

# High-pressure NMR studies towards the understanding of monomer-stabiliser interactions in supercritical carbon dioxide

Márcio Temtem, Teresa Casimiro, Eurico Cabrita, Anjos L. Macedo,  
Ana Aguiar-Ricardo\*

*REQUIMTE/CQFB*, Departamento de Química, Faculdade de Ciências e Tecnologia,  
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

\*Email: [aar@dq.fct.unl.pt](mailto:aar@dq.fct.unl.pt) Fax: +351 212 948 385

## ABSTRACT

In the present work high-pressure NMR is used to investigate monomer-stabiliser interactions between methyl methacrylate, MMA, and Krytox (commercially available carboxylic acid terminated perfluoropolyether oil) in supercritical carbon dioxide.

A high-pressure apparatus, especially designed to prepare and transfer the samples to the high-pressure NMR sapphire tube, was assembled.

In order to mimetize the interactions between MMA and Krytox, a simpler model system where Krytox was replaced by trifluoroacetic acid, TFA, was studied. NMR spectra were obtained for the monomer and the mixture in  $\text{CDCl}_3$  and  $\text{scCO}_2$ , at pressures up to 15 MPa, and at 313.15 K. The observed changes in chemical shifts for MMA + TFA are compared with the results obtained for the MMA + Krytox system. Preliminary data suggests the existence of an interaction between the oxygen atom of the MMA carbonyl group and the proton of the carboxylic acid of Krytox .

## INTRODUCTION

Over the last years there has been an extensive research in the use of supercritical carbon dioxide,  $\text{scCO}_2$ , as a polymerisation reaction medium[1]. Several siloxane and fluorinated co-polymers were identified as effective stabilizers for free radical dispersion polymerisation of different acrylates (e.g. MMA, DEGDMA) in  $\text{scCO}_2$  [2-7]. Also commercially available perfluoropolyethers such as krytox, have been tested with success in this polymerisation [8].

It was suggested that the stabiliser performance was related with the establishment of a hydrogen bond between the carboxylic acid termination of the stabiliser and the ester group of the monomer, leading to a pseudo-graph copolymer. However, these interactions are still not clear [9].

The aim of this work is to apply high-pressure nuclear magnetic resonance, HP-NMR, to investigate these molecular interactions, since this technique offers unique, highly localized structural molecular information [10,11].

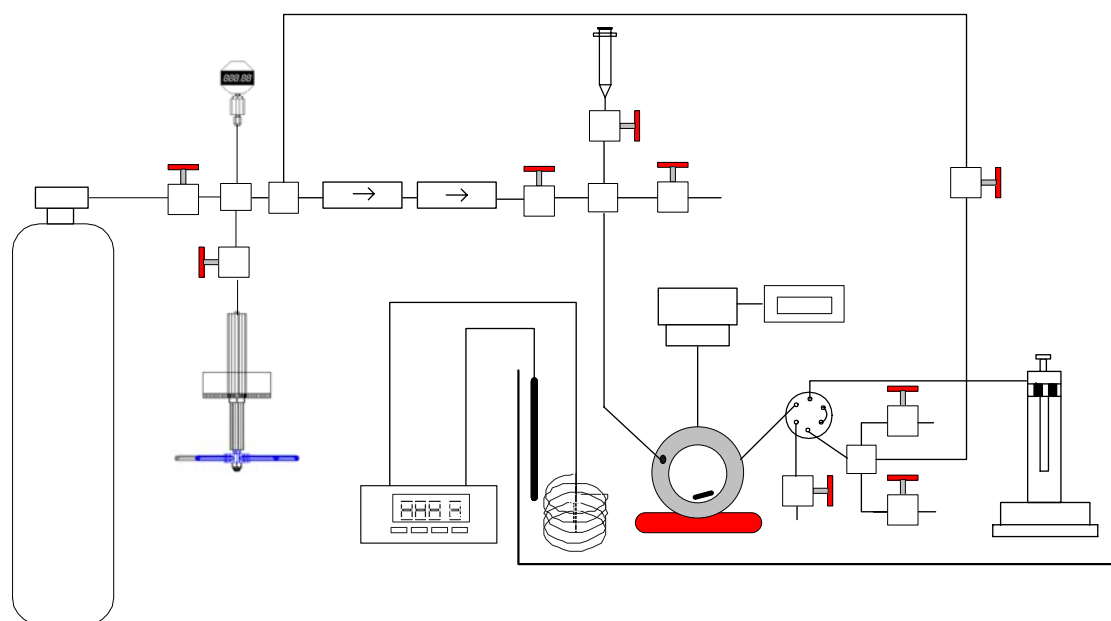
To that end, a new high-pressure apparatus, specially designed to prepare the mixtures under study was assembled. The new apparatus and experimental procedure to fill the HP-NMR tube are described in detail.

$^{19}\text{F}$  and  $^1\text{H}$  NMR spectra of the mixtures of monomer + stabilizer in  $\text{scCO}_2$  are presented. In order to understand this complex system, MMA + TFA was used as a model system to mimetise the MMA + Krytox interactions. The observed changes in the chemical shifts for MMA + TFA in  $\text{CDCl}_3$  and  $\text{scCO}_2$  are compared with the results obtained for the MMA + Krytox system.

## EXPERIMENTAL SECTION

**Materials.** The monomer methyl methacrylate, MMA, was obtained from Aldrich and distilled prior to use. TFA (trifluoroacetic acid) and TMS (tetramethylsilane) were used as received from Merck. Carbon dioxide was obtained from Air Liquide with 99.998% purity. The surfactant, Krytox 157 FSL (Mw 2500), was kindly supplied by DuPont and used without further purification.

**Methods.** The mixtures under study were prepared using a high-pressure apparatus, schematically presented in Figure 1. This apparatus was built around a stainless steel cylindrical cell similar to the one previously described by Sampaio et al.[12] The cell, with capacity of approximately 12.4 cm<sup>3</sup>, has two sapphire windows on top and bottom, and a Teflon o-ring provides the seal at both ends. The cell was immersed in a visual thermostated water bath and it was internally stirred with a magnetic bar and then placed under vacuum conditions.

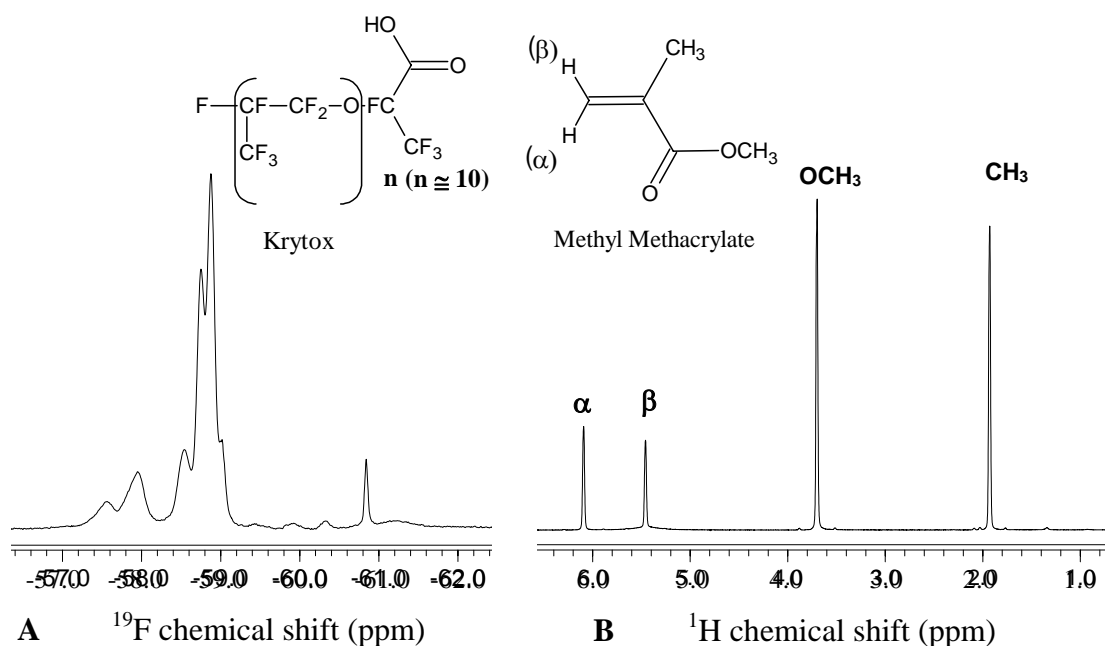


**Figure 1.** Schematic diagram of the apparatus: (1) Hand pump compressor; (2) Filter; (3) Check Valve; (4) Syringe; (5) Temperature controller; (6) Pressure transducer; (7) thermostated water bath; (8) Cell with sapphire windows; (9) HPLC valve; (10) High-pressure NMR tube.

In a typical procedure the reactants were placed into the cell with a syringe. CO<sub>2</sub> was then added at the required pressure with a hand pump (High Pressure Equipment CO., Model 87-6-5) and monitored with a pressure transducer (Setra Systems Inc., Model 204). CO<sub>2</sub> was quantified using the density of pure carbon dioxide[13] at the operating pressure and temperature conditions, assuming that changes in density due to the presence of other compounds were negligible. After 30 min of continuous stirring, the mixture was expanded to the high-pressure NMR sapphire tube already described [14], through the HPLC valve. The system was left to equilibrate for a 30 minutes rest period before closing the HP-NMR tube. High-pressure NMR spectra were obtained at 313 K using a Bruker spectrometer, ARX400, equipped with a temperature control unit. TMS was used as an internal reference for the <sup>1</sup>H NMR chemical shifts.

## NMR RESULTS AND DISCUSSION

In order to understand and clarify the nature of the interactions between the monomer and the surfactant molecule in supercritical conditions,  $^{19}\text{F}$  and  $^1\text{H}$  HP-NMR spectra of the MMA+Krytox system were performed. The  $^{19}\text{F}$  NMR spectrum in Figure 2A, allowed the detection of the larger Krytox molecule in a non-resolved spectrum. Figure 2B shows the  $^1\text{H}$  NMR spectrum of the same mixture, where it is possible to detect the resolved set of resonances obtained for the MMA molecule. Both spectra were obtained in  $\text{scCO}_2$  at 313 K and 18.9 MPa.



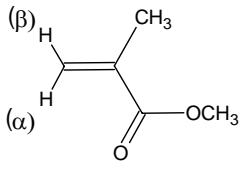
**Figure 2:** A.  $^{19}\text{F}$  NMR spectra of MMA + Krytox in  $\text{scCO}_2$ ; B.  $^1\text{H}$  NMR spectra of MMA + Krytox in  $\text{scCO}_2$ . Both spectra were obtained at 313 K and 18,9 MPa.

In order to establish a valid protocol to study the interactions in these conditions, TFA + MMA was used as a model system. TFA is a strong fluorinated acid that should interact with MMA in a similar way to Krytox, and it is easily characterized by NMR.

NMR chemical shifts reflect the electronic structure in a molecule and therefore can be used to identify and characterize hydrogen bonds[15-17]. The formation of hydrogen bonds shifts electron density from the proton acceptor to the donor, resulting in deshielding of the bridging hydrogen atom. Therefore, a downfield deviation of the proton chemical shift is observed. The  $^1\text{H}$  chemical shifts of MMA in the systems under study, in conventional media using  $\text{CDCl}_3$ , were compared with those observed in  $\text{scCO}_2$ . They are summarized in Table 1.

From this data it can be observed that the shielding in the conventional and in the supercritical medium is similar. In both cases the chemical shifts are shifted downfield when compared to MMA alone. One plausible explanation for such unshielding is the effect of a hydrogen bond between MMA oxygen (carbonyl group) and the carboxylic acid proton. Due to the presence of the conjugated double bond,  $\alpha$  and  $\beta$  protons feel these effects with more intensity, as can be observed in Table 1. The complete assignment of the  $^{19}\text{F}$  NMR spectrum of Krytox is being performed, in order to better characterize the interactions with MMA, and to obtain site-specific information.

**Table 1** – Chemical shifts ( $\delta$ ) and chemical shift differences ( $\Delta\delta$ ) of the  $^1\text{H}$  resonances of MMA and the different systems under study, in  $\text{CDCl}_3$  and in  $\text{scCO}_2$ .



	$\text{CDCl}_3$		$\text{scCO}_2$ (40 °C; 18,6 MPa)		
	MMA $\delta$ (ppm)	MMA + TFA $\Delta\delta$ (ppm)	MMA $\delta$ (ppm)	MMA + TFA $\Delta\delta$ (ppm)	MMA + Krytox $\Delta\delta$ (ppm)
H ( $\alpha$ )	6,1	0,047	6,081	0,039	0,008
H ( $\beta$ )	5,557	0,063	5,441	0,056	0,013
OCH3	3,749	0,044	3,689	0,04	0,009
CH3	1,942	0,005	1,927	0,003	-0,001

## AKNOWLEDGEMENTS

The authors thank Prof. C.J. Elsevier and J.M. Ernstring (Universiteit van Amsterdam) for their help and advice; financial support from Fundação para a Ciência e Tecnologia (FCT), contracts POCTI/35429/QUI/2000, POCTI/42313/QUI/2001 and SFRH/BPD/11665/2002, and by FEDER.

## REFERENCES

- [1] BECKMAN, E.J. J. *Supercrit. Fluids*, Vol.28, **2004**, p.121.
- [2] MAWSON, S., JOHNSTON, K. P., BETTS, D. E., MCCLAIN, J. B., DESIMONE, J. M., *Macromolecules*, Vol.30, **1997**, p.71.
- [3] WANG, W., NAYLOR A., HOWDLE, S. M., *Macromolecules*, Vol. 36, **2003**, p.5424.
- [4] KENDALL, J. L., CANELAS, D. A., YOUNG, J. L., DESIMONE, J. M., *Chemical Reviews*, Vol.99, 1999, p. 543.
- [5] CASIMIRO, T., BANET-OSUNA, A., RAMOS, A. M., NUNES DA PONTE, M., AGUIAR-RICARDO, A., *Proceedings of the 8<sup>th</sup> Meeting on Supercritical Fluids*, Bordeaux, France, Vol.1, **2002**, p.297.
- [6] CASIMIRO, T., PhDThesis, Universidade Nova de Lisboa, Portugal, **2003**.
- [7] GILES, M. R., GRIFFITHS, R.M.T., AGUIAR-RICARDO, A., SILVA, M. M. C. G., HOWDLE, S. M. *Macromolecules*, Vol. 34(1), **2001**, p.20.
- [8] CHRISTIAN, P., GILES, M. R., GRIFFITHS, R. M. T., IRVINE, D.J., MAJOR, R.C, HOWDLE, S. M., *Macromolecules*, Vol. 33, **2000**, p.9222.
- [9] CHRISTIAN, P., HOWDLE, S. M., IRVINE, D.J., *Macromolecules*, Vol. 33, **2000**, p. 237.
- [10] VARGA, T. R., FAZEKAS, Z. S., KATOH, S., HARADA, M., IKEDA, Y., TOMIYASU, H., *Spectrochimica Acta Part A*, Vol. 56, **2000**, p 1781.
- [11] DARDIN, A., DESIMONE, J. M., SAMULSKI, E. T, *J. Phys. Chem. B*, Vol. 102, **1998**, p.1775.
- [12] SAMPAIO, T.C.; BARREIROS, S., in *Methods in Biotechnology, Supercritical Fluid Methods and Protocols*, edited by J.R. Williams, A. A. Clifford, (Humana-Press Inc., Totowa, NJ, **2000**).
- [13] ANGUS, S., ARMSTRONG, B., DE REUCK, K.M., *Carbon Dioxide - International Thermodynamic Tables of the Fluid State-3*; IUPAC, Pergamon Press, Oxford, 1976.
- [14] GAEMERS, S., ELSEVIER, C.J., BAX, A., *Chem. Phys. Letters*, 301, **1999**, p.138
- [15] YONKER, C. R., PALMER, B. J., *J. Phys. Chem. A* , Vol. 105, **2001**, p.308.
- [16] WANG, B., HINTON, J. F., PULAY, P., *J. Phys. Chem. A* , Vol. 107, **2003**, p.4683.
- [17] MIZUNO, K.; OCHI, T.; SHINDO, Y., *J. Chem. Phys.*, Vol. 109, **1998**, p.9502.