ESRF	**Experiment title:** Sol/Gel process in Zr/lactate/polyacrylate systems.	**Experiment number:** 32-1-161
Beamline: BM32	**Date of experiment:** from: March25 to: March 28	**Date of report:** 12-07-00
Shifts: 9	**Local contact(s):** J-L Hazemann	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
Jérôme Rose*[1], Michel Renard*[2], Guy Chauveteau[2], René Tabary[2], Aziz Omari[3], Hervé Toulhoat[2], Hubert Hervet[4]
[1]CEREGE, Physico-chimie des interfaces Europôle de l'Arbois BP 80 13545 Aix-en-Provence France [2]IFP 1-4 Avenue du bois Préaux BP 311 92506 Rueil Malmaison-France [3]MASTER-ENSCPB Av. pey Berland BP108F 33402 Talence cedex-France [4]Laboratoire de physique de la matire condensée du Collge de France, 11 place Marcellin Berthelot. 75231 Paris cedex-France

Report:

Sol-gel processing has gained interest during the past 15 years. A good control of such chemistry and especially the gelation kinetics is an important objective for several applications (ceramic and thin film synthesis, reduction in permeability of filters and porous rocks,). In addition, there is a growing interest in studying the gelation of negatively charged polymers by zirconium because this crosslinker has a lower toxicity than chromium commonly used up to now.

In that context, Chauveteau et al (1999-2000) have developed an original approach and a new model for predicting crosslinking of polyacrylate solutions by Zr-lactate (Zr-La) solutions under shear flow. The complete understanding of gelation process requires to determine the Zr speciation both in Zr-La dilute aqueous solutions and in polymer gels. In a first series of Zr k-edge XAS experiments (cf ESRF report 99), the effects on Zr species of the Zr-La concentration in aqueous solutions and in polyacrylate gels, was investigated. In mother Zr-La solution (72000 ppm), Zr ions are condensed as dimers where the two Zr dodecahedron which are linked by hydroxyl edges are stabilised by 6 lactates as suggested by chemical analysis ([Lactate]/[Zr]=3). After dilution at pH=6, tetramers become the dominant species at 1400 and 800 ppm concentrations. At much lower concentrations, corresponding to that used for gelling, associations between tetramers are observed. Zr species in gels formed at very low Zr concentrations are mainly dimers showing that when carboxylates replace the lactates, associations of tetramers and even dimers can be broken. All these EXAFS results were compared successfully with molecular modelling (ab-initio calculations using DFT) (Rose et al, submitted).

But the 9 runs carried out in 99 did not allowed to analyse the Zr speciation as a function of time after dilution and at the end of gelation.
Thus in 2000, Zr K-edge EXAFS experiments have been carried out with Si (111) monochromator crystals by using the fluorescence detection mode due to the very low concentration of Zr in liquid or gel samples (36 and 72 ppm). The effects of ageing after dilution at 72 ppm (t=20, 120 and 360 mn) on Zr speciation were analysed at 20°C for both pH 5 and 6. Similar Zr speciation kinetic experiments were performed in presence of polymers at a Zr concentration of 36 ppm. During these experiments the temperature was maintained at 20°C±0.2. After each ageing time, the samples were put quickly in a cell to be freeze-dried using liquid nitrogen to block the Zr polymerisation. Due to the extremely low Zr concentrations, ten scans of 40 minutes were recorded for each sample. The noise-to-signal ratio was low for all solutions and gels.
Ageing effect after Zr-La dilution
EXAFS results concerning Zr-La solutions at [Zr]=72 ppm, pH=6 and 5, indicate that Zr polymerisation is a slow process. For both pH after 20 and 120 mn it seems that dimers of Zr are still the dominant species in solution as observed in mother Zr-La solution. This is suggested by the number of Zr atoms (N_{Zr}) around each Zr located at a distance of 3.6Å, found to be close to 1. Oligomerisation of dimers to form tetramers becomes detectable only after ageing time estimated between 120 and 360 mn. At pH=6 N_{Zr} is equal to 1.6±0.3 while at pH 5 N_{Zr}=1.3±0.25. These N_{Zr} values (1.6 and 1.3) suggest that the solution contains a mixture of dimers and tetramers, with an oligomerisation slower at pH=5 than at pH=6.
Ageing effect on the Zr speciation during gelling
The analysis of the Zr speciation during the gelling of polyacrylate solutions at pH 6 indicates that Zr dimers are the major species (N_{Zr}=1) as well after 40 and 120 minutes. After 540 minutes, N_{Zr} slightly increases up to 1.3, suggesting that the polymerisation of Zr occurs but without knowing that if this polymerisation concerns free dimers or dimers bridging two polyacrylate groups on the polymers.
The very satisfactory and important result is that we were able to determine in situ Zr speciation at extremely low concentrations both in aqueous solutions and in polymer gels. Moreover all EXAFS results obtained concerning oligomerisation of Zr and pH effects are in good agreement with both ab-initio molecular modelling and interpretation of rheological studies, giving reliable way to control polymer gelling.
References : (1)Chauveteau G., Tabary R., Renard M., Omari A., (1999), SPE Symposium on Oilfield Chemistry, SPE 50752 (2)G. Chauveteau, A. Omari, R. Tabary, M. Renard, J. Rose (2000) Symposium SPE/DOE Improved Oil Recovery, SPE paper n59317. (3)Rose J., G. Chauveteau, R. Tabary, M. Renard, A Omari, H. Toulhoat, Zirconium Speciation in lactate solutions and Polyacrylate Gels, J.Synchrotron Radiation, XAFS XI Proceedings, submitted.
We would like to thank O.Proux and J-L Hazemann for their precious help during experiments.