DIFFUSION-ORDERED SPECTROSCOPY NMR-DOSY: NEW VERSATILE TOOL TO FOLLOW NITROXYDE MEDIATED POLYMERIZATION OF POLYMETHYL METHACRYLAYE

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ABSTRACT

During the last decade, the use of Diffusion-Ordered Spectroscopy DOSY Nuclear Magnetic Resonance NMR technique, has known a real explosion in many fields. In this work, attention was given for the first use of this technique as efficient tool to follow the Nitroxide Mediated Polymerization NMP of Methyl Methacrylate MMA monomer, well-known as a complex monomer to polymerize by NMP.

The obtained results showed that the applied 2D NMR experiments were successfully curried out to confirm the non-controlled polymerization of pure MMA by NMP. Moreover the livingness of the PMMA chains, growth in the presence of a small styrene amount, were also confirmed using this same versatile tool, without requiring long time analysis or any particular sample preparations, contrary to the chromatographic techniques.

Mots Clés: *Nitroxide mediated polymerization NMP, methacrylic esters, DOSY NMR, Diblock copolymers.*

NOMENCLATURE

Symbols

$<K>$ activation–deactivation equilibrium constant
D diffusion coefficients
$Đ$ dispercity

Subscripts

DOSY Diffusion-Ordered Spectroscopy NMR
MMA methyle methacrylate
min: minutes
NMR Nuclear Magnetic Resonance
NMP Nitroxyde mediated polymerization
SEC Size exclusion chromatography

1. INTRODUCTION

It is well known that the polymerization of methacrylic esters *via* the nitroxyde mediated polymerization technique presented a great challenge for a long time, in reason of their too high activation–deactivation equilibrium constant $<K>$ [1-3]. In 2005, Charleux et *al.* [4,5] showed that the addition of less than 10 mol% of styrene S to Methyl MethAcrylate MMA (2.2 –8.8 mol % based on the monomers) was enough to reach high

conversions control of the NMP of MMA at 90°C, by sufficiently decreasing the value of <*K*>. The percent of *n*-BA required to obtain successful SG1-NMP synthesis of PMMA was much more important, equal to 75% to reach a similar <*K*> value than that obtained when using styrene comonomer [6]**.** All these reported studies were based on theoretical approaches and mainly on the use of H-Nuclear Magnetic Resonance and Size Exclusion Chromatography analysis.

In the other hand, the NMR DOSY technique is described as a method generally used for the identification of different components in mixtures. This technique is mainly based on the pulse field gradient spin-echo NMR experiment accompanied by diffusions of different species [7]. Applying NMR DOSY, two-dimensional spectrums are obtained, correlating the observed diffusion coefficient of each component with corresponding chemical shifts [7-10]**.**

In this contribution, we report the first use of this NMR DOSY technique to demonstrate its efficiency and versatility as analytical tool allowing the follow of the mechanism of the NMP polymerization of PMMA and to check the livingness of polymeric chains *via* corresponding molar masses evolution and their extension, simultaneously.

2. EXPERIMENTAL PART

Different PMMA and block copolymers PMMA, Poly(MMA-*co*-S), Poly(MMA-*b*-BA), Poly((MMA-*co*-S)-*b*-BA) were synthesized via NMP polymerization, using *N*-tert-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide (SG1) as a control agent and 2-methylaminoxypropionic-SG1 alkoxyamine (MAMA BlocBuilder) as the initiator.

For all the polymerizations, samples were withdrawn during the polymerization for further ^{1}H-NMR analyses. All these samples were precipitated twice into a methanol (90/10) mixture for SEC and DOSY analysis. The final products were also precipitated in the same mixture, filtered and dried in a vacuum oven until constant weights were reached.

3. RESULTATS

Two different behaviors were observed when studying the variation of logarithmic monomer concentration *versus* time and the evolution of Mn_{SEC} and $Đ$ *versus* conversion of MMA in presence or not of small amount of styrene. Indeed, the PMMA exhibits features of controlled systems only when adding 10 mol% of styrene, Figure 1.

The comparison between SEC distribution of the two polymers at the first and the last times, illustrates constancy of molar mass of pure PMMA between the two considered times, whereas increase in value of *Mn* is observed in SEC chromatogram of the final sample of P(MMA-*co*-S), without any observed shoulder, Figure 2.

All these observations confirm the non-control of SG1-NMP synthesis of PMMA in absence of styrene [4, 5], generally explained by the development of side reactions in medium reaction when synthesizing PMMA, such as irreversible terminations between the propagating radicals and/or disproportionation reactions *via* hydrogen transfer from propagating radical to free-SG1 nitroxide [3, 11].

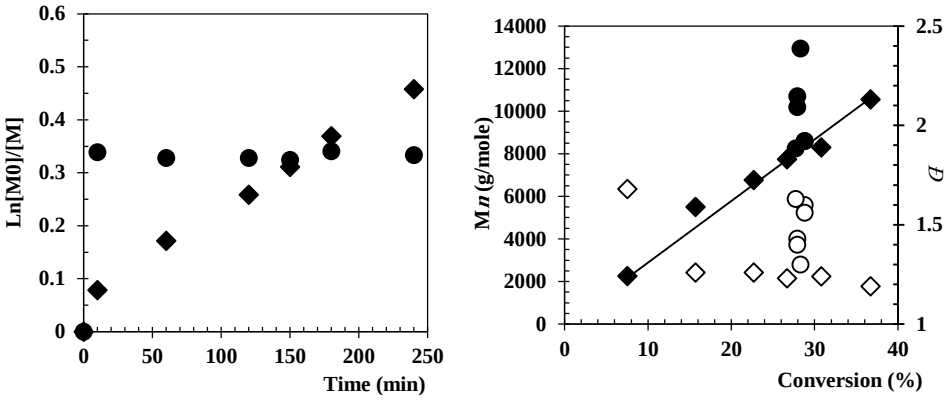

FIGURE 1**.** Bulk polymerizations of MMA and MMA-*co*-S at 80°C : (left) variation of Ln [M]0/[M] *vs.* time and (right) evolution of Mn_{SEC} and *Đ vs.* conversion (pure MMA(●,○) and (MMA-*co*-S) (◆,◇)).

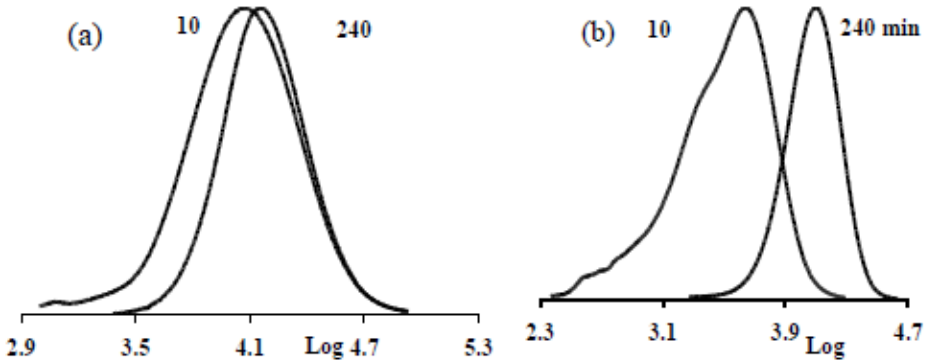

FIGURE 2. Size exclusion chromatograms superposition of (a) PMMA and (b) P(MMA-co-S) depending of time polymerization

In the presence of a small styrene amount, the livingness of the PMMA chains growth were also examined. As reported in bibliography [5], it has been found that the active site of macromolecular chains ends is only present in the P(MMA-co-S) copolymer. Figure 3 illustrates the DOSY spectra of samples at different times of polymerization for both MMA and MMA/S polymerization

We note that the PMMA-*b*-PBA bloc copolymer presents the same value of diffusion coefficient between 0 and 240 min, reflecting the presence of only one species with constant molar mass along the polymerization and thus the confirmation of lack efficiency of the PMMA macro-initiator to extend macromolecular chains due to a high amount of dead chains. However, when a small percent of S to MMA is added, the DOSY ^{1}H spectrum of P(MMA-*co*-S) and P(MMA-co-S)-*b*-PBA show the presence of two different values of diffusion coefficient *D*, confirming the occurrence of diblock formation and consequently the controlled behavior of P(MMA-co-S) to growth the initial chain to reach a block copolymer.

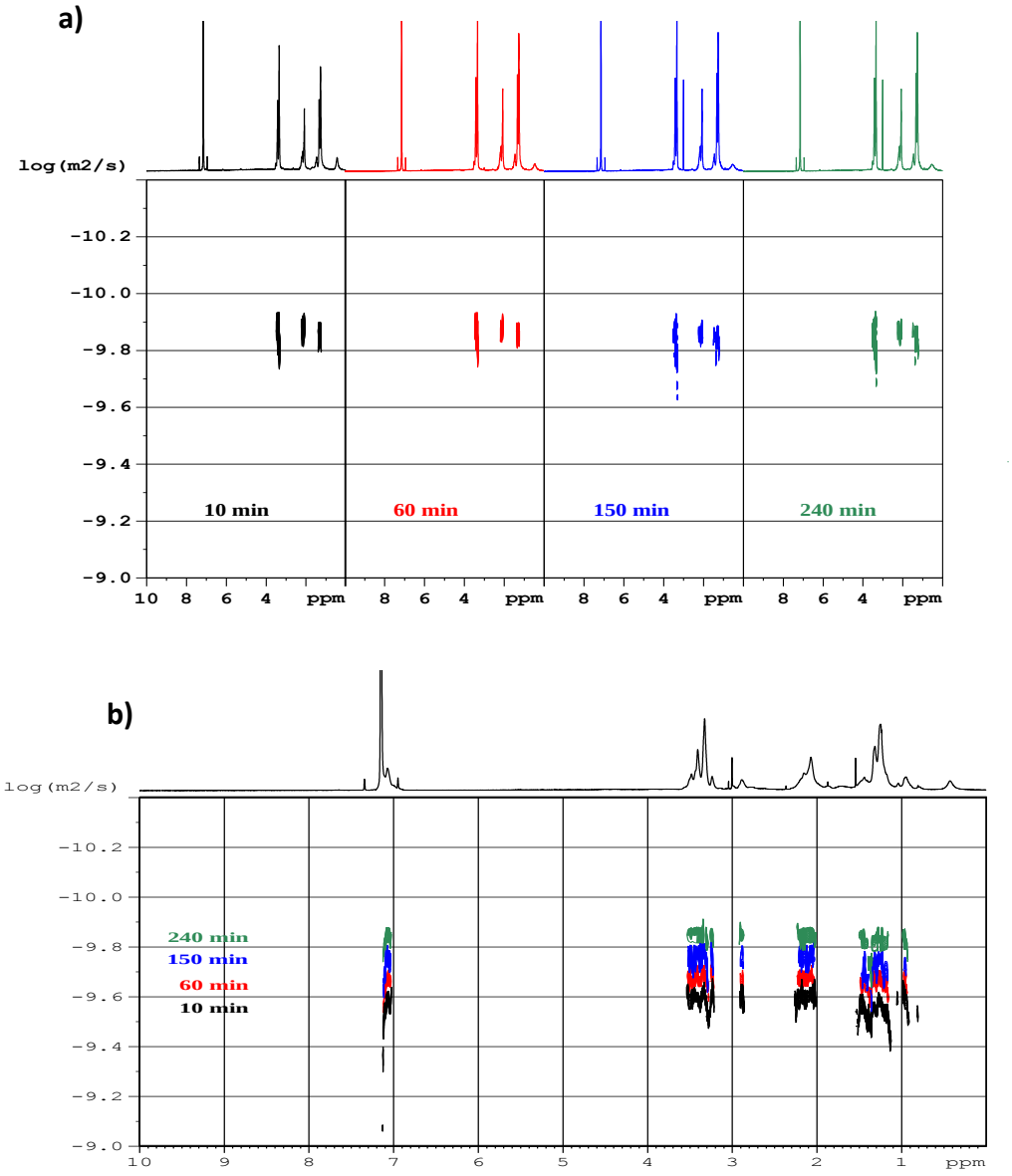

FIGURE 3. DOSY Spectra of PMMA (a) and P(MMA-*co*-S) (b) at 10, 60, 150, and 240 min of polymerization (Polymer concentration = 2 mg/ml).

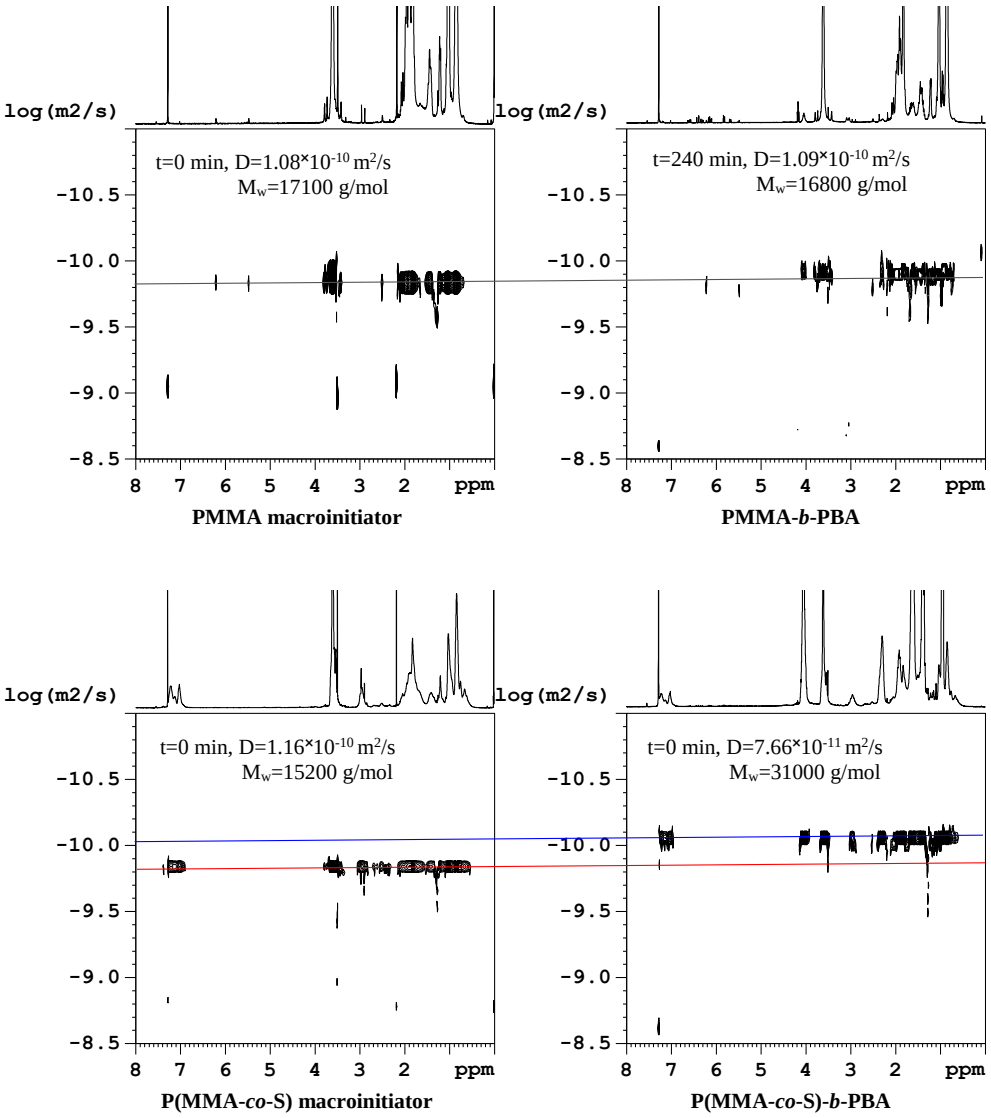

FIGURE 4**.** DOSY NMR of PMMA/PMMA-*b*-PBA (top) and P(MMA-*co*-S)/P(MMA-*co*-S)-*b*-PBA (bottom) macro-initiator/block copolymer couple

4. CONCLUSIONS

In this work, attention was given for the first use of Diffusion-Ordered Spectroscopy (DOSY NMR) technique as efficient tool to give an overview of a mechanism of polymerization in terms of side reactions, molar masses evolution and livingness to synthesize block copolymers. This versatile technique is of great importance for polymer science since it is an powerful analytical tool which can reflect the effective size and shape of polymer chains, and can replace the chromatographic method for physical component separation and molar mass estimation without requiring long time analysis.

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