

**Российская академия наук
Институт синтетических полимерных материалов им. Н.С. Ениколопова**

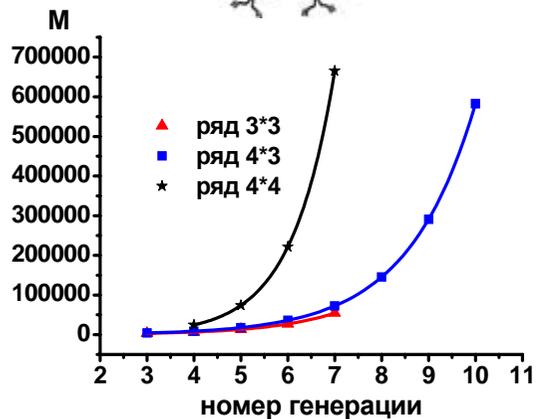
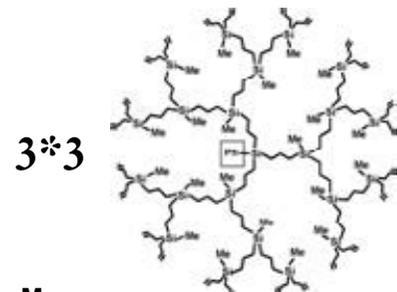
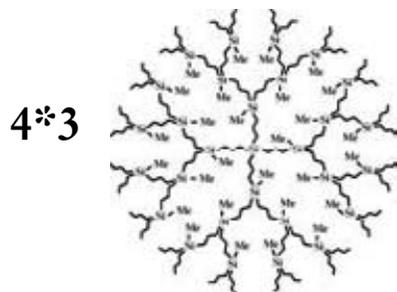
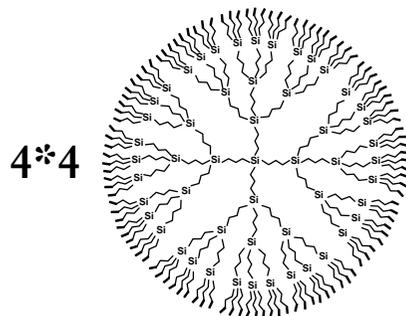
А.М. Музафаров, Н.В.Воронина, И.Б.Мешков, В.В.Казакова, А.Н.Озерин

**"Макромолекулярные нанообъекты, перспективы
использования в полимерных нанокompозитах"**

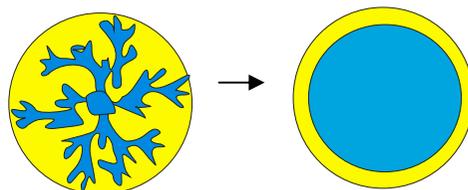


Макромолекулярные нанобъекты

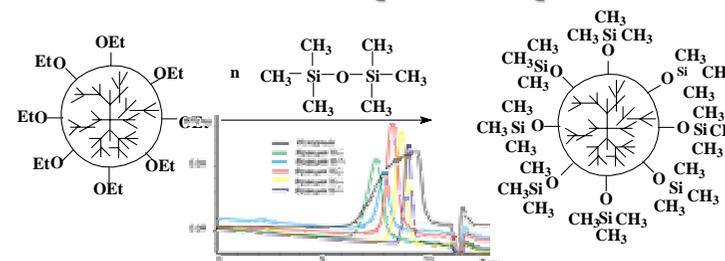
Дендримеры



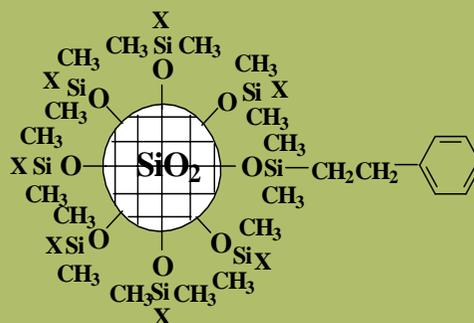
От макромолекулы к частице



Модельные гибридные кремнеземы

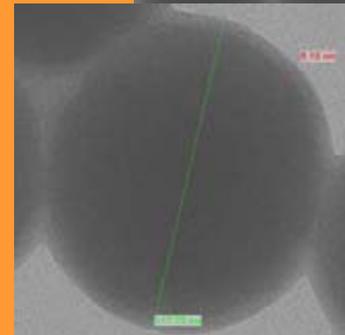
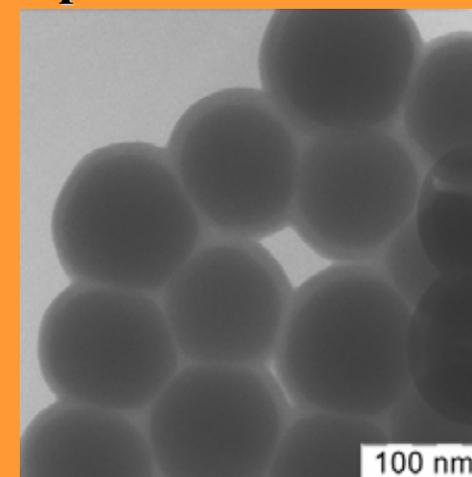


Полимерные нанокompозиты



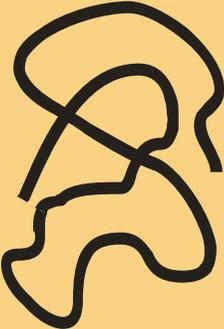
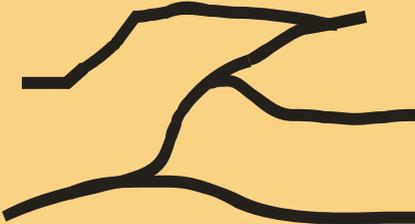
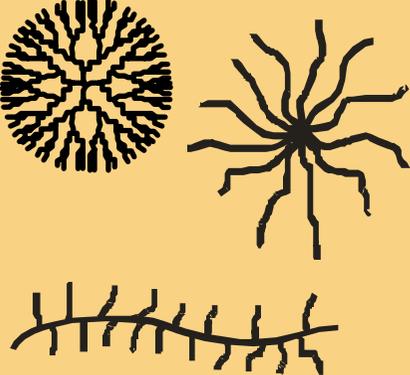
1% 10% 20%

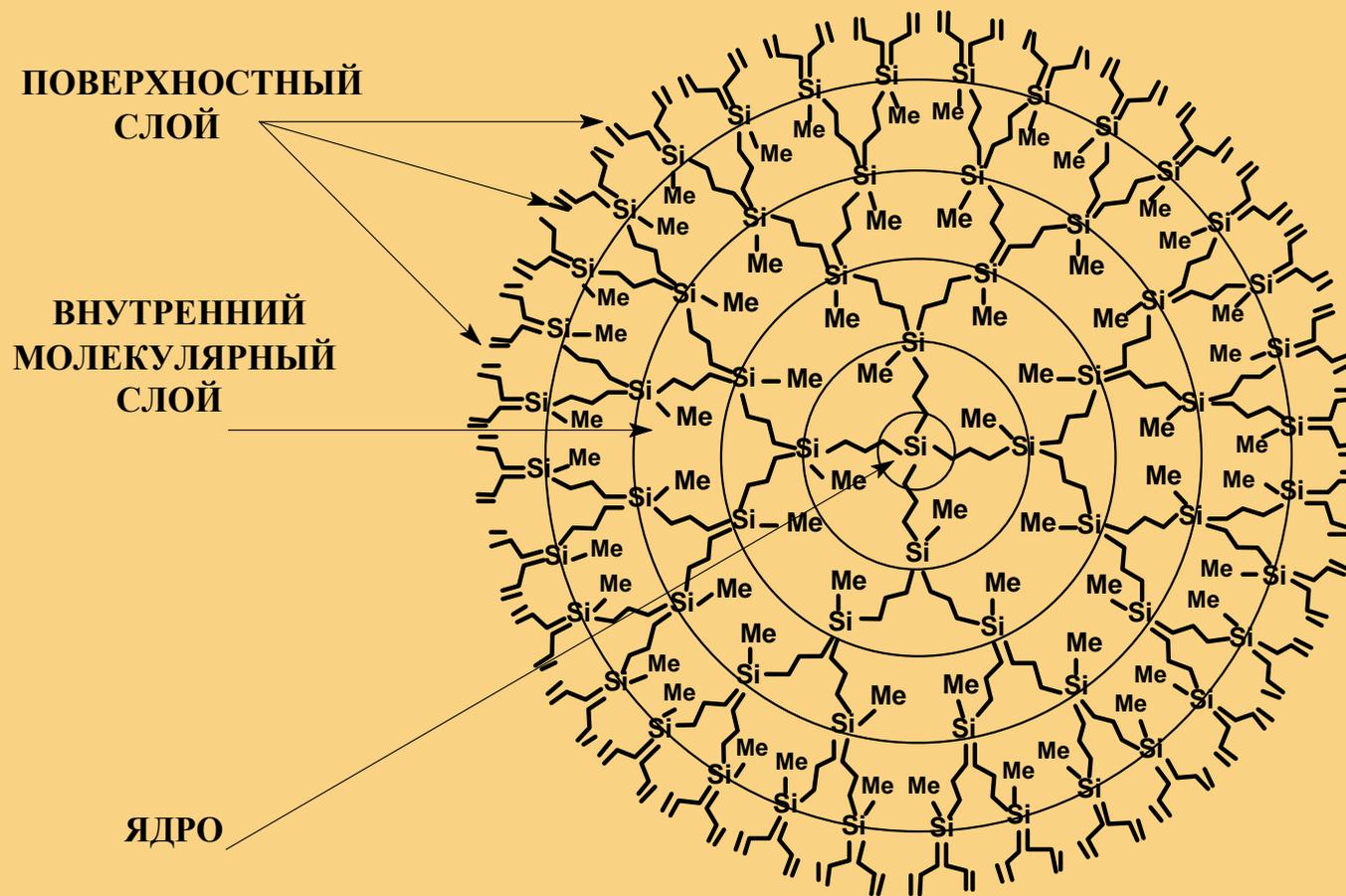
Кремнеземы с функциональным поверхностным слоем





Классификация полимеров по структуре основной цепи

I линейные	II сетчатые	III разветвленные	IV макромолекулы- частицы
			
			<ul style="list-style-type: none">•Дендримеры•Сверхразветвленные полимеры•Молекулярные щетки•Многолучевые звезды•Нано- и микрогели



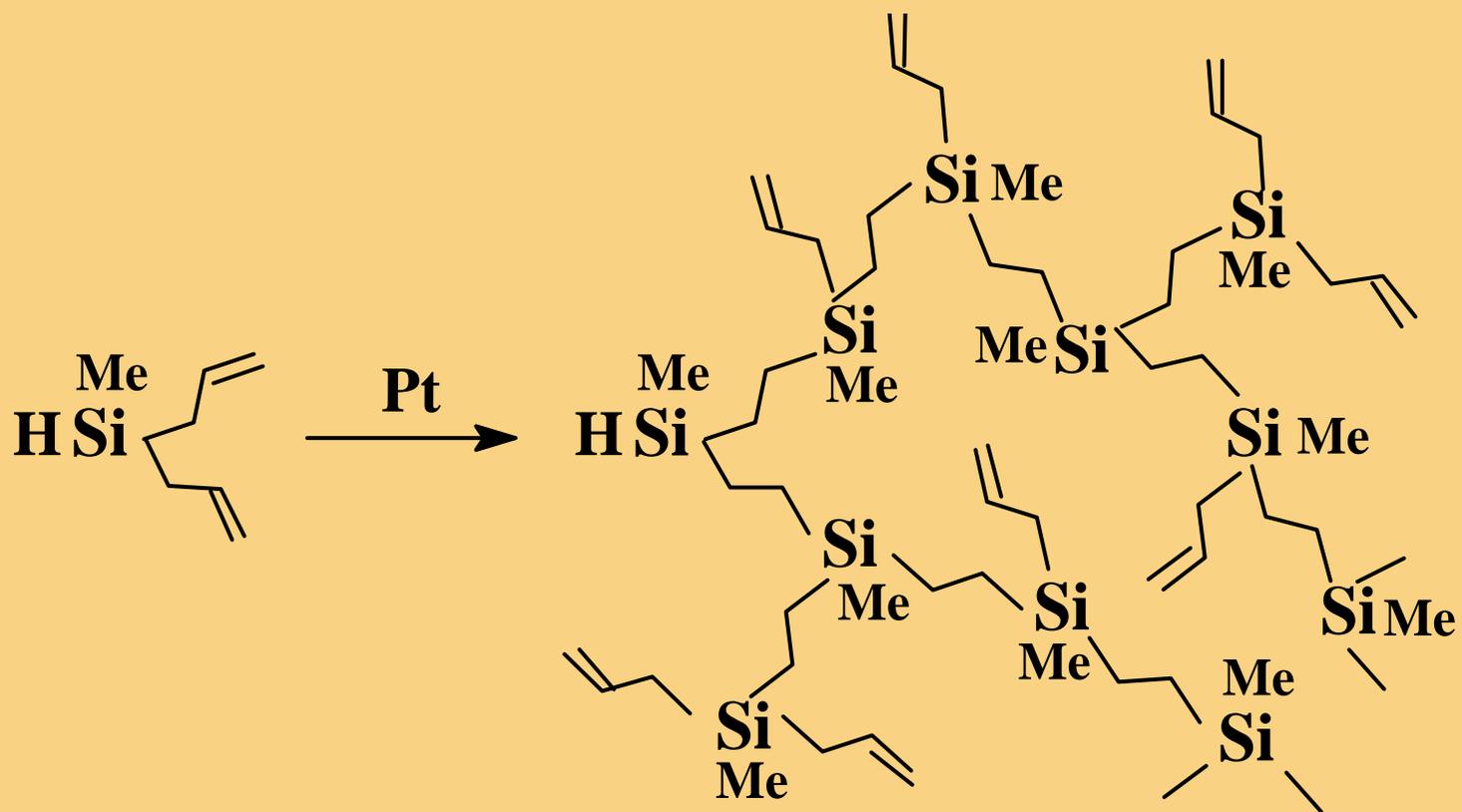
Граничная поверхность:

$$S=4\pi r^2$$

Количество функциональных групп:

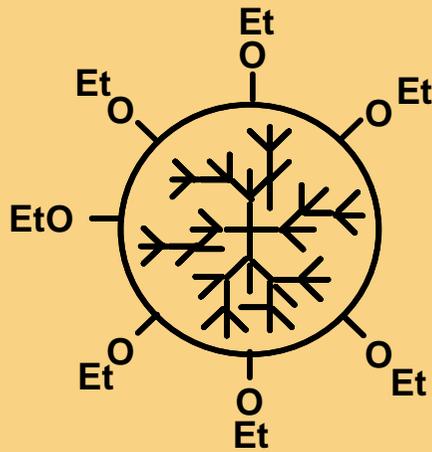
$$Z=N_c * N_b^G,$$

Сверхразветвленные полиаллилкарбосиланы

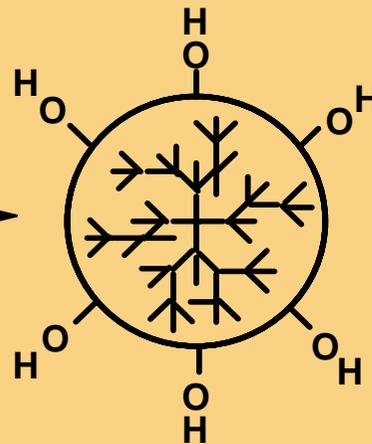
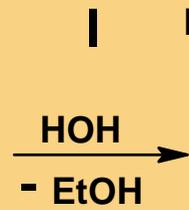


Inorganic dendritic structure

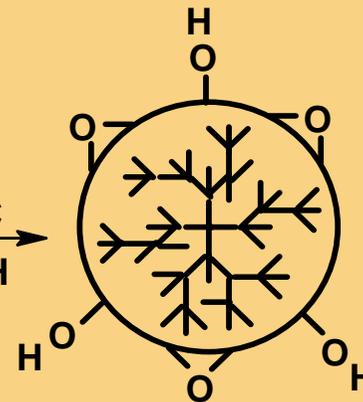
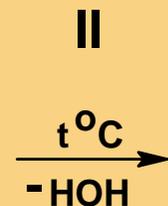
Hydrolysis



Hyperbranched
ethylsilicate



Product of hydrolysis



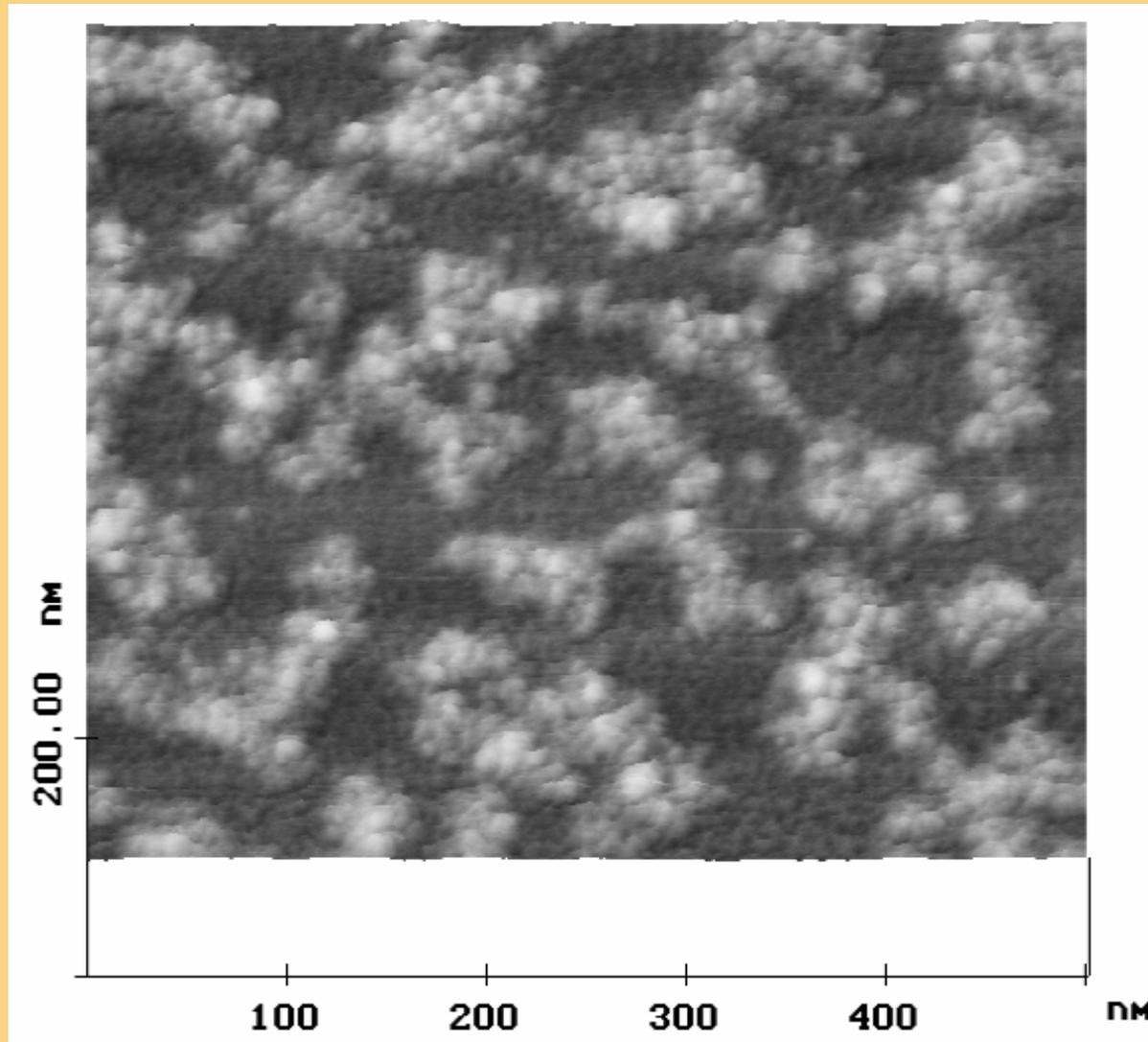
Silica-sol
soluble in water free THF

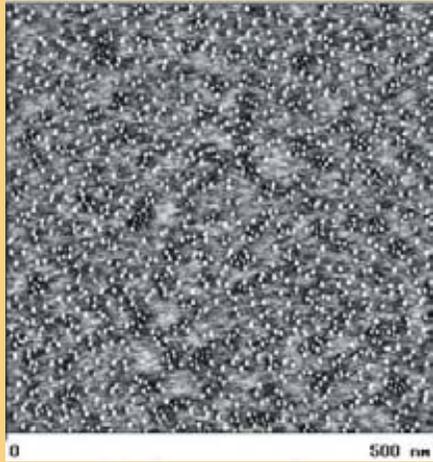


SILICA

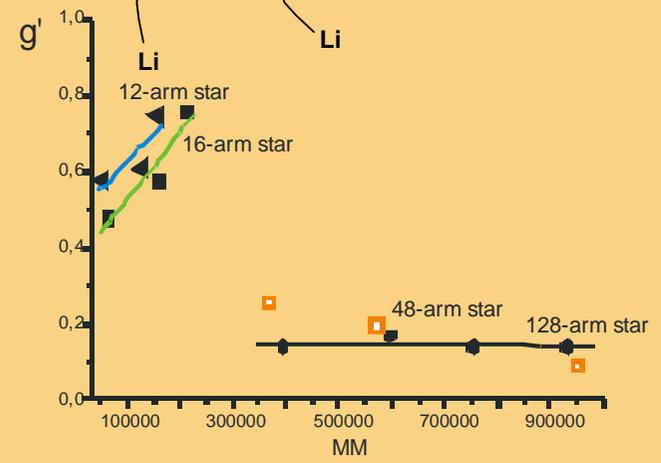
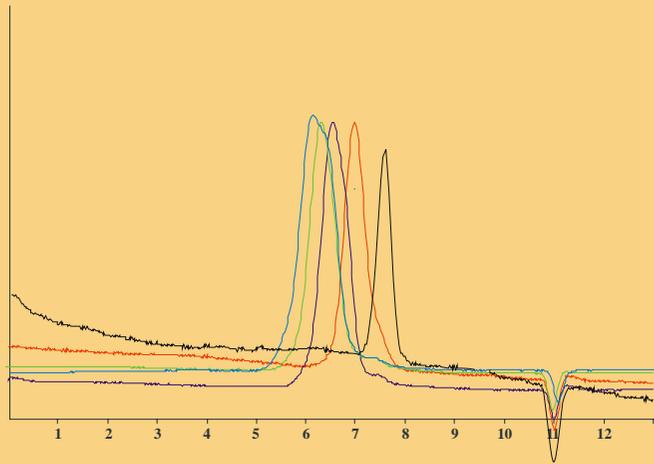
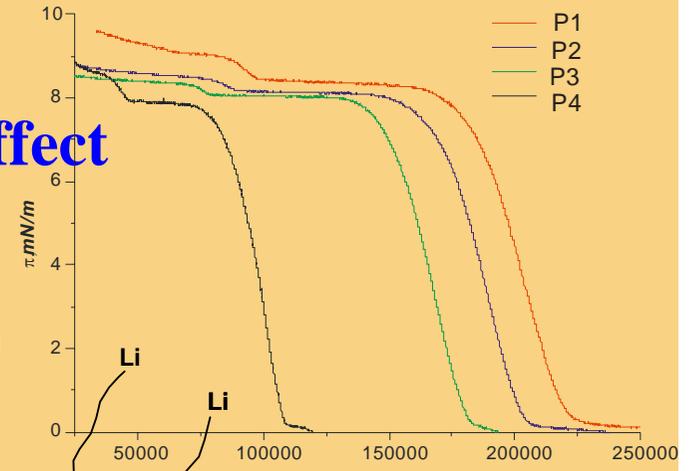
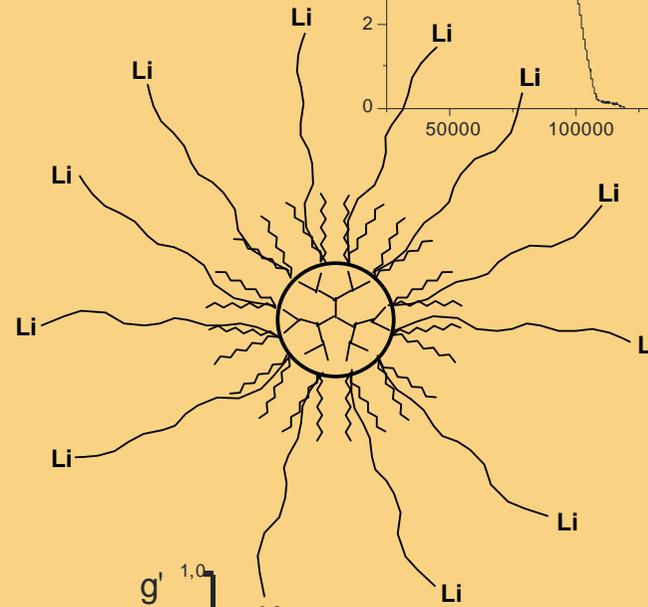
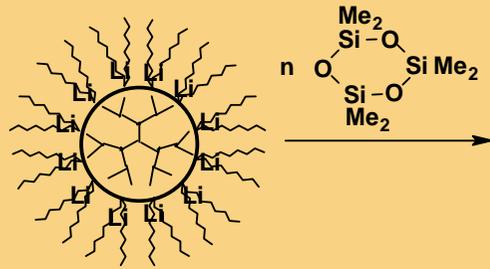
Silica
particles

Scanning force photomicrograph of silica-sol on mica





Molecular Membrane Effect



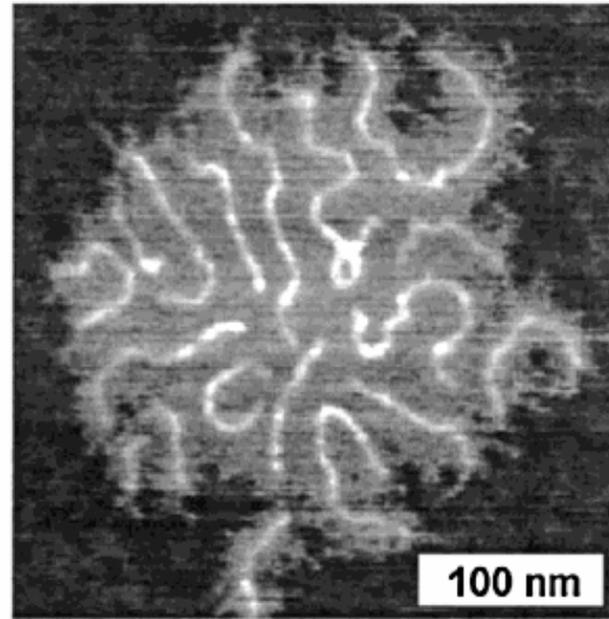
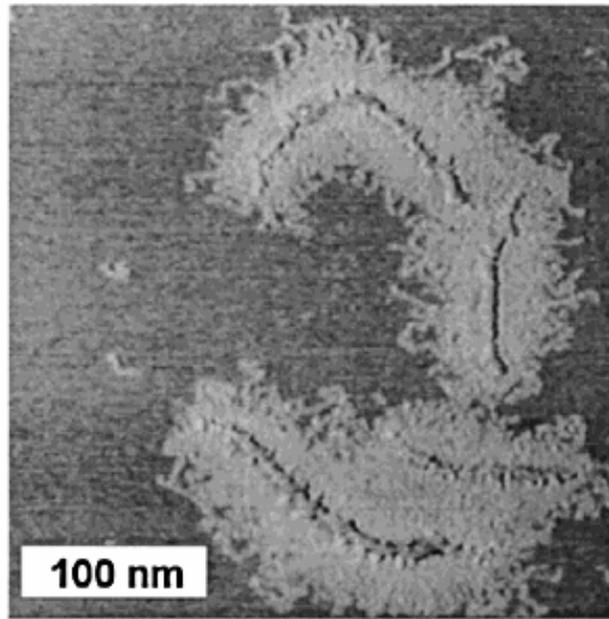
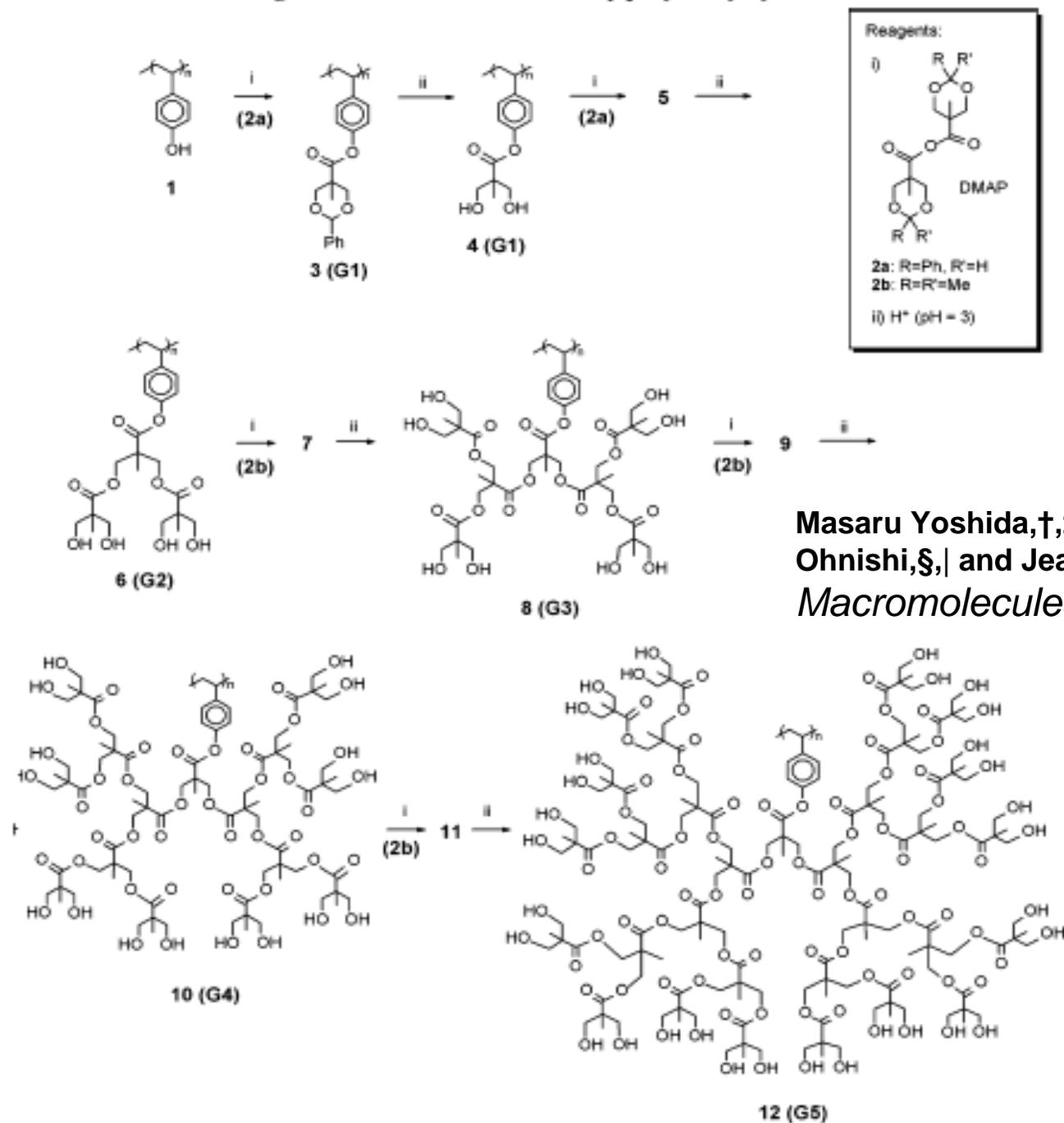


Figure 14. Molecular brushes with poly(*n*-butyl acrylate) side chains of different degrees of polymerization: (a) $n = 52$ and (b) $n = 10$.

Scheme 1. Divergent Dendronization from Poly(*p*-hydroxystyrene) to G5 Alcohol



Masaru Yoshida,^{†,‡} Zachary M. Fresco,[†] Satomi Ohnishi,^{§,||} and Jean M. J. Fréchet*,[†]
Macromolecules **2005**, *38*, 334-344

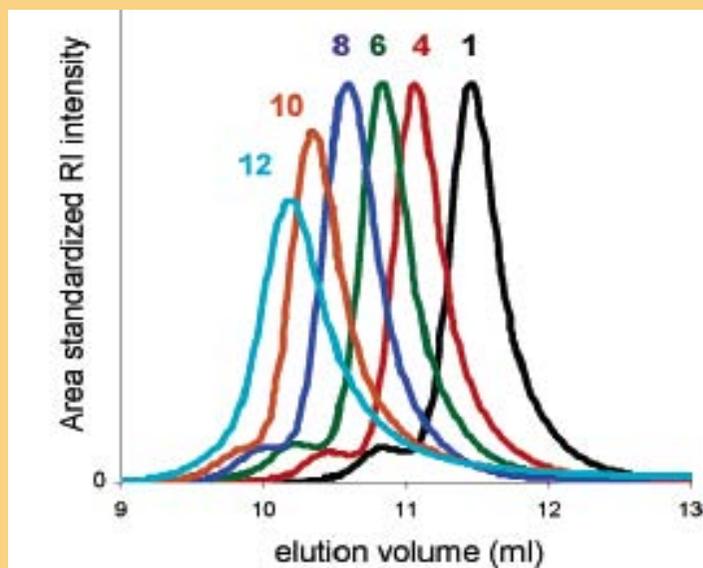
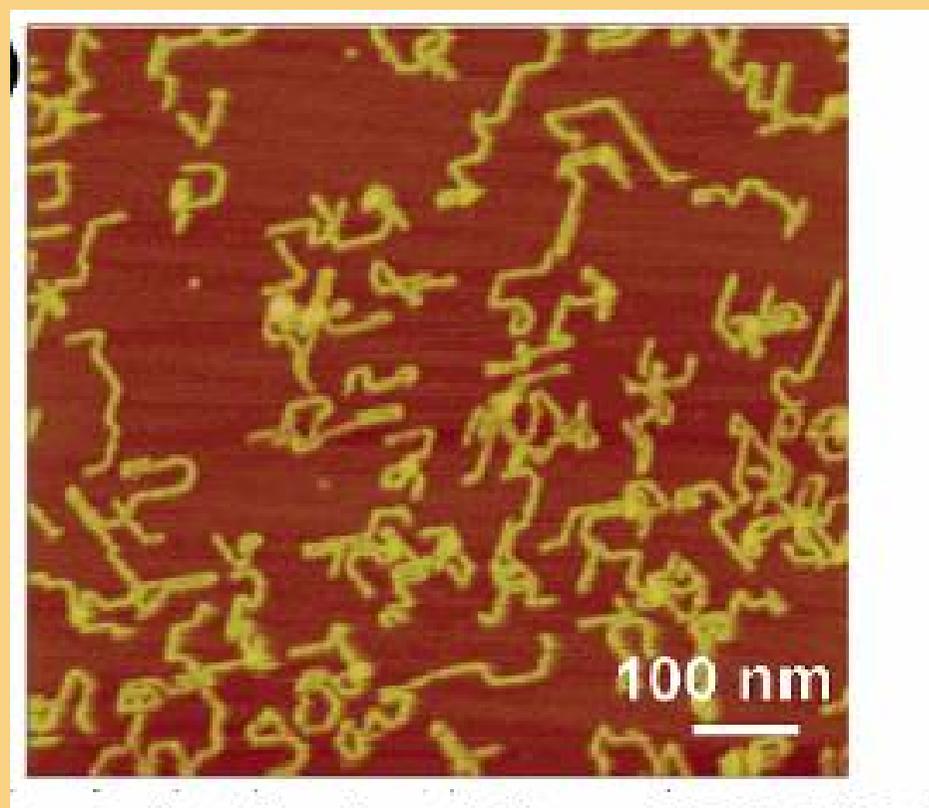
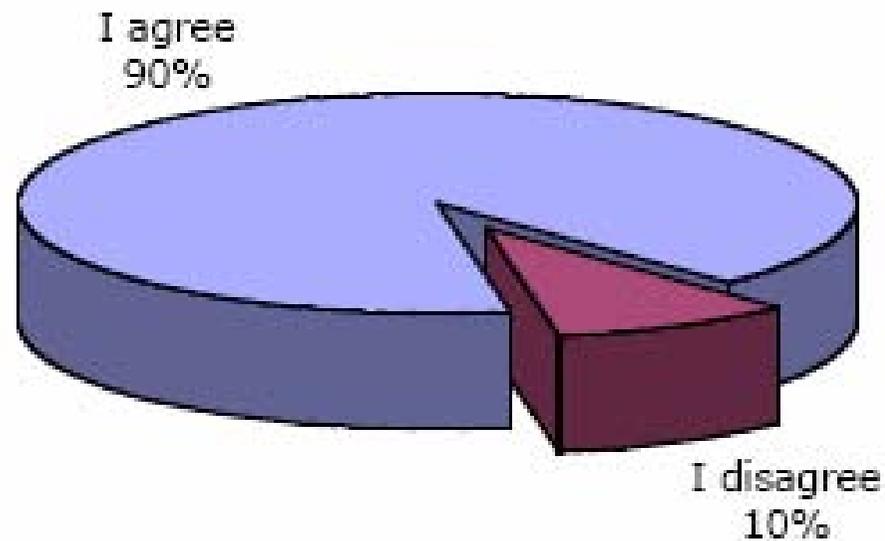


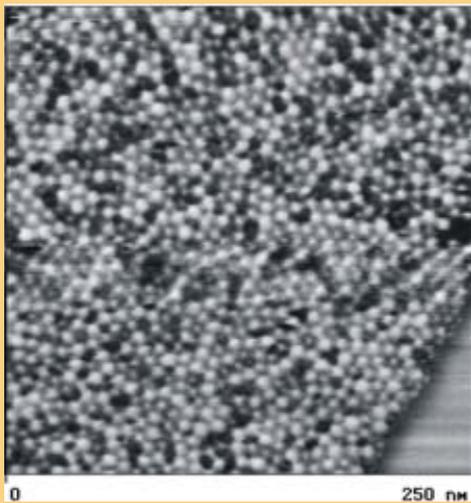
Figure 1. SEC profiles of hydroxylated dendronized polymers.

	M_w	PDI
	153 000	1.05
	379 000	1.05
	286 000	1.08
	752 000	1.08
	587 000	1.08
	1 480 000	1.10
	1 120 000	1.08
	2 600 000	1.08
	2 360 000	1.08
	5 010 000	1.04
	4 630 000	1.04

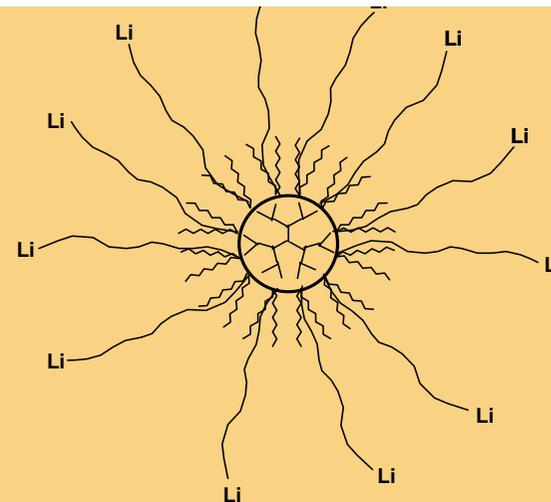
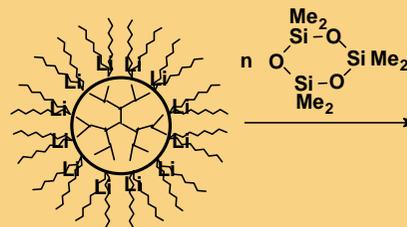


Dendrimers can be considered the most versatile, compositionally & structurally controlled synthetic nanoscale building blocks available today

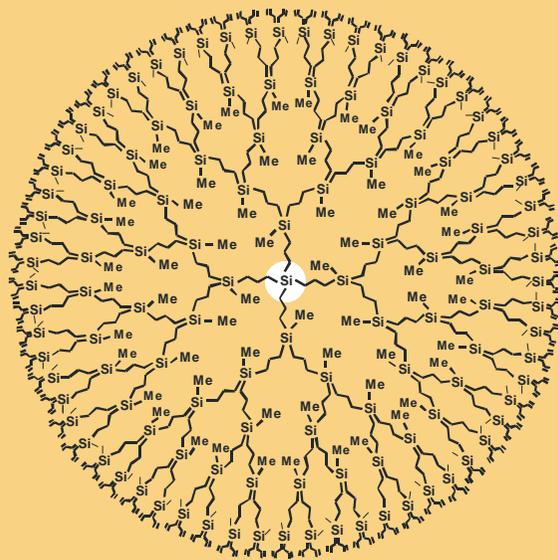




STM image of the 9-th generation of Carbosilane dendrimer on mica



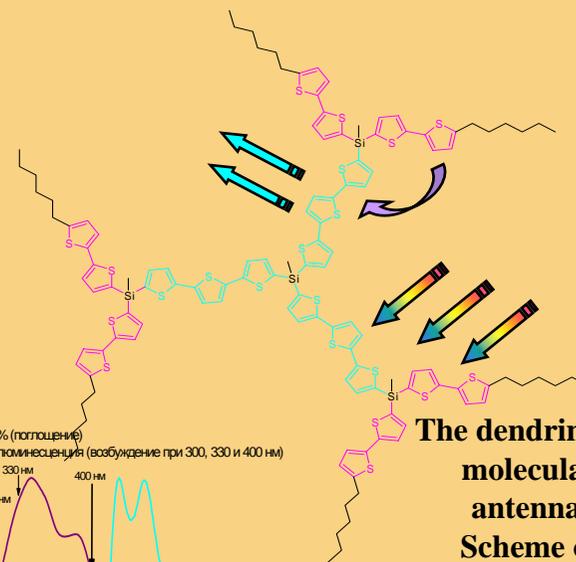
Multifunctional polyolithium (12-128) Initiators of anionic polymerization



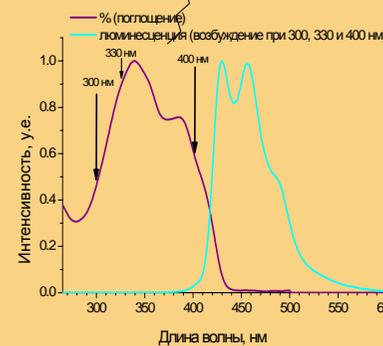
Carbosilane dendrimer



Hexane solution of carbosilane dendrimer Filled by cobalt oxide(II)



The dendrimer – molecular antenna. Scheme of photons transformations, left – absorption and luminescence spectra



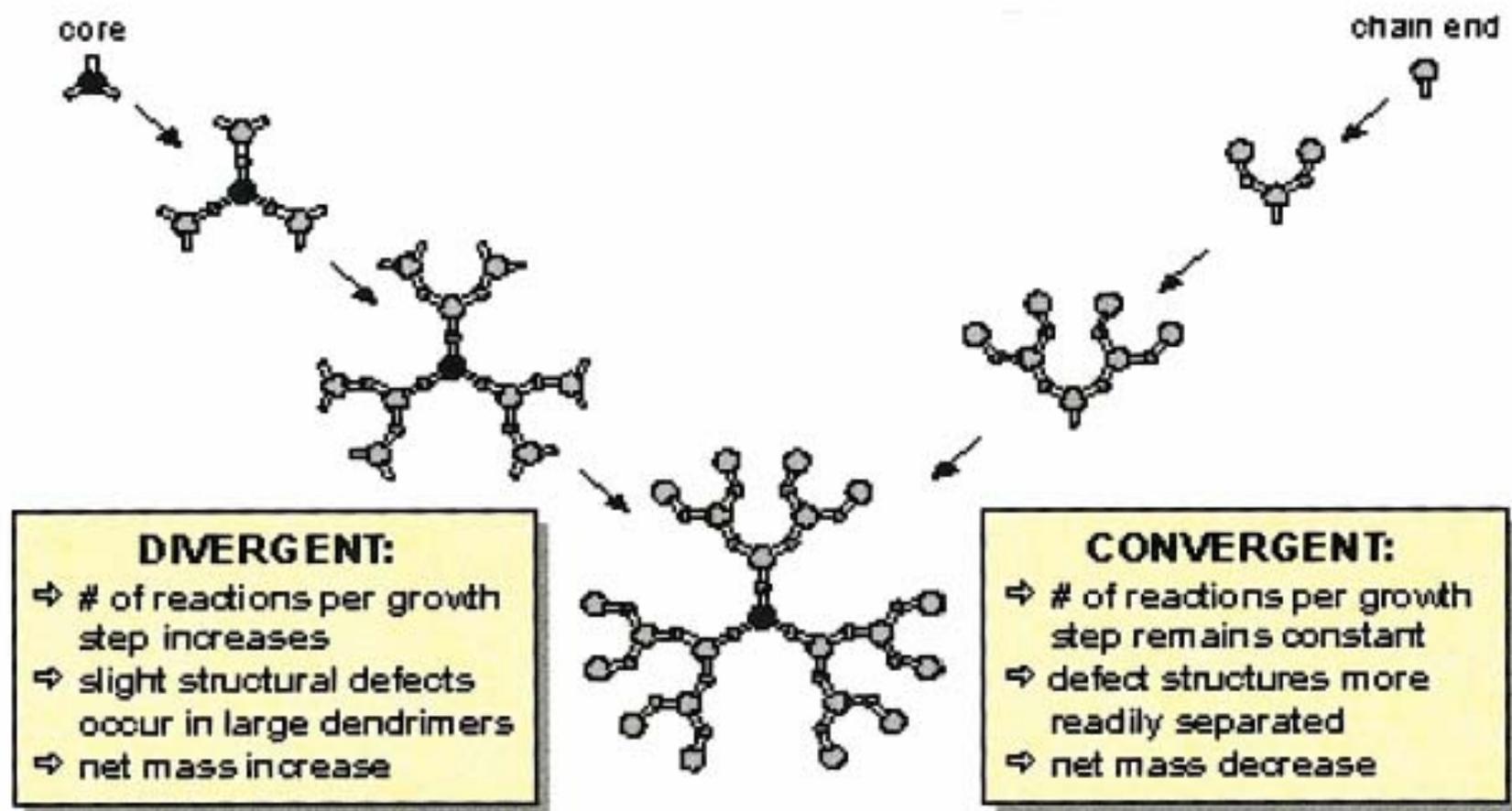
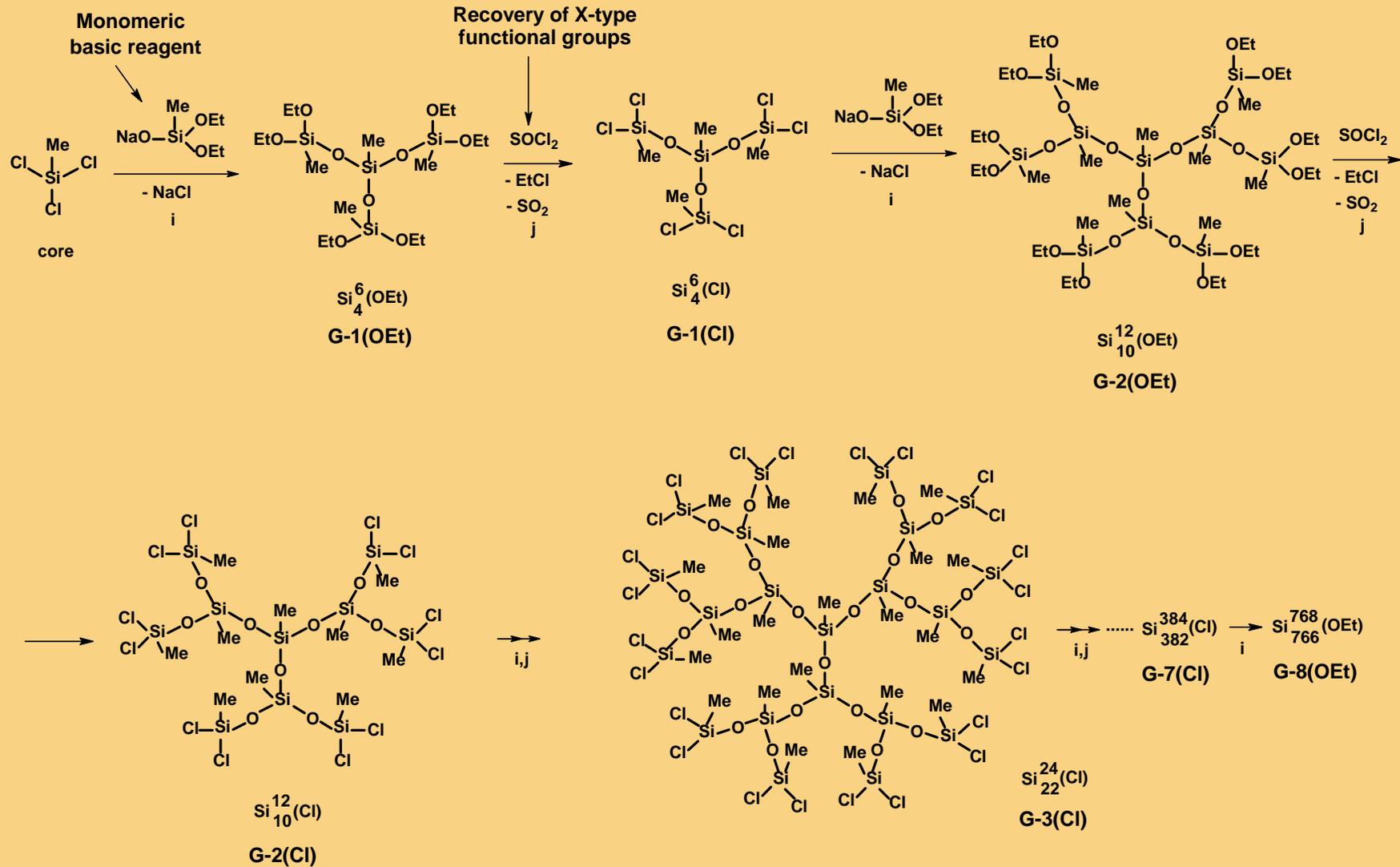


Figure 5. Representation of dendrimer growth by the divergent and convergent methods.

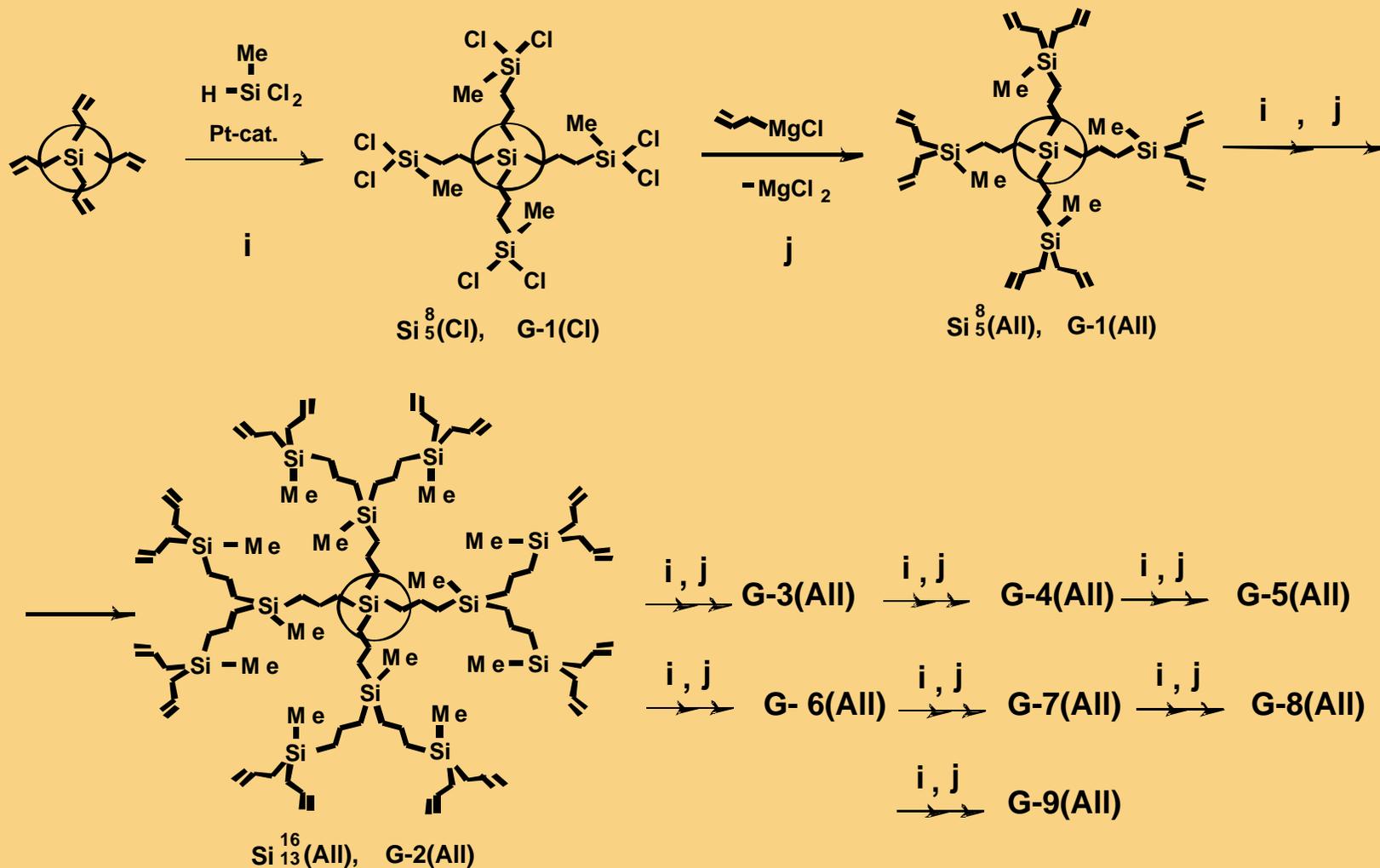


E.A.Rebrov, A.M.Muzafarov, V.S.Papkov, A.A.Zhdanov

Volume-groving polyorganosiloxanes

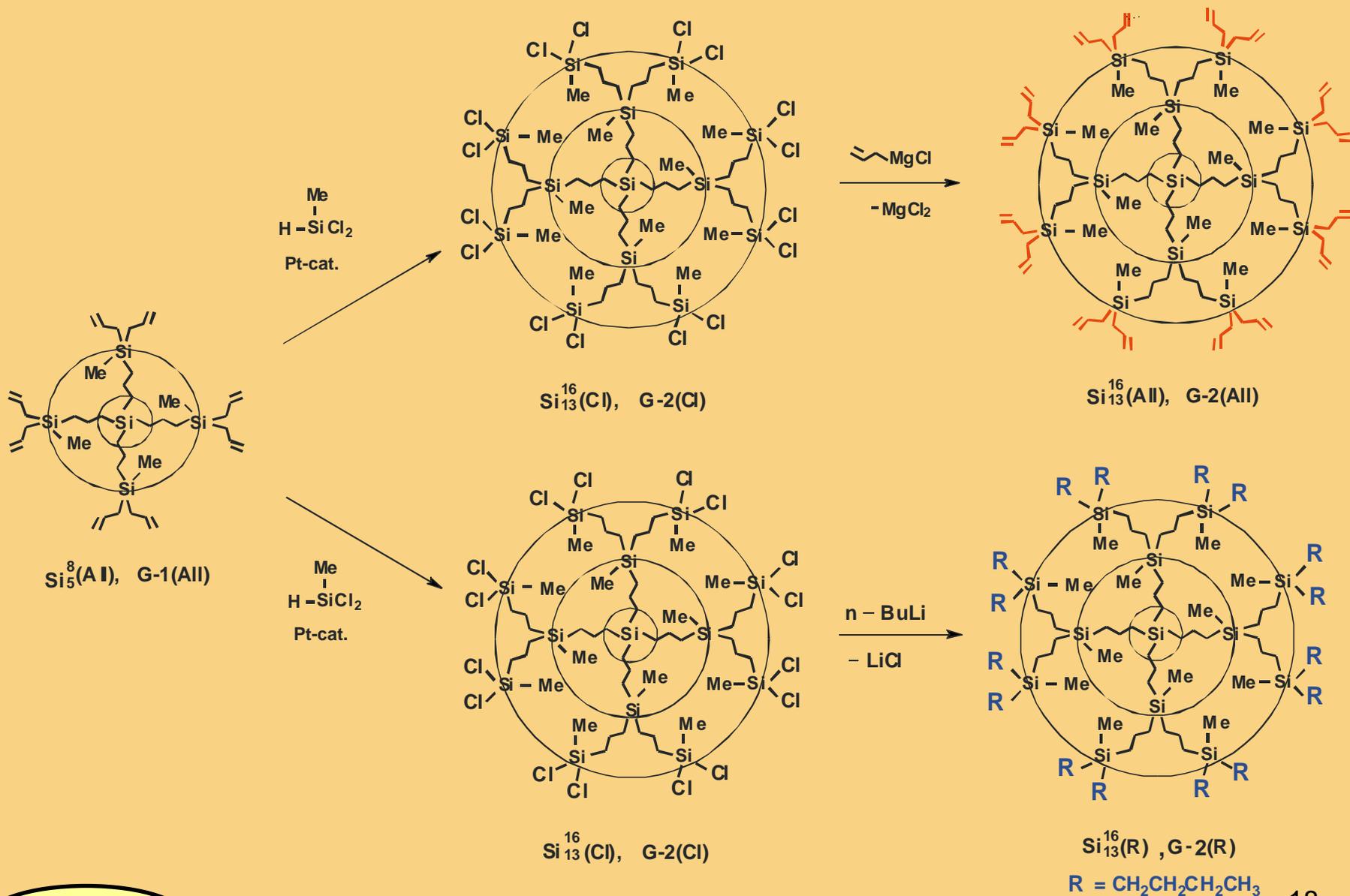
Doklady Chemistry, USSR, 1989, v. 309, №2, p. 376

Divergent scheme of carbosilane dendrimers synthesis

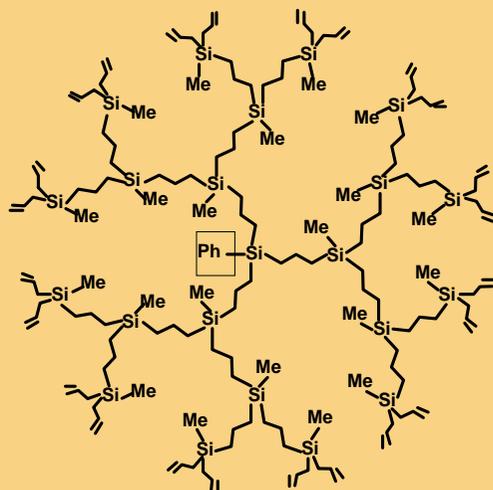


A.Muzafarov, O.B.Gorbatsevich, E.A. Rebrov, G.M.Ignat'eva, T.B.Chenskaya, V.D.Myakouchev, A.F.Bulkin, V.S.Papkov "Organosilicon dendrimers. Volumegrowing polyallylcarbosilanes" Polymer Science, 1993, vol. 35A, No 11, p.1867.

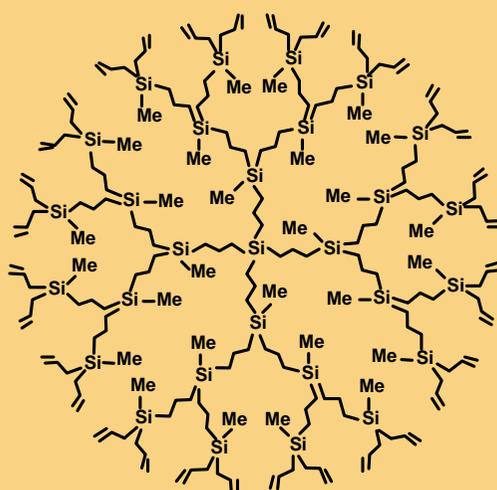
Synthesis of functional and non-functional derivatives of carbosilane dendrimers



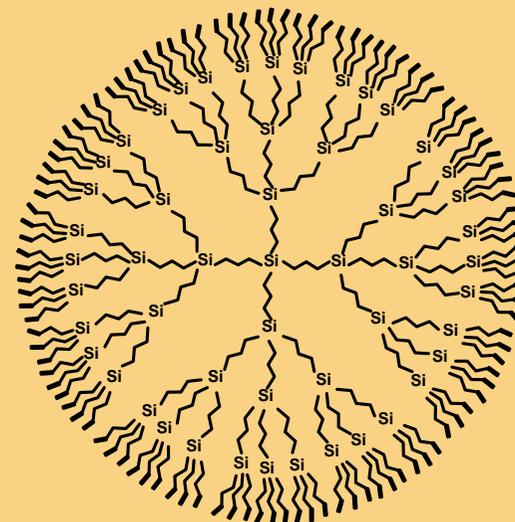
Гомологические ряды карбосилановых дендримеров



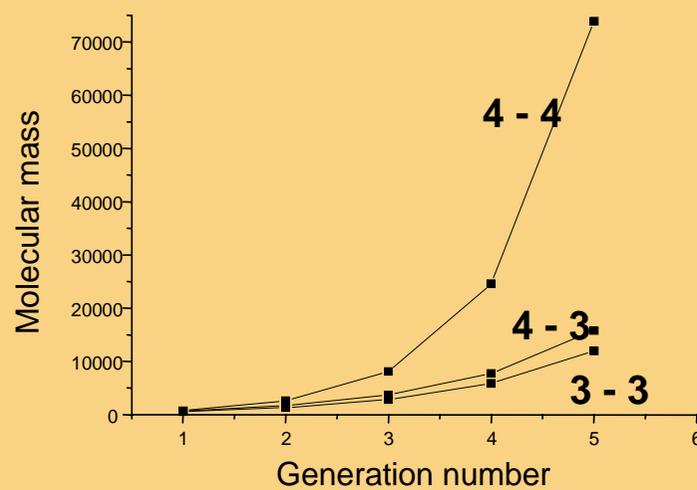
3 - 3



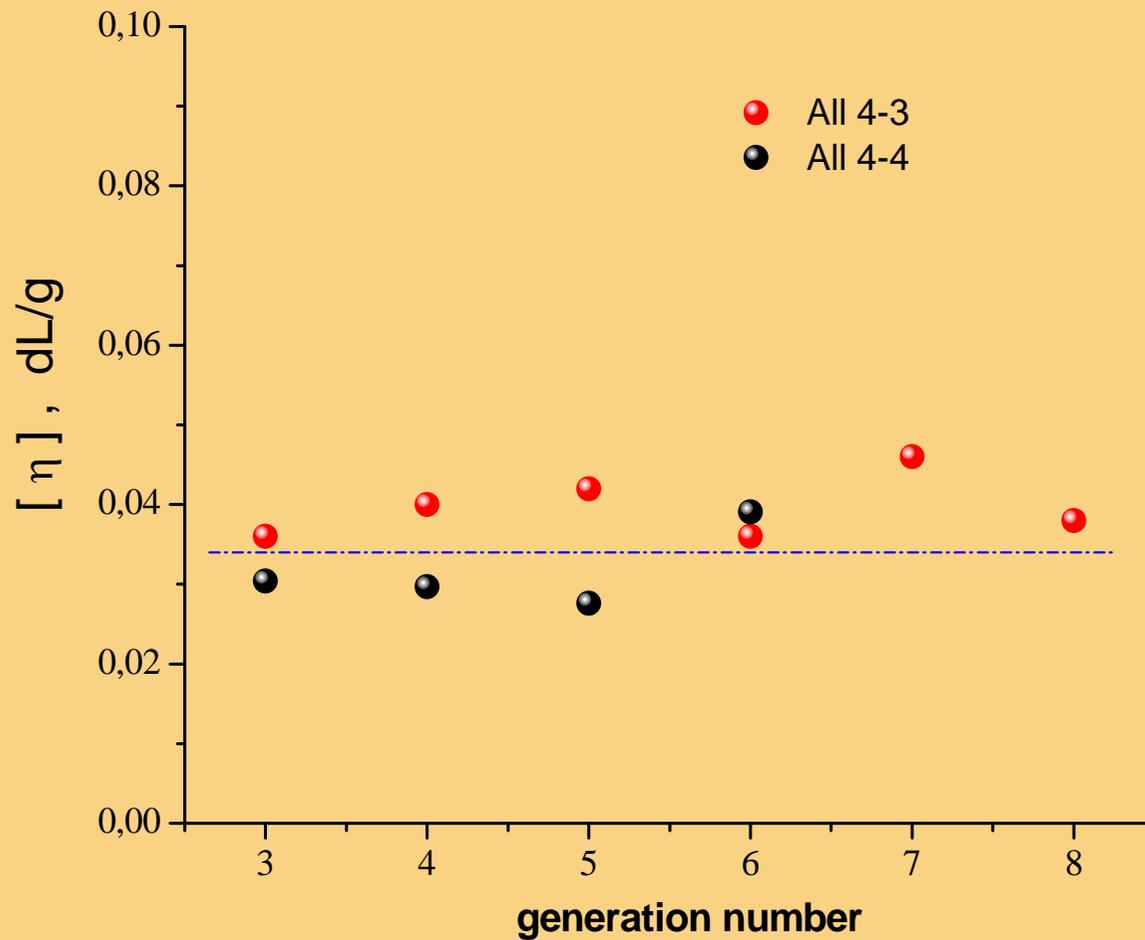
4 - 3



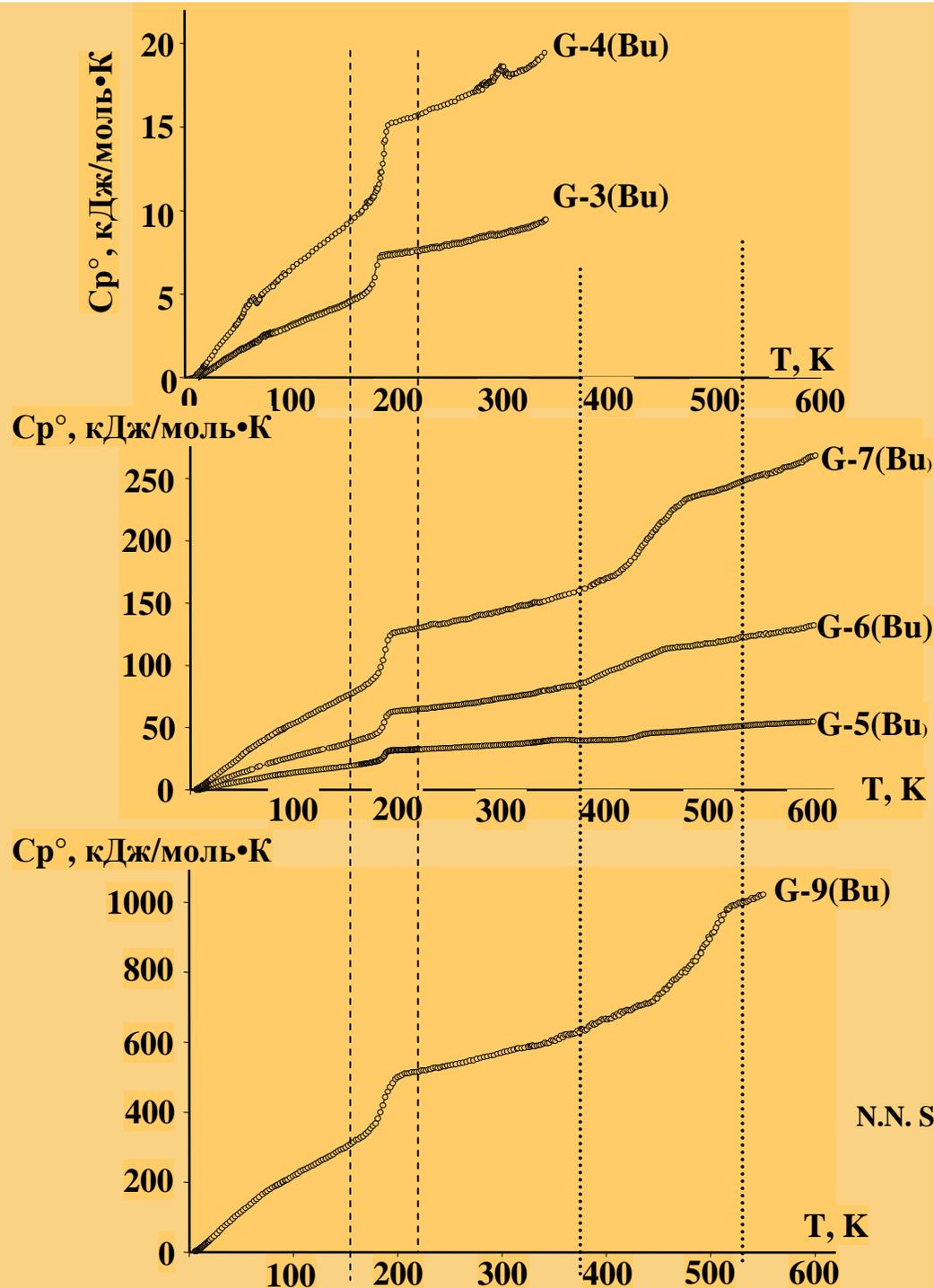
4 - 4



Зависимость характеристической вязкости растворов карбосилановых дендримеров



Зависимость теплоемкости от температуры образцов полибутилкарбосиловых дендримеров 3-9 генераций



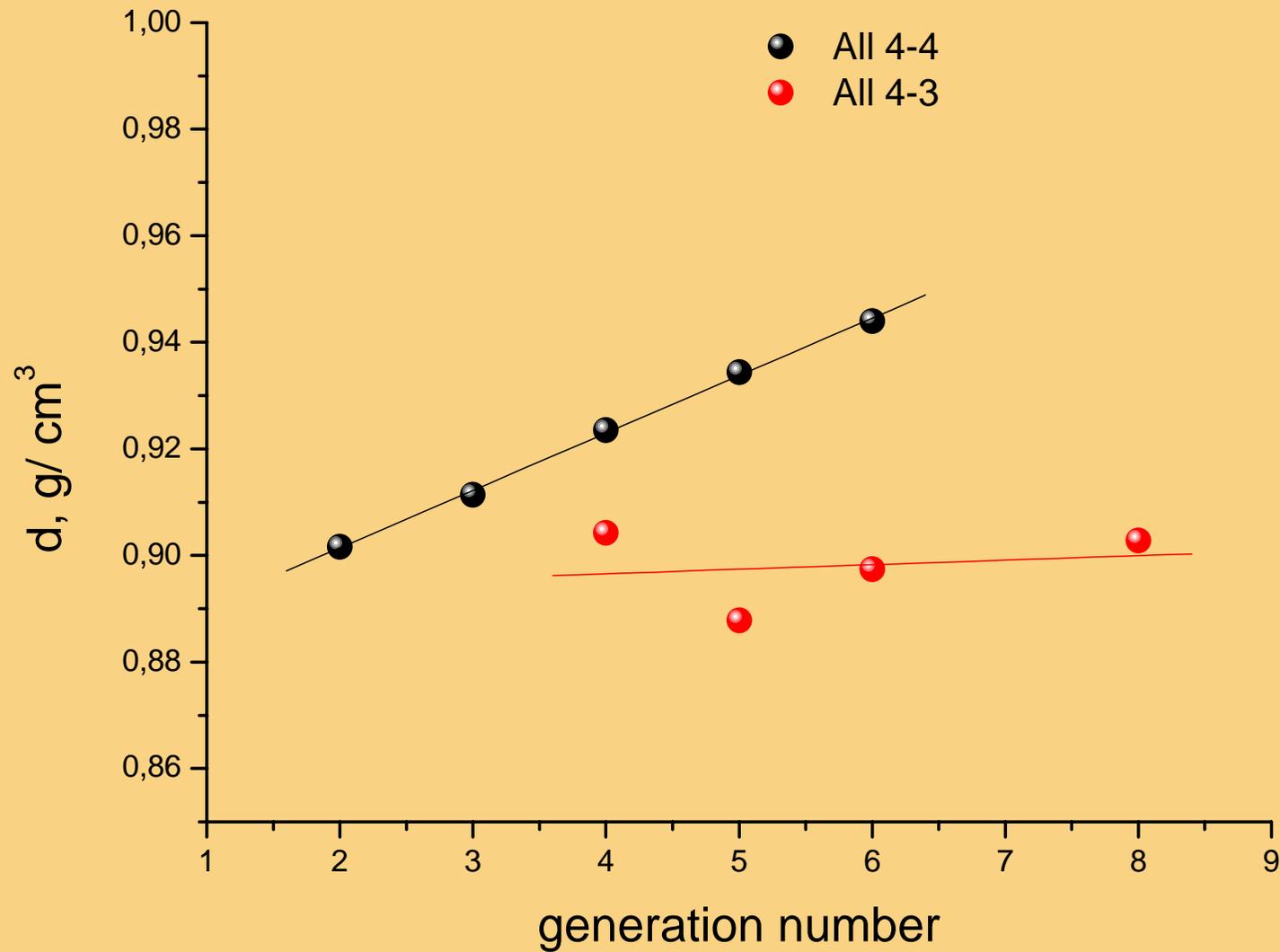
Дендри мер	ΔT , К	T_g , К
G-3(Bu)	174-186	179 ± 1
G-4(Bu)	181-195	186 ± 1
G-5(Bu)	177-195	186 ± 1
G-6(Bu)	178-196	186 ± 1
G-7(Bu)	178-196	186 ± 1
G-9(Bu)	174-204	187 ± 1

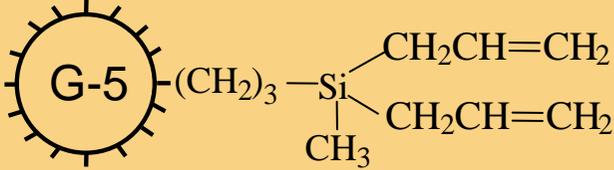
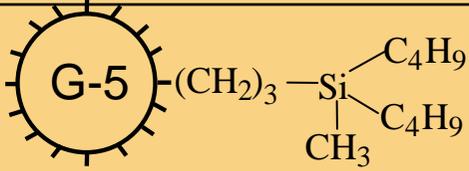
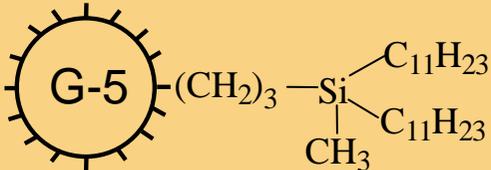
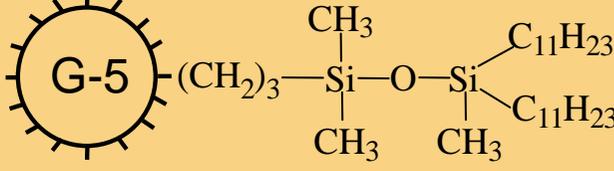
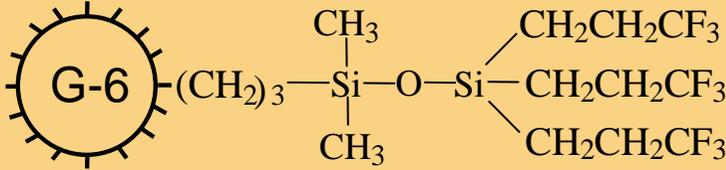
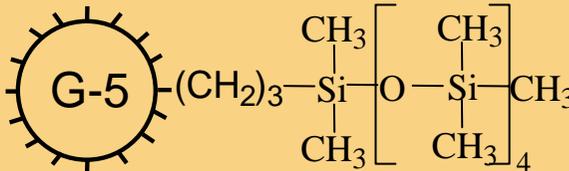
N.N. Smirnova et all. *Thermochimica Acta*. 2006. V.440. P.188-194

N.N. Smirnova et all. *Russ. Chem. Bull.* 2007. in print

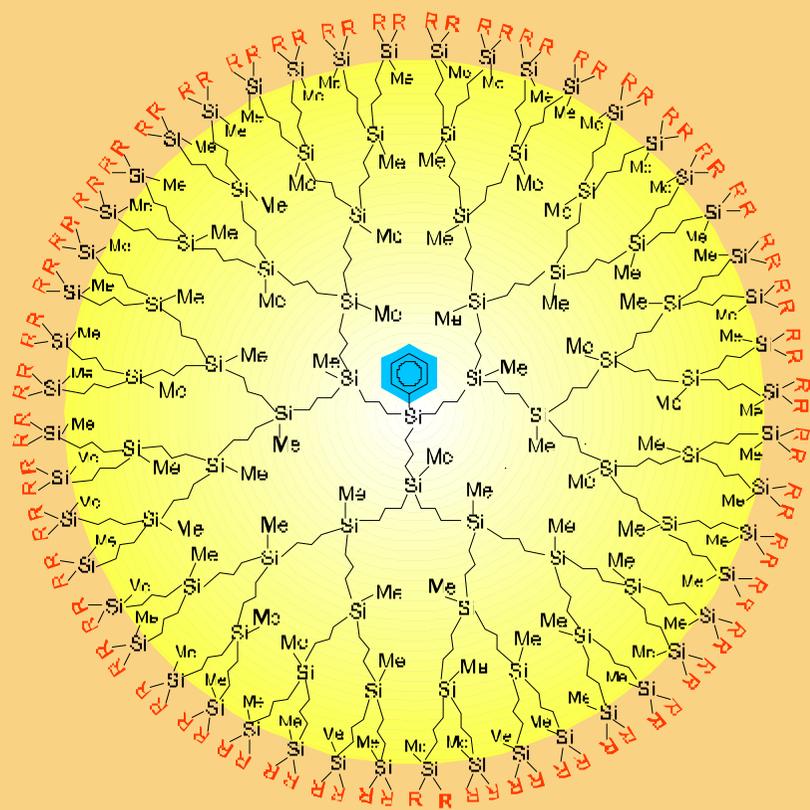
ISPM RAS

Зависимость плотности карбосилановых дендримеров от номера поколения

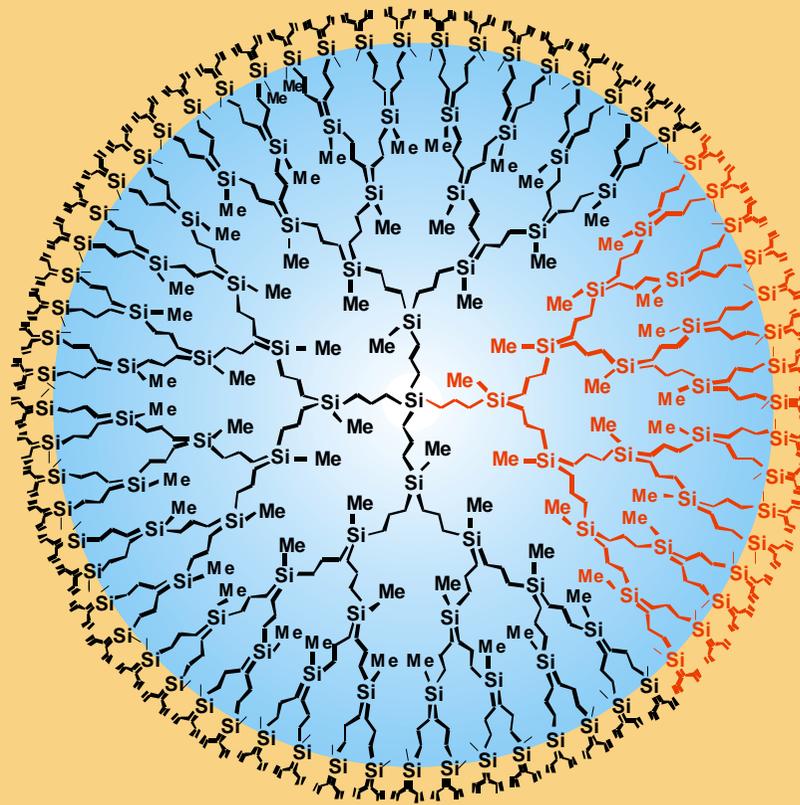


Dendrimers	$T_g, ^\circ\text{C}$
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{CH}_2\text{CH}=\text{CH}_2 \\ \text{CH}_2\text{CH}=\text{CH}_2 \\ \text{CH}_3 \end{matrix}$ </p>	- 93±1
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 \\ \text{CH}_3 \end{matrix}$ </p>	- 87 ± 1
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{C}_{11}\text{H}_{23} \\ \text{C}_{11}\text{H}_{23} \\ \text{CH}_3 \end{matrix}$ </p>	-64 ± 1
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{CH}_3 \\ \text{O} - \text{Si} \begin{matrix} \text{C}_{11}\text{H}_{23} \\ \text{C}_{11}\text{H}_{23} \\ \text{CH}_3 \end{matrix} \\ \text{CH}_3 \end{matrix}$ </p>	-76 ± 3
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{CH}_3 \\ \text{O} - \text{Si} \begin{matrix} \text{CH}_2\text{CH}_2\text{CF}_3 \\ \text{CH}_2\text{CH}_2\text{CF}_3 \\ \text{CH}_2\text{CH}_2\text{CF}_3 \end{matrix} \\ \text{CH}_3 \end{matrix}$ </p>	-50 ± 3
 <p> $(\text{CH}_2)_3 - \text{Si} \begin{matrix} \text{CH}_3 \\ \text{O} - \left[\text{Si} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \right]_4 - \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ </p>	-106.5 ± 1

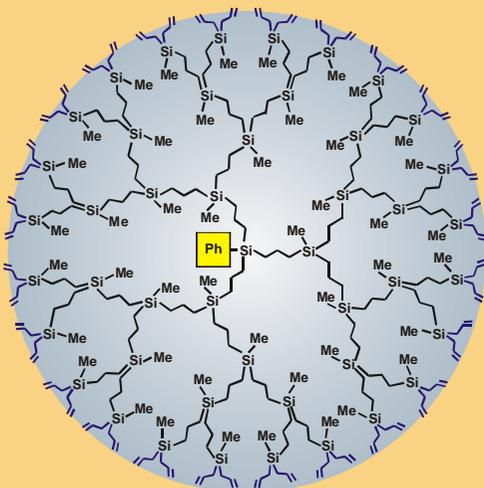
Tail wags the dog...



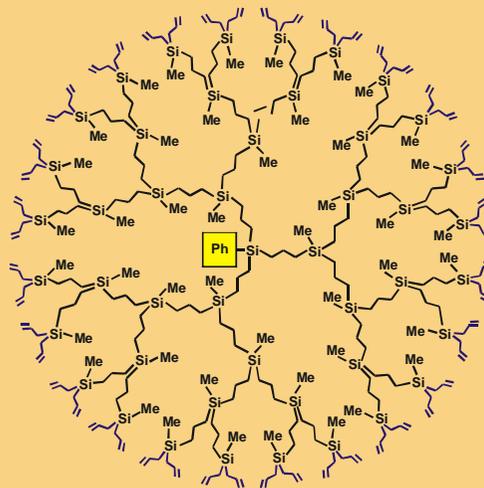
Si_{92}G_5



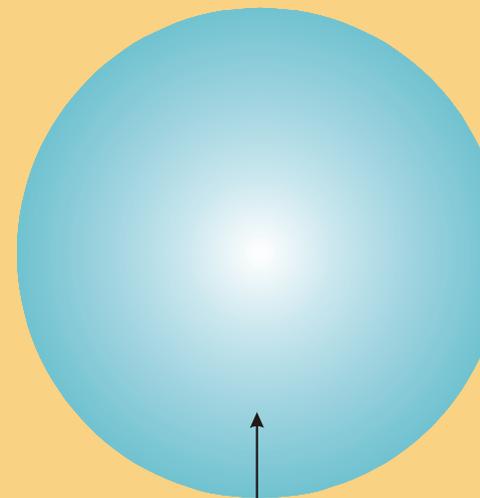
$\text{Si}_{128}\text{G}_5$



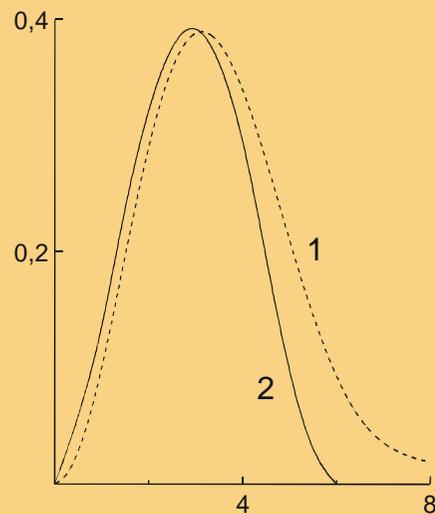
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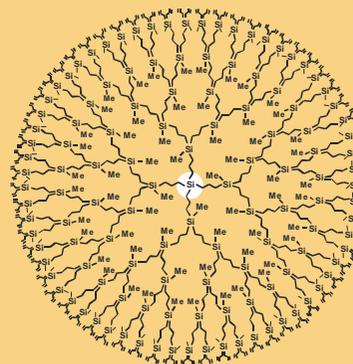
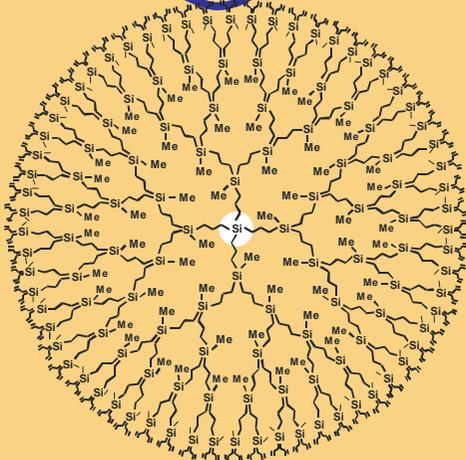
Free space : 30 - 40%



A. Kulkin, G. Ignat'eva, L. Ozerina, A. Islamov,
 R. Muhamedzyanov, N. Shumilkina, V. Myakushev,
 E. Sharipov, A. Muzafarov, A. Ozerin,
Polymer Science, 2002 series A, v. 44, № 12, 1273

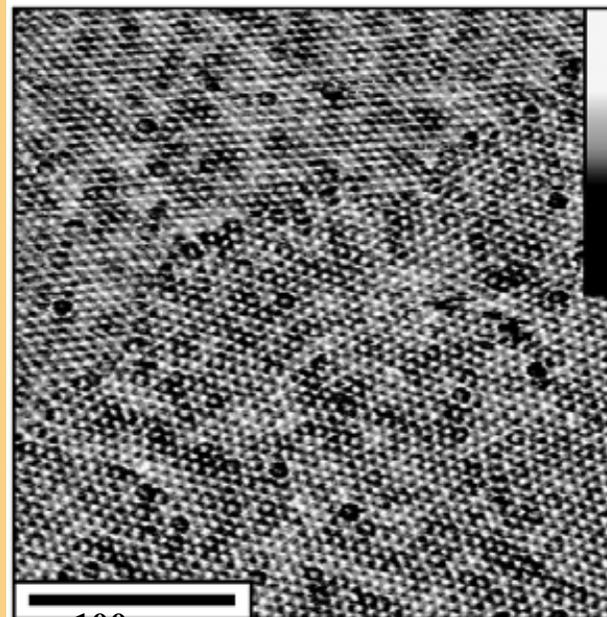
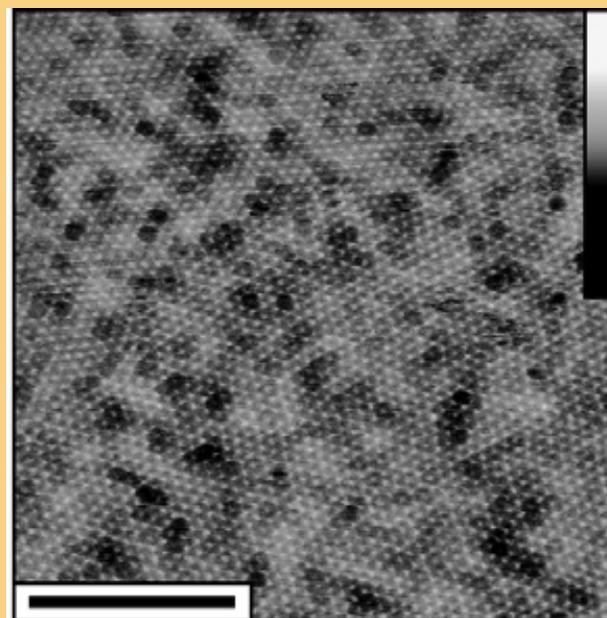
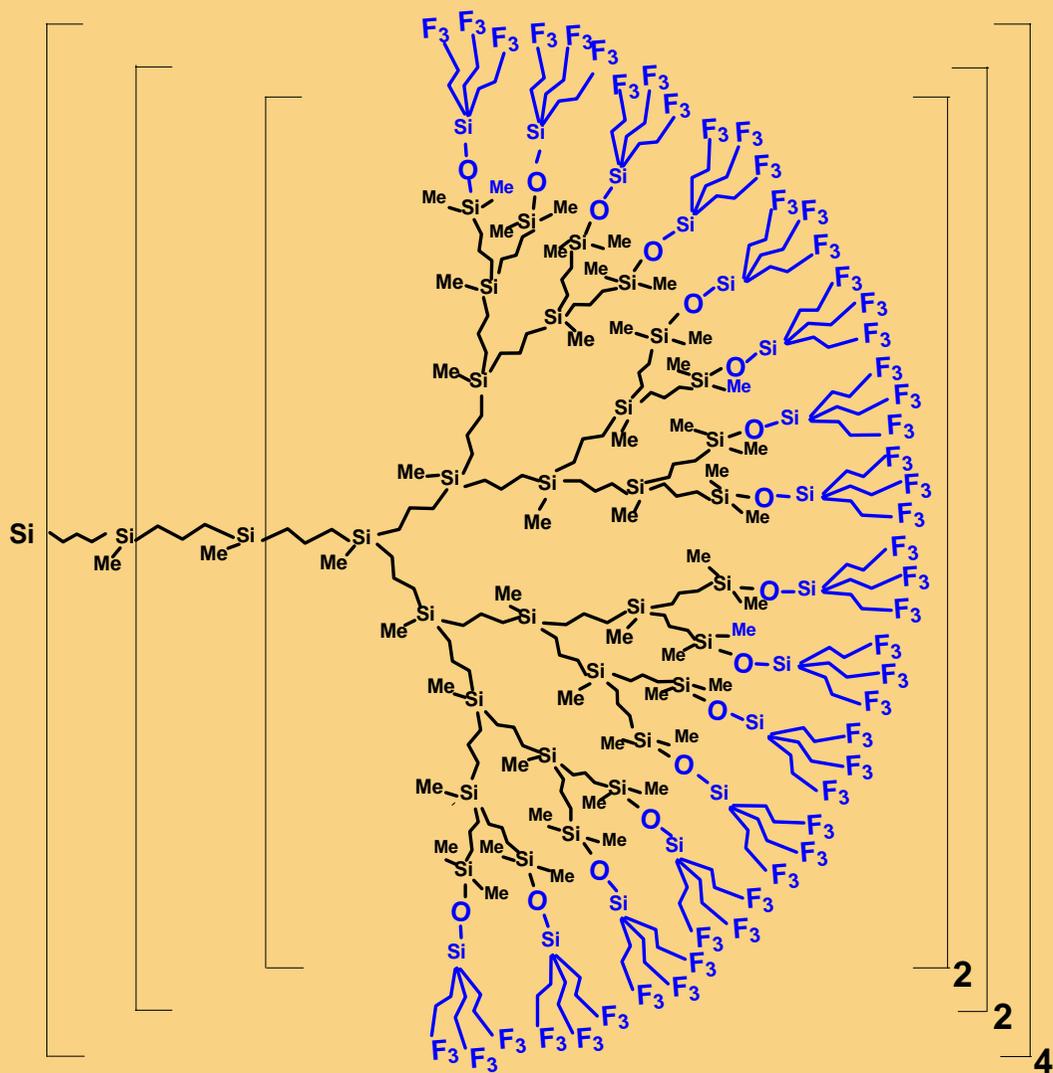
1- SAXS plot G-7 (polyallylcarbosilane dendrimer)

2- theoretical scattering curve of sphere like particle with $R_g = 2.3$ nm

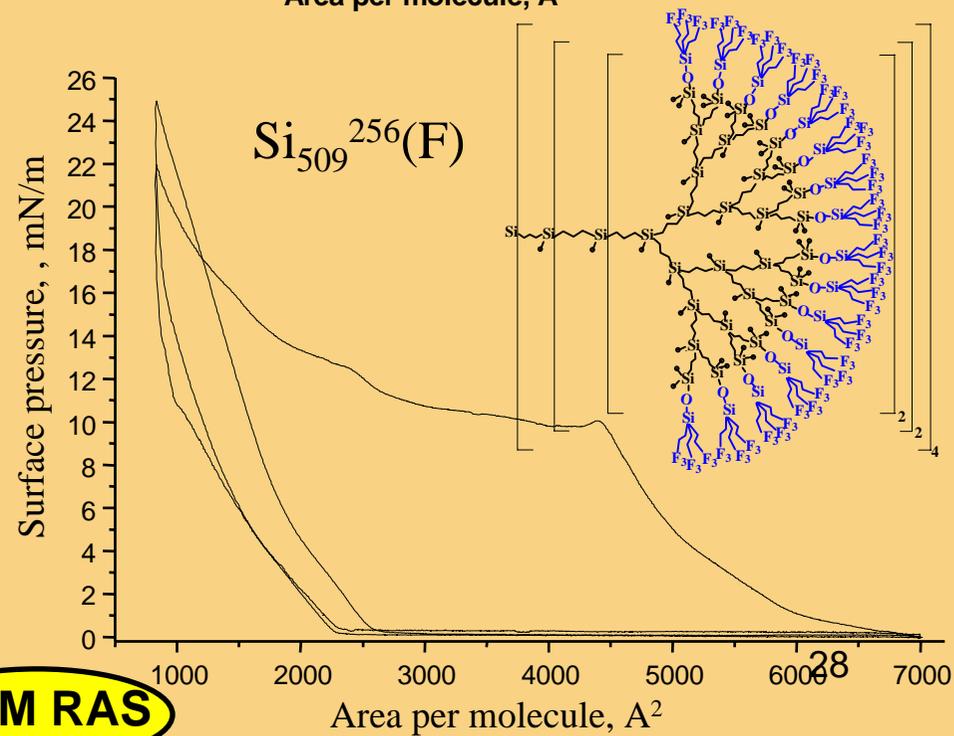
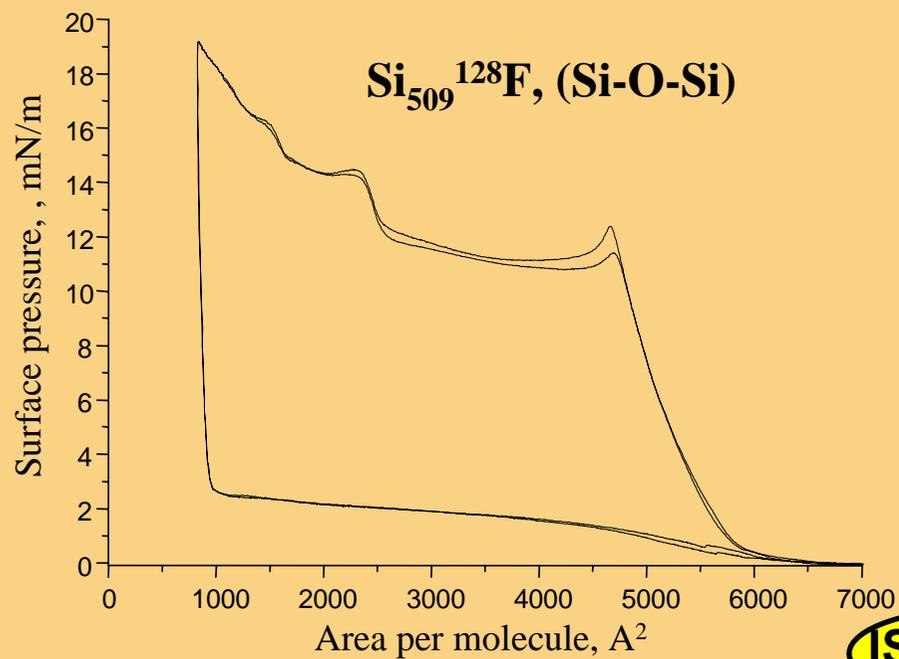
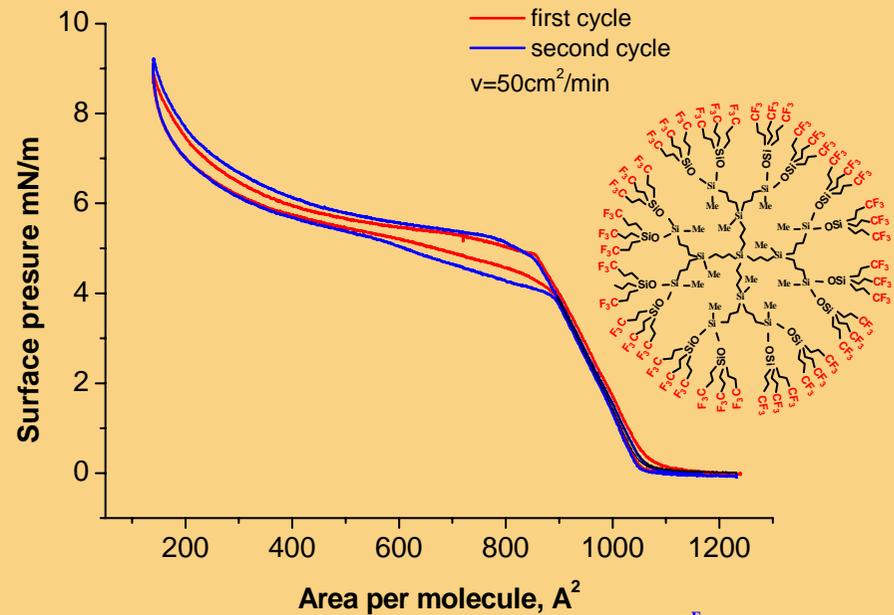
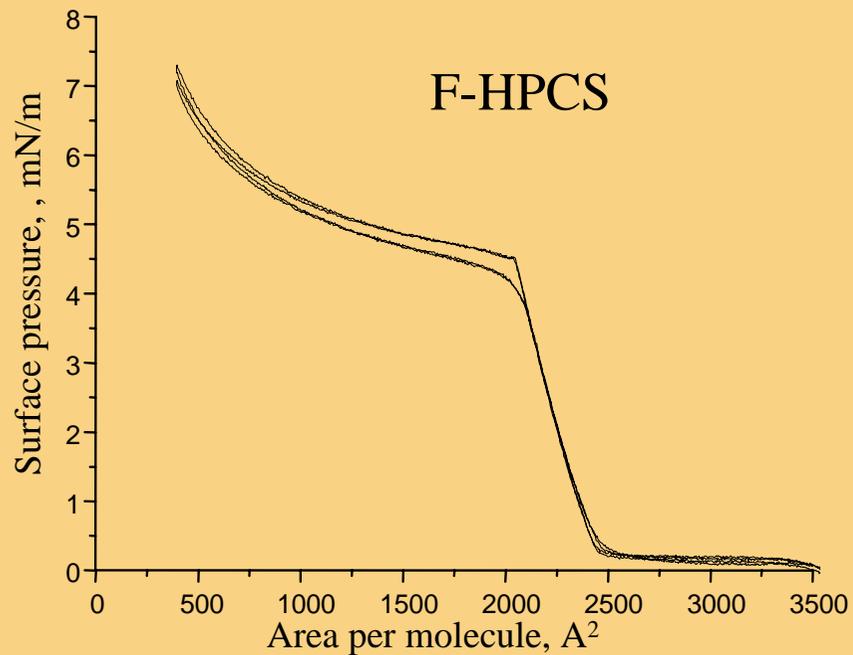


Solvent quality

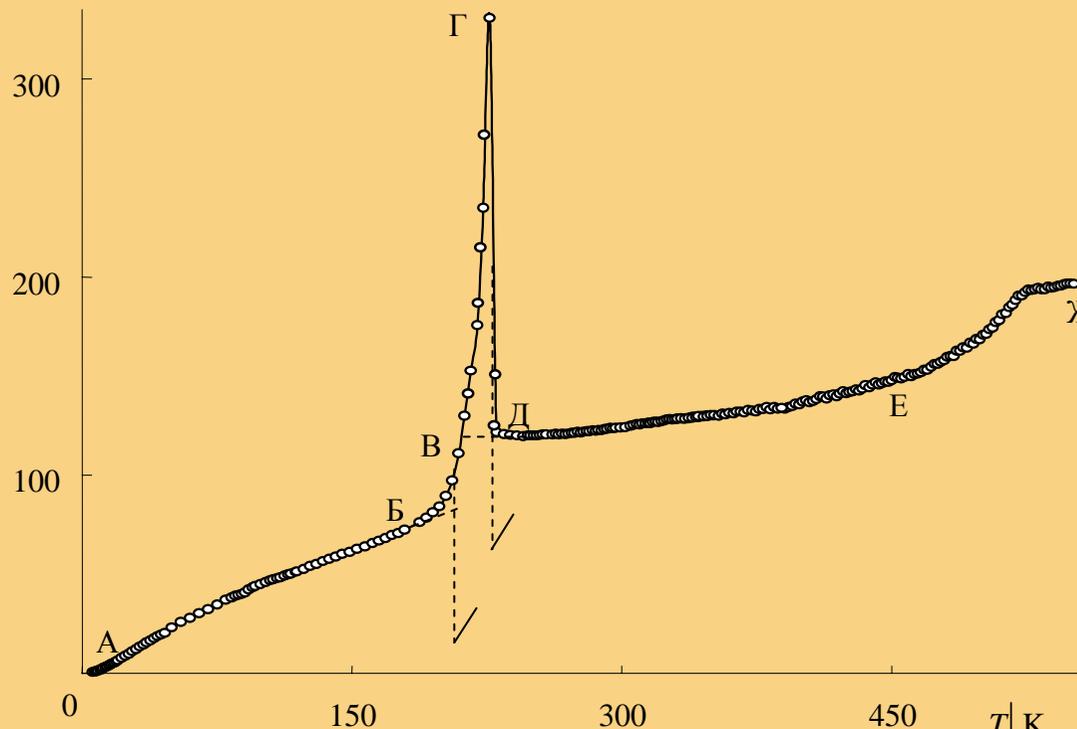
Fluorocarbon Derivatives of Carbosilane Dendrimers of High Generation



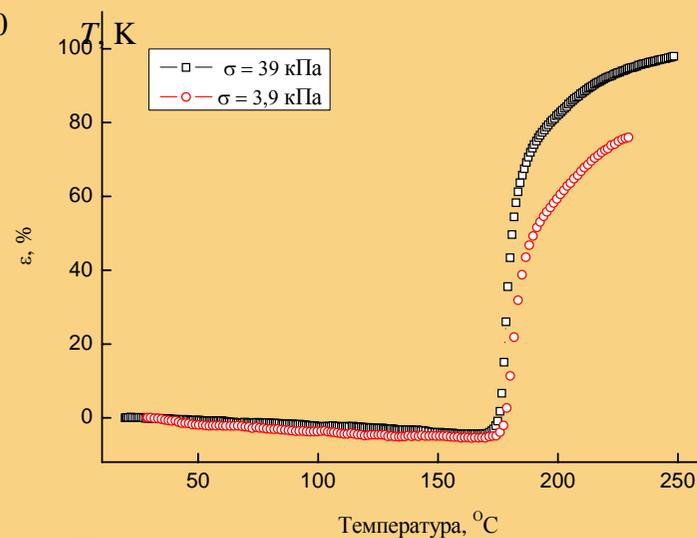
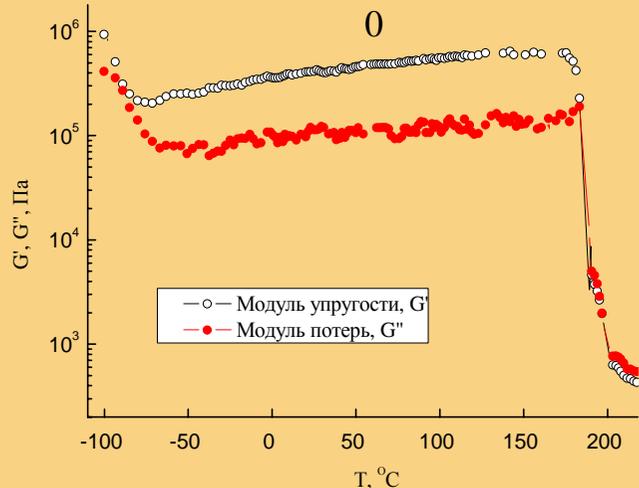
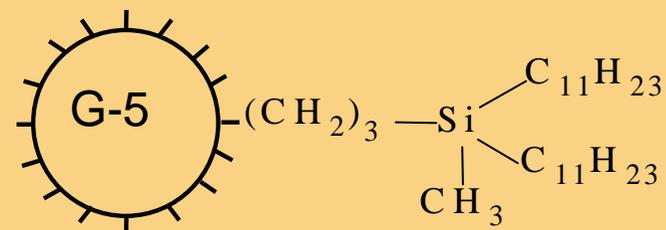
100nm



, кДж/(К моль)

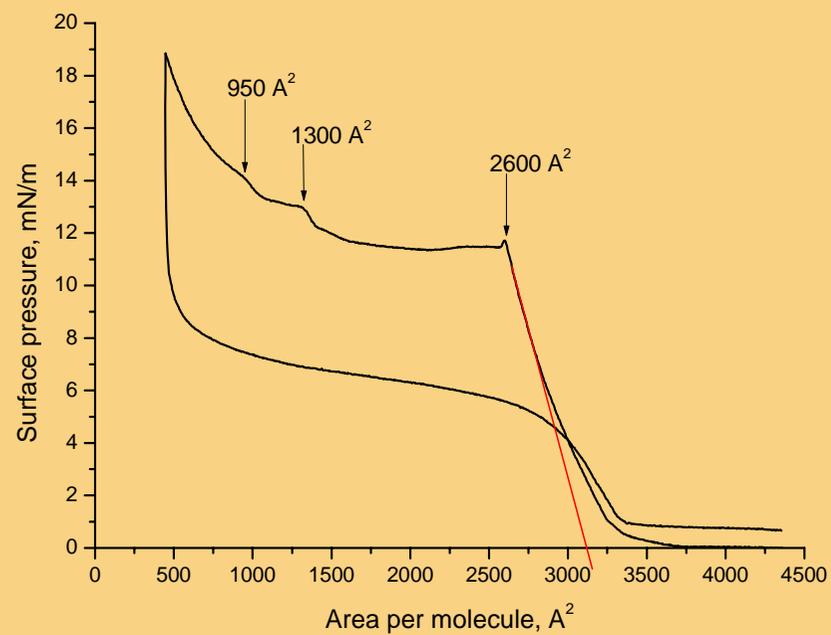
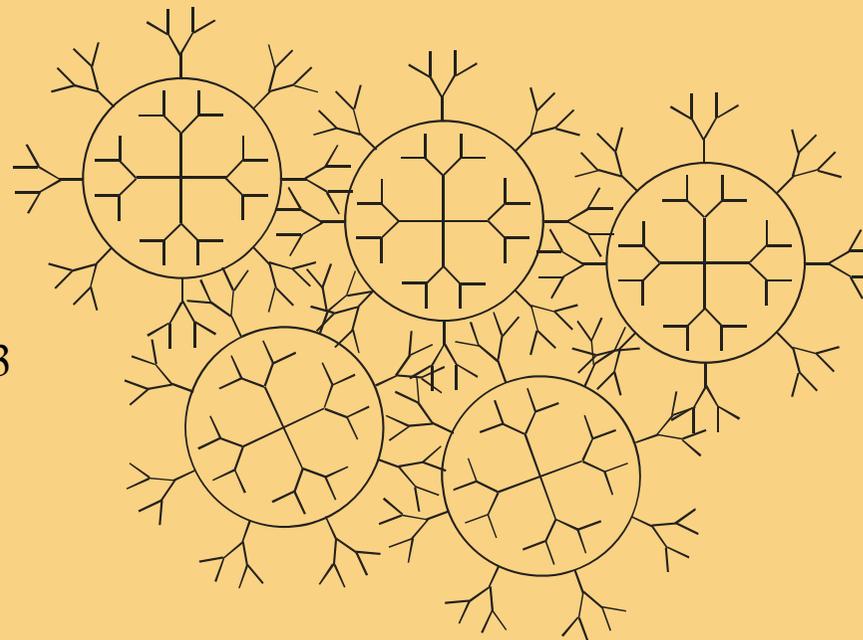
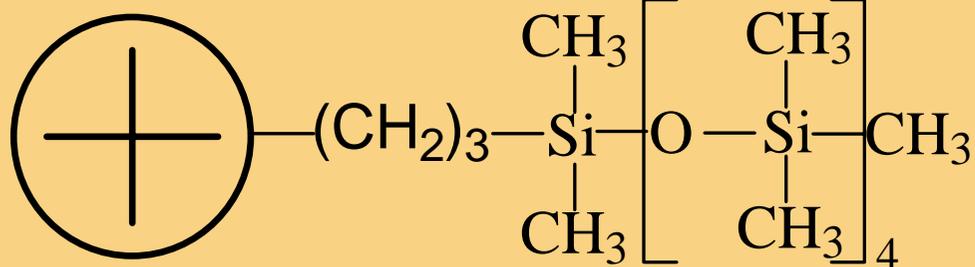


Второй релаксационный переход



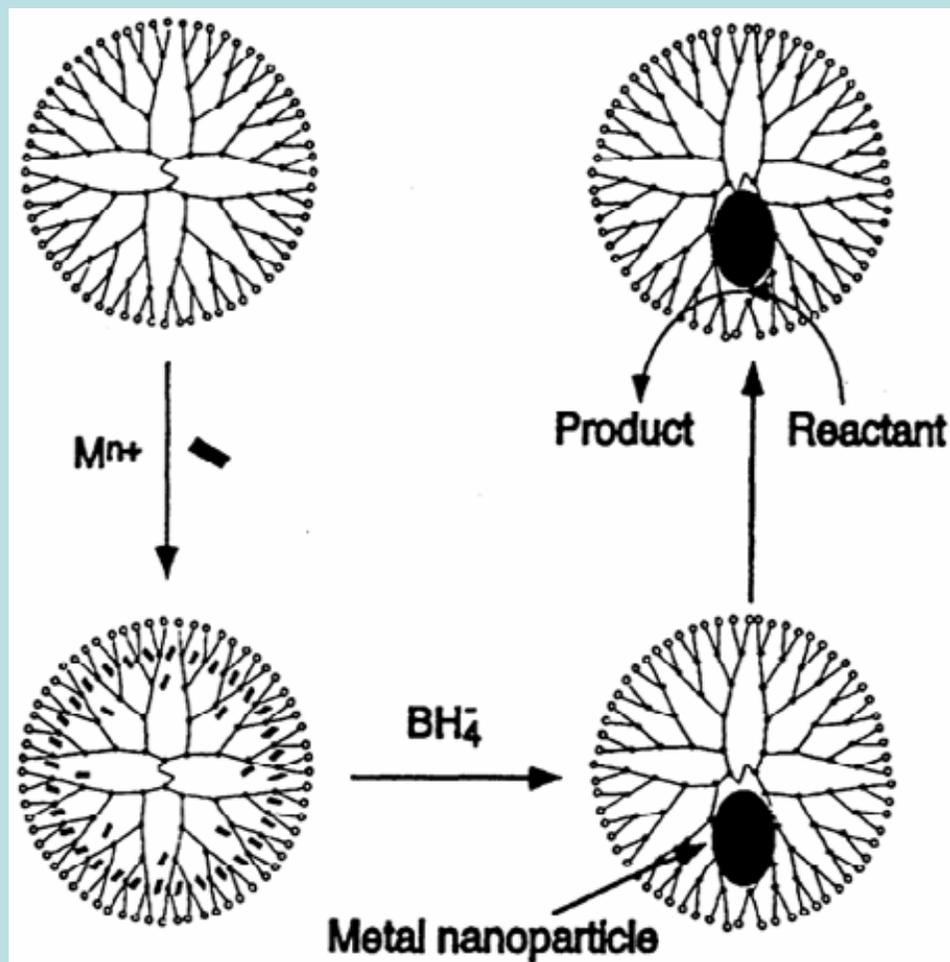
Зависимость динамических модулей дендримера 2 (Gt-26) от температуры в полулогарифмических координатах. Частота 0,63 Гц.

Термомеханические кривые дендримера 2 (Gt-26) при разных сжимающих напряжениях.



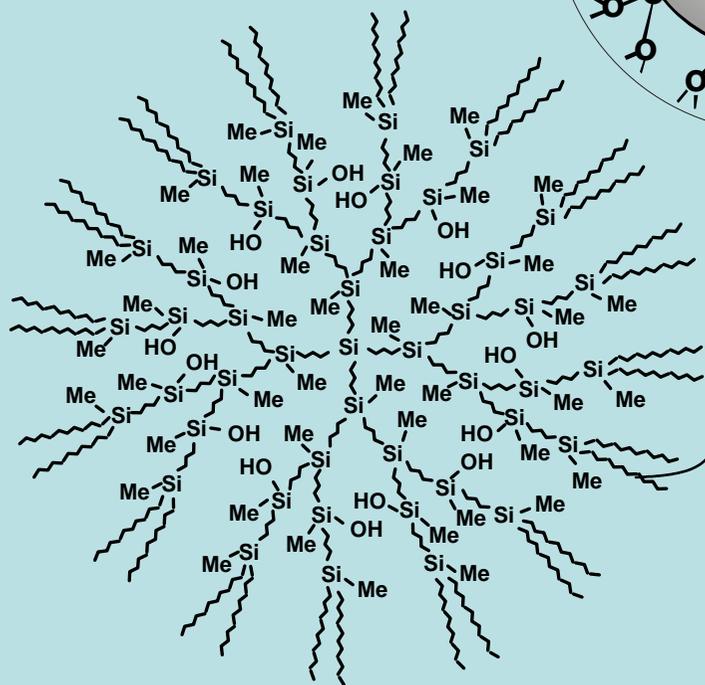
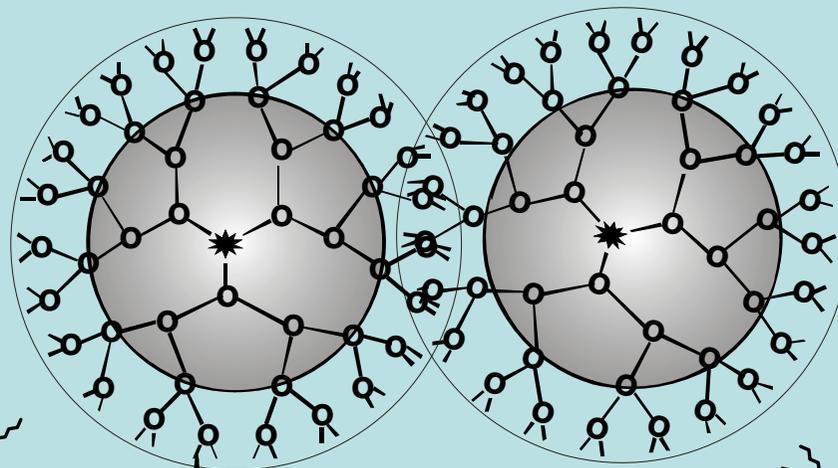


Scheme of step by step nanoclusters formation within dendrimer molecule

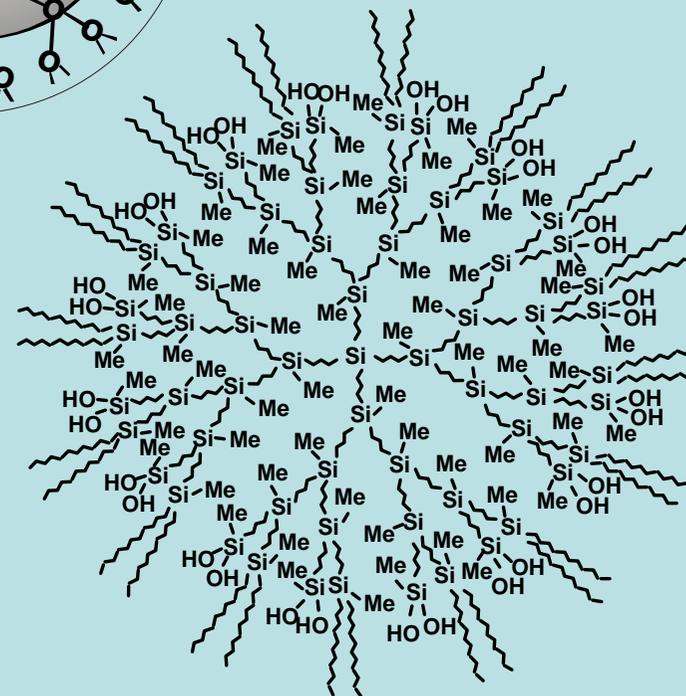


Prof. Crooks R. M.,
USA

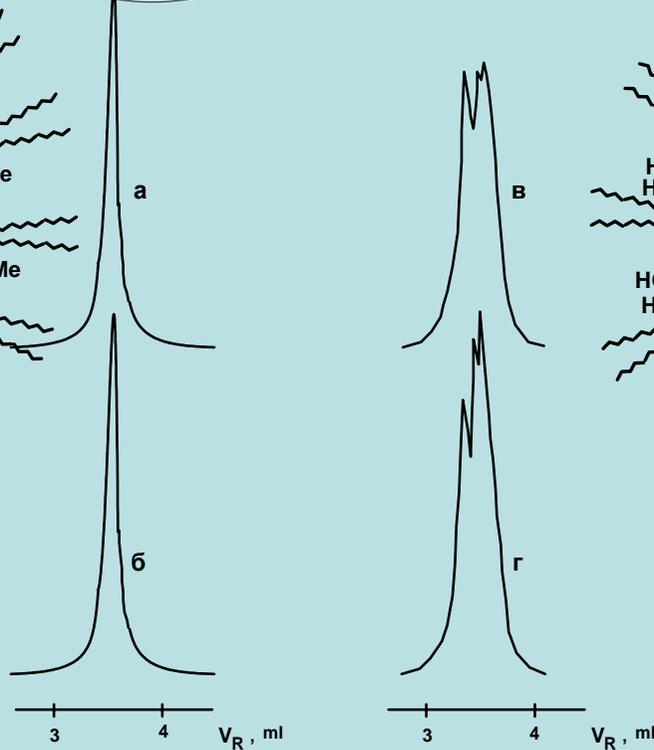
Dr. Balogh L.
USA



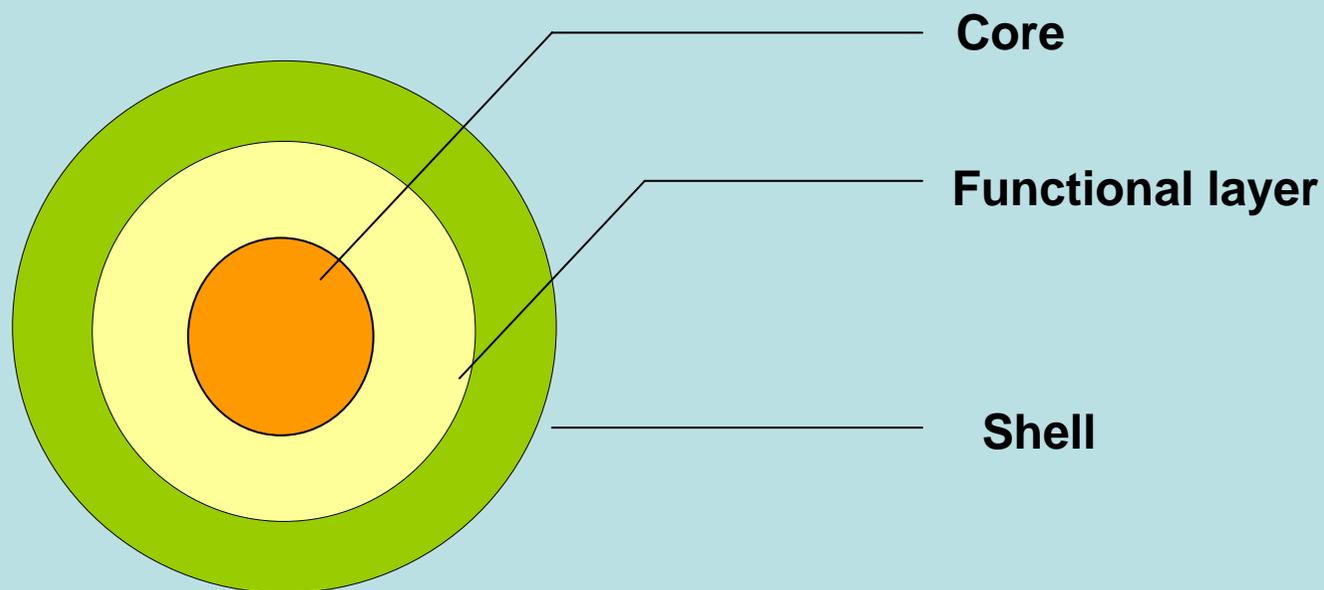
III



IV



Model of dendrimer matrix with active inner sphere



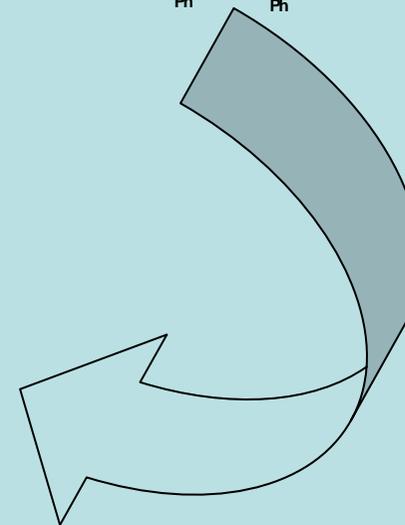
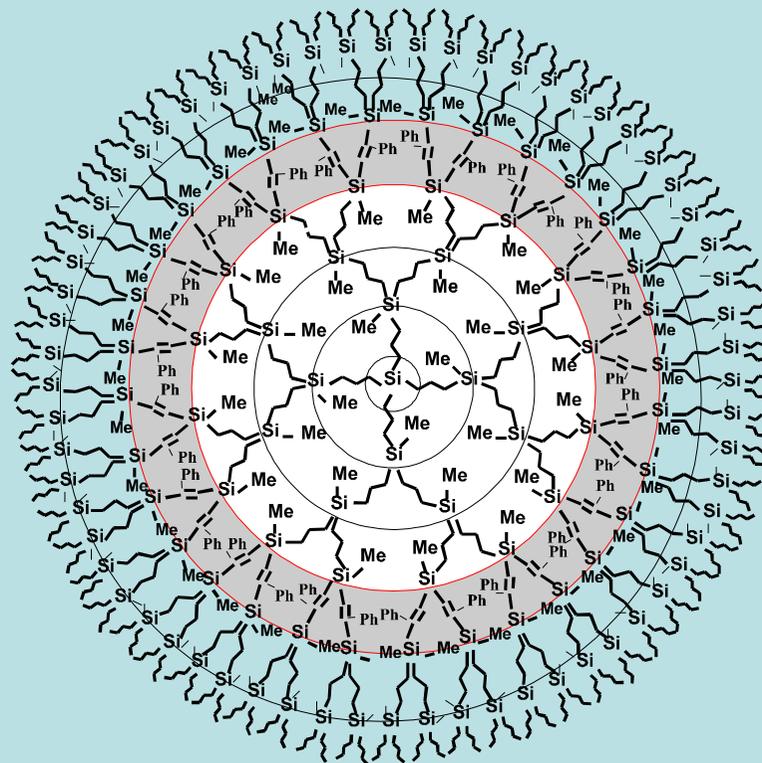
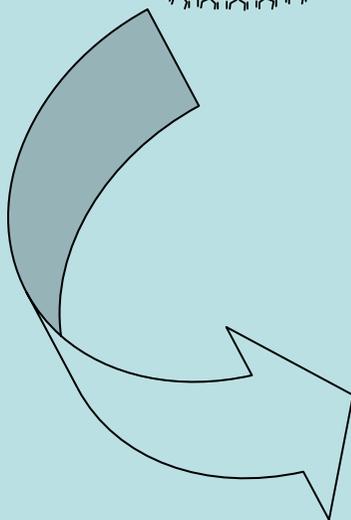
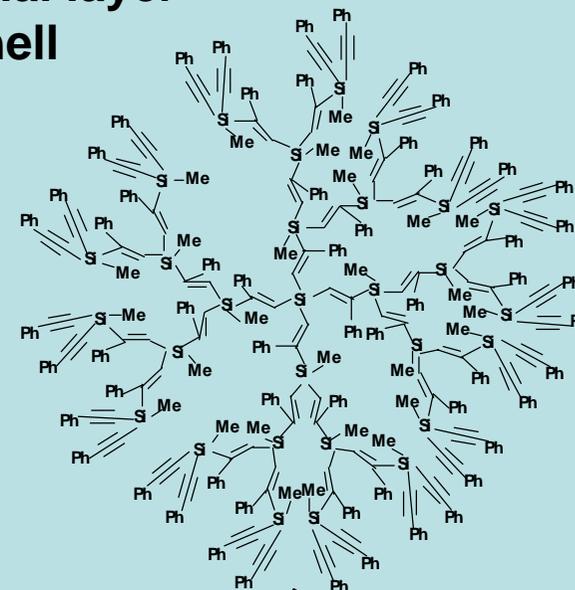
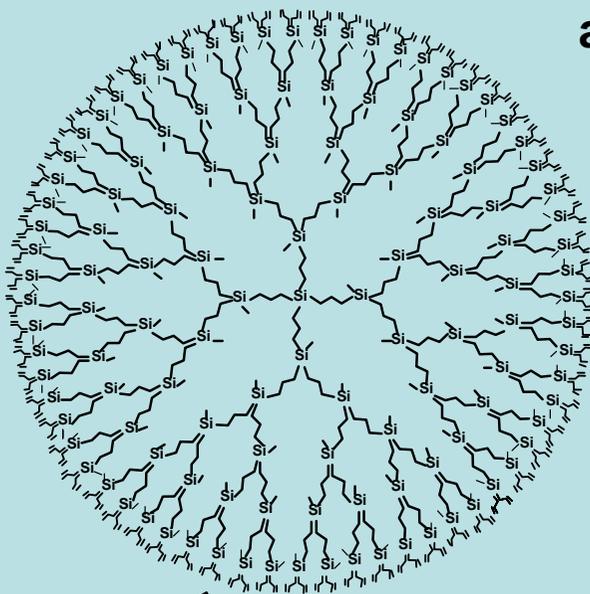
Merits:

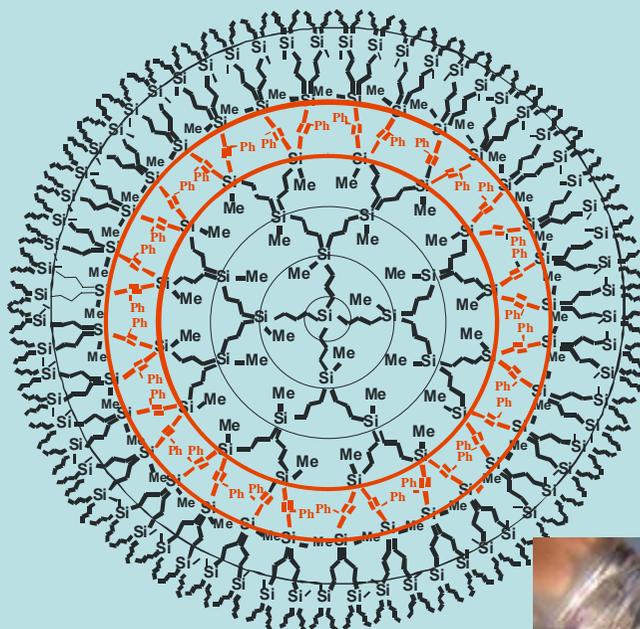
Dendritic clusters are monodispersed

Clusters are stabilized by dendritic structure

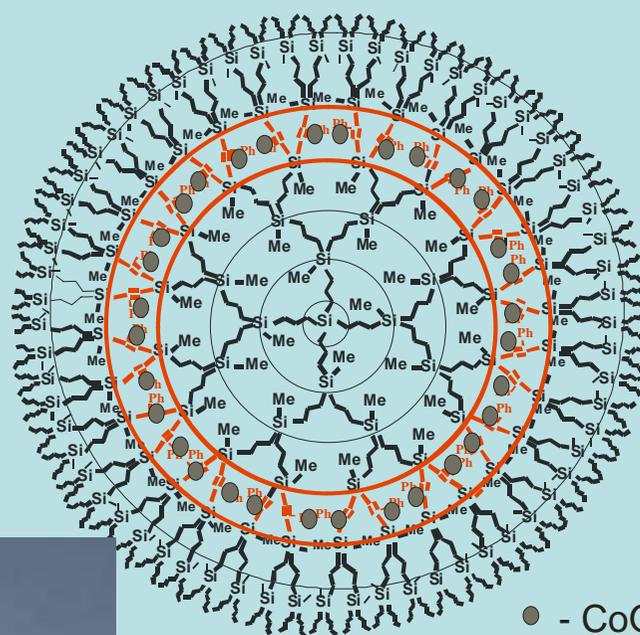
Possibility of cluster localization inside molecule

Dendrimer G5 with inner functional layer and non-functional outer shell



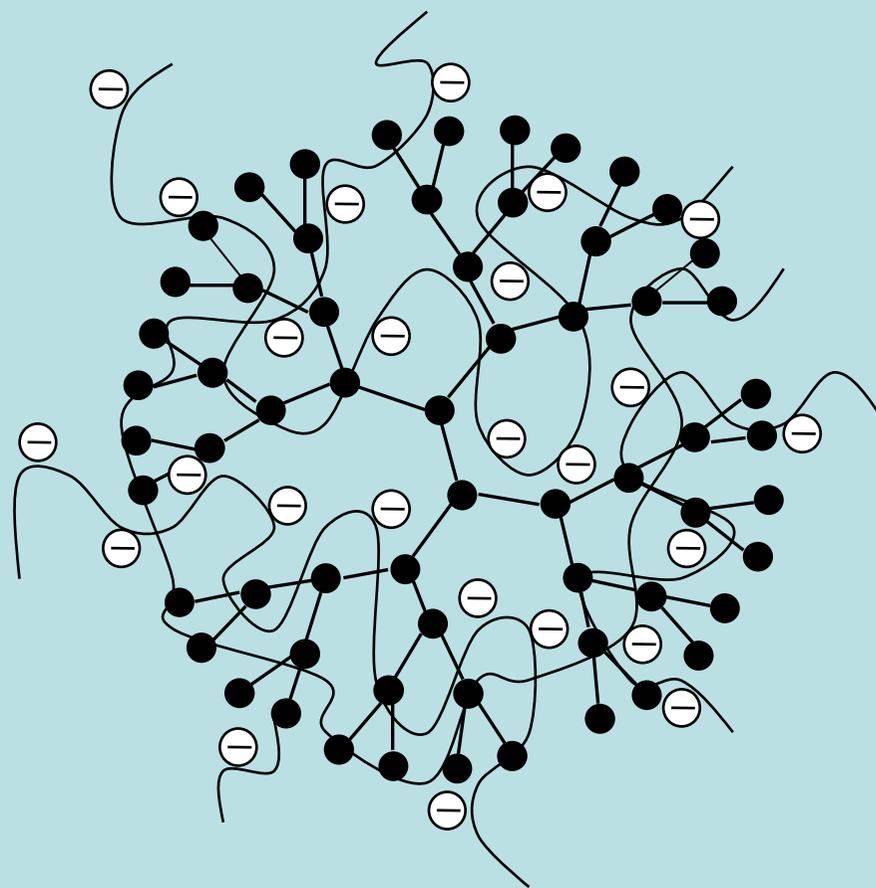


G5 (Bu)

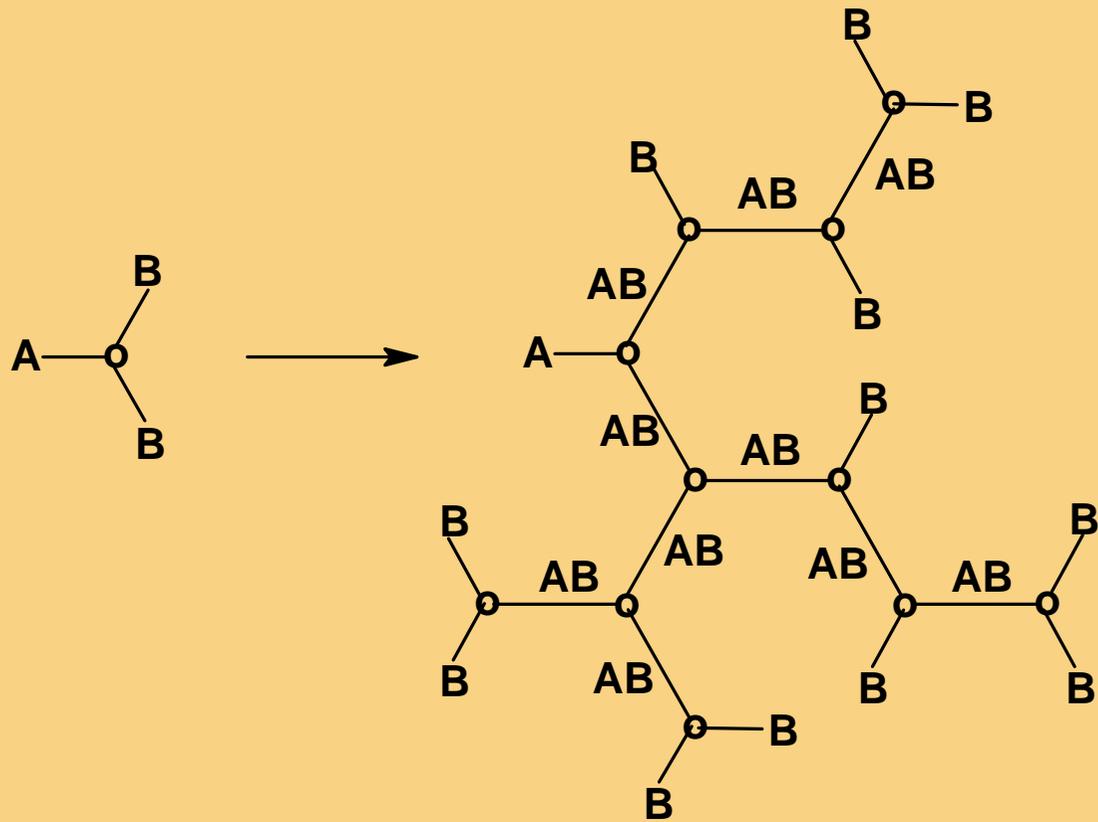


G5 (Bu)+CoO

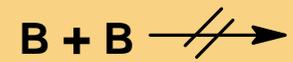
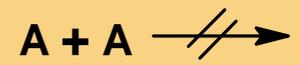




Kabanov V.A., Zezin A.B., Rogacheva V.B., Gulyaeva Zh.G., Zansochova M.F., Joosten J.G.H., Brackman J. Interaction of Astramol poly(propyleneimine) dendrimers with linear polyanions//Macromolecules, 1999, v. 32, № 6, p.1904-1909.

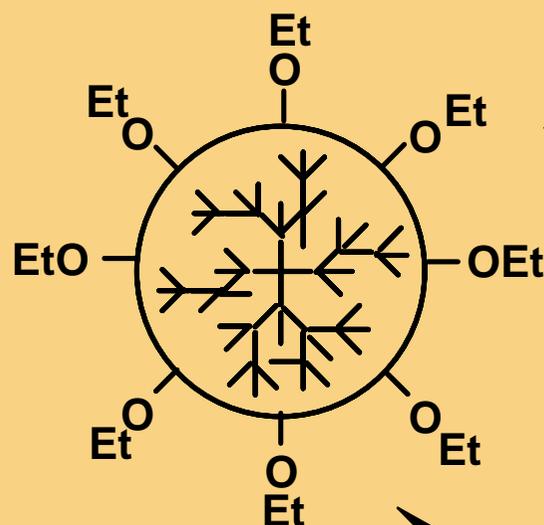
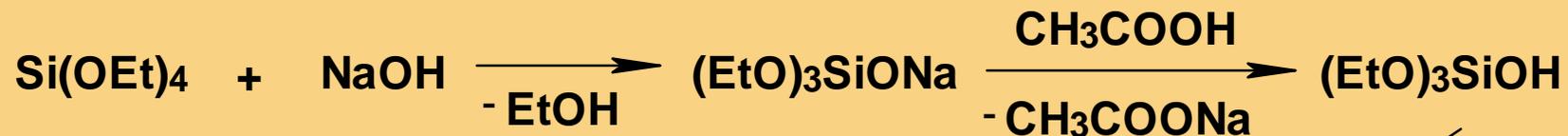


Условия Флори



$$DB = \frac{T+D}{T+D+L}$$

Неорганическая дендритная структура

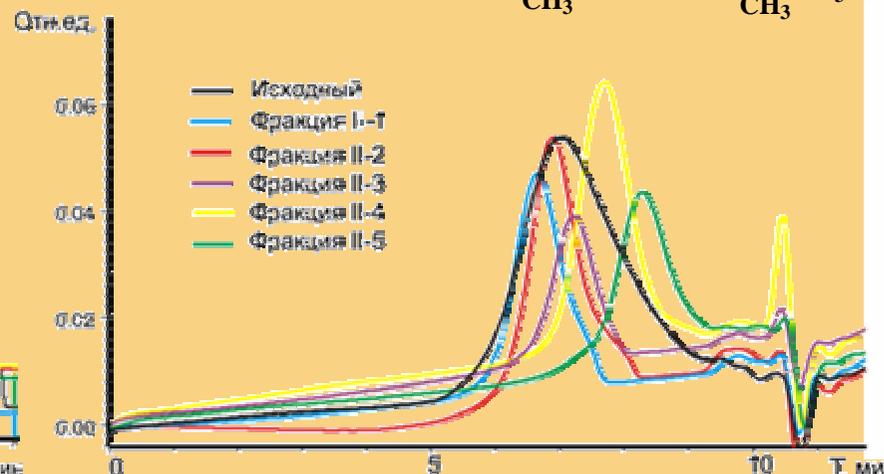
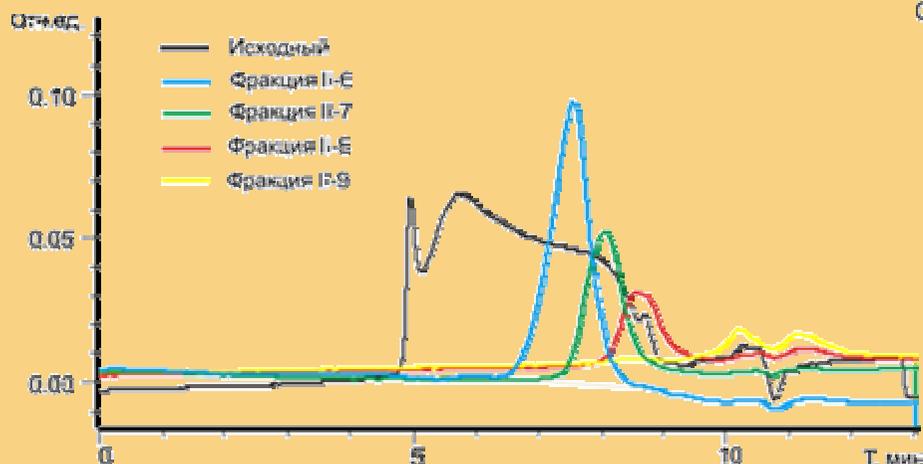
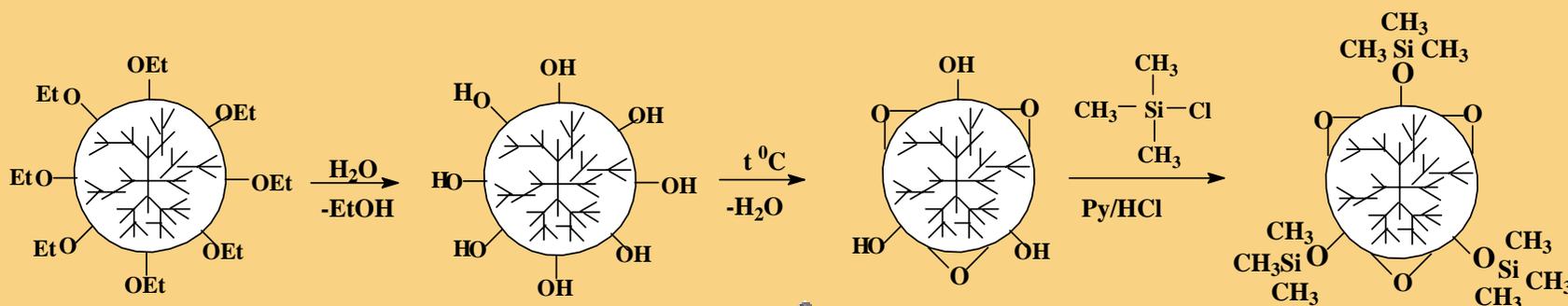
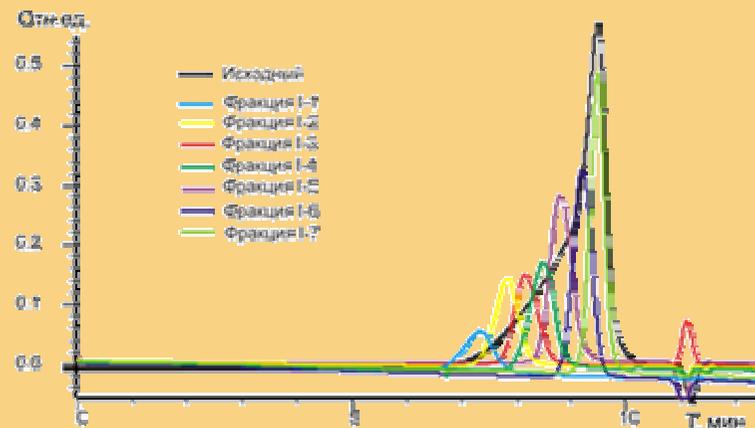
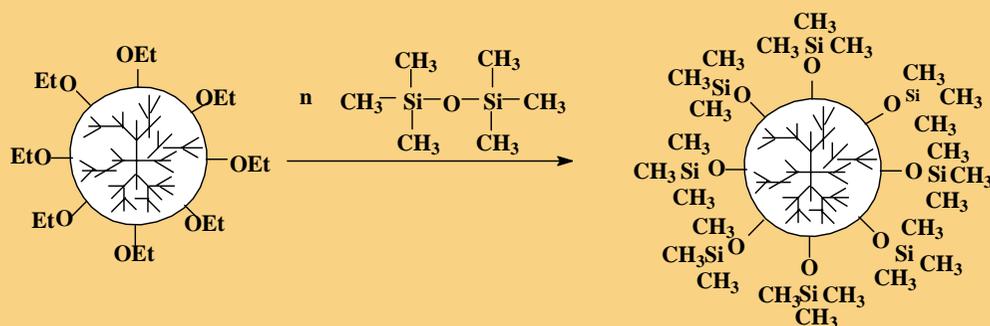


kat.
- EtOH

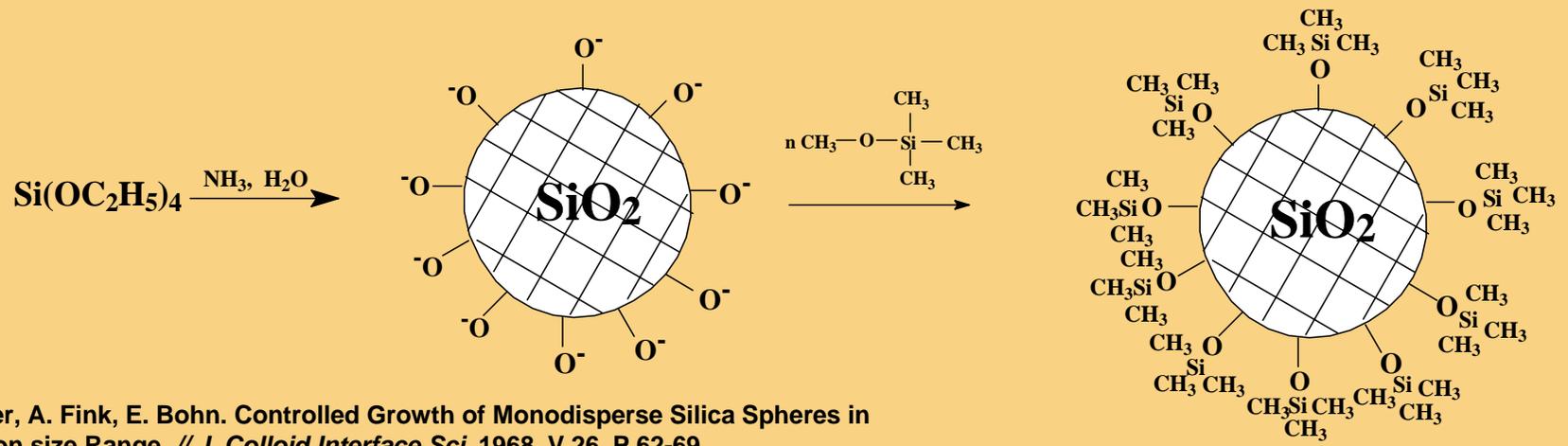
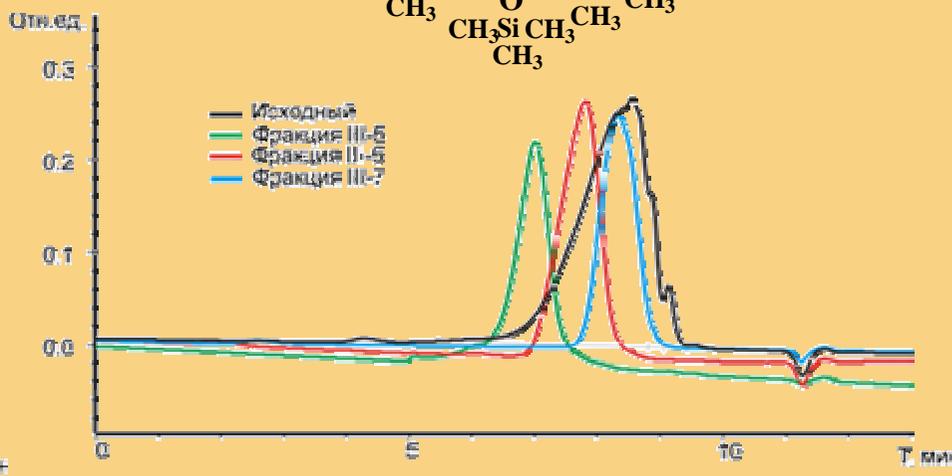
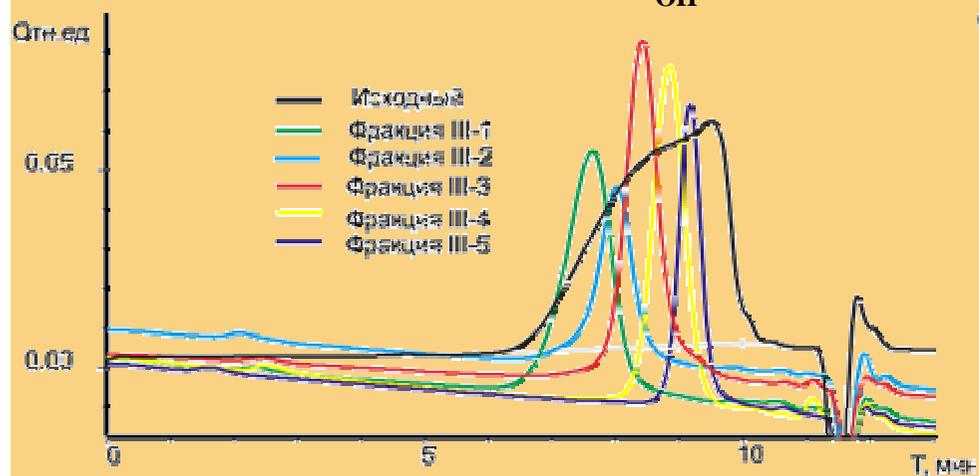
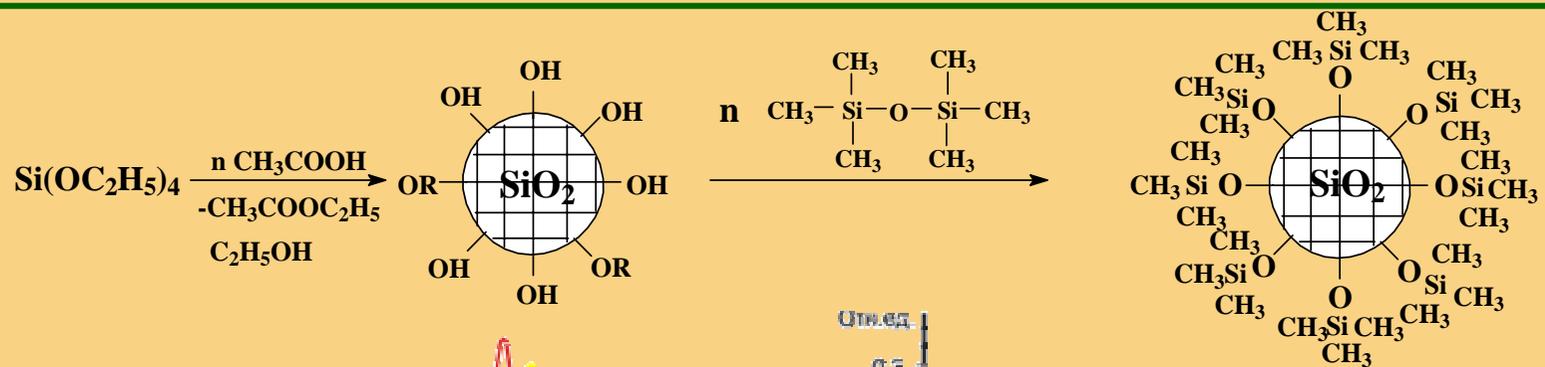


kat.
- CF₃COOEt

Первый и второй способы получения гибридных наночастиц на основе сверхразветвленного полиэтоксисилоксана и силиказоля.

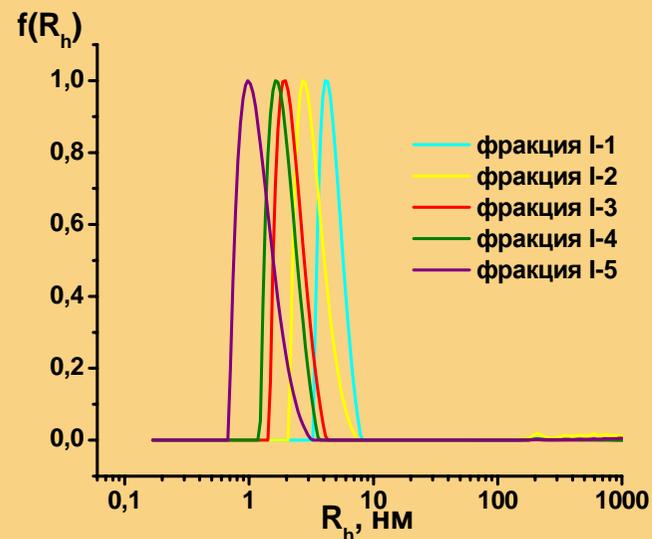
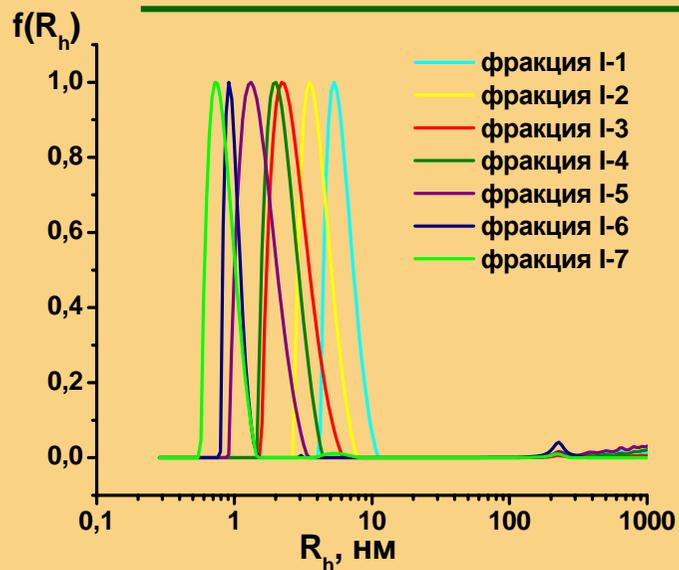


Третий и четвертый способы получения гибридных наночастиц на основе тетраэтоксисилана в кислой и щелочной средах.



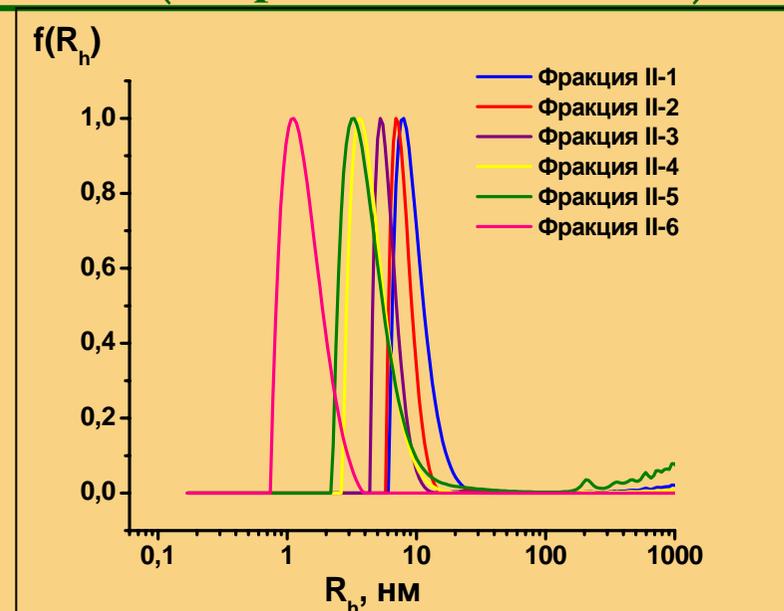
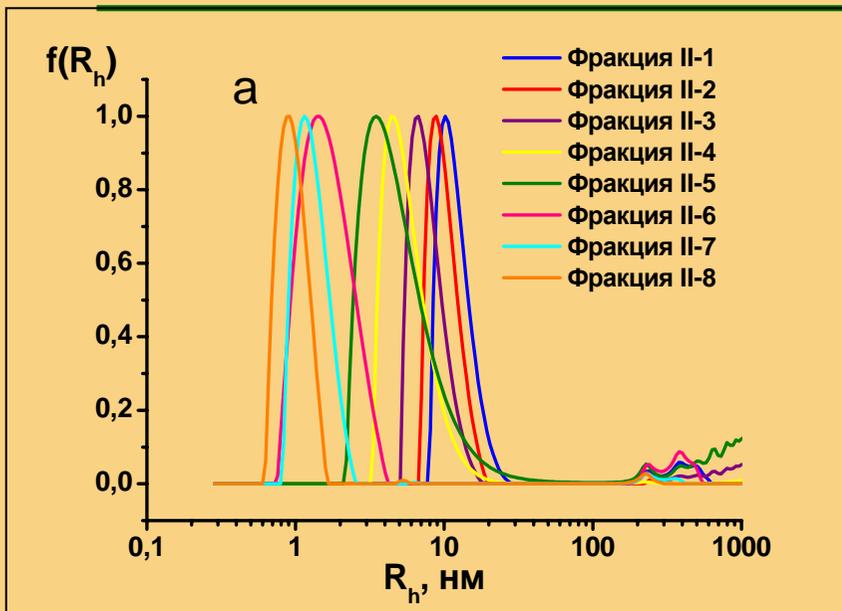
W. Stober, A. Fink, E. Bohn. Controlled Growth of Monodisperse Silica Spheres in the Micron size Range. // *J. Colloid Interface Sci.* 1968, V.26, P.62-69

Гидродинамические свойства наночастиц. Наночастицы на основе полиэтоксисилоксана (первый метод синтеза).



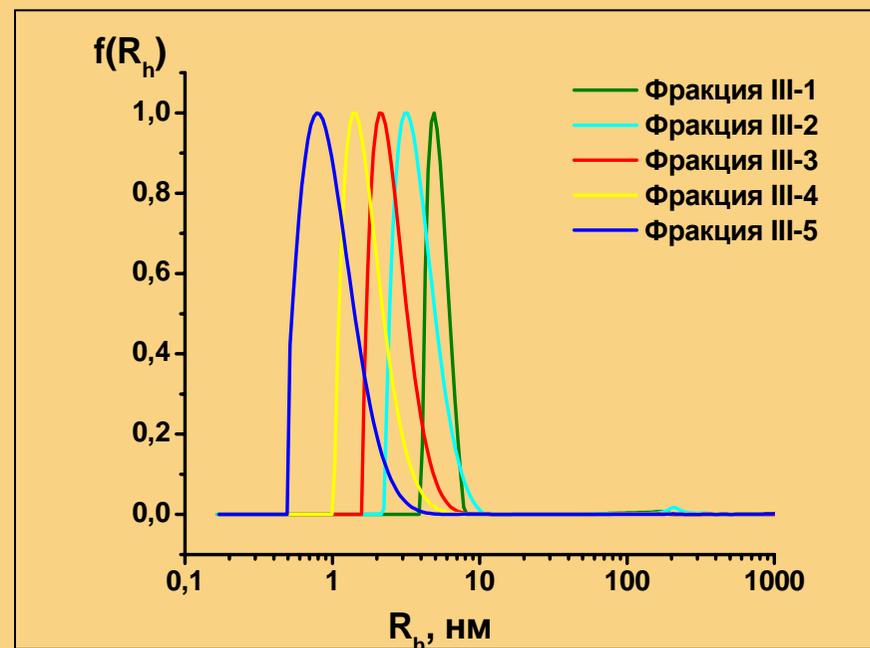
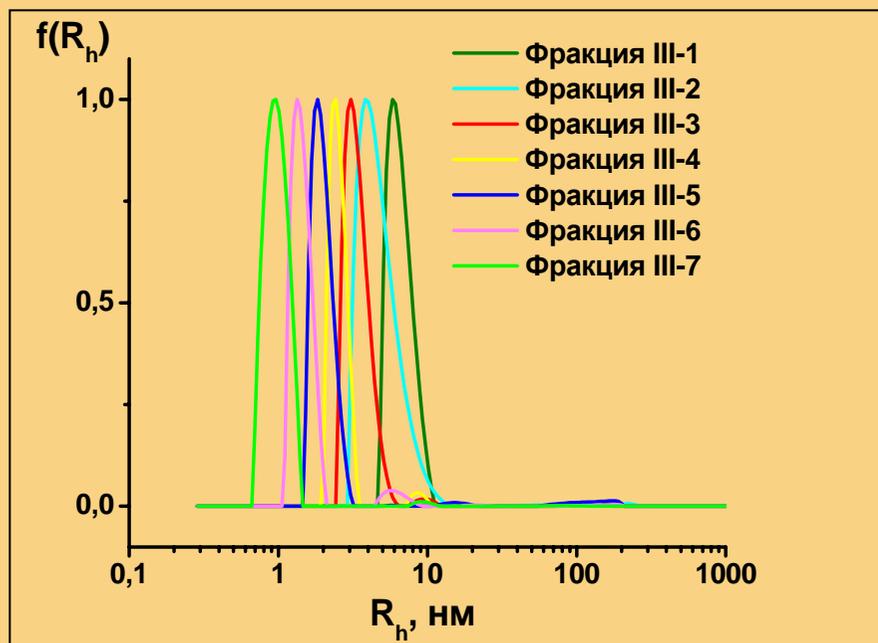
Образец № фракции	M, универсальная калибровка	R, нм (ГПХ) Толуол+2 %ТГФ	R, нм (ДСР) Толуол	R, нм (ДСР) МТБЭ	η (Толуол), дл/г	η (МТБЭ), дл/г
I-1	152000±15000	4,5±0,5	4,1±0,2	5,3±0,3	0,040±0,002	0,061±0,003
I-2	59300±6000	3,0±0,3	2,7±0,2	3,5±0,2	0,033±0,002	0,043±0,002
I-3	34700±3500	2,3±0,2	2,0±0,1	2,2±0,2	0,025±0,001	0,030±0,002
I-4	21500±2000	1,8±0,2	1,7±0,1	2,0±0,1	0,020±0,001	0,028±0,001
I-5	12600±1500	1,4±0,2	1,0±0,1	1,3±0,1	0,017±0,001	0,021±0,001
I-6	6650±1200	1,0±0,2	<1	<1	0,013±0,001	0,019±0,001
I-7	4500±800	0,8	<1	<1	0,010±0,001	0,014±0,001

Наночастицы на основе силиказоля (второй метод синтеза).



Образец	M, универсальная калибровка	R, нм (ГПХ) ТГФ	R, нм (ДСР) Толуол	R, нм (ДСР) МТБЭ	η (Толуол), дл/г	η (МТБЭ), дл/г
№ фракции						
II-1	511000±51000	8,3±0,8	8,0±0,4	10,2±0,5	-	0,072±0,004
II-2	390000±40000	6,9±0,7	7,0±0,4	8,9±0,4	0,055±0,003	0,059±0,003
II-3	220000±22000	5,4±0,5	5,2±0,3	6,7±0,3	0,047±0,002	0,055±0,003
II-4	93000±9000	3,8±0,4	3,6±0,2	4,4±0,2	0,037±0,002	0,041±0,002
II-5	25000±2500	2,4±0,2	3,3±0,2	3,5±0,2	-	-
II-6	11500±1700	1,5±0,2	1,1±0,1	1,5±0,1	0,017±0,001	-
II-7	5000±1000	1,0±0,1	-	1,2±0,1	0,014±0,001	-
II-8	2400±500	0,7±0,1	-	<1	0,012±0,001	-

Наночастицы на основе тетраэтоксисилана (третий метод синтеза).

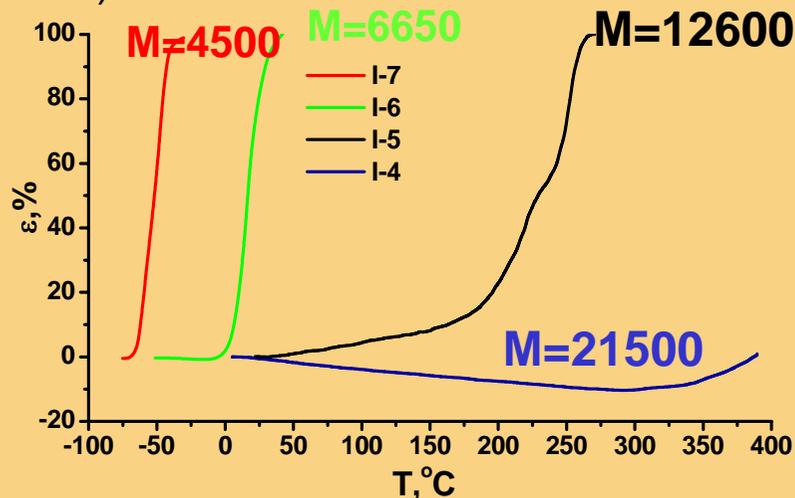


Образец № фракции	M, универсальная калибровка	R, нм (ГПХ)	R, нм (ДСР)	R, нм (ДСР)	η (Толуол), дл/г	η (МТБЭ), дл/г
		Толуол+2 %ТГФ	Толуол	МТБЭ		
III-1	116100±12000	4,5±0,5	4,9±0,2	5,8±0,3	-	0,053±0,003
III-2	61000±6100	3,4±0,3	3,1±0,2	3,8±0,2	-	0,044±0,002
III-3	26800±2700	2,5±0,3	2,1±0,1	3,1±0,2	0,042±0,002	0,042±0,002
III-4	13450±1300	1,8±0,2	1,4±0,1	2,4±0,1	0,033±0,002	0,033±0,002
III-5	8300±1200	1,4±0,2	<1	1,8±0,1	-	-
III-6	7300±1200	1,1±0,2	<1	1,3±0,1	0,019±0,001	0,023±0,001
III-7	3300±700	0,8±0,2	<1	1,0±0,1	0,017±0,001	0,023±0,001

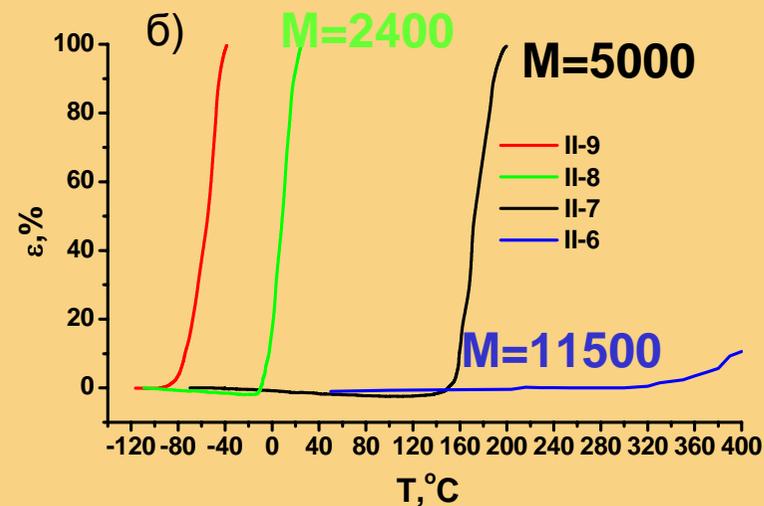
Определение температуры стеклования.

Частицы на основе полиэтоксисилоксана

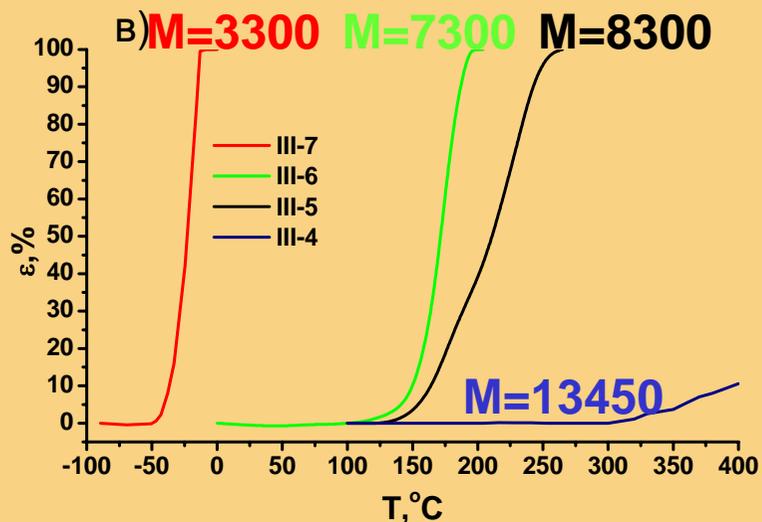
(метод 1)



Частицы на основе силиказоля (метод 2)

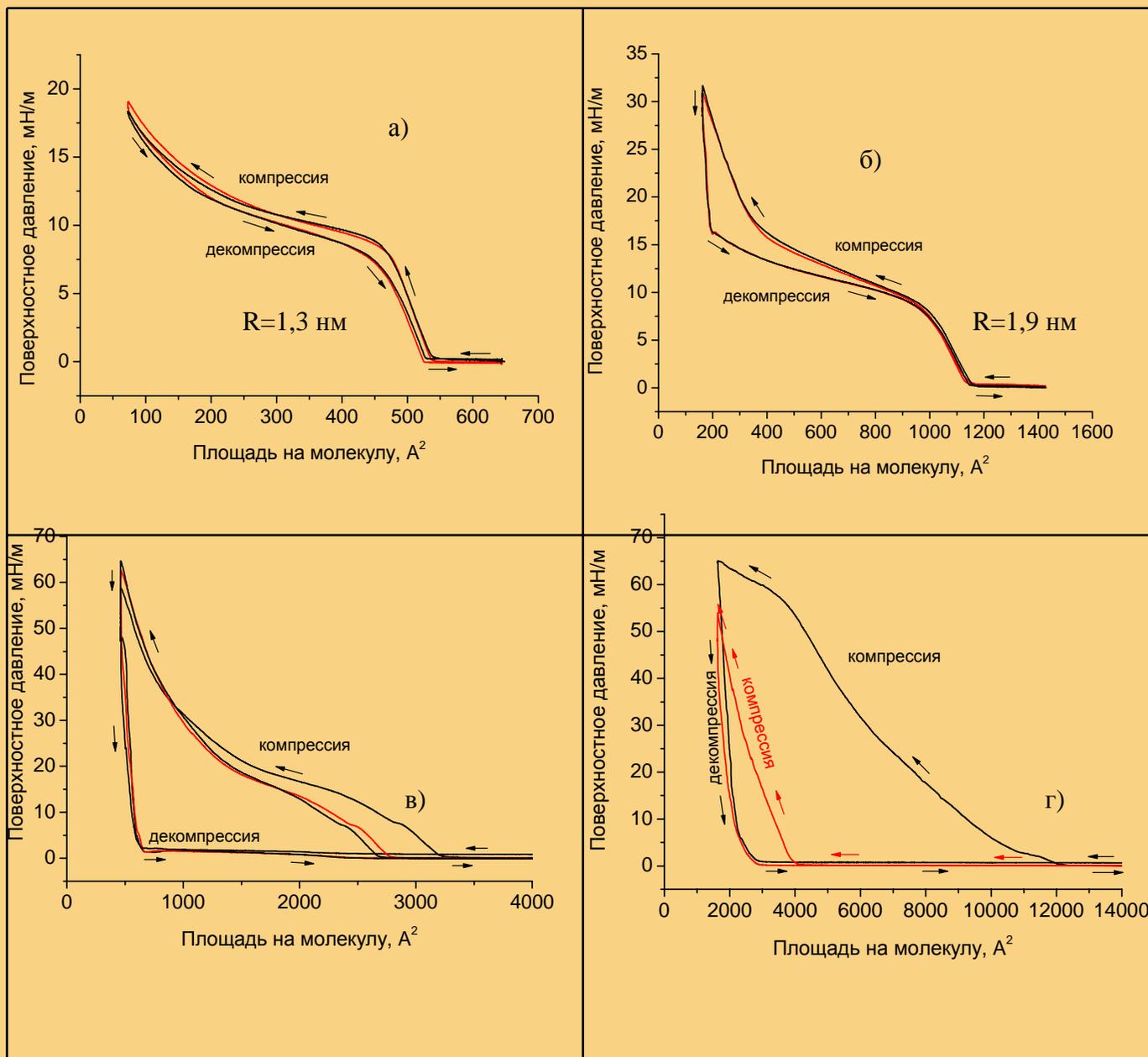


Частицы на основе тетраэтоксисилана
в кислой среде (метод 3)



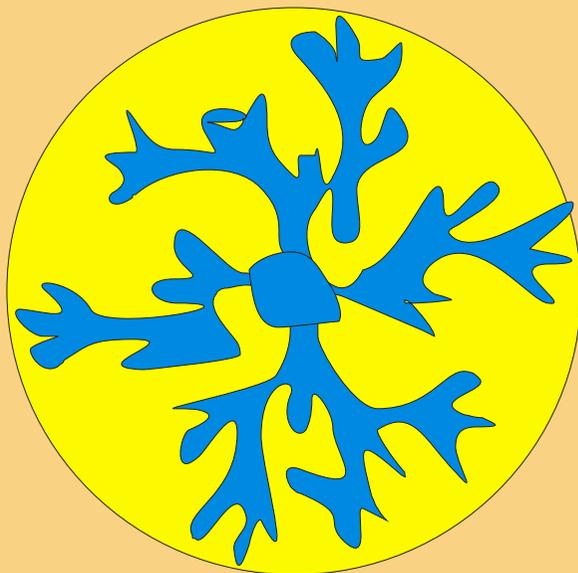
Образец	M	SiO ₂ : (CH ₃) ₃ Si	T _{ст} , °C
I-2	59300	1:0,73	>T _{разл}
I-7	4500	1:1,2	-60
II-4	93000	1:0,5	>T _{разл}
II-8	2400	1:1	0
III-2	61000	1:0,6	>T _{разл}
III-7	3300	1:1,1	-40

Изотермы монослоёв модифицированных кремнеземных частиц на основе тетраэтоксисилана



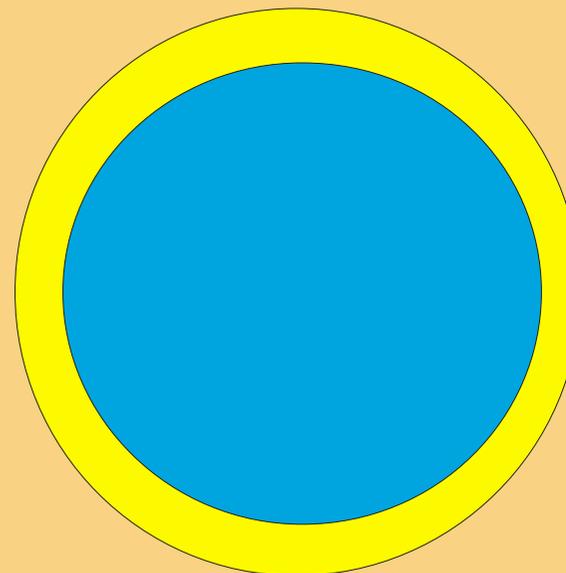
Изотермы поверхностного давления фракций кремнезёмов а)2-3; б)2-2; в)2-1; г)3-1

Модели макромолекулы и частицы.



Макромолекула

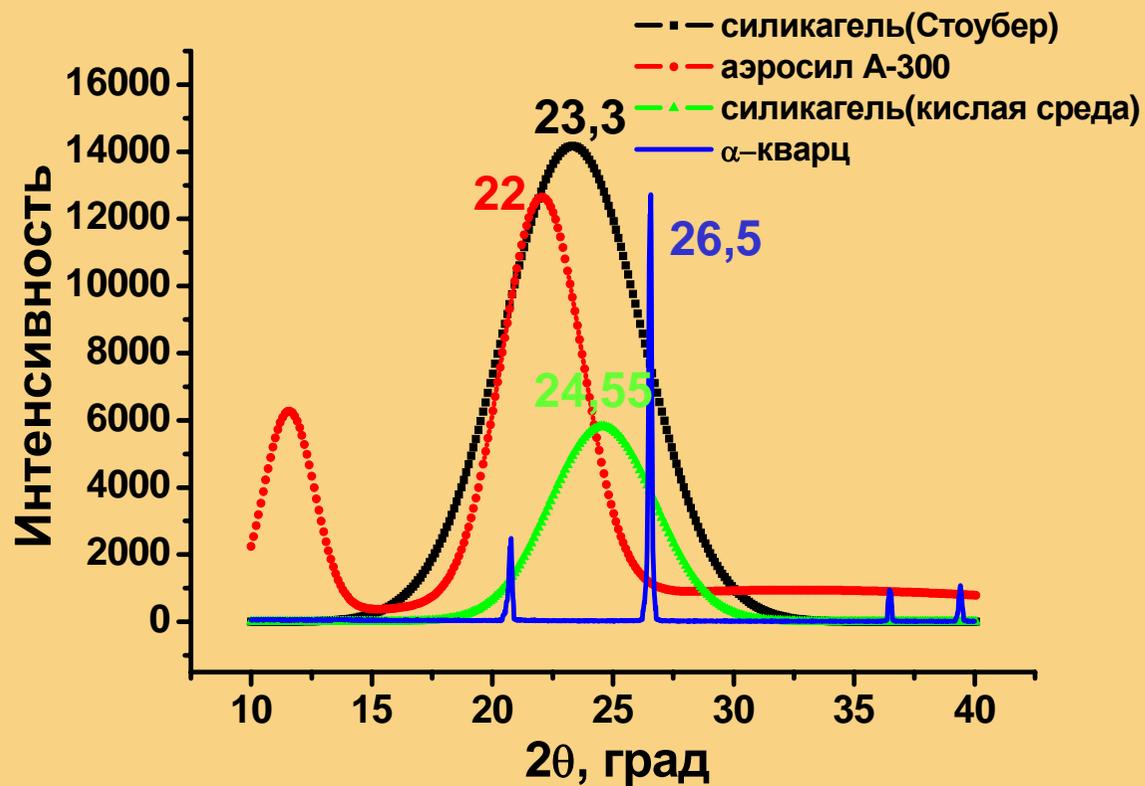
-молекулярная структура
обладает определенной
подвижностью (Тст. <Тразл.)
- полностью сольватируется
растворителем



Частица

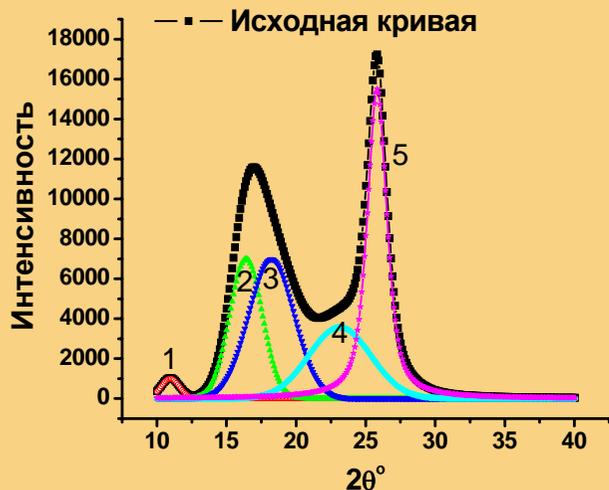
- сольватируется только
поверхностный слой
- ядро жесткая –
частосшитая сетка
(Тст.>Тразл.)

Рентгеновская дифракция в области больших углов



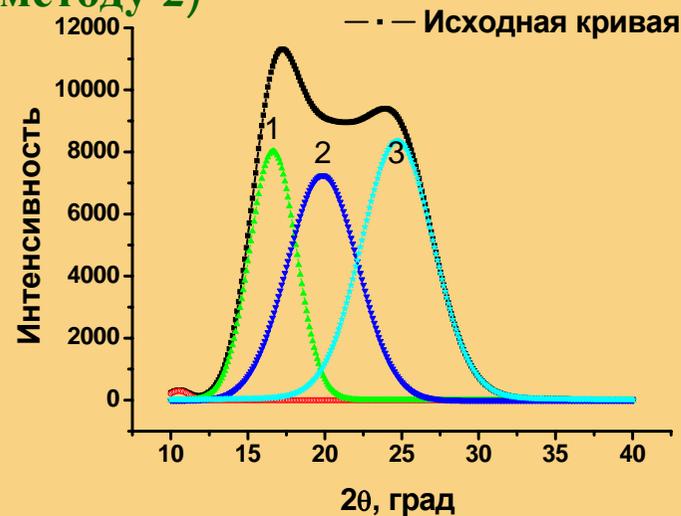
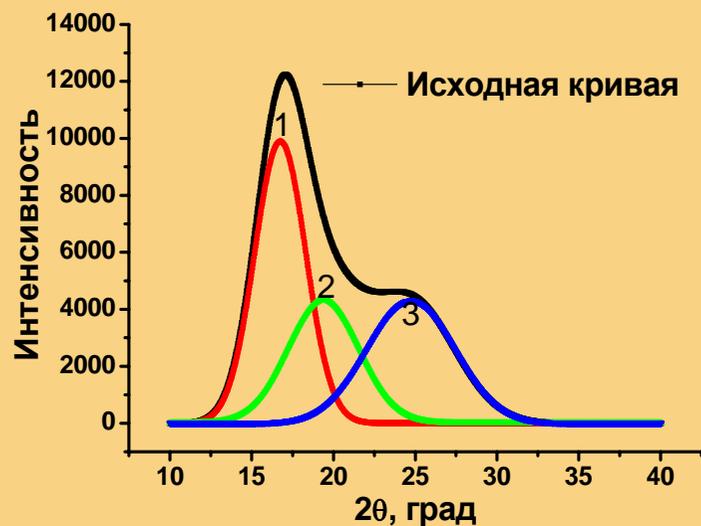
Основной рефлекс α-кварца	Силикагель (кислая среда)	Силикагель (Стоубер)	Аэросил А-300
26,5	24,55	23,3	22

«Полиэтоксисилоксановое» ядро – триметилсилильная оболочка (образцы по методу 1)



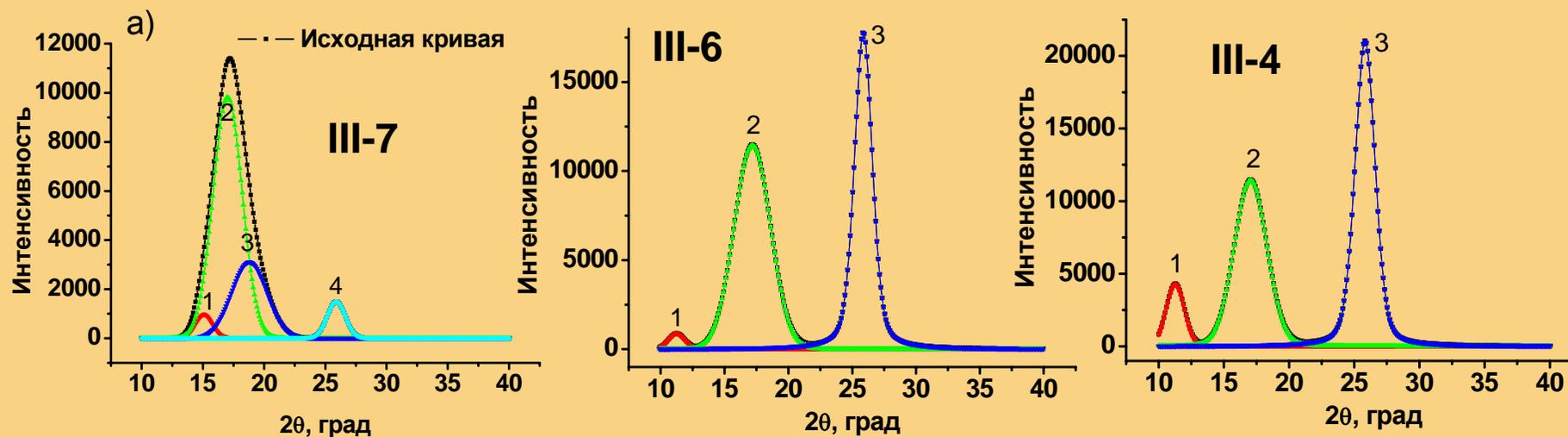
Молек.масса	$T_{ст}$	Содержание SiO_2 , %	$SiO_2:Me_3Si$
59300	$>T_{разл}$	33	1:0,73

Силиказольное ядро – триметилсилильная оболочка (образцы по методу 2)



Молек. масса	$T_{ст}$	C	Содержание SiO_2 , %	$SiO_2:Me_3Si$
2400	0		31,4	1:1
220000	$>T_{разл}$		41	1:1,5

Ядро из «тетраэтоксисилана» – триметилсилильная оболочка. (образцы по методу 3)

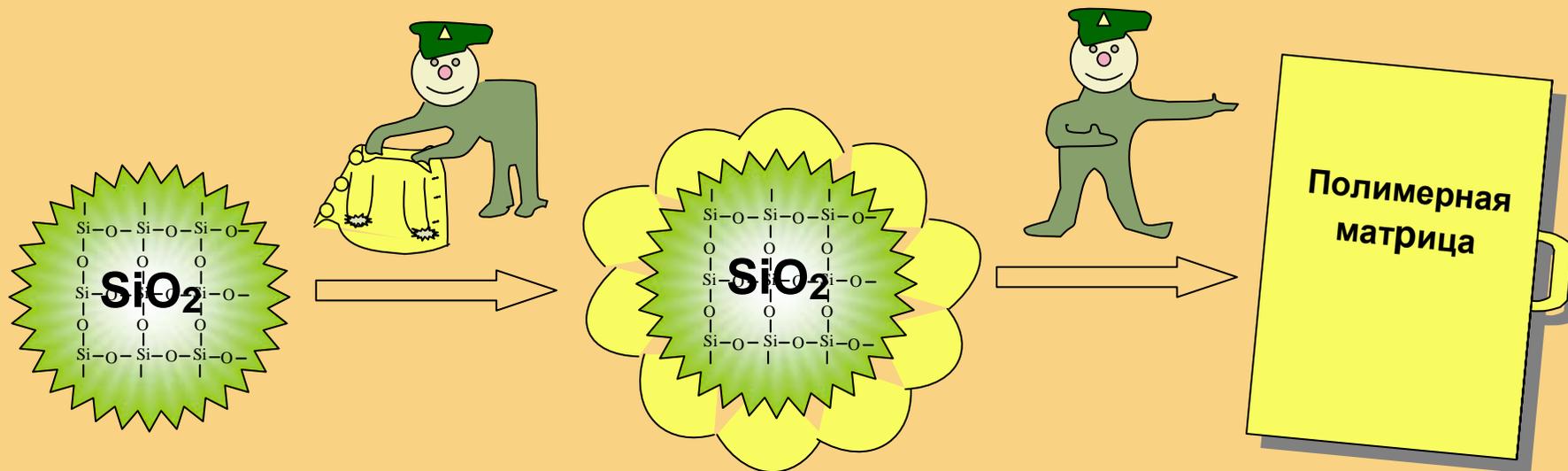


Образец	Вид	Молекулярная масса	$T_{ст}, ^\circ C$	Содержание $SiO_2, \%$	$SiO_2:Me_3Si$
III-7		3300	-50	6,2	1:1,8
III-6		7300	150	46,4	1:1
III-4		13450	$>T_{разл}$	51	1:0,8 ₅₀

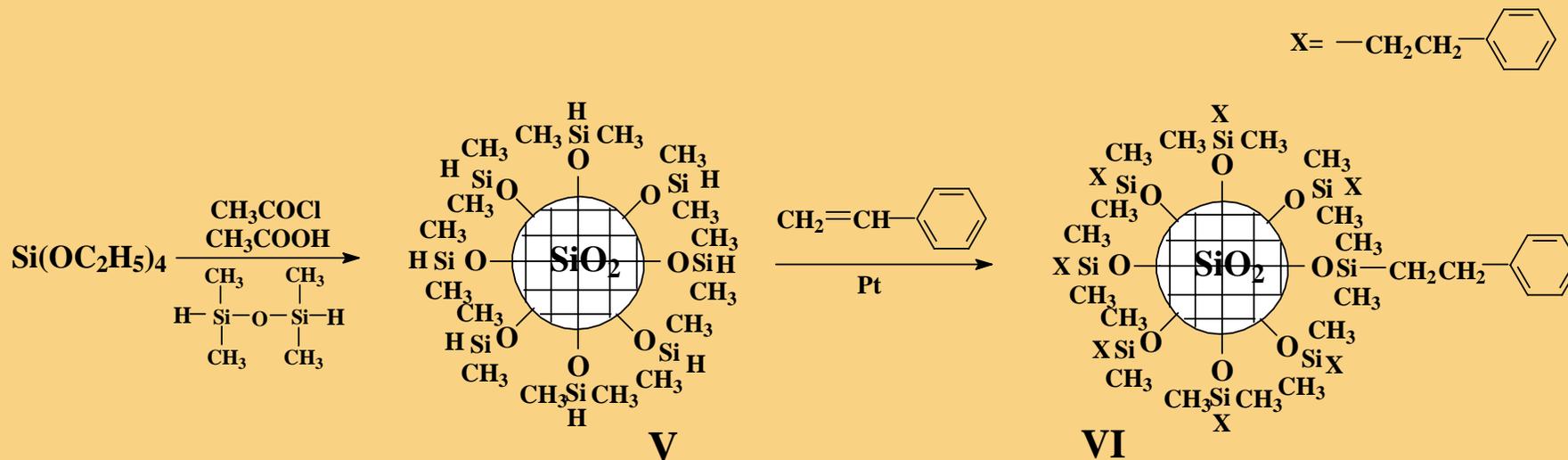
Свойства гибридных наночастиц.

Из полиэтоксисилоксана (первый метод синтеза)				
№	состояние	м.м	R, nm	T _{ст} , C
I-1-I-3	Ч	34700-152000	2-5,3	T _{ст} >T _{разл}
I-4	М-Ч	21500	1,7-2	T _{ст} >T _{разл}
I-5	М	12600	1-1,4	160
I-6	М	6650	1	-5
I-7	М	4500	<1	-60

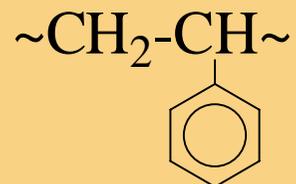
Из силиказоля (второй метод синтеза)					Из тетраэтоксисилана (третий метод синтеза)				
№	состояние	м.м	R, nm	T стекл	№	состояние	м.м	R, nm	T стекл
II-1- II-5	Ч	25000- 512000	2,4-10,2	T _{ст} >T _{разл}	III-1- III-3	Ч	26800- 116100	2,1-5,8	T _{ст} >T _{разл}
II-6	М-Ч	11500	1,1-1,5	T _{ст} >T _{разл}	III-4	М-Ч	13450	1,4-2,4	T _{ст} >T _{разл}
II-7	М	5000	1-1,2	160	III-5	М	8300	1-1,8	170
II-8	М	2400	<1	0	III-6	М	7300	1-1,3	150
II-9	М	-	<1	-80	III-7	М	3300	<1	-50



Синтез кремнезема с 2-фенилэтильными группами для создания нанокompозитов на основе полистирола.

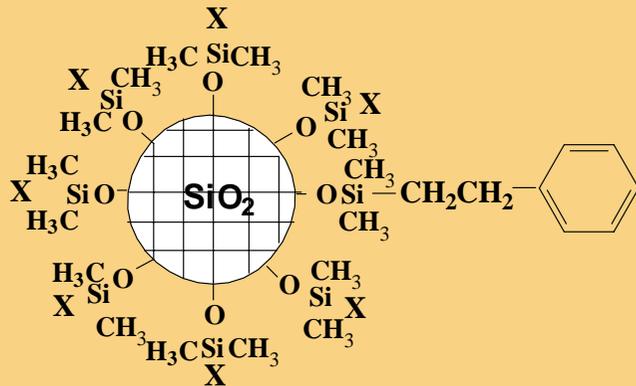


полистирол

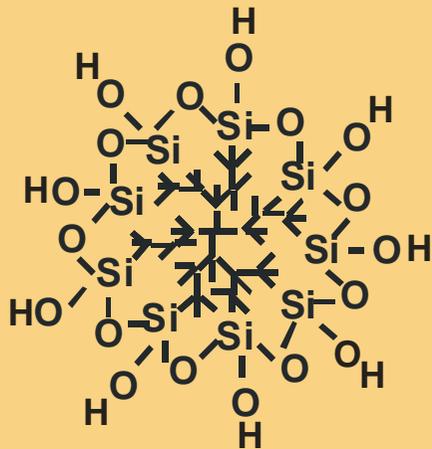


Получение нанокомпозитов на основе полистирола.

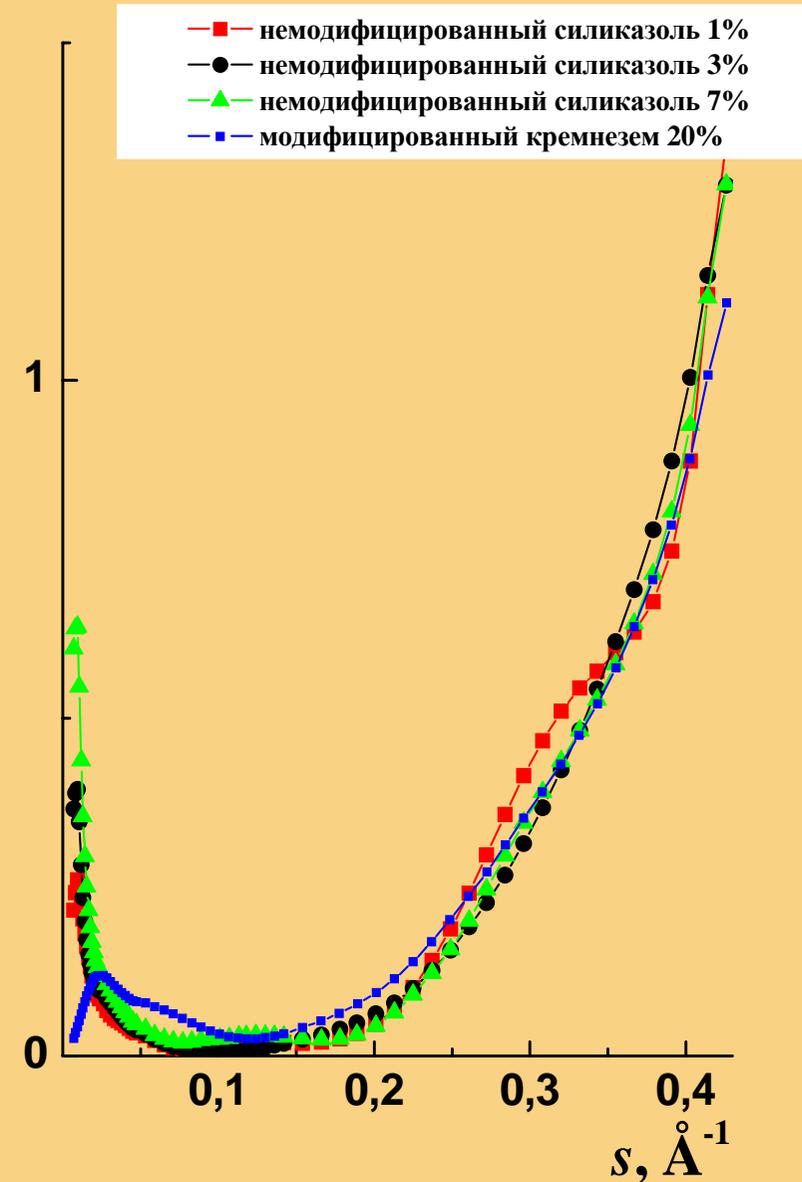
кремнезем, модифицированный
2-фенилэтильными группами

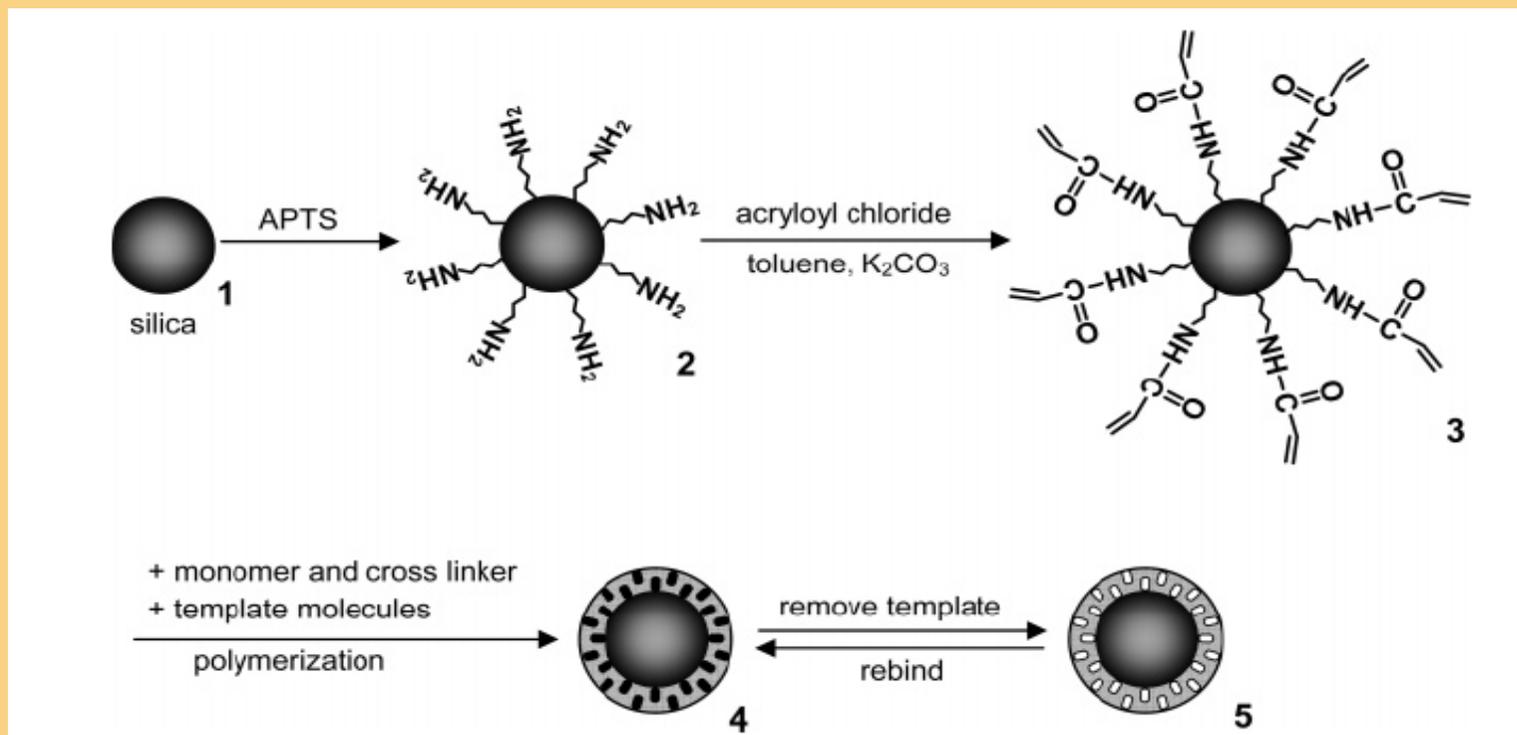


Немодифицированный силиказоль

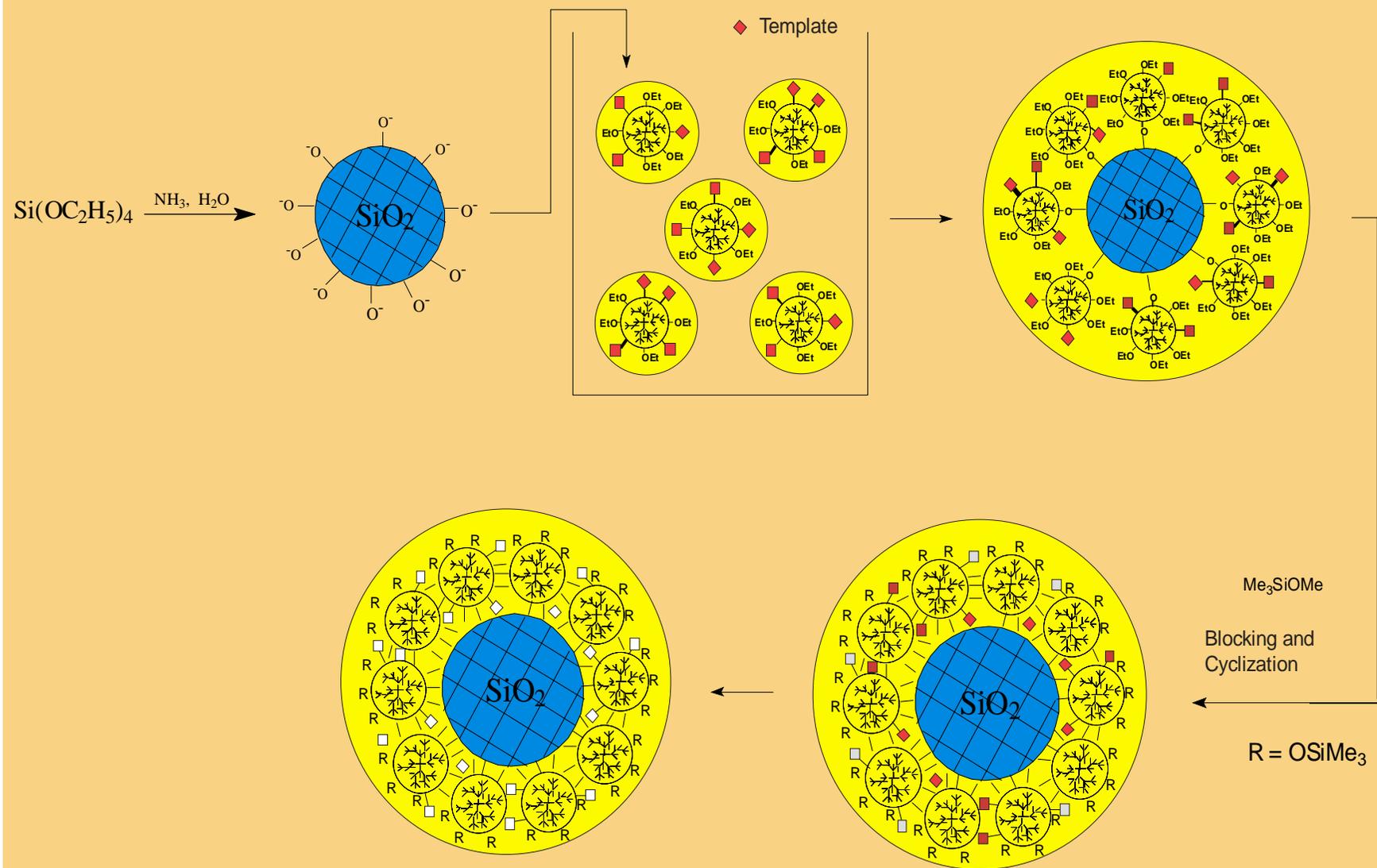


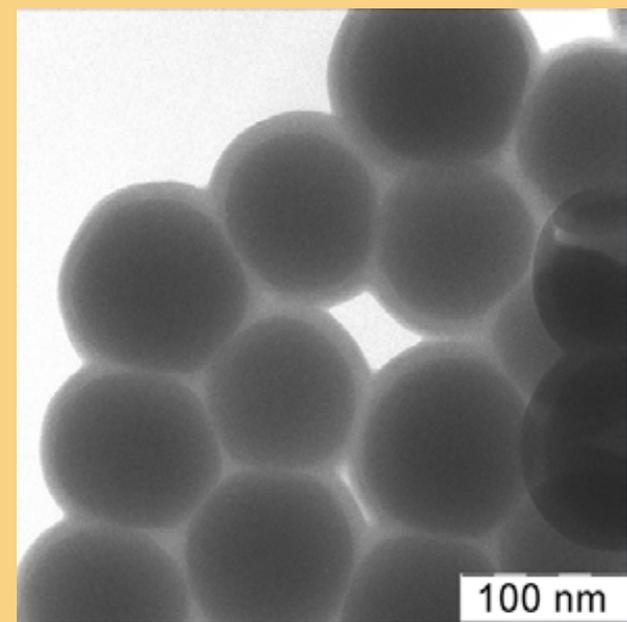
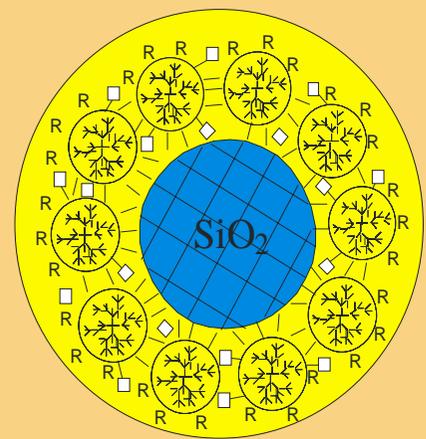
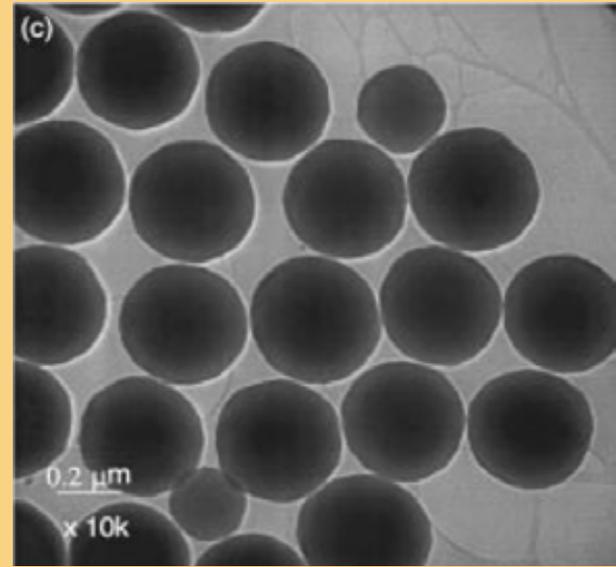
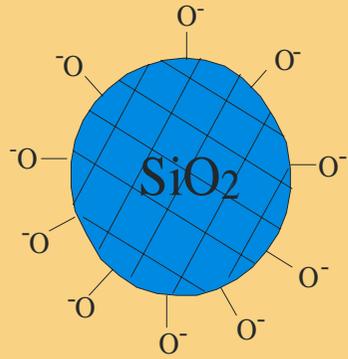
$I*s^2$





D Gao, Z Zhang, M Wu, C Xie G Guan, and D Wang A Surface Functional Monomer-Directing Strategy for Highly Dense Imprinting of TNT at Surface of Silica Nanoparticles. // J. Am. Chem. Soc. 2007, 129, 7859-7866

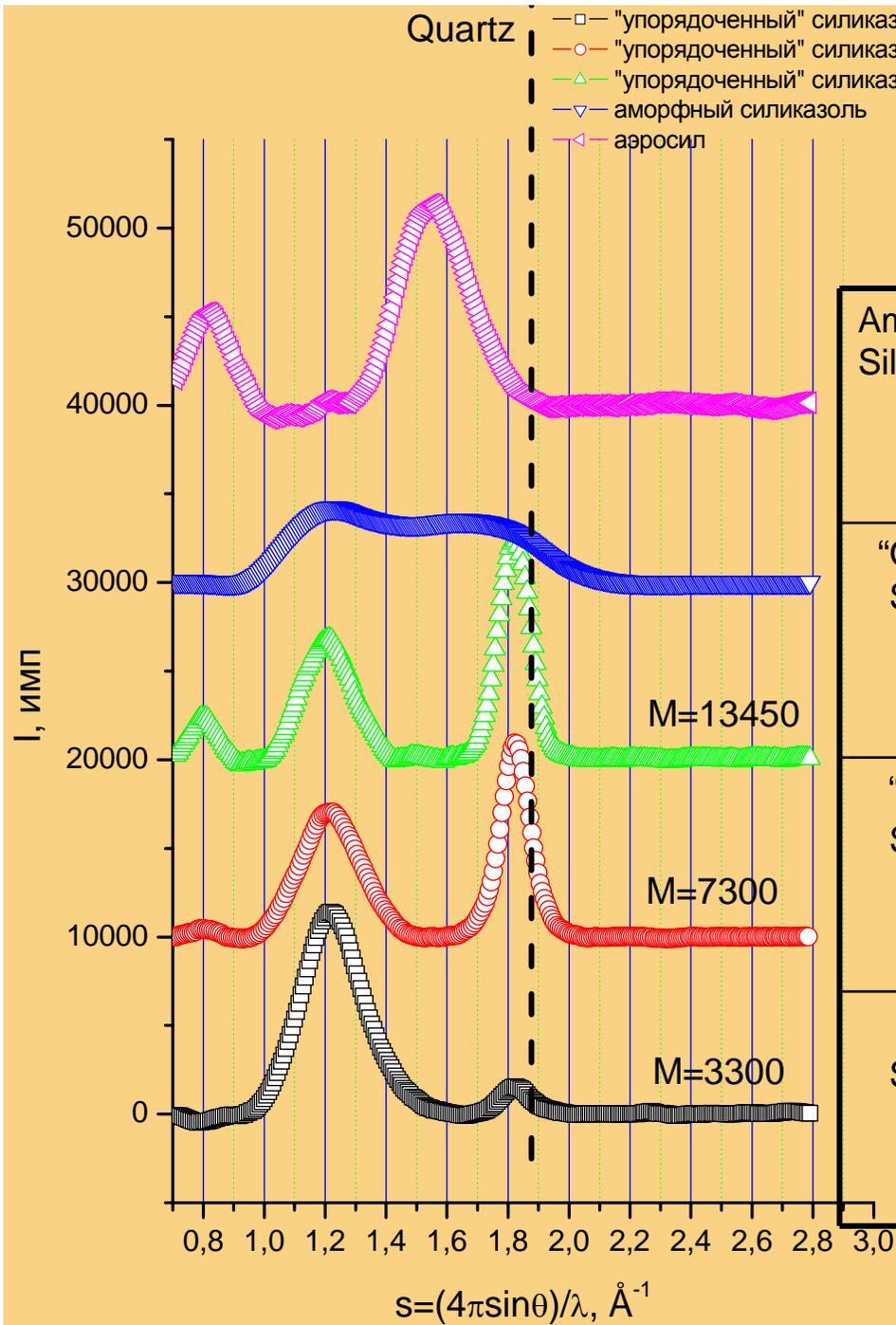




Заключение

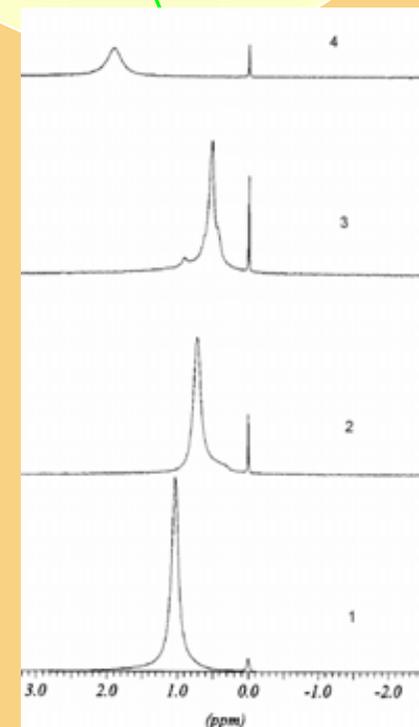
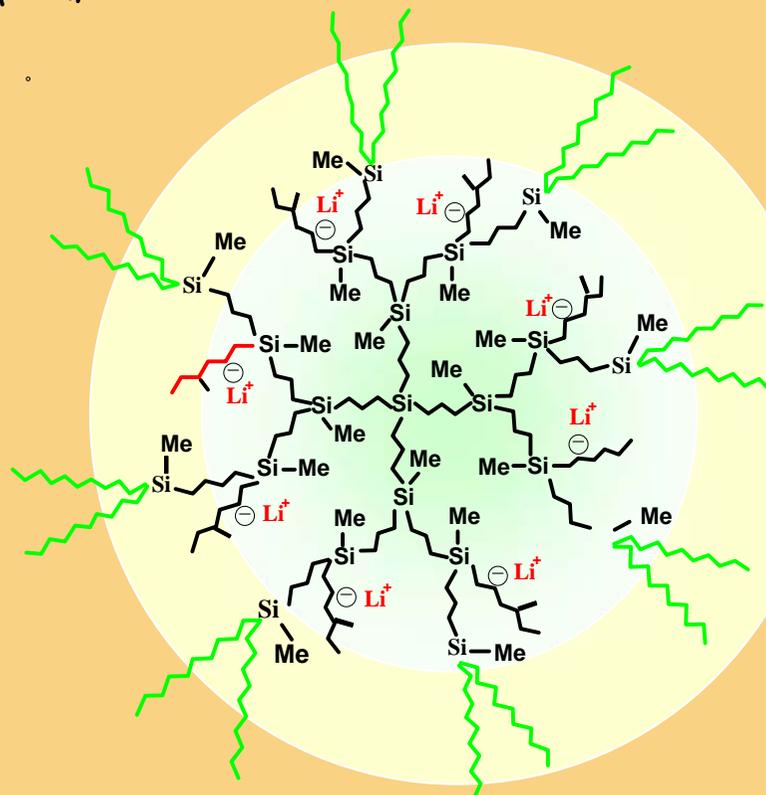
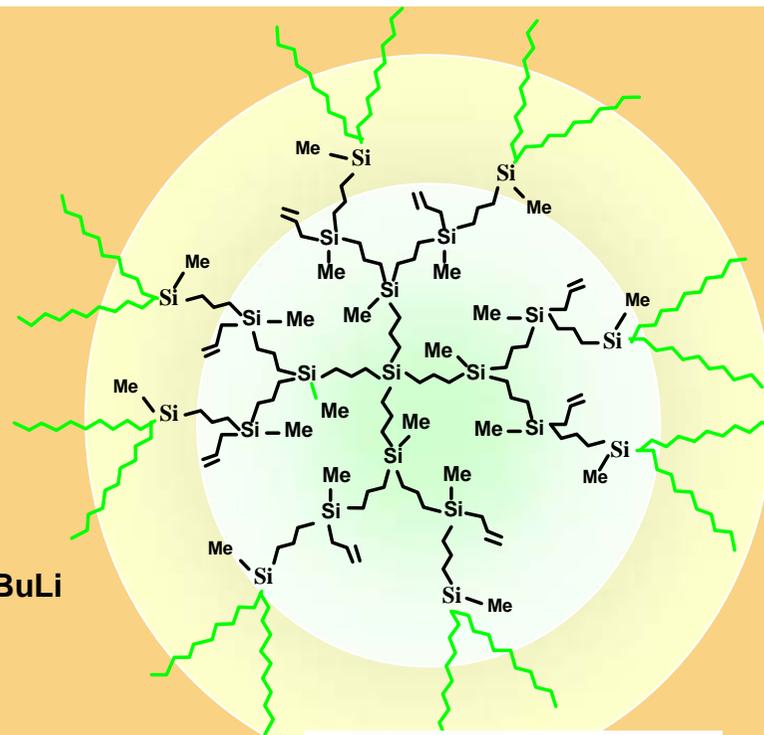
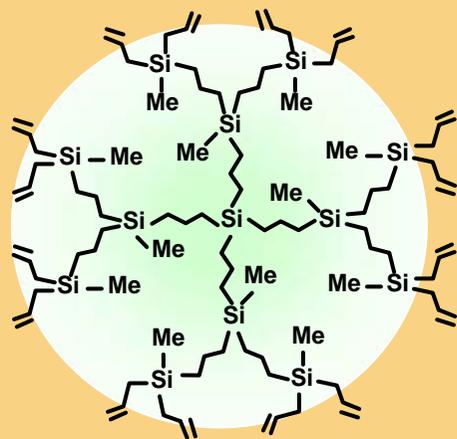
- Синтез и исследование свойств макромолекул- частиц – уникальная образовательная платформа, поскольку предполагает изучение и постоянное переосмысление основ полимерной науки, освоение и создание новых методов синтеза, позволяет моделировать сложнейшие процессы взаимодействия протекающие в полимерных материалах.
- Основная задача, которая стоит перед нами в области полимерных нанокомпозитов, это исследование взаимосвязи размеров и упорядоченности кремнеземного ядра гибридной наночастицы со свойствами полимерного нанокомпозита на ее основе.

Переход макромолекула – частица?

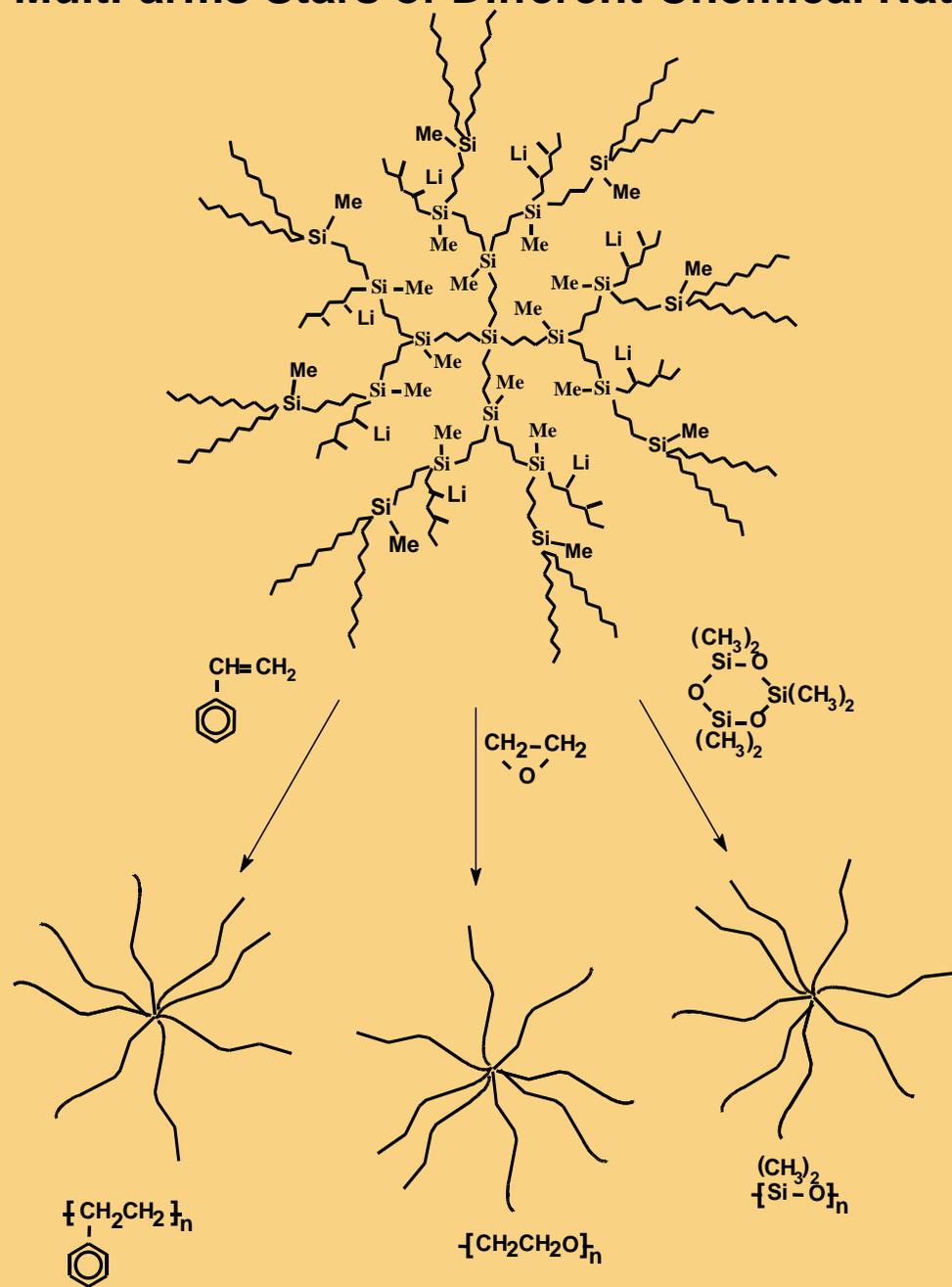


Amorphous Silicasol			$T_g > T_{\text{decomp}}$
"Ordered" Silicasol 3			$T_g > T_{\text{decomp}}$
"Glassy" Silicasol 2			$T_g = 150 \text{ }^\circ\text{C}$
"Liquid" Silicasol 1			$T_g = -50 \text{ }^\circ\text{C}$

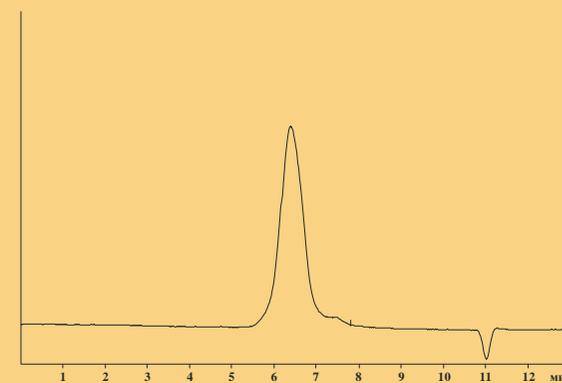
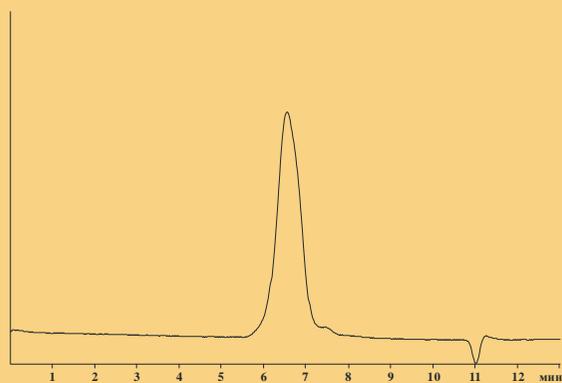
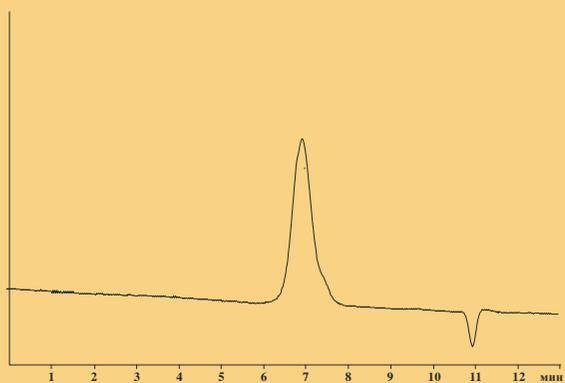
Synthesis of Polylithium initiators



Multi-arms Stars of Different Chemical Nature

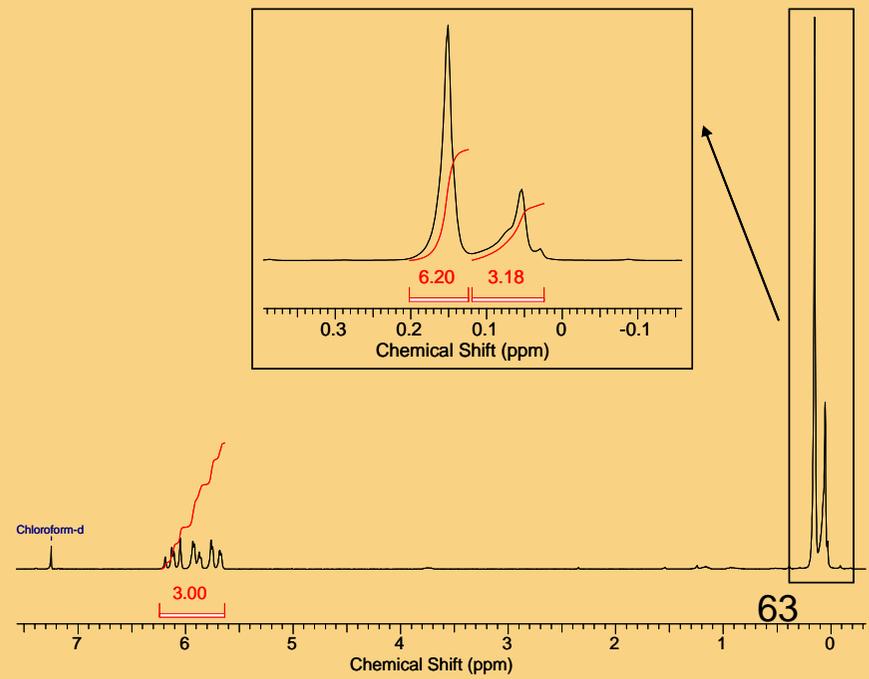
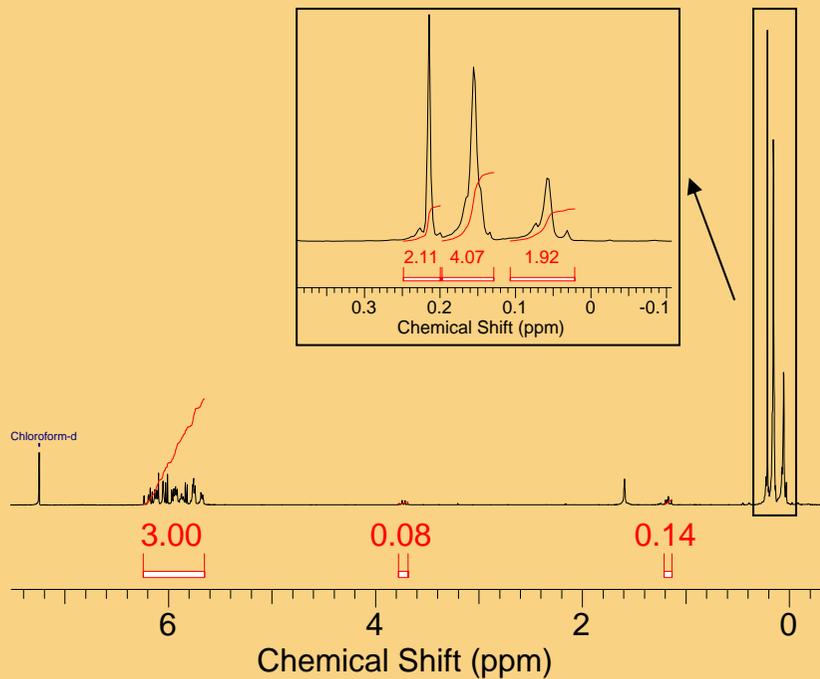
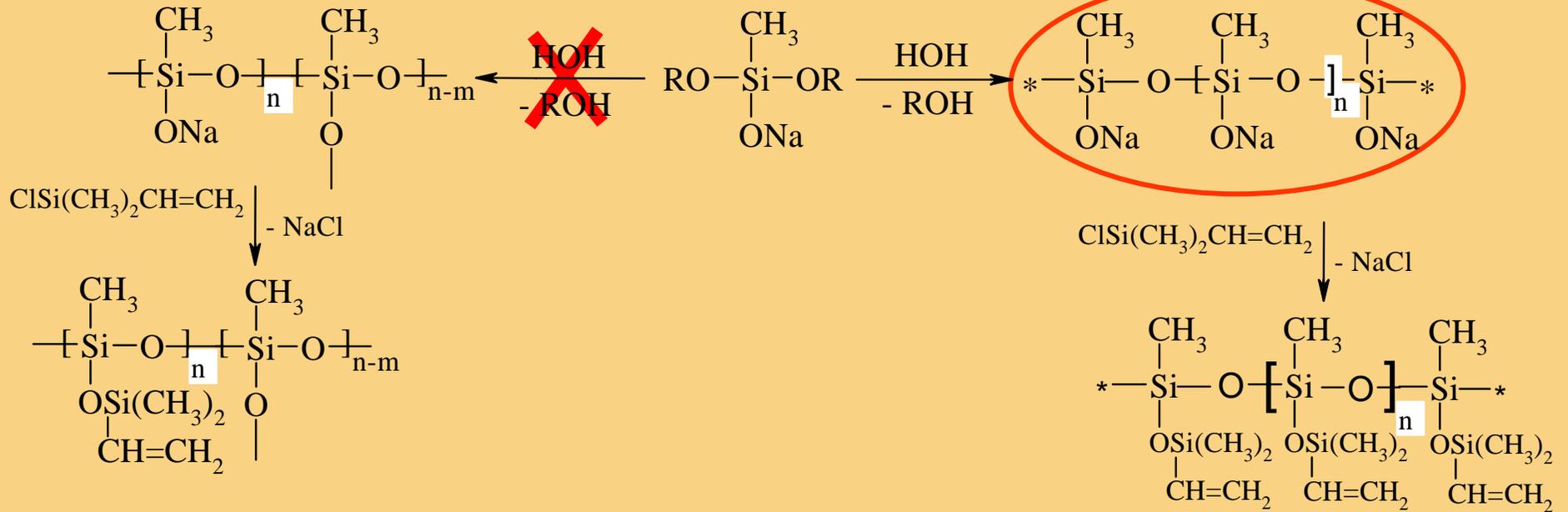


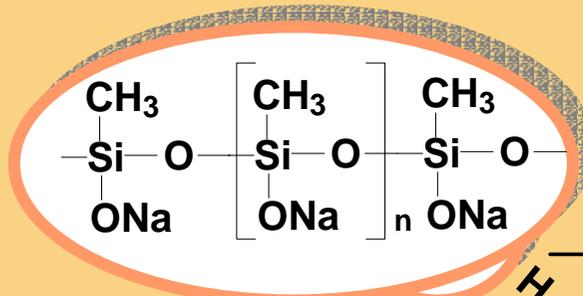
«Российские» 128 лучевые полидиметилсилоксановые звезды



№ опыта	время ч	выход %	конверсия , %	ММ (ГПХ)	ММ (ЯМР)	ММР	звеньев в одном луче	ММ луча
№135.00 1	4	17,2	35	47700	394200	1,11	32	2383
№135.00 2	9	28,3	59	78700	595423	1,15	53	3922
№135.00 3	14	34,0	88	96300	753665	1,18	79	5888
№135.00 4	19	97,6	99	121200	931950	1,23	89	6584

Контроль за эффективностью процесса



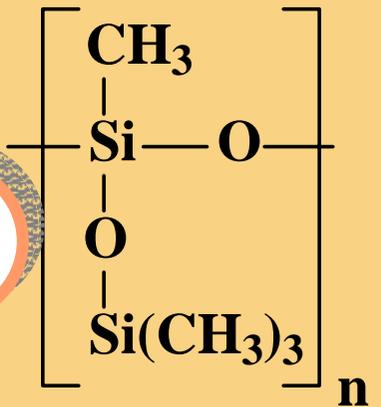


$\downarrow \text{ClSi(CH}_3)_3$

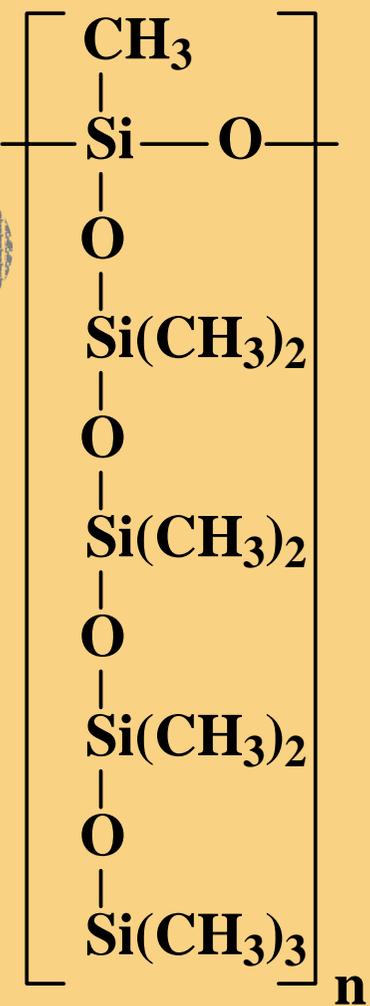
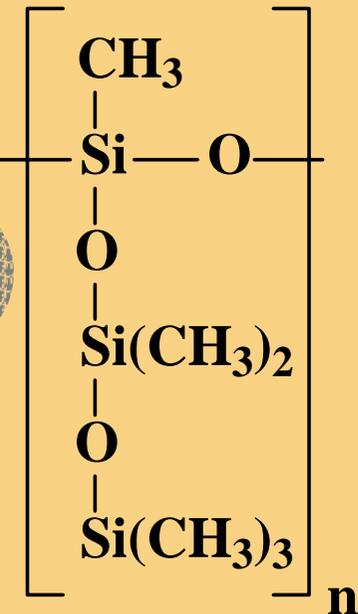
$\downarrow \text{H}_3\text{CC(O)OSi(CH}_3)_3$

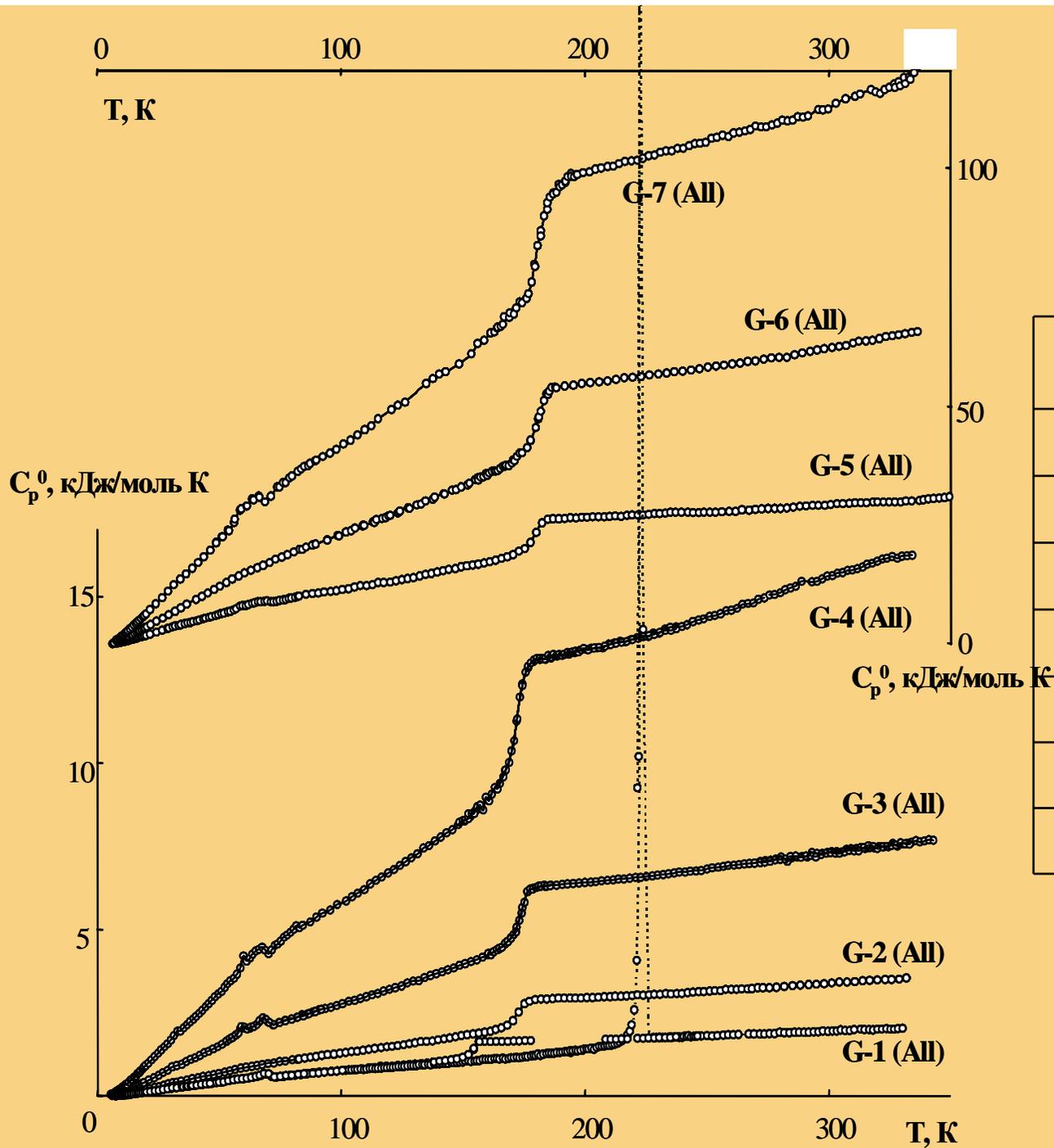
Si 4

Si 1



Si 2





Dendrimer	ΔT , K	T_g° , K
G-1(A11)	150-160	154±1
G-2(A11)	170-180	172±1
G-3(A11)	170-180	172±1
G-4(A11)	170-180	172±1
G-5(A11)	170-180	179±1
G-6(A11)	170-190	180±1
G-7(A11)	170-200	181±1

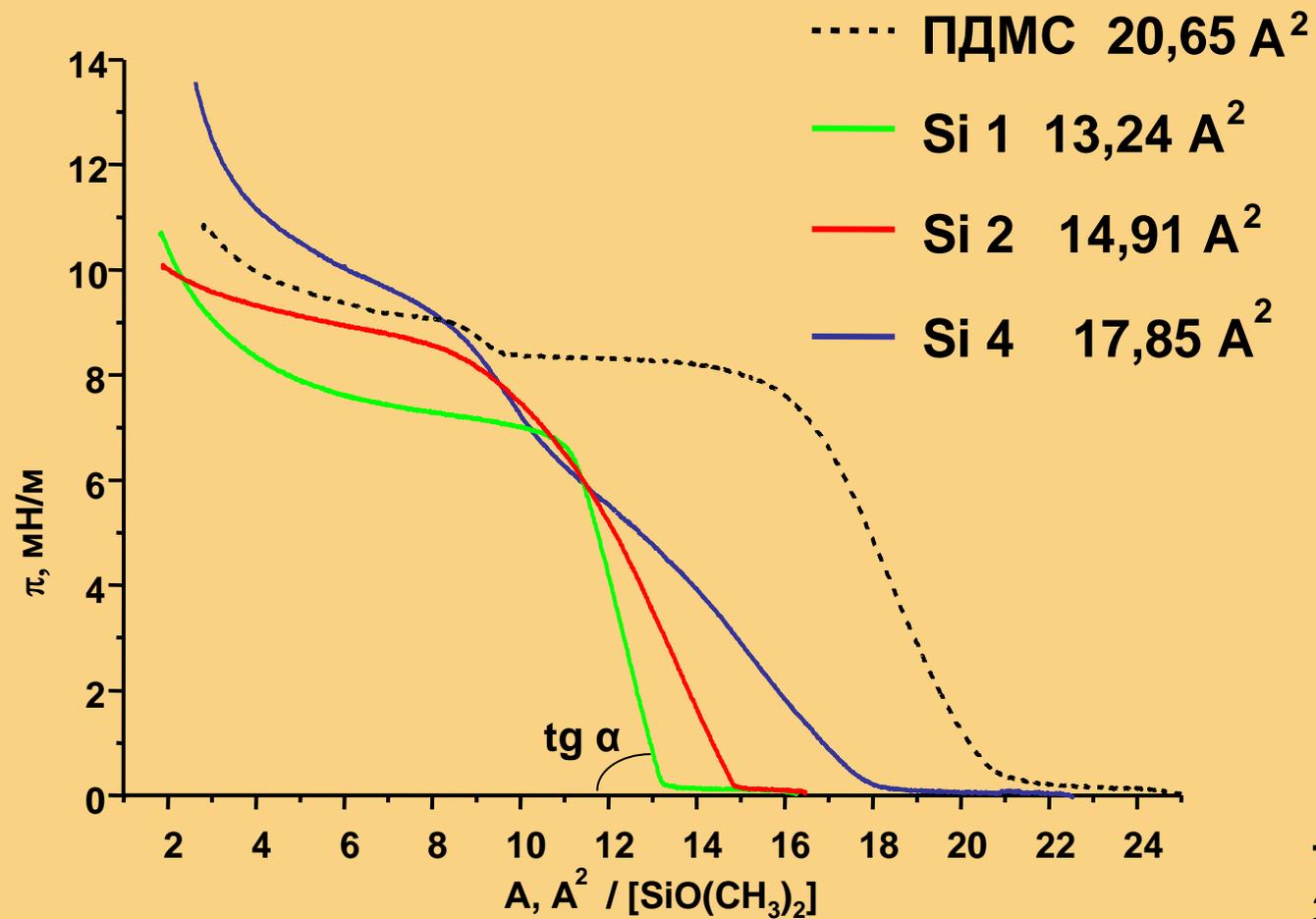


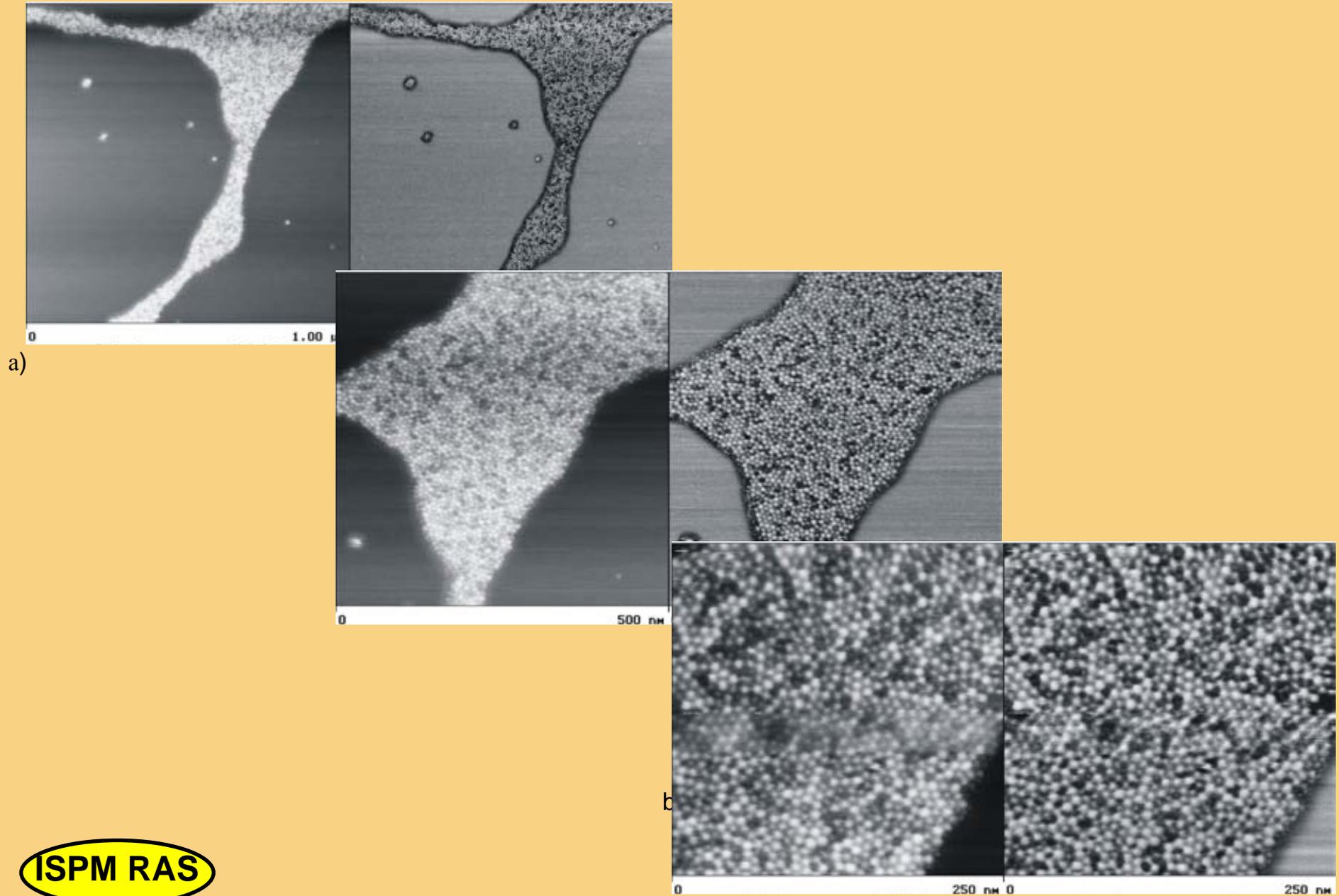
Таблица 2. Значения сдвиговой вязкости полиметилсилоксанов и ПДМС

	ПДМС	Si1	Si2	Si4
Вязкость, η, Па·с	0,27	4,65	1,51	0,17

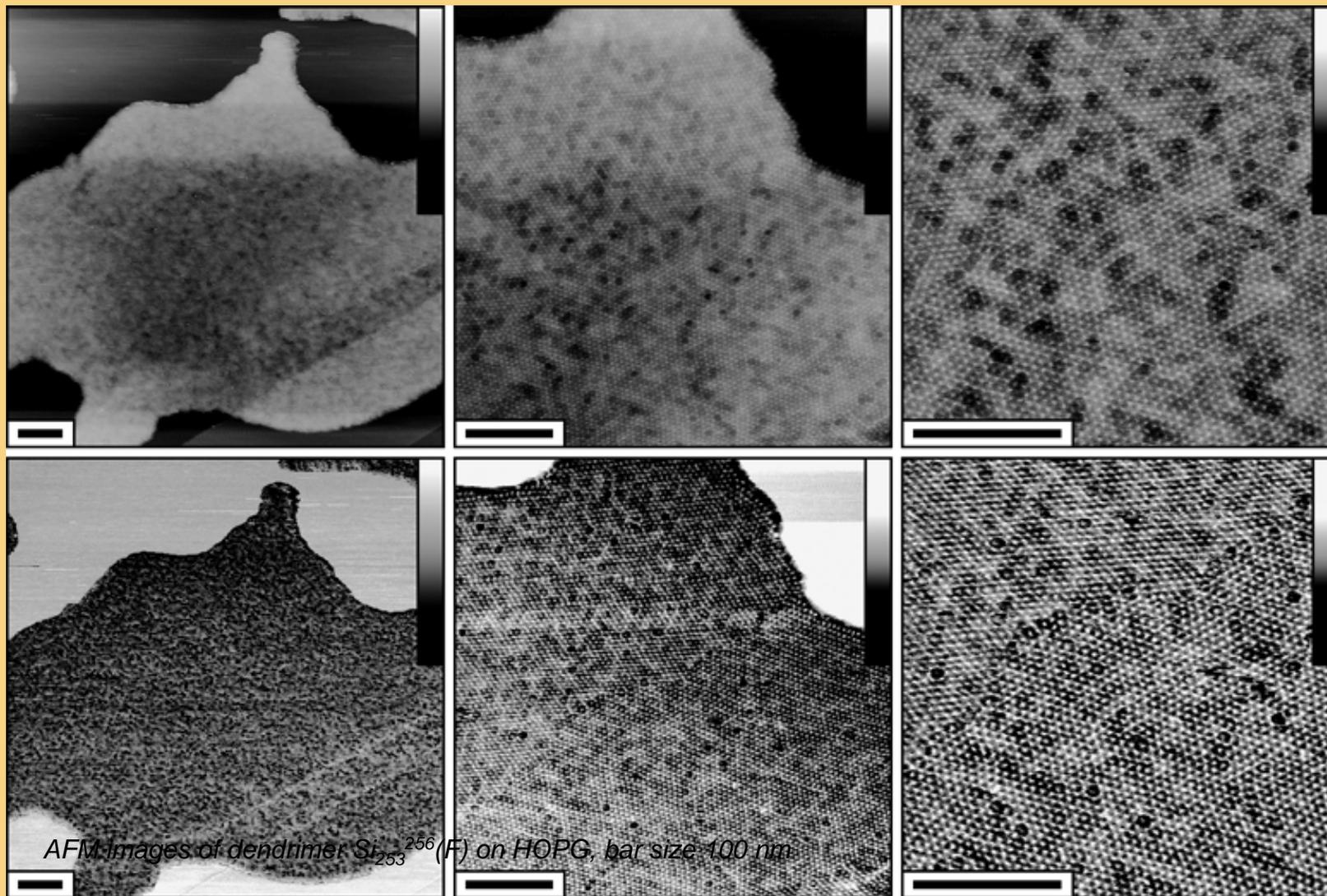
Таблица 3. Значения угла наклона (tg α)

	tg α
Si 1	0.076
Si 2	0.043
Si 4	0.046
ПДМС	0.0246

AFM images of G-9(Bu) on mica

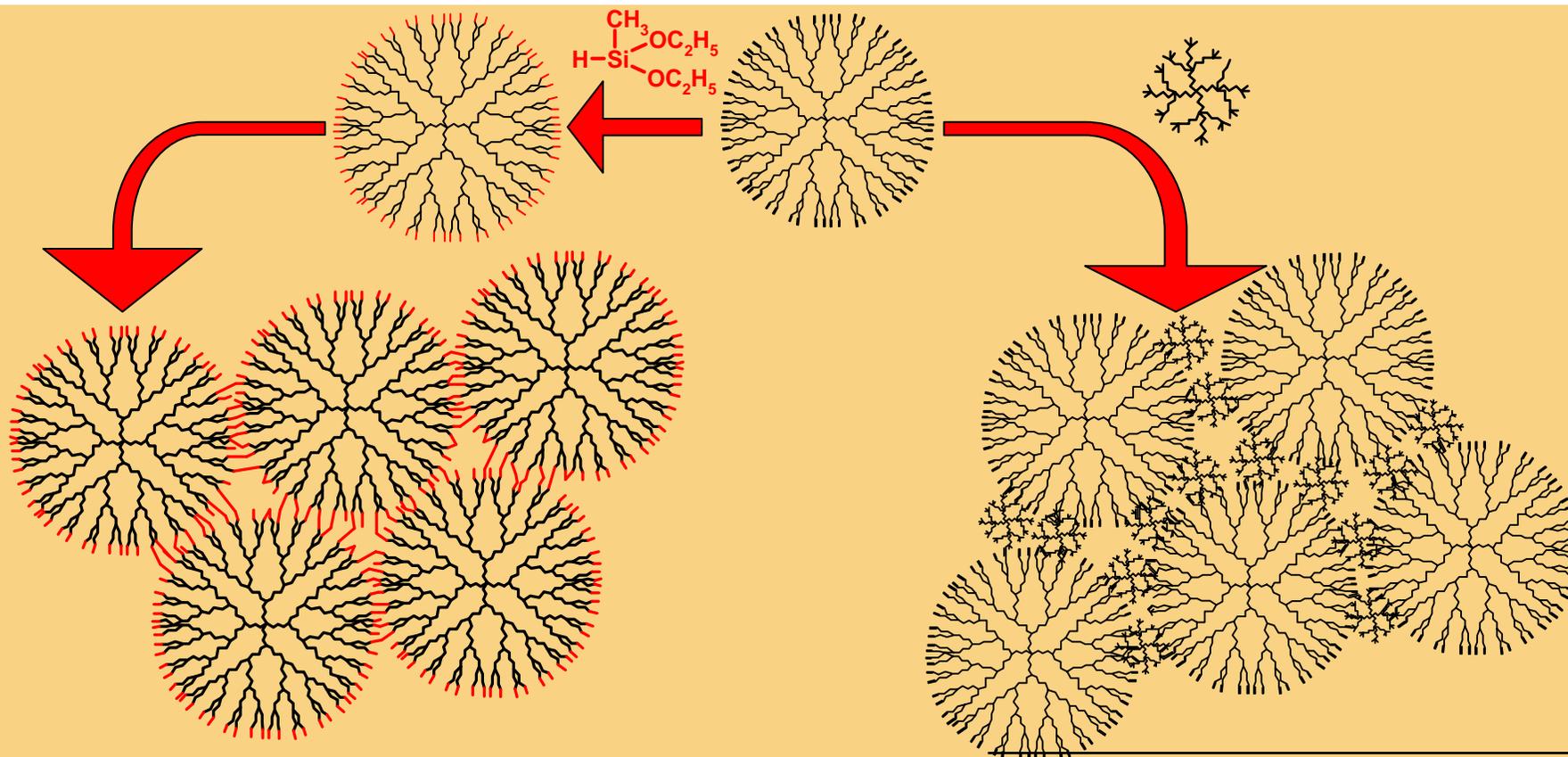


Atomic Force Microscopy



But, is there really a need for high generations dendrimers? According to some experts, the highest generation having practical applications (except for calibration applications) is the 6th generation (G6) dendrimers (for transfection applications). Furthermore, and still according to the same sources, even though phosphorus dendrimers have been synthesised up to G12, the highest generation of these showing interesting properties (both for materials science and for biology) is G4.

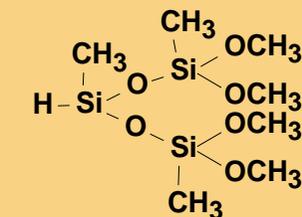
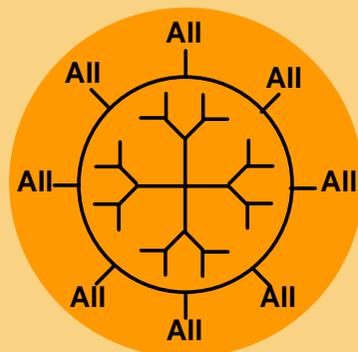
From a medical perspective, some experts agree with the previous argument in that it is unlikely that dendrimers of a generation beyond G4 or G5 will be needed. According to the same source, this is unlikely to be a major issue in the context of new pharmaceuticals given existing developments.



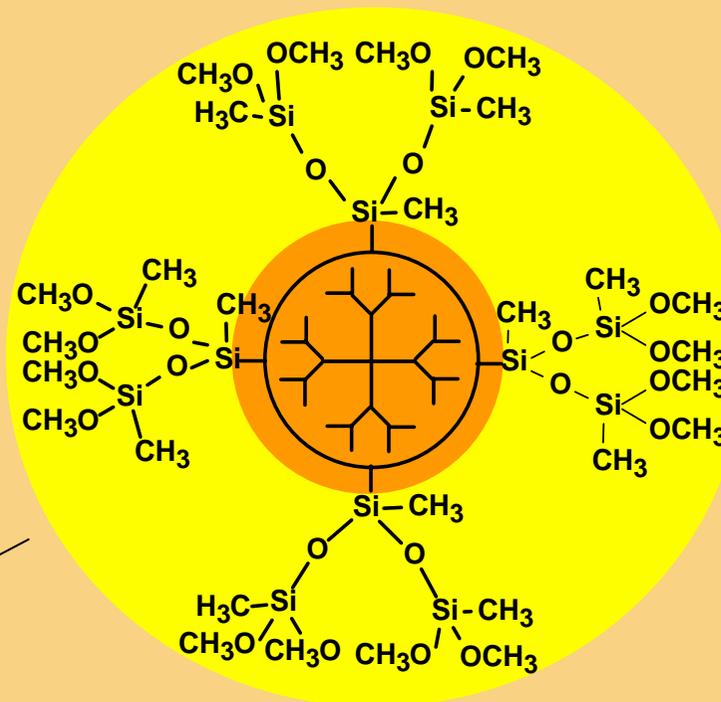
Образец	$\alpha = m_{\text{наб.}} / m_{\text{сух.}}$	
	о-ксилол	метанол
G7 ⁵¹² -3	1.90	1.67
G7 ⁵¹² -10	1.98	1.62
G7 ⁵¹² -25	1.70	1.59
G7 ²⁵⁶ -25	2.83	1.86
G7 ²⁵⁶ -50	1.59	1.09
G7 ⁵¹² (Cl)	1.12	1.03

Образец	$\alpha = m_{\text{наб.}} / m_{\text{сух.}}$	
	толуол	метанол
18(G2)/(G6)-30	1.40	1.12
6(G2)/(G6)-30	1.77	1.01
6(G2)/(G6)-блок	1.38	–
3(G2)/(G6)-30	1.99	–
36(TMDS)/(G6)-30	3.03	1.01
36(TMDS)/(G6)-блок	1.62	1.01
(G2)/(G6)-30	–	72 –

Дендримеры в качестве шаблонов



Pt. cat.



ГИДРОЛИЗ



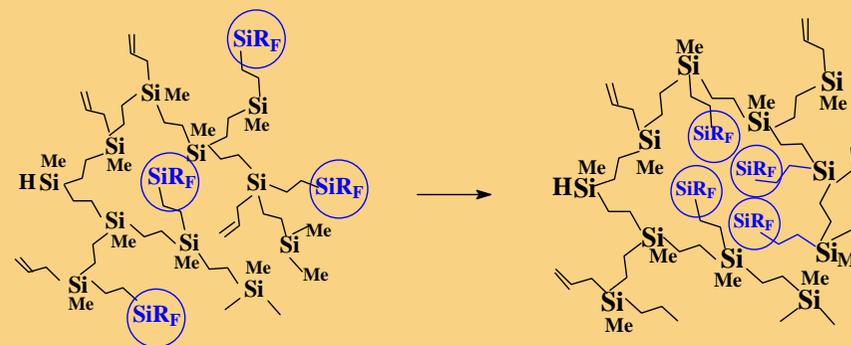
Castle Hill and the Old Town are largely pedestrianized, but there are a couple of car parks where cars and coaches can park for a fee, allowing visitors to walk to the area. Bus 16 runs from Clark Adam tér to



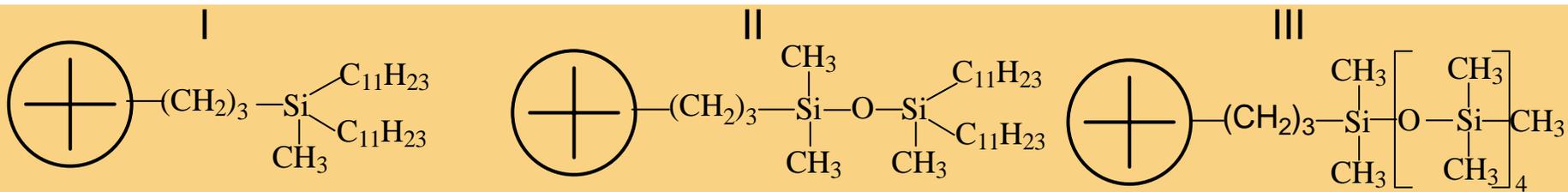
Определение характеристической вязкости фторполимеров в различных растворителях.

Полимер	Mw(ГПХ)	[η], дл/г		Дендример	Растворитель				
		Растворитель			Метилтретбутиловый эфир		Гексафторбензол		
		ТГФ	Гексафторбензол		Γ _[η] , НМ	Γ _{ДСР} , НМ	Γ _[η] , НМ	Γ _{ДСР} , НМ	
РВ	11000	0.15	-						
F-РВ (50%)	23000	0.10	0.08	Si ₅₀₉ ²⁵⁶ (F)	4.03	4.05	3.9	4.2	
F-РВ (100%)	28000	0.08	0.07	Si ₅₀₉ ¹²⁸ F, (Si-O-Si)	3.47	3.7	3.39	3.9	

Полимер	[η], дл/г			
	Растворитель			
	ТГФ	Гексафторбензол	Хлороформ	Толуол
СПКС	0.11	0.06	0.08	0.07
F-СПКС	0.13	0.07	0.02	0.03



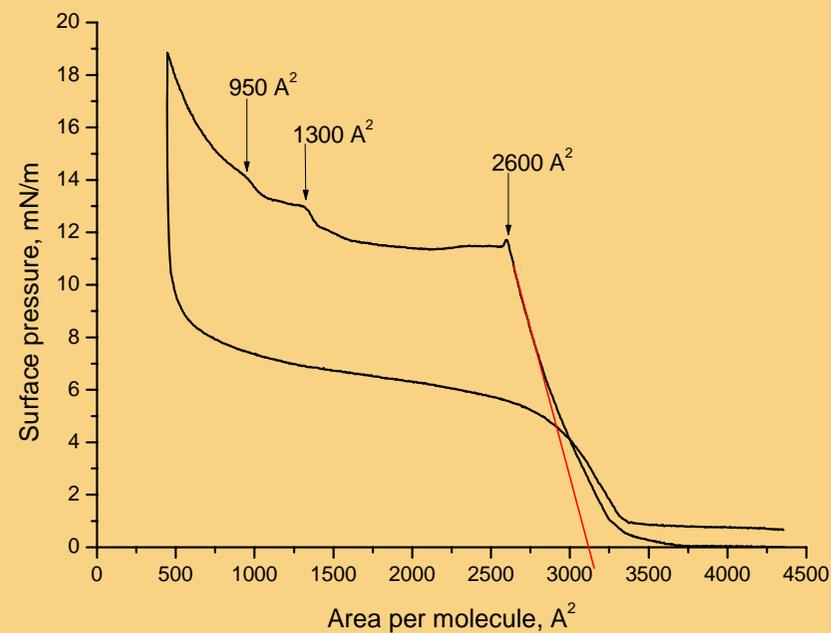
Дендример	[η], дл/г		
	Растворитель		
	ТГФ	Метилтретбутиловый эфир	Гексафторбензол
G-6(AlI)	0.04	-	-
Si ₅₀₉ ²⁵⁶ (F)	0.02	0.03	0.03
Si ₅₀₉ ¹²⁸ F, (Si-O-Si)	0.03	0.03	0.03



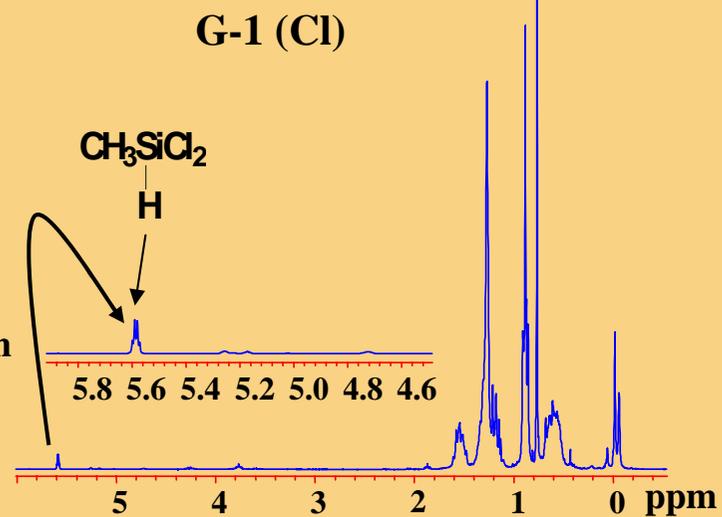
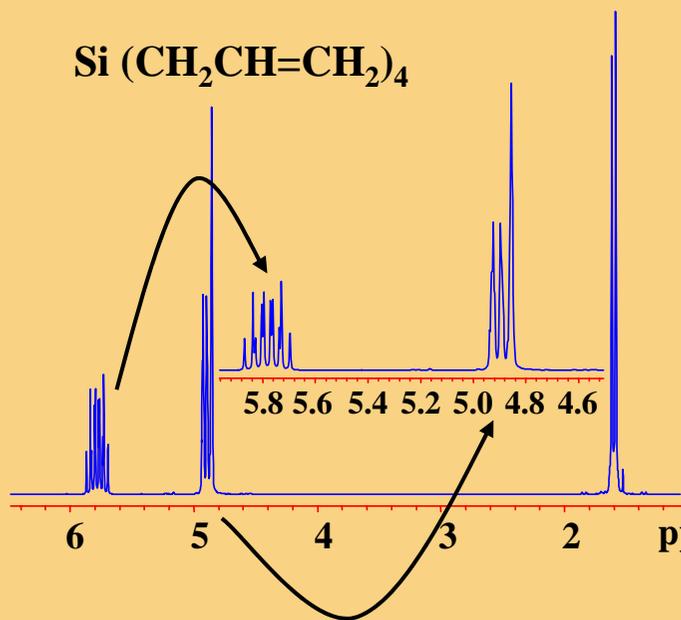
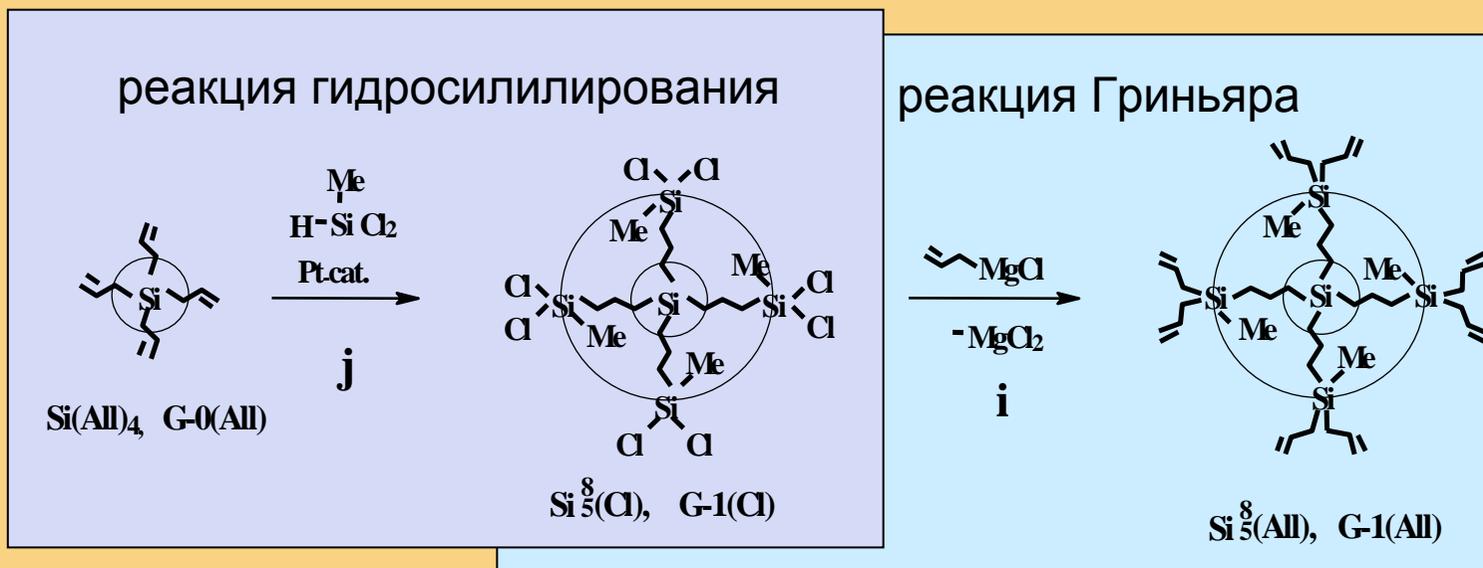
Viscosity

	Mw(calc.), g/mol	$[\eta]$ (toluene), dl/g	$[\eta]$ (THF), dl/g
I	61257	0.047 ± 0.005	0.051 ± 0.001
II	70748	0.038 ± 0.002	0.031 ± 0.001

Langmuir isotherm (III)



Контроль за полнотой протекания реакций



Функциональный анализ

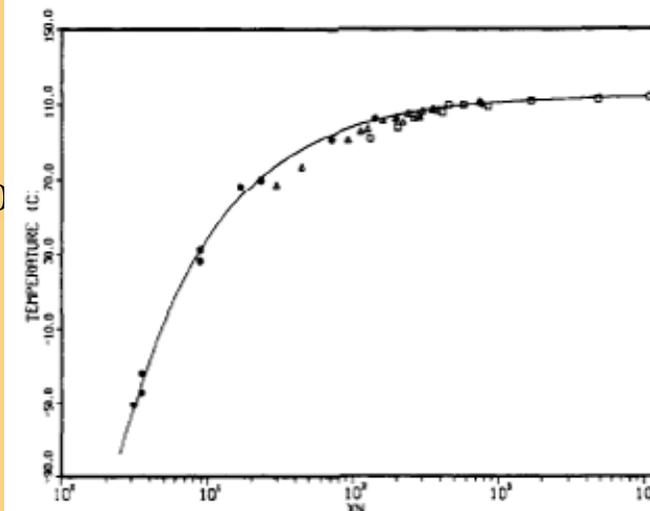
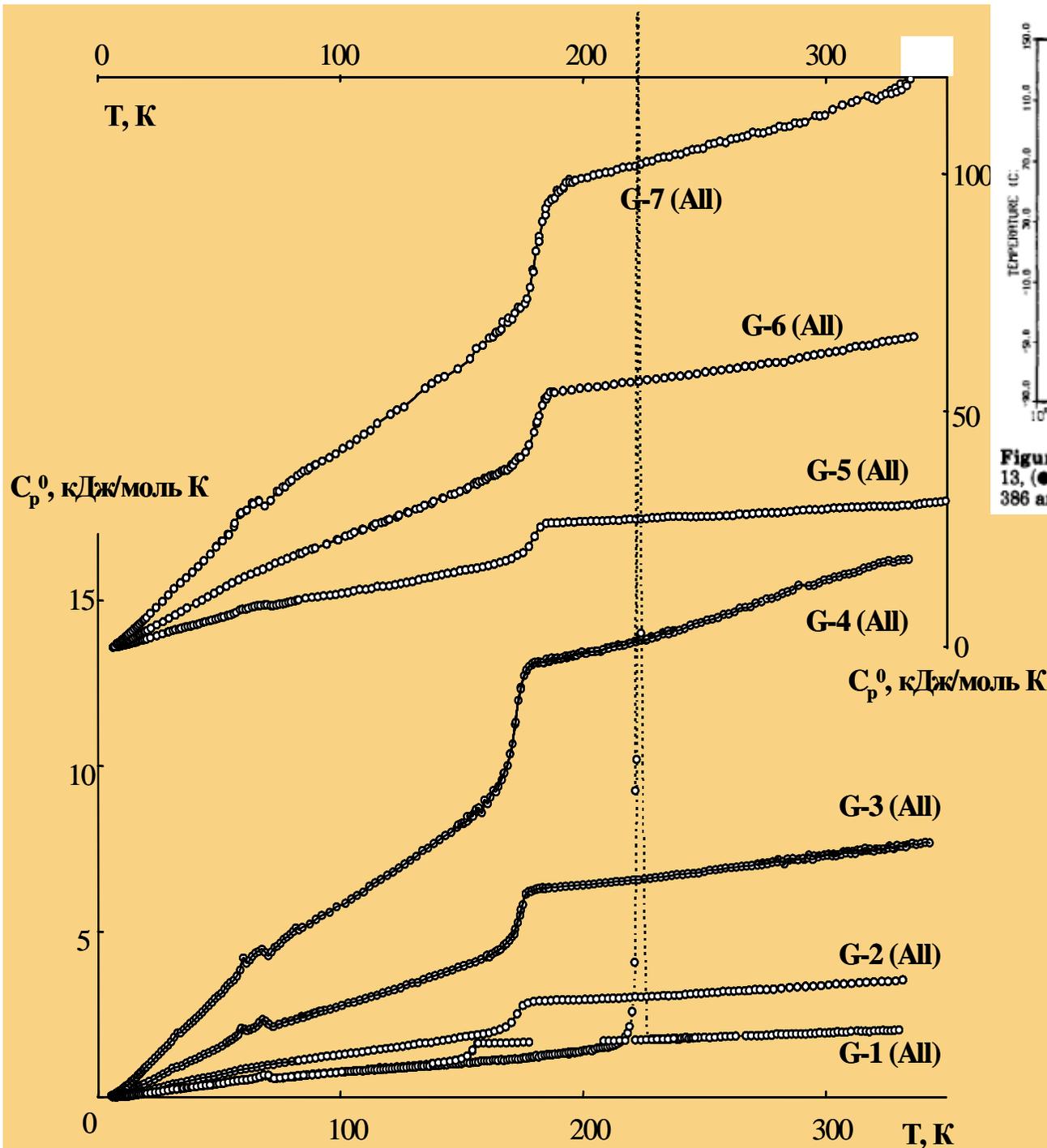
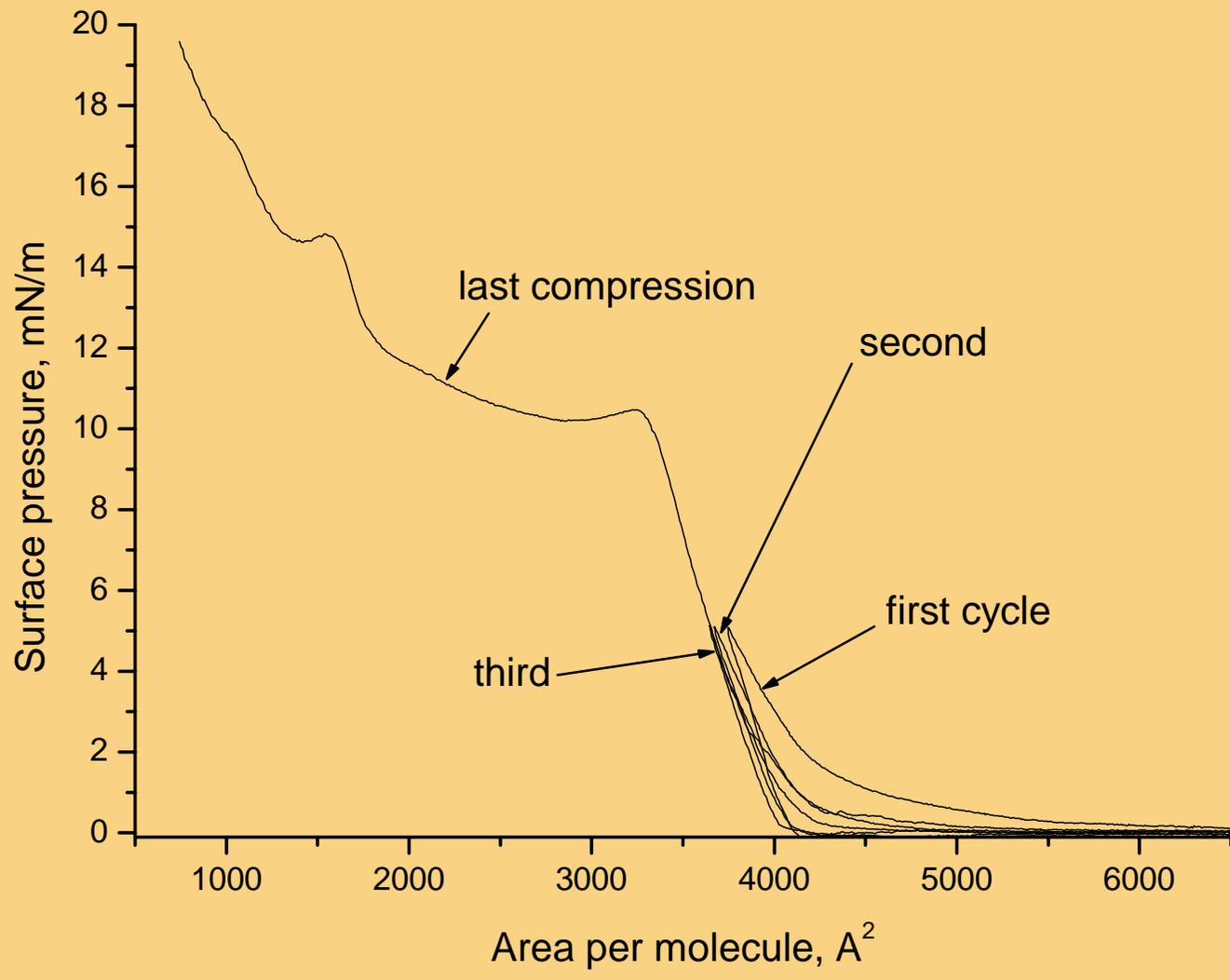
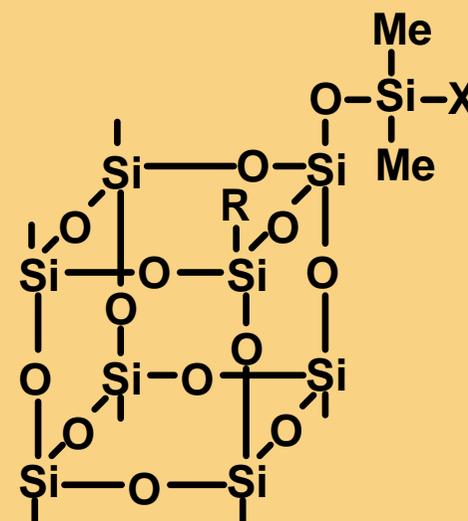
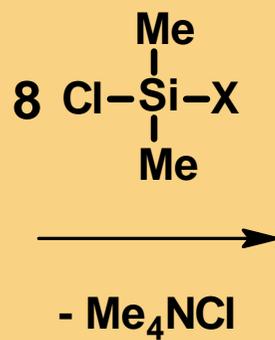
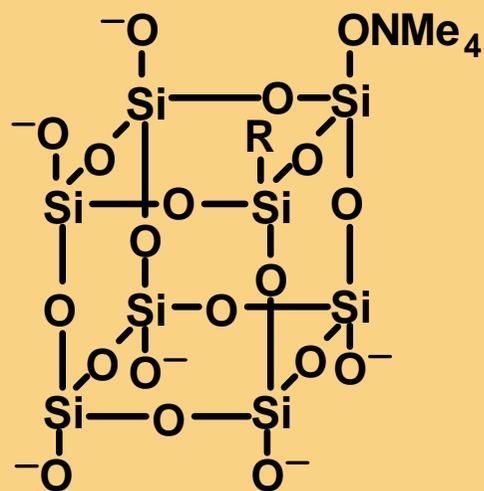
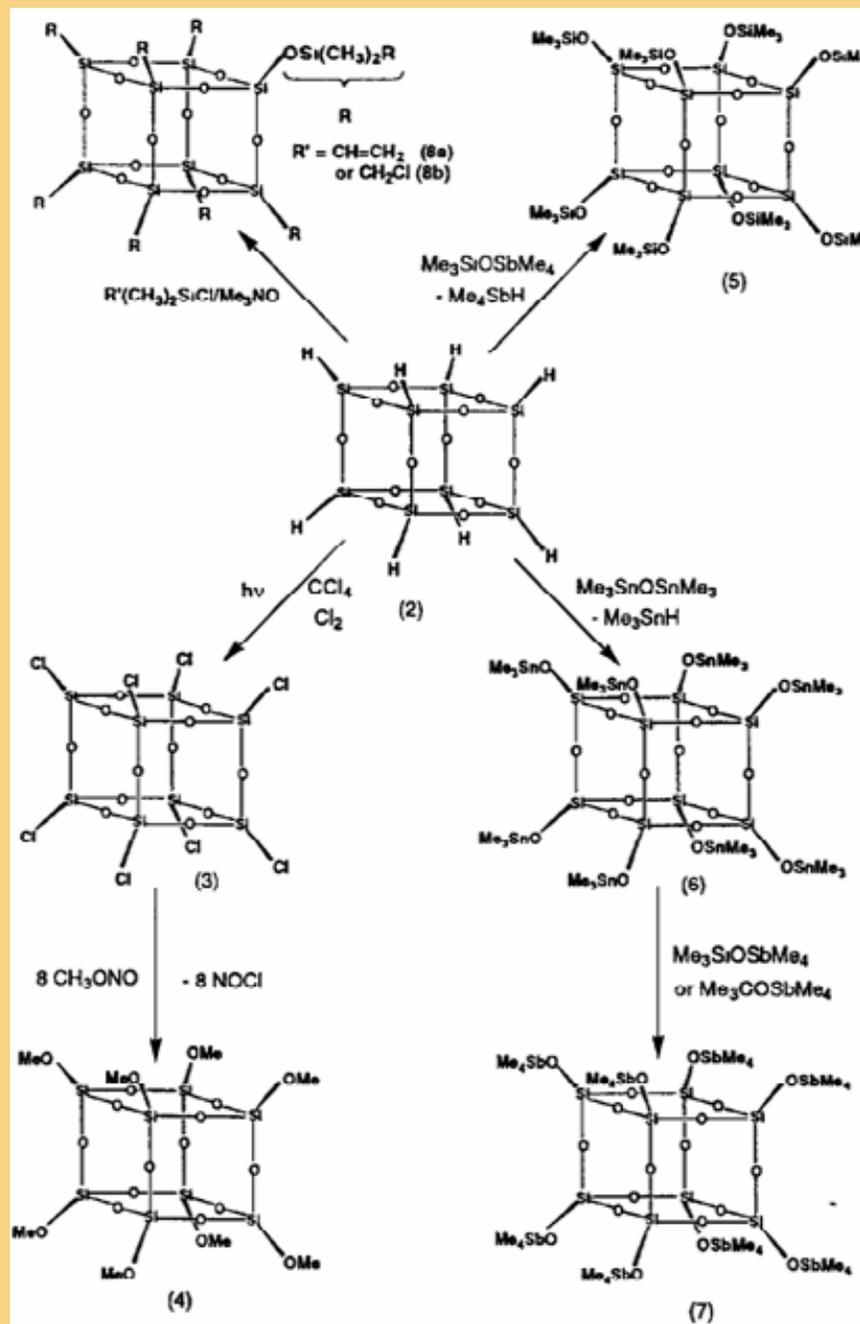


Figure 1. T_g as a function of X_n for PMMA: (Δ) ref 12, (\blacksquare) ref 13, (\bullet) this work, Table I. Solid line fitted to eq 4 with $T_{g^0} = 386$ and $K = 353$.

Дендример	ΔT , K	T_g^0 , K
G-1(A11)	150-160	154 \pm 1
G-2(A11)	170-180	172 \pm 1
G-3(A11)	170-180	172 \pm 1
G-4(A11)	170-180	172 \pm 1
G-5(A11)	170-180	179 \pm 1
G-6(A11)	170-190	180 \pm 1
G-7(A11)	170-200	181 \pm 1







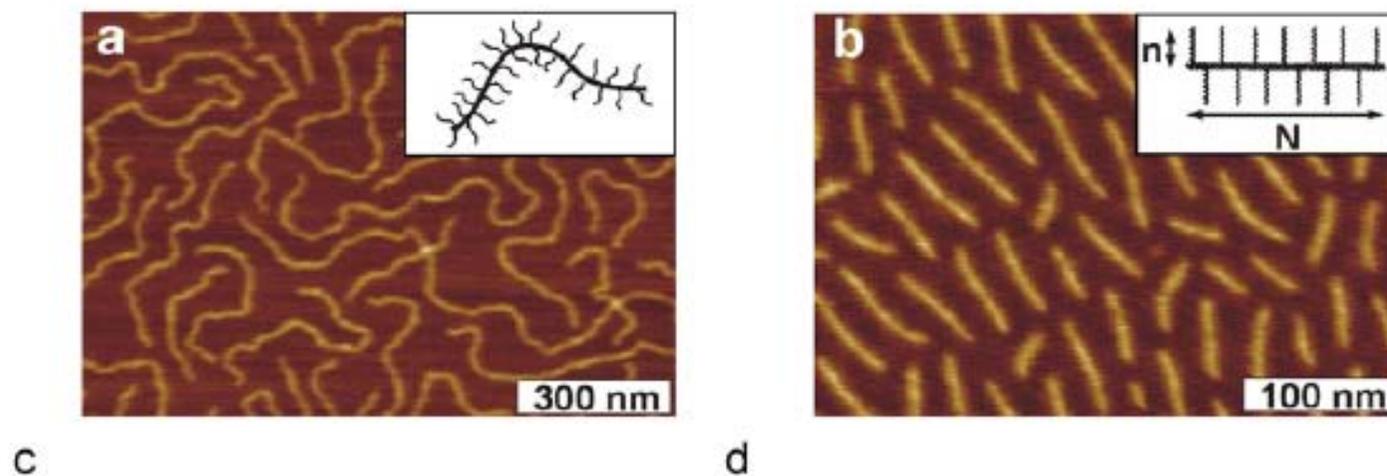
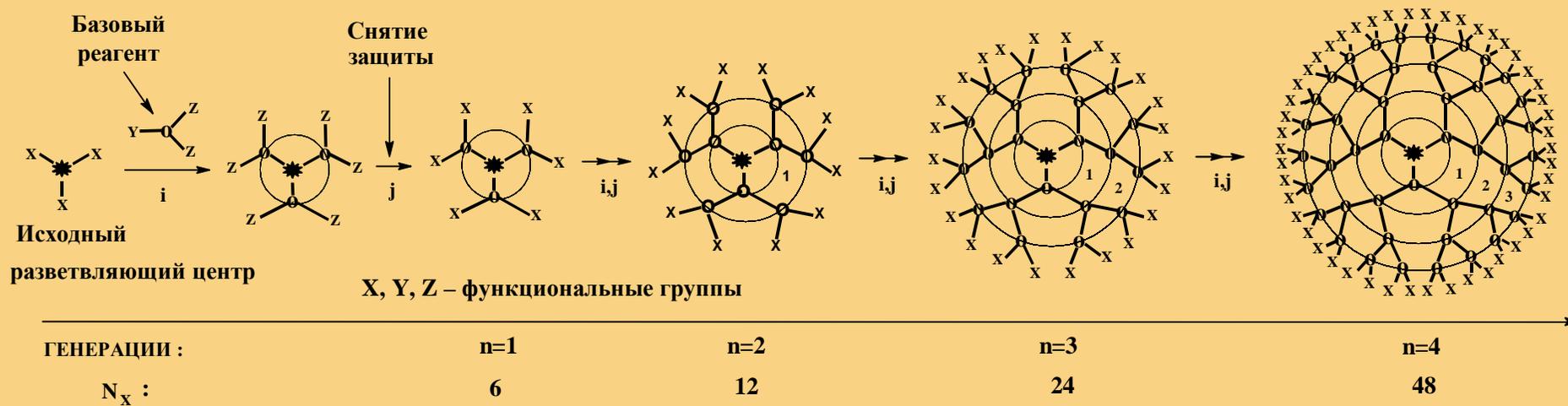


Fig. 16. Brush molecules change from (a) flexible to (b) rod-like conformation with increasing degree of polymerization of side chains n .

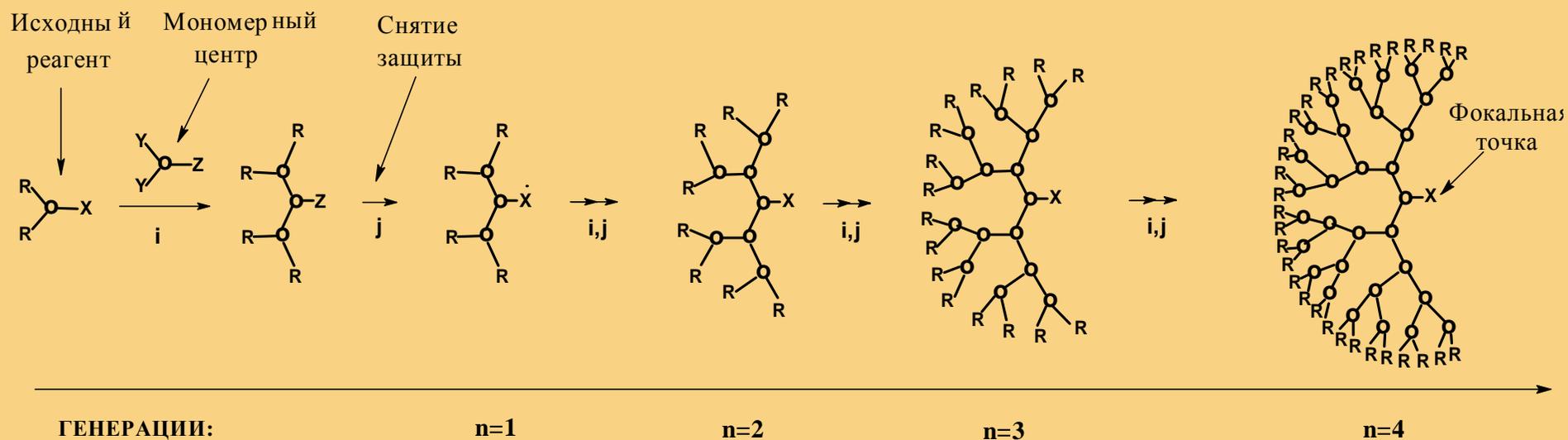
Дендримеры – это высокоупорядоченные, пространственно гиперразветвленные, полностью ациклические образования, построенные по закону ветвящегося дерева.



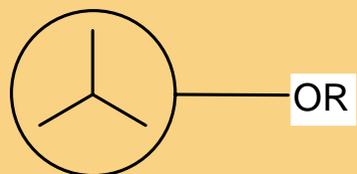
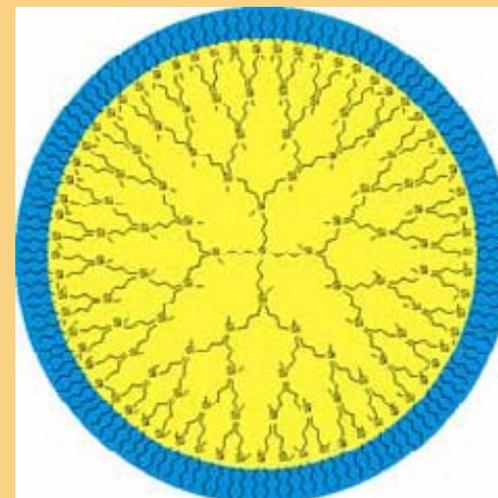
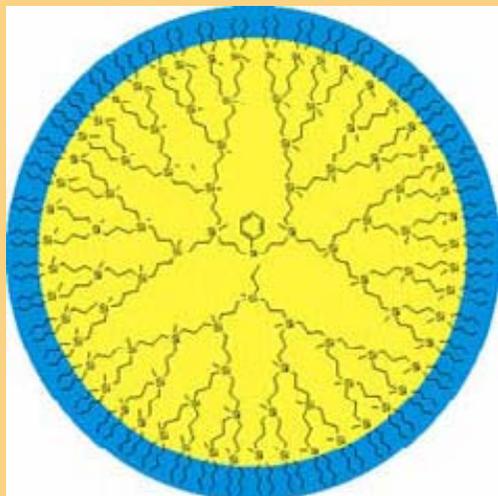
$$N_X = 3 \cdot 2^n - \text{ количество концевых функциональных групп}$$

Дивергентная схема синтеза дендримеров.

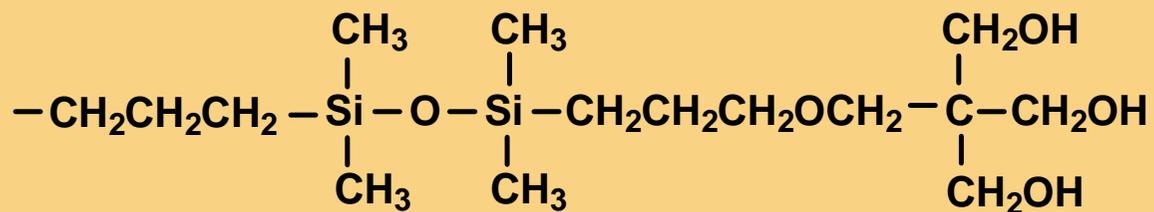
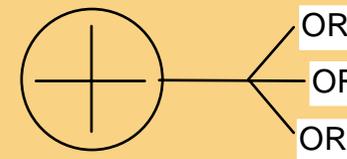
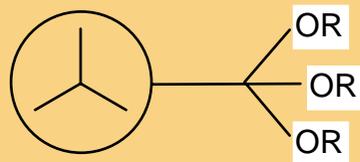
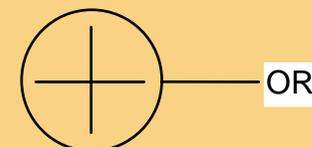
Конвергентная схема синтеза дендримеров



Diphilic dendrimers G3-G5 with different density of outer shell



$R = \text{SiMe}_3 \text{ or } \text{H}$



A number of diphilic carbosilane dendrimers



32 OH-groups



96 OH-groups



64 OH-groups



192 OH-groups



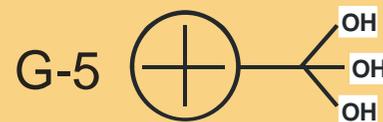
96 OH-groups



288 OH-groups

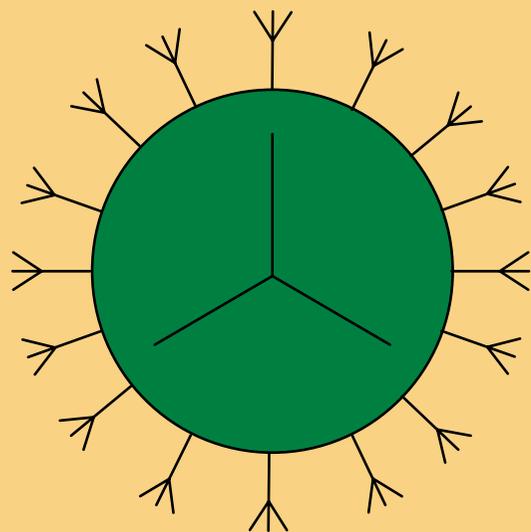


128 OH-groups

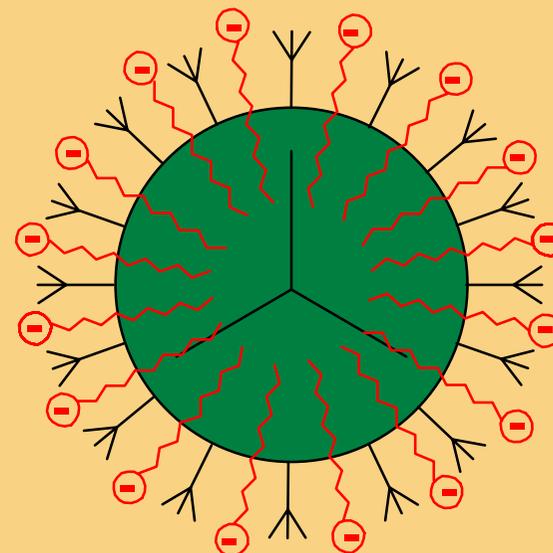


384 OH-groups

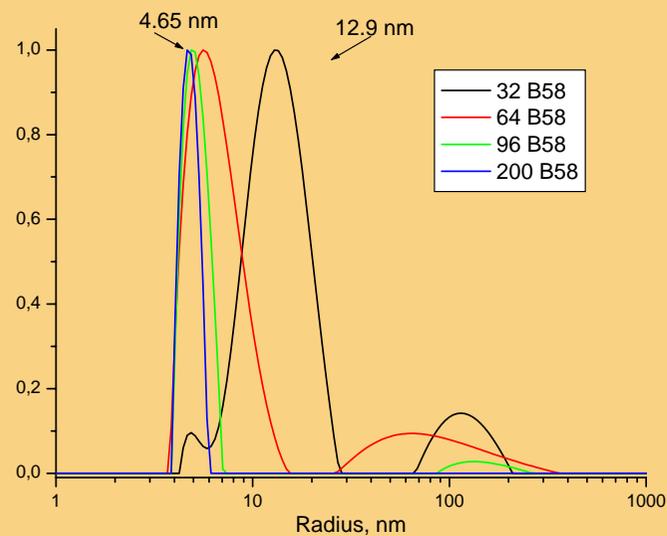
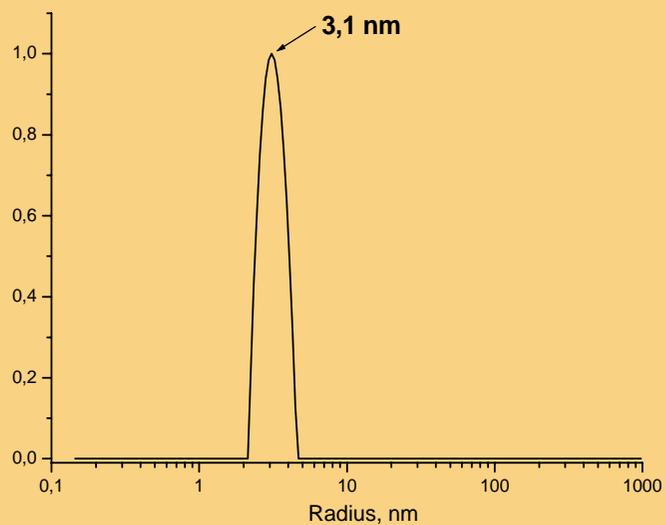
Hydrophilic dendrimer – SDS



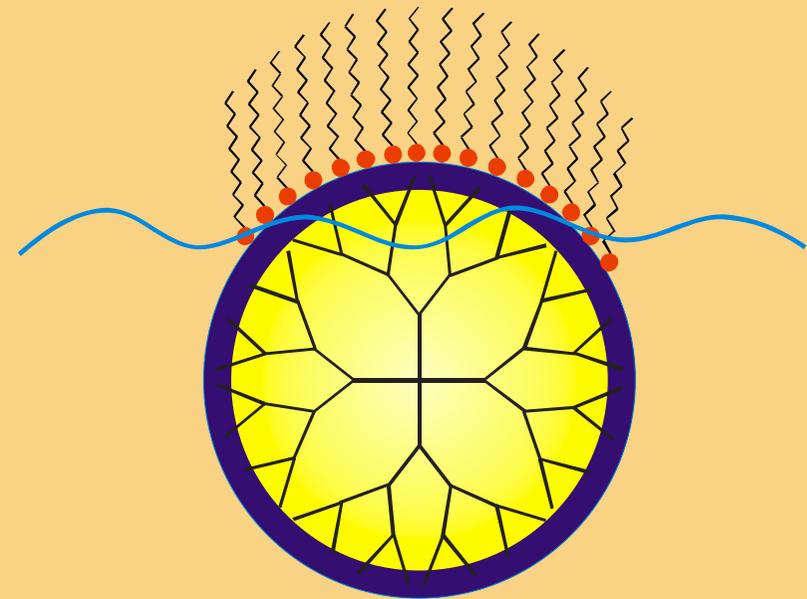
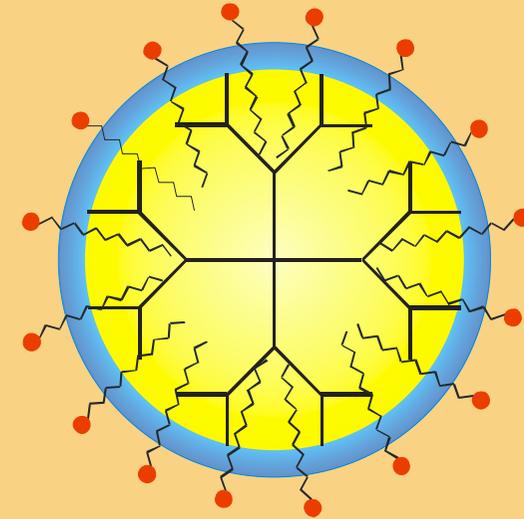
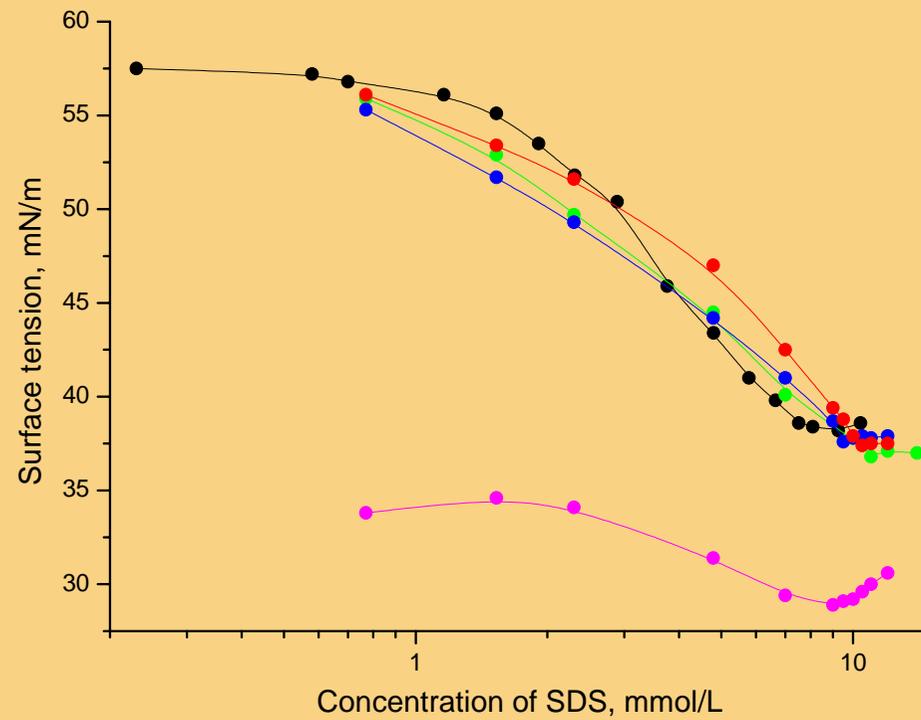
Surfactant



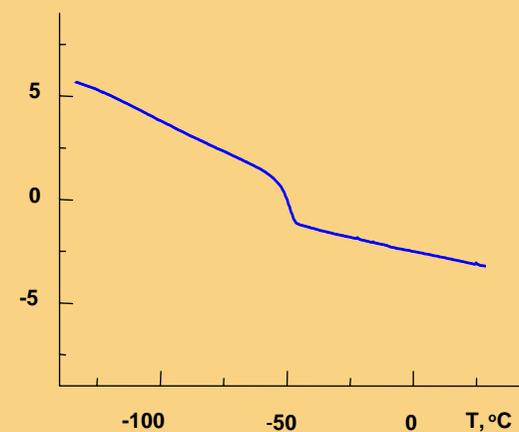
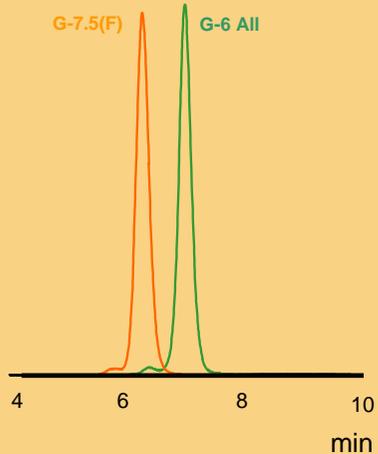
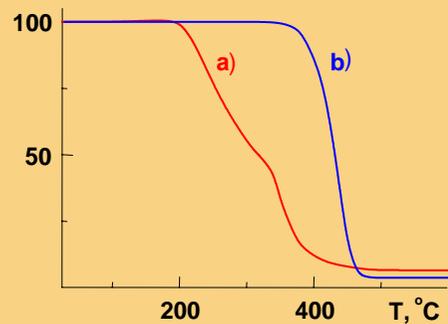
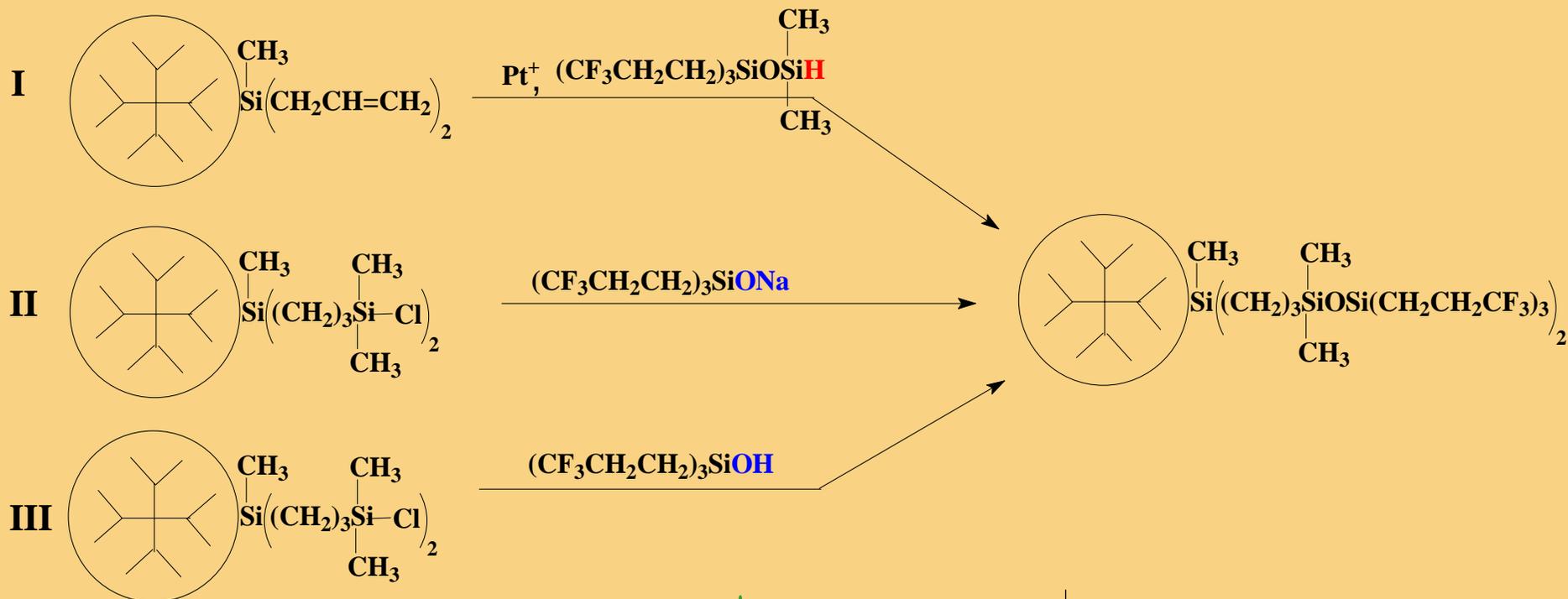
DLS data:



From Quantity to Quality Transformations

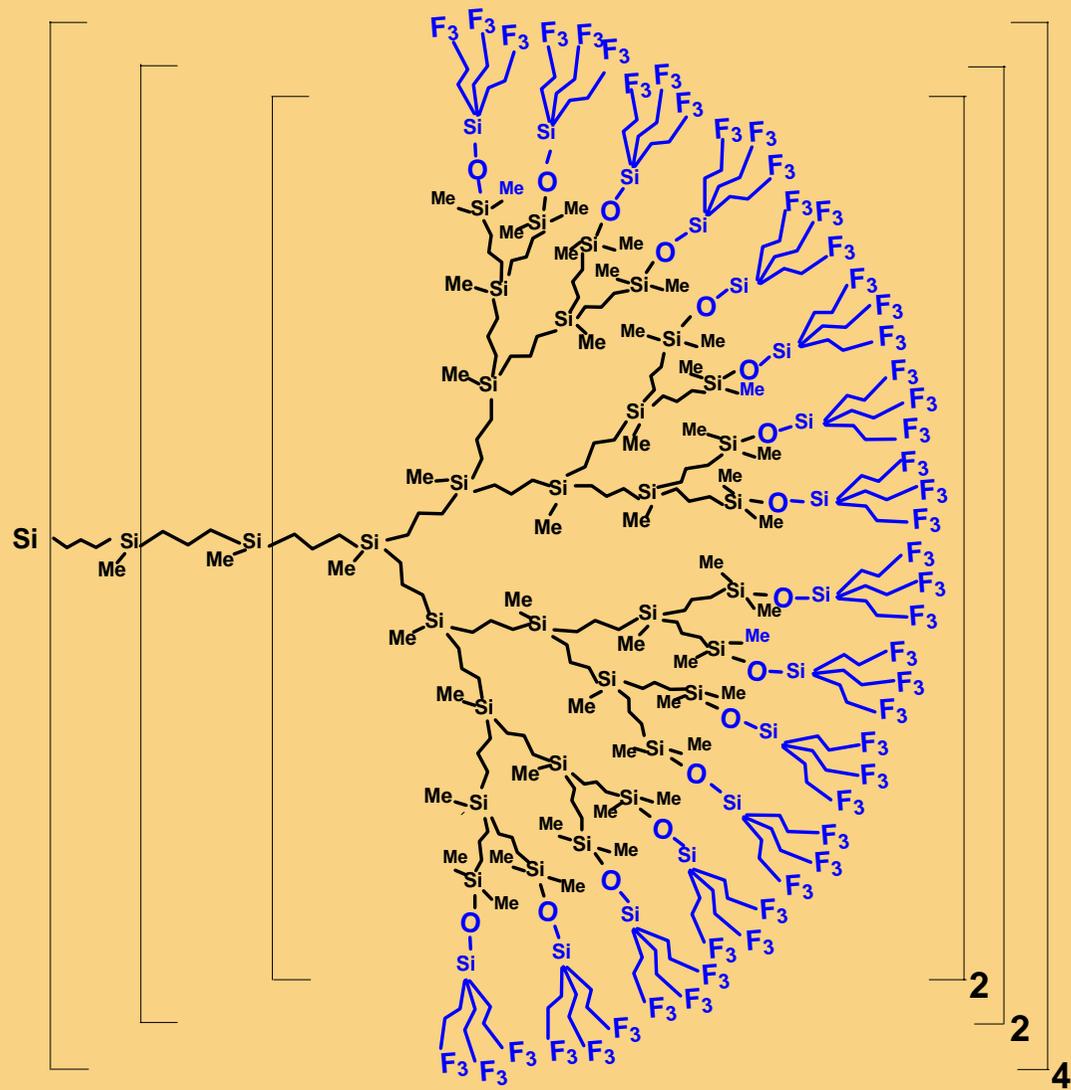
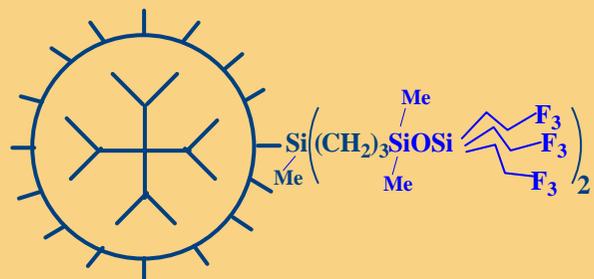


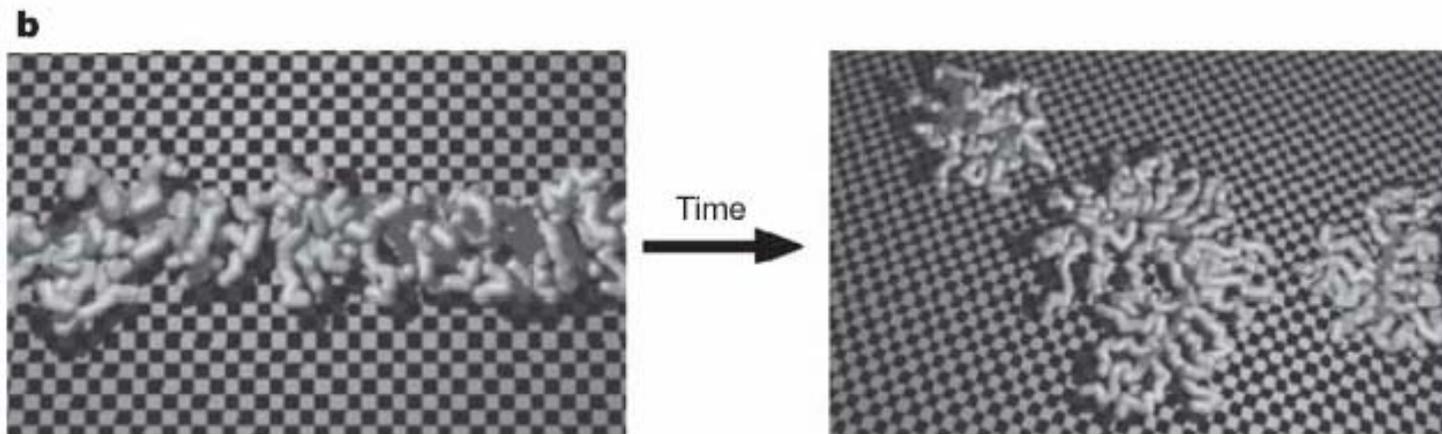
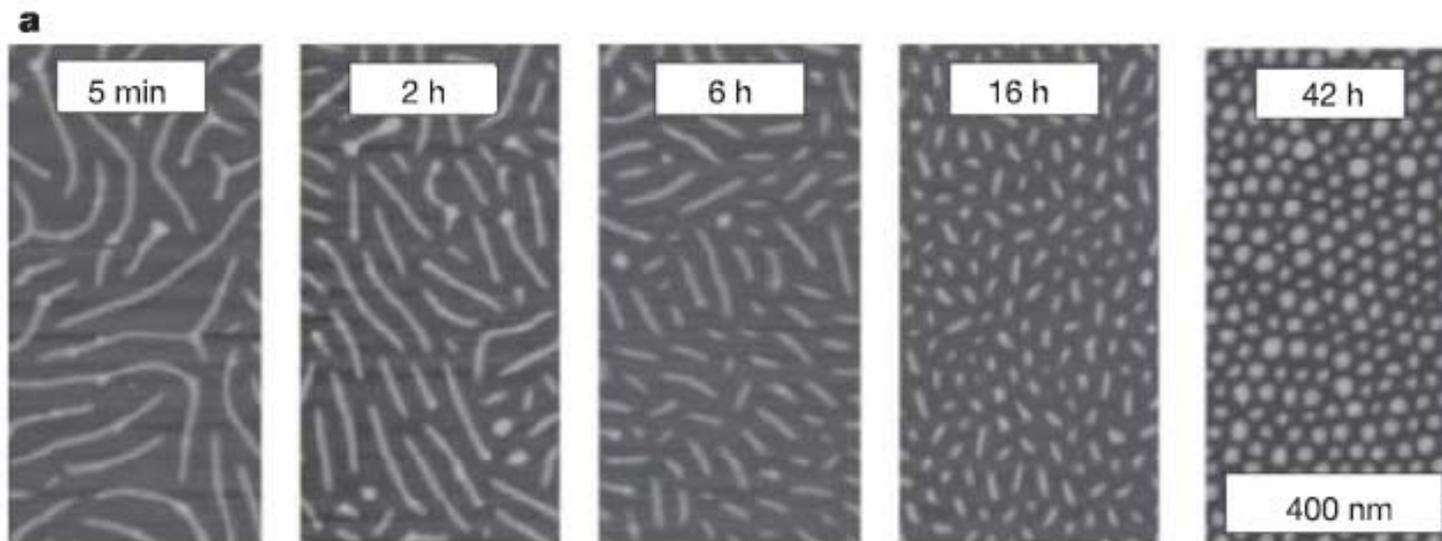
Fluorocarbon derivatives of carbosilane dendrimers of high generation





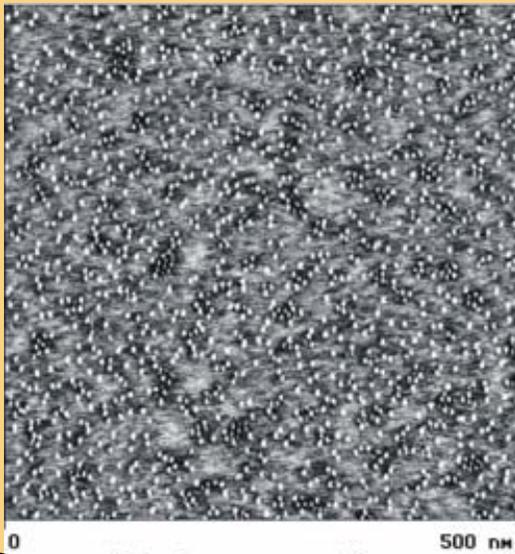
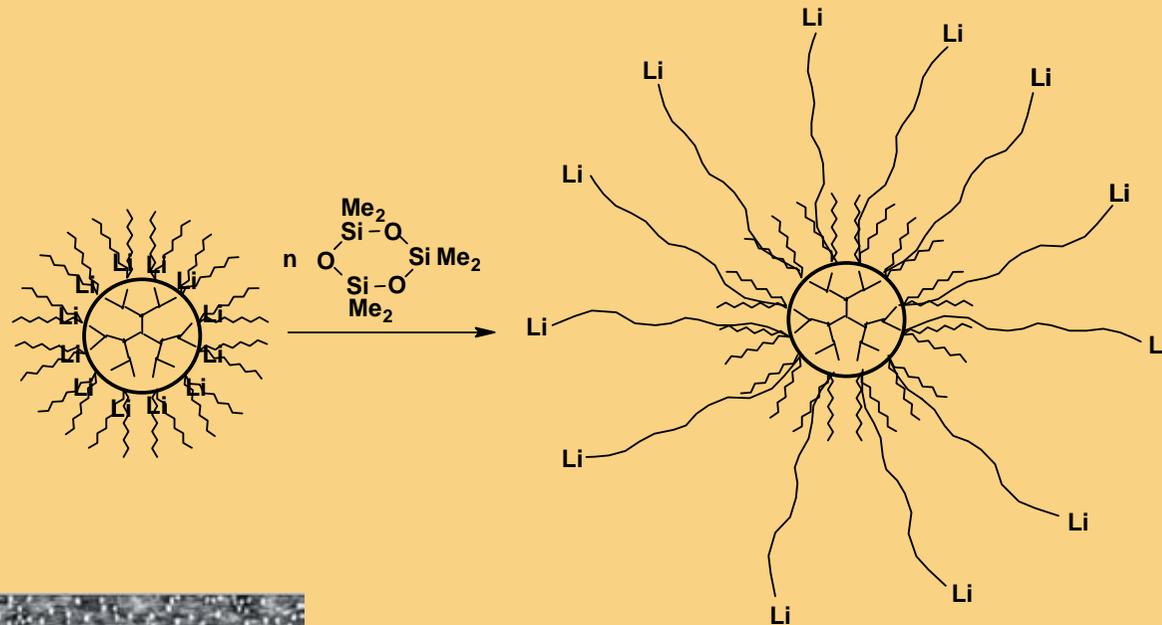
Pt cat.



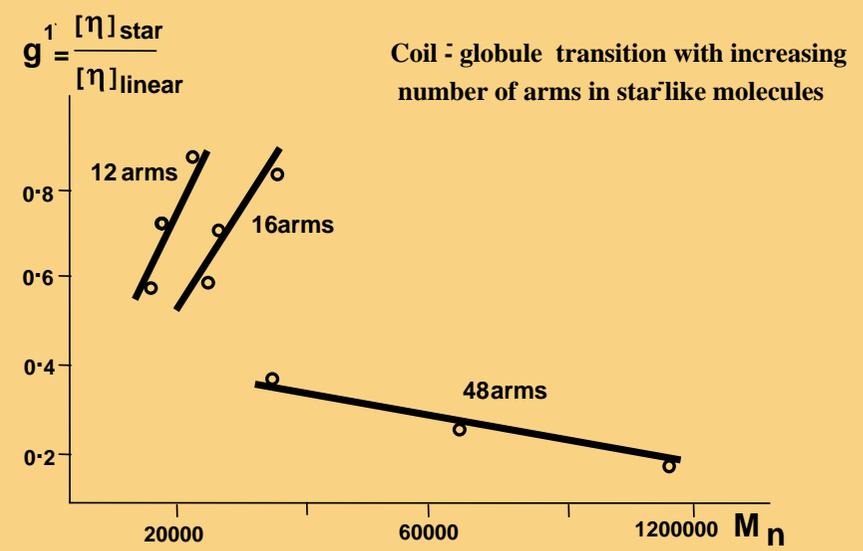


Adsorption-induced degradation of macromolecules. a, The molecular degradation of brush-like macromolecules with long side chains ($n \approx 140$) on mica was monitored using AFM height imaging after each sample was exposed for different time periods (as indicated in the images) to a water/propanol (99.8/0.2wt/wt%) substrate.

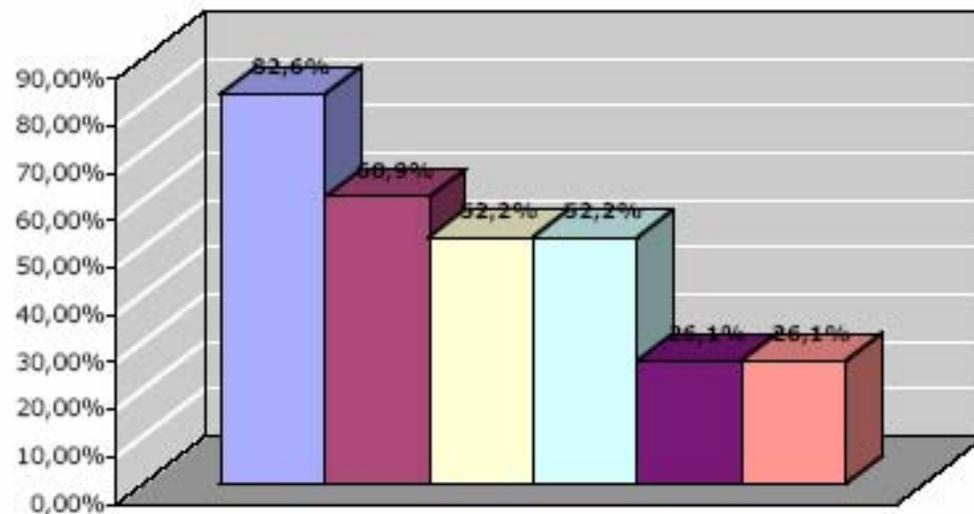
Molecular Membrane Effect



ISPM RAS



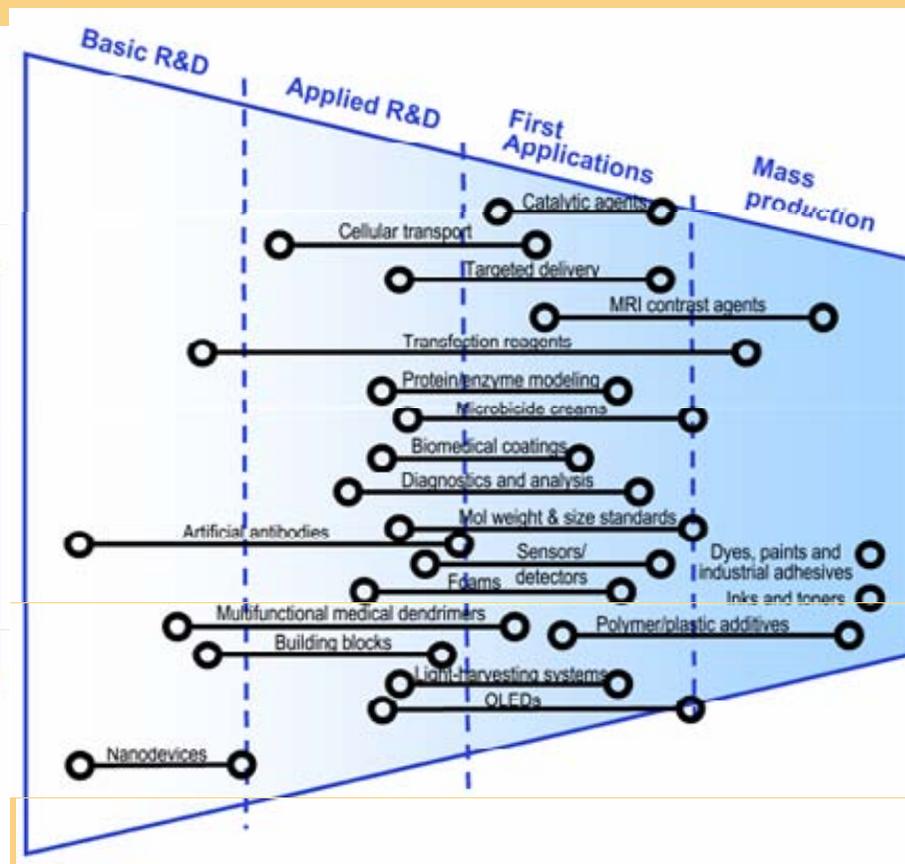
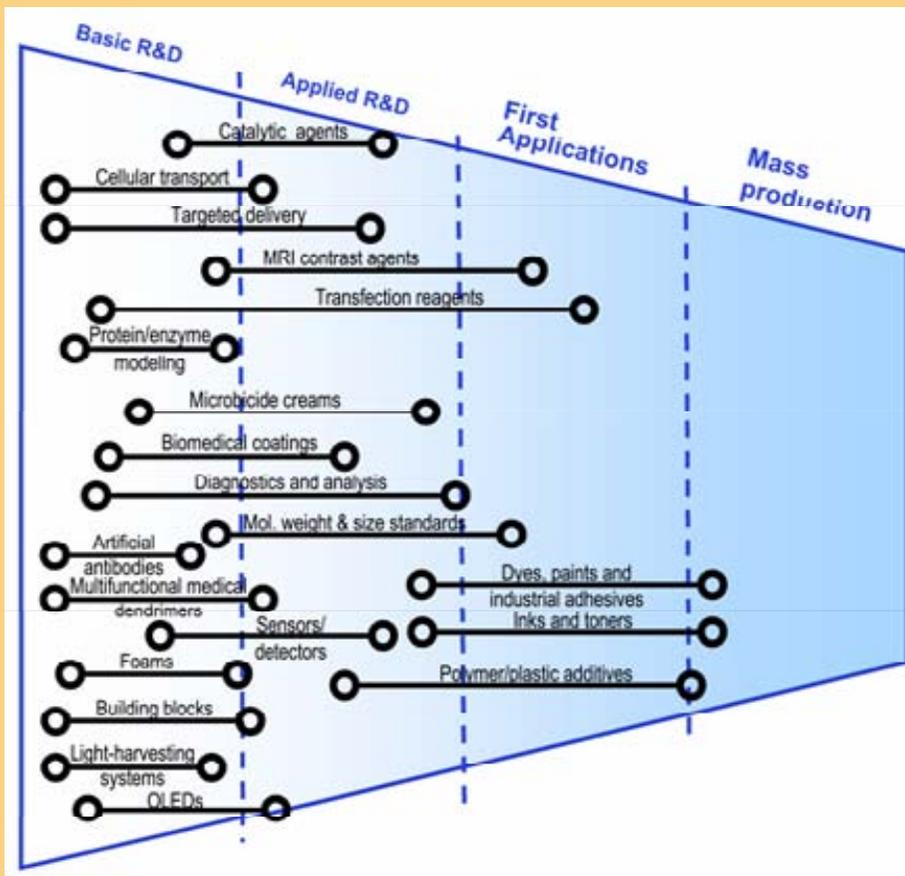
Most potentially exploitable properties of dendrimers

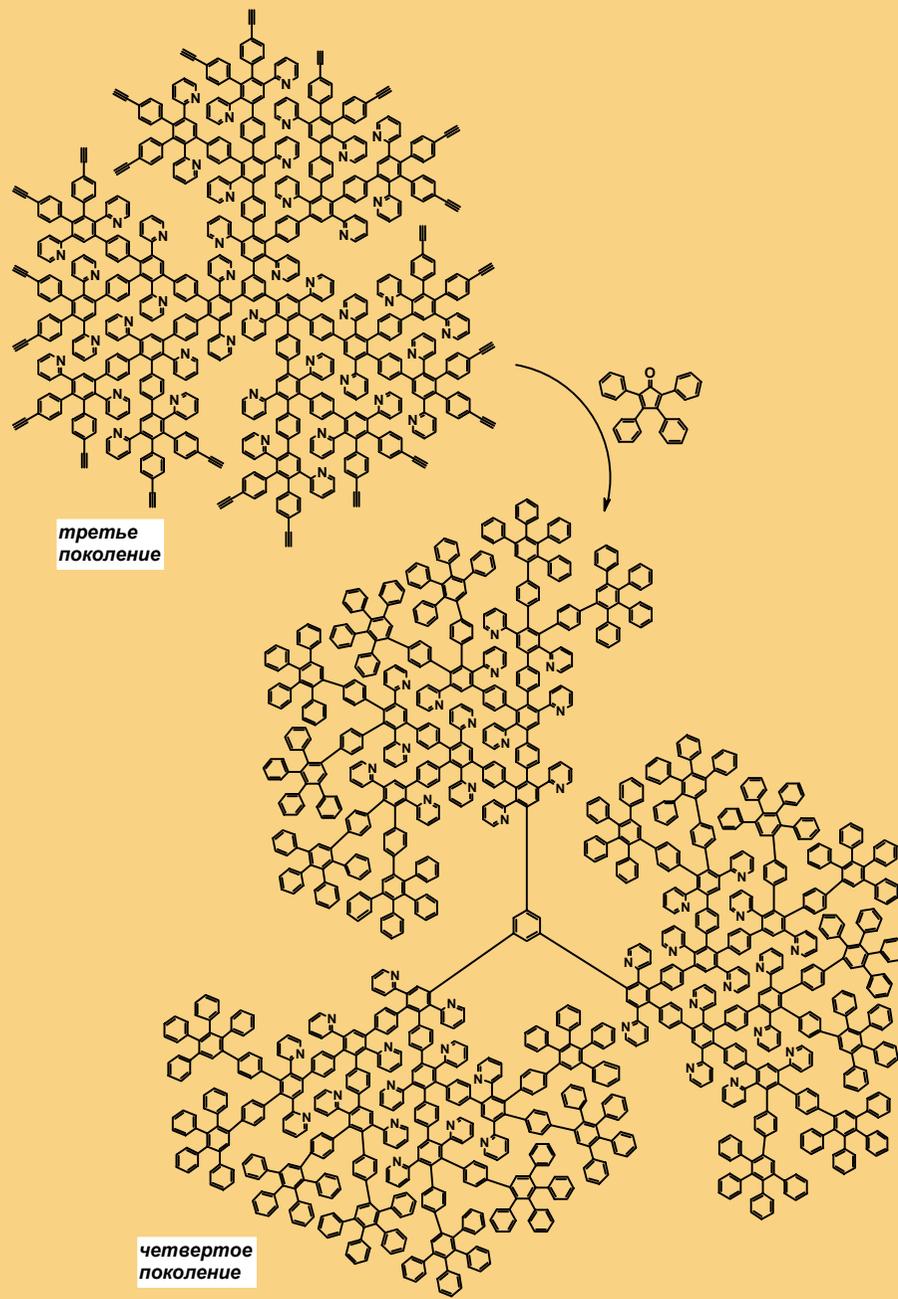


- Polyvalency: the outer shell of a dendrimer can be multiply functionalized
- Defined architecture, size and shape control
- Monodispersity: step-wise synthetic processes enable dendrimers with highly uniform sizes
- Loading capacity: can be used to carry and/or store a wide range of molecules
- Biocompatibility / low toxicity
- Transfection properties: to transport genetic material into cell interiors

Now

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$T_g > T$ разл.

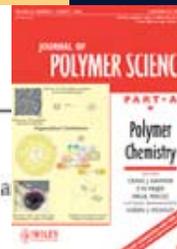


Series Editor J. Matison
Volume Editors P. Dvornic · M. J. Owen

Silicon-Containing Dendritic Polymers

HIGHLIGHT

From the Discovery of Sodiumoxyorganoalkoxysilane to the Organosilicon Dendrimers and Back



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ABSTRACT: Upon being discovered 20 years ago, sodiumoxyorganoalkoxysilanes became the key to the world of organosilicon dendrimers. First considering the great variety of objects that had appeared in this area during the last 20 years, the organosilicon dendrimers are still one of the most actual objects in this class. Above all, this is true concerning the carbosilane systems. The high reactivity of the

functional groups, the well controlled chemistry of their transformations, and the interest of the molecular skeleton are the reasons for making these systems highly actual in two main respects as model objects for the deep research of the dendrimers' properties and as polyfunctional substrates for numerous derivations. In this review, we were mainly focusing on the importance of the former part. In the

conclusion, we showed the motivation for further development of this area both in regard of synthesis of new carbosilane systems and further development of siloxane dendrimers. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 95–103, 2008

Keywords: dendrimers; glass transition; hydrogen-containing polymers; hyperbranched; networks; polysiloxanes



AZIZ M. MUZAFAROV

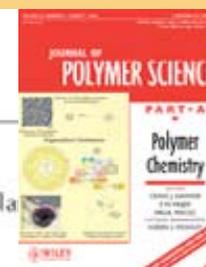
Professor A.M. Muzafarov graduated from Andrianov Chair of Moscow Institute of Fine Chemical Technology in 1971, obtained his Ph.D. in 1981 with Professor A.A. Zhdanov, on the subject of high functional organosilicon oligomers and hyperbranched polymers. He achieved his Dr. of Chemistry degree in 1997 on the subject of Organosilicon dendrimers and hyperbranched systems. In 2006 together with E.A. Rebrov, he received I.V. Lebedev Award of Academy of Sciences of Russia for the investigation of organosilicon dendrimers and hyperbranched systems. From 1995 up till now he is the Head of the

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Polymer Data Handbook Second Edition

EDITED BY James E. Mark

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