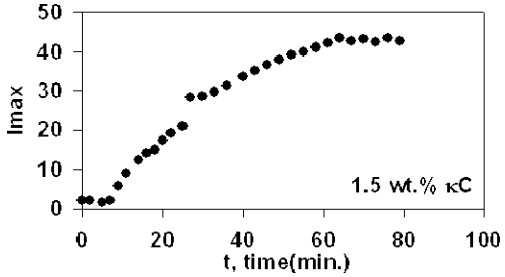

Fig. 3 Fluorescence intensity 427 nm variation of the pyranine, bonded to the PAAm for 1.5 wt.% κC concentrations, versus reaction time

The series given by Eq. 3 is convergent. The first term of the series expansion is dominant at large t, which correspond to the last stage of the swelling. As it is seen from Eq. 4 τ_n is inversely proportional to the squared of α_n, which are the roots of the Bessel functions. If $n>1$, then α_n increases and τ_n decreases very rapidly. Therefore kinetics of swelling in the limit of large t or If τ_1 is much larger than the rest of τ_n [26] all high order terms ($n\geq 2$) in Eq. 3 can be dropped so that the swelling and shrinking can be represented by the first order kinetics [25]. In this case Eq. 3 can be written as

$$\frac{W_t}{W_\infty} = 1 - B_1 e^{-t/\tau} \tag{5}$$

where τ_1 as taken as τ. Eq. 5 allows us to determine the parameters B_1 and τ. if one knows the behaviour of W_t as a function of t. Here it is important to note that Eq. 5 satisfies the following equation

$$\frac{dW_t}{dt} = \frac{1}{\tau}(W_\infty - W) \tag{6}$$

which suggest that the process of swelling should obey the first order kinetics. The higher order terms ($n\geq 2$) can be considered as fast decaying perturbative additions to the first order kinetics of the swelling in the limit of large t.

Experimental

AAm, BIS, APS and pyranine were dissolved in 10 ml distilled water (pH 6.5) by heating. The heated mixture

Table 1 Experimentally measured parameters of PAAm hydrogel for various amounts of κC during gelation process

PAAm [M]	κC (wt.%)	$t_c(s)$	β
2	0.5	300±5	0.54
2	1.0	480±5	0.41
2	1.5	720±5	0.56
2	2	960±5	0.55
2	2.5	1320±5	0.82
2	3	1140±5	0.80

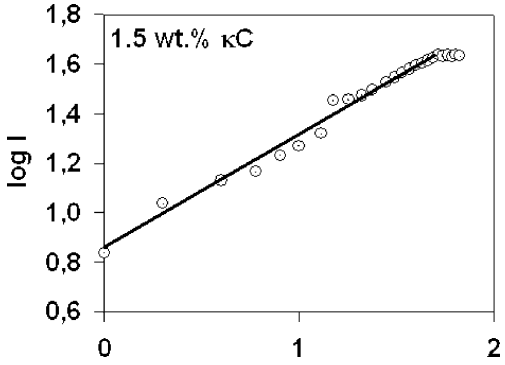

Fig. 4 Double logarithmic plot of the intensity I versus time curves above t_c for 1.5 wt.% κC. The β exponents were determined from the slope of the straight lines

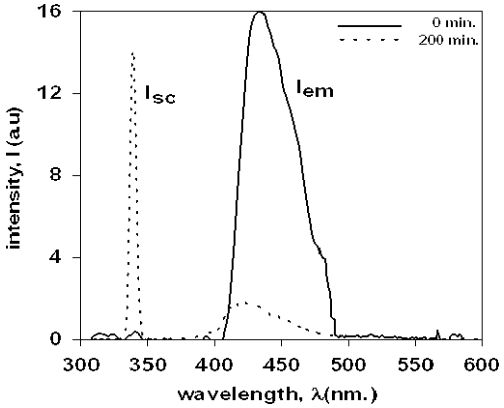

Fig. 6 Fluorescence spectra of pyranine during the swelling process for 0.5 wt.% κC content composite gel. The numbers indicate the swelling times

solution where the number of crosslinker per AAm monomer was fixed was held at 80 ^{0}C. Then varying amounts of κ-carrageenan (0.5 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.% and 3 wt.%) were added. At the last stage 2 μ*l* TEMED was added. The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller. All measurements were made at 90° position and slit widths were kept at 5 nm. Pyranine was excited at 340 nm during in situ gelation and swelling experiments and variation in the fluorescence spectra and emission intensity of the pyranine were monitored as a function of time.

Results and discussion

Gelation process

Figure 1 shows typical fluorescence spectra of pyranine at different stages of the PAAm- κC copolymerization. At the beginning of the reaction, only the 508 nm-peak exists, then the intensity of the new (short-wavelength) peak started to increase as the intensity of the 508 nm-peak (long-wavelength peak) decreased during the course of AAm polymerization. Shift to the short wavelengths and increase in the intensity of short-wavelength peak during the polymerization should be due to the neutralization of SO^{-3} groups of some of the pyranines in the reaction mixture. Therefore, the disappearing of the 508 nm peak at the end of the polymerization reaction, as shown in Fig. 1, can only be attributed to the binding of the pyranines to the PAAm gel.

We have conducted the gelation experiments for various amounts of κ-carrageenan. Since 508 nm- peak (corresponding to free pyranines in the sample cell) does not shift during the whole polymerization process, one may have a chance for real time monitoring of the polymerization by means of the change in the free pyranine intensity versus reaction time. Figure 2 presents the fluorescence intensity of the free pyranine from the reaction mixture as a function of the reaction time for 1.5 wt.% of κ-carrageenan. As seen in Fig. 2 that the fluorescence intensity of the free pyranines first decreased rapidly to some value (initial stage) then started to

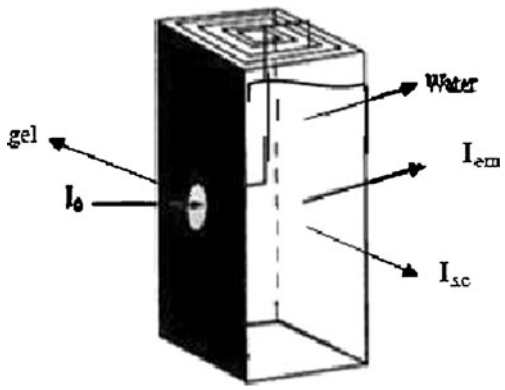

Fig. 5 The position of PAAm-κC composite gel in the fluorescence cell during swelling in water. I_0 is excitation (340 nm), I_{sc} is scattered (340 nm) and I_{em} is emission (427 nm) maximum light intensities, respectively. PAAm- κC composite gel located on the black cartoon with circular hole

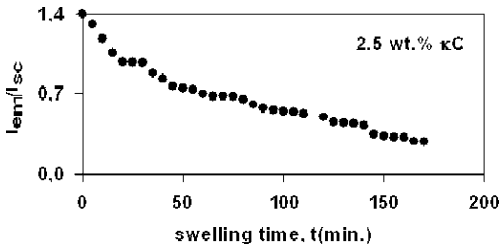

Fig. 7 Corrected fluorescence intensities of pyranine, I (=I_{em}/I_{sc}) during the swelling process for 2.5 wt.% κC concentrations

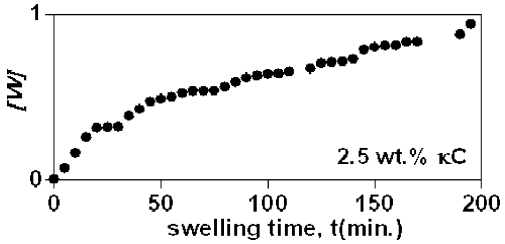

Fig. 8 The plots of water uptake, W versus swelling time, t for PAAm-κC composite gel swollen in water for 2.5 wt.% κC contents

increase suddenly up to some point (gelation stage), and then decreased to zero at the end of the reaction (final stage) for all carrageenan contents.

Figure 3 shows the fluorescence intensities from the bonded pyranine against the reaction time for 1.5 wt.% of κ-carrageenan. Since the maxima of the spectra (corresponding to bonded pyranine) shifts from 400 nm to 427 nm as the polymerization progresses, one does not have a chance to monitor the intensity in the time drive mode of the spectrometer (ten possible data in one second). Therefore, we monitored the fluorescence spectra in the relatively large periods of time and plotted the intensity corresponding to the maxima of the spectra as a function of time, in Fig. 3. Using the Eqs. 1 and 2 and the values for t_c summarized in Table 1 we calculated β exponents as function of κ- carragenan (κC) concentration. Figure 4 represents the log-log plots of the typical intensity-time data above the gel point, for 1.5 wt.% κC concentration where the slope of the straight lines, close to the gel points, give β exponents. The produce β values are listed in Table 1 for various amounts of κ-carrageenan, where β obeyed the percolation result for less κ-carrageenan content (<2.0 wt.%) however classical results were produced at high κ-carrageenan concentration (>2.0 wt.%).

Swelling process

After gelation process, a disc-shaped gel samples were placed on the wall of 1×1 quartz cell filled with water for

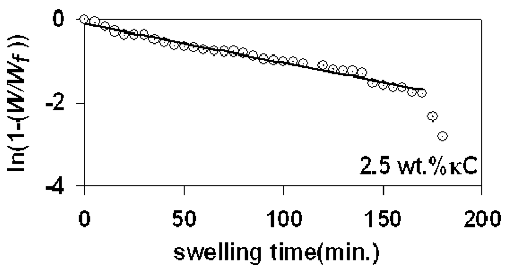

Fig. 9 Fit of swelling time data between 0 min and 170 min. in Fig. 9 to Eq. 10 for PAAm- 2.5 wt.% κC content composite gel swollen in water

Table 2 Experimentally measured parameters of PAAm hydrogel for various κC content during sweeling process

κC (wt.%)	$a_i\times10^{-2}$ (m)	$a_f\times10^{-2}$ (m)	$r_i\times10^{-2}$ (m)	$r_f\times10^{-2}$ (m)	τ (min)	$D\times10^{-9}$ (m^2s^{-1})
0.5	0.108	0.190	0.300	0.535	160	6.96
1.0	0.095	0.188	0.350	0.588	185	4.44
1.5	0.105	0.215	0.356	0.780	188	1.68
2.0	0.090	0.158	0.305	0.520	200	1.06
2.5	0.110	0.183	0.380	0.570	233	0.97
30.	0.110	0.170	0.405	0.595	240	0.31

a_i the initial disc thickness, a_f the final disc thickness, r_i the initial radius of the disc, r_f the final radius of the disc, τ fluorescence time constant, D fluorescence cooperative diffusion coefficient

the swelling experiments. The position of the gel and the incident light beam for the fluorescence measurements are shown in Fig. 5 during swelling in water. Here one side of the quartz cell is covered by black cartoon with a circular hole to collimate the light beam so that minimize the effect of changes in the volume.

Figure 6 shows the emission spectra of PAAm-κC composites during the swelling process in pure water for 2.5 wt. % κC. It can be seen that as the water uptake is increased fluorescence intensity, I_{em} decreases and the scattered light intensity, I_{sc} increases. Since the increase in I_{sc} corresponds to increase in turbidity of the swelling gel, then we have defined corrected fluorescence intensity, I as I_{em}/I_{sc}.

Figure 7 shows the variations of the corrected pyranine intensities, I ($=I_{em}/I_{sc}$) of PAAm-κC composites versus swelling time during hydrogel swelling for 2.5 wt. % κC concentrations, respectively. It can be seen that as the swelling time, t, is increased, quenching of excited pyranines increase due to water uptake. It has also to be noted that quenching becomes more efficient at higher κC concentrations.

In order to quantify these results the collisional type of quenching mechanism may be proposed for the fluorescence intensity, I from the hydrogel sample during the swelling process, where the following relation can be used [5],

$$I^{-1} = I_0^{-1} + k_q\tau_0[Q] \tag{7}$$

Here, k_q is quenching rate constant, τ_0 is the lifetime of fluorescence probe and Q is the quencher.

Integration and reorganization of the above relation for low quenching efficiency, $(\tau_0 k_q[Q] << 1)$ produces the following useful equation,

$$W = \left(1 - \frac{I}{I_0}\right)\frac{\upsilon}{k_q\tau_0} \tag{8}$$

Here water uptake, W was calculated over differential volume by replacing Q with W as

$$W = \int_{a_0}^{a_\infty} [W] d\upsilon \tag{9}$$

where υ is the swollen volume of the gel at the equilibrium swelling, which can be measured experimentally. k_q was obtained from separate measurements by using Eq. 8 where the infinity equilibrium value of water release and uptake, W_f was used for all κC concentrations. Since τ_0 (≈ 5 ns.) is already known from the dry gel, and measured values of W can be calculated from the measured I values at each swelling steps.

Here, it is assumed that k_q values do not vary during swelling processes, i.e. the quenching process solely originates from the water molecules.

Plots of water uptake, W versus swelling time are presented in Fig. 8. The logarithmic form of the data in Fig. 9 is fitted to the following relation produce from Eq. 3

$$\ln\left(1 - \frac{W}{W_f}\right) = \ln B_1 - \frac{t}{\tau} \tag{10}$$

Here, τ is the time constant, measured by fluorescence technique. Using Eq. 10 linear regressions of curves provide us with B_1 and τ values. Taking into account the dependence of B_1 on R, one obtains R values and from α_1-R dependence α_1 values were produced [27]. Then using Eq. 10, cooperative diffusion coefficients D were determined for these disc-shaped hydrogels and found to be around 10^{-9} m^2/s. Experimentally obtained τ and D values are summarized in Table 2, where a and r values are also presented for each gel sample. It should be noticed that D values decrease as the κC concentrations are increased.

Increasing κ-carrageenan(κC) content decelerates the swelling process of the gel which results smaller values of D for the composite system. This phenomenon can be explained by assuming that the less carrageenan content composite gels are loosely formed gels which contain less double helices than the densely formed gels, formed with more carrageenan content. It is understood that due to high water absorbance capability, densely formed gels swell much slower than loosely formed gels, which result to produce large D values. It means that moister absorption capacity of carrageenan is much higher than PAAm.

Conclusion

Results for swelling have shown that the steady-state fluorescence technique is quite powerful and can be used to monitor swelling kinetics of PAAm- κC composite gels in water. Observations around the gel point, t_c for PAAm-κC composite gels showed that the gel fraction exponent β obeyed the percolation result for less κ-carrageenan content (<2.0 wt.%) however classical results were produced at high κ-carrageenan concentration (>2.0 wt.%). The Li- Tanaka equation can be employed to determine the swelling time constants τ and cooperative diffusion coefficients D for the swelling processes. It is observed that loosely formed composite gels which contain less κ- carrageenan than densely formed gels swell much faster, providing larger cooperative diffusion coefficients. It is observed that densely formed gels contain more double helices and more lattice dislocations and swell slower than loosely formed gels which may contain less double helices and less lattice imperfections [28].

References

1. Tanaka T (1978) Collapse of gels and the critical endpoint. Phys Rev Lett 40(12):820–823
2. Meena R, Prasad K, Mehta G, Siddhanta AK (2006) Synthesis of the Copolymer hydrogel κ-carrageenan-graft-PAAm: evaluation of its absorbent and Adhesive properties. J App Poly Sci 102 (6):5144–5152
3. Falshaw R, Bixler H, Johndro K (2001) Structure and performance of commercial kappa-2 carrageenan extracts I. Structure analysis. Food Hydrocoll 15(4–6):441–452
4. Barrow GM (1962) Introduction to molecular spectroscopy. McGraw-Hill, New York
5. Birks JB (1965) Photophysics of aromatic molecules. Willey, (Interscience), London
6. Jager WF, Volkers AA, Neckers DC (1995) Solvatochromic fluorescent probes for monitoring the photopolymerization of dimethacrylates. Macromolecules 28(24):8153–8158
7. Schaeken TC, Warman JM (1995) Radiation-induced polymerization of a mono- and diacrylate studied using a fluorescent molecular probe. J Phys Chem 99(16):6145–6151
8. Miller KE, Krueger RH, Torkelson JM (1995) Mobility-sensitive fluorescence probes for quantitative monitoring of water sorption and diffusion in polymer coatings. J Polym Sci B Polym Phys 33 (17):2343–2349
9. Vatanparast R, Li S, Hakala K, Lemmetyinen H (2000) Monitoring of curing of polyurethane polymers with fluorescence method. Macromolecules 33(2):438–443
10. Erçelen Ş, Klymchenko AS, Demchenko AP (2000) Ultrasensitive fluorescent probe for the hydrophobic range of solvent polarities. Anal Chim Acta 464(2):273–287
11. Jager WF, Sarker AM, Neckers DC (1999) Functionalized 4-(Dialkylamino)-4′-nitrostilbenes as reactive fluorescent probes for monitoring the photoinitiated polymerization of MMA. Macromolecules 32(26):8791–8799
12. Pekcan Ö, Yilmaz Y, Okay O (1997) Real time monitoring of polymerization rate of methyl methacrylate using fluorescence probe. Polymer 38(7):1693–1698
13. Pekcan Ö, Yilmaz Y, Okay O (1994) Fluorescence technique for studying the sol-gel transition in the free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. Chem Phys Lett 229(4–5):537–540

14. Aktas DK, Evingür GA, Pekcan Ö (2007) Study on swelling of hydrogels (PAAm) at various temperatures by using fluorescence technique. J Mat Sci 42(20):8481–8488
15. Yilmaz Y, Uysal N, Gelir A, Guney O, Aktaş DK, Gogebakan S, Oner A (2009) Elucidation of multiple- point interactions of pyranine fluoroprobe during the gelation. Spectrochimica Acta Part A: Mol Biomolecular Spect 72(2):332–338
16. Flory PJ (1941) Molecular size distribution in three dimensional polymers. I. Gelation. J Am Chem Soc 63(11):3083–3090
17. Stockmayer WH (1943) Theory of molecular size distribution and gel formation in branched- chain polymers. J Chem Phys 11(2):45–54
18. Stauffer D, Coniglio A, Adam M (1982) Gelation and critical phenomena. Adv Polym Sci 44:103–158
19. Stauffer D (1985) Introduction to percolation theory. Taylor and Francis, London
20. de Gennes PG (1988) Scaling concepts in polymer physics. Cornell University Press, Ithaca
21. Hermann HJ (1986) Geometrical cluster growth models and kinetic gelation. Phys Rep 136(3):153–224
22. Stauffer D, Aharony A (1994) Introduction to percolation theory, 2nd edn. Taylor and Francis, London (second printing)
23. Yilmaz Y, Erzan A, Pekcan Ö (1998) Critical exponents and fractal dimension at the sol- gel phase transition via in situ fluorescence experiments. Phys Rev E 58(6):7487–7491
24. Yilmaz Y, Erzan A, Pekcan Ö (2002) Slow Release percolate near glass transition. Euro Phys J E: Soft Matter and Biological Physics 9(2):135–141
25. Li Y, Tanaka T (1990) Kinetics of swelling and shrinking of gels. J Chem Phys 92(2):1365–1371
26. Tanaka T, Sato E, Hirakowa Y, Hirotsu S, Peetermans J (1985) Critical kinetics of volume phase transition of gels. Phys Rev Lett 55(22):2455–2458
27. Shibayama M, Tanaka T (1993) Volume phase transition and related phenomena of polymer gels. Adv Polym Sci 109:1–62
28. Kara S, Tamerler C, Arda E, Pekcan Ö (2003) Photon transmission study on swelling of k- carrageenan gels prepared in various concentrations. Int J Bio Macro 33:235–245