Óbudai Egyetem

mta ttk

Óbuda University

Doctoral School on Materials Sciences and Technologies

3rd semester progress presentation : Spring 2017/18

"Application of calixresorcinarenes as sensors in the detection of heavy metals ions in the environment"

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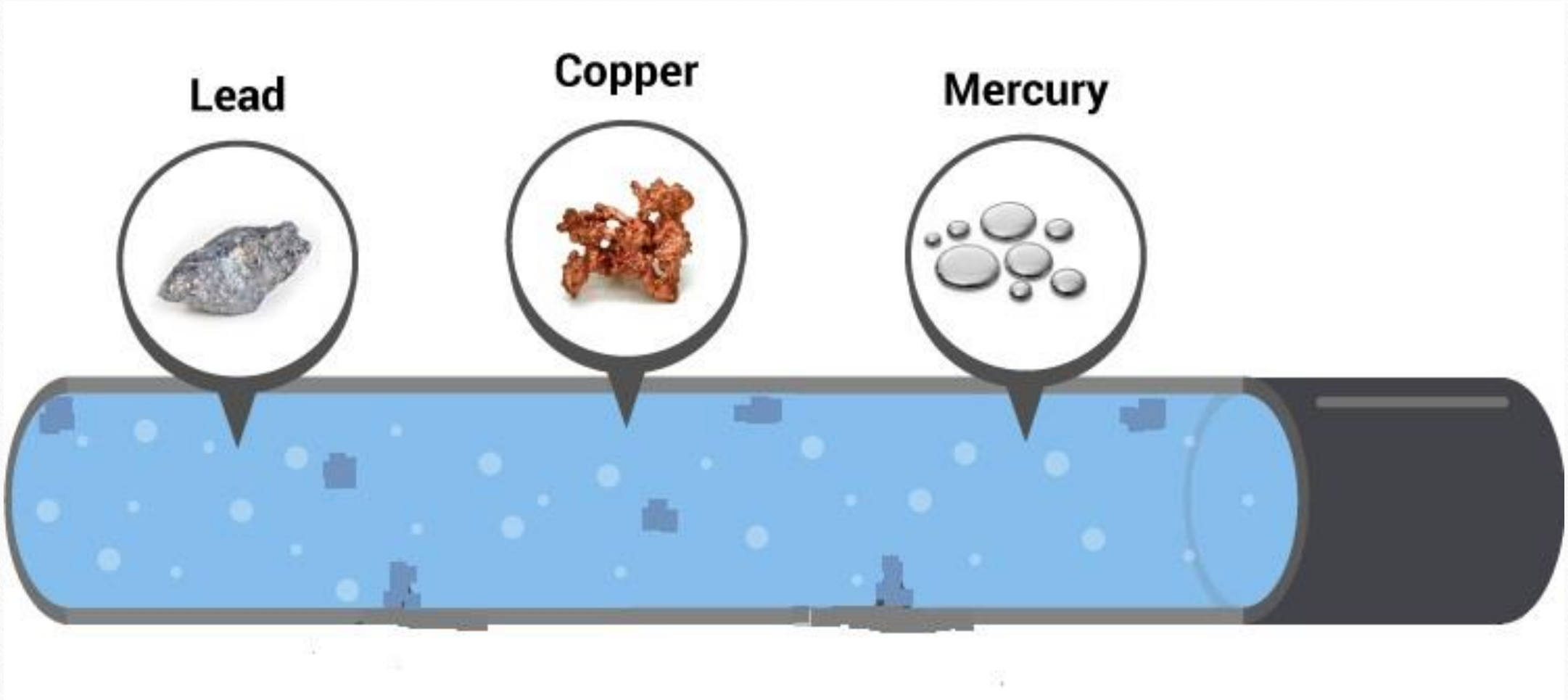
Supervisor: Dr. Shaban Abdul

Budapest 21 June 2018

Outlines

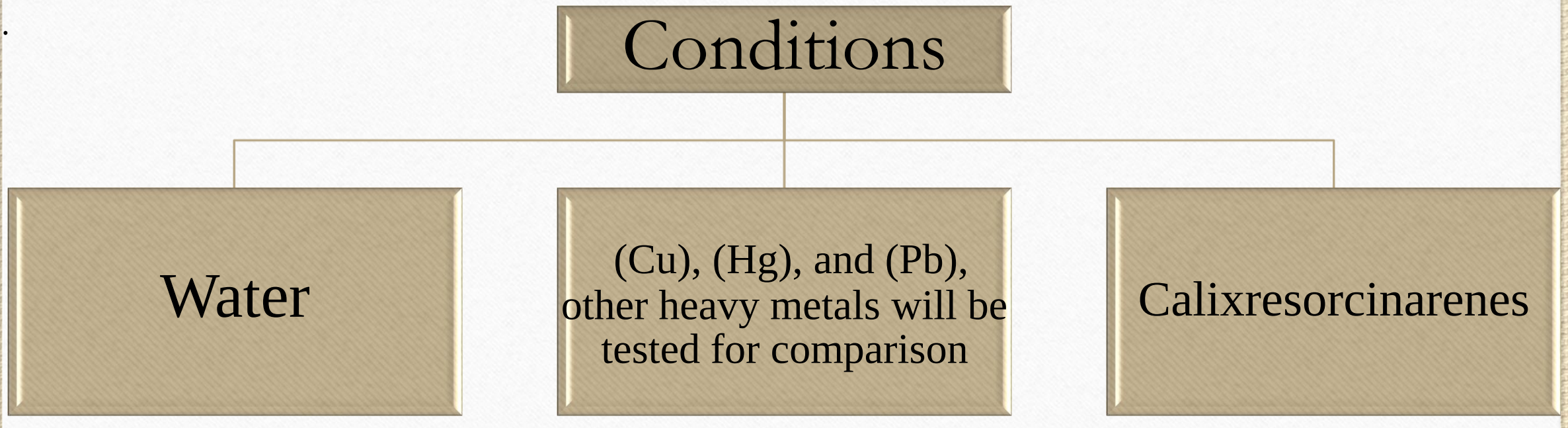

Introduction
Topic of research and previous results
Results of the actual semester
Future planned tasks
Conclusion

Introduction: Heavy metals toxins



Topic of research

"The application of calixresorcinarenes sensors in the detection of heavy metals ions in the environment"



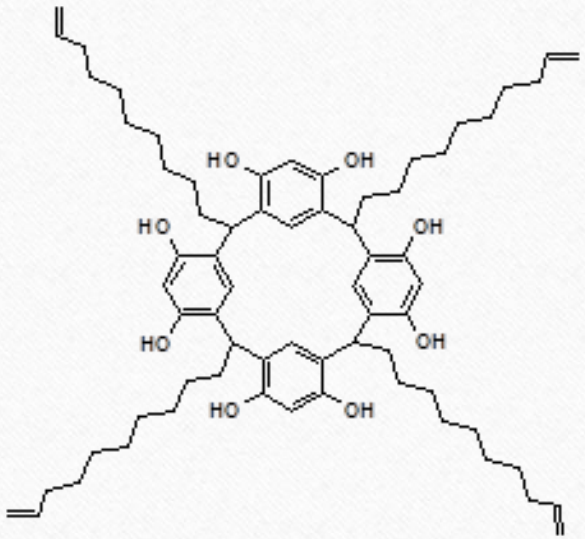
Previous results

Synthesis

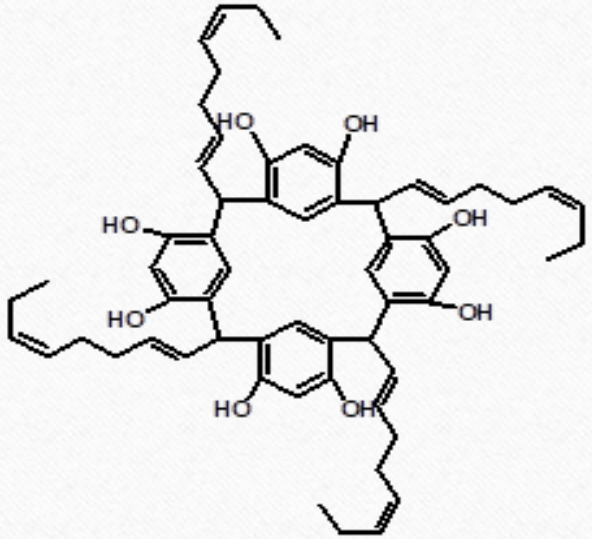
- Synthesis of macrocycles by condensation reaction

- LAR 1001: C-undecenylcalix[4]resorcinarene,
- LAR 2001: C-trans-2, cis-6-nonadienylcalix[4]resorcinarene,
- LAR 3001: C-undecenylcalix[4]resorcinarene-O- (R+)-α-methylbenzylamine,
- LAR 4001= 6001: C-undecenylcalix[4]resorcinarene-O-(S-)-α-methylbenzylamine,
- LAR 5001= LAR 8001: C-undecylcalix[4]resorcinarene,
- LAR 7001 : tert-Butylcalix(4)arene.

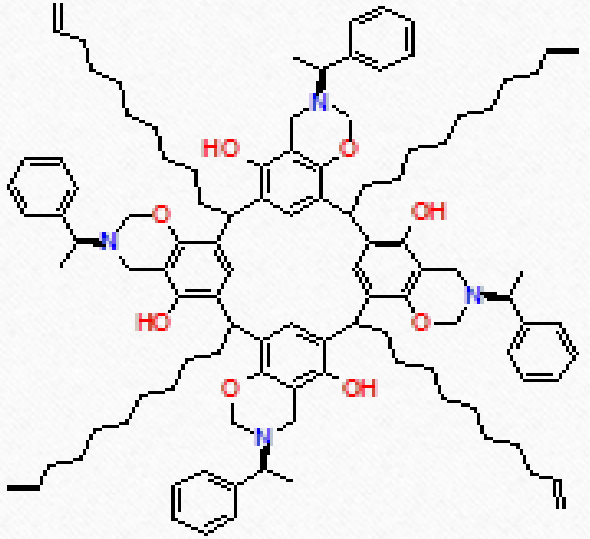
Previous results



LAR 1001

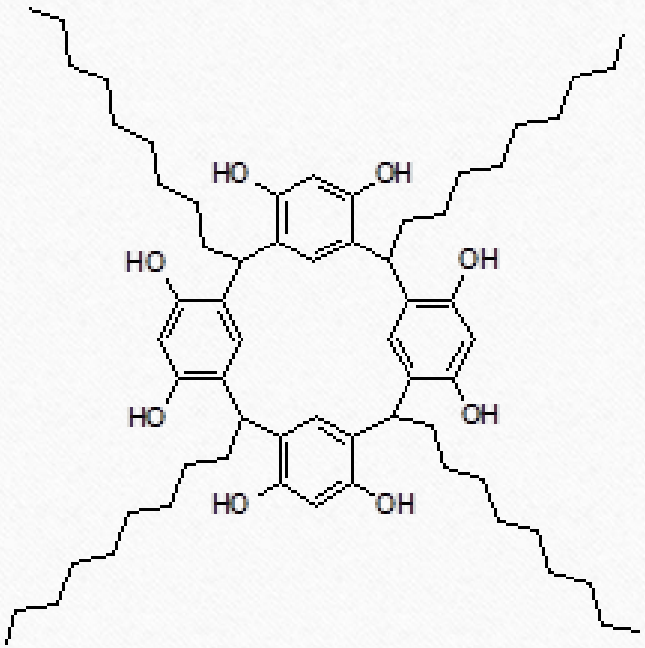


LAR 2001

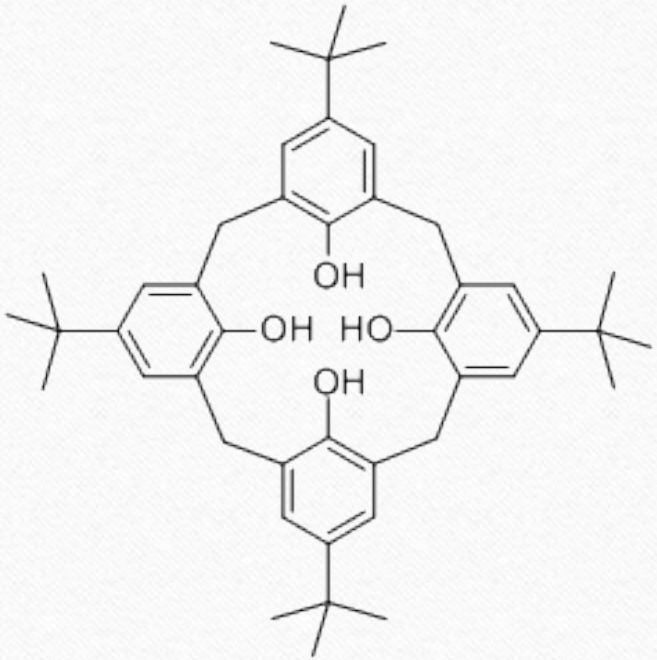


LAR 3001, LAR 4001, LAR 6001

Previous results



LAR 5001, 8001



LAR 7001

Previous results

Characte-rization

- To know the properties of the molecules

- Melting points,
- L-B isotherms,
- B.A.M. images,
- Simulation of size of macrocycles,
- QCM-I detection of lead ions in aqueous solution

Results of the actual semester

Characterization of macrocycles

FTIR measurements : to define the functional groups,

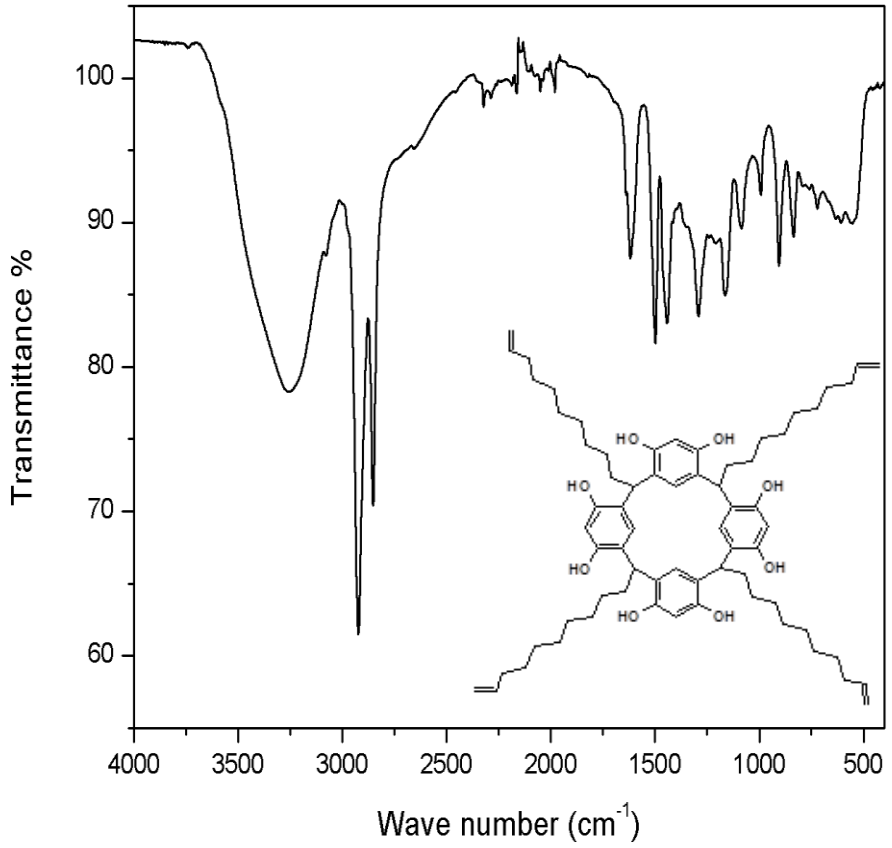
TG-DSC coupled with *MS* : to study the thermal behavior,

XRD : to evaluate the crystallinity.

Results of the actual semester: FTIR Measurements

To define the functional groups that can help in the determination of the structure

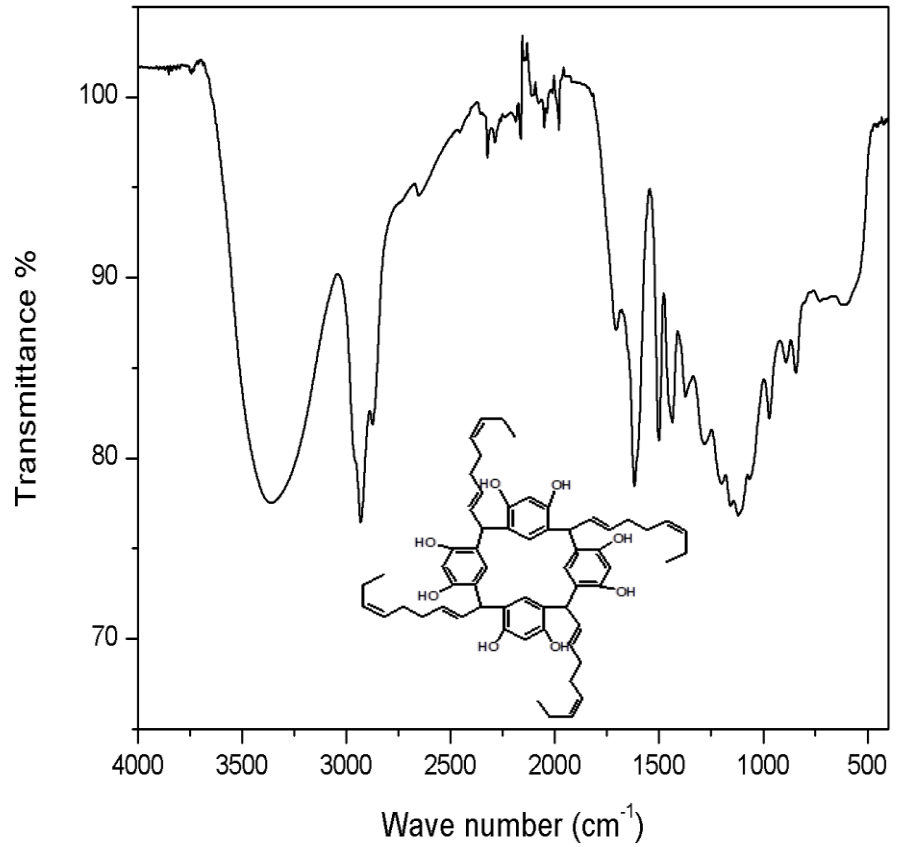
Results of the actual semester: FTIR Measurements



	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	3255	Associated O-H	Stretching	Strong and large
	1166	C-O	Stretching	Medium
	1292	O-H	In plan deformation	Medium
Vinyl	3077	=C-H	Stretching	Medium
	3034	=C-H	Stretching	Medium
	1822	C-H	Deformation harmonics	Medium
	1622	C=C	Stretching	Medium
Aromatic	3074	=C-H	Stretching	Medium
	1500	C=C	Stretching	Medium
	1440	C=C	Stretching	Medium
	1980	C-H	Deformation harmonics	Small
	835	C-H	Out plan deformation	Medium to small
Alkane	2925	CH_2	Asymmetric stretching	Strong
	2853		Symmetric stretching	Medium
	721		Rocking	Medium to small

LAR 1001

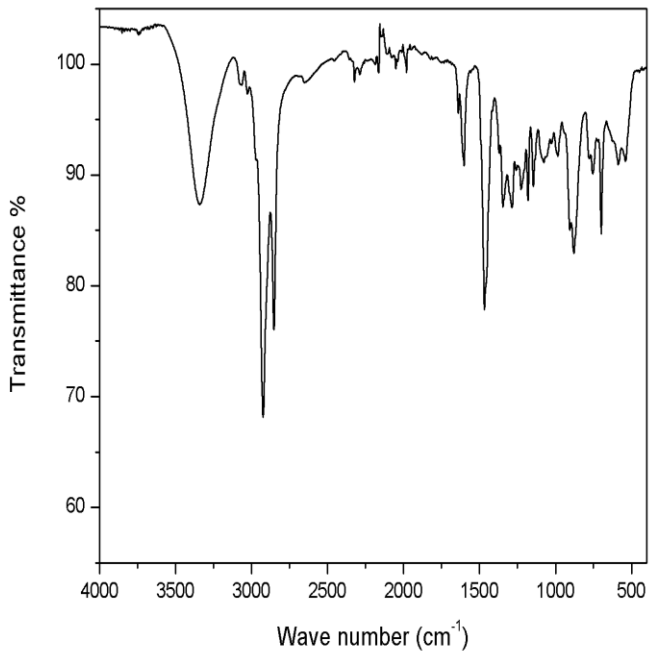
Results of the actual semester: FTIR Measurements



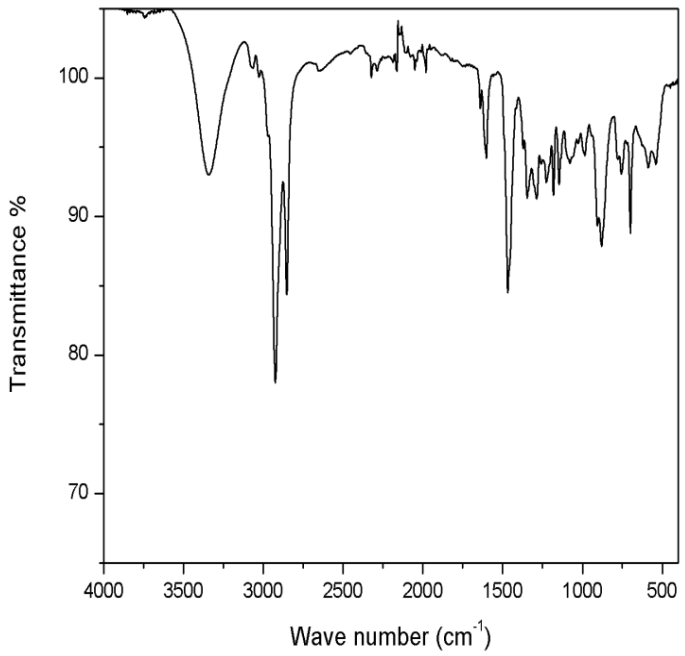
		Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol		3361	Associated O-H	Stretching	Strong and large
		1201	C-O	Stretching	Strong
		1373	O-H	In plan deformation	Strong
Aromatic		1598	C=C	Stretching	Small
		1560	C=C	Stretching	Small
		1500	C=C	Stretching	Medium
		1437	C=C	Stretching	Medium
		1707	C-H	Deformation harmonics	Small
		890	=C-H	Out plan deformation	Medium
Alkene	Cis	1652	C=C	Stretching	Medium
		727	=C-H	Out plan deformation	Medium
	Trans	1683	C=C	Stretching	Medium
		1288	=C-H	In plan deformation	Medium
		971	=C-H	Out plan deformation	Strong
		1620	C=C	Stretching	Strong
Alkane		2931	CH_2	Asymmetric stretching	Strong
		2874	CH_3	Symmetric stretching	Strong
		1437	CH_3	In plan deformation	Medium
		729	CH_2	Rocking	Medium

LAR 2001

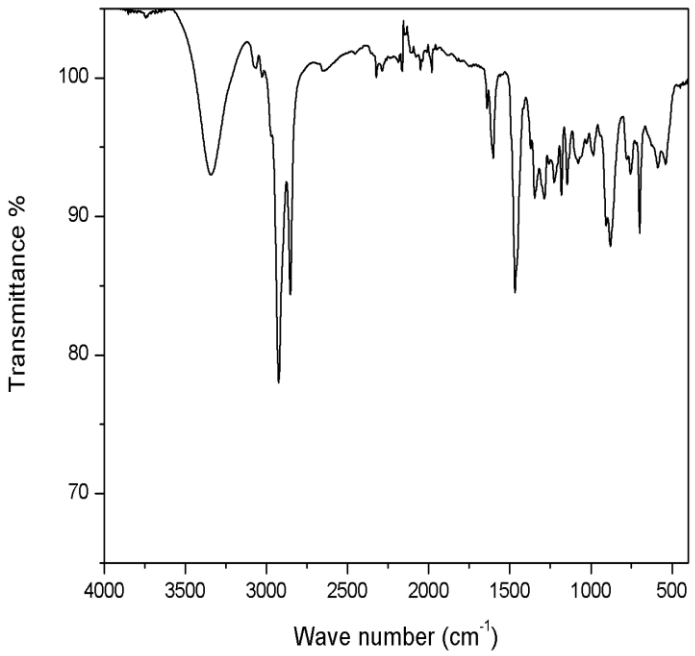
Results of the actual semester: FTIR Measurements



LAR 3001

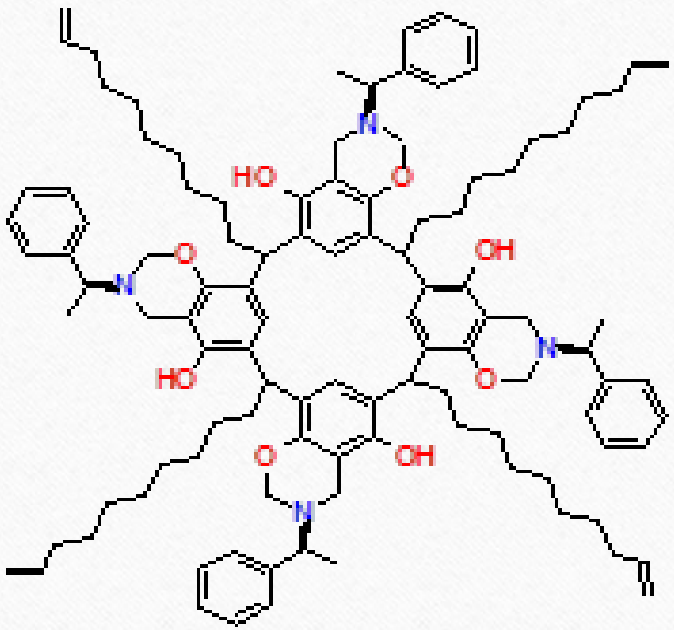


LAR 4001



LAR 6001

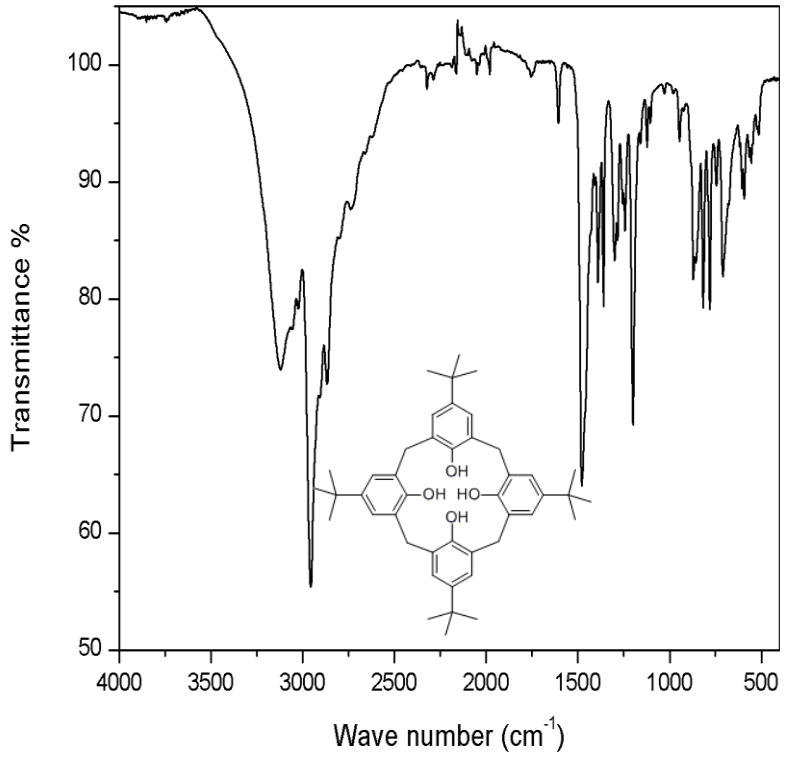
Results of the actual semester: FTIR Measurements



They've the same spectra, the difference is in configuration 'R' and 'S'

	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	3340	Associated O-H	Stretching	Strong & large
	1226	C-O	Stretching	Medium
	1348	O-H	In plan deformation	Medium
Vinyl	3070	=C-H	Stretching	Small to medium
	3027	=C-H	Stretching	Small to medium
	1822	C-H	Deformation harmonics	Small
	1640	C=C	Stretching	Small to medium
	907	=C-H	Out plan deformation	Strong
	880	=C-H	Out plan deformation	Strong
Aromatic	3030	=C-H	Stretching	Small
	1602	C=C	Stretching	Small
	1560	C=C	Stretching	Small
	1540	C=C	Stretching	Small
	1468	C=C	Stretching	Medium
	1980	C-H	Deformation harmonics	Small
5H adj.	778	=C-H	Out plan deformation	Medium
1H adj.	750	=C-H	Out plan deformation	Medium
	880	=C-H	Out plan deformation	Medium
Tertiary amine	1145	C-N	Stretching (Aliphatic amine)	Small
Cyclic ether	1181	C-O	Stretching	Medium to strong
Alkane	2853	CH_3	Symmetric stretching	Strong
	1468	CH_3	Symmetric plan deformation	Medium
	2925	CH_2	Asymmetric stretching	Strong
	700	CH_2	Rocking	Medium
	2970	C-H	Stretching	Small
	1346	C-H	Out plan deformation	Small

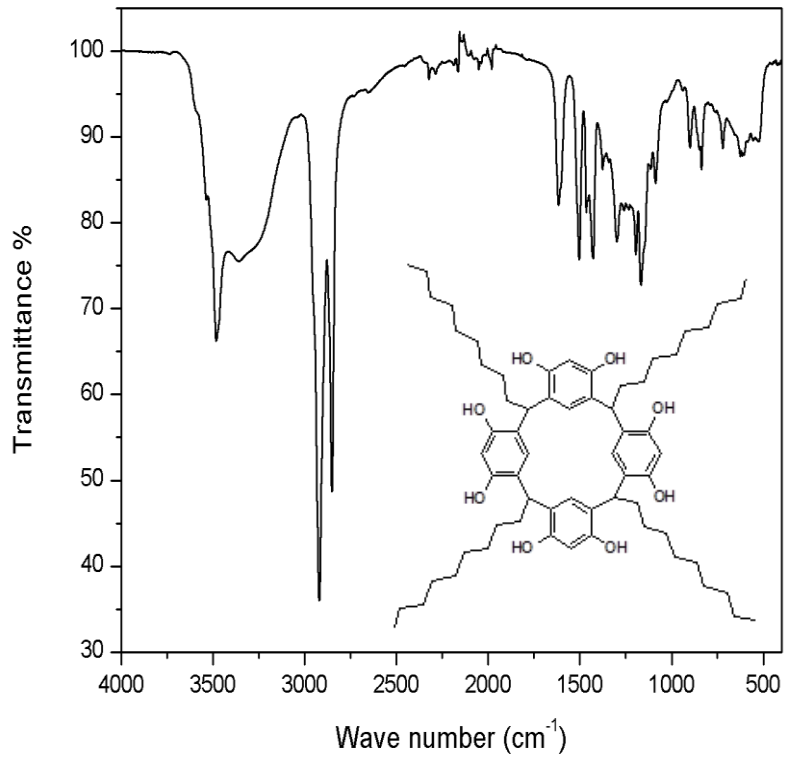
Results of the actual semester: FTIR Measurements



	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Phenol	3123	Associated O-H	Stretching	Strong & large
	1200	C-O	Stretching	Strong
	1360	O-H	In plan deformation	Medium to strong
Aromatic cycle	3024	=C-H	Stretching	Medium
	1606	C=C	Stretching	Small
	1575	C=C	Stretching	Small
	1539	C=C	Stretching	Medium
	1480	C=C	Stretching	Small
	1755	C-H	Deformation harmonics	Small
	872	=C-H	Out plan deformation	Small to medium
Alkane	2956	CH_3	Asymmetric stretching	Strong
	2867	CH_3	Symmetric stretching	Strong
	1391	CH_3	In plan deformation(T-butyl)	Medium
	1361	CH_3	In plan deformation(T-butyl)	Strong
	1280	C-C (Tert-butyl chain)	stretching	Small

LAR 7001

Results of the actual semester: FTIR Measurements



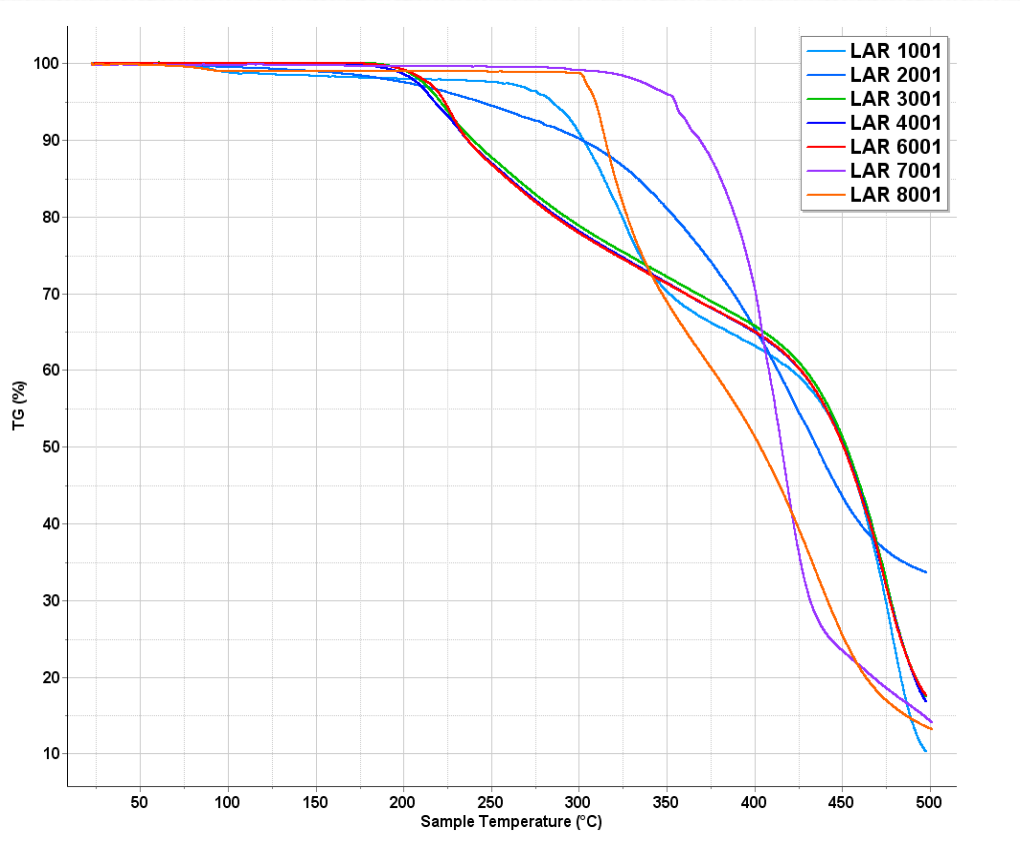
	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	**3481**	Associated O-H	Stretching	Strong & large
	1196	C-O	Stretching	Medium to strong
	1377	O-H	In plan deformation	Medium
Aromatic	**3038**	=C-H	Stretching	Very small
	1616	C=C	Stretching	Medium
	1503	C=C	Stretching	Medium
	1464	C=C	Stretching	Medium
	1979	C-H	Deformation harmonics	Small
	900	=C-H	Out plan deformation	Small
Alkane	**2850**	CH_3	Symmetric stretching	Strong
	1430	CH_3	Asymmetric plan deformation	Medium
	2922	CH_2	Asymmetric stretching	Strong
	1465	CH_2	Scissoring	Medium
	722	CH_2	Rocking	Medium
	1342	C-H	In plan deformation	Very small
	1166	Linear chain C-C	Stretching	Small

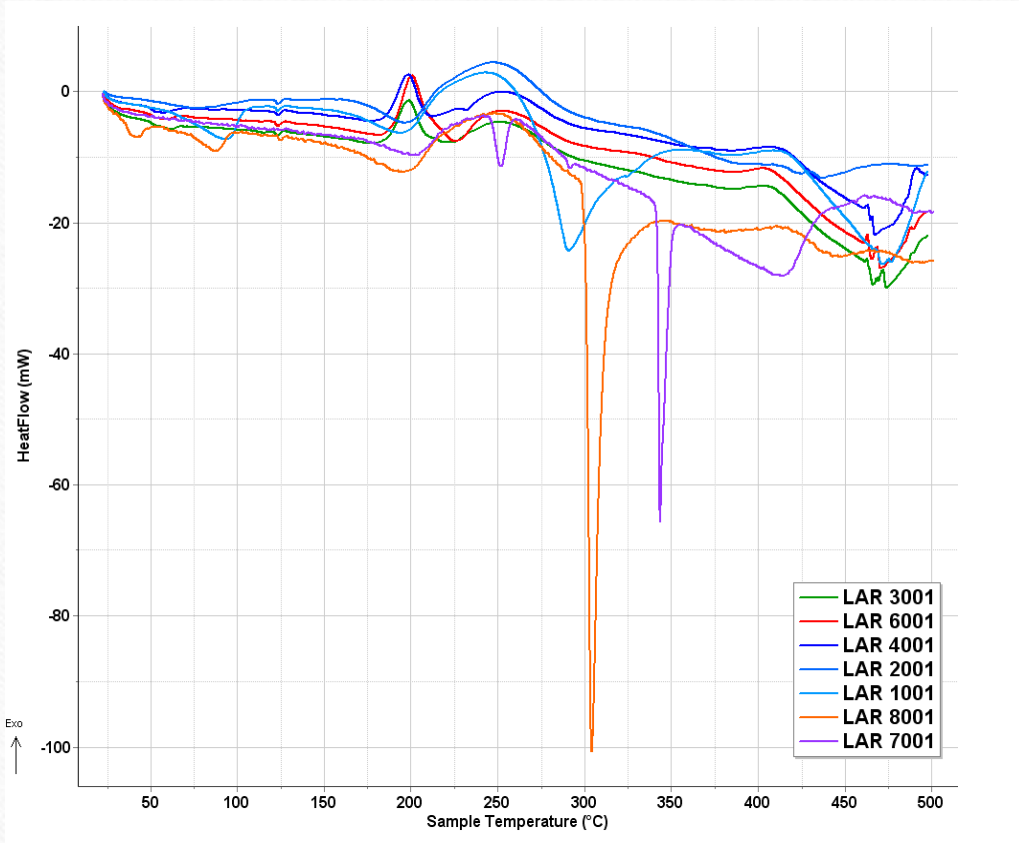
LAR 8001

Results of the actual semester: TG and DSC

To study the thermal behavior :
-Determine the purity,
-Confirm the melting points.

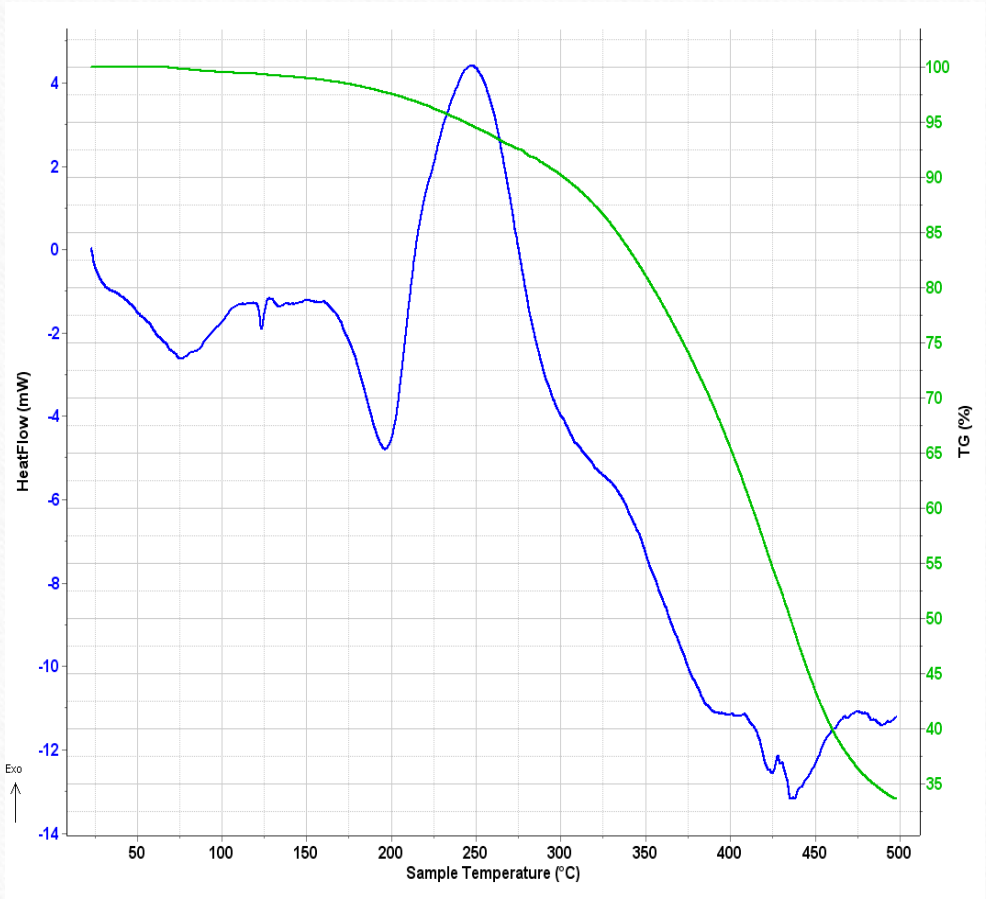
Results of the actual semester: TG and DSC / Heat Flow





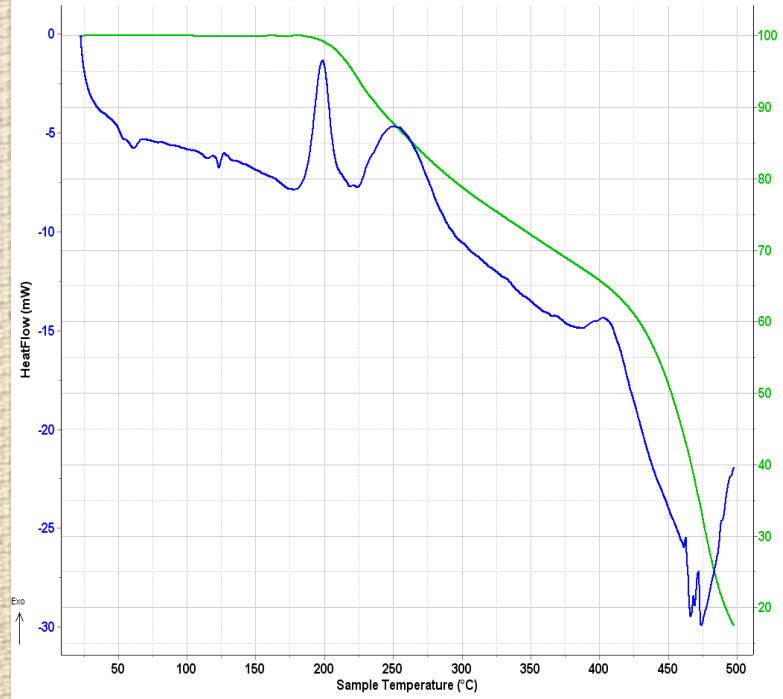
Results of the actual semester: TG-DSC

LAR 1001

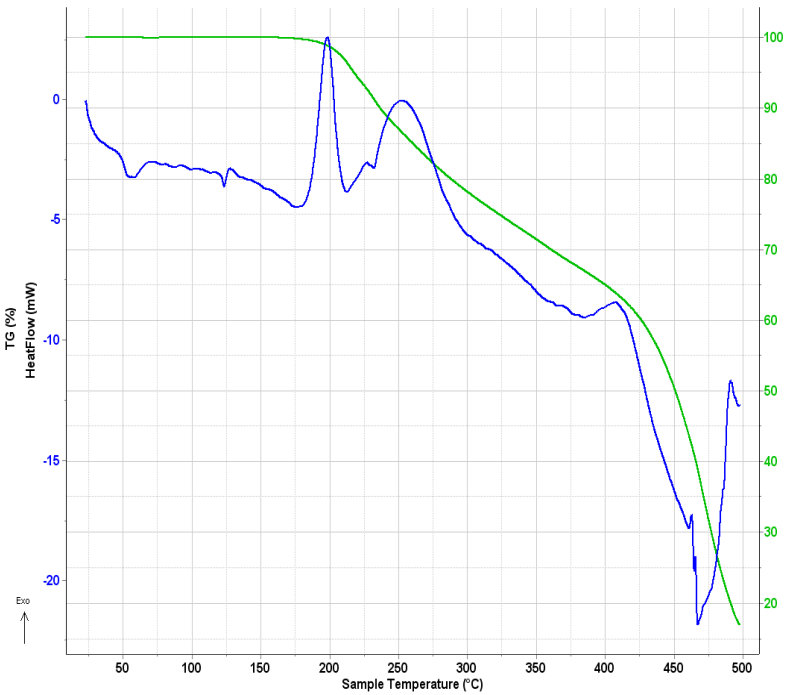


LAR 2001

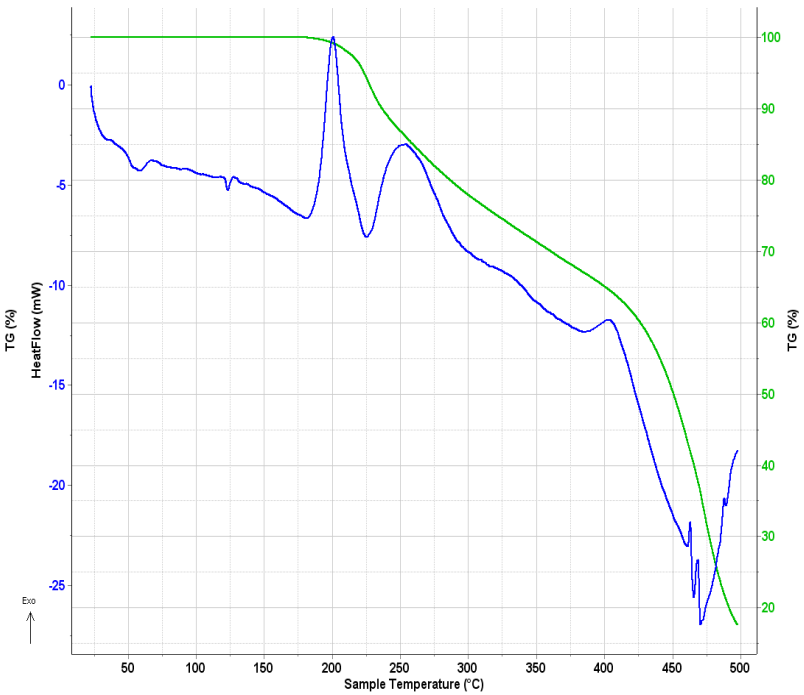
Results of the actual semester: TG-DSC



LAR 3001

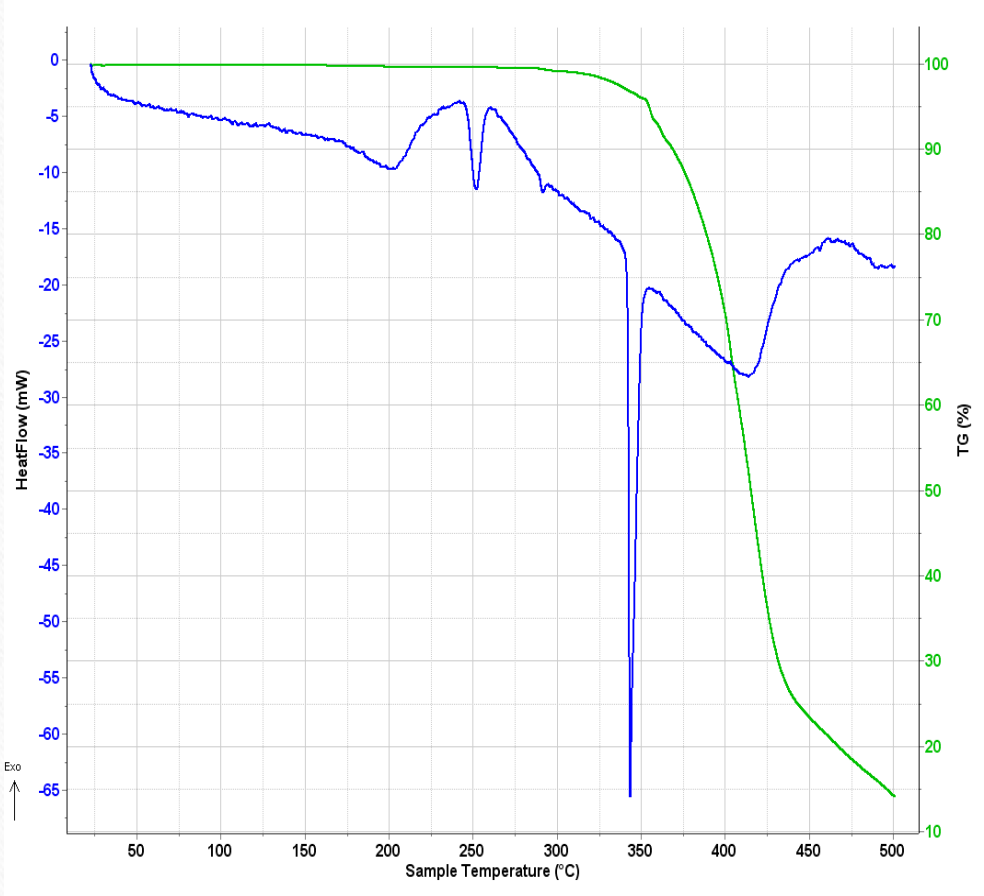


LAR 4001

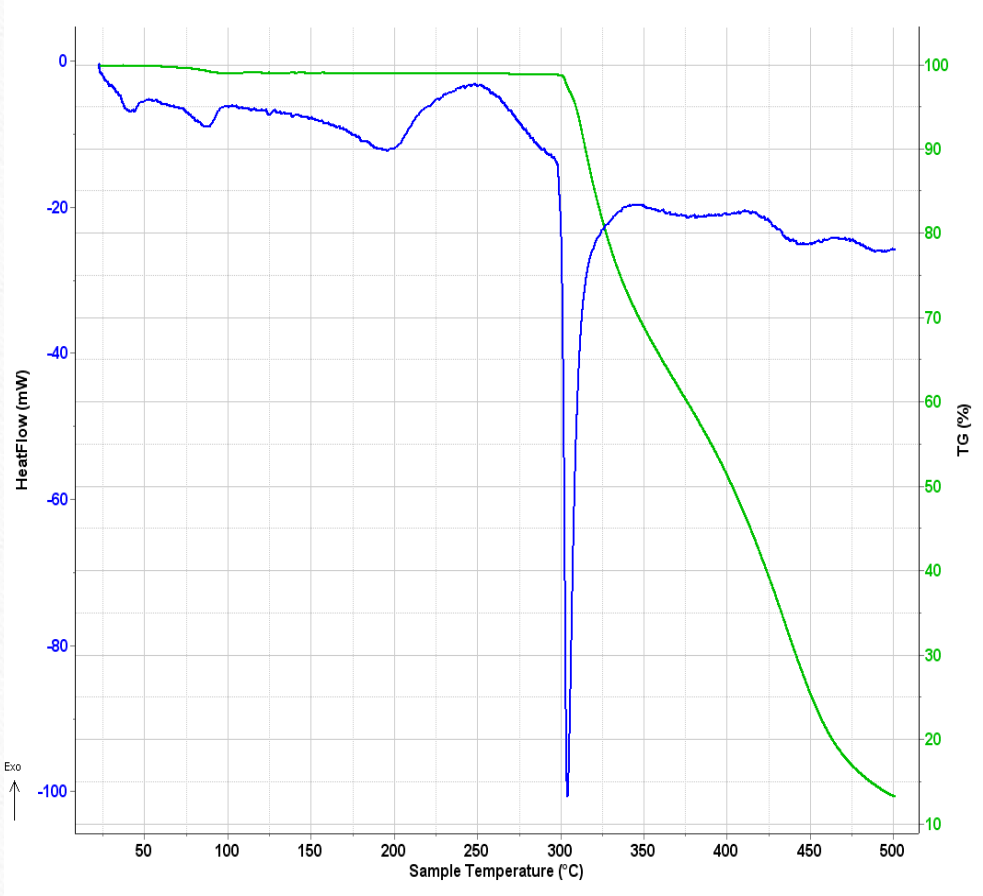


LAR 6001

Results of the actual semester: TG-DSC



LAR 7001



LAR 8001

Results of the actual semester: TG-DSC

Experimental and DSC Melting points

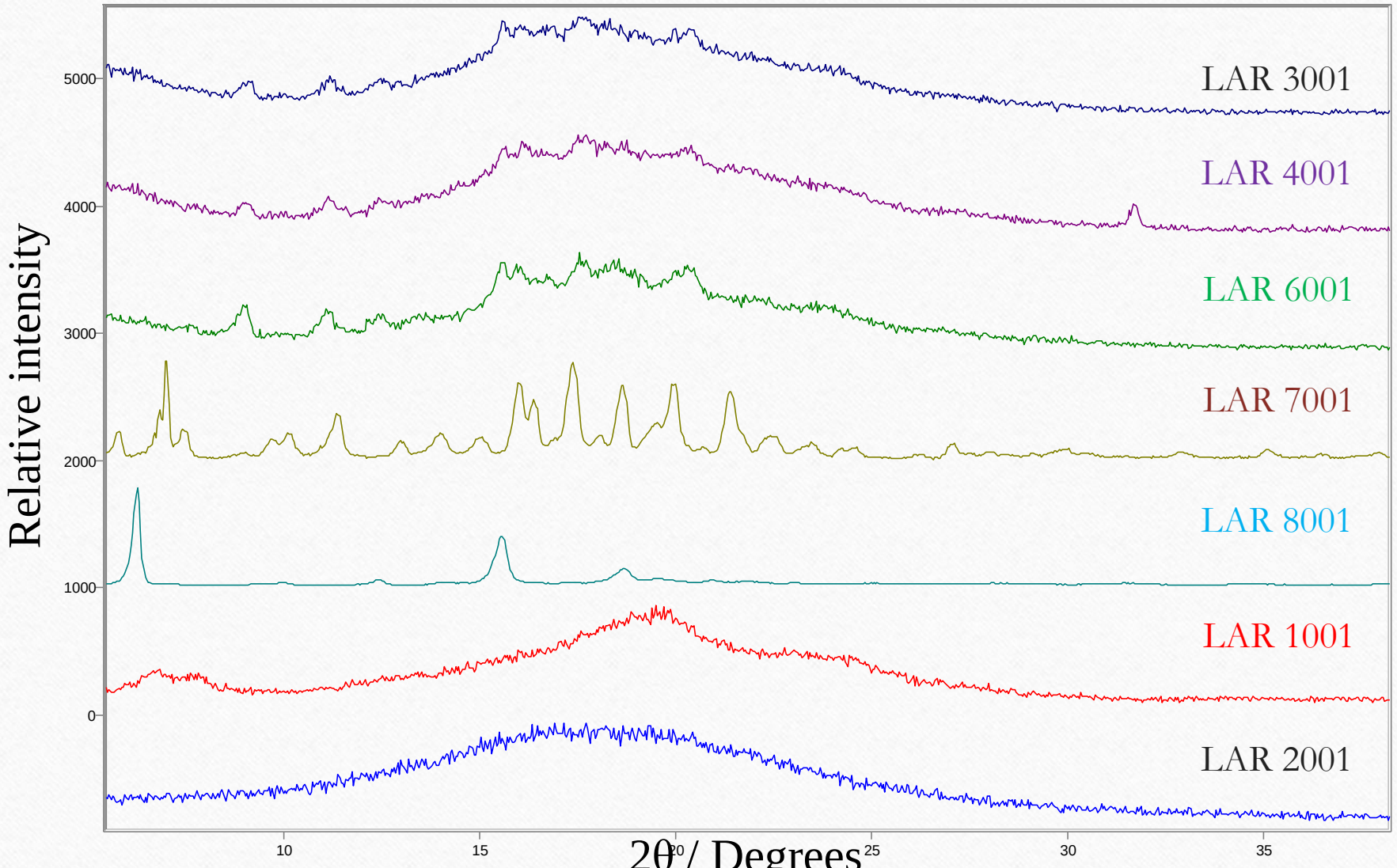
Codes	Exp M.P.	DCS M.P. (Onset)	Pic maximum
LAR 1001	277	269.5	289.9
LAR 2001	No thermal event	No thermal event	No thermal event
LAR 3001	70	48.7	61.0
LAR 4001	75.6	48.4	53.8
LAR 6001	70	49.2	59.0
LAR 7001	315	342.2	343.6
LAR 8001	285	300.7	304.2

The results are in good agreement

Results of the actual semester : XRD Analysis

To study the crystallinity

Results of the actual semester : XRD Analysis



Results of the actual semester

Subject Title & Neptune codes	Lecturers	No. of credits
Seminar on Materials science (OATATSZ1ND)	Dr. Borsa Judit	3
Cellulose chemistry (OATCSZM1ND)	Dr. Borsa Judit	6
Application of polymers in 3D microtechnology (OATPOAM1LD)	Dr. Pap Andrea	6
Environmental chemistry (OATENCH1ND)	Dr. Shaban Abdul	6
Research project III (OATKUTP3ND)	Dr. Shaban Abdul	10
Research Report III (OATBESZ3ND)	Dr. Shaban Abdul	6
Total credits		37

Future planned tasks

- Continuation of the characterization using methods as : AFM, ESEM, NMR,
- Try to prove the complexation process between the sensing materials and the heavy metals ions by UV,
- Perform electrochemical measurements using EIS,
- Modification of the sensor surface by the immobilization of the macrocycles and perform detection measurements using the QCM-I,
- Submission of a publication and another one is on the way.

Conclusions

- IR results showed all the functional groups belonging to the structures of the molecules,
- TG-DSC measurements confirmed the purity of the samples and the melting points were similar to those determined directly,
- XRD patterns gave us an idea about the degree of crystallinity of all the macrocycles.

Köszönöm a figyelmet!