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Structural investigation on gamma-irradiated polyacrylamide hydrogels using small-angle neutron scattering and ultraviolet–visible spectroscopy

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Abstract. Small-angle neutron scattering (SANS) and ultraviolet (UV)–visible spectroscopic techniques are used to investigate the microstructural changes in polyacrylamide (PAAm) hydrogels on gamma irradiation. SANS measurements have revealed the presence of inhomogeneities in nanometre scale and reduction of their size with increase in dose. Analysis of SANS data also revealed the increase in the correlation length with increase in dose. The extinction coefficient obtained from the UV–visible spectroscopic studies exhibited $\lambda^{-\beta}$ dependence between 500 and 700 nm and is understood to arise from the existence of scatterers (inhomogeneities) in submicron scale in PAAm hydrogels. The increase in value of exponent β with increase in dose indicates that the size of scatterers decrease with increase in dose.

Keywords. Polyacrylamide hydrogels; small-angle neutron scattering; UV–visible spectra; gamma irradiation; inhomogeneities.

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1. Introduction

Over the past few decades several interesting properties and applications of polyacrylamide (PAAm) hydrogels have been explored after selectively modifying their molecular structures using various processes such as hydrolysis [1–4], or immobilizing external components such as colloidal crystals [5], crown ether (CE) [6] and various functional groups [7–9] within their networks. For instance, Tanaka *et al* [1] have studied the phase transition behaviour of hydrolysed PAAm hydrogels in various concentrations of acetone/water mixture. Their study showed that unhydrolysed PAAm hydrogels de-swell continuously with increase in concentration of acetone. We have reported that the PAAm hydrogels swell initially in the presence of various concentrations of nitric acid and exhibit de-swelling at long times due to hydrolysis [2]. Okay *et al* [4] have studied the effect of hydrolysis on spatial inhomogeneities of PAAm hydrogels and reported that the extent of hydrogel inhomogeneity decreases drastically with increase in aging time which is attributed to the hydrolysis of amide groups into acrylate groups. Structural parameters of hydrogels have been determined by employing small-angle neutron scattering (SANS), dynamic light scattering and electron microscopy techniques and also by equilibrium swelling theory [10,11].

Here, for the first time, we report the effect of γ-irradiation on inhomogeneities and correlation length (also known as mesh size) of PAAm hydrogels that were synthesized using photopolymerization method. SANS and ultraviolet (UV)–visible spectroscopic measurements were carried out on γ-irradiated PAAm hydrogels to understand the influence of γ-irradiation on the microstructure of PAAm hydrogels.

2. Experimental

Disc-shaped PAAm hydrogels (43 mm diameter and 1 mm thickness) with various concentrations of the polymer (10%, 15% and 20% w/w) keeping crosslinker concentration fixed at 1% w/w and also with various concentrations of crosslinker (1%, 1.5% and 2% w/w) for a fixed concentration of polymer (20% w/w) were prepared by photopolymerization using the procedure described in [2,10]. Disk-shaped hydrogel samples were immersed in water for a week to reach equilibrium. Samples with higher N,N′-methylene bisacrylamide (MBA) concentration appeared turbid as compared to those with lower MBA and lower PAAm concentrations. Water-swollen PAAm hydrogels were irradiated in a gamma chamber with ^{60}Co as the source. Irradiation was carried out for several cumulative doses from 10 to 200 Mrad to study equilibrium swelling. The dose rate was 0.45 Mrad/h. Degree of swelling (DoS) measurements have been carried out by weighing the hydrogel before and after every cumulative irradiation. DoS is defined as

$$\mathrm{DoS} = (W - W_0)/W_0, \tag{1}$$

where W_0 is the equilibrated weight of the unirradiated hydrogel and W is the weight of the γ-irradiated hydrogel.

SANS experiments were performed using a SANS diffractometer at the Dhruva reactor, BARC, Trombay, India [12]. The scattered intensity $I(q)$ was recorded in the q-range of 0.017–0.35 Å^{-1} and all SANS profiles were corrected for the background and direct beam contributions. JASCO 650 UV–visible spectrophotometer was used to record the UV–visible transmission in the wavelength range of 200–900 nm. UV–visible spectra were recorded before and after every dose of irradiation. All the measurements were done at room temperature.

3. Results and discussion

Unirradiated PAAm hydrogels with 1% MBA and different PAAm concentrations (10, 15 and 20%) swelled about 10 to 15 times from their dried state to fully equilibrated swollen state and the degree of swelling observed is in agreement with that reported by Lira *et al*

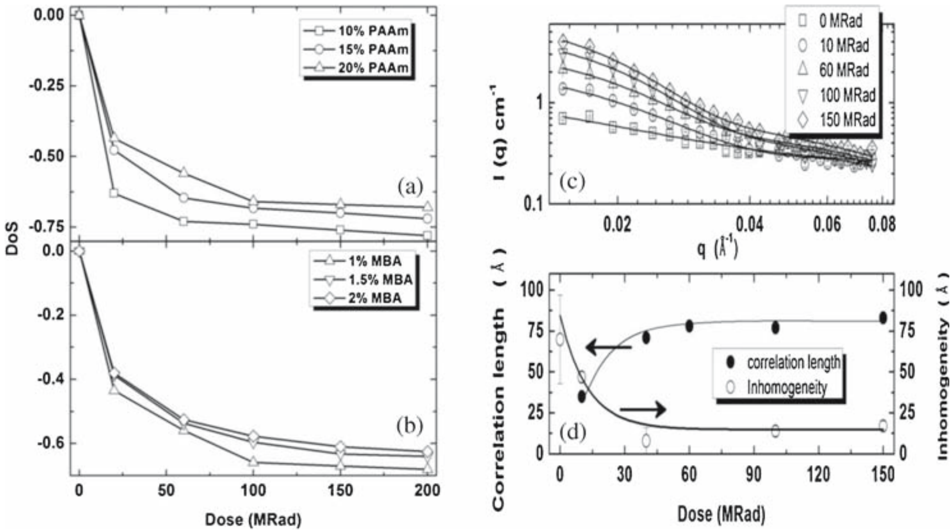

Figure 1. DoS of PAAm hydrogels as a function of dose. (**a**) Various PAAm concentrations (10%, 15% and 20%) with 1% MBA. (**b**) Different MBA concentrations (1%, 1.5% and 2%) with 20% PAAm. (**c**) SANS profiles for 10% PAAm hydrogels with 1% MBA as a function of dose. Solid lines are fits to eq. (2). (**d**) Influence of γ-irradiation on the correlation length and size of inhomogeneities of 10% PAAm hydrogel with 1% MBA. The solid lines are guides to the eye.

[11]. To determine the degree of swelling/de-swelling of PAAm hydrogels on irradiation, the swollen state of the respective unirradiated gel was taken as the reference state. Figures 1a and 1b show DoS for hydrogels as a function of dose for different PAAm concentrations with 1% MBA and for different MBA concentrations with 20% PAAm. It can be noticed that PAAm hydrogels de-swell around 60–75% on γ-irradiation for all concentrations of PAAm as shown in figures 1a and 1b. On γ-irradiation the crosslinking increases. Hence, PAAm hydrogels are expected to de-swell. The evidence for increase in crosslinking with increase in dose comes from the SANS studies discussed below.

To understand the microstructural changes in PAAm hydrogels on γ-irradiation, we have carried out SANS and UV–visible spectroscopic studies on the PAAm hydrogels, before and after γ-irradiation. Figure 1c shows SANS profiles for 10% PAAm hydrogel with 1% MBA for different doses of γ-radiation. At low-q region, SANS intensity, $I(q)$ is found to increase with increase in dose and this suggests that crosslinking density in the hydrogel increases with increase in dose. The increase in $I(q)$ with dose is similar to Hecht *et al* [13] observations of increased scattered intensity with increase in the crosslinker concentration in the PAAm hydrogels. In the present study, the increase in crosslinking density leads to decrease in DoS with dose (figures 1a and 1b). This implies that SANS results are consistent with the results obtained from macroscopic swelling measurements.

Hydrogel network parameters viz., correlation length ξ and size of the inhomogeneities Ξ were extracted by fitting the SANS data to the following equation:

$$I(q) = I_{\mathrm{G}}(0)\exp\left(-\Xi^2 q^2/2\right) + I_{\mathrm{L}}(0)/\left(1+\xi^2 q^2\right), \quad (2)$$

where $I_G(0)$ and $I_L(0)$ are coefficients of Gaussian and Lorentzian terms. The variations of ξ and Ξ as a function of dose are shown in figure 1d. Notice that correlation length increases and size of inhomogeneities decreases with increase in dose. It can be seen that size of inhomogeneity as well as mesh are in the same order of magnitude. Hence, there is a need for checking the uniqueness of the fit. We have checked by performing the fit to eq. (2) at each dose with different initial guess values for ξ and Ξ and ending with the best fit to the SANS profile with ξ and Ξ as shown in figure 1d. The observation of increase in correlation length with increased dose constitutes evidence for increased crosslink density in our PAAm on γ-irradiation. Further, the observation by Hecht *et al* [13], the increase in correlation length with the increase in crosslinker concentration in PAAm hydrogels, also supports our observations. Also, the existence of nanometre-sized inhomogeneities in 10% PAAm hydrogel with 1% MBA revealed by SANS data is in good agreement with the results reported by Furukawa *et al* [14]. We have measured scattering profiles of hydrogels with 15% and 20% PAAm concentration and found the scattered intensity to be very low as compared to that of 10% PAAm hydrogel. The data were hence not subjected to further analysis and also is not shown here. The increase in polymer concentration

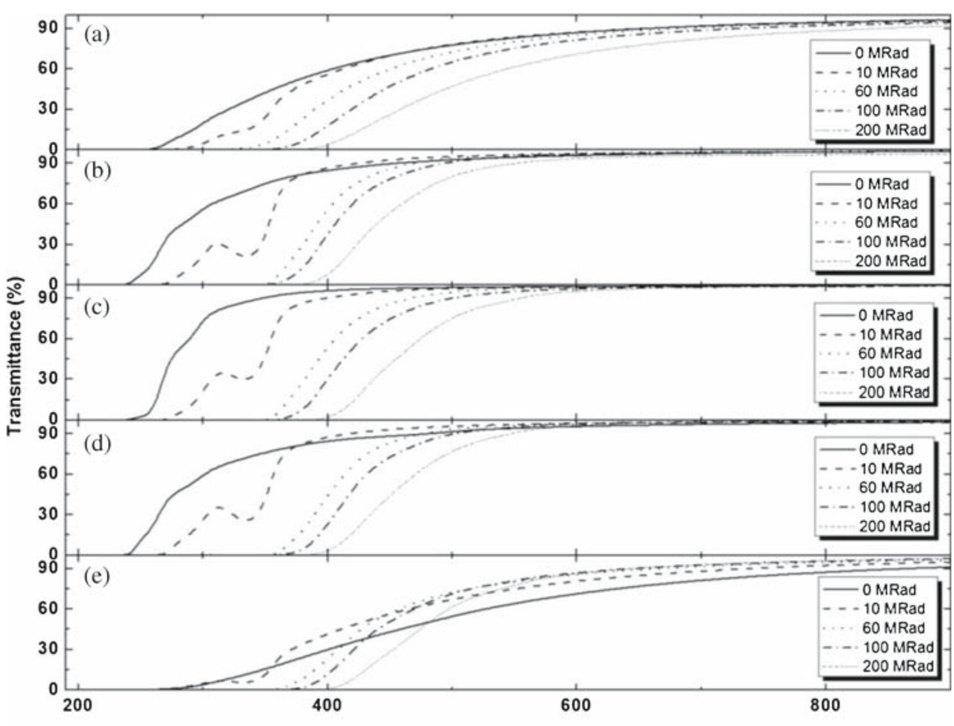

Figure 2. UV–visible spectra of hydrogels having various PAAm concentrations with fixed crosslinker (1% MBA) as a function of dose. (**a**) 10% PAAm, (**b**) 15% PAAm and (**c**) 20% PAAm. UV–visible spectra of PAAm hydrogels with different crosslinker concentrations and same amount (20%) of PAAm as a function of dose: (**d**) and (**e**) are for 1.5% and 2% MBA respectively.

lowers the contrast with respect to solvent (D_2O used for SANS measurements) resulting in poor scattering from these samples.

Furukawa *et al* [14] have carried out light scattering studies on PAAm hydrogels and reported the existence of two types of inhomogeneities: one with size in nanometre scale and the other in the submicron scale. Our SANS measurements also confirmed the existence of nanometre-sized inhomogeneities (figure 1c). As the scattering of submicron-sized inhomogeneities is predominantly in the visible region, UV–visible transmission studies have been carried out to provide not only evidence for their presence but also to know the influence of γ-irradiation on their size and resulting changes in the transmission of PAAm hydrogels. Figure 2 shows UV–visible transmission spectra recorded on PAAm hydrogels irradiated by different doses of γ-irradiation. A shift in cut-off wavelength (i.e., wavelength at which transmittance reaches zero) towards higher wavelength with increase in the dose of γ-irradiation in all PAAm hydrogels with different polymer or MBA concentrations can be noticed. This redshift in cut-off wavelength with an increase in dose of γ-irradiation indicates that PAAm hydrogels turn opaque to UV rays.

Further insight about the submicron-sized inhomogeneities is obtained by analysing the UV–visible transmission data in terms of the extinction coefficient which is obtained using the equation [15,16]

$$\tau = 1/h \ln 1/T = c\lambda^{-\beta}, \tag{3}$$

where h is the thickness of the hydrogel and T is the transmittance, $c = 24\pi^3 V_p^2 N_p \left[\left(n^2-1\right)/\left(n^2-1\right)\right]^2$, β is the exponent, V_p is the volume of the spherical scatterer, λ is the wavelength, N_p is the number density of scatterers and n is the relative refractive index. The extinction coefficient showed $\lambda^{-\beta}$ dependence between $\lambda = 500$ and 700 nm and such dependence arises when scatterers (i.e. inhomogeneities) in submicron scale exist in the PAAm hydrogels (figure 3a). The exponent β as well as constant c are found to increase monotonically with increase in dose (figures 3b and 3c). The value

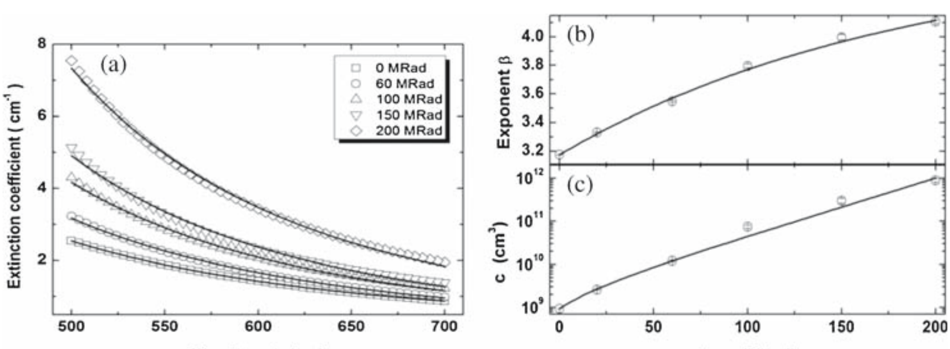

Figure 3. (**a**) Variation of extinction coefficient of 10% PAAm hydrogel with 1% MBA as a function of wavelength before and after different cumulative γ-irradiation. Solid lines are fits to eq. (3). (**b**) and (**c**) show variation of exponent β and constant c as a function of dose, respectively for 10% PAAm hydrogel with 1% MBA. Lines are guides to the eye.

of β increasing from 3.2 to 4.1 suggests that scatterers with size in the submicron scale shrink with increase in dose and our observations are consistent with that reported by Heller *et al* [17]. Further, we also observe a dip at 332 nm in the UV–visible transmission spectrum (figure 2) in PAAm hydrogels that are irradiated to dose of 10 Mrad and disappeared at higher doses. It may be mentioned here that Moharram *et al* [18] also observed a peak close to 300 nm in the absorption spectrum when irradiated by a dose of 2 Mrad to 8 Mrad and a decrease in peak height upon further increase in the dose to 10 Mrad. Observations of Moharram *et al* corroborate our observation of dip at 332 nm which is genuine. We attribute this dip to the formation of carbonyl groups existing with saturated aldehydes upon irradiation based on the assignment reported by Moharram *et al* [18] and also by Rao and Murthy [19]. Thus, γ-irradiation has strong influence on microstructure as well as on the optical properties of PAAm hydrogels and have implications in their applications.

4. Conclusions

Swelling behaviour and microstructural changes of PAAm hydrogels upon γ-irradiation were investigated using SANS and UV–visible spectroscopic studies. The analysis of SANS profiles and UV–visible transmission spectra revealed the presence of nanometre and submicron inhomogeneities in PAAm hydrogels, respectively. It is shown that size of nanometre as well as submicron scale inhomogeneities decrease with an increase in dose. The cut-off wavelength is shown to increase with an increase in dose of γ-irradiation. These observations have implications in designing PAAm hydrogel-based UV filters.

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