

Cell Mineral Interface Group

Physical-chemical dynamics of macromolecules at the solid-liquid interface

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Adsorption behaviour of the macromolecules on the mineral surface

Two types of interactions are of central importance for the adsorption process:

Chemical interactions, which can include Van der Waals interactions, hydrogen bonding, hydrophobic effects, and conformational changes etc.

Electrostatic interactions, that can be either repulsive or attractive.

The driving force for the **adsorption of uncharged polymers** is of a chemical nature.

Adsorption of charged polymers makes, apart from the chemical contribution, an electrostatic contribution which can counteract or reinforce the former.

Electrostatic interactions and conformational effects are strongly interrelated and might complicate the adsorption process of charged polymers.

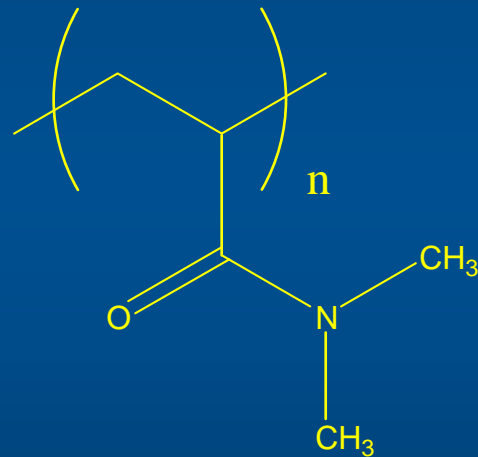
The theoretical understanding of the adsorption of more complex polyelectrolytes and proteins is far from complete.

C-MI

Fluorescently-labelled synthetic macromolecules

Synthetic macromolecule

Poly(N,N-dimethylacrylamide)



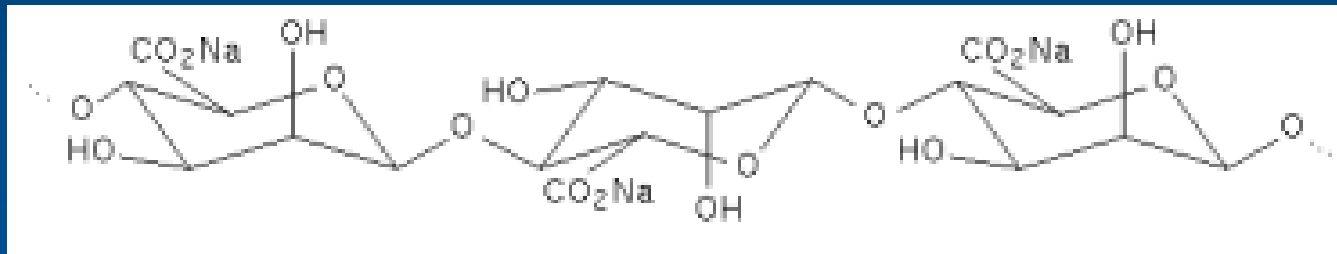
PDMAc

C-MI

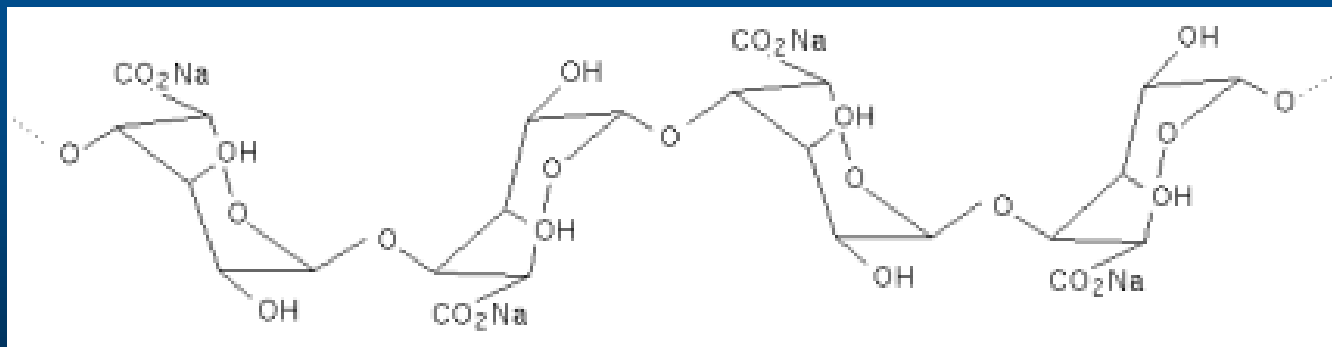
Fluorescently-labelled natural polysaccharides

Alginate –

linear copolymer of β -D-mannuronic acid and α -L-guluronic acid



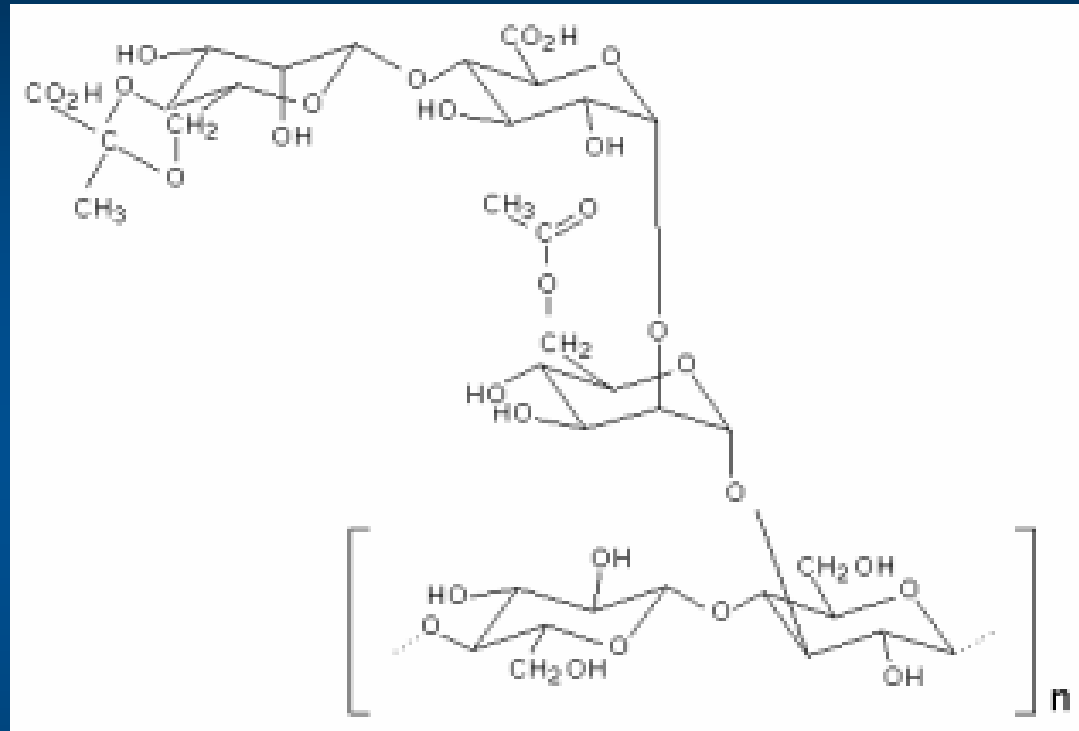
Poly(mannuronic acid) sodium salt



Poly(guluronic acid) sodium salt

Xanthan gum

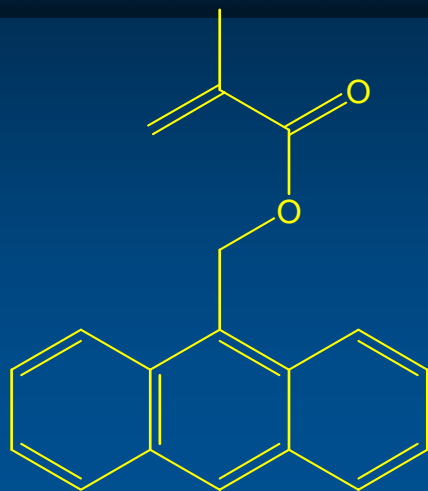
The backbone is β 1-4-D-glucose. Every alternate glucose residue has a three sugar side chain consisting of two mannose residues with a glucuronic acid residue between them. 60-70% of the mannose residues nearest the main chain can carry a C6 acetyl group and pyruvate residues can be found on 30-40% of the terminal mannose residues.



Xanthan is produced as a twin stranded, right handed five fold helix. The stability of the helix is strongly affected by ionic environment.

Adsorption of xanthan on silica and kaolinite depends on salinity and temperature of the mixture.

(M.Page, J.Lecourtier, C.Noik, Fossy. Journal of Colloid and Interface Science 1993, 161, 450-454)

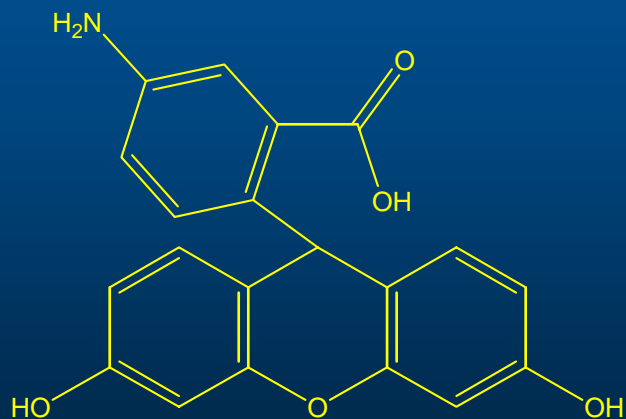


(9-anthryl)methyl methacrylate (AMMA)

- **Sensitivity**

- **Intramolecular effects**
(single polymer chains)

Introduce a label (ca. 1 wt%) into polymer during synthesis or modification of the polymer



5-aminofluorescein

Label provides information on

its environment (openness of polymer coil)
(Intensity and lifetime measurements)

how fast polymer moves in solution
[Time-resolved anisotropy measurements (TRAMS)]

Fluorescence intensity measurements

provide a direct method for determination of the amount of polymer adsorbed using a fluorescent label attached to an adsorbate. The adsorbent and associated adsorbed layer is separated from the suspension by centrifugation and the concentration of adsorbate left in the supernatant is quantified through fluorescence from label. It is possible to study the adsorption of polymers from very dilute solutions.

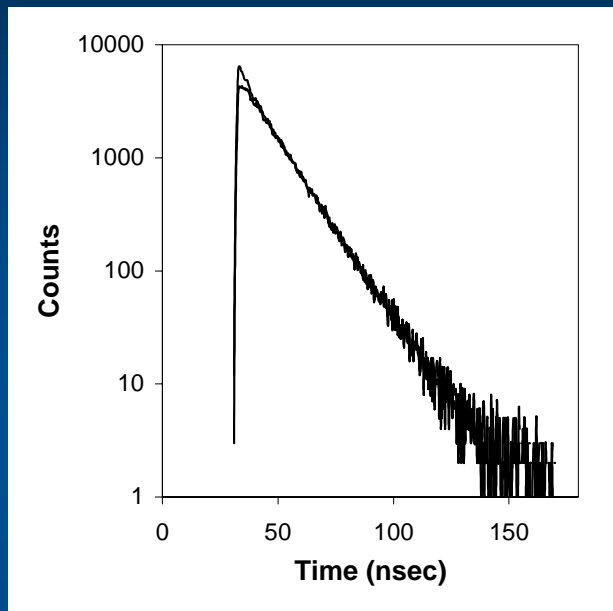
Time-resolved anisotropy measurements (TRAMS)

The anisotropy of the luminescence emitted by an electronically species is a function of the extent to which molecular reorientation occurs within the timescale imposed by the excited state. Anisotropy measurements provide a means of studying molecular dynamics.

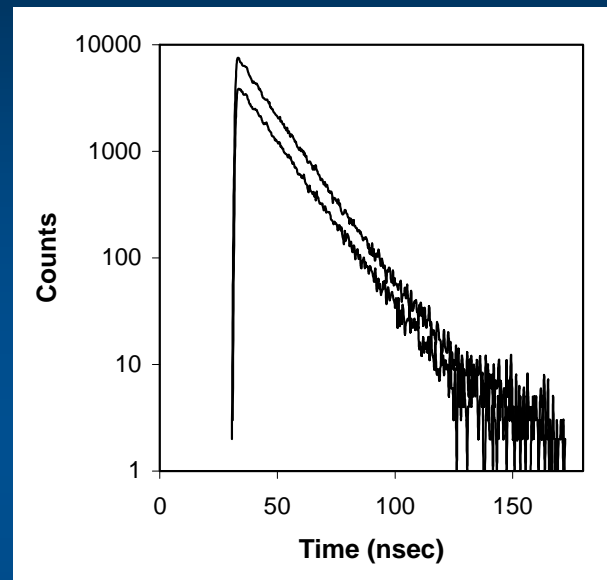
It can be imagined that the mobility of the polymer in adsorbed state would be lower than those in the bulk solution. Therefore, comparison of the segmental motions of polymers in the adsorbed state with those in the bulk solution should allow to make reasonably detailed conclusions regarding the conformations of the polymers in the adsorbed state.

In TRAMS the orthogonal components of luminescence intensity $I_{||}$ and I_{\perp} are analysed as a function of time. These decay data can be transformed into a time-dependent anisotropy function $R(t)$, that contains reorientational information.

Using direct analyses we can produce the fits to the data and the result of such fits is **correlation time** (τ_c).

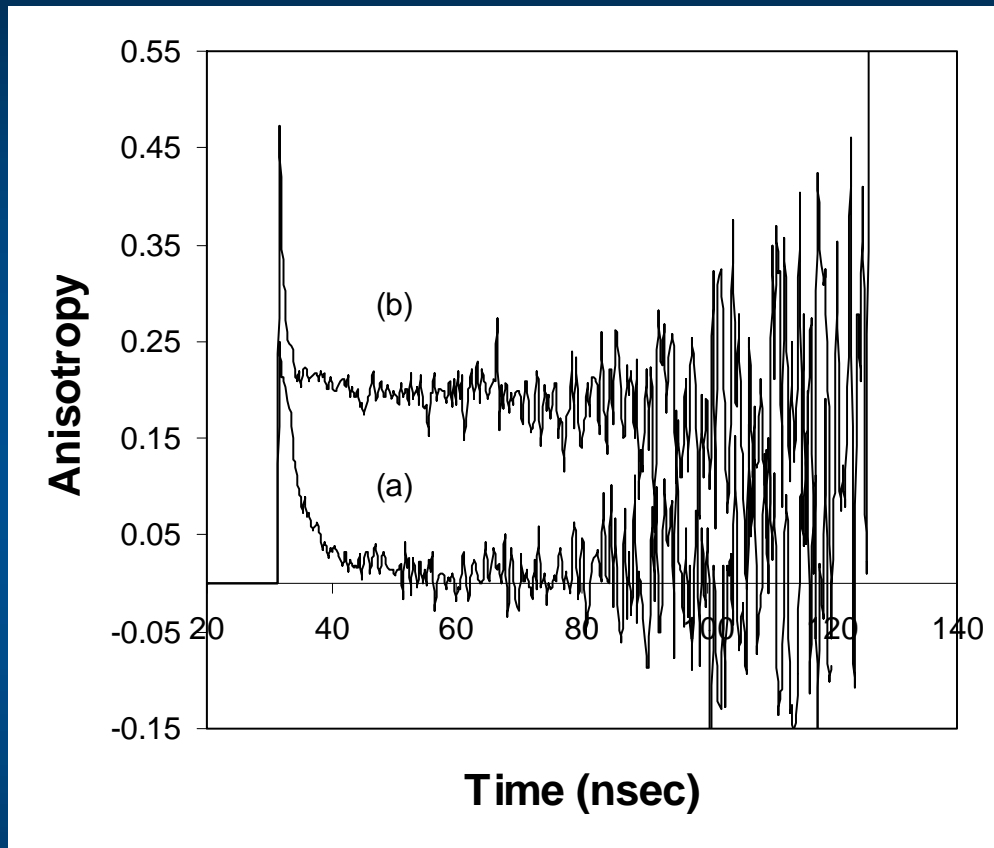
Time-resolved anisotropy measurements
(TRAMS)

(a)



(b)

Components of fluorescence intensity (at 450 nm), $I_{\parallel}(t)$ (upper curve) and $I_{\perp}(t)$ (lower curve), analysed in the planes parallel and perpendicular, respectively, to that of vertically polarized excitation (at 370 nm) for AMMA-labelled poly(DMAC) (10^{-2} wt.% in water) in the absence of silica (a) and at silica concentration of 1 wt%.

Time-resolved anisotropy measurements
(TRAMS)

$$R(t) = A \exp(-t/\tau_c) + B$$

τ_c is characteristic of the segmental motion of PDMAC in the system

Time-resolved fluorescence anisotropy data of aqueous AMMA-labelled poly(DMAC) solution (10^{-2} wt.%) in the absence (a) of silica and (b) at silica concentration of 1 wt%. $\lambda_{\text{ex}}=370\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$.

**Adsorption and conformational behaviour of macromolecules
at silica-water interface**

Concentration effect (polymer/colloid concentration ratio)

pH dependence

Ionic strength effect

Fluorescence spectroscopy measurements

Steady-state fluorescence intensity

Lifetime measurements

Time-resolved anisotropy measurements (TRAMS)

UV spectroscopy measurements

Transmission electron microscopy (TEM)

Dynamic light scattering (DLS)

C-MI

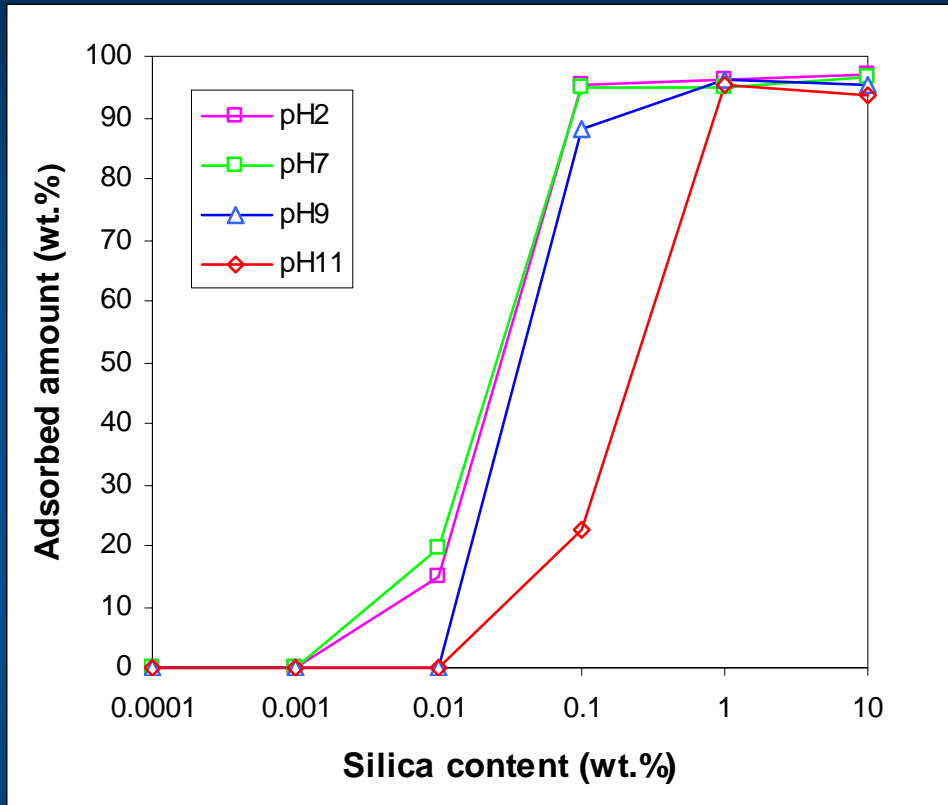
Extent of the adsorption of poly(N,N-dimethylacrylamide) on the silica surface

The adsorbed amount of AMMA-labelled poly(DMAC) on the colloidal silica in water at various pHs.

Polymer/silica ratio (wt/wt)	Polymer content (wt.%)	Silica content (wt.%)	pH	Adsorbed amount (wt.%)	Adsorption density ($\mu\text{g m}^{-2}$)
1/100	10^{-2}	1	2	96.07	41.8
1/100	10^{-2}	1	7	94.90	41.3
1/100	10^{-2}	1	9	96.37	41.9
1/100	10^{-2}	1	11	95.37	41.5
1/10	10^{-2}	10^{-1}	2	95.36	415
1/10	10^{-2}	10^{-1}	7	94.86	412
1/10	10^{-2}	10^{-1}	9	88.14	383
1/10	10^{-2}	10^{-1}	11	22.50	97.8
1/1	10^{-2}	10^{-2}	2	14.85	645
1/1	10^{-2}	10^{-2}	7	19.44	845
1/1	10^{-2}	10^{-2}	9	0	0
1/1	10^{-2}	10^{-2}	11	0	0
1/0.1	10^{-2}	10^{-3}	all range	0	0

- Poly(DMAC) adsorbs over all range of pH.
- The adsorbed amount of AMMA-labelled poly(DMAC) of the colloidal silica particles depends on the amount of the mineral surface available for adsorption (number of adsorption sites)

Extent of the adsorption of poly(N,N-dimethylacrylamide) on the silica surface



Adsorption of AMMA-labelled poly(DMAC) on the colloidal silica as a function of polymer/silica ratio at various pHs. Conc. of polymer in the solution is 10^{-2} wt.%.

The adsorption of the polymer is close to complete at the polymer to silica ratio 1/100 over all range of pH.

It is believed that adsorption occurs through a three-step process:

- (i) transport from bulk to the surface
- (ii) attachment to the surface
- (iii) rearrangements in the adsorbed layer

C-MI

Ionic strength effect on the adsorption of poly(N,N-dimethylacrylamide) on the silica surface

The adsorbed amount (wt%) of AMMA-labelled poly(DMAC) on the colloidal silica in water at various pHs.

pH	Polymer/silica ratio (wt/wt)	CaCl ₂ concentration (mol/l)				
		0	0.0001	0.0005	0.001	0.002
2	1/1	14.85	22.92	22.84	22.97	23.04
	1/10	95.36	98.76	99.24	99.4	99.15
	1/100	96.07	99.14	99.48	98.91	99.34
7	1/1	19.44	14.82	17.89	11.74	8.06
	1/10	94.86	89.92	93.84	92.99	90.32
	1/100	94.9	97.9	90.43	97.6	95.75
9	1/1	0	0	0	0	0
	1/10	88.14	76.29	70.51	77.67	82.80
	1/100	96.37	84.42	88.84	91.63	92.84
11	1/1	0	0	0	0	0
	1/10	22.5	0	0	0	0
	1/100	95.37	~1	~1	~2	~2

Adsorption behavior of poly(DMAC) depends on the amount of calcium salt present in the system and varies with the pH of the solution:

No effect on adsorption behavior at low pH.

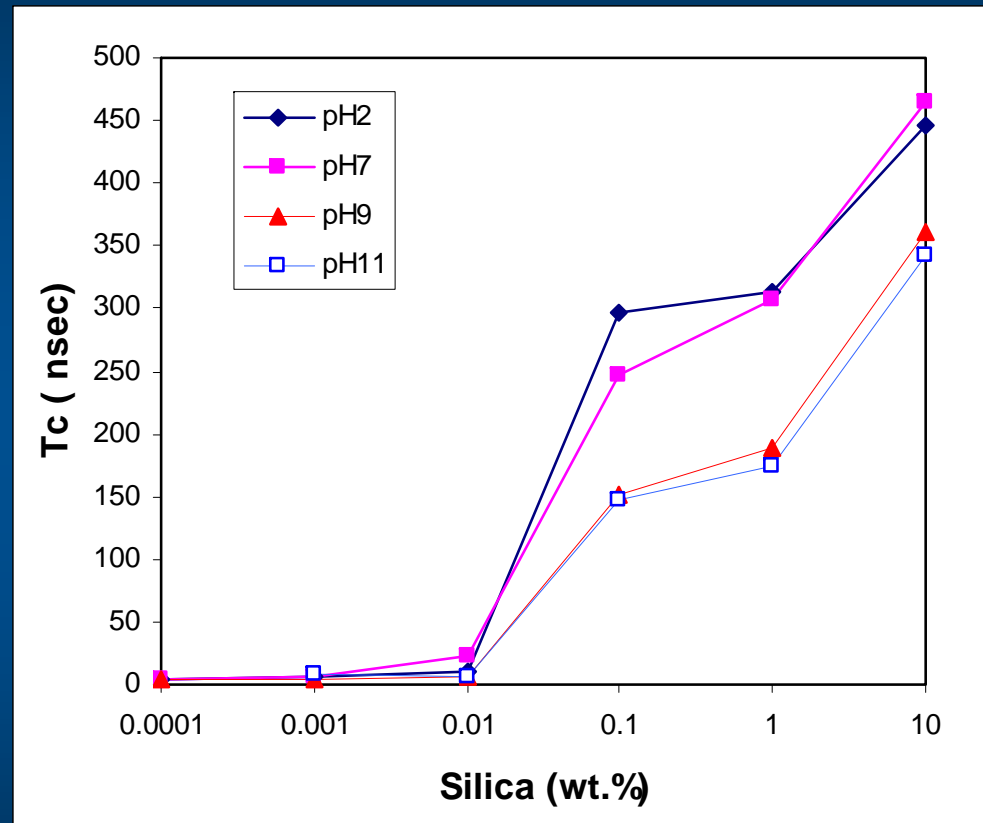
The extent of adsorption is highly decreased in the presence of calcium salt at high pH of the solution.

C-MI Conformational behaviour of polymer on colloidal silica

TRAMS data are responsive to adsorption of the AMMA-labelled poly(DMAC) to the surface of the silica particles

Concentration, pH effect

Rotational behaviour of AMMA-labelled poly(DMAC) in water (10^{-2} wt%) as a function of silica colloid concentration.



The segmental mobility is dependent upon the concentration of silica in the adsorption system.

The conformations adopted by the polymer in the adsorbed state are very different from that in the bulk solution. Slow relaxation (high τ_c value) indicates that the polymer “lies flat” upon the colloid surface in adsorption.

C-MI Conformational behaviour of polymer on colloidal silica

Calcium salt effect

on τ_c (ns) of the polymer .

pH	Polymer/silica ratio (wt/wt)	CaCl ₂ concentration (mol/l)				
		0	0.0001	0.0005	0.001	0.002
2	1/1	10.68	7.78	7.20	10.71	10.48
	1/10	296.54	303.36	371.29	475.59	492.98
	1/100	345.38	346.52	480.78	467.48	500.93
7	1/1	23.44	6.34	6.83	5.07	4.74
	1/10	247.05	231.21	234.51	264.8	186.52
	1/100	308	351.78	271.36	353.59	346.18
9	1/1	6.97	5.3	5.45	4.56	5.8
	1/10	150.62	63.81	27.44	30.85	56.66
	1/100	287	274.56	74.62	21.51	8.71
11	1/1	6.36	6.1	3.5	3.2	3.3
	1/10	146.35	5.11	4.22	5.66	3.7
	1/100	174.7	5.41	3.15	4.93	3.88

Low pH Essentially no effect on rotational behavior of the polymer changing Ca salt content in the polymer/colloid system.

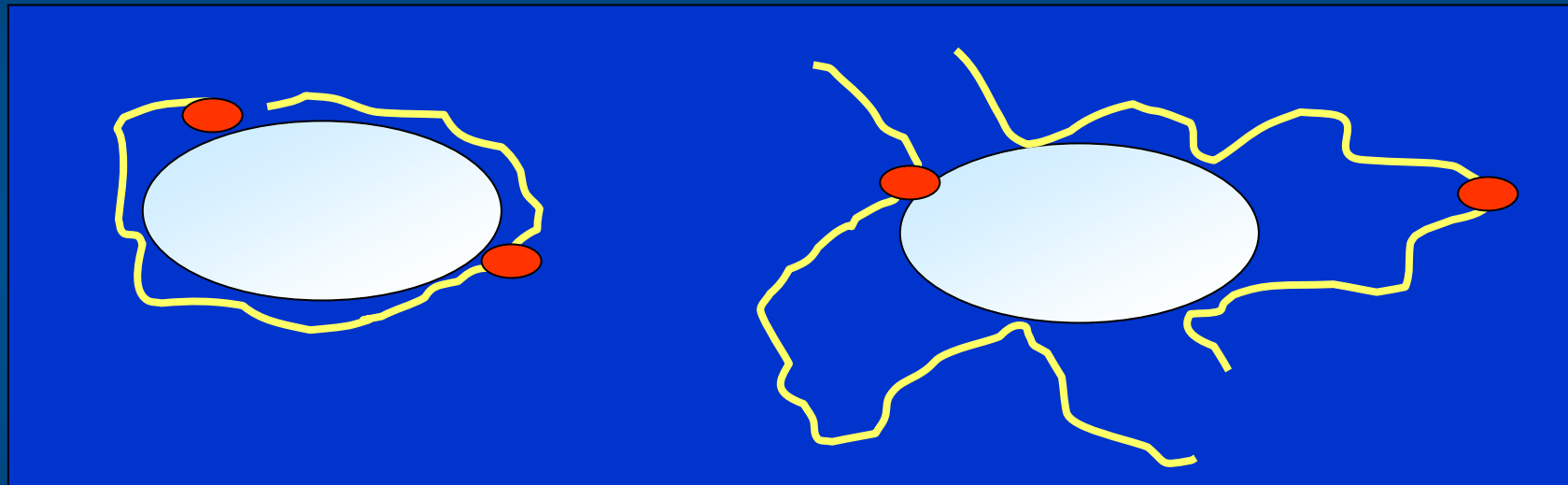
High pH Correlation time decreases with the increasing of CaCl₂ content. Segmental mobility of adsorbed polymer increases with increasing salt concentration.

The addition of salt depresses the adsorption forces due to charge screening effects.

C-MI Conformational behaviour of polymer on colloidal silica

In 1951 Jenckel and Rumbach proposed a model incorporating a combination of 'trains', 'loops' and 'tails' to describe the conformations of adsorbed polymers.

(E. Jenckel, R. Rumbach. Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie 1951, 55, 612-618)



Flat

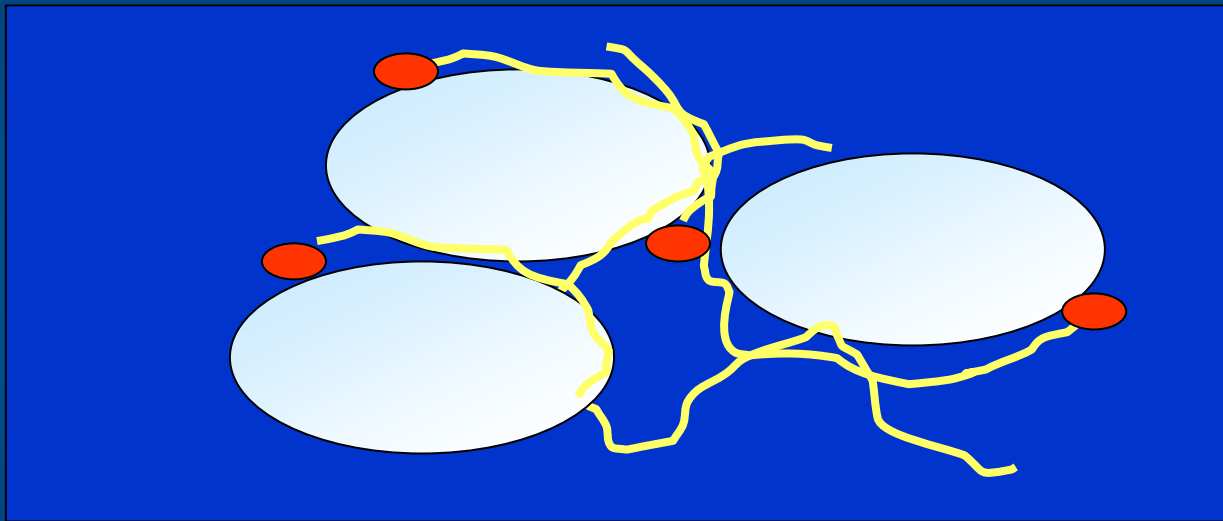
Loops & Tails

● Fluorescent label

At low silica contents where polymer adsorption is incomplete, the fluorescence anisotropy decay curves will contain contributions from both adsorbed species and "free" polymer, in solution. Mean value of τ_c will be a composite of correlation times of segments of adsorbed species existing in varying proportions as loops, tails and trains according to the amount of surface available.

C-MI Conformational behaviour of polymer on colloidal silica

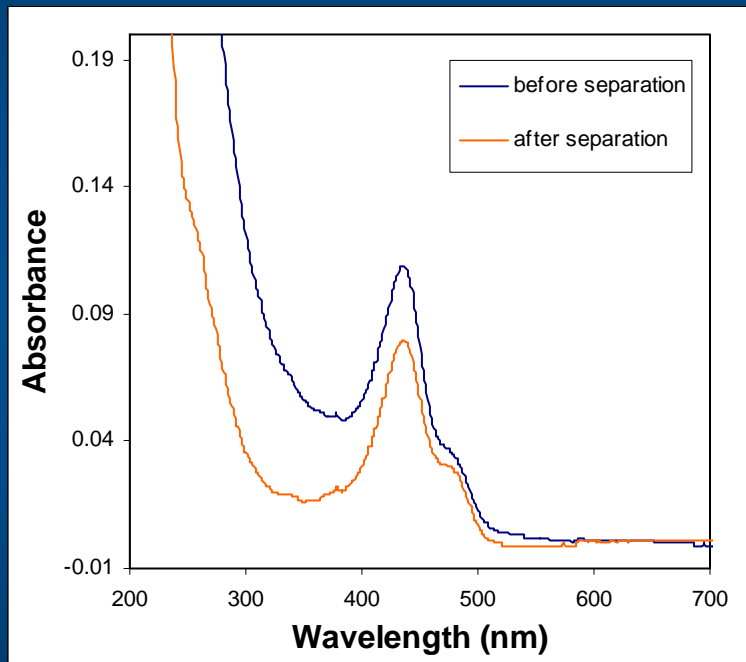
Slow relaxation (high τ_c value) at higher colloid concentration in the system occurs on a timescale comparable to that expected for the rotation of whole particle in the aqueous colloidal dispersion and indicates that the polymer “lies flat” on colloid surface in adsorption.



The introduction of further amounts of colloidal silica into the system may cause the rearrangement of polymer conformations in the adsorbed state.

In the systems with higher adsorbent to polymer ratios, the polymer may adopt “flatter” conformation in which more segments exist in “train” and/or “small loops” conformations, which are characterized by longer correlation times. However, introduction of even greater amounts of adsorbent offers the polymer the chance of forming bridges between adsorbent particles.

Evaluation of the extent of alginates adsorption onto the colloidal particles by UV spectroscopy



Separation of the polymer from the solution

without silica at pH3 ~11 wt%
containing silica at pH 3 ~27 wt%

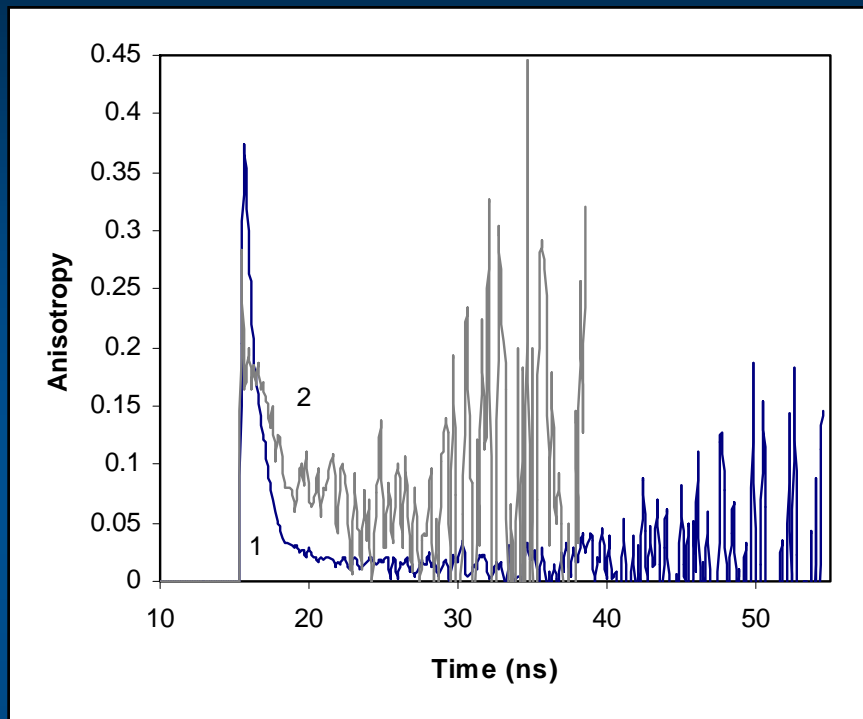
No separation (adsorption) of the polymer at pH6, pH9.

The charged polymer becomes protonated and flocculated at low pH. The flocculation is enhanced in the presence of silica colloid.

Normalised absorbance spectra of fluorescein-labelled alginate in water (10^{-2} wt%) at silica concentration of 1 wt% at pH 3 before and after separation by centrifugation.

C-MI

Conformational behaviour of alginates in water as a function of pH, Ca salt and colloid content



No effect on rotational behaviour (segmental mobility) of the polymer changing polymer/silica ratio over all range of pH.

TRAMS can sense interactions of alginic acid with CaCl_2 .

Time-resolved fluorescence anisotropy data of aqueous fluorescein-labelled alginic acid (10^{-2} wt.%) solution at pH 9 in the absence of CaCl_2 (1) and at CaCl_2 concentration of 0.0015 M (2). $\lambda_{\text{ex}} = 495 \text{ nm}$, $\lambda_{\text{em}} = 550 \text{ nm}$.

$[\text{CaCl}_2]$ (mol/l)	0	0.00005	0.0015
pH 2.5	1.36 ± 0.04	1.84 ± 0.16	4.80 ± 0.45
pH 9	1.45 ± 0.04	1.15 ± 0.02	5.33 ± 0.54

- To identify the conformation adopted by the synthetic polymer at the liquid/silica interface (further analysis of TRAMS and other exp.data)
 in progress
- To assess particle size, morphology and degree of dispersion of the colloidal systems by transmission electron microscopy, dynamic light scattering.
 in progress
- Surface charge determination experiments of the mineral phase (potentiometric titration)
- Adsorption experiments of fluorescently labelled biopolymers (alginates, xathan) on the mineral surface (UV, steady-state and time-resolved fluorescence spectroscopy)
 in progress
- The adsorption experiments of macromolecules on other mineral phase