Theme 1

Classification, Basic Methods of Obtaining, Structural Features and Properties of Hybrid Nanoparticles and Organic-Inorganic Nanocomposites

General Concept for Design of Organic-Inorganic Nanocomposites via Nanoscale Combination of Components

Organic component:

Monomer,
Oligomer,
Polymer

(flexibility, lightness, ease of mechanical treatment)

Inorganic component:

SiO_2, TiO_2, ZrO_2, Al_2O_3, zeolites...,

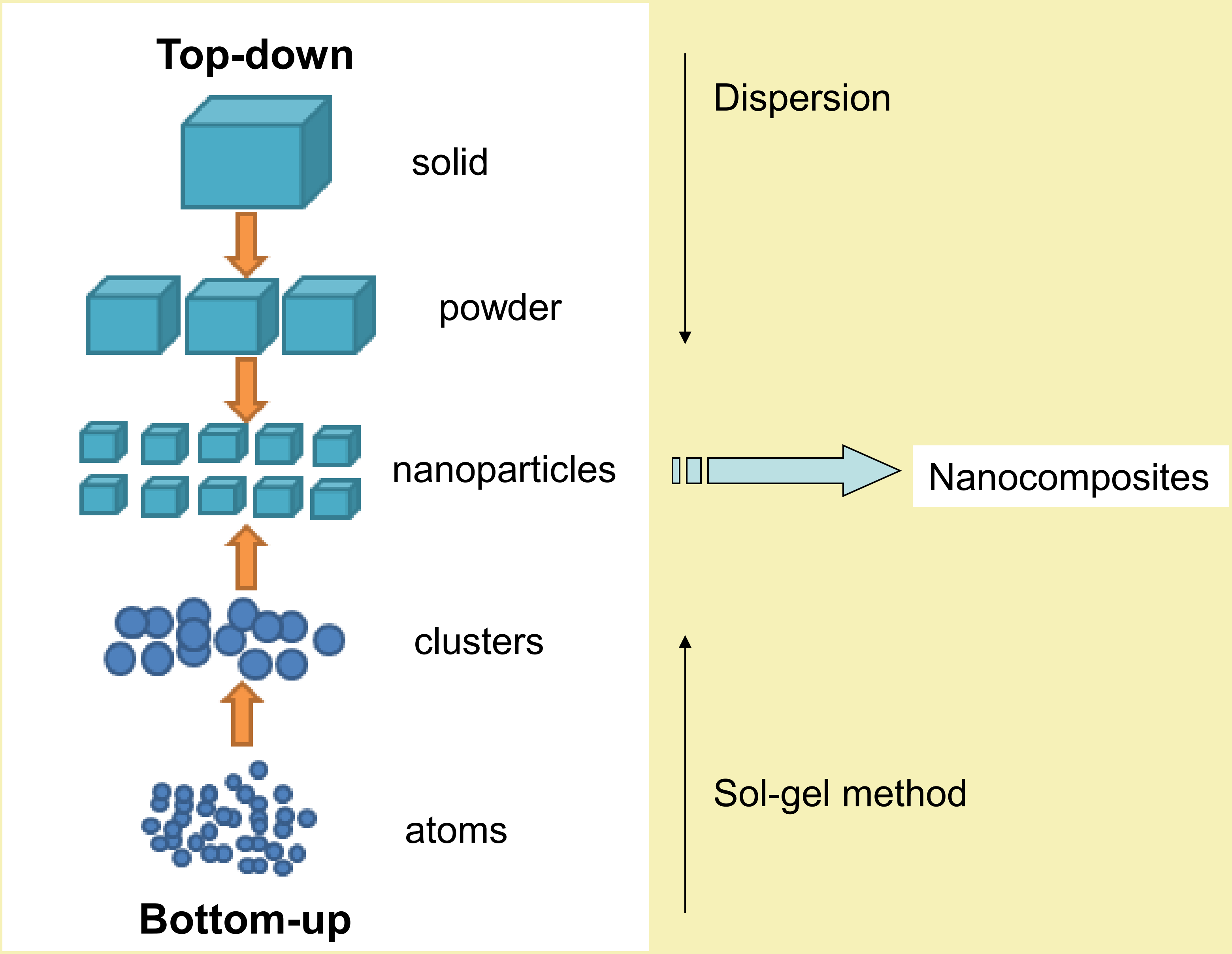
(thermal and chemical stability, mechanical strength)

Functional additives:

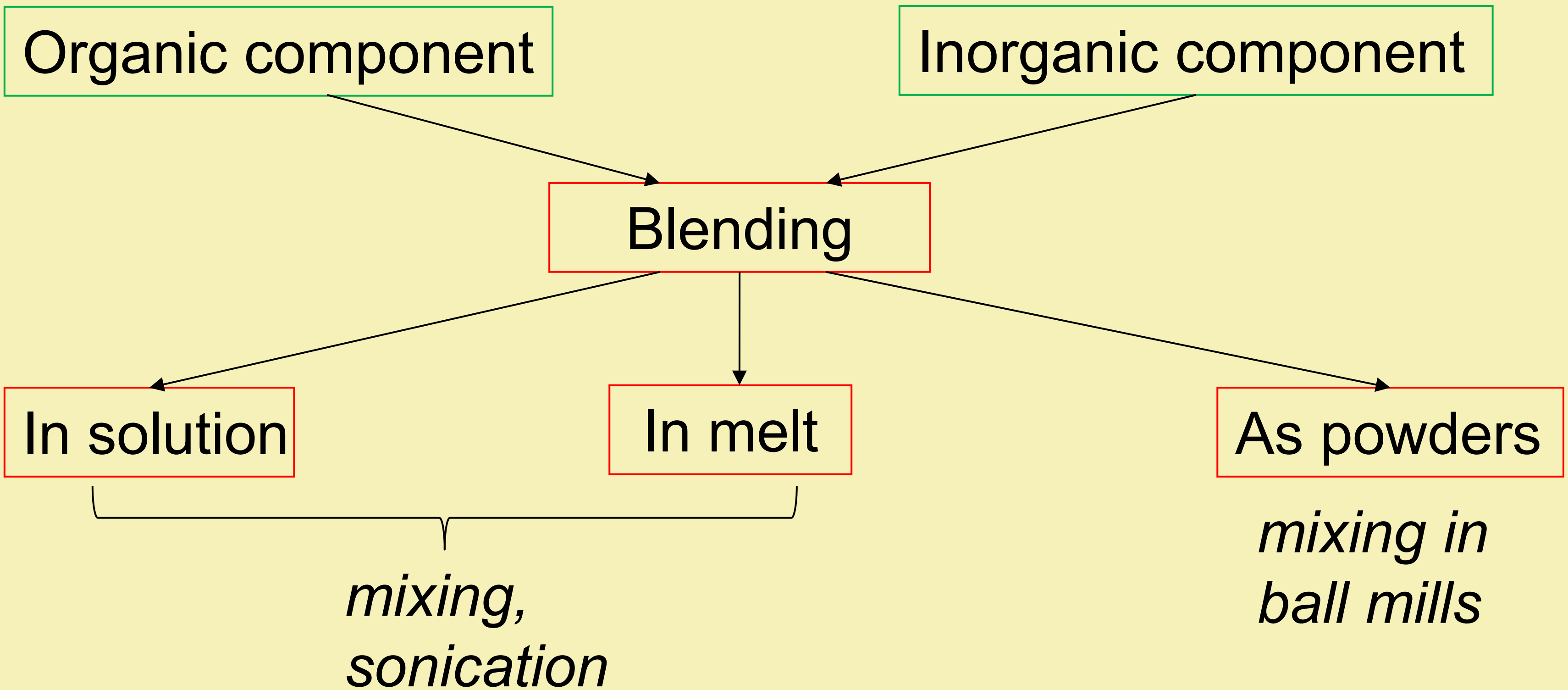
Acids, salts, complexes, dyes, nanofillers (POSS-derivatives, carbon nanotubes, layered silicates, etc.)

(electrical, magnetic, optical properties)

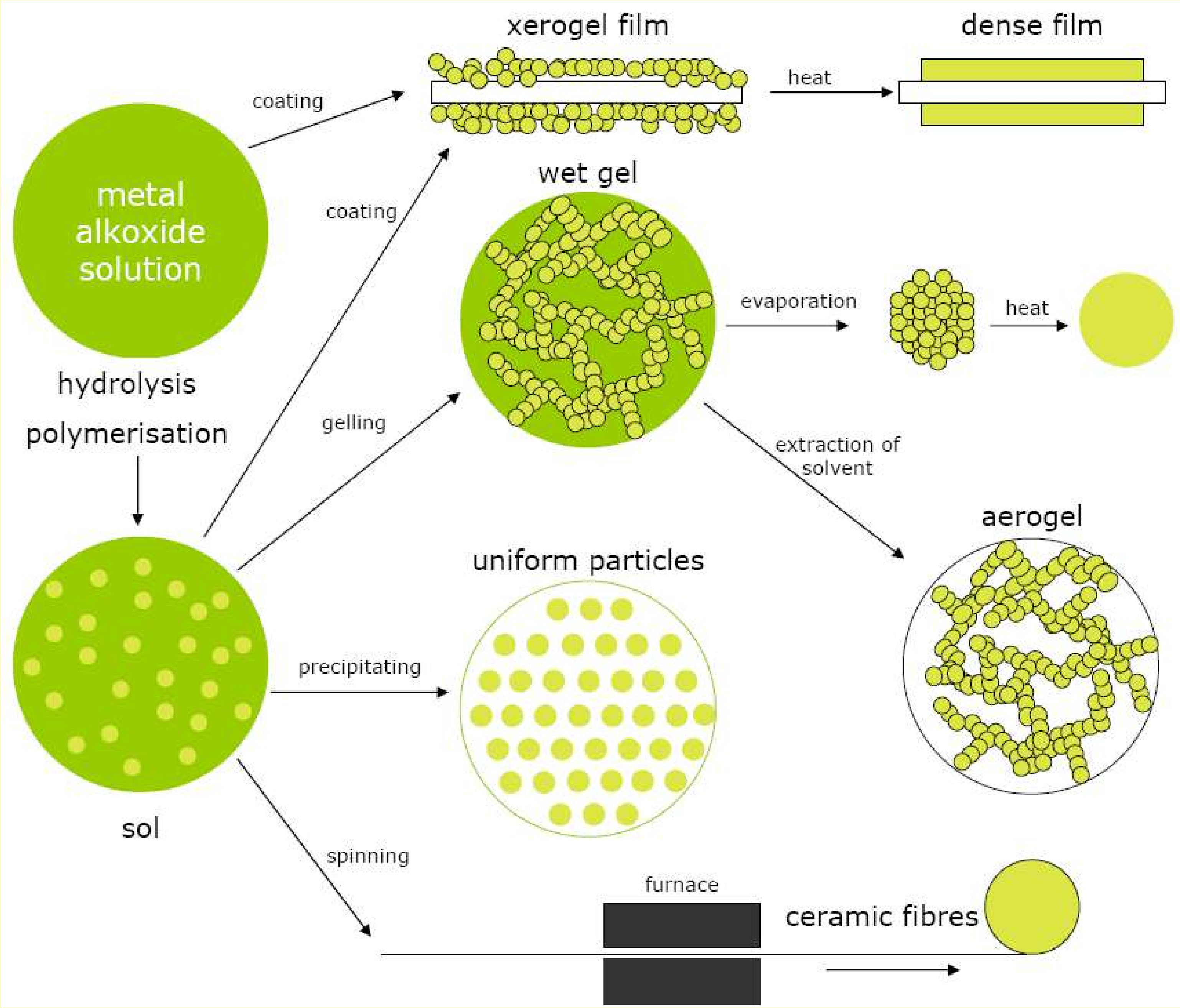
Methods of Obtaining the Organic-Inorganic Nanocomposite Systems



Methods of Realization of Obtaining the Organic-Inorganic Nanocomposites by "Top-Down" Technique



Sol-Gel Method



Res. J. Chem. Sci. – 2015. - V.5, N12. – P.98-105.

Types of Nanocomposites According to Type of Interaction Between Organic and Inorganic Component

Polymer-based hybrids prepared by sol-gel

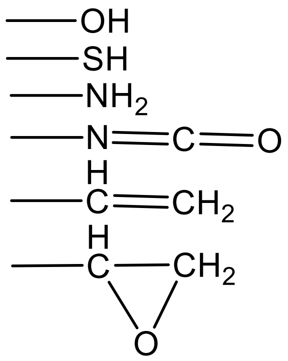
Class I

Physical interactions

Class II

Chemical interactions

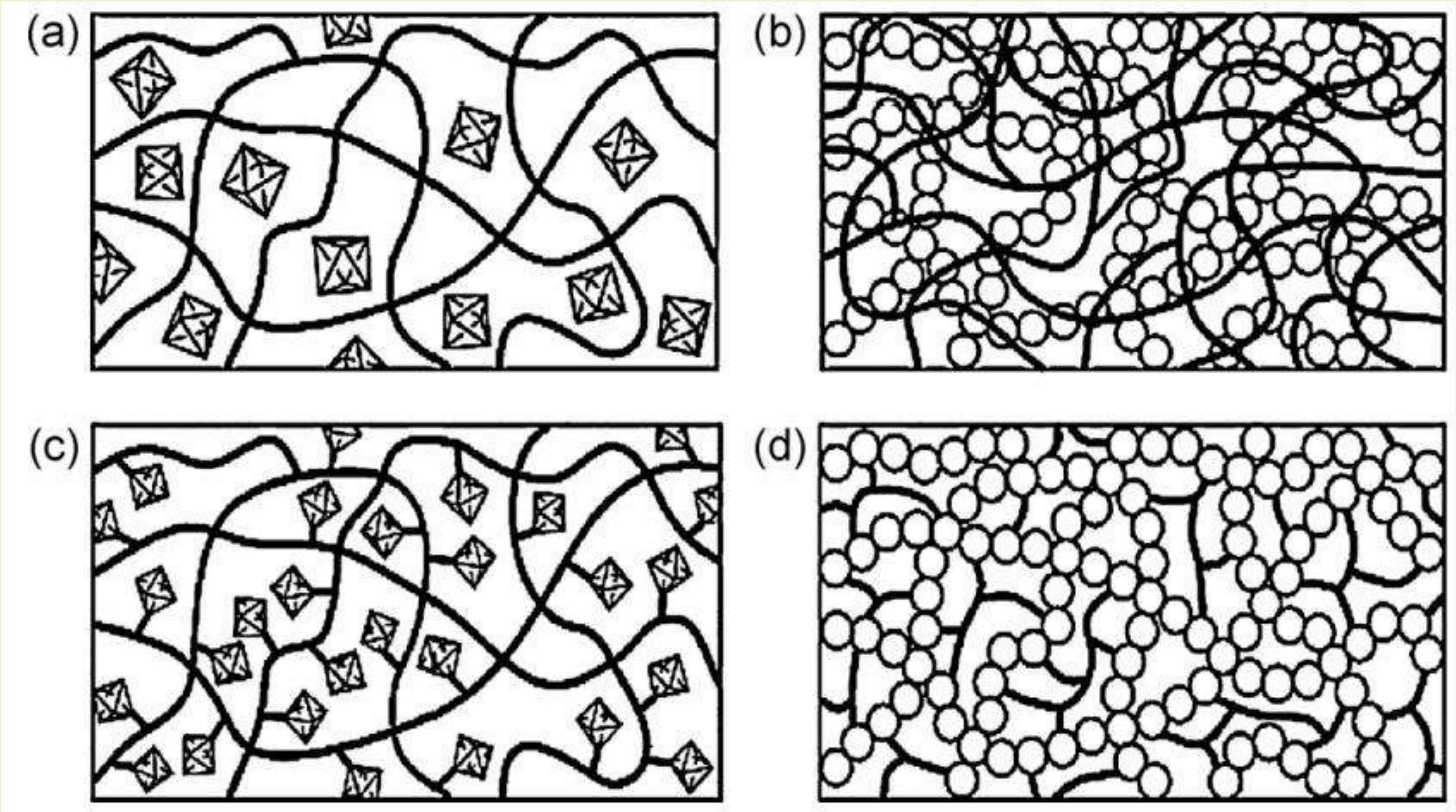
Functionalized polymers by metal alkoxides; Polymers and alkoxides of metals with reactive groups:



Compabilizers are added to improve component compatibility

Kim C.S. Hybrid and hierarchical composite materials Chapter 2. Organic-inorganic polymer hybrids: Synthetic strategies and applications / C.S. Kim, C. Randow, T. Sano. - Switzerland: Springer International Publishing, 2015, P.11-63.

Types of Nanocomposites with Different Type of Interaction Between Organic and Inorganic Component



(a) an organic polymer containing chemically unbound inorganic nanoparticles; (b) interpenetrating networks, including chemically interconnected ones; (c) an organic polymer containing chemically bound inorganic groups or nanoinclusions; (d) nanocomposite obtained by simultaneous polymerization and polycondensation of organo-inorganic monomers.

Progr. Polymer Sci. - 2011. - Vol.36, №7. - P. 945-979.

Basic Definitions

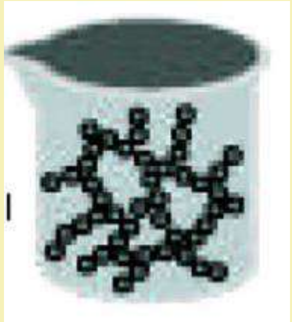
Sols are ultramicroheterogenic dispersion systems with liquid or gaseous dispersion media, the particle sizes of which range from 1 to 100 nm. Sols occupy an intermediate position between true solutions and coarse dispersed systems (suspensions, emulsions). Short-range forces (Van der Waals, Coulomb) predominate between the particles.

SOL IS A COLLOIDAL SOLUTION

GEL IS A SOL WITH COLLOIDAL PARTICLES FORMING SPATIAL NETWORK OF BONDS

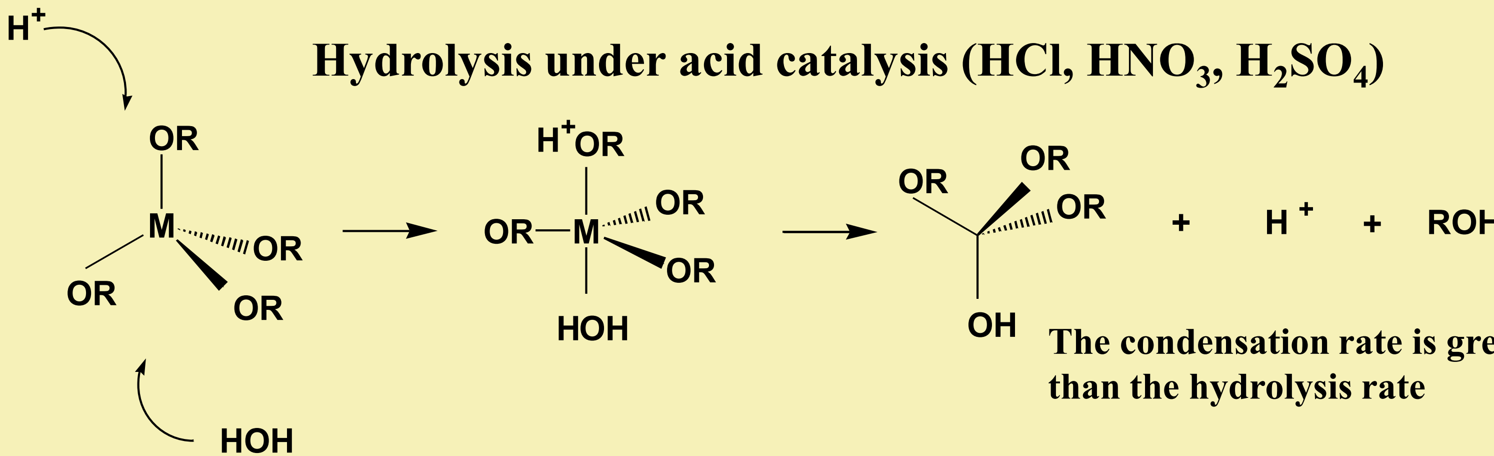
XEROGEL IS A DRIED GEL

AEROGEL IS A GEL DRIED UNDER SUPERCRITICAL CONDITIONS



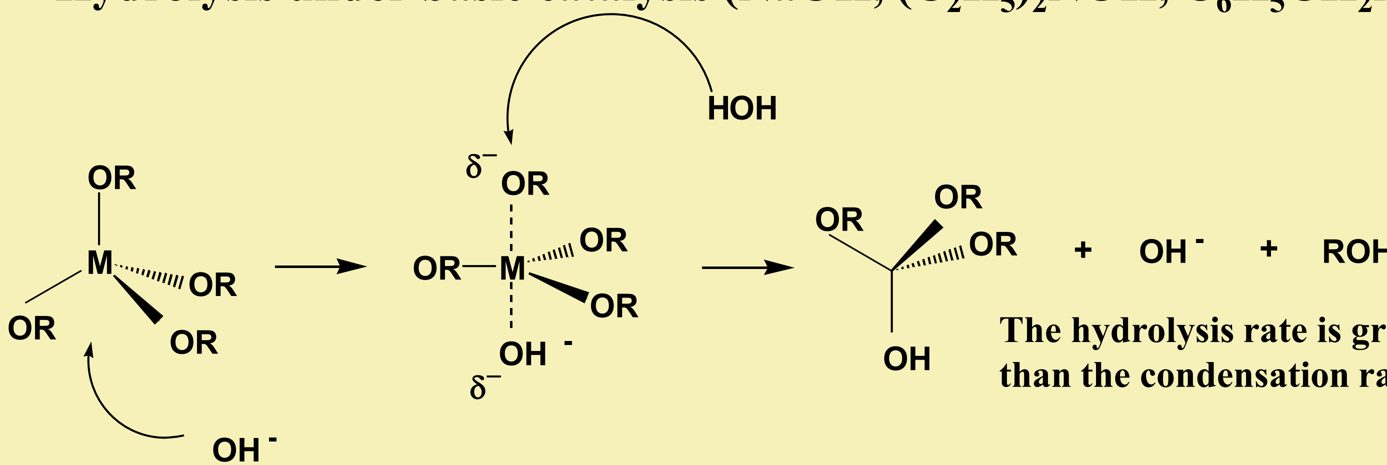
Hydrolysis of Alkoxide Precursors

Hydrolysis under acid catalysis (HCl, HNO_3, H_2SO_4)



The condensation rate is greater than the hydrolysis rate

Hydrolysis under basic catalysis (NaOH, $(C_2H_5)_2NOH$, $C_6H_5CH_2N(CH_3)_2$)



The hydrolysis rate is greater than the condensation rate

It is less common to carry out neutral catalysis using salts($(C_4H_9)_2Sn(OOCC_{11}H_{23})_2$, NaF)

Metal Alkoxides Used for the Sol-gel Process

Alkyl		*Alkoxy*	
methyl	$\bullet CH_3$	methoxy	$\bullet OCH_3$
ethyl	$\bullet CH_2CH_3$	ethoxy	$\bullet OCH_2CH_3$
n-propyl	$\bullet CH_2CH_2CH_3$	*n*-propoxy	$\bullet O(CH_2)_2CH_3$
iso-propyl	$H_3C(\bullet C)HCH_3$	*iso*-propoxy	$H_3C(\bullet O)CHCH_3$
n-butyl	$\bullet CH_2(CH_2)_2CH_3$	*n*-butoxy	$\bullet O(CH_2)_3CH_3$
sec-butyl	$H_3C(\bullet C)HCH_2CH_3$	*sec*-butoxy	$H_3C(\bullet O)CHCH_2CH_3$
iso-butyl	$\bullet CH_2CH(CH_3)_2$	*iso*-butoxy	$\bullet OCH_2CH(CH_3)_2$
tert-butyl	$\bullet C(CH_3)_3$	*tert*-butoxy	$\bullet OC(CH_3)_3$

The most widely used is alkoxide of silicon ($Si(OC_2H_5)_4$), aluminum ($Al(OCH(CH_3)_2)_3$), tin ($Sn(OCH_2CH(CH_3)_2)_4$) and alkoxydes of d-elements in the highest degree of oxidation, such as zirconium ($Zr(OCH(CH_3)_2)_4$) and titanium ($Ti(OCH_2CH(CH_3)_2)_4$).

Chlorides of these metals are less commonly used.

Brinker C.J., Scherer G.W. Sol-gel science: the physics and chemistry of sol-gel processing / London: Academic Press., Inc., 1990, 908 p.

Condensation of Alkoxide Precursors

$$\equiv Si\text{–}OH + \equiv Si\text{–}OR \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + ROH$$

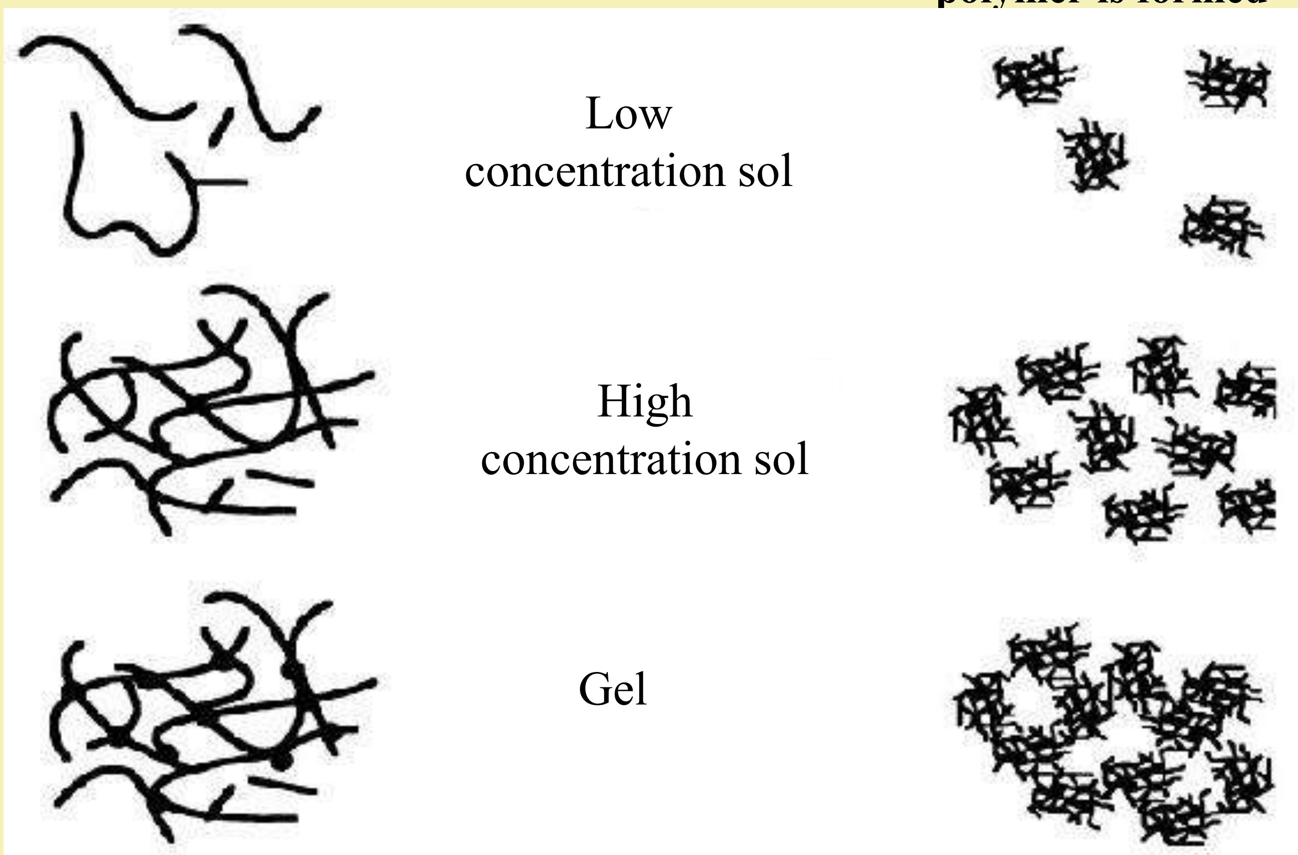
$$\equiv Si\text{–}OH + \equiv Si\text{–}OH \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + H_2O$$

ACID CATALYSIS

A network-like polymer is formed

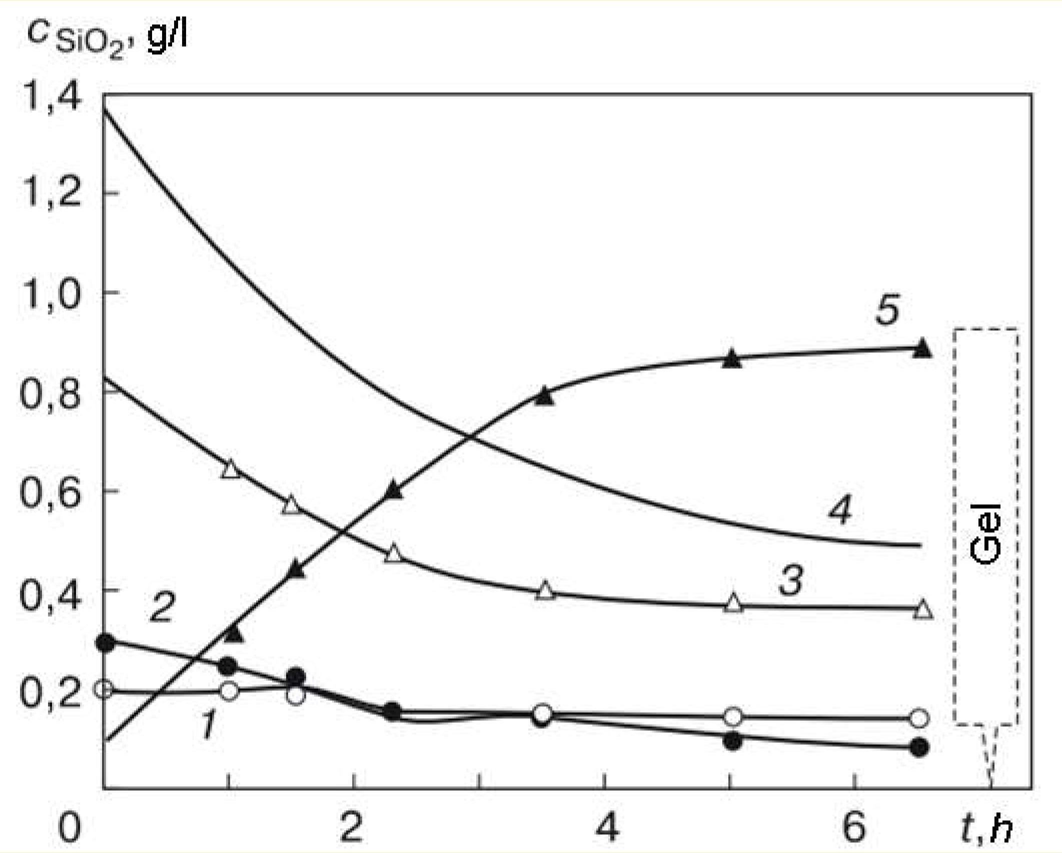
BASIC CATALYSIS

A highly branched polymer is formed



Mater. Horiz. - 2016 - V.3. - P.91-112

Kinetics of Polycondensation



Kinetic curves of aging of silicic acid (c_{SiO2} = 33.8 g/l; $pH_{initial}$ = 4.0, 293 K):

1 – monomer fraction;

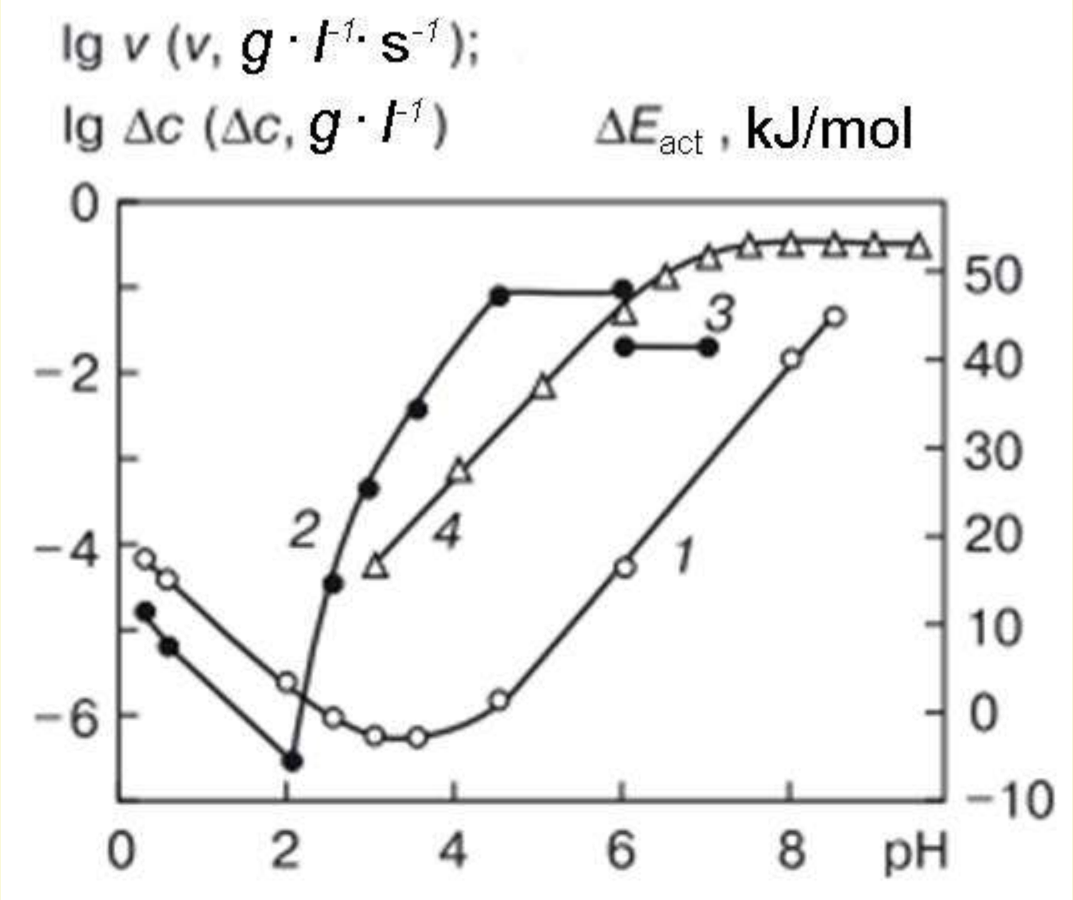
2 – low molecular weight fraction;

3 – higher oligomers;

4 – total concentration of "active fractions";

5 – macromolecular acids.

Kinetics of Polycondensation



Influence of pH on various parameters of polycondensation process (c_{SiO2} = 1.45 g/l; 293 K): reaction rate **ν** (1), activation energy **Δ*E*** (2 – without stirring, 3 – under stirring and buffer conditions); the difference in the "active" (thermodynamic) concentration of the monomer **Δc** in the volume of the solution and the surface layer of particles (4)

Thermodynamics of Nucleation

Gibbs-Volmer theory

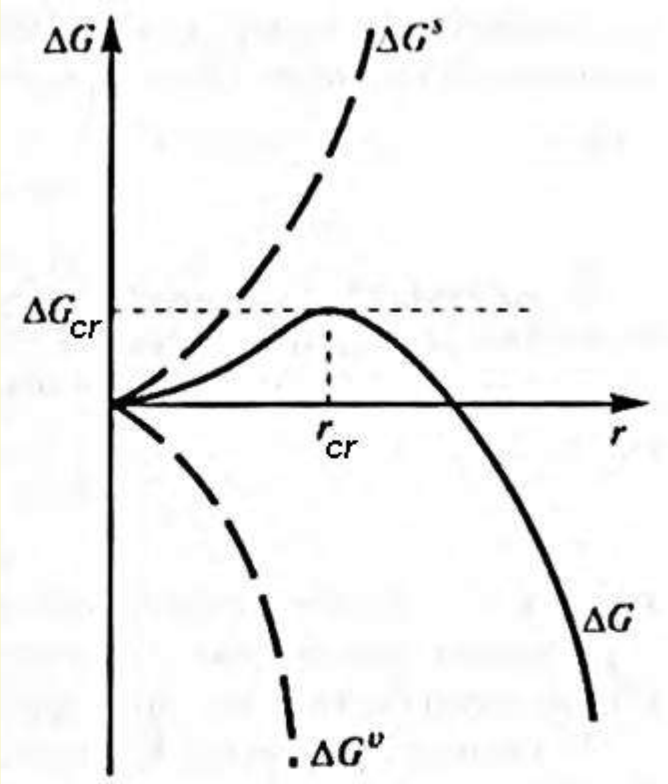
Formation of nucleus with critical radius r_{cr} (as the radius increases, the value of Gibbs free energy ΔG becomes negative, that indicates their **stability**) is described by dependency:

$$\Delta G_{cr} = \frac{4}{3}\pi r_{cr}^{\ 2}\sigma = \frac{1}{3}\sigma s_{cr},$$

σ – surface tension at the nucleus/environment interface; s_{cr} – nucleus interface.

This dependence can be expressed by equilibrium concentration (c_e) and critical concentration of the saturated solution (c_{cr}) of silicic acid based on the volume of the molecule of the latter V_M in the nucleus.

$$\Delta G_{cr} = \frac{16\pi\sigma^3 V_M^2}{3(RT)^2 \ln^2(c_{cr}/c_e)},$$



Dependence of Gibbs energy of nucleus formation ΔG on the nucleus radius: ΔG^s – surface component; ΔG^v – volume component

Thermodynamic Stability of Dispersed Systems

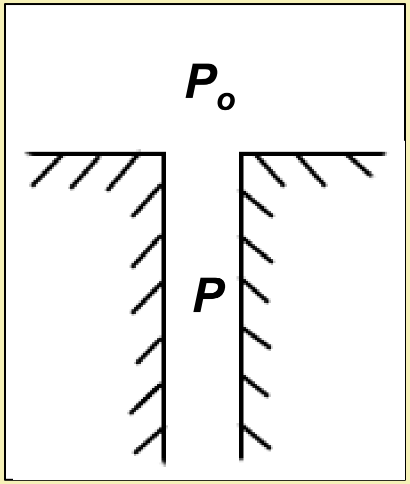
Sedimentation (kinetic) stability –the ability of dispersed systems to maintain a uniform distribution of particles of the dispersed phase in the dispersed medium

Resistance to gravity

Aggregate resistance – the ability of the particles of the system to maintain the degree of dispersity or in other words not to stick together and not to form aggregates under the influence of various factors

Resistance to adhesion of particles

It is characterized by a splitting pressure: $\Pi = P - P_o$



This parameter characterizes the surface forces that carry out work to increase the Gibbs thermodynamic potential dG:

$$\Pi = \left(\frac{dG}{dh}\right)_{T,P,\mu}$$

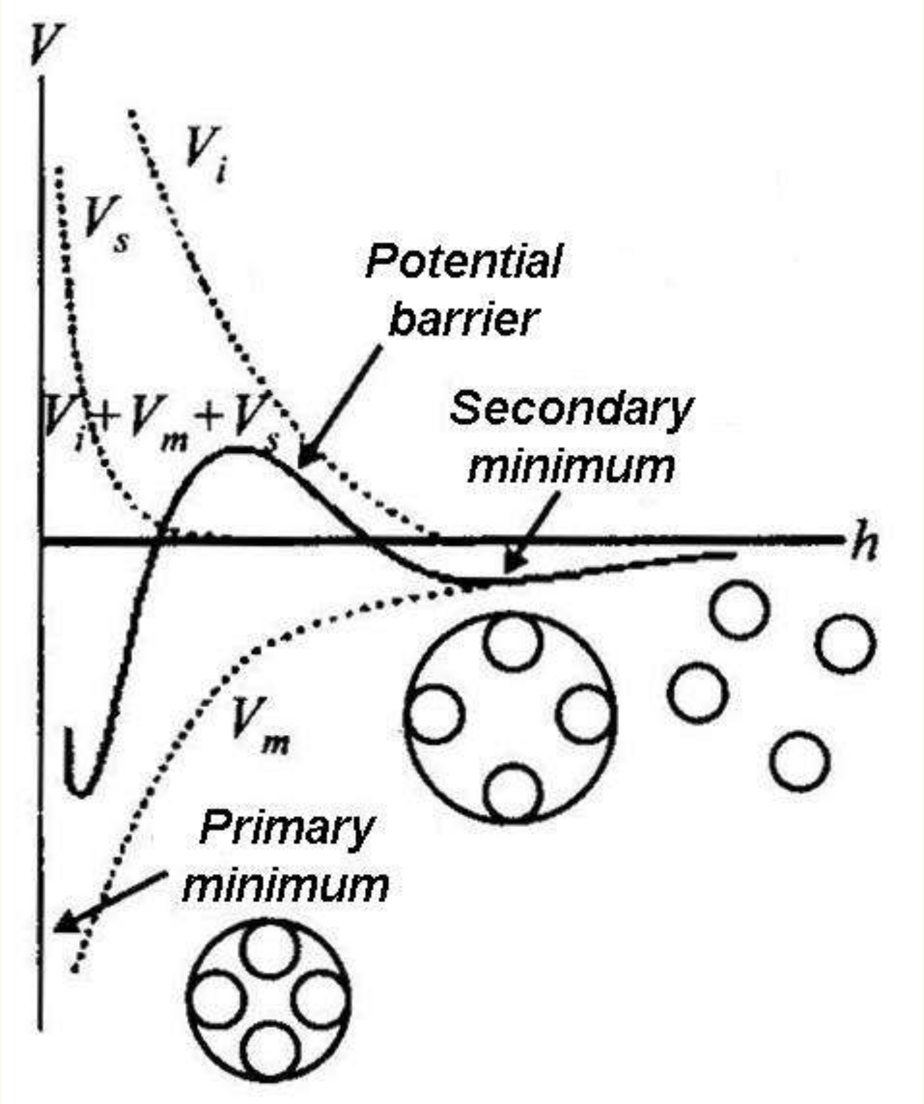
The theory of stability of Deryagin-Landau-Fairway-Overbeck (DLFO)

$\Pi(h) = \Pi_i(h) + \Pi_m(h) + \Pi_s(h)$,
$\Pi_i(h)$ – *ion-electrostatic component associated with the overlapping of the double electric layer;* ***$\Pi_m(h)$*** – *molecular component associated with the Van der Waals forces;* ***$\Pi_s(h)$*** – *structural component associated with overlapping boundary layers in which the fluid structure differs from the bulk.*

The total potential energy of the pairwise interaction of particles

$V = V_i + V_m + V_s$,

V_i *- ion-electrostatic component;* ***V_m*** *- molecular component;* ***V_s*** *– structural component.*



The dependence of energy of pairwise interaction of the particles (***V***) on the distance (***h***) between them.

Rheological Properties of Dispersed Systems

$$\boldsymbol{\tau} = \boldsymbol{\tau}_d + \boldsymbol{\eta}^* \cdot \frac{\boldsymbol{d\varepsilon}}{\boldsymbol{dt}},$$ (Shvedov-Bingham equation)

τ – shear stress; τ_d – limit shear stress; η^*– plastic viscosity, which is determined by the angle of inclination of the straight line BC (at the figure) and takes into account the part of the deformation resistance which is proportional to the shear rate; ε – deformation; t – time.

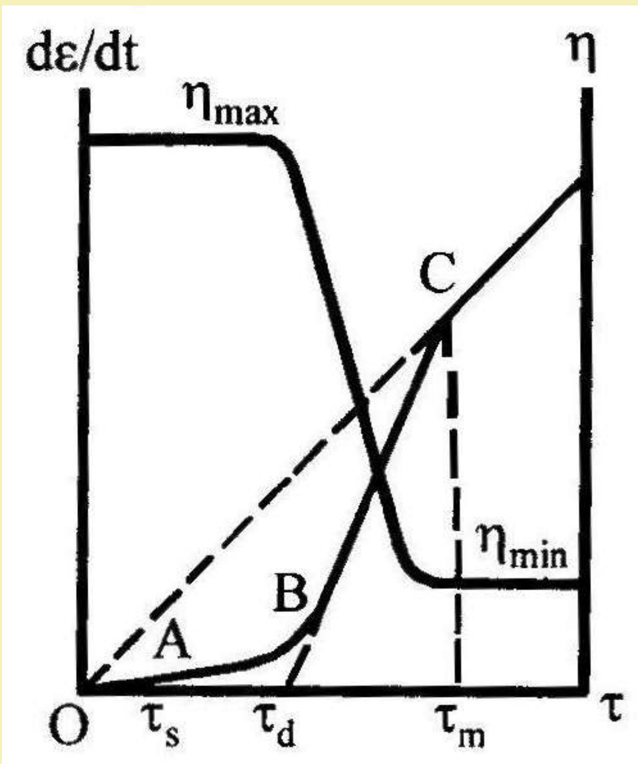
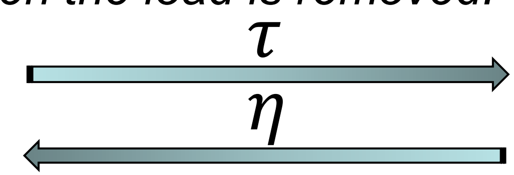
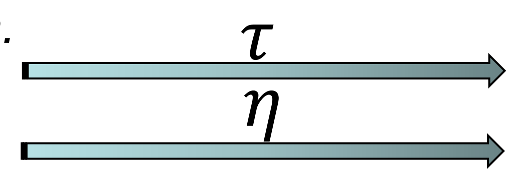


Figure: τ_s – maximum static shear stress below which the system does not flow; τ_d – limit dynamic shear stress (yield strength according to Bingham); τ_m – limit dynamic shear stress (Bingham's yield strength) at which the structure of the system is completely destroyed.

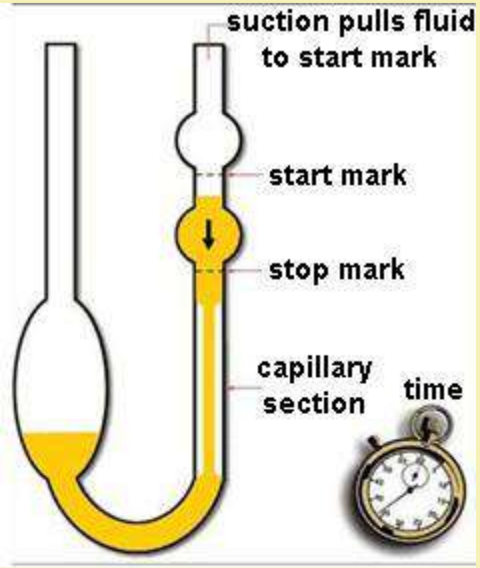
Thixotropy *- the ability of the system to restore structure when the load is removed.*



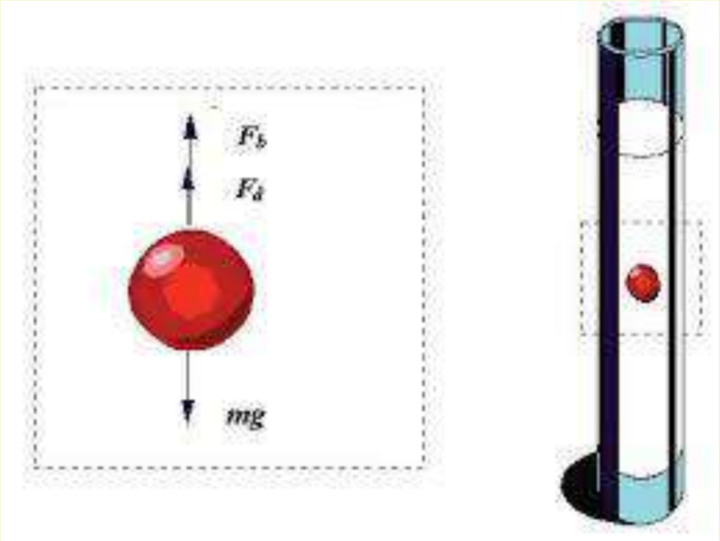
Dilatancy *is a reversed to* ***thixotropy*** *phenomenon.*



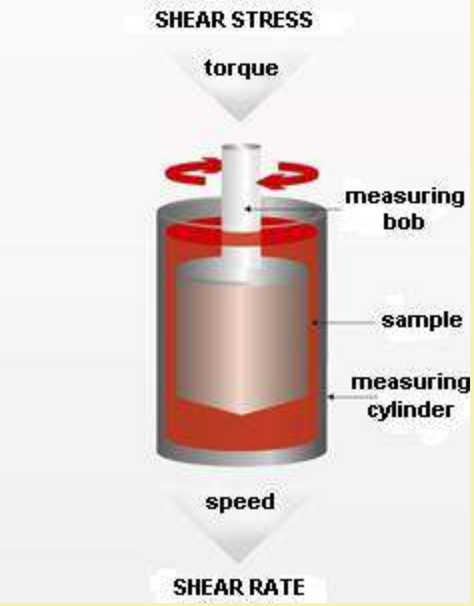
Methods of Measuring Viscosity



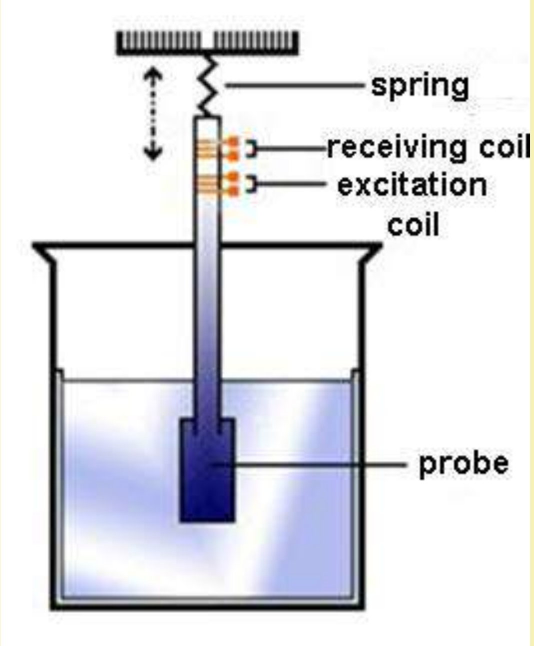
Capillary method



Falling ball method

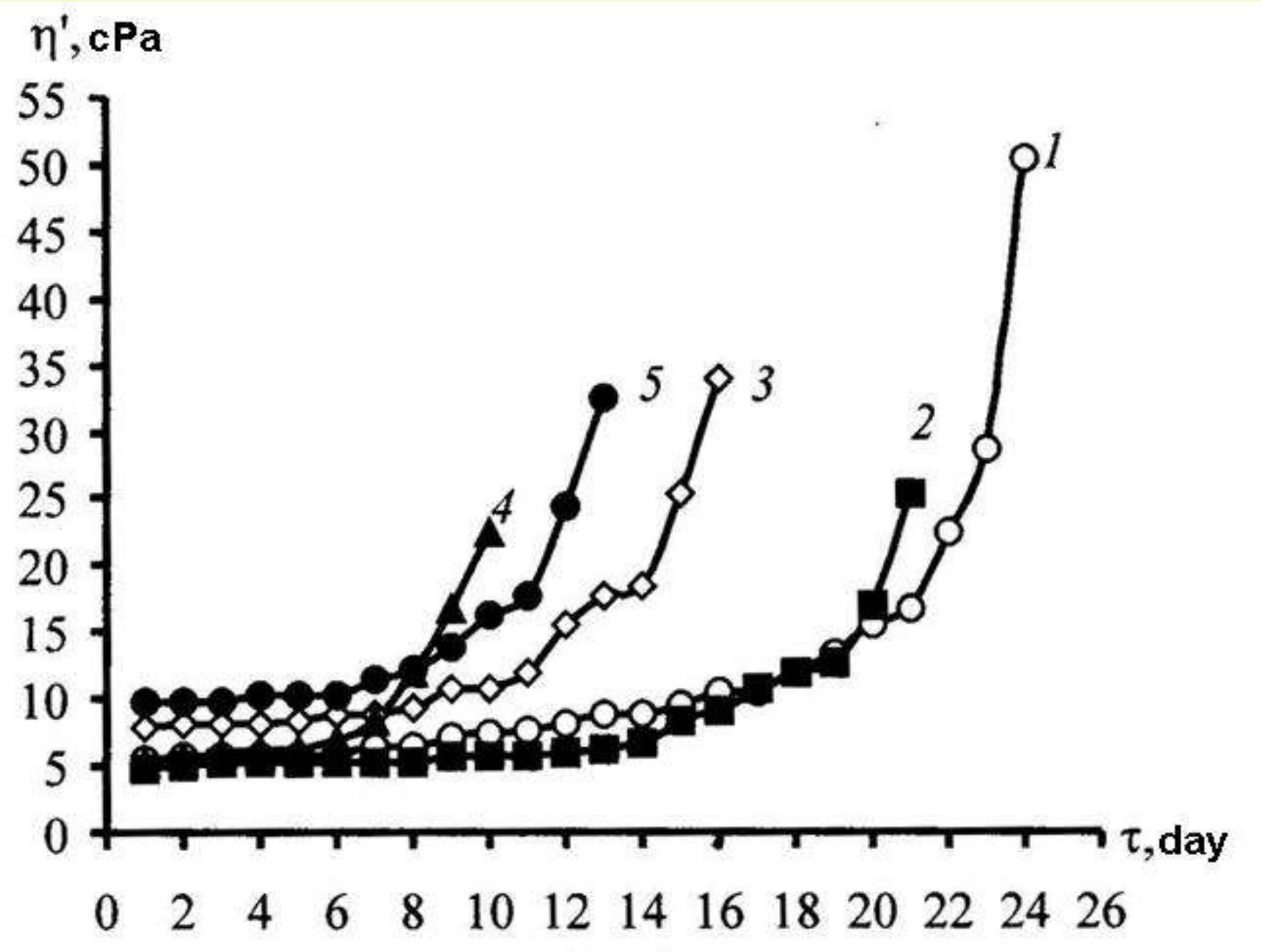


Rotary method



Ultrasonic method

Kinetics of Structural Viscosity of Silica During Maturation



Changes in the structural viscosity of silica based on $Si(OEt)_4$ over time :

1 – silica obtained with an equivalent amount of water;

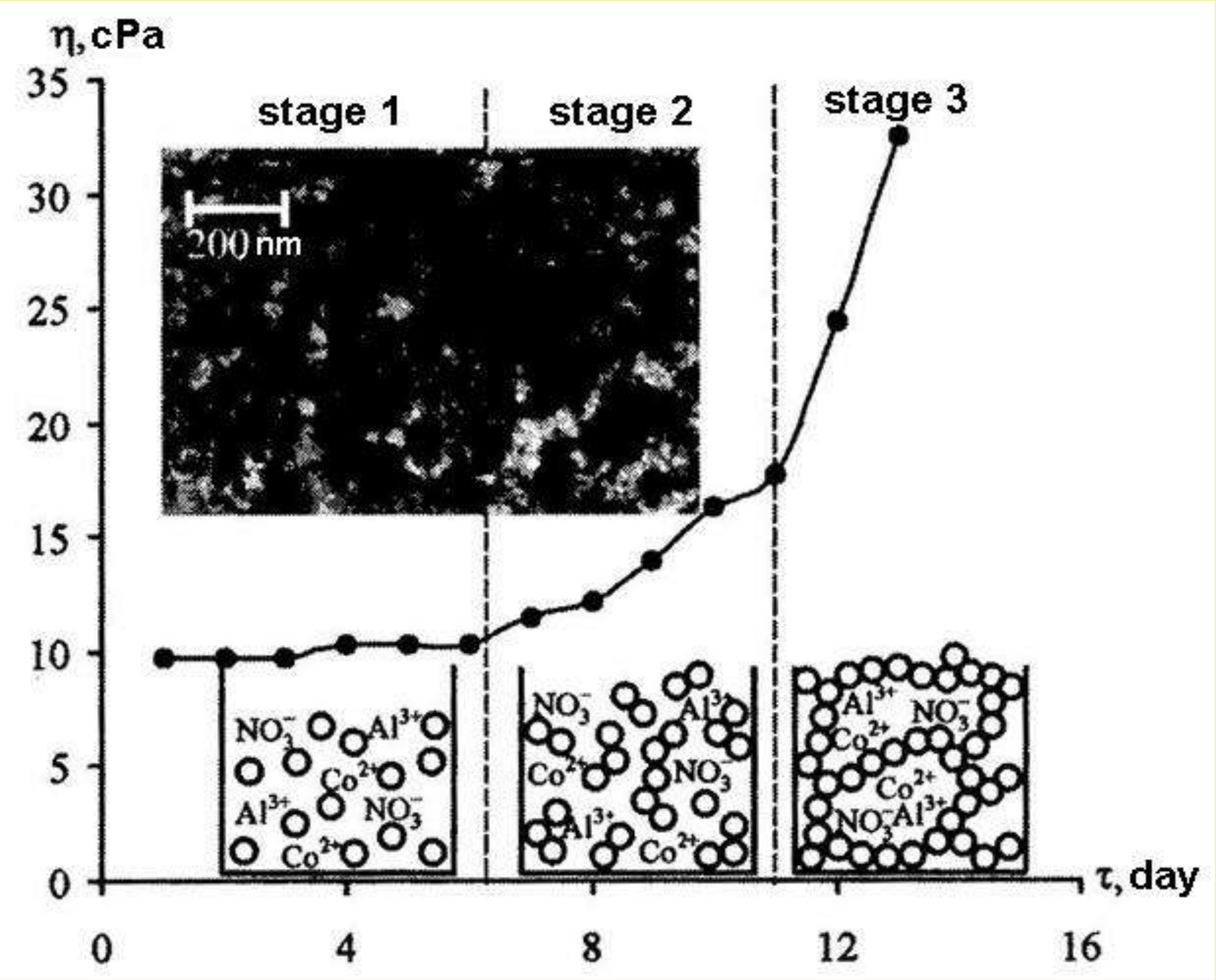
2 – silica obtained with excess water;

3 – silica modified by $Al(NO_3)_3$;

4 – silica modified by $Co(NO_3)_2$;

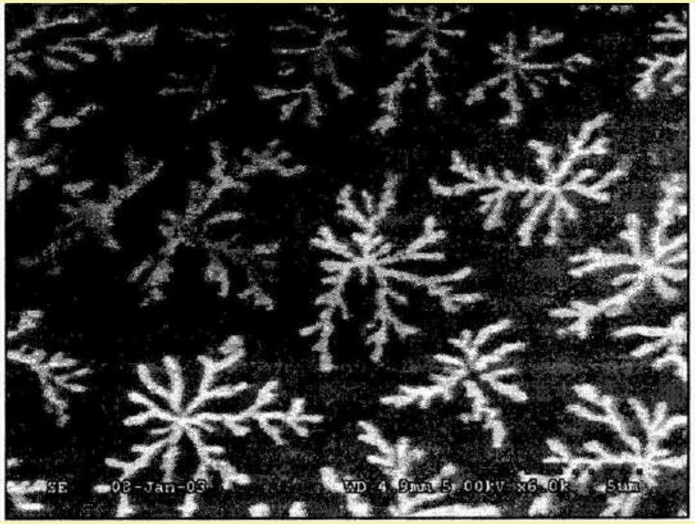
5 – silica modified by $Al(NO_3)_3$ та $Co(NO_3)_2$

Kinetics of Silica Viscosity During Gelation

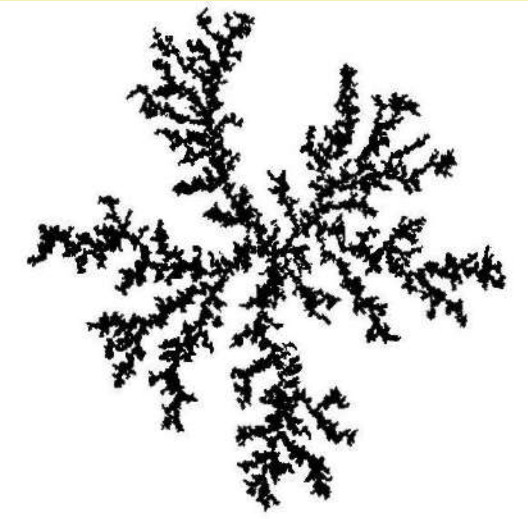


Schematic representation of the stages of gelation of silica based on $Si(OEt)_4$ modified by $Al(NO_3)_3$ and $Co(NO_3)_2$ (TEM image of sol on the 2nd day of maturation are inserted)

A Fractal Approach to Estimating the Structure of Dispersed Systems

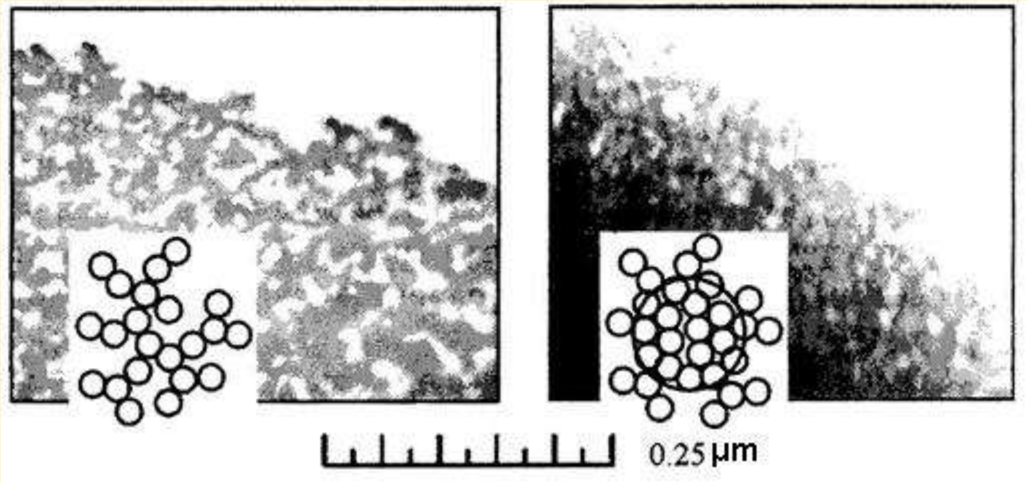


Fractal structures in glass (image obtained by electron microscopy)



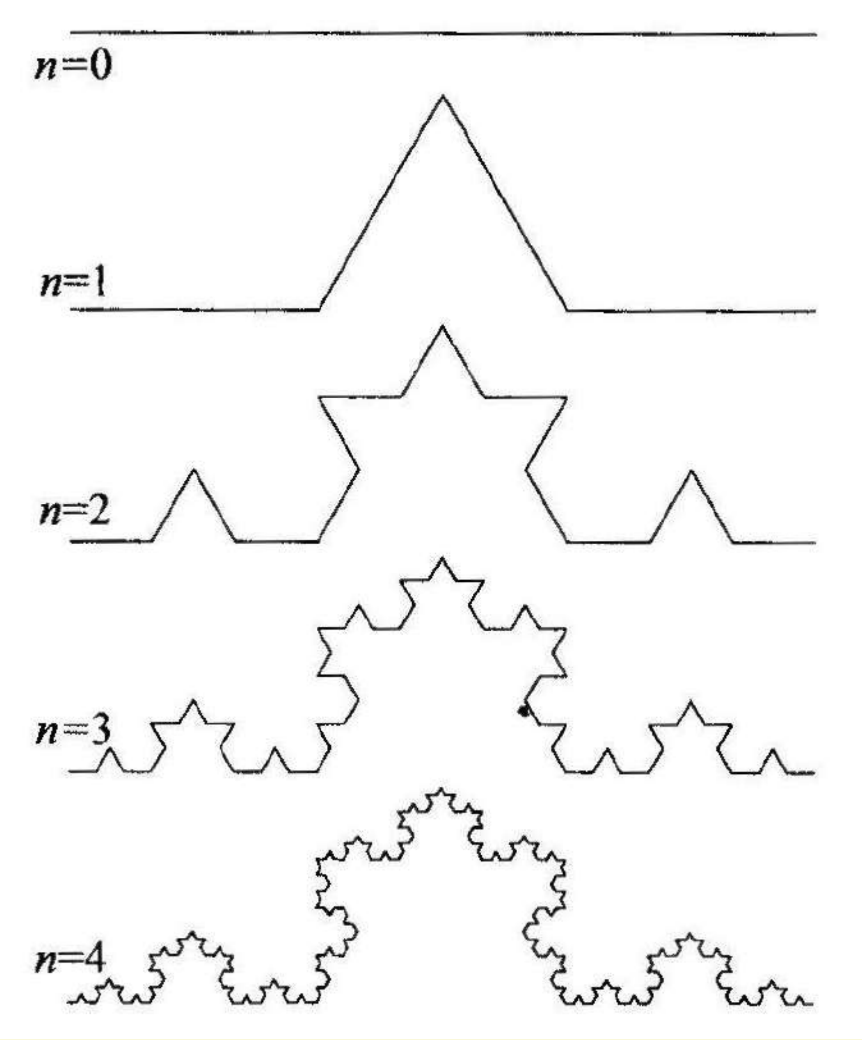
Witten-Sander fractal unit obtained by computer simulation

Brinker C.J., Scherer G.W. Sol-gel science: the physics and chemistry of sol-gel processing / London: Academic Press., Inc., 1990, 908 p.



Scheme illustrating the formation of a fractal aggregate of mass (left) and surface (right) type in phosphosilicate xerogel according to the results of small-angle X-ray scattering

General Concept of Fractal



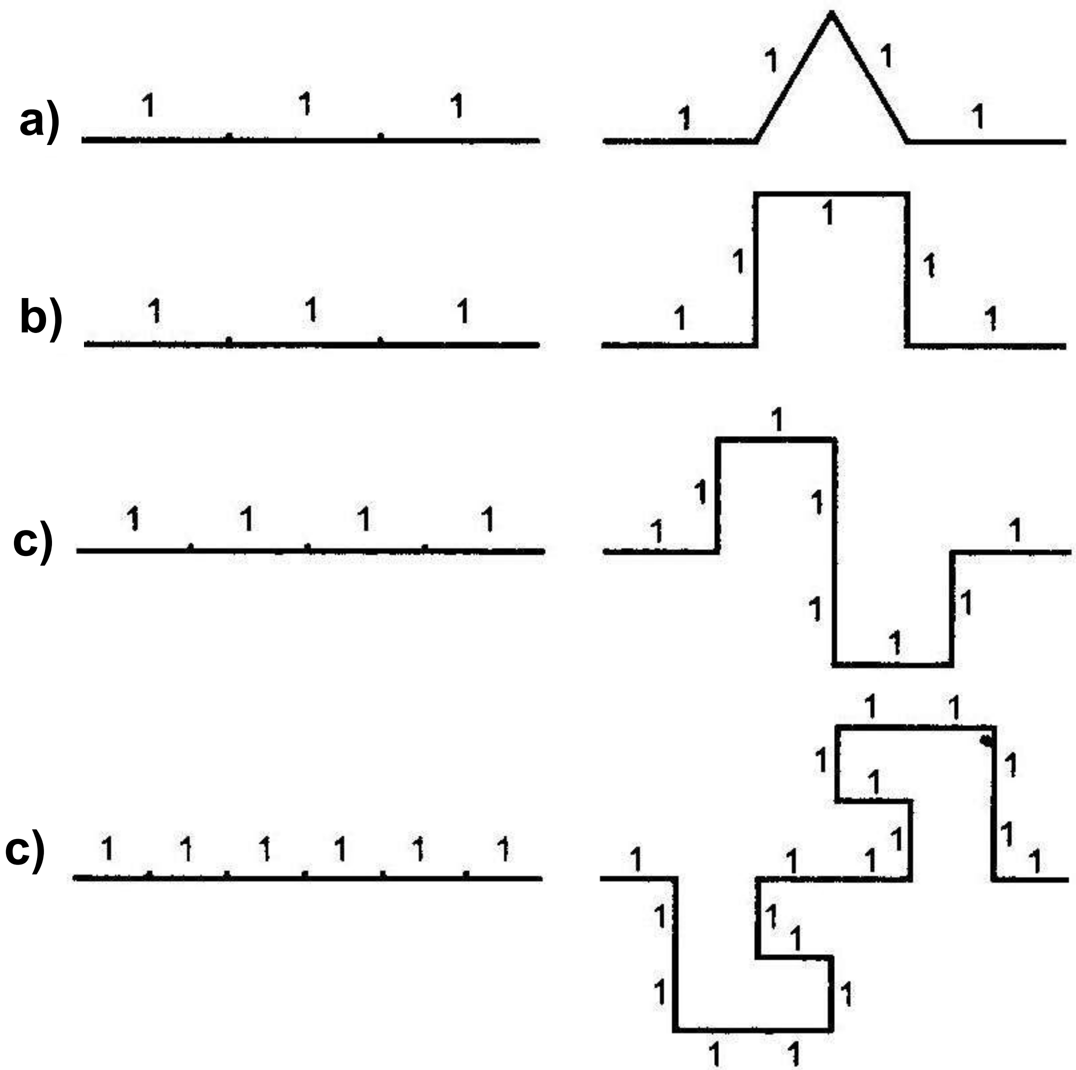
An example of the first generations
of the Koch triad curve

Length of the line: $L = a \cdot \left(\frac{R}{a}\right)^{D}$,

a *– elementary element length;* R *– distance between the ends of the line;* ***D – fractal dimension.***

Fractal dimension *– ratio of logarithms of distances between endpoints of the forming element along the broken line and the straight line (for the Koch curve it is* $\frac{ln4}{ln3} = 1{,}2618$*)*

Examples of Dependencies of Fractal Dimensions Depending on Structure of the Forming Element of the Koch Curves



$$D = \frac{\ln 4}{\ln 3} \approx 1{,}262$$

$$D = \frac{\ln 5}{\ln 3} \approx 1{,}465$$

$$D = \frac{\ln 8}{\ln 4} = 1{,}5$$

$$D = \frac{\ln 18}{\ln 6} \approx 1{,}613$$

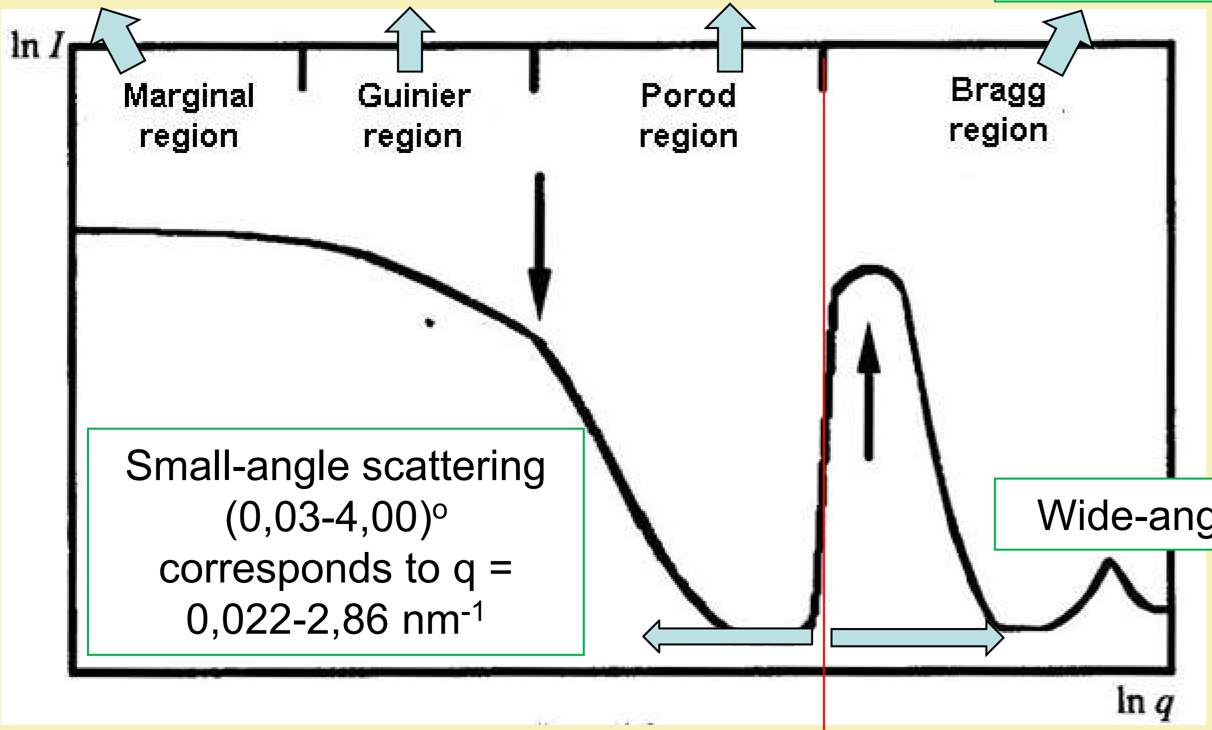
Study of Structure of Fractal Systems by the Method of Small-angle X-ray Scattering

Number average MM and concentration of monomers

Radius of inertia (R_g) of fractal aggregates

Fractal dimension

The nature of ordering at distances comparable to the length of the chemical bond



Small-angle scattering (0,03-4,00)^o corresponds to q = 0,022-2,86 nm^{-1}

Wide-angle scattering

Small-angle X-ray scattering curve: *I – scattering intensity; q – wave vector*

The fractal dimension is determined by the tangent of angle of linear section inclination (tg $\alpha = \beta$) in the Porod region

Study of Structure of Fractal Systems by the Method of Small-angle X-ray Scattering

Guinier Region

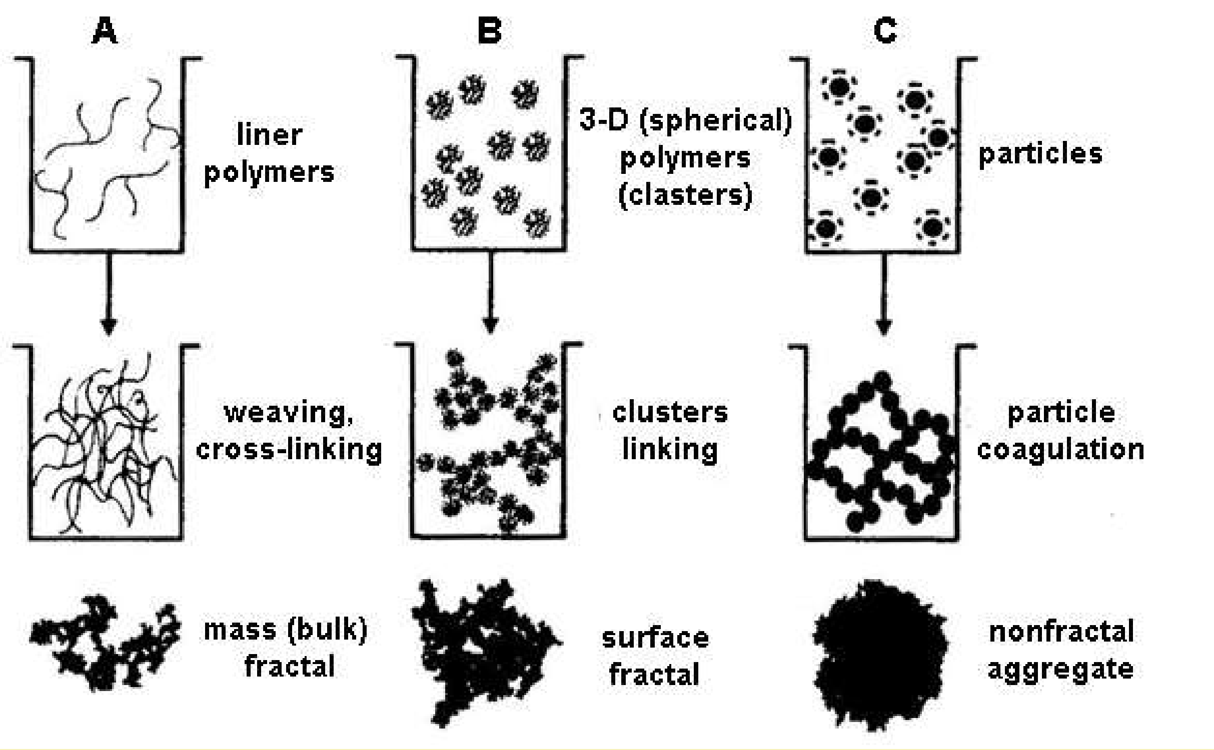
The radius of inertia (rotation) of fractal aggregates is determined by the ratio

$$\alpha = \frac{-q^2 \cdot R_g^2}{3}$$

Porod Region

$|\beta| = 1 \div 3$ ⇨ Mass fractal with fractal dimension $D_f = |\beta|$

$|\beta| = 3 \div 4$ ⇨ Surface fractal with fractal dimension $D_s = 6 - |\beta|$

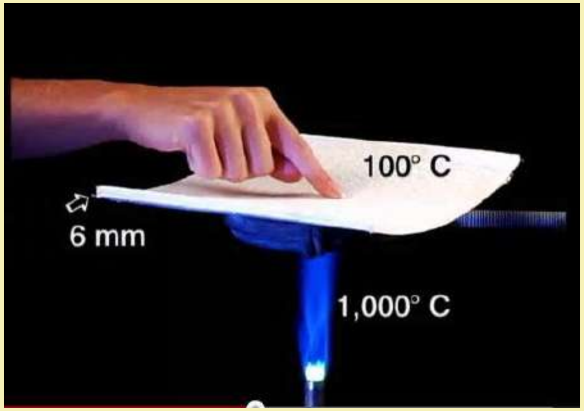


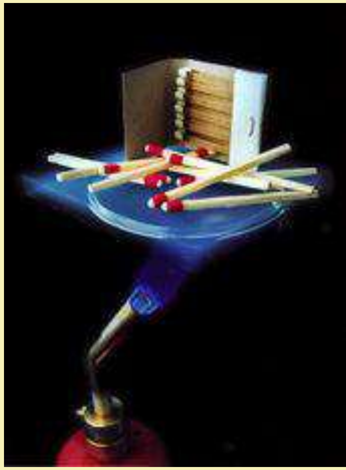
Types of polymers, gelation and fractal organization in polymeric sol-gel systems:
A – in acidic medium;
B – in basic medium;
C – in colloidal sol-gel systems

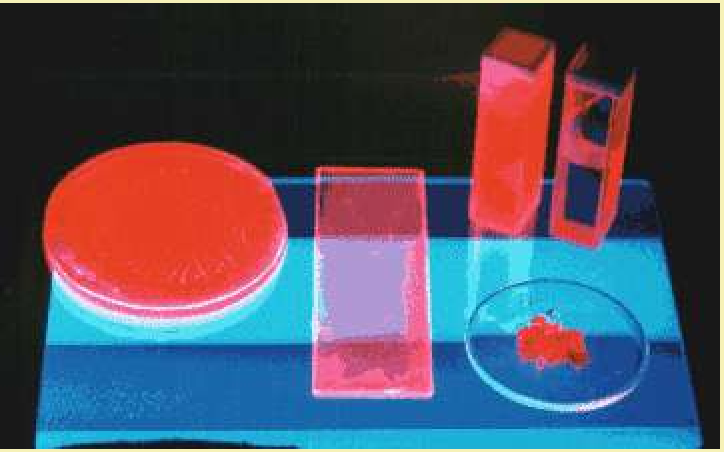
Applications of Hybrid Materials

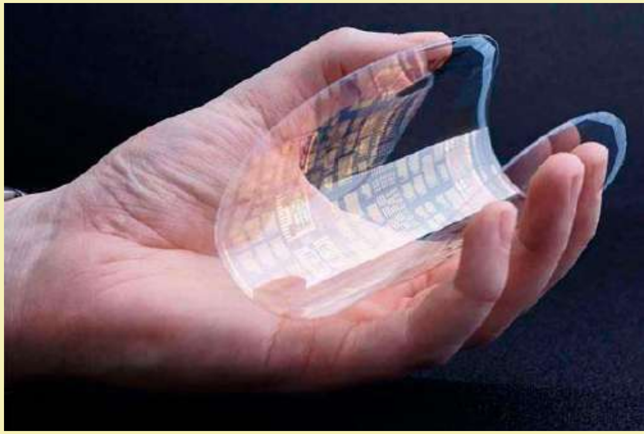
Coatings	High homogeneity, possibility of obtaining hybrid coatings
Fibers	Possibility of extraction from solution, possibility to prevent high melting point, possibility of extraction of fibers from extremely high-temperature oxides, purity (optical fibers)
Powders	Monodisperse spherical particles, lower temperature of obtaining sintered ceramic masses, elimination of grinding process
Monoliths	Monoliths, plates (glass), cores, tubes, lower process temperatures, cleanliness
Hollow spheres	Special shells for nuclear fuel (deuterium, tritium)
Porous products	Substrates for catalysts, narrow pore distribution (i.e. the possibility of obtaining material with the same pore size)

Materials Obtained Using Sol-gel Technology









Thanks for your attention!