Nanocomposites composed of HEUR polymer and magnetite iron oxide nanoparticles: structure and dynamics

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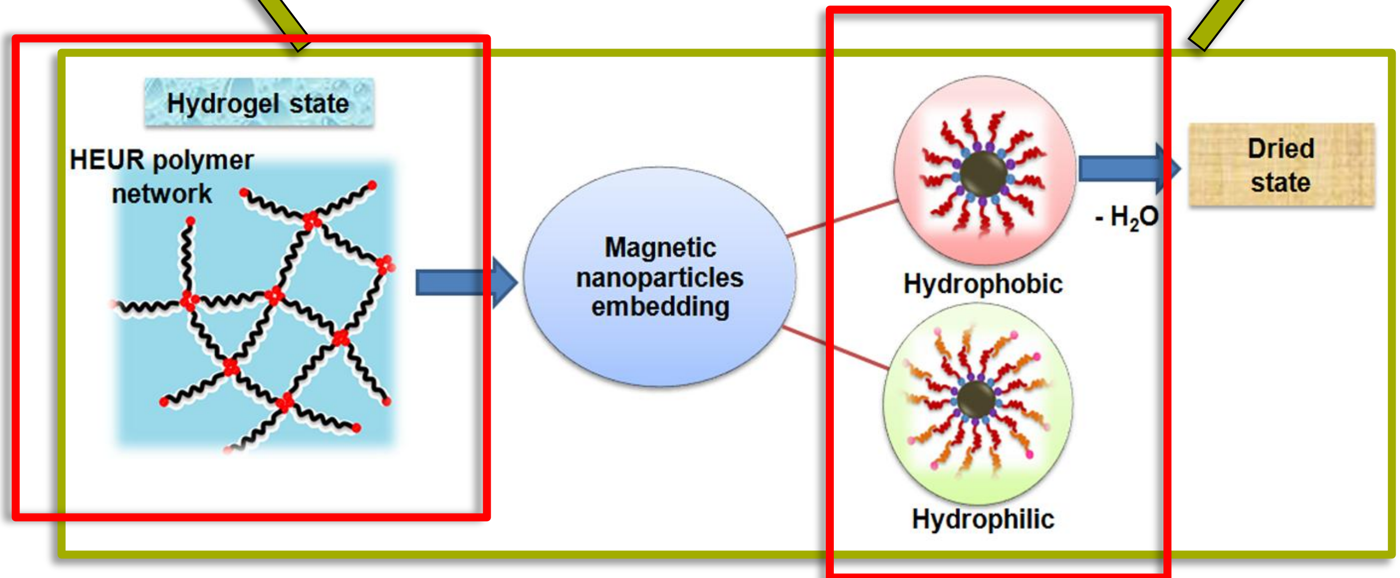
2nd internal biennial science meeting of the MLZ, Grainau,15-18 June 2015

MLZ is a cooperation between:

Outline

structural investigation of the nanocomposites as hydrogels and as dry films using SANS[1]

magnetic properties of the dried state[1]



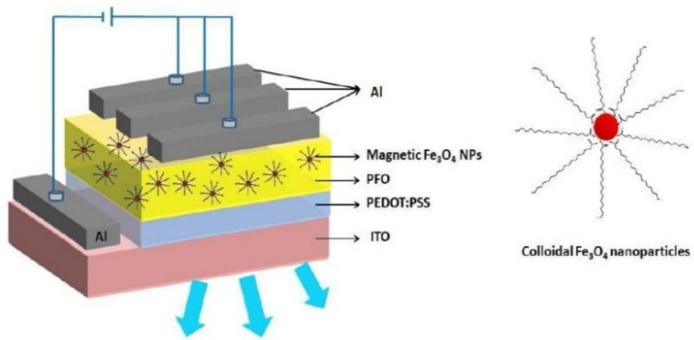
1. Polymer matrix

2. Magnetite nanoparticles

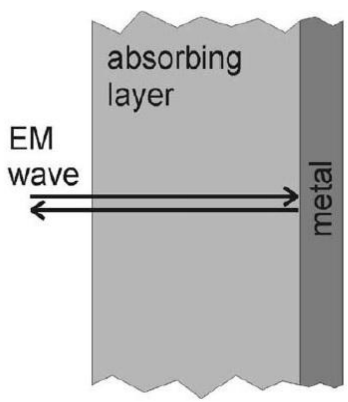
Dynamics through Dielectric Spectroscopy measurements

[1]*A.Campanella et al, Polymer, 60 (2015),176-185*

Possible applications of magnetic nanocomposites

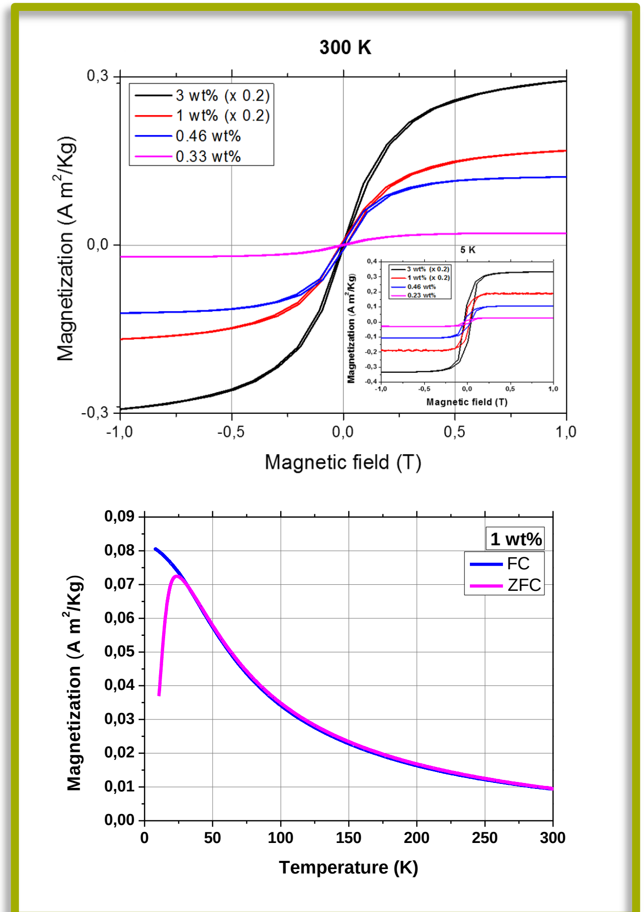


OLED devices with MNPs as dopant[1]



EM absorbers[2]

3



[1] *M. Kus, F. Ozel, N. M. Varal, and M. Ersoz, Progress in Electromagnetics Research, 2013, 134, 509-524*
[2] *V. B. Bregar , IEEE Transactions on Magnetics, 2004, 40, 1679-1684*
[3] *A.Campanella et al, Polymer, 60 (2015),176-185*

1. polymer matrix

HEUR polymers**: H**ydrophobically modified **E**thoxylated **UR**ethanes

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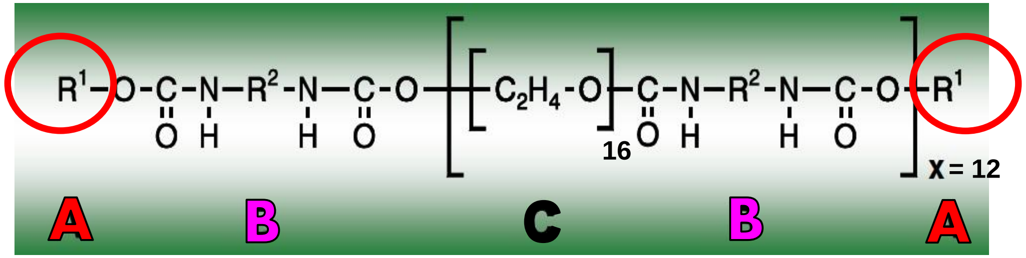
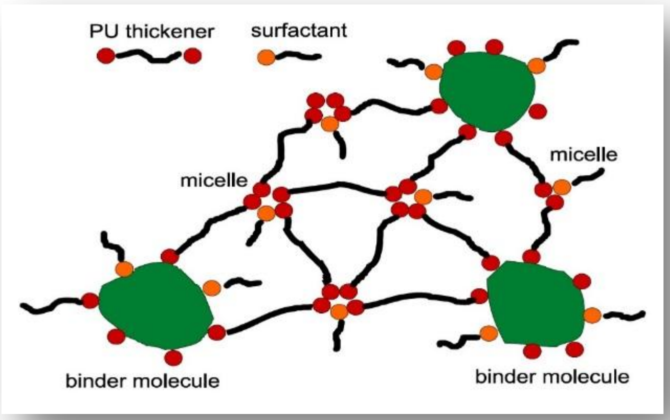
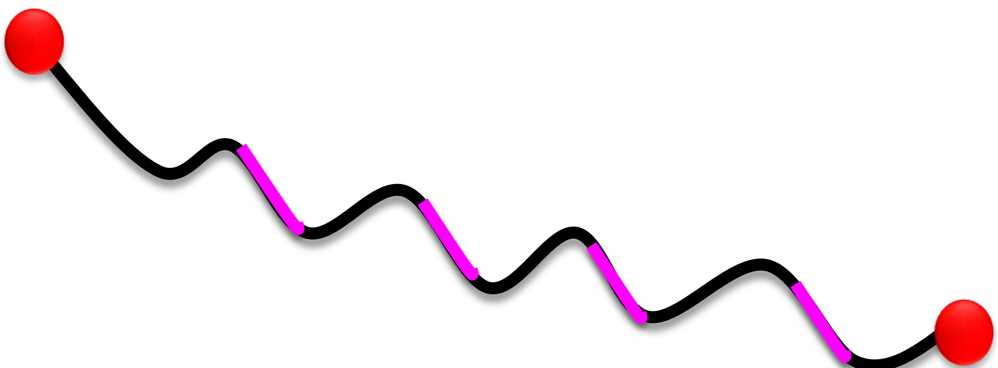


A. long alkyl chains (C_{22}) **B**. Urethanes groups ($R^2=C_4$) **C.** PEO

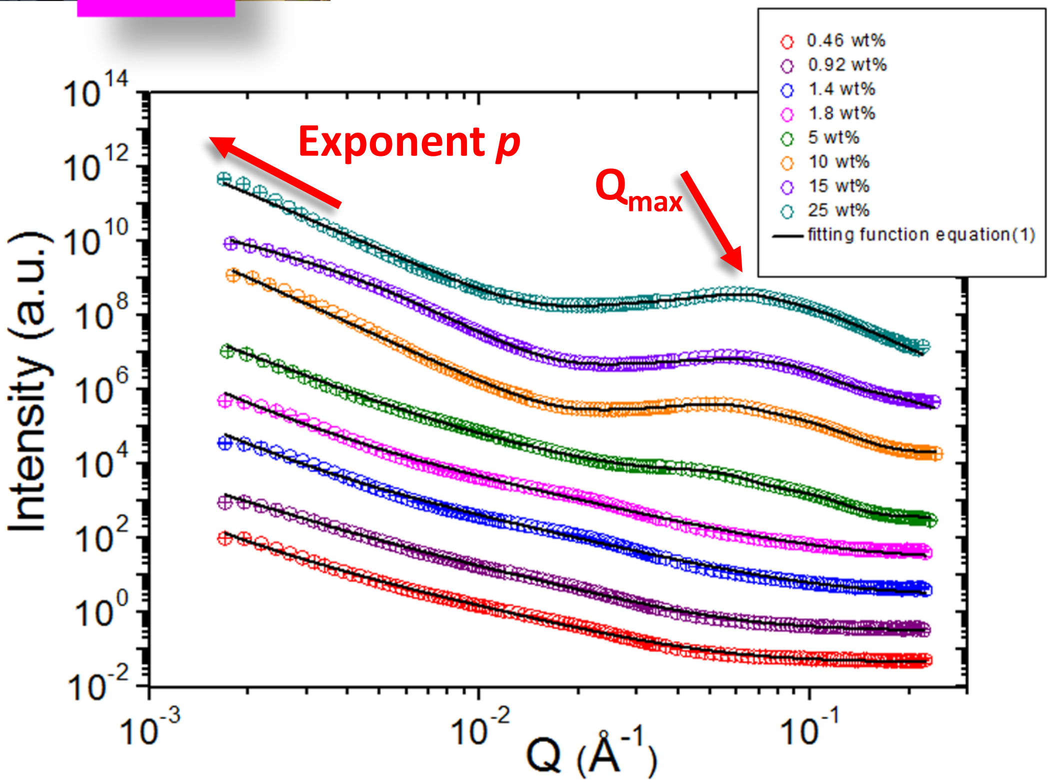


micelles as junction points immobilise hydrophobic particles

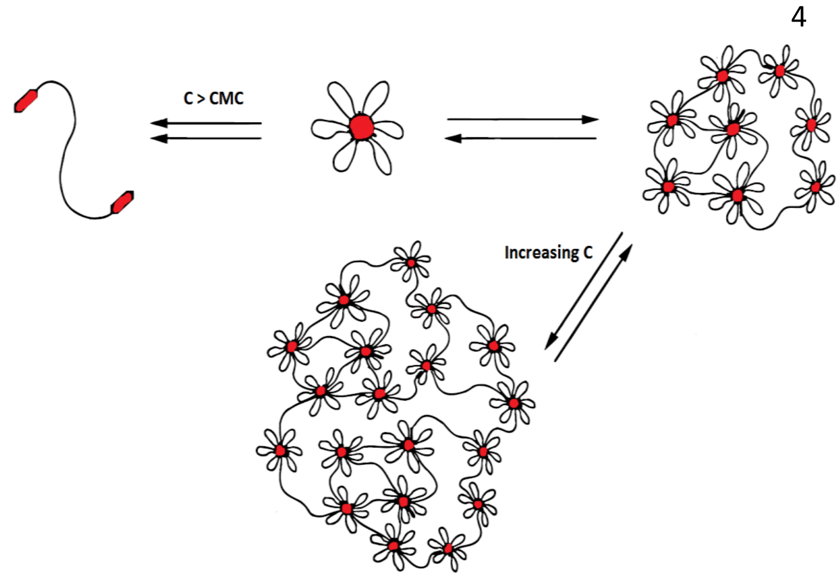


Telechelic polymer

1. polymer matrix
structure and aggregation properties



[4]



CMC = (2.89 ± 0.13) x 10^{-4} g/L

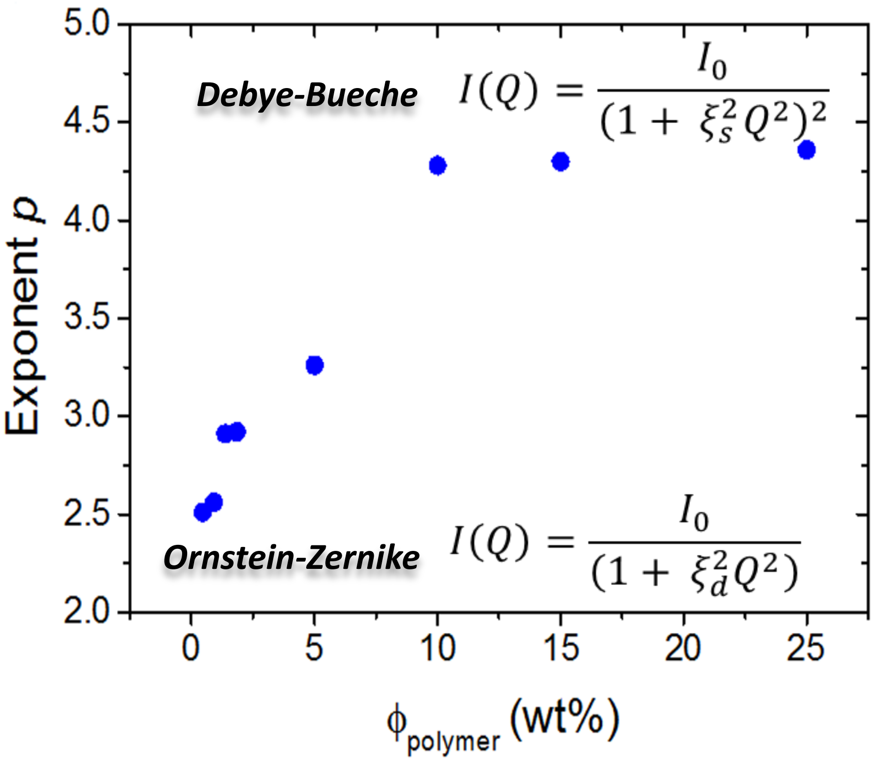
[5]

$$f(Q) = A_1\, Q^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432 Q R_g)}{(QR_g)^4} + bgr$$

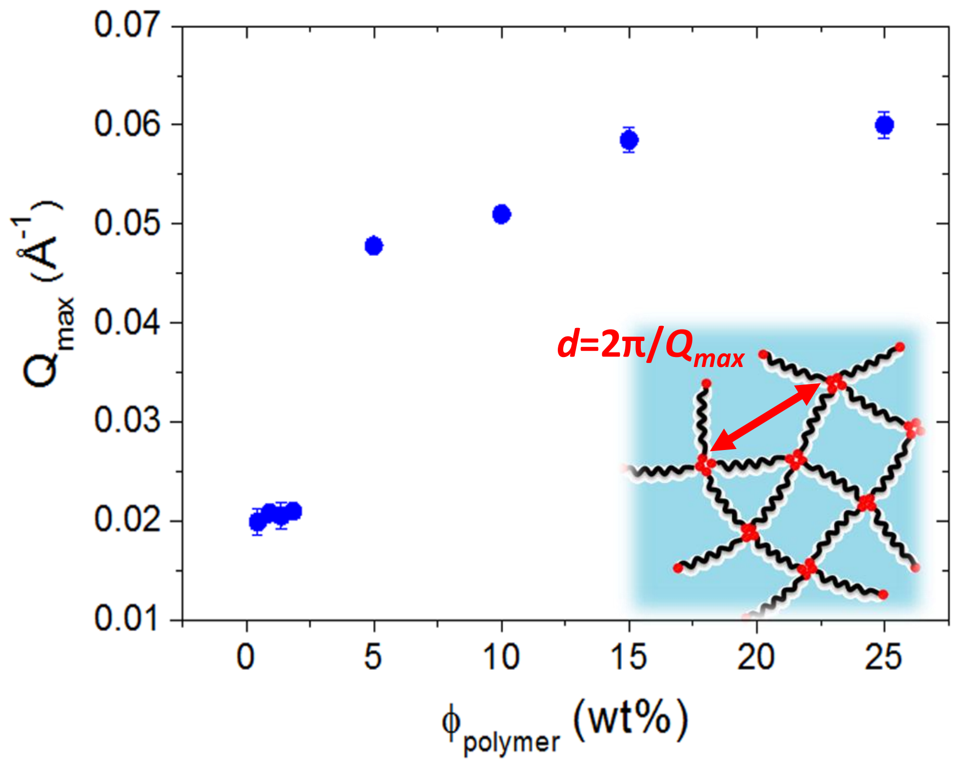
[4] K.C. Tam, Jenkins R.D., Winnik M.A., Basset D.R., *Macromolecules*, 1998, 31, 4149-4159
[5] C.Frank, H.Frielinghaus, J.Allgaier, *Lagmuir*, 2007, 23, 6526-6535

1. polymer matrix structural parameters

scattering fluctuations contributions



decrease of the domain spacing

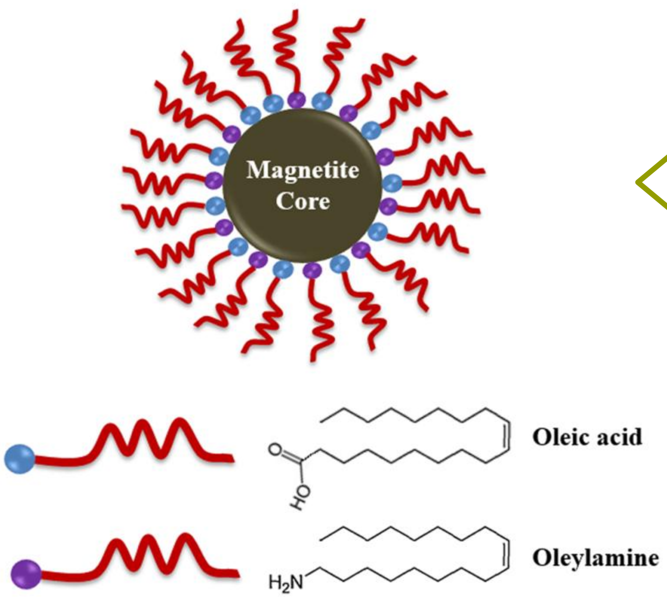


“open” gel → large fractal-like structure

polymer network becomes denser

2. magnetic nanoparticles

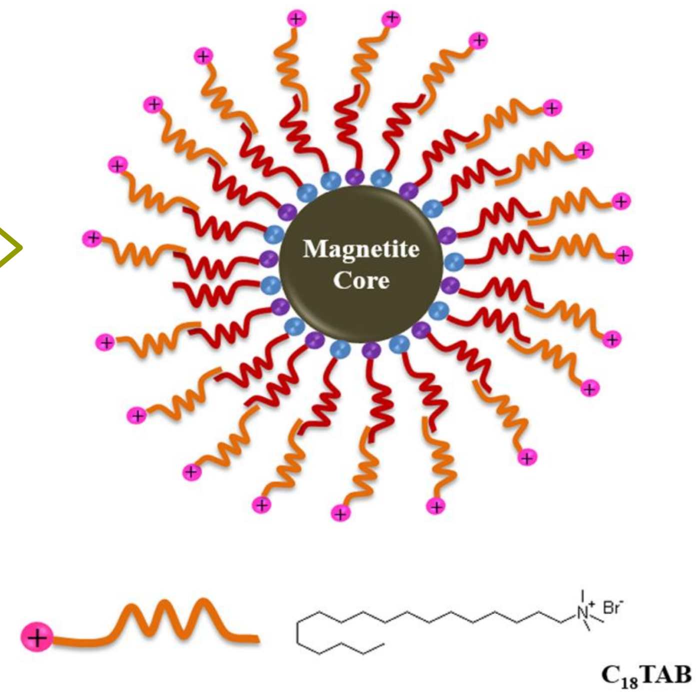
hydrophobic magnetite nanoparticles



dry film and hydrogel nanocomposites

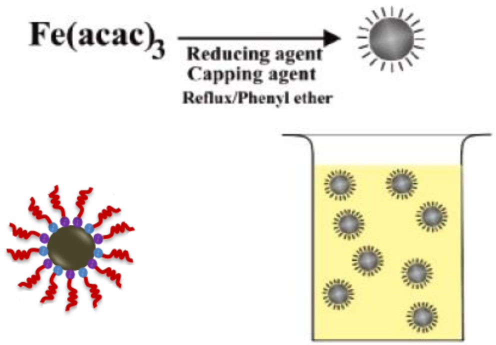
different coatings

hydrophilic magnetite nanoparticles

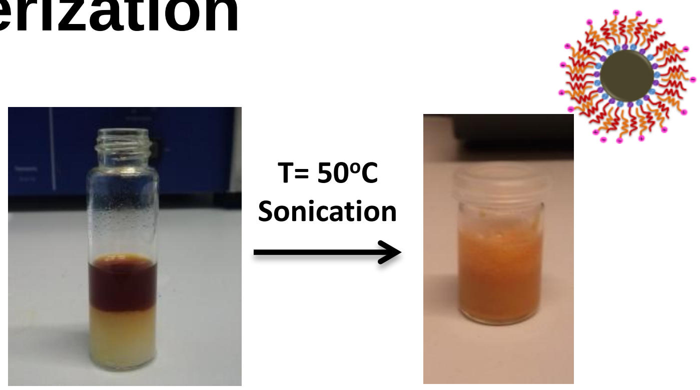


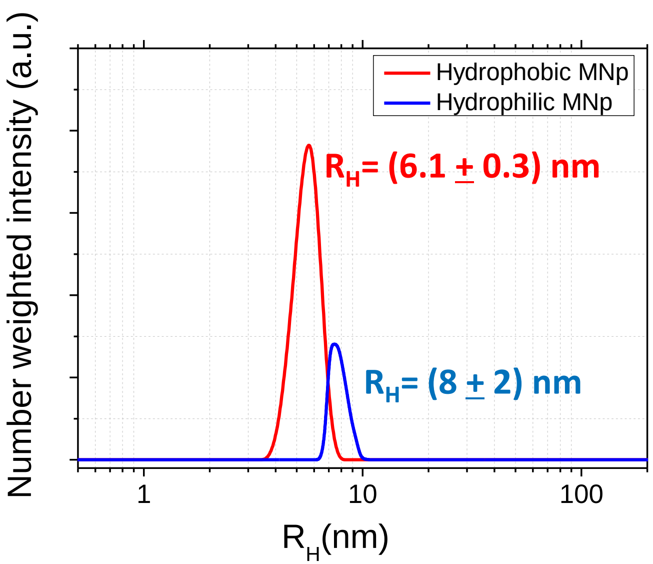
hydrogel nanocomposites

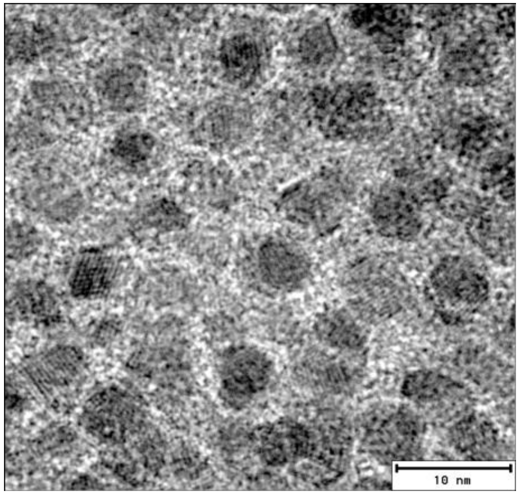
2. magnetic nanoparticles preparation and characterization



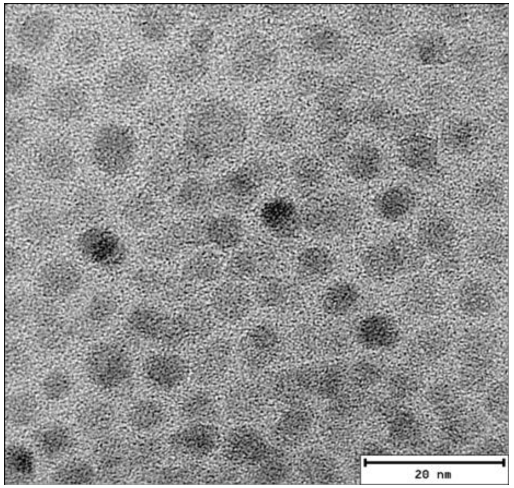
- 1,2-hexadecanediol
- oleic acid and oleylamine







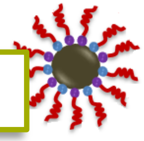
Hydrophobic MNp

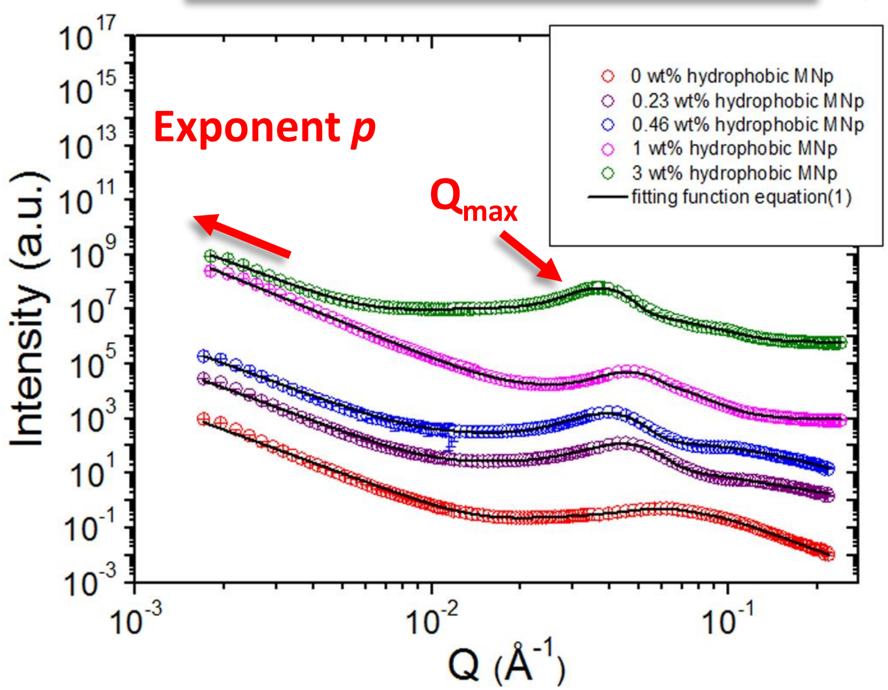


Hydrophilic MNp

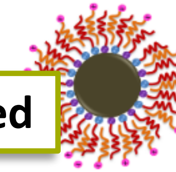
HEUR-magnetite nanoparticles nanocomposites hydrogel state

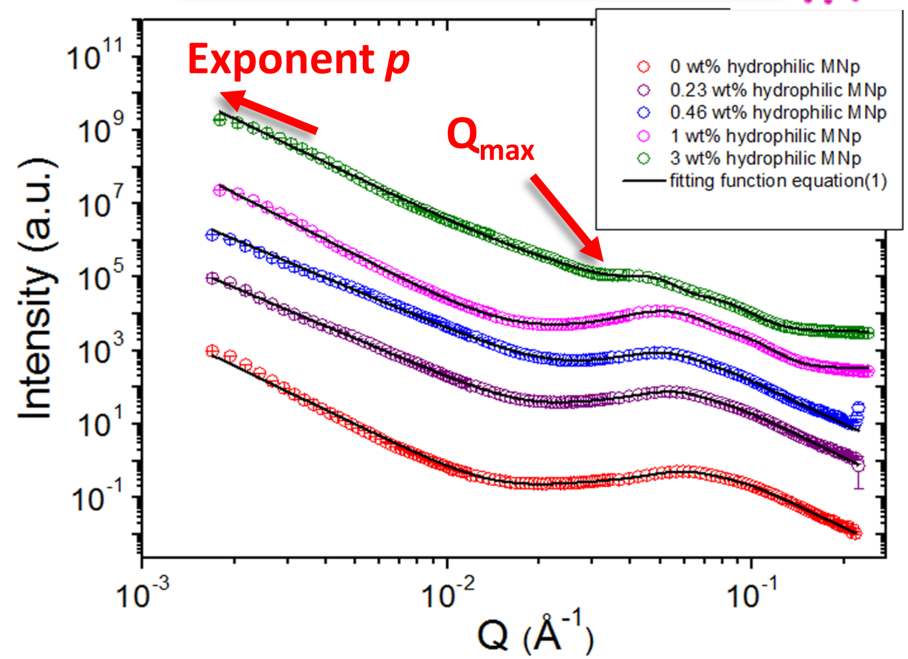
hydrophobic MNp embedded





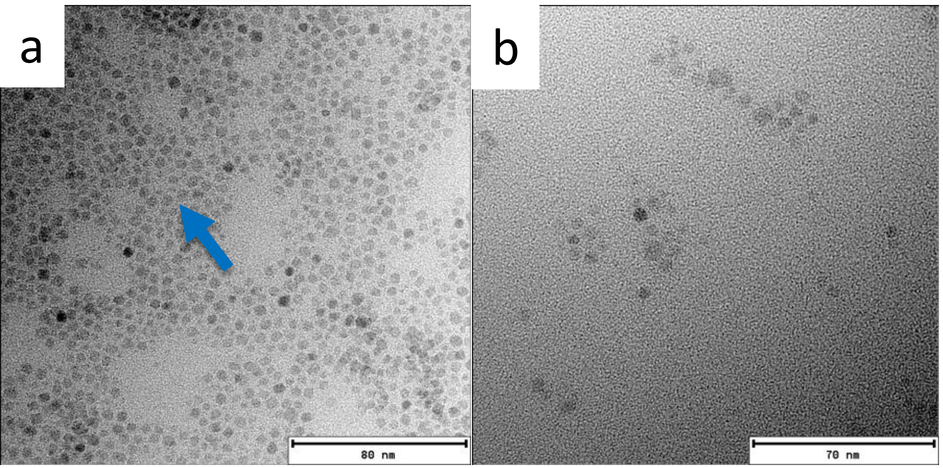
hydrophilic MNp embedded





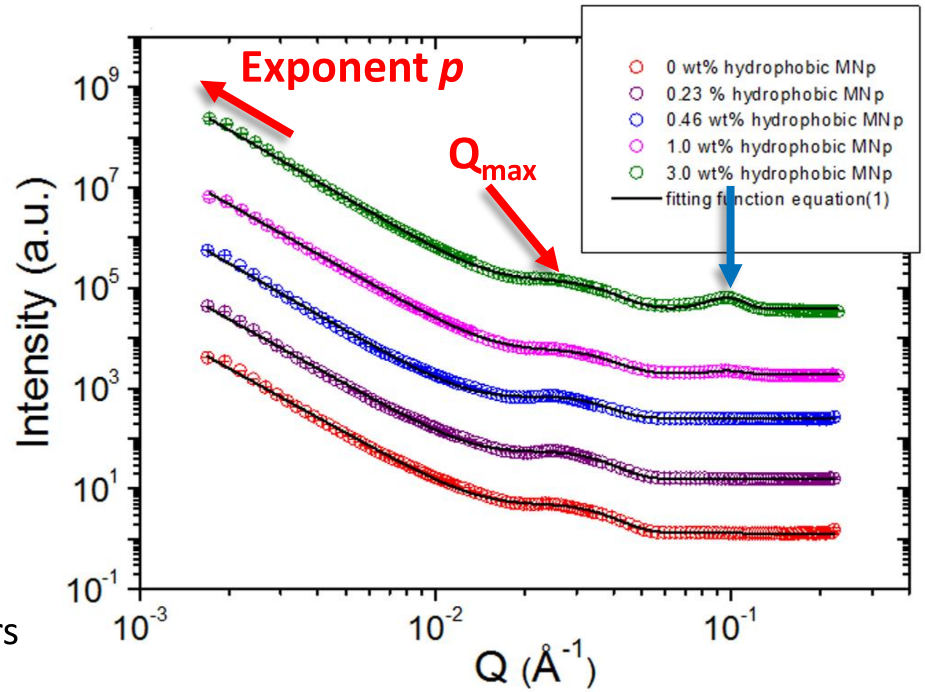
$$f(Q) = A_1\, Q^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432 Q R_g)}{(QR_g)^4} + bgr$$

HEUR-magnetite nanoparticles nanocomposites dried state



1 wt% MNp content

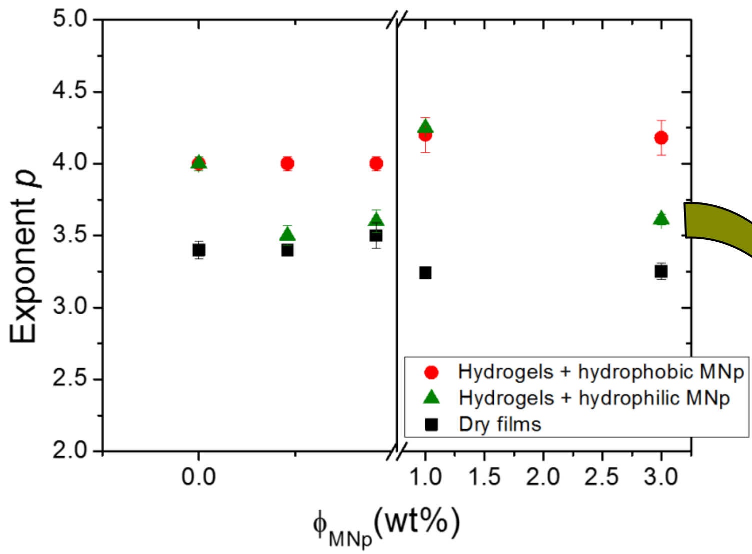
a) mesh-like structure **b)** single MNp and small clusters

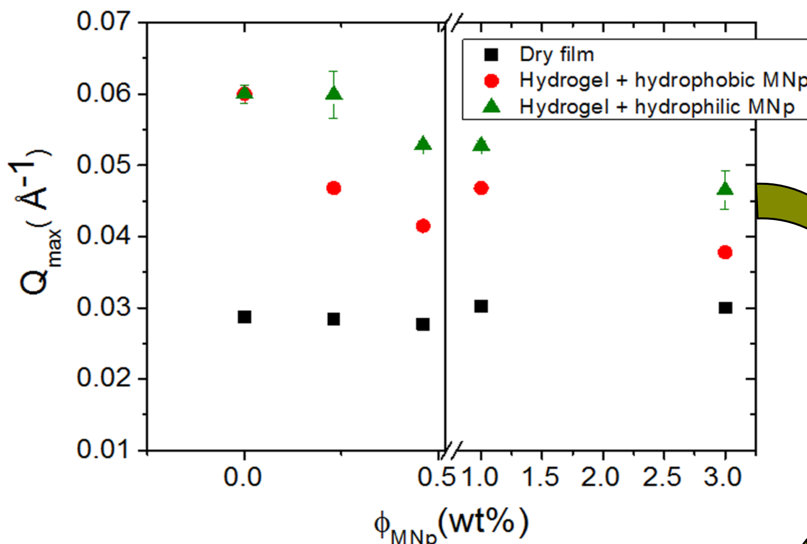


$$Je^{-k^2(Q-Q_{max})^2}$$

$$f(Q) = A_1\, Q^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432 Q R_g)}{(QR_g)^4} + bgr$$

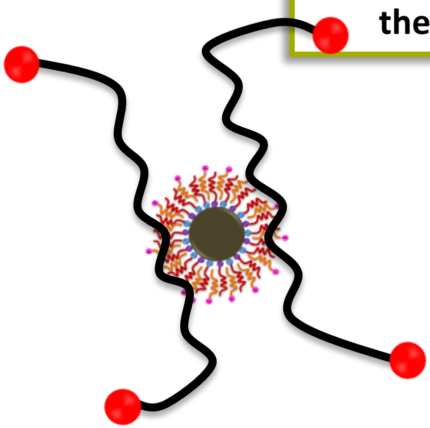
HEUR-magnetite nanoparticles nanocomposites structural parameters



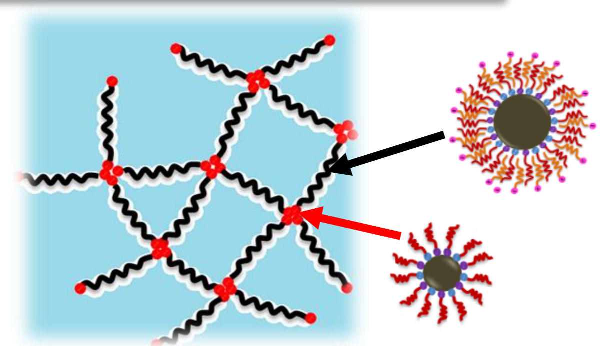


decrease of the cross-links of the polymer network

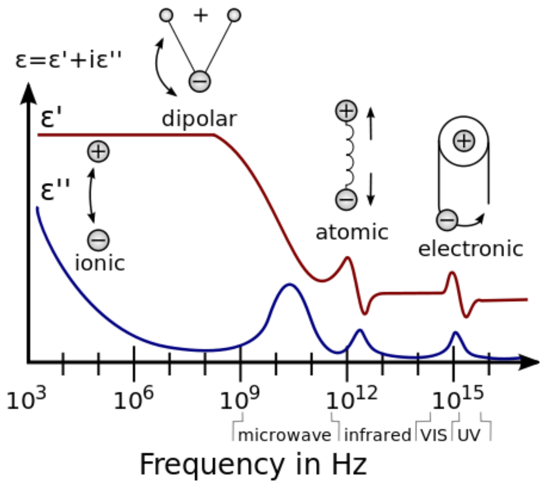
only for hydrogel nanocomposites: decrease of the domain spacing $d=2\pi/Q_{max}$

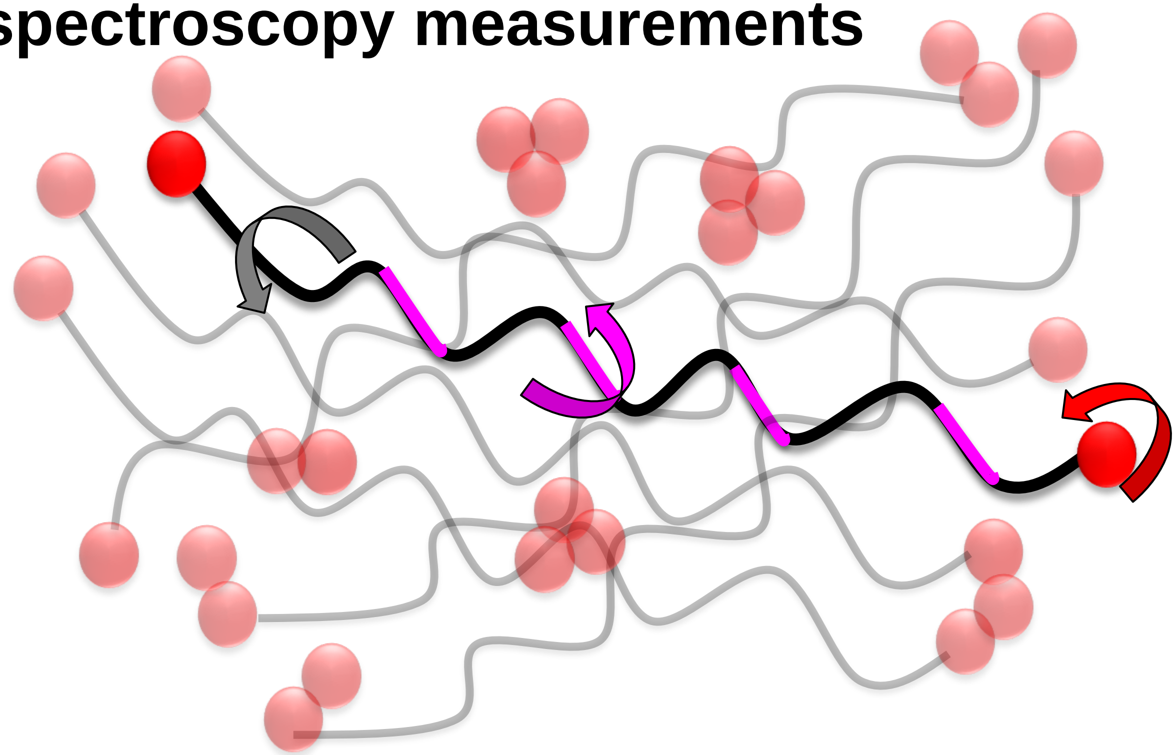


by combining the 2 results



dynamics of the HEUR-MNp nanocomposites dielectric spectroscopy measurements





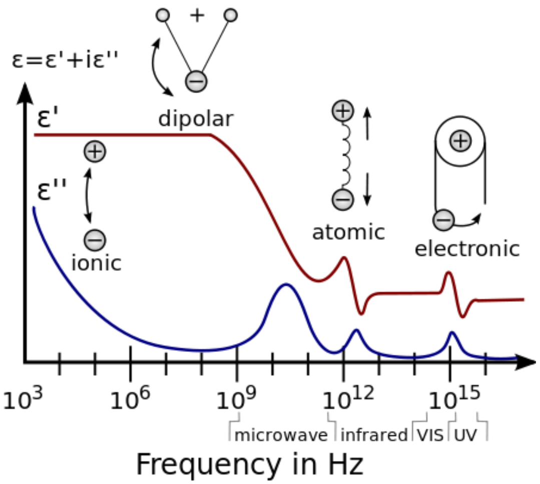
$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{\{1+(i\omega\quad)^{1-\alpha}\}^\beta}$$

$$\omega_{\max} = \left(\frac{\sin\left(\frac{\pi\alpha}{2(\beta+1)}\right)}{\sin\left(\frac{\pi\alpha\beta}{2(\beta+1)}\right)}\right)^{1/\alpha} \tau^{-1}$$

$$\tau_{max} = (2\pi\omega_{max})^{-1}$$

? **Contributions of the blocks to the polymer relaxations**

dynamics of the HEUR-MNp nanocomposites
dielectric spectroscopy measurements



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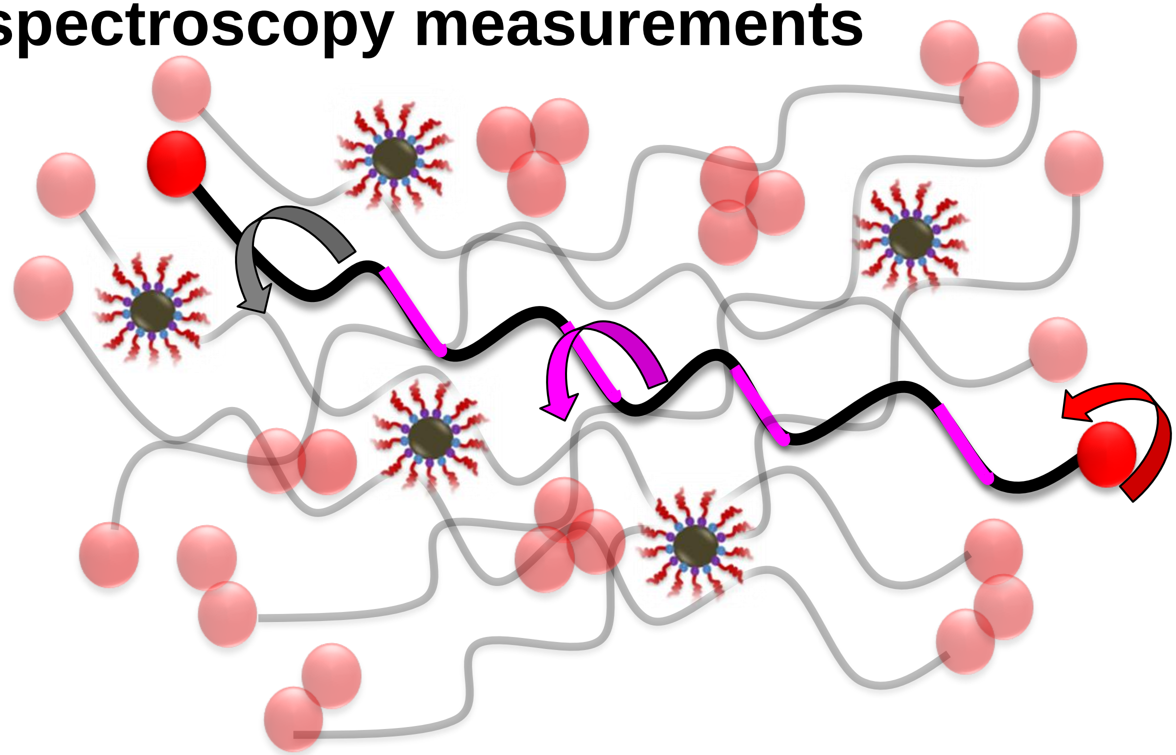
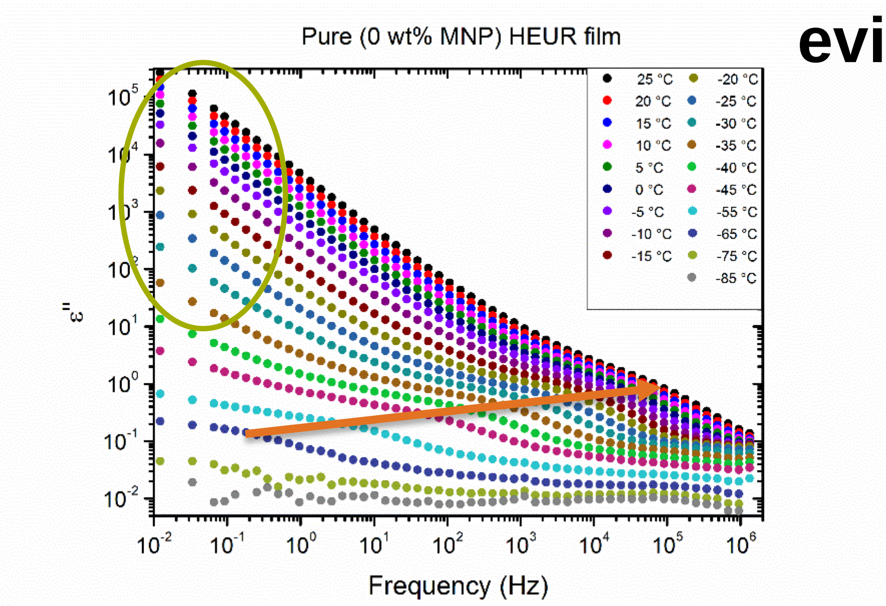


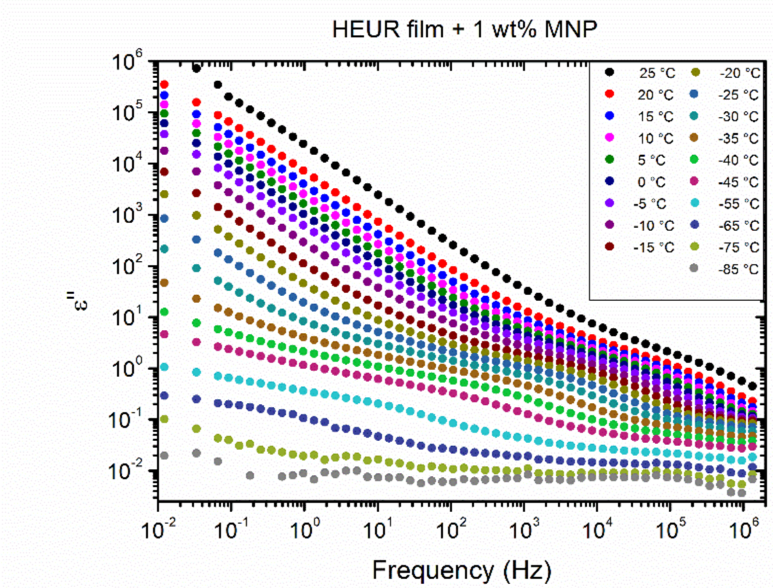
?? **Addition of the MNp**

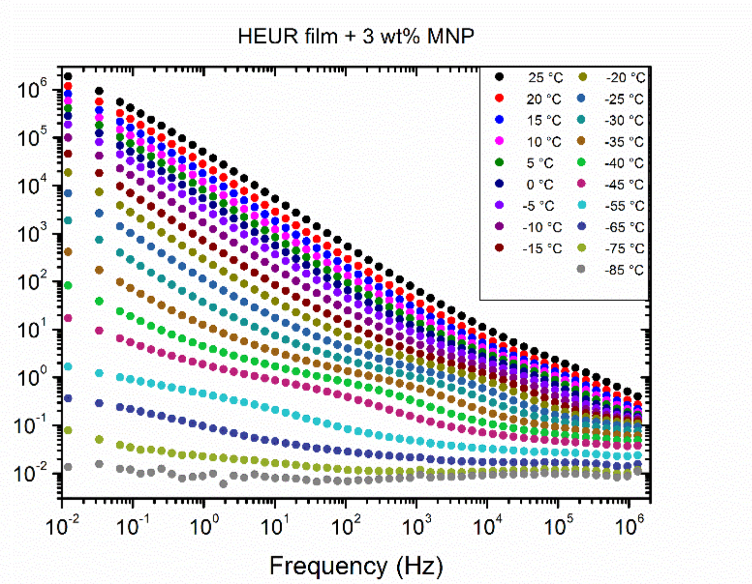
dielectric spectroscopy measurements: evidences



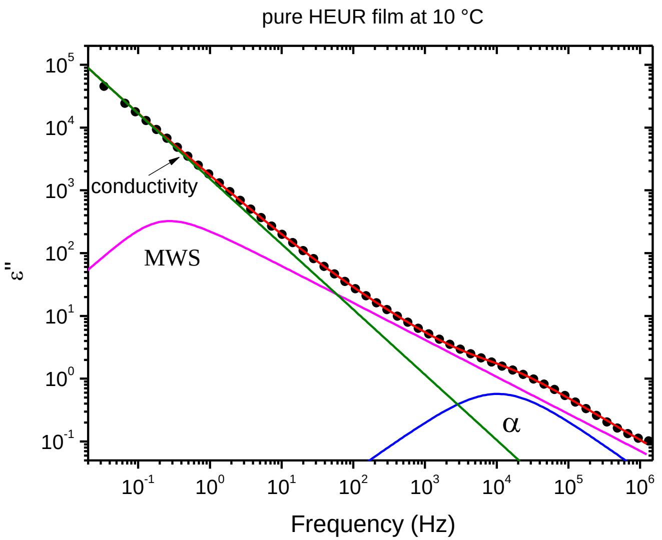
$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{\{1+(i\omega\ )^{1-\alpha}\}^{\beta}} + jk\omega^{-s}$$ [6,7]

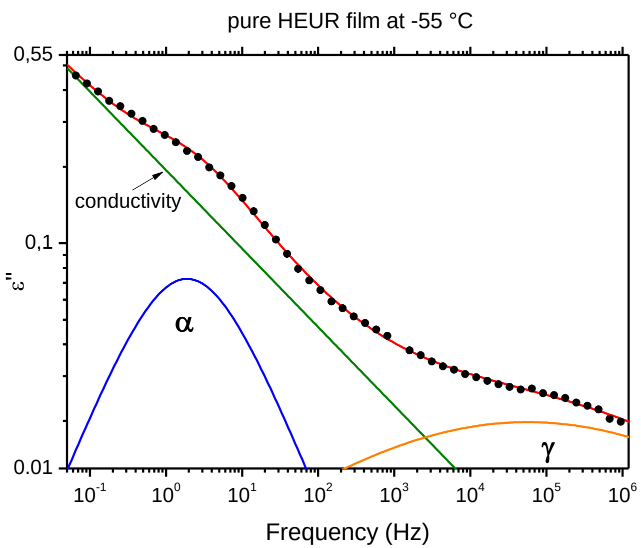
1 main relaxation process at T>T_g

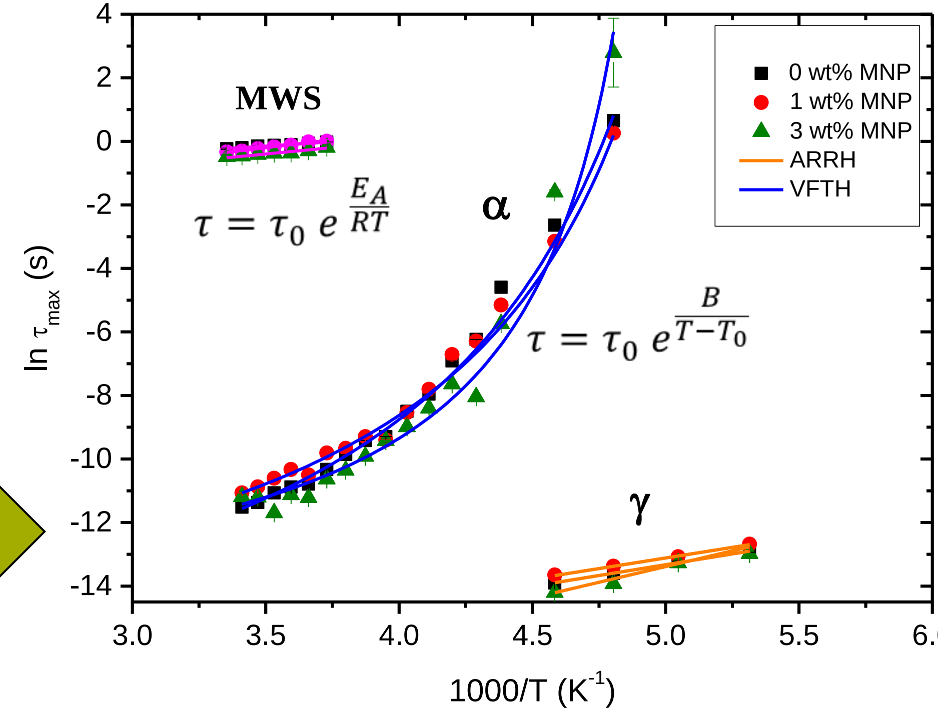




dielectric spectroscopy measurements: Data analysis







MNP (wt%)	E_A [MWS] (KJ/mol)	E_A [γ] (KJ/mol)	T_g(°C) calc.	T_g(°C) exp.	Fragility index,m (%)
0	4.45 ±0.15	11.3 ± 0.7	-71.1 ± 1.2	-73	68
1	8.35±0.62	11.1± 0.3	-71.5 ± 5.7	-74	68
3	6.73±0.78	16.5± 0.9	-67.3 ± 7.1	-71	82

[6] J.J. Fontanella et al, *Solid State Inonics*, 1983, 8, 333-339

[7] G. Fanggao et al, *Il nuovo cimento*, 1994,16D, 855-864

summary and conclusions

- development of an easy formulation path to prepare superparamagnetic nanocomposites
- at concentration 0.46 wt% and 0.92 wt%:in D_2O, the HEUR telechelic polymer forms an homogeneous “open gel” structure, in which the interactions between the hydrophilic main polymer chains are negligible. Increasing the concentration up to 25 wt% the polymer molecules form an inhomogeneous network rich in entanglements between different polymer chains
- nanocomposites: above a concentration of 0.8 wt% MNp tend to form large clusters and large, dense MNp clusters coexist with isolated MNp. The hydrophobic MNp are embedded in the hydrophobic domains of the HEUR polymer network, while the hydrophilic MNp stay in the aqueous phase within the polymeric network and cut or suppress some crosslinks
- the relaxation measurements on the dry films show 3 main relaxation processes: MWS polarization, α-relaxation and a very weak γ-relaxation. For the film with 3wt% MNP we observed lower T_g (higher fragility index) and a slower γ-relaxation than the other 2 nanocomposites were observed. The interpretation of the results is still in progress

acknowledgements

JÜLICH
FORSCHUNGSZENTRUM

Jülich Centre
for Neutron Science

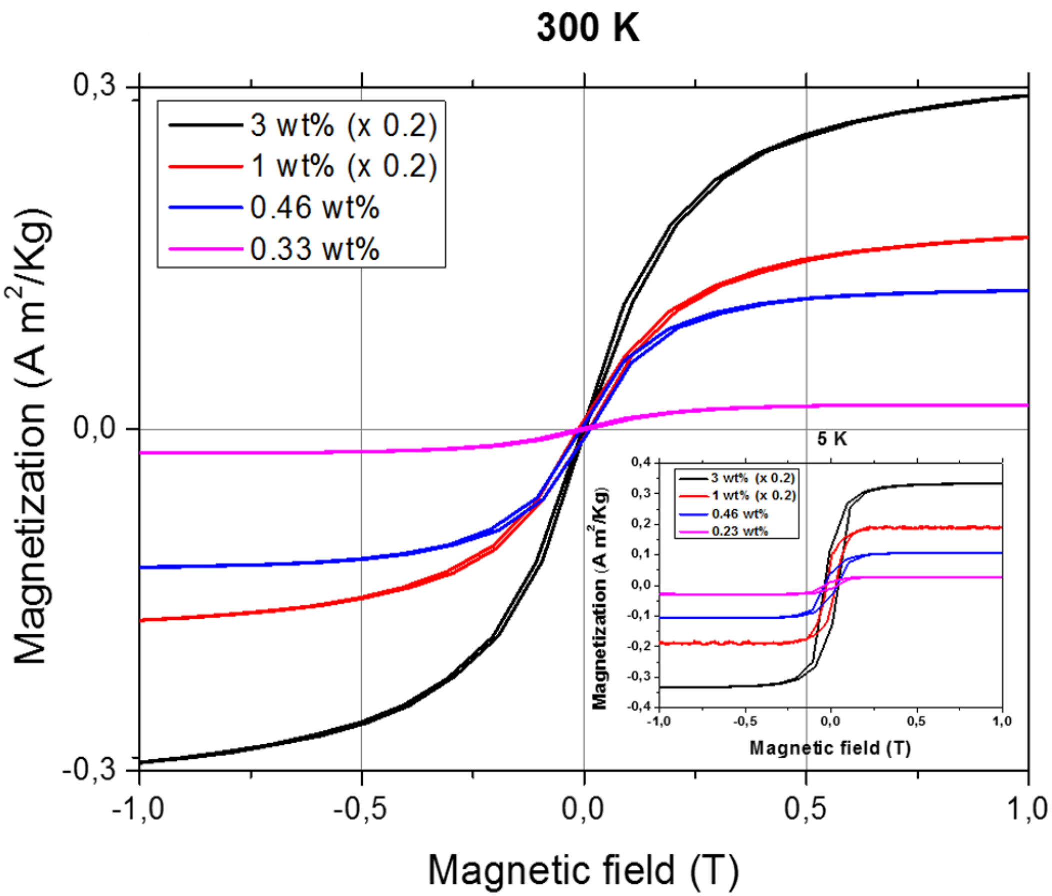
TU München Lehrstuhl für
Funktionelle Materialien

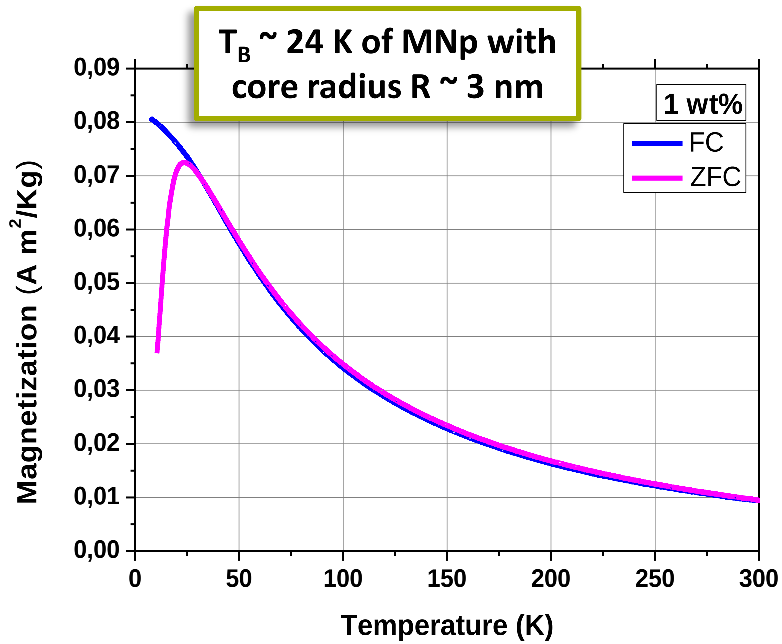
YOU for your attention!

outlook

- Perform dielectric spectroscopy measurements at smaller temperature steps
- Dielectric spectroscopy measurements on the HEUR films with increasing MNP concentration
- Dielectric spectroscopy measurements on the HEUR hydrogels with and without MNP
- Additional insights about the dynamics: Spin-echo measurements on the nanocomposites as hydrogels

HEUR-magnetite nanoparticles nanocomposites as dry films magnetic response





superparamagnetic MNp properties are conserved in the final nanocomposite formulation

Back up
Fitting model

$$f(Q) = A_1\, x^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432QR_g)}{(QR_g)^4} + bgr$$

Simple power law describing long-range fluctuations:
Information about the overall structure (fractal nature of the network)

Back up
Fitting model

$$f(Q) = A_1\, x^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432QR_g)}{(QR_g)^4} + bgr$$

↓

Scattering cross section according to Teubner-Strey Theory (arising from Landau termodynamic approach)

↓

Describing 2-phase systems (microemulsion)→ in our case the 2 phases are the hydrophobic and the hydrophilic domains

Back up
Fitting model

$$f(Q) = A_1\, x^{-p} + \frac{A_2}{(Q_{max}^2 + \xi^{-2})^2 - 2(Q_{max}^2 - \xi^{-2})Q^2 + Q^4} + \frac{A_3\, Erf^{12}(0.432 Q R_g)}{(Q R_g)^4} + bgr$$

Empirical terms: permits the expansion of the model to large Q-range. It takes into account the fractal nature and it is used to describe the power law Q^{-4} at large Q values

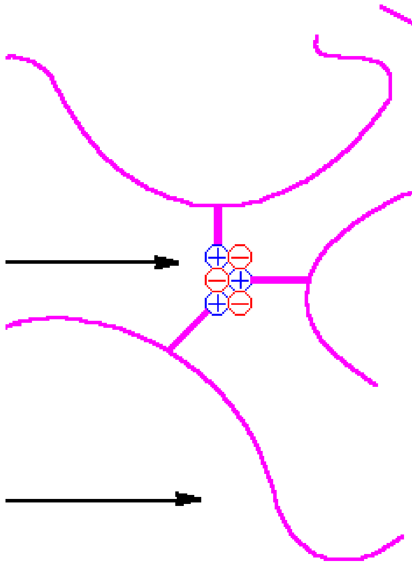
Gyration radius of the scattering objects: $R_g \leq 2\pi / Q_{max}$

Back up
Application of the fitting model

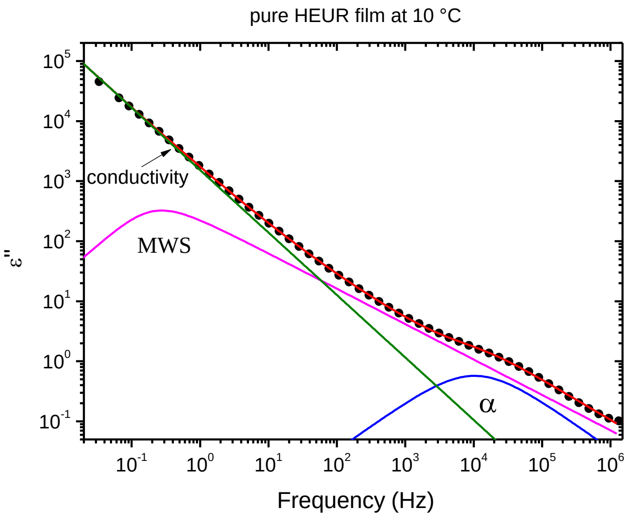
- Microemulsions
- Bicontinuous microemulsions composed of nonionic surfactants with linear and Branched Hydrocarbon Tails

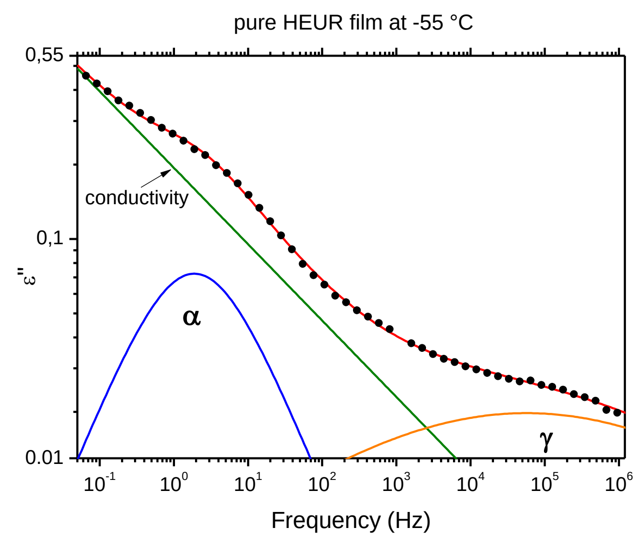
Polyetheretherketone SPEEK/ silsesquioxane SQO nanoparticles composites for DMFC
high scattering intensity at low-Q range because of the presence of inhomogenities >1 μm→ large hydrophobic mesh in the ionomer;

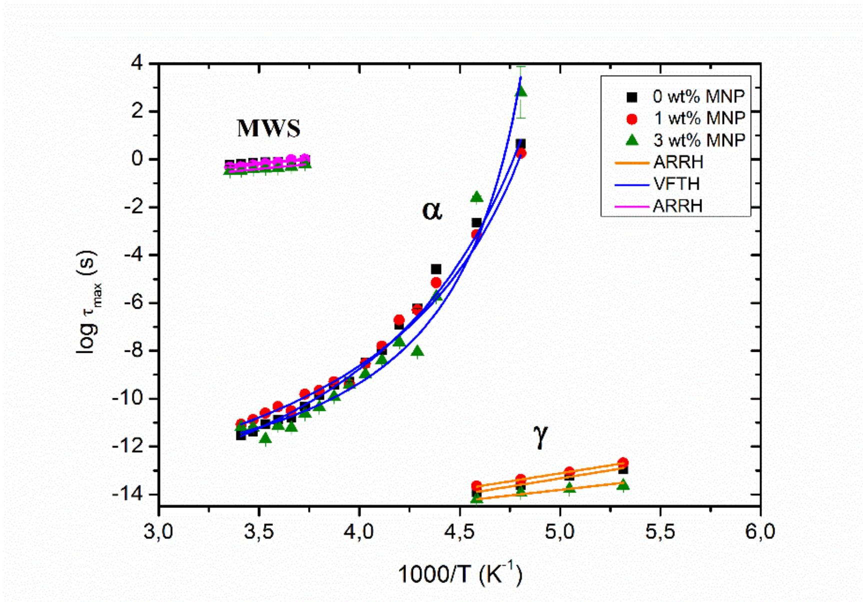
broad hump due to the formation of ionic domains.



dielectric spectroscopy measurements: Data analysis





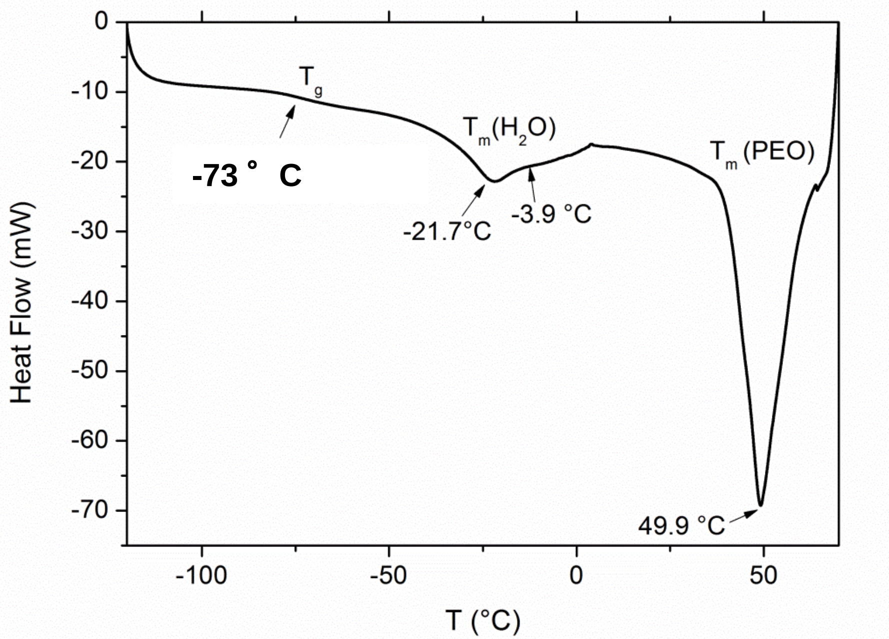


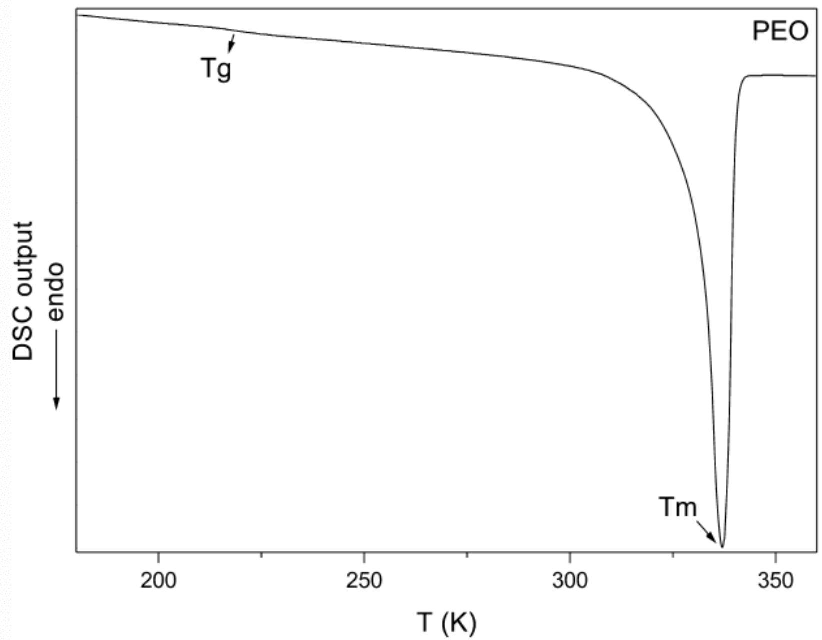
- **MWS interfacial polarization** at -5ºC<T<25 ºC: due to the microphase separation inside the system (SANS results) at -5ºC<T<25 ºC
- **α-relaxation** at T>-75 ºC (T_g) : : originates mainly from the PEO backbone portion[6]
- **γ-relaxation** visible from T=-55 ºC : crankshaft motions of methylene groups[7]

[6] J.J. Fontanella et al, *Solid State Inonics*, 1983, 8, 333-339

DSC measurements on the nanocomposites as dry films

Pure HEUR film



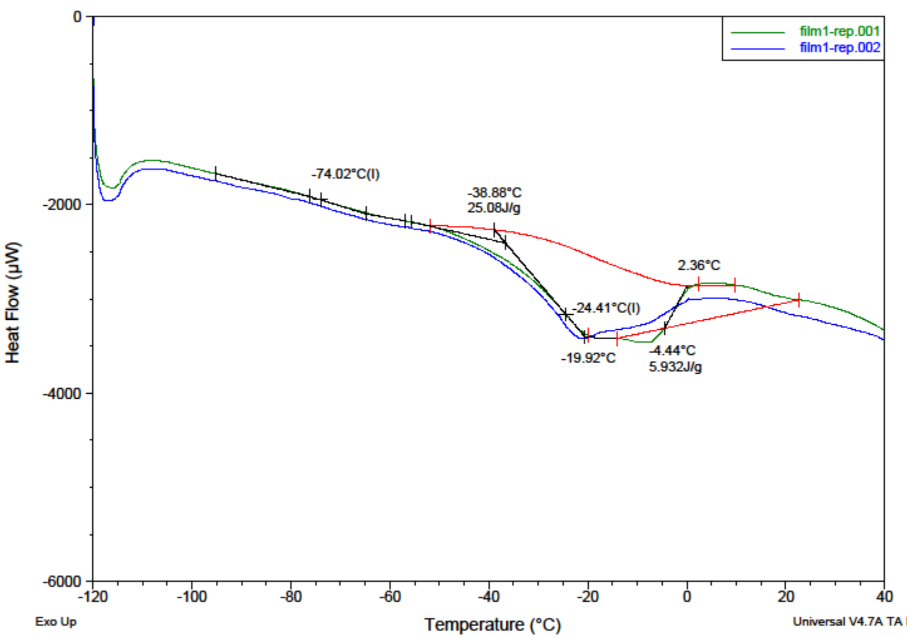


M_w PEO portion in HEUR polymer ≈ 8848 g/mol

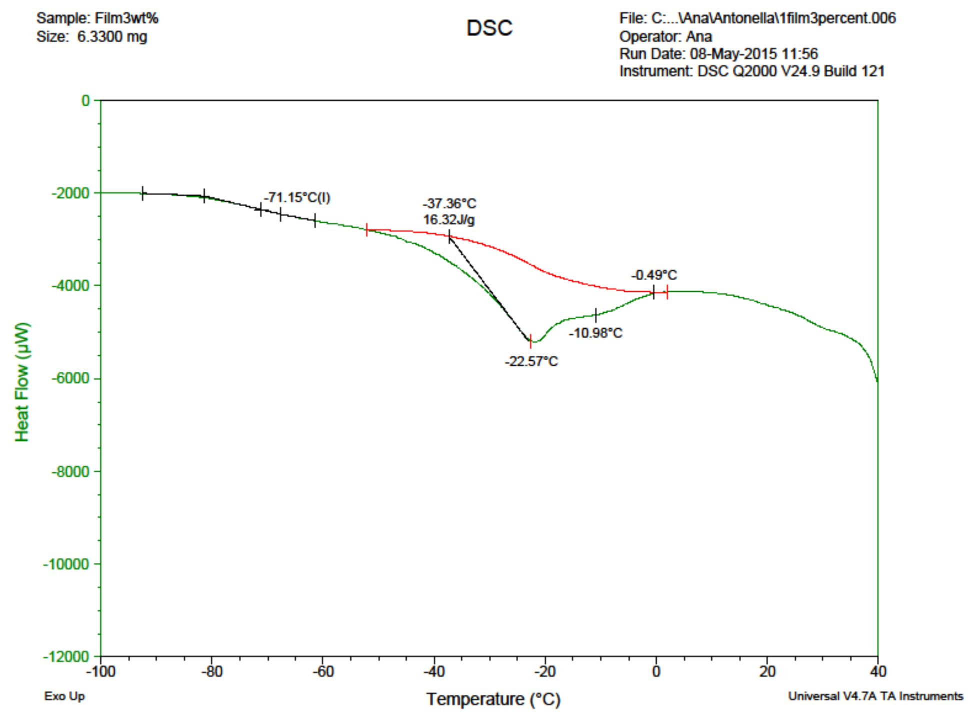
Cristallinity degree→ to be calculated

DSC measurements on the nanocomposites as dry films

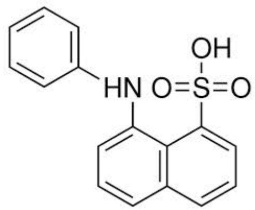
Pure HEUR film+1wt% MNP film



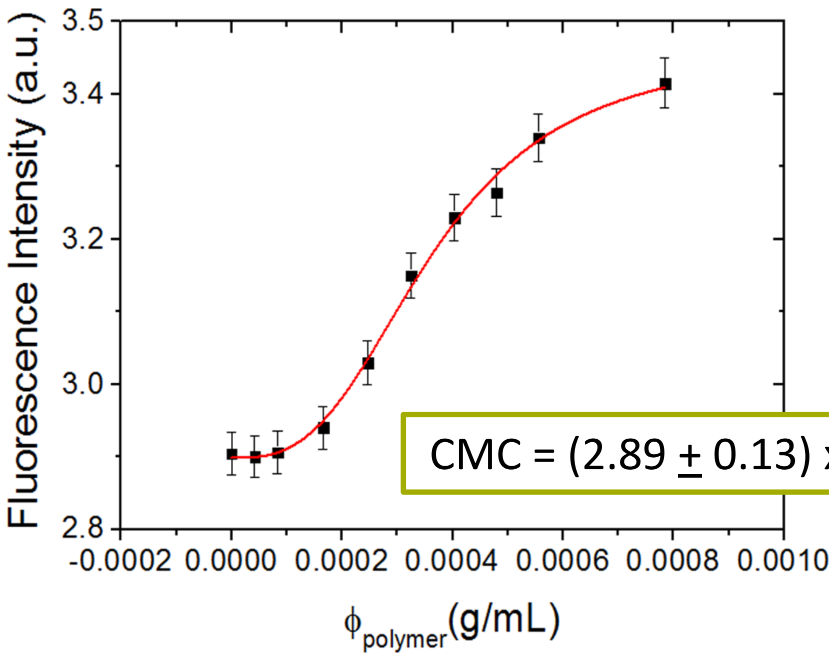
Pure HEUR film+3wt% MNP film



1. Polymer matrix
Structure and Aggregation properties

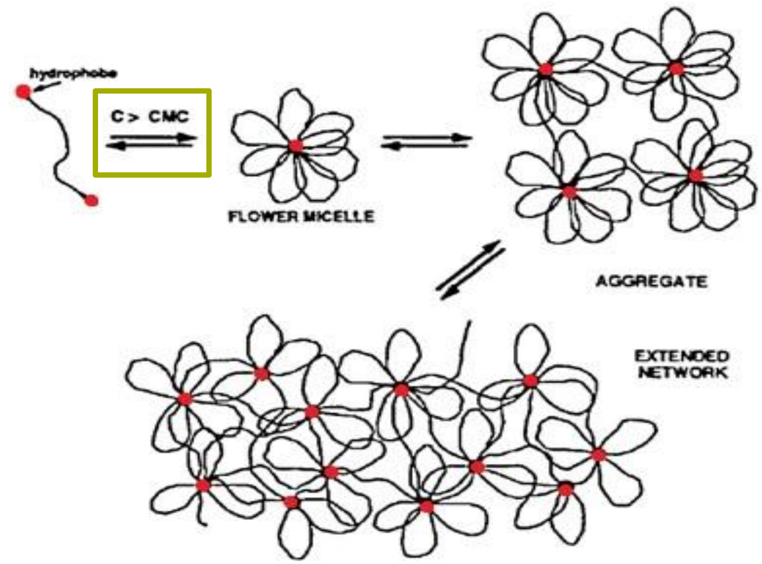


λ_{max} = 480 nm



CMC = (2.89 ± 0.13) x 10^{-4} g/L

[4]



[4] *A.N. Semenov, J.F. Joanny, and A.R. Khokhlov, Macromolecules **1995**,28, 1066-1075*

[1] *A. Campanella,et al, Polymer,60(2015),176-185*