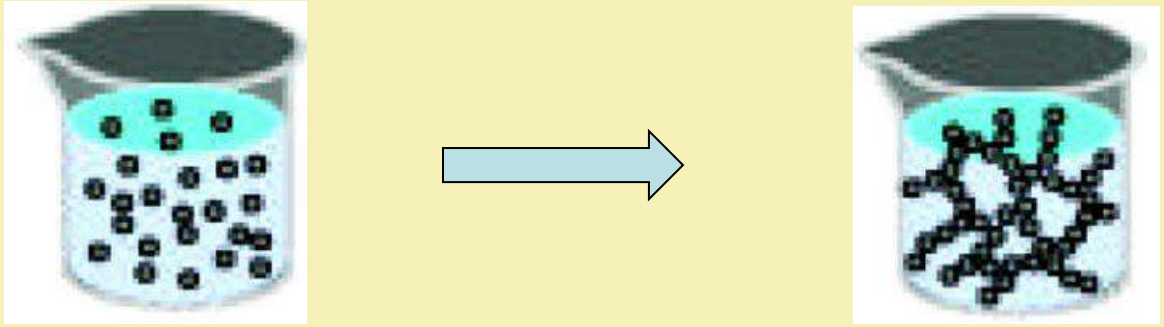
Theme 2

Fundamentals of Sol-Gel Synthesis of Hybrid Nanocomposites and Features of Obtaining Functionalized Polyhedral Oligosilsesquioxanes

Sol-Gel Method. Basic Concepts

«Sol-gel systems»	«Sol-gel synthesis»	«Sol-gel technology»

Sols — ultramicroheterogenic dispersion systems with liquid or gaseous dispersion medium having particle sizes ranging from 1 to 100 nm.
Sols occupy an intermediate position between true solutions and coarse dispersed systems (suspensions, emulsions). Short-acting forces prevail between the particles (Van der Waals, Coulomb).



SOL – COLLOID SOLUTION

GEL – SOL WITH COLLOIDAL PARTICLES THAT FORM A SPATIAL NETWORK OF BONDS

Sol-Gel Process Steps

1st step – obtaining sol

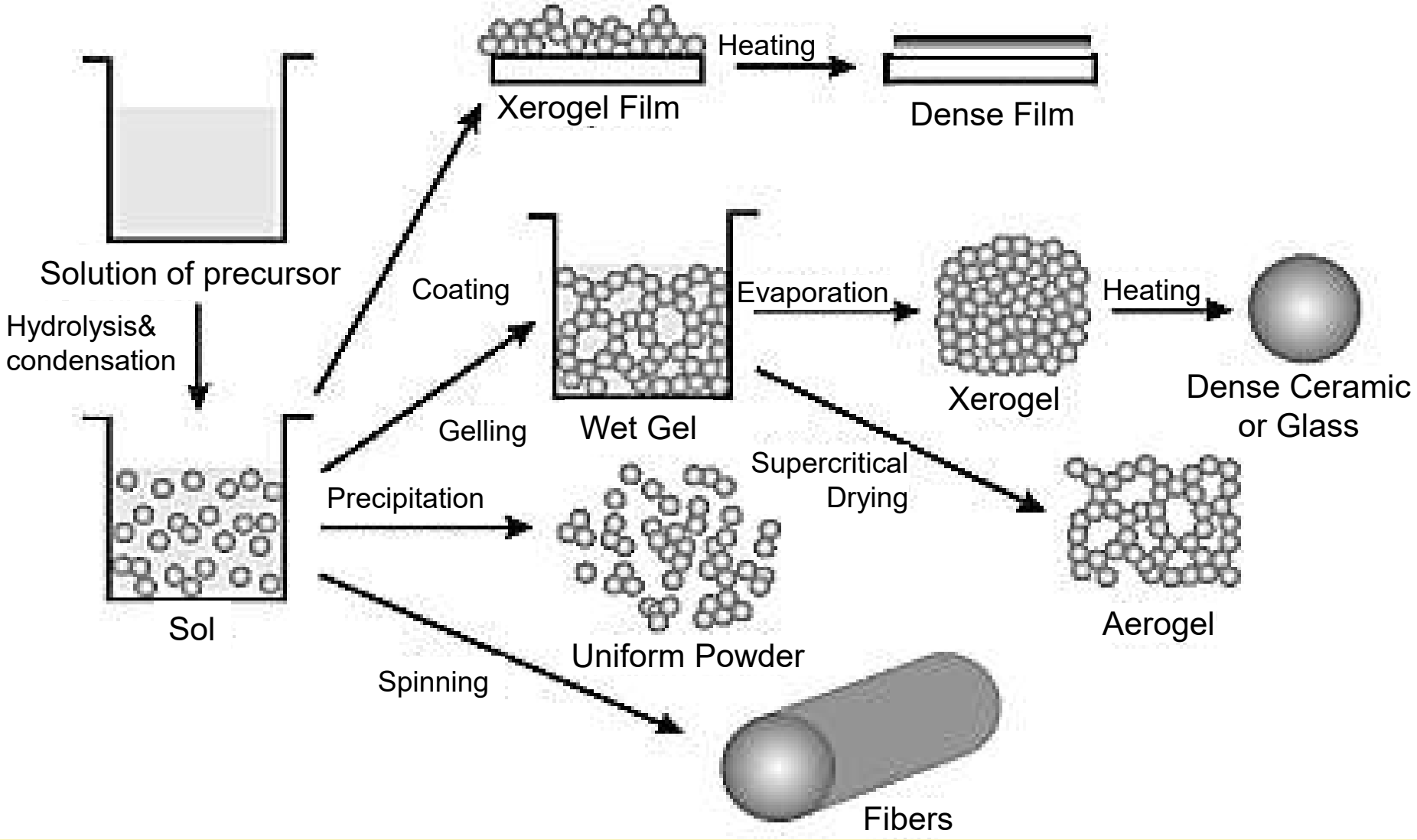
- Colloid sol
- Polymeric sol

2nd step – gelation

3rd step – drying gel

4th step – annealing

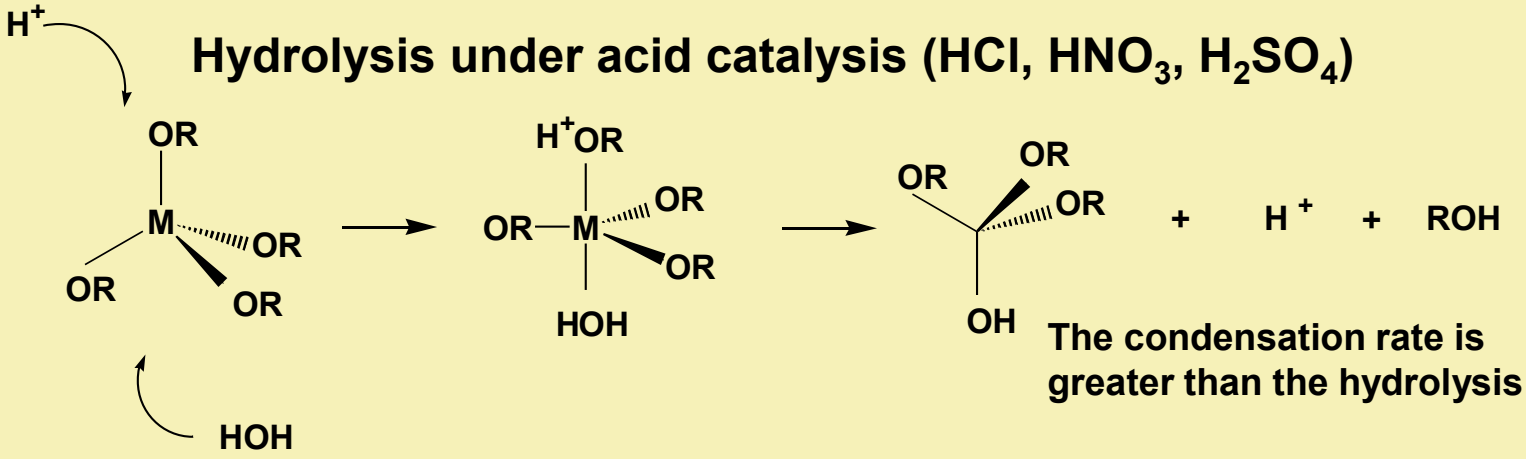
Sol-Gel Method



Niederberger M., Pinna N. Chapter 2. Aqueous and Nonaqueous Sol-Gel Chemistry. In: Metal Oxide Nanoparticles in Organic Solvents. Engineering Materials and Processes / M. Niederberger, N. Pinna. London: Springer, 2009, P. 7-18

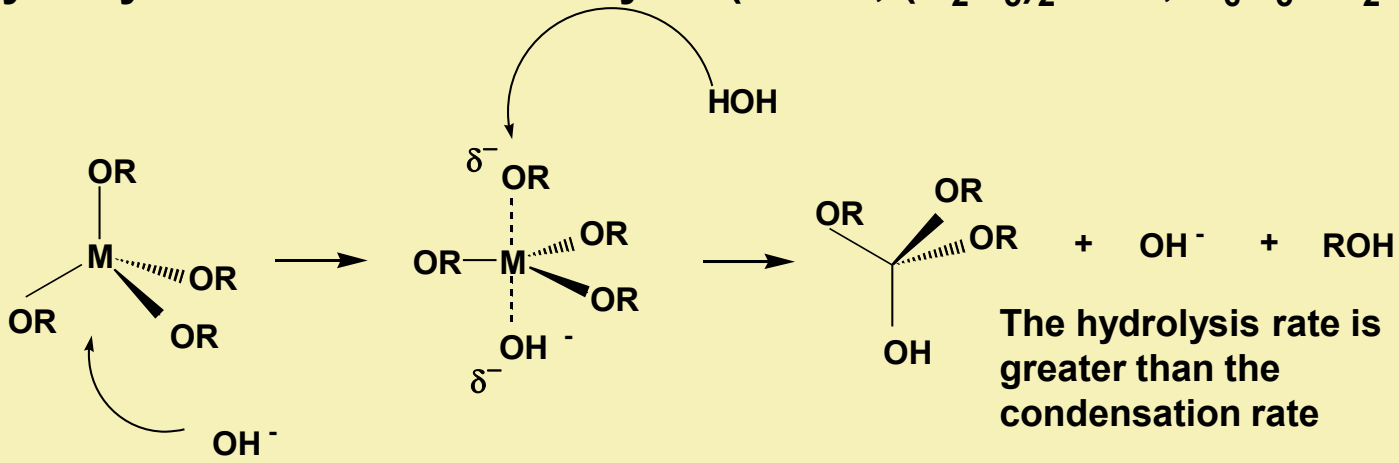
Hydrolysis of Alkoxide Precursors

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

Neutral catalysis is carried out rarely 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.

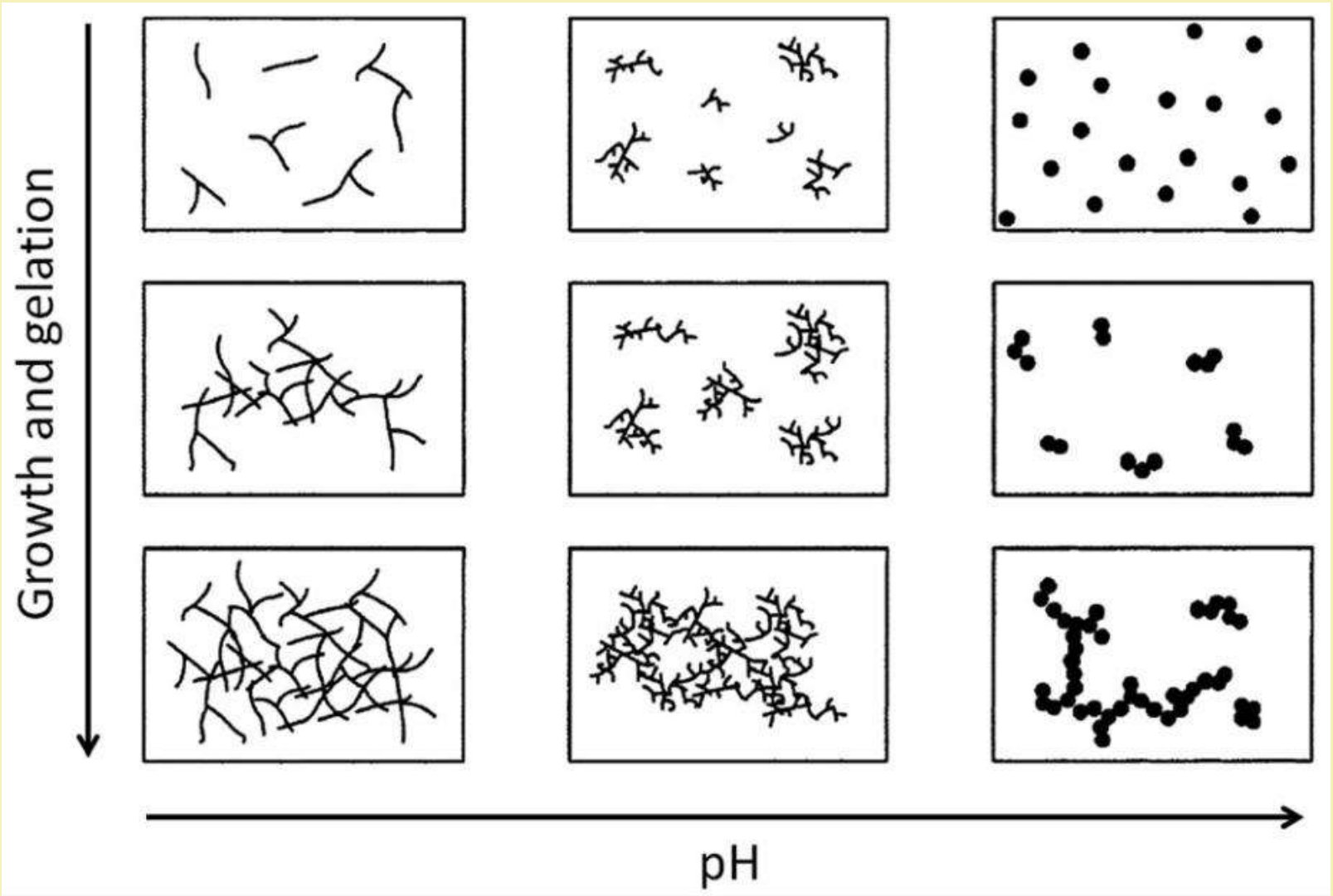
Brinker C.J., Scherer G.W. Sol-gel science: the physics and chemistry of sol-gel processing / London: Academic Press., Inc., 1990, 908 p.

Functionalized Metal Alkoxides for the Sol-gel Process

abbreviation	name	chemical struture
APMDES	aminopropyl methydiethoxysilane	$H_2N(CH_2)_3(CH_3)Si(OC_2H_5)_2$
APMDMOS	(3-acryloxypropyl)methydimethoxysilane	$CH_2{=}CHCOO(CH_2)_3(CH_3)Si(OCH_3)_2$
APTES (APTS, APTEOS, APrTEOS)	3-aminopropyltriethoxysilane	$H_2N(CH_2)_3Si(OC_2H_5)_3$
APTMS (APTMOS, APrTMOS)	3-aminopropyltrimethoxysilane	$H_2N(CH_2)_3Si(OCH_3)_3$
APTMS (APTMOS)	(3-acryloxypropyl)trimethoxysilane	$CH_2{=}CHCOO(CH_2)_3Si(OCH_3)_3$
APTMS (APTMOS)	aminophenyltrimethoxysilane	$H_2NPhSi(OCH_3)_3$
TESPT	bis(triethoxysilylpropyl)tetrasulfane	$(C_2H_5O)_3Si(CH_2)_3S_4(CH_2)_3Si(OC_2H_5)_3$
DDS	dimethyldichlorosilane	$(CH_3)_2SiCl_2$
GPS (GPTS, GOTMS, GPTMOS, KH560)	3-glycidoxypropyltrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane	$CH_2(O)CHCH_2O(CH_2)_3Si(OCH_3)_3$
ICPTES	3-isocyanatopropyltriethoxysilane	$OCN(CH_2)_3Si(OC_2H_5)_3$
MMS	methacryloxymethyltriethoxysilane	$CH_2{=}C(CH_3)COOCH_2Si(OC_2H_5)_3$
MPS (MPTMS, MPTS, MAMSE, MATMS, MSMA, TPM, MEMO, KH570)	methacrylic acid 3-(trimethoxysilyl) propyl ester, 3-(trimethoxysilyl)propyl methacrylate, 3-methacryloxypropyltrimethoxysilane	$CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
MPTES	methacryloxypropyltriethoxysilane	$CH_2{=}C(CH_3)COO(CH_2)_3Si(OC_2H_5)_3$
MPTS	mercaptopropyl triethoxysilane	$SH(CH_2)_3Si(OC_2H_5)_3$
MTES	methyltriethoxysilane	$CH_3Si(OC_2H_5)_3$
PTMS	phenyltrimethoxysilane	$PhSi(OCH_3)_3$
VTES	vinyltriethoxysilane	$CH_2{=}CHSi(OC_2H_5)_3$
VTS	vinyltrimethoxysilane	$CH_2{=}CHSi(OCH_3)_3$

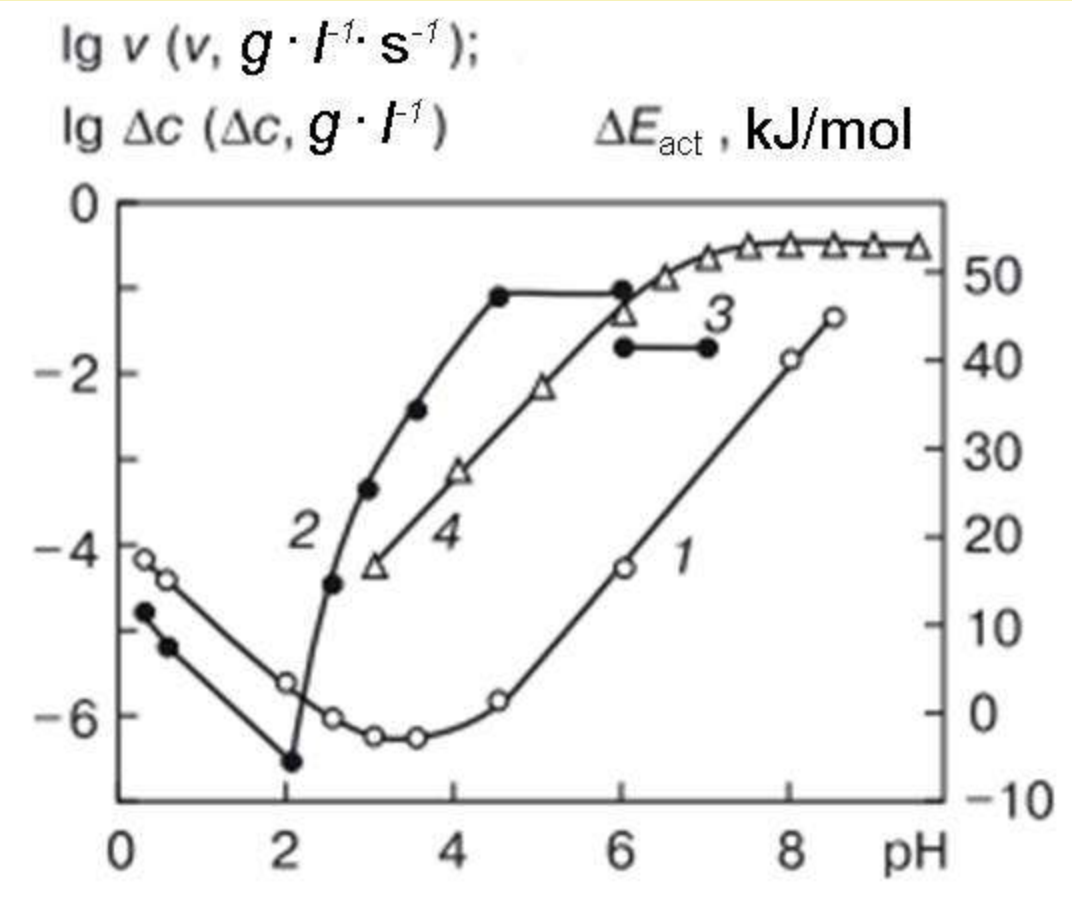
Chem. Rev. – 2008. – V.108. – P.3893–3957

The Effect of pH on the Sol-Gel Process



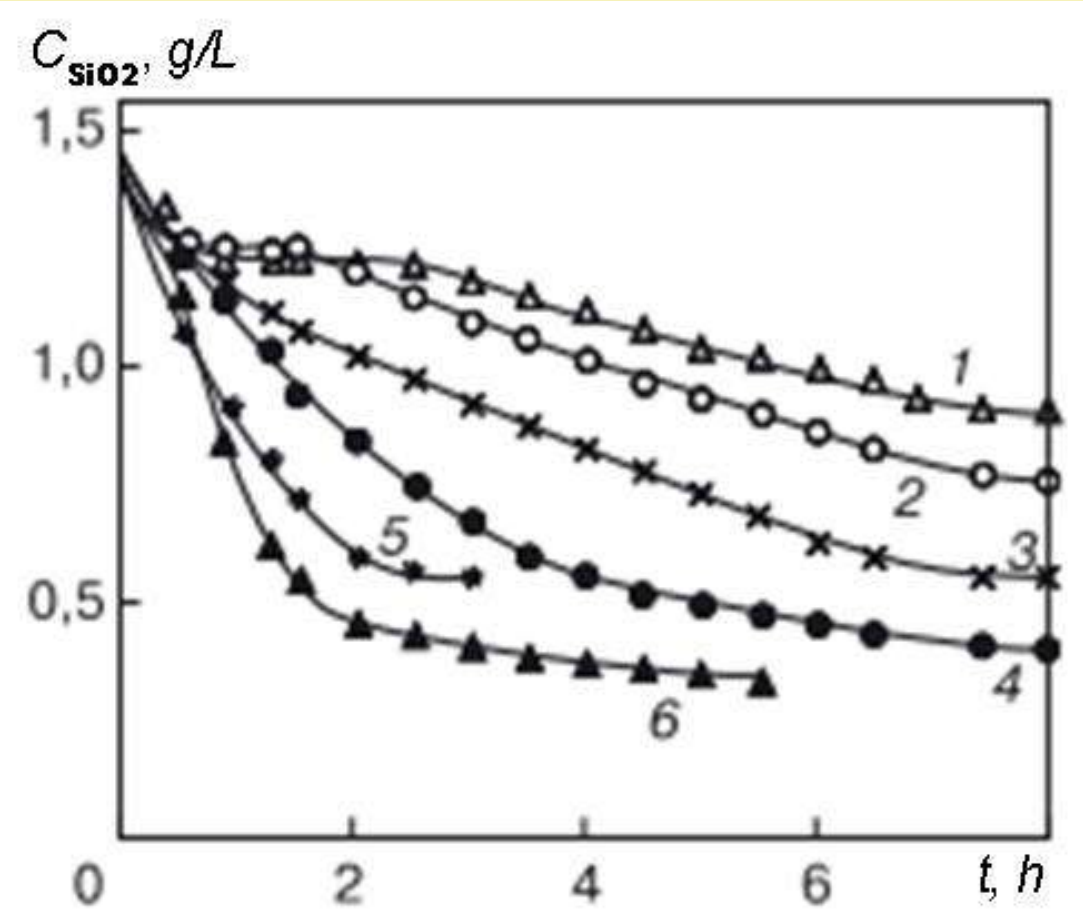
Mater. Horiz. - 2016 - V.3. - P.91-112

Kinetics of Polycondensation



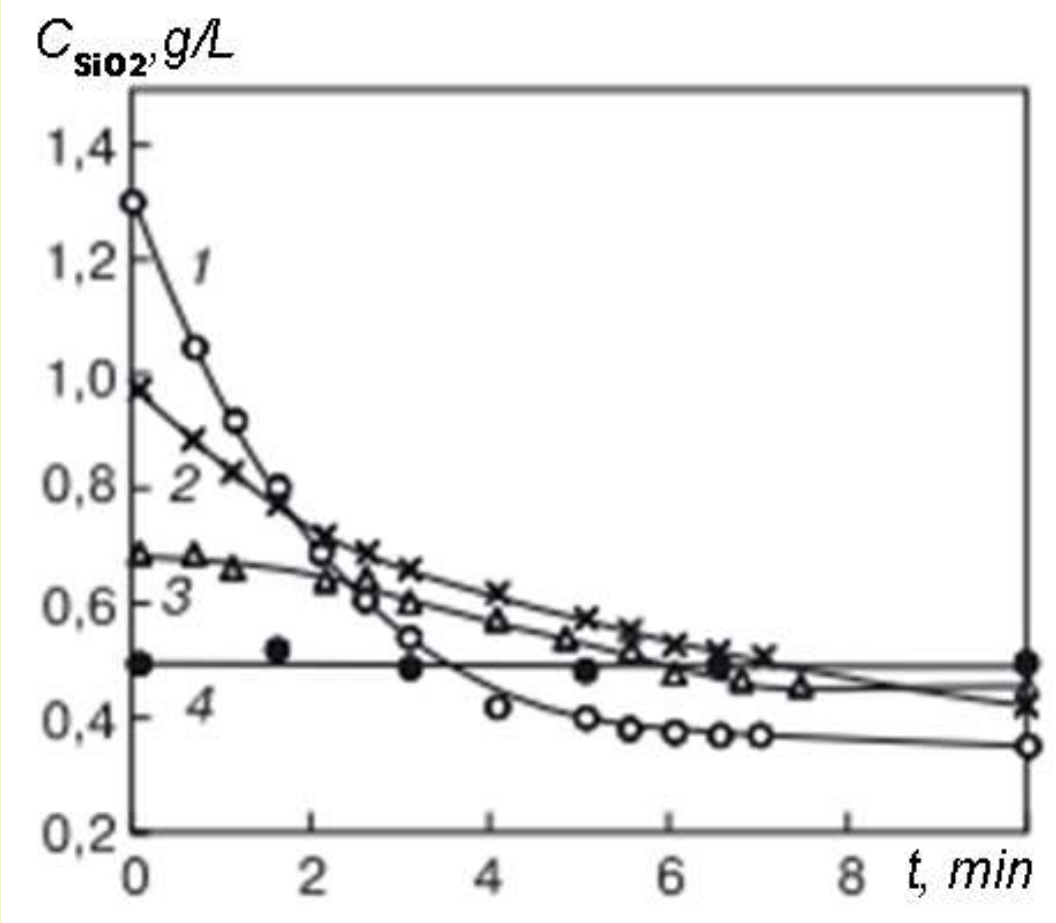
Influence of pH on various parameters of polycondensation process (c_{SiO2} = 1.45 g/l; 293 K): reaction rate **ν** (1), activation energy ΔE (2 – without stirring, 3 – under stirring and buffer conditions); the difference in the "active" (thermodynamic) concentration of the monomer **Δc** in the volume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

Influence of Temperature on Sol-Gel Process



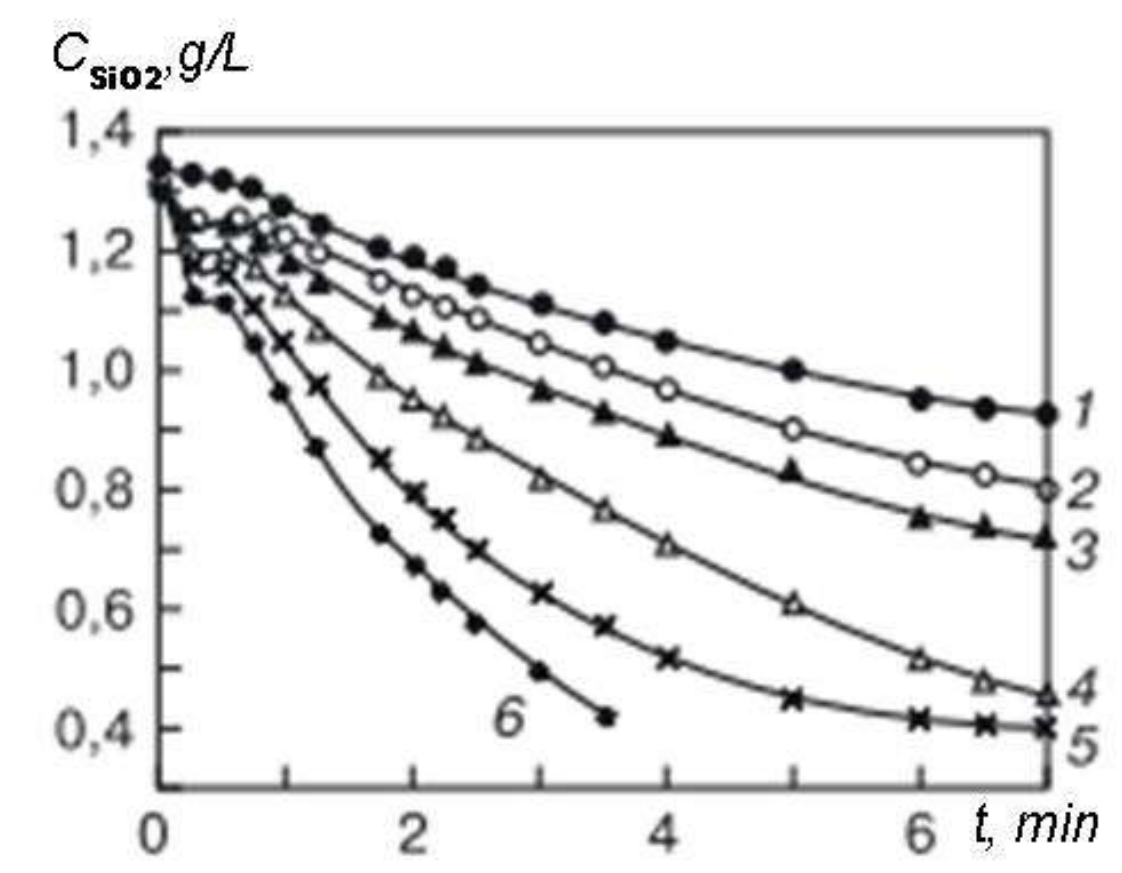
Influence of temperature on the kinetics of changes in the concentration of silicic acid:
1 – 20°C; 2 – 30°C; 3 – 40°C; 4 – 60°C; 5 – 80°C; 6 – 90°C
(c_{SiO2}=1,45 g/L; $pH_{initial}$ = 4,75)

Influence of Monomer Concentration on Sol-Gel Process



Kinetics of change of concentration of monomer in solutions of silicic acid with different initial concentration, g/L:
1 – 1,5; 2 – 1,0; 3 – 0,7; 4 – 0,5
($pH_{initial}$ = 8,2; 293 K)

Effect of Presence of Salt on Sol-Gel Process

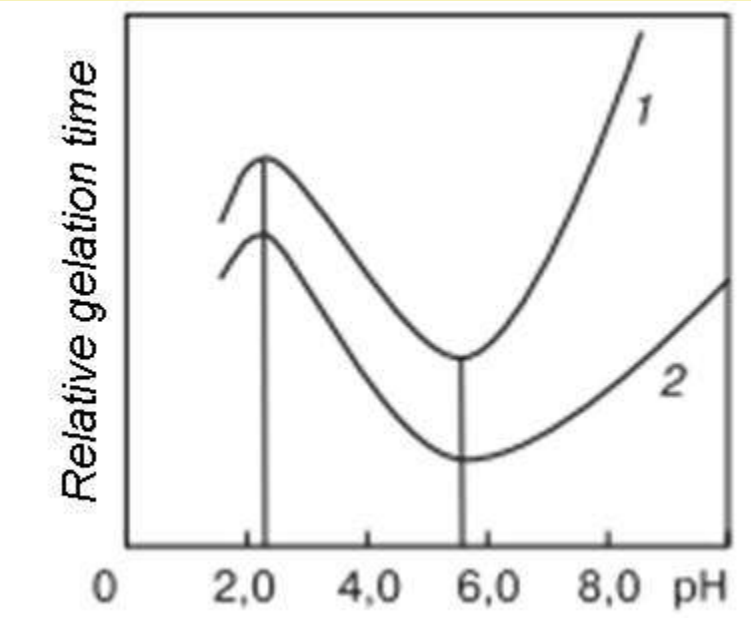


Kinetics of change of concentration of silicic acid at initial pH of 4.8 and concentration NaCl, M:

1 – *0*; 2 – *0,05*; 3 – *0,2*; 4 – *0,6*; 5 – *1,0*; 6 – *1,5*

(c_{SiO2}=*1,45* g/L; *303* K)

Influence of pH and Presence of Salt on Gelation



Influence of pH on the relative gelation time for silica sols :
1 – *in the absence of electrolytes*; 2 – *in the presence of electrolytes*

Speed of gelation

pH ≈ 2,0

$$CH_3COOH > H_3PO_4 > HCl > HNO_3 > H_2SO_4$$

pH ≈ 3,0-5,0

$$HCl > H_2SO_4 > H_3BO_3 + HCl > H_3PO_4$$

pH ≥ 6,0

$$HCl > H_2SO_4 > H_3PO_4 > H_3BO_3 + HCl$$

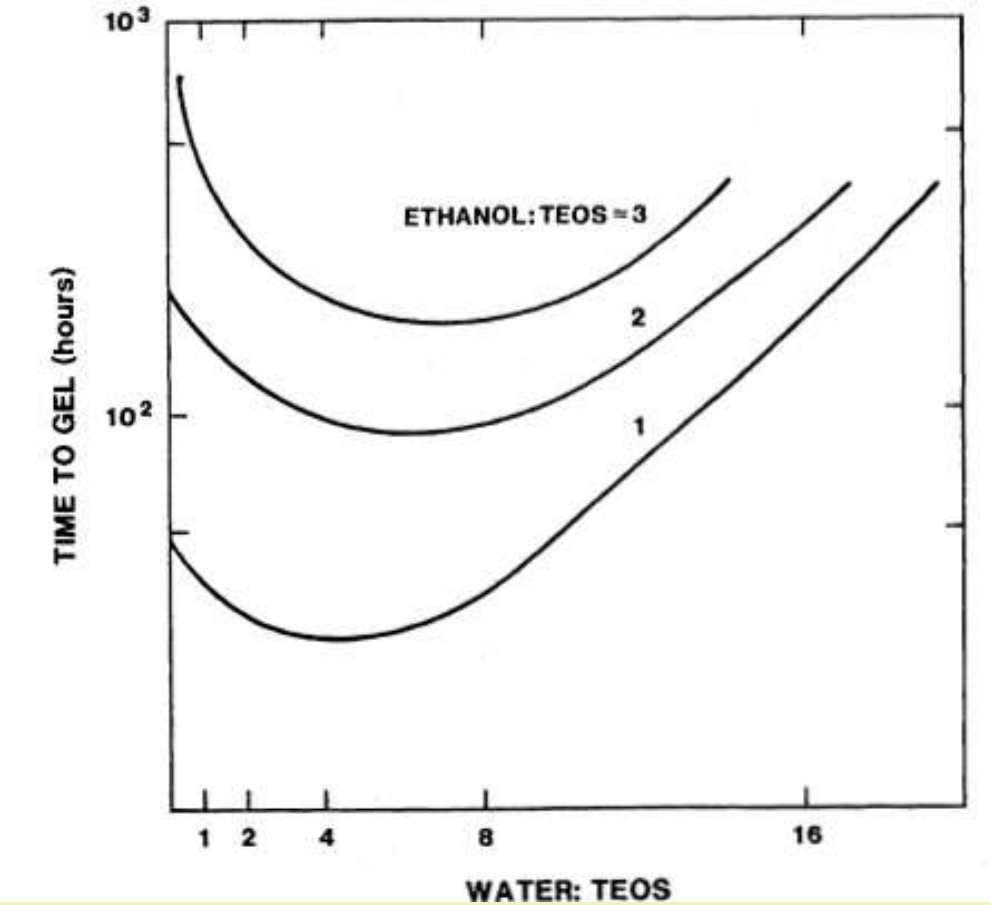
Influence of Amount of Water on Sol-gel Process and Structure of Condensation Products

Acidic catalysis

H_2O : Si

Branching

Basic catalysis



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

Influence of Solvent on Sol-Gel Process

pH > 7 → OH^-

pH < 7 → H^+

Aprotic solvents are not capable of hydrogen bonding and therefore enhance nucleophilicity of OH^-

Protic solvents form hydrogen bonds and therefore enhance H^+ electrophilicity

Physical Properties of Typical Solvents.

	MW	bp	ρ	n_D	ε	η	μ
Protic							
water H_2O	18.01	100.00	1.000	1.333	78.5	10.1	1.84
methanol CH_3OH	32.04	64.5	0.791	1.329	32.6	5.4	1.70
ethanol C_2H_5OH	46.07	78.3	0.785	1.361	24.3	10.8	1.69
2-ethoxyethanol $C_4H_{10}O_2$	90.12	135	0.93	1.408	—	—	2.08
formamide CH_3ON	45.04	193	1.129	1.448	110	33.0	3.7
Aprotic							
dimethylformamide C_3H_7NO	73.10	152	0.945	1.430	36.7	7.96	3.86
dioxane 1,4 $C_4H_8O_2$	88.12	102	1.034	1.422	2.21	10.87	0
tetrahydrofuran C_4H_8O	72.12	66	0.889	1.405	7.3	—	1.63

bp: °C. n_D: 20°. η: millipoise.
ρ: g/cm³ at 20°C. Dielectric constant, ε: at 25°C. Dipole moment, μ: debyes.

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

Reduce the activity of catalysts

Promote transesterification

Increase the viscosity of the system that reduces the rate of hydrolysis

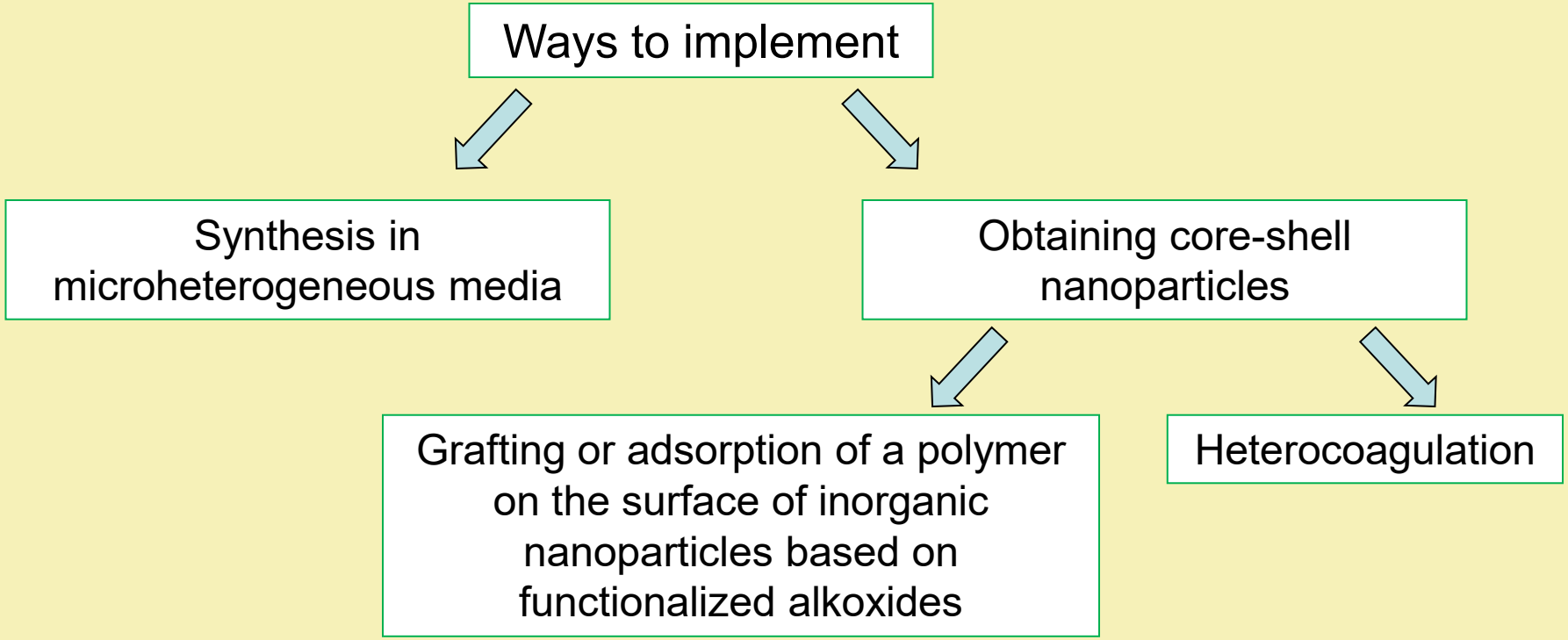
Polarity of solvent

Intensity of interaction between adjacent sol particles

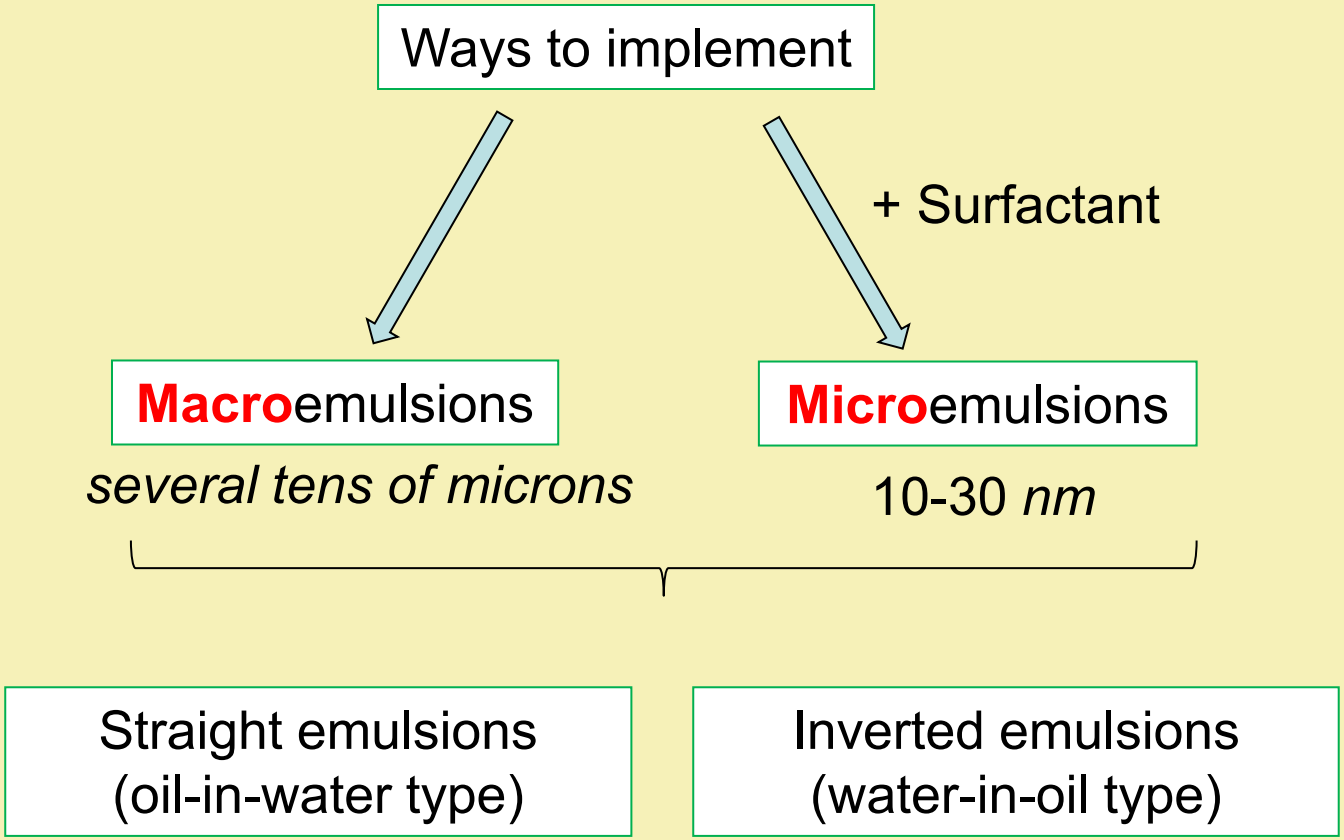
Sol-Gel Synthesis in Heterogeneous Media

Advantages :

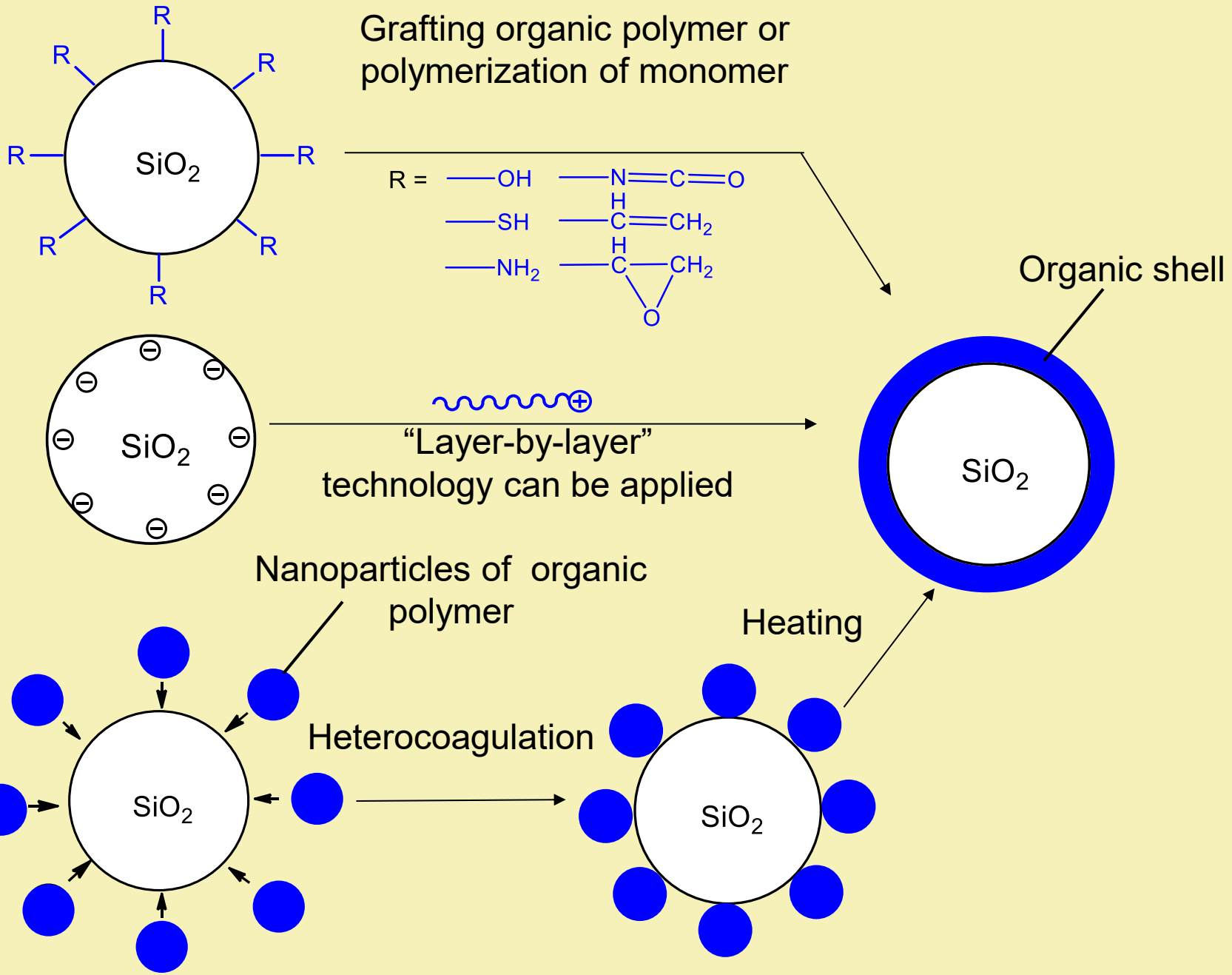
- exact variation in size, morphology, and shape of inorganic nanoparticles;
- producing nanoparticles of the type "inorganic core - organic shell" or "polymer core - inorganic shell";
- obtaining mesoporous materials with controlled size and pore shape



Sol-Gel Synthesis in Microheterogenic Media

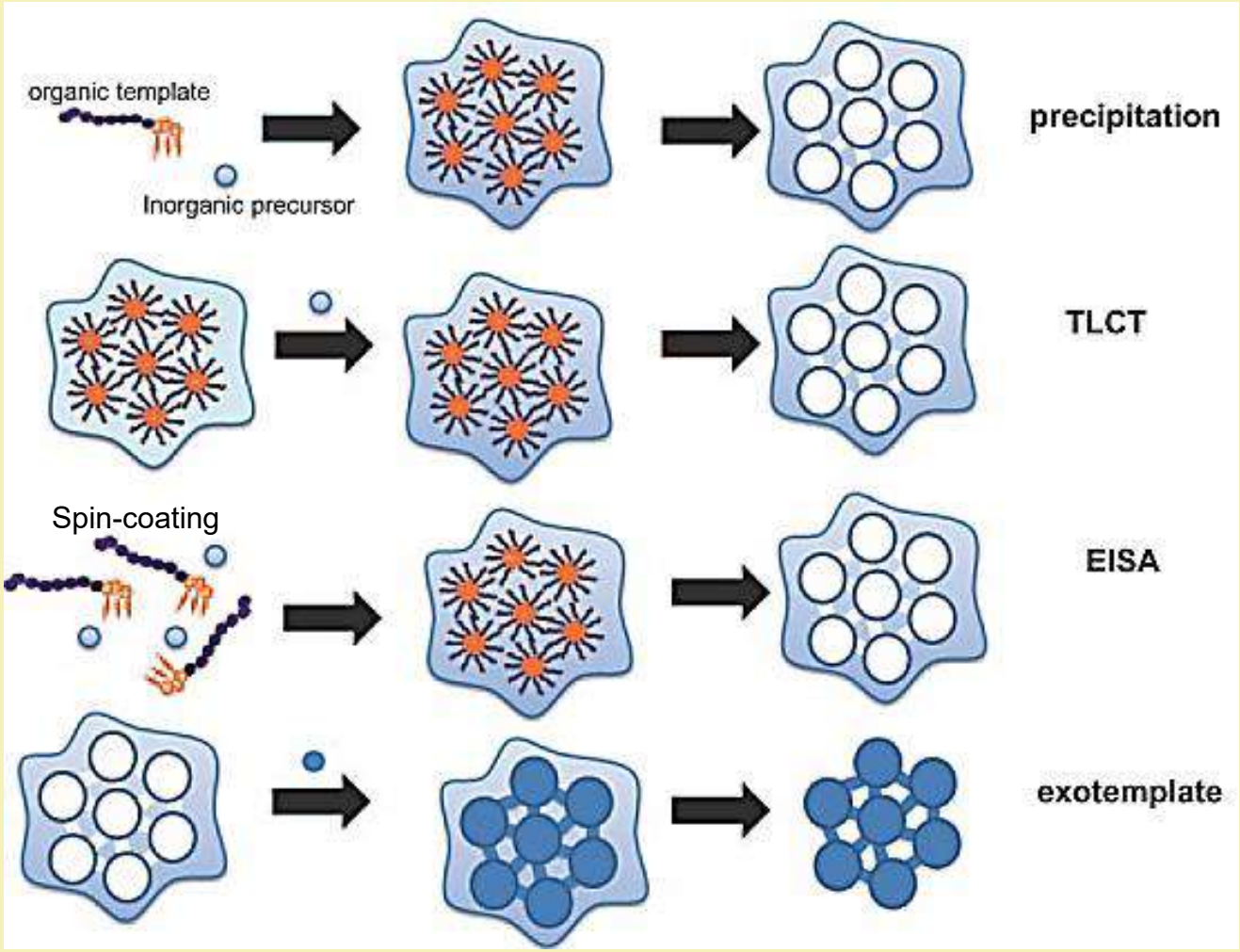


Obtaining Core-shell Nanoparticles



Template Approach in Sol-gel Synthesis

This approach allows to produce a porous hybrid materials with adjustable shape and size (macro-, nano- and mesopores) of pores

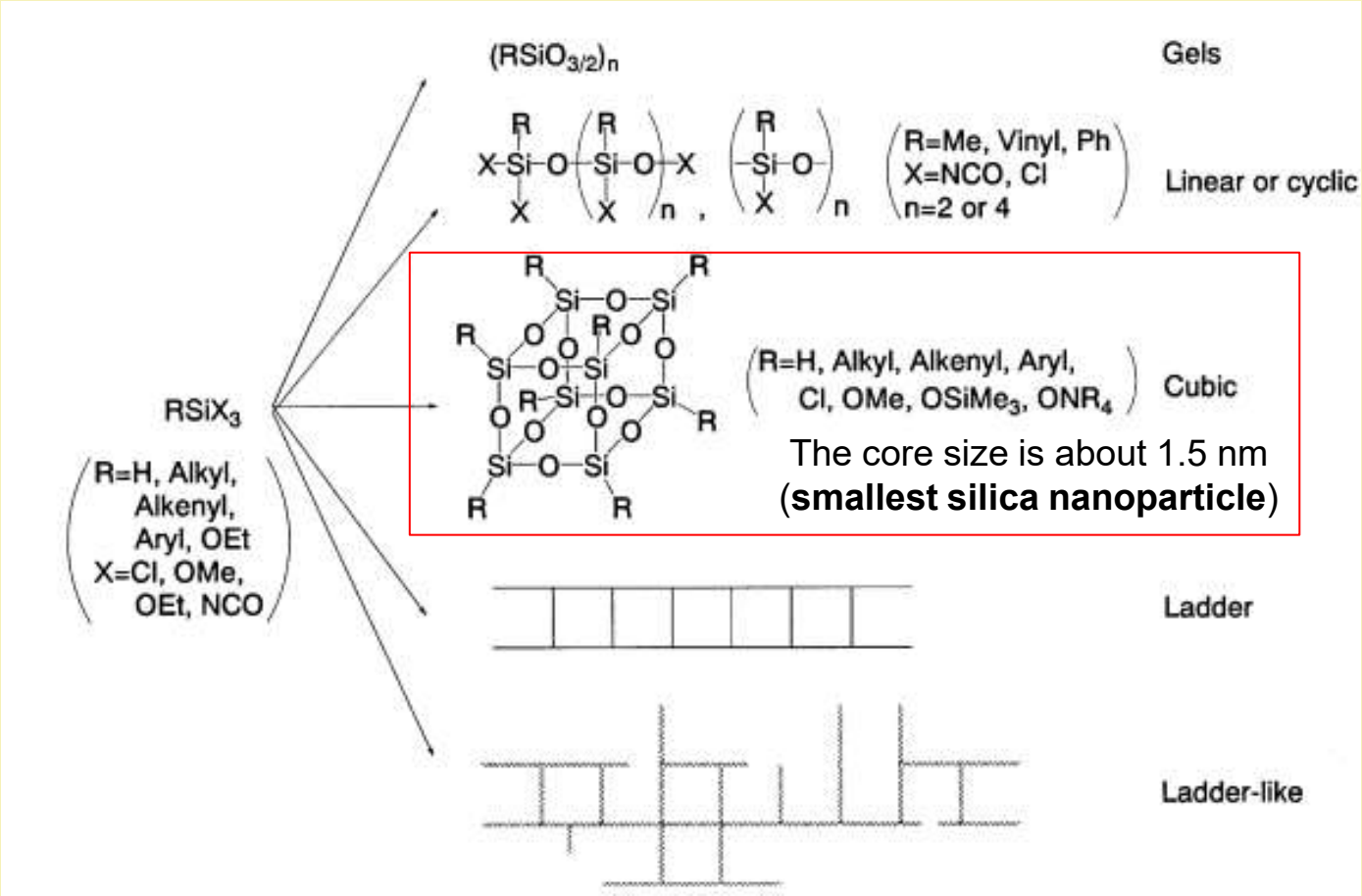


Surfactants and salts are used as templates. Removal of templates is carried out by extraction or heat treatment (annealing)

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.

Synthetic pathways leading to the generation of mesoporous inorganic materials: The direct precipitation, the true liquid crystal templating (TLCT), the evaporation-induced self-assembly (EISA), and exotemplating route

Synthesis of Polyhedral Oligomeric Silesquioxanes (POSS)



Formation of POSS is facilitated by excess water and use of alkaline catalyst

R =

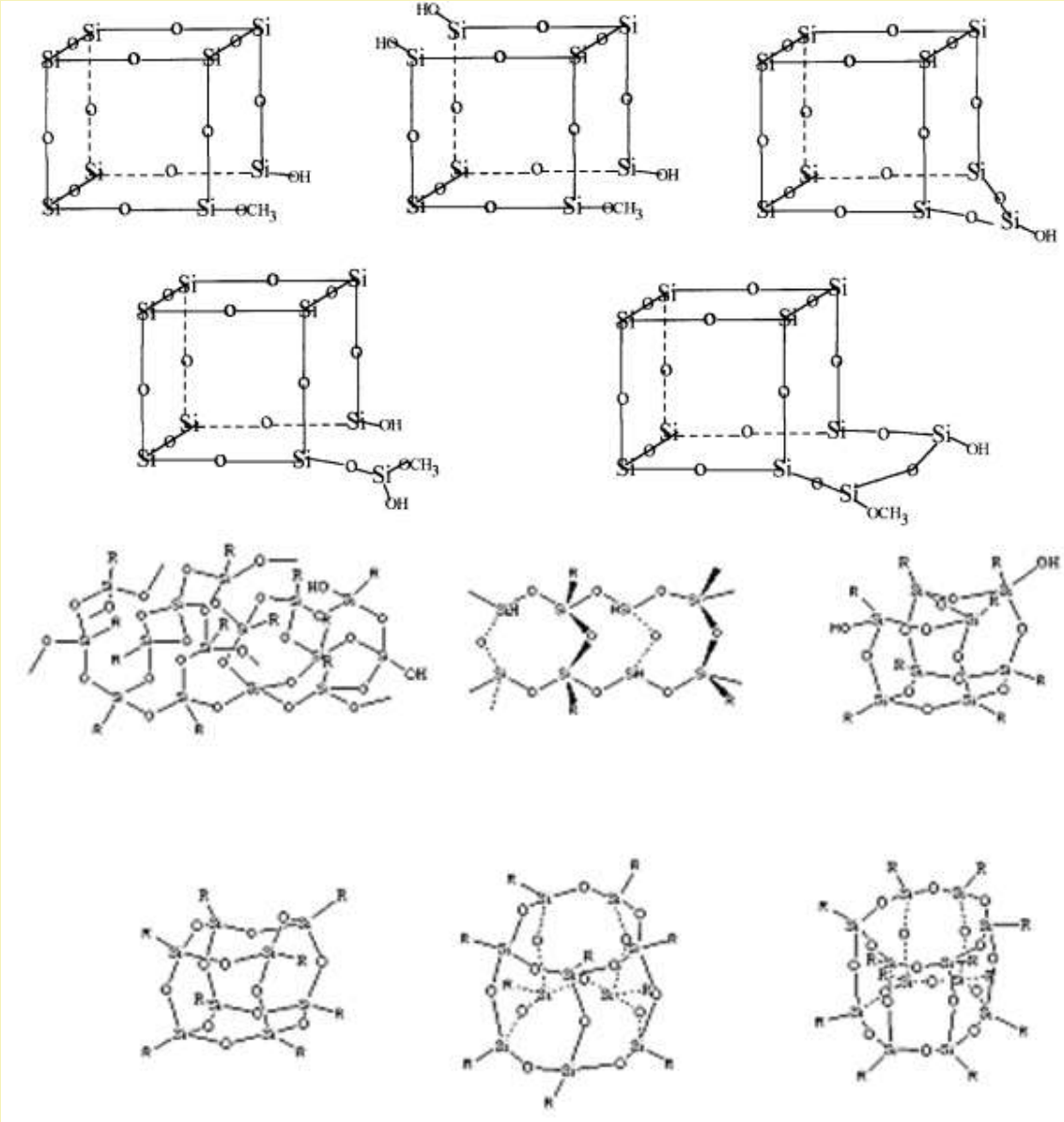
- **organic non-reactive substituent for improved solubility in solvents or compatibilization with a nanocomposite polymer matrix;**

- **functional substituent with certain chemical (reactive, including polymerizable) and physical (ionic, optically active groups, substituents with magnetic properties, etc.) function**

Prog. Polym. Sci. – 2004. – V.29. – P.149–182.

Synthesis of Polyhedral Oligomeric Silesquioxanes (POSS)

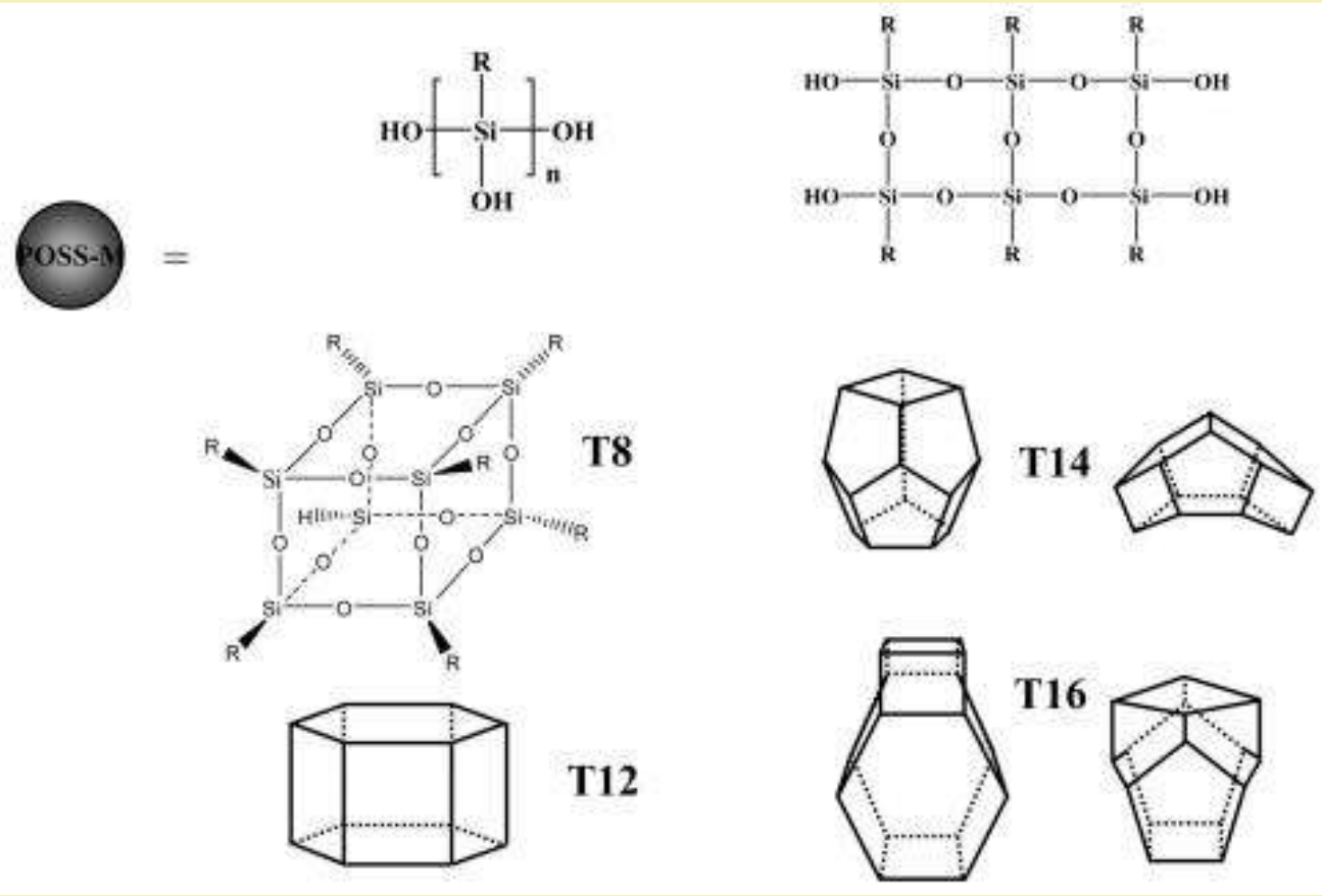
During synthesis of POSS the partially and completely condensed structures of different types are also formed. They are named “POSS-M” (POSS-mixture).



Macromolecules. – 2001. – Vol. 34. - P. 6904-6914

J. Macromol. Sci. Polymer Rev. – 2009. – V.49. – P. 25-63

Synthesis of Polyhedral Oligomeric Silesquioxanes (POSS)



Langmuir. – 2009. – Vol. 25. - P. 1196-1209

Functionalized Organic-Inorganic Sol-Gel Materials

Type I

Sol of hybrid nanoparticles

+

Functional additive:

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

(electrical, magnetic, optical properties)

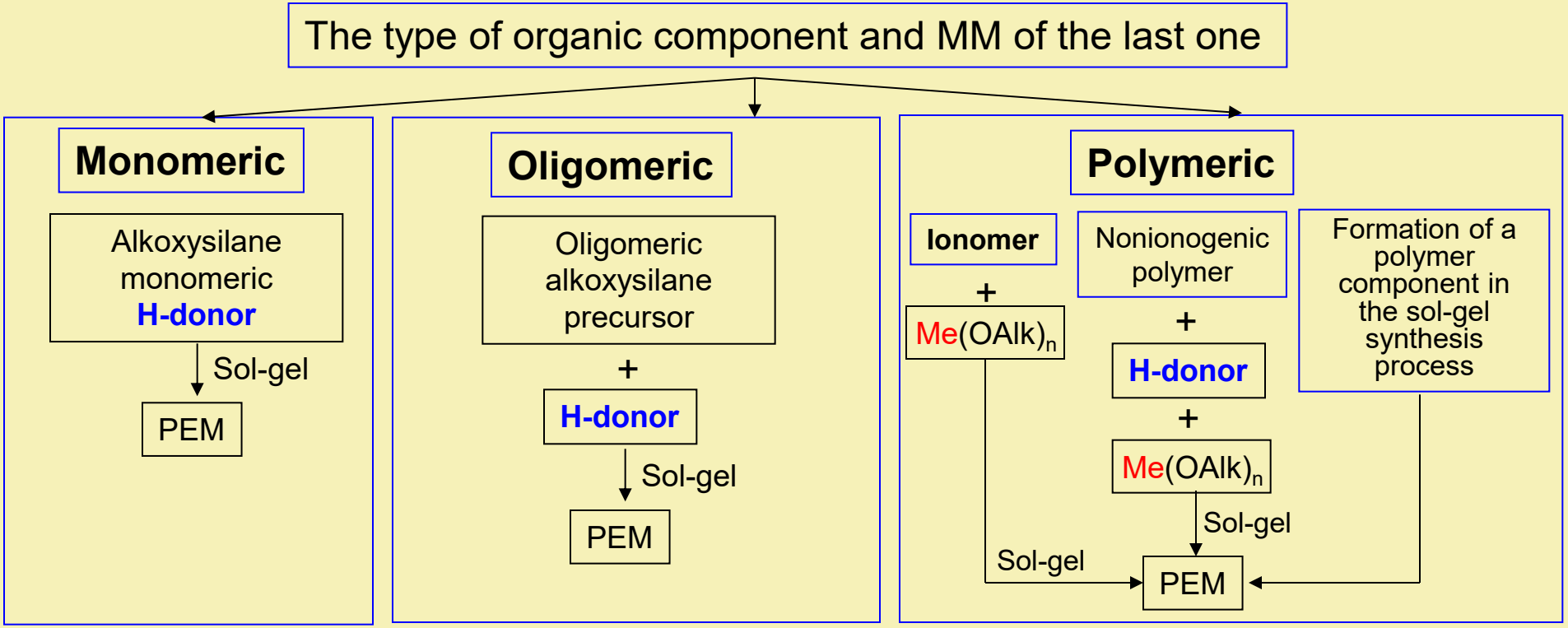
Type II

Sol hybrid nanoparticles, the organic component of which contains a functional group

Gel

Finished product

Organic-Inorganic Proton-Exchange Membranes (PEMs) Obtained by Sol-Gel Method

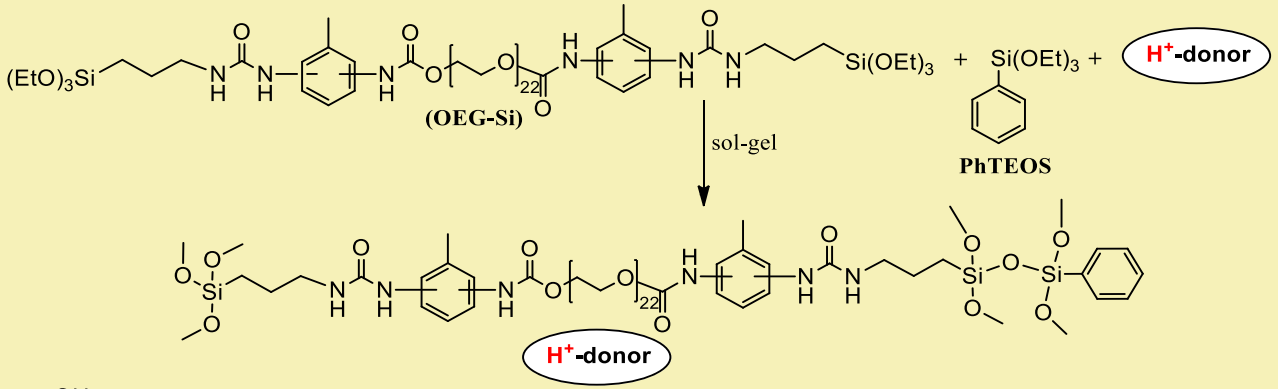


An approach to creation of hybrid organic-inorganic PEM by sol-gel method with an anhydrous conductivity mechanism was proposed. It is based on the synthesis and use in the production of PEM a sulfonic acid proton-donors of monomeric and oligomeric type of different chemical structure, capable and incapable of sol-gel transformation, and filmforming oligoether segmented dialkoxysilyl precursors capable of self-organization in the sol-gel synthesis due to urethane and urea fragments in their composition with formation of ordered proton-conducting channels.

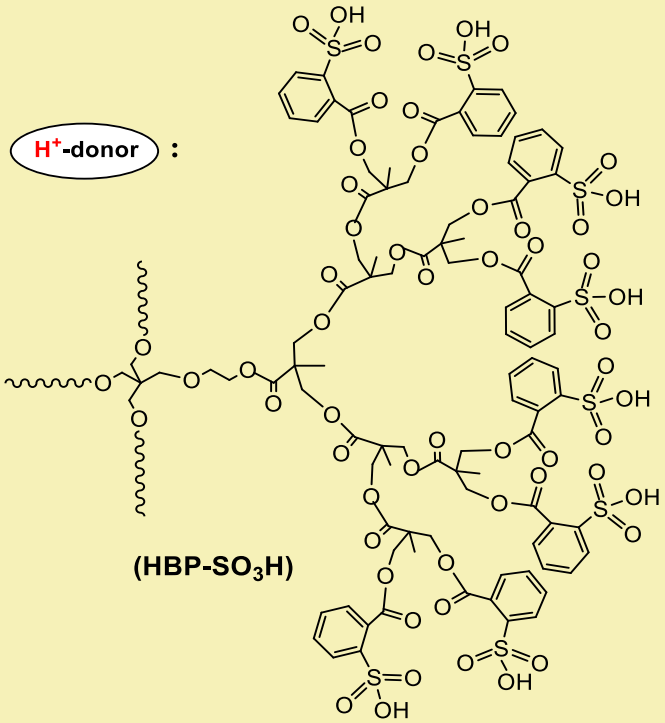
Basic Physicochemical Properties of Hybrid PEM

PEM	Oligomeric precursor		Monomeric proton-donor	T_g, °C	SEC, meqiv/g	σ_{dc}, S/cm (100°C)
	Name	%wt.	Name			
OEG-Si/M-1(20)	OEG-Si	80	M-1	68	0,39	$3{,}53\cdot10^{-6}$
OEG-Si/M-1(40)	OEG-Si	60	M-1	69	0,57	$1{,}05\cdot10^{-5}$
OEG-Si/M-2(20)	OEG-Si	80	M-2	80	0,57	$4{,}17\cdot10^{-6}$
OEG-Si/M-2(40)	OEG-Si	60	M-2	93	0,76	$2{,}04\cdot10^{-6}$
OEG-Si/M-3(20)	OEG-Si	80	M-3	86	0,31	$5{,}37\cdot10^{-8}$
OTMG-Si/M-1(20)	OTMG-Si	80	M-1	-67	0,36	$3{,}71\cdot10^{-9}$
OTMG-Si/M-2(20)	OTMG-Si	80	M-2	-68	0,42	$1{,}0\cdot10^{-9}$
OTMG-Si/M-2(40)	OTMG-Si	60	M-2	-69	0,51	$3{,}0\cdot10^{-10}$
OEGM-Si/M-1(20)	OEGM-Si	80	M-1	-19	0,34	$1{,}10\cdot10^{-6}$
OEGM-Si/M-1(40)	OEGM-Si	60	M-1	-19	0,60	$1{,}17\cdot10^{-7}$

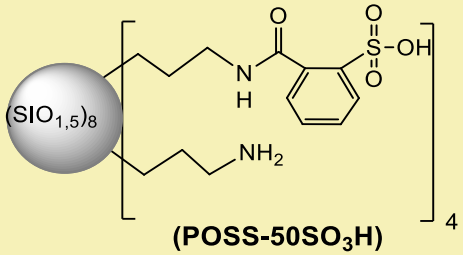
Sensory Proton-Conducting Composites Based On Sulfonate Derivatives of Hyperbranched Polyester Polyol and POSS



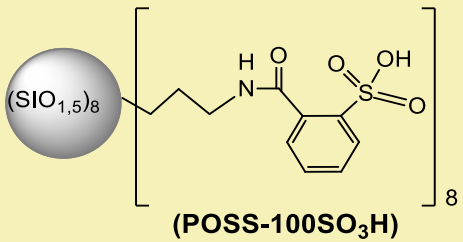
H⁺-donor :



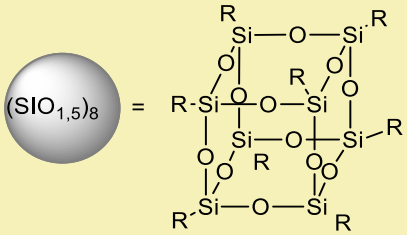
(HBP-SO_3H)



(POSS-50SO_3H)



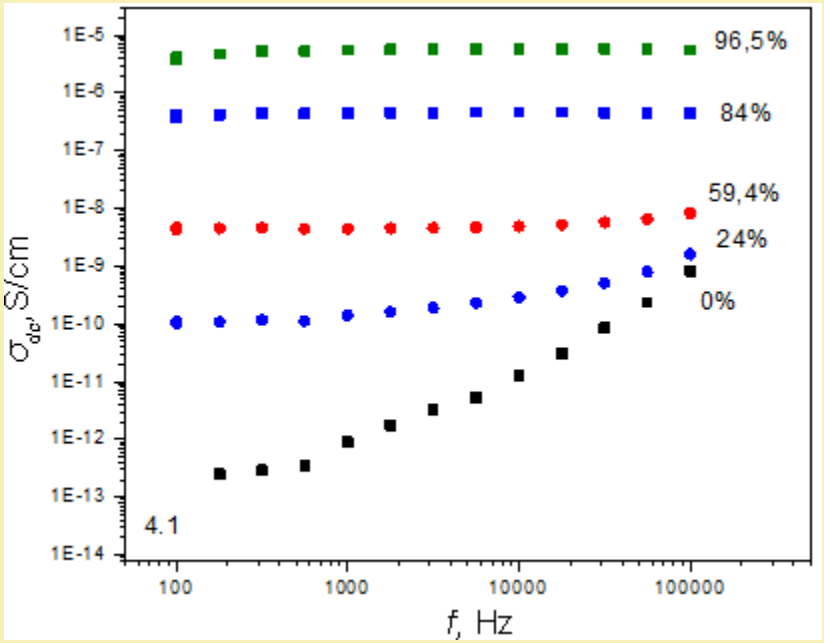
(POSS-100SO_3H)



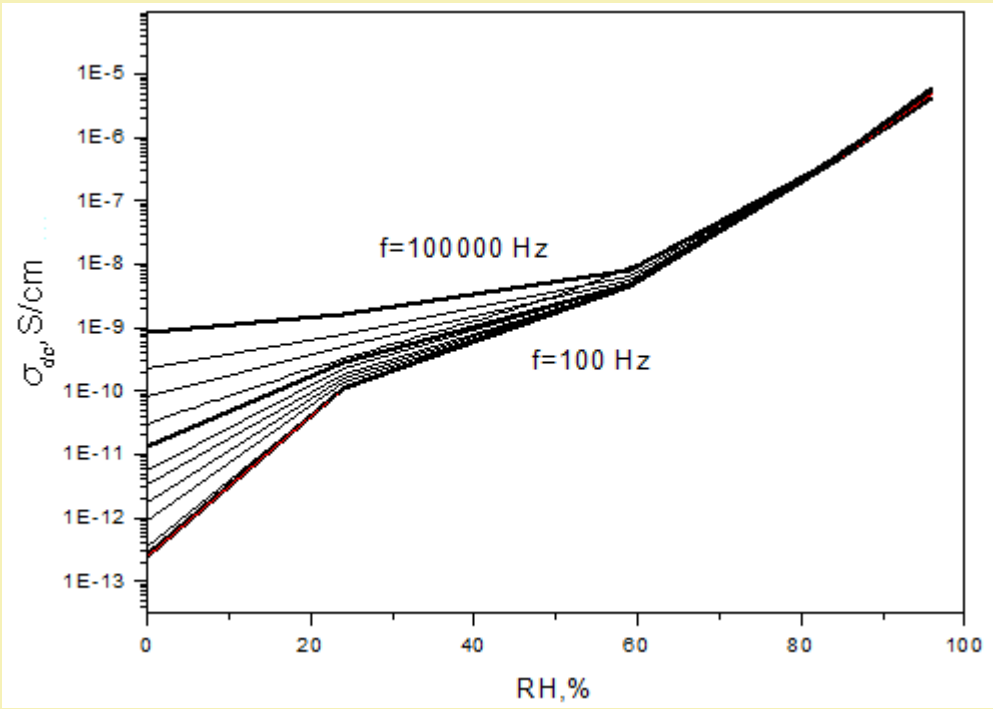
The proton-conducting compositions based on sulfonate derivatives of hyperbranched polyester polyol and octahedral oligosilesquioxane were used as the sensing medium.

Sample	σ_{dc}, S/cm	
	20°C	100°C
OEG-Si-50HBP-SO_3H	$3{,}24\cdot10^{-7}$	$1{,}64\cdot10^{-4}$
OEG-Si-50POSS-50SO_3H	$2{,}15\cdot10^{-8}$	$4{,}03\cdot10^{-5}$
OEG-Si-50POSS-100SO_3H	$1{,}46\cdot10^{-6}$	$3{,}98\cdot10^{-5}$

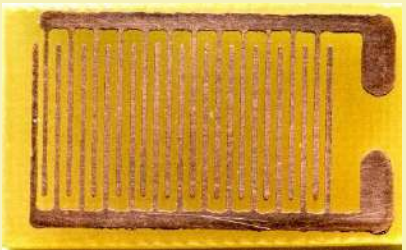
Sensory Characteristics of the Developed Materials



Frequency dependences of ionic conductivity of a resistive sensor at different relative humidity values and 293 K based on the sample **OEG-Si-50POSS-100SO_3H**

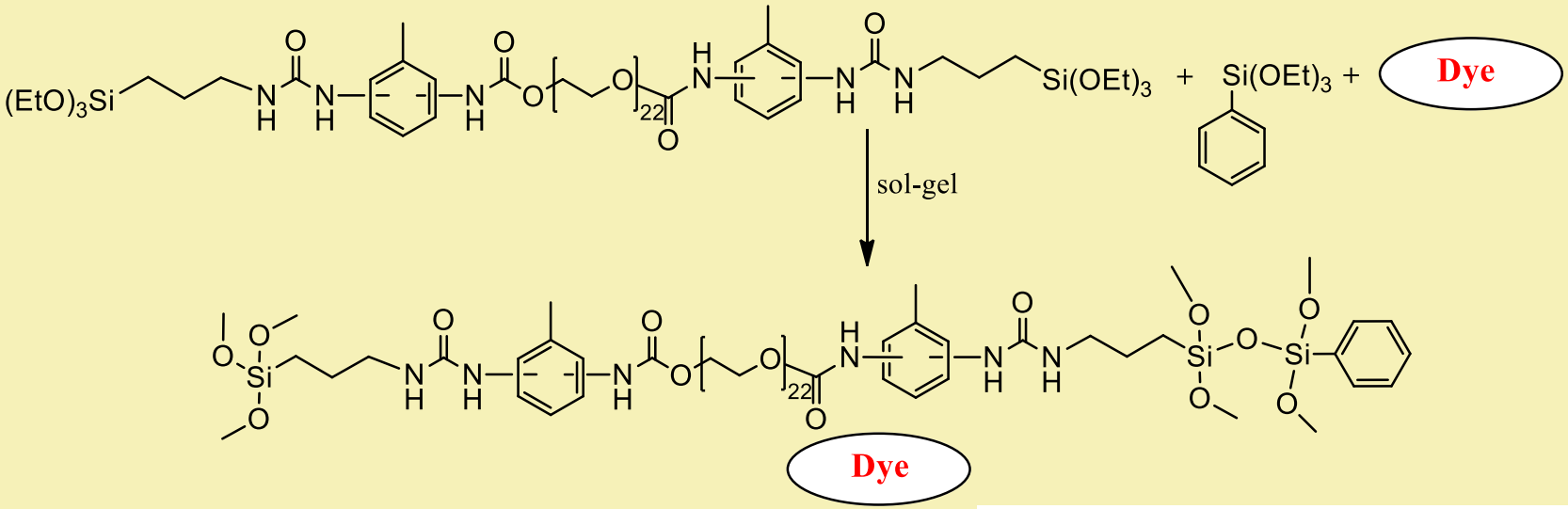


Moisture sensor calibration schedule based on the sample **OEG-Si-50POSS-100SO_3H** (isofrequency dependences of ionic conductivity of the sensor on relative humidity)

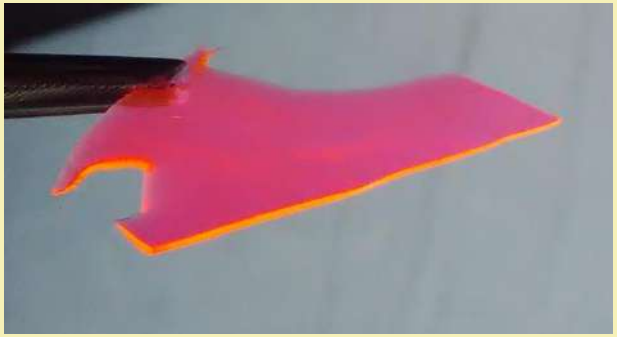


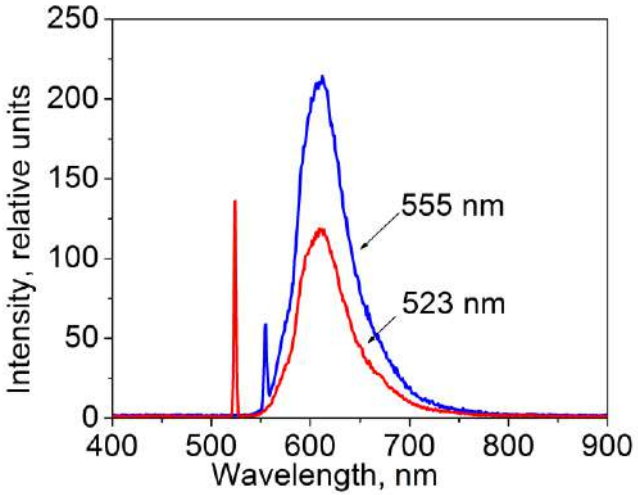
Humidity sensor substrate

Hybrid Organic-Inorganic Optically Active Nanomaterials



Dye - polymethine dye №1П synthesized at the Institute of Organic Chemistry of the NAS of Ukraine





Fluorescence spectrum of the synthesized material

Thanks for your attention!