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Title: Effect of Embedded Polyelectrolyte Chains on Microstructure of Polyacrylamide Hydrogels

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In the present work we have studied the dynamics of chemically cross – linked polyacrylamide (PAAm) hydrogels with and without incorporating polyelectrolyte (pel) chains using dynamic light scattering (DLS) technique. A non – ergodic approach to analyze the intermacromolecular systems suggests stiffening of cross – linked junctions as the concentration of foreign species is increased. Thus the dynamics of parent gels is distinctly different from those in presence of pel chains. To further confirm our observation we have fit the intermediate scattering function to a straight line equation and used it to calculate the diffusion coefficient of the network. It was found that the diffusion coefficient decreased as we increased the added pel chain concentration. The decreased diffusion coefficient indicates an enhanced frozen – in structures in gel matrix.

EFFECT OF EMBEDDED POLYELECTROLYTE CHAINS ON MICROSTRUCTURE OF POLYACRYLAMIDE HYDROGELS

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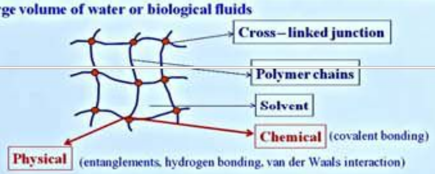
INTRODUCTION

HYDROGELS:

Three dimensional cross – linked network of polymer chains imbibing large volume of water or biological fluids



- Cross – links – Prevents fluid to flow out
- Trapped fluids – Structural integrity to gel matrix

Structurally flexible, biocompatible, permeable and smart response to external stimuli viz, pH, salt, temperature, electric field

➢ Generally Gels are known to have a heterogeneous structure and their characteristics is influenced by numerous factors

ELEMENTS INFLUENCING GEL STRUCTURE

- ❑ Polymer concentration
- ❑ Cross – linking density
- ❑ Solvent Quality
- ❑ Solution pH
- ❑ Aging of Gels
- ❑ Temperature
- ❑ Incorporation of foreign particles – Nano particles, surfactants, Polyelectrolytes

Sodium sulfonated polystyrene (NaPSS) incorporated in Polyacrylamide (PAAm) gel matrix

POLYACRYLAMIDE (PAAm) HYDROGEL:

➢ Chemically cross – linked gel (monomers are kind of stitched together by cross – linkers which are usually bi – or multi – functional)

➢ Monomer: Acrylamide (AAm)
Cross – linker: N,N' methylene bisacrylamide (BIS)

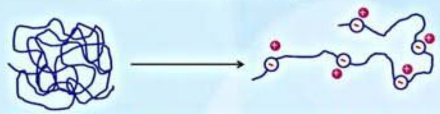
APPLICATIONS

- Drug treatment
- Ophthalmic operations
- Separation of chemical systems
- Plastic surgery
- Cell culture studies
- Horticulture
- Heavy metal removal
- Sensors
- Water purification
- Biomaterial transport

POLYELECTROLYTES

Ionizable polymer chains - basically dissociates into macroions and counterions

$$NaCl \longrightarrow Na^+ + Cl^-$$

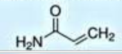


- Polyelectrolytes are of great importance as most of the known biological as well as some of the non – biological polymers are charged.
- Polyelectrolytes are extensively used as transport vehicles for drugs and biomaterials, in water treatment.

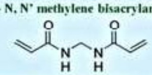
EXPERIMENTAL SECTION

MATERIALS:

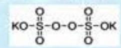
- Monomer - Acrylamide (AAm) – C_3H_5NO



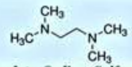
- Cross – linker - N, N' methylene bisacrylamide (Bis) – $C_7H_{10}N_2O_2$



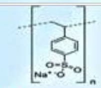
- Initiator – Potassium Persulfate (KPS) – $K_2S_2O_8$



- Activator – N, N, N', N' tetramethylethylenediamine (TEMED)



- Entrapped Polyelectrolyte: Sodium Sulfonated Polystyrene, 1000kDa

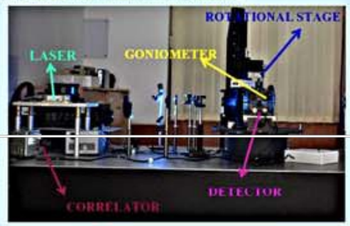


SAMPLE PREPARATION

Respective Stock Solution AAm, BIS, KPS → Filtered Stock Solution AAm, BIS, KPS → Mix appropriate amounts of Filtered Stock Solution → Add Powdered NaPSS & vortex it → Add activator, mix and leave overnight for gelation

DYNAMIC LIGHT SCATTERING (DLS)

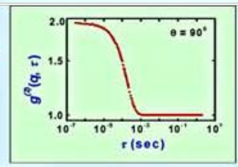
- Used to study dynamics of fluid systems: polymer solutions, colloids, nano particles
- Typically measures time average intensity – intensity correlation function whereas theoretically it is ensemble average
- DLS has recently been used to analyze dynamics in non – ergodic systems viz, hydrogels, glass, concentrated polymer melts



ERGODIC SYSTEM

- All scatterers are free to undergo Brownian excursions
- Therefore in Ergodic systems: $\langle I \rangle_E = \langle I \rangle_T$

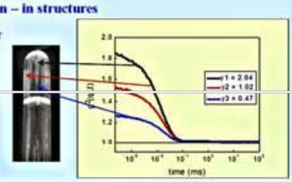
$$g_2(q,\tau) = 1 + \beta |g_1(q,\tau)|^2$$



NON - ERGODIC SYSTEM

- All scatterers are not free to move and contribution to scattered electric field: Fluctuating component and Frozen – in structures
- Therefore in Non - Ergodic systems: $\langle I \rangle_E \neq \langle I \rangle_T$

✓ $g^{(2)}(q,0) < 2$
✓ $g^{(2)}(q,t)$ varies with position



Pusey & van Megan Method: *Physica* A, 157, 705 (1989)

a. Measures $g^{(2)}(q,\tau)$ at one point of the sample
b. Measures $\langle I \rangle_T$ at the same point of the sample
c. Measure $\langle I \rangle_E$ by rotating the sample

By comparing all these values ISF $f(q,t)$ can be calculated

$$g_T^{(2)}(q,t) = 1 + Y^2\left[f^2(q,t) - f^2(q,\infty)\right] + 2Y(1-Y)\left[f(q,t) - f(q,\infty)\right]$$

Intermediate Scattering Function (ISF)

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

Long time ISF: $f(q,\infty) = \frac{(Y-1)}{Y} + \frac{\sqrt{1-\sigma_I^2}}{Y}$

For diffusive mode: $f(q,t) \propto e^{-Dq^2t}$

$$f(q,t) = 1 - D_C(q)\, q^2 t + \ldots \qquad D_A = YD_C/\sigma_I^2$$

REFERENCES

1. T. R. Hoare and D. S. Kohane, Polymer 49, 1993 – 2007 (2008); 2. A. Tangri, IJPCBS 4, 951-959 (2014); 3. G. Gerlach and K.F. Arndt, Hydrogels sensors and Actuators, O. Okay: Springer Series on Chemical Sensors and Biosensors, 2009; Vol 6, p1.; 4. O. Okay and W. Oppermann, Macromolecules 40, 3378 – 3387 (2007); 5. C. Rochas and E. Geissler, Macromolecules 47, 8012 – 8017 (2014); 6. W. Wang and S. A. Sande Polymer Journal, 1 – 9 (2014); 7. P. N. Pusey and W. Van Megen, Physica A 157, 705 – 741 (1989); 8. C. Gelfi and P. G. Righetti, Electrophoresis 2, 213 – 219 (1981)

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