Experimental report

09/02/2020

Proposal: 9-11-1967 **Council:** 10/2019

Title: Smart gels of sequence-controlled polymers in organic solvents

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Francois TOURNILHAC

Experimental team: Henrique TREVISAN
Francois TOURNILHAC

Local contacts: Lionel PORCAR

Samples: Toluene D8
Toluene in toluene D8 (5 vol%)
Alt-C18 + 1/8 molar bipyridine in toluene D8 (5 vol%)
Alt-C18 + 1/4 molar bipyridine in toluene D8 (5 vol%)
Alt-C18 + 1/4 molar bipyridine D8 in toluene D8 (5 vol%)
Alt-C18 + 1/1 molar bipyridine D8 in toluene D8 (5 vol%)
Alt-C18 in toluene D8 (5 vol%)
Alt-C18 + 1/2 molar bipyridine in toluene D8 (5 vol%)
Alt-C18 + 1/1 molar bipyridine in toluene D8 (5 vol%)
Alt-C18 + 1/8 molar bipyridine D8 in toluene D8 (5 vol%)
Alt-C18 + 1/2 molar bipyridine D8 in toluene D8 (5 vol%)

Instrument	Requested days	Allocated days	From	To
D22	1	1	08/02/2020	09/02/2020

Abstract:

Sequence control is an emerging discipline of polymer science. In this movement, the objective of our researches is to implement novel functions in polymer materials through the control of sequence in copolymers. We previously reported physical gelation behavior of alternating copolymers consisting of monomers with long alkyl chain and phenol side groups in aromatic solvents; the SANS study performed at ILL revealed the presence of wormlike micellar objects. Since then, we observed by rheology the possibility of tuning the properties of these organogels, by controlled addition of small molecules. The current proposal aims to analyse the associated structural changes.

Neutron scattering report: experiment 9-11-1967 at the ILL (Grenoble)

Smart gels of sequence-controlled polymers in organic solvents

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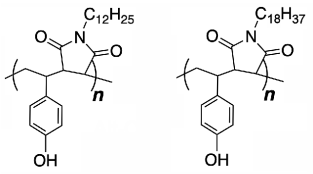
During this experiment beamtime, two different types of self-assembled structures made of sequence-controlled copolymers have been investigated. The base materials Alt-C12 and Alt-C18 (figure 1) are alternated copolymers of vinyl phenol and n-alkyl maleimide units, already investigated at the ILL (D22) during the DIR-158 experiment.[1,2]



Alt-C12 Alt-C18

These compounds have polysurfactant structure. They show partial to complete solubility in organic solvents and insolubility in water.
In a first series of experiments, thermoreversible organogels formed in toluene at different concentrations in the presence of 1/4 molar amount of bypyridines A, B, C, D with respect to the repeat unit were investigated as a function of temperature.
In the second series of experiments, emulsions made by precipitation from solutions in a water-miscible solvent such as acetone and THF were considered. On the basis of calculated SLD values, isotope labelling was used to increase or decrease the contrast between the two solvents present in the system see description of all samples in the table in appendix.

Note: *The sample named* 5% alt C12 + bipy B *in slot 17 in the second series is in reality* 5% alt C12 + bipyD.

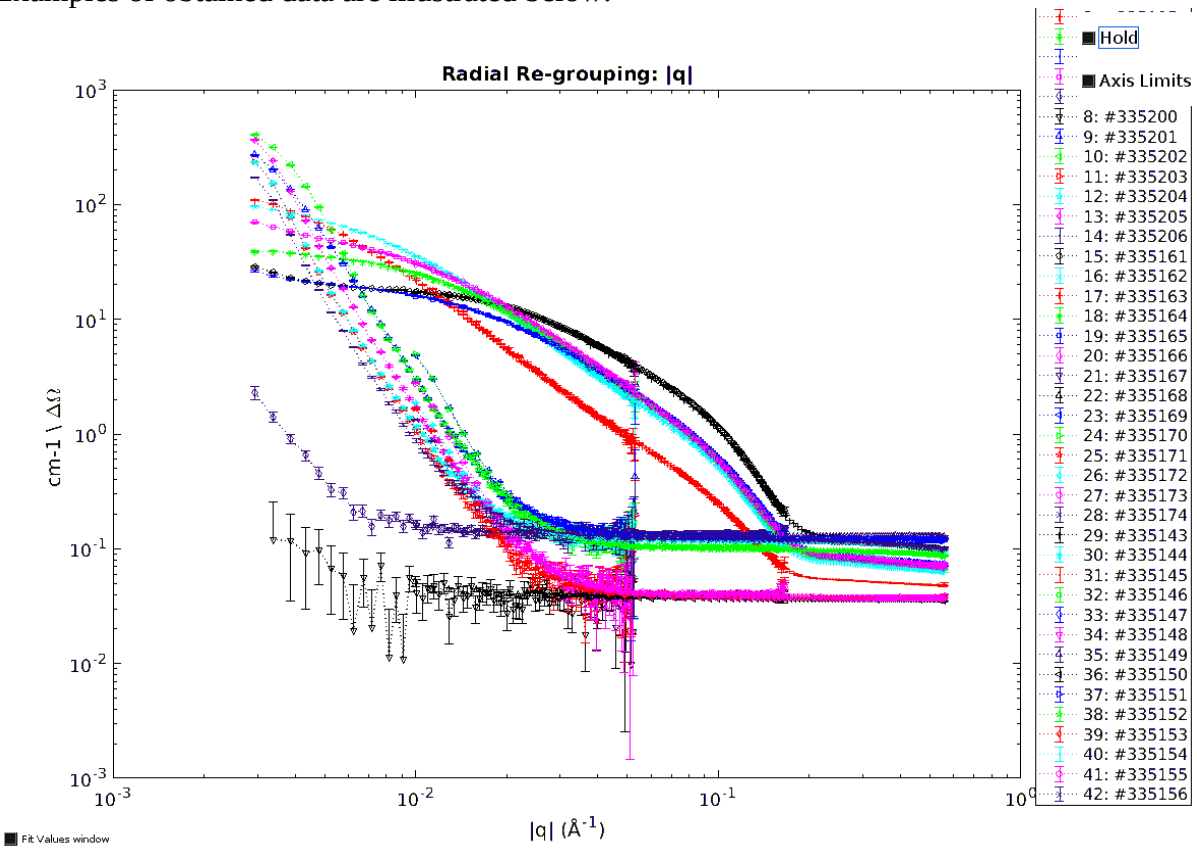
All experiments were performed on line D22 at the Institute Laue Langevin under the responsability of Lionel Porcar. The radiation was monochromatic and sample-to-detector distances D = 1.5 m, 5.6 m and 17.6 m were used at λ = 6 Å. Additionally, D = 17.6 m was used at λ = 11.5 Å thus covering a momentum transfert range from 0.001 $Å^{-1}$ to 0.55 $Å^{-1}$. Chemistry labs at the beamline and in the science building were utilised.

Samples of solutions were prepared via dissolution in toluene D8, acetone D6, D_2O or H_2O/D_2O mixtures. Samples of emulsions were prepared by first dissolving the polymer in either acetone, THF or dioxane then adding 10-fold volume of water. All samples were analyzed at 25°C by DLS (Malvern nonosizer 90) at PSCM.

The samples were held in quartz Hellma cells with a 1 mm path; cell volume = 300 µL. The temperature was imposed by a circulating fluid in the cell's holder rack. SANS data were collected at four different temperatures, the actual temperature was measured close to the samples at any time (see table). Additionally a last scan was performed at 25°C after cooling from 90°C to ensure a data collection of all sample with an uniform temperature history.

Interestingly B10, B5 and β10 samples (10% AltC18-bipyB, 5% AltC18-bipyB and 10% AltC12-bipyB) did clearly show a pink colour after the experiment.

Examples of obtained data are illustrated below:



Reduced data were downloaded directly from the ILL data portal site.[3] SANS results in D_2O and toluene D8 will be fitted with different models with the help of SASView fitting modules to elucidate the structure of solutions and organogelsgels. In addition for emulsions, quantitative evaluation of interphase density will be performed as described in ref 4. The results will be combined with other existing data from rheology, cryoTEM, DLS, UV-visible reflectometry and upcoming SAXS data to give a featured description of the self-assembled phases.

1 F. Tournilhac, E. Cazares-Cortes, M. Ouchi, L. Porcar, B. Tarus, DOI: 10.5291/ILL-DATA.DIR-158.
2 K. Nishimori, E. Cazares-Cortes, J.-M. Guigner, F. Tournilhac, M. Ouchi. *Polym. Chem.* 2019, **10**, 2327
3 F. Tournilhac, H. Trevisan, L. Porcar, DOI: 10.5291/ILL-DATA.9-11-1967.
4 I. Grillo, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2003, **225**, 153160

25 C		Tournilhac F., Trevisan H., Porcar L.					8-9 february 2020		9-11-1967			
Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam						223	191	159	141	
3	MTC	Empty cell						224	192	160	142	
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64	225	193	161	143	**225**
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64	226	194	162	144	**226**
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64	227	195	163	145	**227**
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64	228	196	164	146	**228**
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64	229	197	165	147	**229**
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64	230	198	166	148	**230**
10	R1	H_2O	13.5 vol%	D_2O			5.39		199	167	149	**199**
11	R2	D_2O	-	D_2O			6.33		200	168	150	**200**
12	A	Alt C12 + Acetone D6	0.045 vol%	R1	0.75	5.39	5.39	231	201	169	151	**231**
13	B	Alt C12 + Acetone H6	0.045 vol%	D_2O	0.75	0.27	6.33	232	202	170	152	**232**
14	C	Alt C12 + THF D8	0.045 vol%	D_2O	0.75	6.35	6.33	233	203	171	153	**233**
15	D	Alt C12 + THF H8	0.045 vol%	D_2O	0.75	0.18	6.33	234	204	172	154	**234**
16	E	Alt C18 + THF D8	0.045 vol%	D_2O	0.54	6.35	6.33	235	205	173	155	**235**
17	F	Alt C18 + THF H8	0.045 vol%	D_2O	0.54	0.18	6.33	236	206	174	156	**236**

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Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam										
3	MTC	Empty cell										
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64					
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64					
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64					
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64					
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64					
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64					
10	C18T	Alt C18	50 mg/mL	Toluene D8	0.54		5.64	237	264	273	282	**237**
11	C12T	Alt C12	50 mg/mL	Toluene D8	0.75		5.64	238	265	274	283	**238**
12	β10	Alt C12 + BipyB	100 mg/mL	Toluene D8	0.88		5.64	239	266	275	284	**239**
13	β5	Alt C12 + BipyB	50 mg/mL	Toluene D8	0.88		5.64	240	267	276	285	**240**
14	β2	Alt C12 + BipyB	25 mg/mL	Toluene D8	0.88		5.64	241	268	277	286	**241**
15	α5	Alt C12 + BipyA	50 mg/mL	Toluene D8	0.88		5.64	242	269	278	287	**242**
16	χ5	Alt C12 + BipyC	50 mg/mL	Toluene D8	0.93		5.64	243	270	279	288	**243**
17	δ5	Alt C12 + BipyD	50 mg/mL	Toluene D8	0.93		5.64	244	271	280	289	**244**
18	C18A	Alt C18	50 mg/mL	Acetone D6	0.93		5.39	245	272	281	290	**245**

40 C		Tournilhac F., Trevisan H., Porcar L.					8-9 february 2020		9-11-1967			
Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam										
3	MTC	Empty cell										
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64	366	321	306	291	**366**
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64	367	322	307	292	**367**
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64	368	323	308	293	**368**
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64	369	324	309	294	**369**
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64	370	325	310	295	**370**
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64	371	326	311	296	**371**
10	C18T	Alt C18	50 mg/mL	Toluene D8	0.54		5.64	372	327	312	297	**372**
11	C12T	Alt C12	50 mg/mL	Toluene D8	0.75		5.64	373	328	313	298	**373**
12	β10	Alt C12 + BipyB	100 mg/mL	Toluene D8	0.88		5.64	374	329	314	299	**374**
13	β5	Alt C12 + BipyB	50 mg/mL	Toluene D8	0.88		5.64	375	330	315	300	**375**
14	β2	Alt C12 + BipyB	25 mg/mL	Toluene D8	0.88		5.64	376	331	316	301	**376**
15	α5	Alt C12 + BipyA	50 mg/mL	Toluene D8	0.88		5.64	377	332	317	302	**377**
16	χ5	Alt C12 + BipyC	50 mg/mL	Toluene D8	0.93		5.64	378	333	318	303	**378**
17	δ5	Alt C12 + BipyD	50 mg/mL	Toluene D8	0.93		5.64	379	334	319	304	**379**
18	C18A	Alt C18	50 mg/mL	Acetone D6	0.93		5.39	380	335	320	305	**380**

60 C		Tournilhac F., Trevisan H., Porcar L.					8-9 february 2020		9-11-1967			
Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam										
3	MTC	Empty cell										
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64	395	423	437	451	**395**
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64	396	424	438	452	**396**
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64	397	425	439	453	**397**
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64	398	426	440	454	**398**
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64	399	427	441	455	**399**
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64	400	428	442	456	**400**
10	C18T	Alt C18	50 mg/mL	Toluene D8	0.54		5.64	401	429	443	457	**401**
11	C12T	Alt C12	50 mg/mL	Toluene D8	0.75		5.64	402	430	444	458	**402**
12	β10	Alt C12 + BipyB	100 mg/mL	Toluene D8	0.88		5.64	403	431	445	459	**403**
13	β5	Alt C12 + BipyB	50 mg/mL	Toluene D8	0.88		5.64	404	432	446	460	**404**
14	β2	Alt C12 + BipyB	25 mg/mL	Toluene D8	0.88		5.64	405	433	447	461	**405**
15	α5	Alt C12 + BipyA	50 mg/mL	Toluene D8	0.88		5.64	406	434	448	462	**406**
16	χ5	Alt C12 + BipyC	50 mg/mL	Toluene D8	0.93		5.64	407	435	449	463	**407**
17	δ5	Alt C12 + BipyD	50 mg/mL	Toluene D8	0.93		5.64	408	436	450	464	**408**

90 C		Tournilhac F., Trevisan H., Porcar L.					8-9 february 2020		9-11-1967			
Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam										
3	MTC	Empty cell										
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64	535	493	479	465	**535**
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64	536	494	480	466	**536**
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64	537	495	481	467	**537**
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64	538	496	482	468	**538**
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64	539	497	483	469	**539**
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64	540	498	484	470	**540**
10	C18T	Alt C18	50 mg/mL	Toluene D8	0.54		5.64	541	499	485	471	**541**
11	C12T	Alt C12	50 mg/mL	Toluene D8	0.75		5.64	542	500	486	472	**542**
12	β10	Alt C12 + BipyB	100 mg/mL	Toluene D8	0.88		5.64	543	501	487	473	**543**
13	β5	Alt C12 + BipyB	50 mg/mL	Toluene D8	0.88		5.64	544	502	488	474	**544**
14	β2	Alt C12 + BipyB	25 mg/mL	Toluene D8	0.88		5.64	545	503	489	475	**545**
15	α5	Alt C12 + BipyA	50 mg/mL	Toluene D8	0.88		5.64	546	504	490	476	**546**
16	χ5	Alt C12 + BipyC	50 mg/mL	Toluene D8	0.93		5.64	547	505	491	477	**547**
17	δ5	Alt C12 + BipyD	50 mg/mL	Toluene D8	0.93		5.64	548	506	492	478	**548**

25 C		Tournilhac F., Trevisan H., Porcar L.					8-9 february 2020		9-11-1967			
Nb in rack	Short name	Sample name	Concentration	Solvent	SLD solid	SLD cosolvent	SLD solvent	Manip 1	Manip 2	Manip 3	Manip 4	Filename
λ (Å)								11.5	6	6	6	
D (m)								17.6	17.6	5.6	1.5	
1	MTB	Empty beam										
2	BB	Blocked beam										
3	MTC	Empty cell										
4	B10	Alt C18 + BipyB	100 mg/mL	Toluene D8	0.67		5.64	563	577	605	619	**563**
5	B5	Alt C18 + BipyB	50 mg/mL	Toluene D8	0.67		5.64	564	578	606	620	**564**
6	B2	Alt C18 + BipyB	25 mg/mL	Toluene D8	0.67		5.64	565	579	607	621	**565**
7	A5	Alt C18 + BipyA	50 mg/mL	Toluene D8	0.67		5.64	566	580	608	622	**566**
8	C5	Alt C18 + BipyC	50 mg/mL	Toluene D8	0.67		5.64	567	581	609	623	**567**
9	D5	Alt C18 + BipyD	50 mg/mL	Toluene D8	0.72		5.64	568	582	610	624	**568**
10	C18T	Alt C18	50 mg/mL	Toluene D8	0.54		5.64	569	583	611	625	**569**
11	C12T	Alt C12	50 mg/mL	Toluene D8	0.75		5.64	570	584	612	626	**570**
12	β10	Alt C12 + BipyB	100 mg/mL	Toluene D8	0.88		5.64	571	585	613	627	**571**
13	β5	Alt C12 + BipyB	50 mg/mL	Toluene D8	0.88		5.64	572	586	614	628	**572**
14	β2	Alt C12 + BipyB	25 mg/mL	Toluene D8	0.88		5.64	573	587	615	629	**573**
15	α5	Alt C12 + BipyA	50 mg/mL	Toluene D8	0.88		5.64	574	588	616	630	**574**
16	χ5	Alt C12 + BipyC	50 mg/mL	Toluene D8	0.93		5.64	575	589	617	631	**575**
17	δ5	Alt C12 + BipyD	50 mg/mL	Toluene D8	0.93		5.64	576	590	618	632	**576**