A comparison of ensemble, non-ergodic and heterodyne method on Acrylamide/Sodium acrylate gel

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ABSTRACT SUMMARY

The dynamics of Acrylamide/Sodium acrylate (AAm/SA) hydrogel was studied by dynamic light scattering. Three methods of data evaluation was compared. Two modes of motion was seen and both diffusion coefficients was found to increase with SA content regardless of method chosen.

INTRODUCTION

Hydrogels are hydrophilic crosslinked polymer networks which have gained reasonable research interest because of their myriad of applications. They have been used in controlled drug delivery applications, separation technology, diapers, fertilizers, metal extraction etc[1]. In all of these applications structure plays a vital role. Hydrogel structure, degree of crosslinking and swelling governs the drug release rate which is an important parameter in drug delivery. Thus to use hydrogel in drug delivery, precise knowledge of hydrogel structure and dynamics is needed. Thus in the present study the dynamics of AAm/SA gel is investigated and three methods of data evaluation is compared.

EXPERIMENTAL METHODS

The hydrogels were prepared by free radical polymerization. To study the dynamics of gels, dynamic light scattering experiments were carried out. Time averaged intensity correlation function (ICF) $g_T^{(2)}(q,t)$ was measured for 30 minutes at a single position which also gives $\langle I(q) \rangle_T$ using a 7004- ALV multitau correlator. Ensemble averaged scattered intensity $\langle I(q) \rangle_E$ was measured by rotating the sample cell at a speed of 6rpm using a stepper motor.
Non-ergodic: The intermediate scattering function $f(q,t)$ was determined from $g_T^{(2)}(q,t)$ using Pusey and van Megan method 2.

$$f(q,t) = \frac{Y-1}{Y} + \frac{(g_T^{(2)}(q,t) - \sigma_I^2)^{1/2}}{Y} \qquad (1)$$

Where σ_I^2 is the mean square intensity fluctuation and $Y = \langle I(q) \rangle_E / \langle I(q) \rangle_T$
The short time expansion is given by

$$f(q,t) = 1 + Dq^2t + .. \qquad (2)$$

D is the corrected diffusion coefficient and is related to apparent diffusion coefficient by $D = D_A \sigma_I^2 / Y$
Heterodyne: For a non-ergodic medium like polymer gels D_A as well as $\langle I(q) \rangle_T$ varies with sample position. However $\langle I(q) \rangle_T$ has two contributions

$$\langle I(q) \rangle_T = I_c(q) + \langle I_F(q) \rangle_T$$

Where the intensities are due to frozen structures and concentration fluctuations. In this case $D = D_A/2 - X_p$
and $X_p = \langle I_F(q) \rangle_T / \langle I(q) \rangle_T$

RESULTS AND DISCUSSION

The ISF $f(q,t)$ was constructed using equation 1 in non-ergodic approach. The curve was fitted with standard equation to obtain D values. In heterodyne case D was found out by plotting a curve of $\langle I(q) \rangle_T / D_A$ v/s $\langle I(q) \rangle_T$. In the case of ensemble average, the obtained ICF was directly fitted to a single plus stretched exponential function. The values obtained from the fitting are presented It is seen that the diffusion coefficient value depends on the technique chosen and also to the extent the frozen in component taken into account.

CONCLUSION

The dynamics of AAm/SA gel was studied by use of dynamic light scattering and three methods of data evaluation is done. It is seen that diffusion coefficient value depends greatly on frozen in structures and also type of hydrogel formed and method chosen.

REFERENCES

1. Ferfera-Harrar, H et al. *J Appl Polym Sci*. 2014, 131, 1-14.
2. Pusey, P.; Van Megan, W. *Physica A*. 1989, 157, 705-741.

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1. INTRODUCTION

- Hydrogels are three dimensional crosslinked polymer network swollen in solvent medium of water.
- Capable of absorbing substantial amount of water.
- Exhibits both solid and liquid like behaviour.
- Common examples are: Polysaccharides, DNA/RNA, Mucin-lining the stomach, intestines etc.
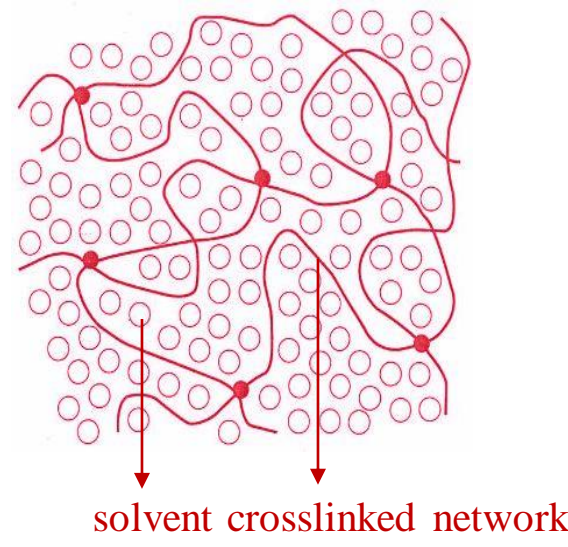
solvent crosslinked network

Classification: Based on cross-linking types

Physical gel

- Non-covalently crosslinked like hydrogen bonding, Vander Waals force or simply by physical entanglement.
- Thermo-reversible gels,
- Shows sol-gel phase transition.
- Ex: Agarose, gelatin, alginate etc.

Chemical gel

- Covalently crosslinked
- Permanent or strong gels.
- Ex: Poly acrylic acid, Poly acrylamide, Poly vinyl alcohol, Poly sodium acrylate etc.
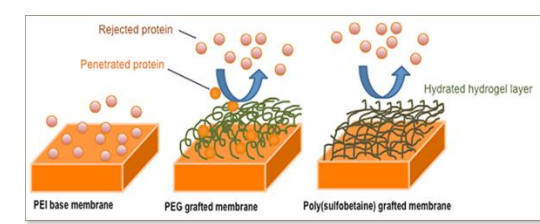
Factors effecting hydrogel structure

- ✓ Polymer concentration
- ✓ Crosslink density
- ✓ Solution pH
- ✓ Temperature
- ✓ Solvent quality
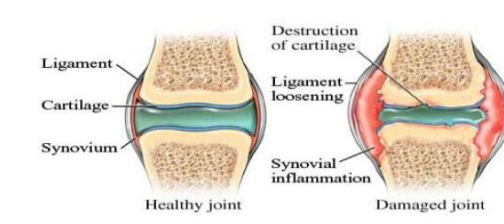- ✓ Salts

Why AAm/SA gel ?

- ✓ Excellent response to external stimuli with __applications__ in.
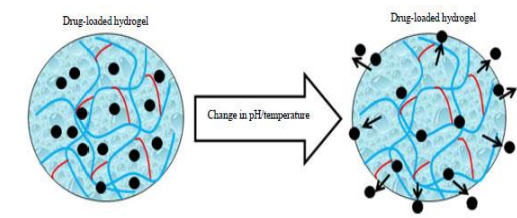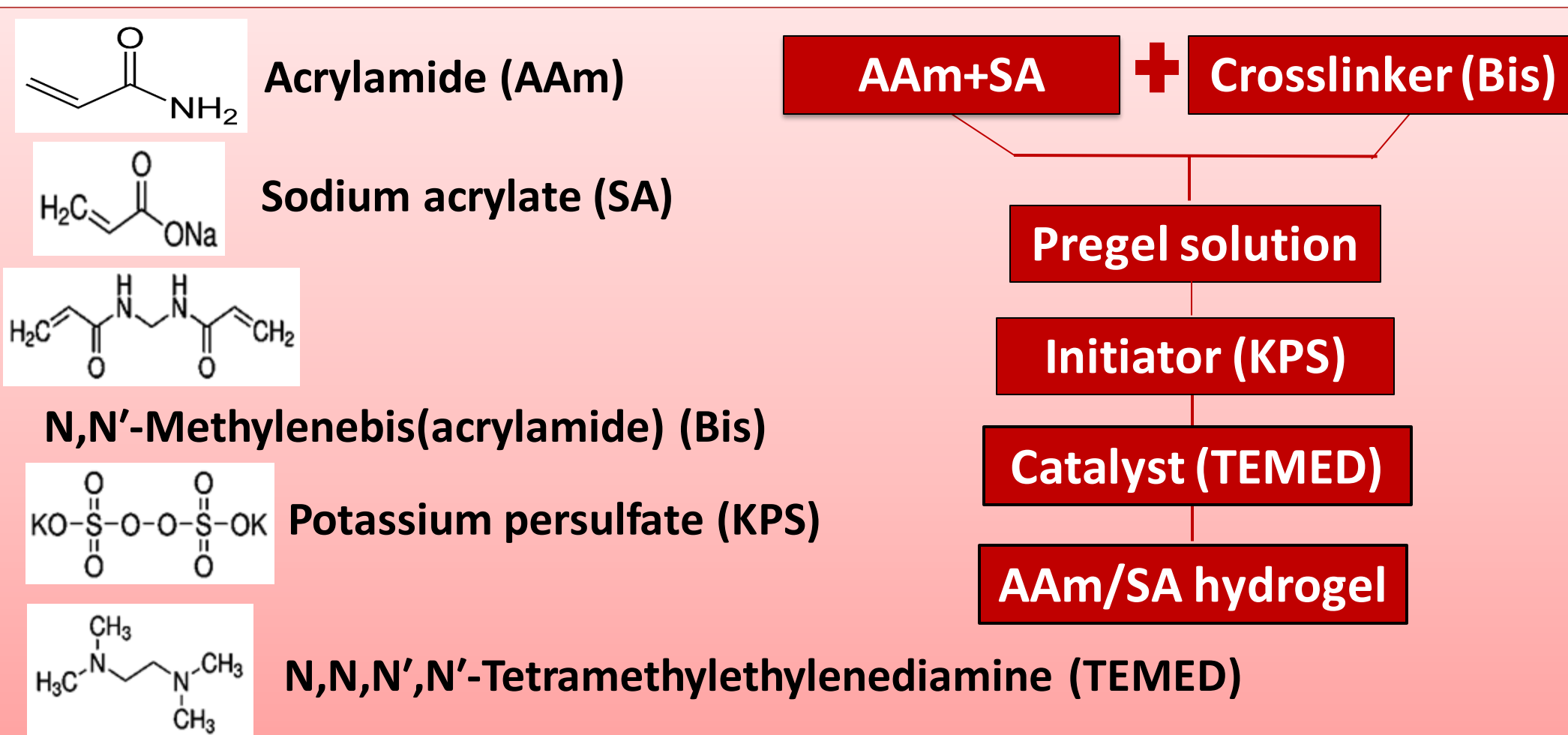
Drug Delivery   Separation Technology   Tissue Engineering

Objectives

1. To investigate the diffusive dynamics of hydrogels
2. Study the effect of comonomer content on dynamics of hydrogels
3. Compare the methods of data evaluation

2. METHODOLOGY

Acrylamide (AAm)

Sodium acrylate (SA)

N,N'-Methylenebis(acrylamide) (Bis)

Potassium persulfate (KPS)

N,N,N',N'-Tetramethylethylenediamine (TEMED)

AAm+SA ➕ Crosslinker (Bis)
→ Pregel solution
→ Initiator (KPS)
→ Catalyst (TEMED)
→ AAm/SA hydrogel

Dynamic light scattering (DLS)

- Measure time averaged intensity correlation function (ICF) $g_T^{(2)}(q,t)$ which is practically same as ensemble averaged ICF, $g_E^{(2)}(q,t)$ for ergodic samples.

- However this is not the case for non-ergodic samples like **Gels & Glasses**

- Three separate methods being employed to measure the ensemble averaged correlation functions
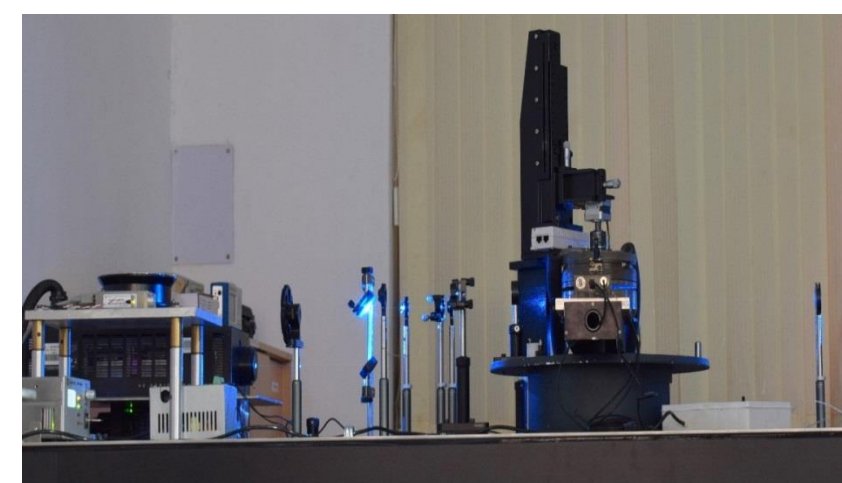
DLS setup in lab

Direct Ensemble averaged Method:

$Directly\ measure\ ,g_E^{(2)}(q,t)$ by rotating the sample at a constant speed

Non-Ergodic Method:

The intermediate scattering function $f(q,t)$ was determined from single measurement of $g_T^{(2)}(q,t)$ and by comparing them with $\langle I(q)\rangle_E$ and $\langle I(q)\rangle_T$

$$f(q,t) = \frac{Y-1}{Y} + \frac{(g_T^{(2)}(q,t) - \sigma_I^2)^{1/2}}{Y}$$

σ_I^2 is the mean square intensity fluctuation & $Y = \langle I(q)\rangle_E / \langle I(q)\rangle_T$

The short time expansion is given by

$$f(q,t) = 1 + Dq^2t + ..$$

$$D = D_A \sigma_I^2 / Y$$

D-corrected diffusion coefficient
D_A-apparent diffusion coefficient

Heterodyne Method:

By measuring $g_T^{(2)}(q,t)$ at large number of positions (~ 100) and by comparing them with absolute intensity value, $\langle I(q)\rangle_T$ as a function of position.
For gels D_A as well as $\langle I(q)\rangle_T$ varies with sample position. $\langle I(q)\rangle_T$ has two contributions

$\langle I_F(q)\rangle_T$-Intensities due to frozen structures
$I_c(q)$-Intensities due to concentration fluctuations.

$$\langle I(q)\rangle_T = I_c(q) + \langle I_F(q)\rangle_T$$

$$D = D_A/2 - X_p$$

$$X_p = \langle I_F(q)\rangle_T / \langle I(q)\rangle_T$$

3. RESULTS AND DISCUSSION

(a) Non-ergodic:

- The ISF $f(q,t)$ was constructed using equation.
- ISF at short times decays from 1 and at long times decays incompletely.
- The plot of $f(q,\infty)$ vs SA concentration is plotted which shows incomplete decay arising from frozen in structures

- The above figure depicts the fitting to the equation described above.
- The residual plot is plotted in the inset.
- From fitting τ is obtained from which cooperative diffusion coefficient D_C is calculated

(b) Heterodyne :

- Figure depicts the speckle patterns of the sample measured at fifty different sample positions.
- $\langle I\rangle_T$ varies arbitrarily with sample position.
- Red line indicates the average equivalent to $\langle I\rangle_E$.
- The obtained apparent diffusion coefficient D_A shows a strong dependence on $\langle I\rangle_T$.
- The data collapses into a straight line and values of D_C and $\langle I_F\rangle_T$ are evaluated.

- The intercept is below 1 suggesting non-ergodicity of samples.
- The correlation function is fitted with the equation for fifty different positions from which D_A is calculated

(c) Ensemble average:

- The ensemble averaged correlation function was directly measured by rotating the sample cell using stepper motor and fitted to equation and inset depicts the fitted curve

Comparison

- All the three methods of data evaluation is compared.
- The cooperative diffusion coefficient increases with increasing SA content.
- As correlation length is inversely proportional to D_C mesh size thus decreases.

- The slow diffusion coefficient is compared in above figure.
- It is seen that as the SA concentration increases, the slow diffusion coefficient increases initially and then saturates.

4. CONCLUSION

- ✓ The dynamics of AAm/SA hydrogel was studied by dynamic light scattering
- ✓ Three methods of data evaluation was compared.
- ✓ The diffusion coefficient is seen to increase with increase in SA content.
- ✓ Mesh size decreases, may be attributed to increasing crosslinking efficiency of crosslinker.

5. REFERENCES

1. Ferfera-Harrar, H et al. J Appl Polym Sci. 2014, 131, 1-14.
2. Pusey, P.; Van Megan, W. Physica A. 1989, 157, 705-741.

6. ACKNOWLEDGEMENTS