Structural and kinetic modification of aqueous hydroxypropylmethylcellulose (HPMC) induced by electron beam irradiation

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ABSTRACT: Electron beam was irradiated on 10% and 20% hydroxypropylmethylcellulose (HPMC) aqueous solutions with different doses to make gel films. As increasing dose, the gel fraction of the film increased sharply above a critical dose and then decreased gradually after passing a maximum. The scission/cross-linking ratio and the critical dose were determined using the Charlesby-Rosiak equation as 0.52 and 9 kGy for 10% gel and 0.43 and 14 kGy for 20% gel, respectively. The gel fraction for 20% HPMC film was lower at low dose and higher at high dose than that for 10% film. The behavior of the swelling ratio of the gel film was just opposite to that of the gel fraction. The cross-linking density of the gel estimated from the Flory theory linearly increased with irradiation dose at low dose, passed a maximum around 100 and 160 kGy for 10% and 20% films, respectively, and decreased at high dose. These results suggest the competition of scission and cross-linking induced by indirect effect of irradiation. Dielectric relaxation measurement by time domain reflectometry and RF impedance/material analyzer revealed two characteristic relaxations of chain motions around 100MHz and of orientation of free water around 20GHz. From the dose dependence of the relaxation parameters determined by fitting to a combined equation of Cole-Cole type and KWW type, a coupling of motions of HPMC molecules and water molecules was strongly suggested. The critical dose for gelation was coincident with the dose for the maximum of τ_h and the minimum of $\Delta\varepsilon_h$ together with the minimum of τ_m and the maximum of $\Delta\varepsilon_m$, where τ_h and $\Delta\varepsilon_h$ denote the relaxation time and the relaxation strength for free water molecular motion and τ_m and $\Delta\varepsilon_m$ the corresponding ones for HPMC molecular motion. The characteristic behavior was discussed in terms of the increase of affinity between HPMC and water and the constrained molecular motion in the gel network.

Keywords: hydroxypropylmethylcellulose (HPMC); electron beam irradiation; gel fraction; swelling; dielectric spectroscopy; coupled molecular motion

Introduction

In radiation chemistry, polymers were classified into two types: scission polymers and cross-linking polymers, and most biopolymers were placed into the scission polymers[1,2]. Recent developments in this field proved, however, that a variety of biopolymers could be cross-linked in aqueous solution or paste-like state and modified to form hydrogels by irradiation of high-energy electromagnetic waves such as β-ray and γ-ray, only if the irradiation condition of the total irradiation dose, the dose rate, the temperature, the biopolymer concentration, and the coexisting cations was properly controlled[3-7]. Since the radiation-induced hydrogels are prepared without any toxic chemical reagents or additives and the products are biodegradable, they have attracted growing attention as an environmentally-friendly materials for industrial and pharmaceutical applications[6,7]. To control the physicochemical properties of the hydrogels it is necessary to study the relationship between the irradiation condition and the characteristics of the resultant materials. The hydrogel prepared by β-ray irradiation consists of three-dimensional cross-linked polymer network and enclosed aqueous solution of branched biopolymer molecules with a distribution of the degree of polymerization and branch. In this study we measured the fraction of the polymer network f, the swelling ratio Q_v and the dielectric properties of the hydrogel of one of cellulose derivatives, hydroxypropylmethylcellulose (HPMC) to characterize the electron beam radiation-induced hydrogel as a function of irradiation dose and HPMC concentration. The critical dose for cross-linking is estimated from the observed gel fraction by using the Charlesby-Rosiak equation. The cross-linking density of the polymer network q of the hydrogel is estimated from the swelling ratio of the dried hydrogel by assuming the Flory theory for equilibrium swelling. Dielectric spectroscopy gives us the information of the molecular motion of the polymer network, the enclosed polymers and solvent water. To study the molecular motion of the molecules in the hydrogel is even challenging from academic aspect, since the interaction of the molecules such as hydrogen bonding and hydrophobic bonding plays important roles in stabilizing complex states observed in temperature-concentration phase diagrams[8-11].

Extensive data already obtained for HPMC are useful for discussion of the physical properties of newly prepared hydrogels[12-18].

Experimental Section

HPMC (60SH-50) is a gift from Shin-Etsu Chemical Co. The viscosity-average molecular weight is 10.4×10^4 and the nominal degree of substitution of methoxyl group (DS) and the molecular substitution of hydroxypropoxyl groups (MS) per anhydroglucose unit are 1.9 and 0.25, respectively, and the nominal density is 1.26 g/cm^3. In order to prepare 10 wt% and 20 wt% homogeneous solutions, HPMC was first dispersed in 2/3 of desired amount of MilliQ water at 80°C and then remaining 1/3 amount of water at 4°C was added to it. The final solution was obtained by dissolving thoroughly with gentle stirring at 4°C for two days. For irradiation the solution was put into a nylon bag and heat-sealed after the removal of air by a vacuum pump to yield a liquid plate (1mm x 10cm x 10cm). Electron beam from a 2 MeV accelerator at Takasaki Radiation Chemistry Research Institute was used to prepare hydrogel films at the irradiation parameters of the current being 1mA, the voltage 2 MeV and the dose per pass 1 kGy. A portion of the gel film was freeze-dried and the weight W_i was measured. Then the freeze-dried gel film was soaked in a large amount of water to extract soluble parts in the gel film at 20 ^{o}C for two weeks. The remaining insoluble solid was freeze-dried again and the weight W_n was measured. The gel fraction f was obtained from these values as $f=W_n/W_i$. The final sample of the freeze-dried insoluble solid was soaked in water at 20 ^{o}C. The weight of the swollen hydrogel was constant after 10 h. The volume of the dried film V_n and that of the swollen gel V_s was calculated from the weights at the initial state and the equilibrium after 48 h soaking together with the densities of HPMC and water, and the swelling ratio $Q_v=V_s/V_n$ was determined. Four sheets of the finally obtained hydrogel prepared from 10 wt% and 20 wt% HPMC solutions was stacked in layers at high humidity condition to obtain the sample for dielectric spectroscopy study. The dielectric measurements were performed using a combination of Time Domain Reflectometry (TDR)(Agilent Technologies, HP54120T)[19] and RF Impedance/Material Analyzer (Agilent

Technologies, HP54120T) at 25 °C. The observed dielectric spectroscopic data were fitted to the equation

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\sigma}{j\omega\varepsilon_0} + \frac{\Delta\varepsilon_h}{1 + (j\omega\tau_h)^{\beta_h}} + \frac{\Delta\varepsilon_l}{1 + (j\omega\tau_l)^{\beta_l}} + \Delta\varepsilon_m \int_0^\infty \left[-\frac{d\varphi(t)}{dt} \right] e^{-j\omega t_m} dt$$

$$\varphi(t) = \exp\left[-\left(\frac{t}{\tau_m}\right)^{\beta_{KWW}} \right]$$

(1)

where $\varepsilon_\infty, \varepsilon_0$, σ, $\Delta\varepsilon$, τ, and β are the permitivity at limiting high frequency, the permitivity of vacuum, the DC conductivity, the relaxation strength, the relaxation time, and the shape parameter indicating the broadness of the relaxation curve, respectively. Smaller β values ($0<\beta<1$) give broader symmetric relaxation curves. The subscripts h, m, and l indicate the Cole-Cole type free water relaxation process, the KWW type micro-Brownian motion of HPMC, and the electrode polarization/ the counter ion process, respectively. The corresponding relaxations are hereafter called the h-, m- and l-relaxation. The detailed analyzing procedure and the adequacy were reported elsewhere[20-25].

Results and Discussion

Figure 1 shows the dose dependence of gel fraction f of hydrogel prepared from HPMC aqueous solutions at 10 wt% and 20 wt%, which we hereafter call 10% gel and 20% gel, respectively. The dose dependence of sol fraction s=(1-f) is conventionally described by Charlesby-Rosiak equation[26]:

$$s + \sqrt{s} = \frac{p_0}{q_0} + (2 - \frac{p_0}{q_0})(\frac{D_v + D_g}{D_v + D})$$

(2)

where p_0 and q_0 are the degradation and cross-linking densities, respectively, D; the absorbed dose, D_v; the virtual dose required for changing the molecular weight distribution to the most probable distribution and D_g; the critical dose for gelation. The data were fitted to Eq. (2) by a least squares method and the

parameters of p_0/q_0, D_v and D_g were determined as 0.52, -4.04 kGy and 9.3 kGy, respectively, for 10% gel and 0.43, 4.16 kGy and 13.6 kGy for 20% gel, respectively. The values of $p_0/q_0<1$ mean the predominance of cross-linking. The dashed lines in Fig. 1 show the calculated ones using Eq. (2) with these parameters. While Eq. (2) could express a monotonous increase of gel fraction, in the real experiment for the HPMC solution, however, as increasing dose the gel fraction of the film increased sharply above a critical dose and then decreased gradually after passing of a maximum. Therefore, since Eq. (2) deviates from the real one to higher value of $s+\sqrt{s}$ at low dose, the critical dose D_g obtained using Eq. (2) should be taken as the lower minimum. The solid lines in Fig. 1 were drawn for the guide of eyes. The real D_g may be around 10kGy for 10% gel and 20 kGy for 20% gel. The gel fraction for 20% gel was lower at lower dose and higher at higher dose than that for 10% gel. The cross-linking of polymer molecules is in general produced by direct effect due to the radical formation along the irradiated polymer molecules and indirect effect due to the attack of hydroxide radicals yielded in irradiated water molecules to the polymer molecules. The higher sensitivity of more dilute (10%) solution to the irradiation dose at low dose suggests a larger contribution of indirect effect. This result is common to cellulose derivatives[6]. At high dose when the cross-linking density is quite high, the motility of polymer molecules decreases. In that case since the diffusion of polymer radicals is requisite for cross-linking, further cross-linking is difficult to yield but scission becomes predominant. The deviation of observed gel fraction from that of Charlesby-Rosiak equation, especially the decrease of the gel fraction at high dose, could be attributed to this effect and/or the breaking of polymer network due to the brittleness resulting from excess inhomogeneity of cross-linking points. It is known that polysaccharides are modified by gamma-ray, neutron ray and X-ray as typically by breaking of glycosidic linkages and the introduction of carboxyl and carbonyl groups[1,27-29]. Although the concentration of radicals is usually much higher during electron beam irradiation than gamma-ray irradiation, the main breaking points along the polysaccharides may not be changed.

Figure 2 shows the swelling ratio as a function of irradiation dose. As increasing dose the swelling ratio Q_v decreases at low dose, passes a minimum and finally increases at high dose. Q_v for 10% gel is lower at low dose and higher at high dose than that for 20% gel. These are just opposite to the behavior of gel fraction. The uptake of water by the hydrogel is determined by the elastic force of the polymer network relative to the decrease of free energy due to the dilution, and vice versa. The cross-linking density is estimated from the swelling ratio data by assuming the Flory equation as[30]

$$\ln(1-\phi_g) + \phi_g + \chi\phi_g^2 + \frac{\rho_p \upsilon}{M_c}\left(\phi_g^{1/3} - \frac{\phi_g}{2}\right) = 0$$

$$q = \frac{w}{M_c}$$

(3)

where ϕ_g, ρ_p, ν, M_c and χ are the volume fraction of HPMC (dried HPMC gel), the density of HPMC, the molar volume of water, the average molecular weight of the chain between cross-linking points, and the thermodynamic interaction parameter. χ was estimated from the reported empirical value of second virial coefficient A_2, 1.38×10^{-3} cm^3 mol/g^2, for a similar HPMC sample (Mw=127,000, DS=1.9 and MS=0.15)[31] as 0.468. The dose dependence of q is shown in Fig. 3. As increasing dose, q increases above the critical dose, passes a maximum and finally decreases. The critical dose for the starting of swelling and the dose for the maximum q are obtained around 10kGy and 100kGy for 10% gel and 20kGy and 160kGy for 20% gel, respectively. The critical doses for the starting of swelling agree fairly well with the critical doses of gelation D_g determined from gel fraction by eye as shown in Fig. 1. From the definition of q, the average number of monomer unit between the cross-linking points n is equal to 1/q. From Fig. 3, at the maximum cross-linking density condition, n is estimated around 100-500. If the effects of dangling chains could be neglected, the ratio of the numbers of cross-linking points and the terminal point in the polymer network is around 100. Measurements for gel fraction and swelling of HPMC (M~3.1-3.5x10^5, DS=1.4 and 1.9, MS=0.25 and 0.20) gels prepared by electron beam irradiation were performed by Pekel et al. in narrower range of irradiation dose[18]. The behavior of gel fraction

agrees well with ours in the overlapping experimental region. On the other hand, the swelling ratio is smaller than one third of ours, the considerable discrepancy of which cannot be attributed to the difference in the molecular weight M and the degree of substitution of methoxyl and hydroxypropoxyl groups. This could be rather resulted from the difference of preparation procedure of dried samples, i.e., we dried the sample by means of freeze-drying but Pekel et al. dried in air and a vacuum oven.

A typical example of the dispersion and absorption curves in the dielectric spectroscopy is shown in Fig. 4 for the hydrogel prepared from 10 % gel at irradiation dose of 50 kGy. Relaxation parameters for each process were obtained from fitting procedure of Eq. (1) to the experimental data. The solid lines in Fig. 4 were calculated from Eq.(1) together with the parameters thus determined. The dose dependences of the parameters for h-, m- and l-relaxation processes are shown in Fig. 5(a), (b), (c). Lower frequency side of the l-relaxation process is not exactly analyzed in the present frequency region because of a lack of the longer time behavior than the observed time domain. However, relaxation parameters for l-relaxation process were tentatively estimated to exactly determine other parameters for m- and h-relaxation processes. The relaxation parameters thus obtained for the l-process are not discussed in the present paper. The relaxation time of high frequency process τ_h takes the value around 10ps, which corresponds to the rotational diffusion of free water[32]. The decrease in the relaxation strength of high frequency process $\Delta\varepsilon_h$ with increasing percentage of weight of HPMC also supports the relaxation mechanism of free water. The tendency of the concentration dependence of β_h shown in Fig. 5(a) is similar to those usually obtained in various aqueous systems for which the β_h value decreases with increasing relaxation time[25,33] and the relaxation time is conventionally explained by the free volume concept. Usually, the relaxation process observed around 100MHz is attributed to the reorientation of bound water molecules and/or chain motions. Bound water has been considered to form two-dimensional network via hydrogen bond on the surface of proteins and DNA. The concentration dependence obtained for the relaxation time of free water is not shown for bound water[22]. In the present case of HPMC aqueous solution, it is considered that the surface does not offer hydrogen-bonding sites

to form network structure of bound water. The large concentration dependence for the relaxation time obtained in the present study also suggests that the m-process is closely related with polymer chain motions, which is largely affected by the concentration.

In this study, though hydration water is not directly reflected in the m-process, the chain dynamics is affected by hydration. We cannot identify each contribution of free polymer molecules enclosed in the gel network and the side chains of the network polymer to the m-relaxation process at this stage. Therefore, full understanding awaits the study of the dielectric spectroscopy for the rehydrated gel from completely washed freeze-dried hydrogel, the study of which is performed in the near future.

However, the present results show how relaxation parameters reflect the scission and cross-linking processes by electron beam irradiation for the first time. In h-relaxation in Fig. 5(a), a maximum of τ_h and a minimum of $\Delta\varepsilon_h$ appear around 10kGy for 10% gel and around 20-30kGy for 20% gel. The irradiation dose for the extreme values coincides with the critical dose for the starting of gelation and swelling both for 10% and 20% gels, as indicated by the arrows. A hump in τ_h and a depression in $\Delta\varepsilon_h$ are found at higher dose both for 10% and 20% gels. The dose for these small changes seems slightly lower for 10% gel than that for 20% gel, which might be related to the maximum of the gel fraction observed in Fig. 1. β_h, the index of inhomogeneity of relaxation motion decreases with increasing dose from unity for no irradiation. In m-relaxation in Fig. 5(b), a minimum in τ_m and a maximum in $\Delta\varepsilon_m$ are observed at 10kGy for 10% gel and 20-30kGy for 20% gel. A slight depression in τ_m and a hump in $\Delta\varepsilon_m$ are also found at high dose around 100 kGy. β_m monotonously decreases with increasing dose from 0.8 at 0 dose (no irradiation). The completely contrasting dose dependences of the relaxation time and the relaxation strength for h-relaxation and m-relaxation together with the increase of inhomogeneity with increasing dose strongly suggest a coupling of free water motion and polymer motion, i.e., a cooperative motion of different kind of molecular dynamics, resulting in slow dynamics of water. In the irradiation of electron beam the cross-linking is predominant in the initial stage according to the value of $p_0/q_0 < 1$. Since the branching of polymer molecules results in smaller contact area with surrounding solvent

molecules and the free energy is lowered, the affinity between the polymers and the solvent water should be increased[34]. The initial increase of τ_h and the decrease of $\Delta\varepsilon_h$ combined with the decrease of τ_m and the increase of $\Delta\varepsilon_m$ could be explained if we assume that an amount of free water with higher mobility is associated with polymer molecules to raise the mobility of them.

Around 10kGy for 10% gel and around 20kGy for 20% gel, three-dimensional polymer network with infinite molecular weight appears. The motion of polymer chains is constrained by being fixed to the network at the one end of the polymer. In contrast the water molecules associated to polymer molecules could be liberated from the polymer chains. This brings about the following decrease of τ_h and the increase of $\Delta\varepsilon_h$ combined with the increase of τ_m and the decrease of $\Delta\varepsilon_m$. As the branching at the side chain of the network increases with further irradiation, then the affinity increase becomes gradually predominant again, resulting in the behavior similar to the initial irradiation process of the increase of τ_h and the decrease of $\Delta\varepsilon_h$ combined with the decrease of τ_m and the increase of $\Delta\varepsilon_m$. The small humps in τ_h and $\Delta\varepsilon_m$ and the depressions in $\Delta\varepsilon_h$ and τ_m in the range of 50-150 kGy could be related to the maximum of gel fraction and cross-linking density and the minimum of swelling. Therefore, the final decrease in τ_h and the increase of $\Delta\varepsilon_h$ combined with the increase of τ_m and the decrease of $\Delta\varepsilon_m$ could be related to the scission of the polymer network. Similar results on a decrease in the relaxation strength from that estimated from the water amount were reported for emulsion with the wall materials of different lengths of glyceryl group of n-gryceryl monomyristate[19]. Those emulsion systems and proteins[35,36] also indicate that hydrophobic interaction decreases the relaxation strength for water, and this result corresponds well to the present dose dependence. The validity of the picture of irradiation-induced gelation proposed in the above could be further investigated by a light scattering measurement of the polymer solution enclosed in the hydrogel.

Conclusions

HPMC hydrogel was prepared in aqueous solution by indirect effect of electron beam irradiation. The critical dose for gelation D_g and the cross-linking density of the hydrogel were determined from gel fraction and swelling ratio measurements. Dielectric spectroscopy measurements strongly suggested cooperative change of motions of HPMC molecules and water molecules. Characteristic sharp and moderate peaks in the relaxation time and the relaxation strength for h- and m-relaxations were related to D_g and the peaks of gel fraction as a function of irradiation dose.
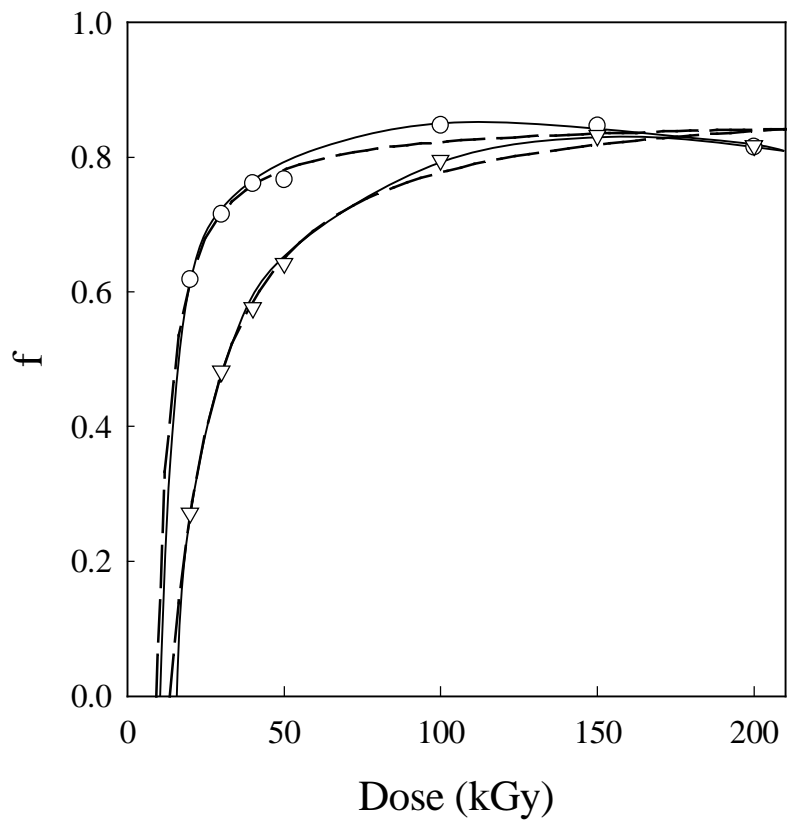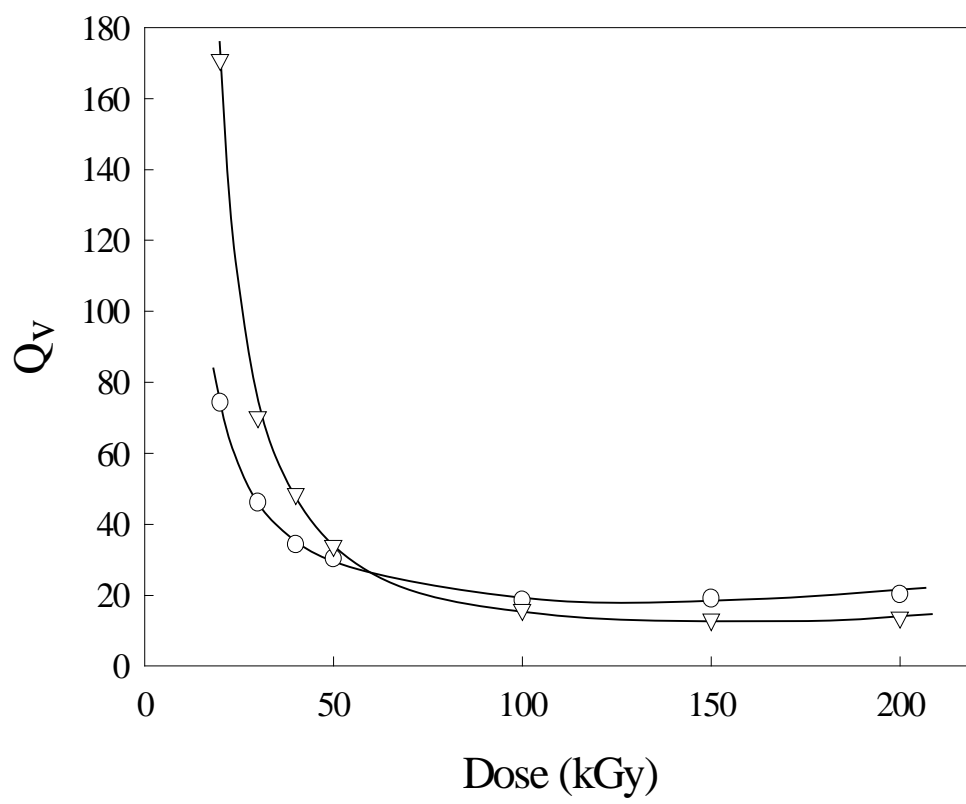
Figure 1. Furusawa et al. 12

Figure 2. Furusawa et al.

The figure plots $q / 10^{-4}$ (y-axis, from 0 to 80) versus Dose (kGy) (x-axis, from 0 to 200).
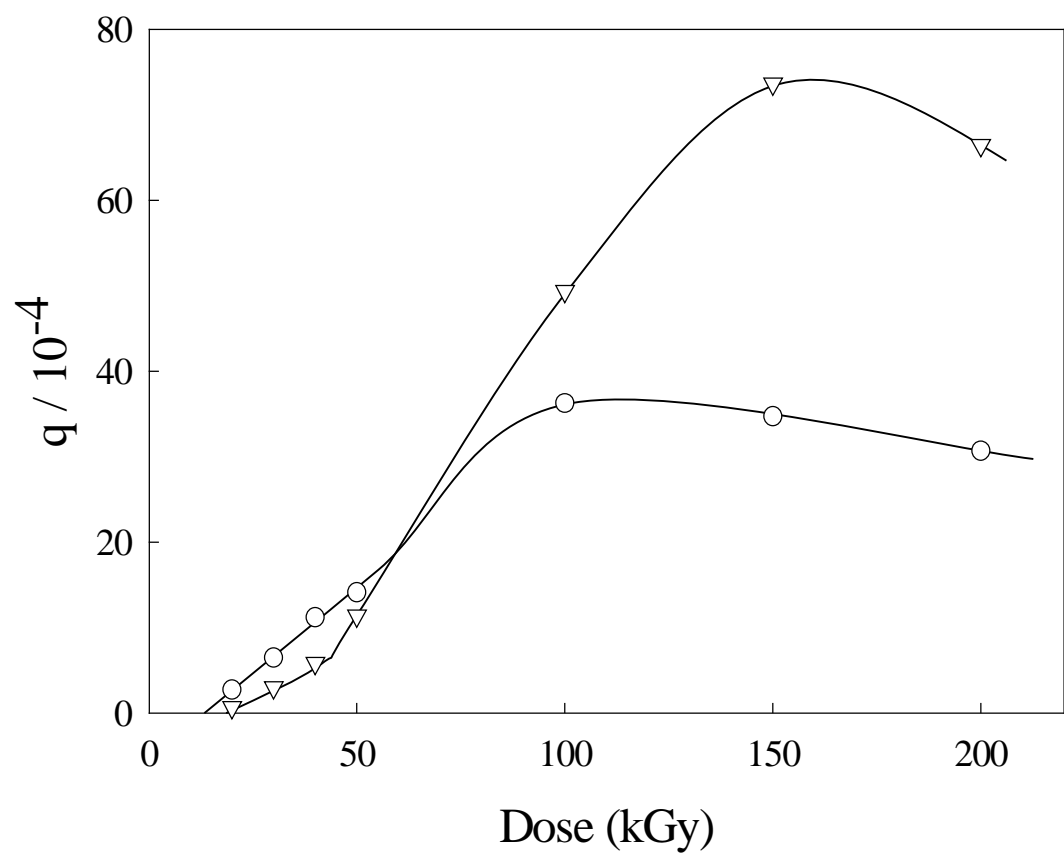
Figure 3. Furusawa et al.
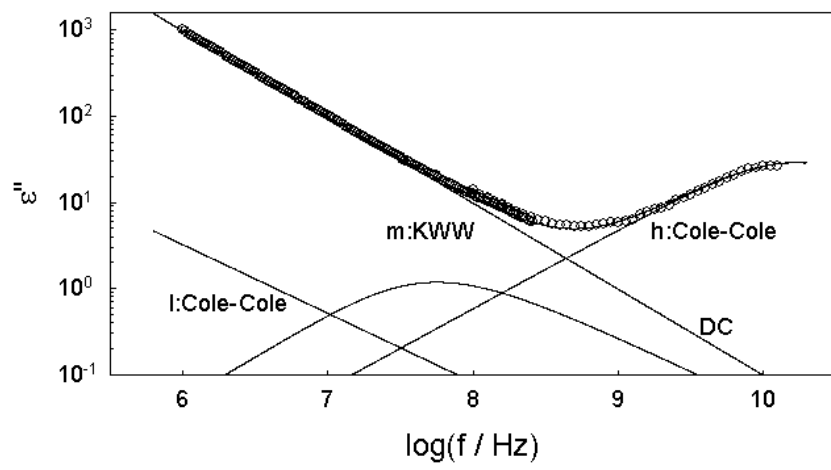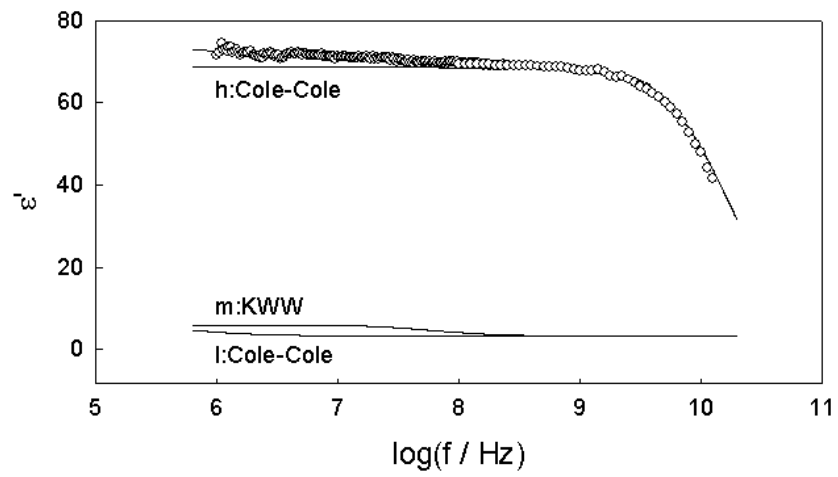
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Figure 4. Furusawa et al.

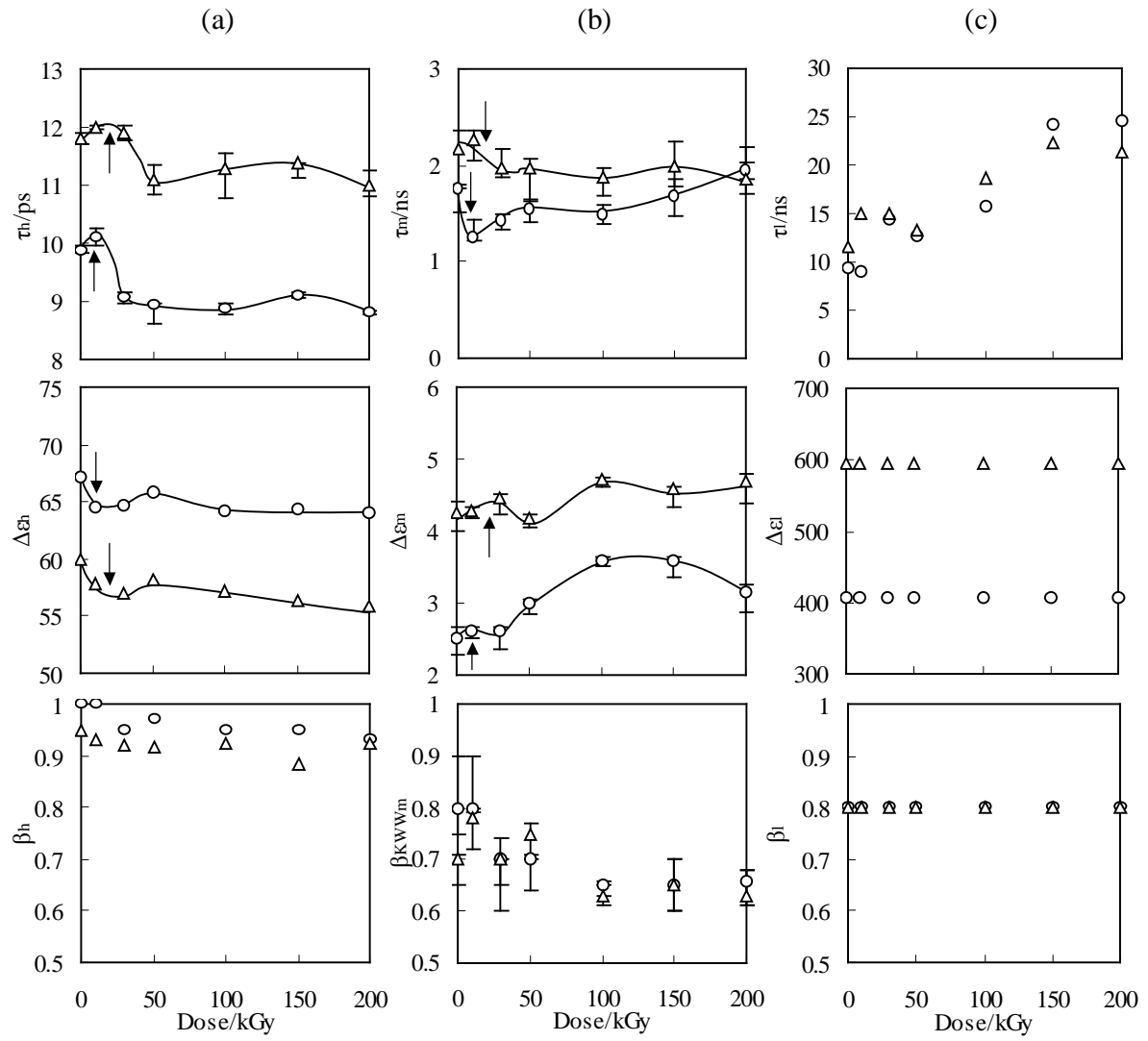(a)   (b)   (c)

Figure 5. Furusawa et al.

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Figure captions

Figure 1 Gel fraction of hydrogel prepared from HPMC aqueous solutions at 10 wt% ( ) and 20 wt% ( ). Dashed lines are calculated from Eq. (2) with parameters given in the text and solid lines are drawn for the guide of eyes.

Figure 2 Swelling ratio of hydrogel prepared from HPMC aqueous solutions at 10 wt% ( ) and 20 wt% ( ).

Figure 3 Cross-linking density of hydrogel prepared from HPMC aqueous solutions at 10 wt% ( ) and 20 wt% ( ).

Figure 4 Dielectric dispersion and absorption curve at 25 $^{\circ}$C for hydrogel prepared at irradiation dose of 50kGy from HPMC aqueous solutions at 10 wt% ( ). The solid lines are the calculated ones using Eq. (1).

Figure 5 Dose dependence of dielectric parameters for h-relaxation (a), m-relaxation (b) and l-relaxation (c) for hydrogel prepared from HPMC aqueous solutions at 10 wt% ( ) and 20 wt% ( ). The arrows indicate the critical dose for gelation determined from the measurement of gel fraction.

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