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Article

DOSY Experiments to Monitor Block Copolymer Polymerization

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Abstract. Block copolymers are a class of polymeric materials made by the covalent bonding of at least two macromolecular chains each with a different chemical nature. The performance of these materials is highly dependent on the physical and chemical properties of the constituting blocks, especially with regard to their chemical composition and molecular weight distribution. Usually, the block copolymer molecular weight is determined using Size-Exclusion Chromatography (SEC). In addition to traditional techniques, Diffusion Order SpectroscopY (DOSY) was introduced in the early 90s to obtain polymer composition and molecular weight information. In the present work, we have successfully used DOSY as a method to monitor block copolymer polymerization as well as to account for the SEC results of a typical analysis.

Keywords: Diffusion Ordered NMR Spectroscopy, Pulsed-field-gradient NMR, Block copolymer, Molecular weight.

Resumen. Los copolímeros en bloque son un grupo de polímeros constituidos por al menos dos cadenas poliméricas de diferente naturaleza química unidas por un enlace covalente. El desempeño de estos materiales está ligado a las propiedades físicas y químicas de cada uno de sus bloques, especialmente a su composición química y distribución de peso molecular. Usualmente, el peso molecular de estos materiales es determinado por Cromatografía de exclusión (CE). Adicionalmente a las técnicas tradicionales, la espectroscopia de difusión ordenada (DOSY) se introdujo a principios de los 90s en el análisis de polímeros para obtener información de la composición y peso molecular. En el presente trabajo se ha utilizado con éxito el método DOSY para monitorear la polimerización de un copolímero en bloques y explicar los resultados de CE en un análisis de rutina.

Palabras clave: Espectroscopia de Difusión Ordenada por RMN, Gradientes de campo magnético pulsados RMN, Copolímero en bloques, Peso molecular.

Introduction

All synthetic copolymers are made up of at least two different chemical species, having multiple distributions of various characteristics such as molecular weight and composition. Precise analysis of copolymers with multivariate distributions is a difficult task and a single separation method is often not able to provide complete information. Size-Exclusion Chromatography (SEC) is the most popular tool for determining the number average molecular weight (Mn), the weight average molecular weight (Mw) and the molecular weight distribution (polydispersity) of polymers [1, 2]. However, in co-elution of species the analysis of copolymers is complex, so SEC has been coupled with other chromatographic techniques to measure molar mass and chemical composition independently [3, 4]. Furthermore, chromatographic conditions for a 2D experiment at critical conditions are specific for just one copolymer. On the other hand, Diffusion NMR spectroscopy, a non-invasive technique with the advantage of requiring little sample preparation, has become a helpful and powerful tool to analyze complicated mixtures without the need for previous chemical separation [5-9]. In the polymer field, this technique has been used in the characterization of homopolymers [10-15] and block copolymers [16].

Translational self-diffusion relies on a simple principle: small molecules moving quickly in solution are associated with large diffusion coefficient values and their NMR resonances appear partially or fully attenuated when compared to those of larger molecules moving more slowly. Usually, the diffusion coefficient (**D**) is experimentally determined by monitoring the signal intensity decay in a 1D pulsed-field gradient spin-echo experiment (PFGSE) spectrum as a function of the applied gradient strength [17]. In optimal conditions and in the absence of signal overlap, the signal intensity of a given resonance decays as described by eq. 1 when using rectangular gradients:

$$A_g = A_o \exp\left(-\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\, \mathbf{D}\right) \qquad (1)$$

where A_g and A_o are the signal intensities in the presence and absence of gradient, respectively, γ is the gyromagnetic ratio, g is the strength of the diffusion gradients, **D** is the diffusion coefficient of the observed spins, δ is the length of the diffusion gradient and Δ is the separation time between the leading edges of the two diffusion pulsed gradients.

Diffusion Order SpectroscopY (DOSY) is a very convenient processing scheme which produces two-dimensional correlation maps showing chemical shifts and diffusion coefficients on the horizontal and vertical axis, respectively [5]. In the present work, DOSY was used as a method to monitor block copolymer polymerization as well as to interpret the SEC results of a typical analysis.

Results and Discussion

The sample under study was designed to be a methyl methacrylate-butyl acrylate (MMA-BA) block copolymer and synthesized accordingly under a controlled two step process to obtain a block copolymer with low polydispersity. A SEC chromatogram was performed at the end of each step (Figure 1). The first chromatogram shows a single peak with Mw of 12682 as expected. The second SEC chromatogram also shows a single peak suggesting that only one component is present in the sample. However, the experimental Mn and Mw are lower than the expected value, indicating that the block copolymer with the desired Mw was not formed. Due to these results, NMR was used as a complementary technique to further characterize the sample.

To corroborate the sample composition and confirm the presence of the two blocks, the ^{1}H NMR spectrum of the sample under study was acquired. The resulting spectrum does contain the signals expected for the copolymer but it is impossible to establish whether they belong to the homopolymer or to the corresponding block copolymer (Figure 2).

DOSY experiments were then performed to determine if the ^{1}H signals belong to the same macromolecule. Figure 3 shows the DOSY spectra of the sample. In the spectra, the ^{1}H signals corresponding to PMMA and PBA are aligned on a different horizontal line indicating different diffusion coefficients. This constitutes unequivocal proof of the presence of at least two species with different hydrodynamic radii instead of the desired block copolymer. It is important to mention that if the ^{1}H signals of both blocks had been perfectly aligned on the horizontal line of the DOSY, the pattern would have indicated that the signals belonged either to the same macromolecule or to molecules with the same diffusion coefficient. If so, the diffusion coefficient value of the block copolymers MMA-BA should be lower than that of the mixture of MMA and BA homopolymers. Furthermore, when a given sample contains a mixture of block copolymers and homopolymers with different molecular weight, a deviation from pure monoexponential behavior is observed.

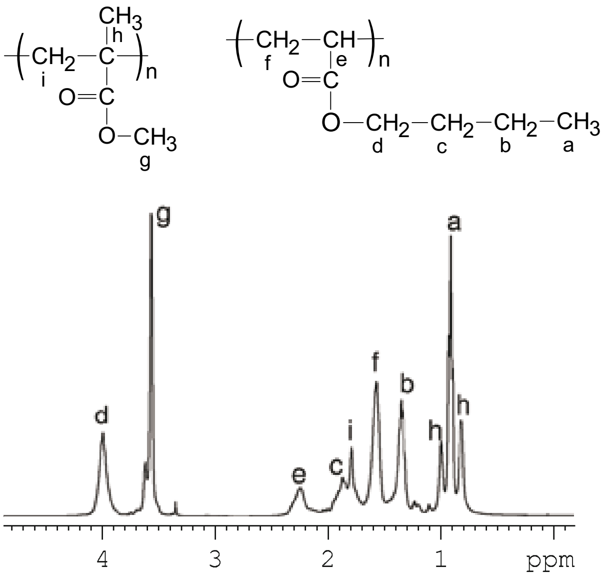

Fig. 2. ^{1}H NMR spectrum (400 MHz) of the target polymerized block copolymers dissolved in $CDCl_3$ at 298 K. Chemical structure of MMA is shown at the top-left and BA at the top-right. The resonances labelled with low case letter are assigned to each particular chemical group.

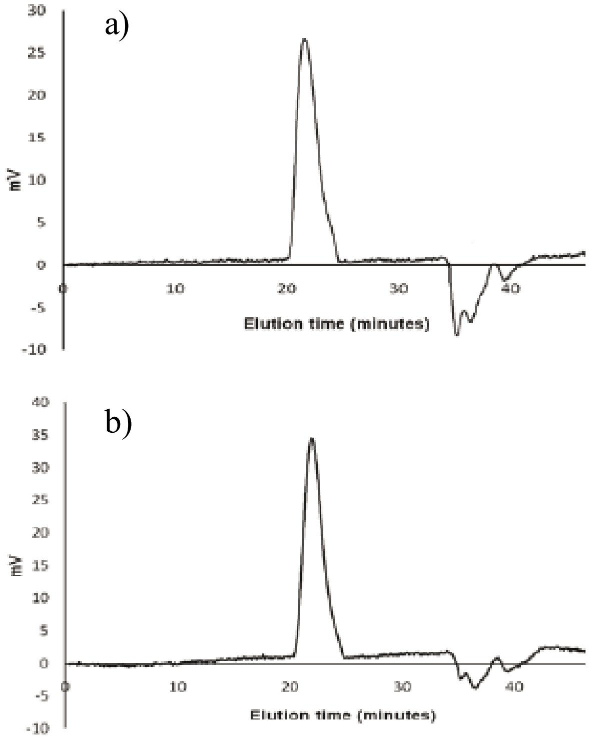

Fig. 1. SEC chromatograms of the polymerization products after each step of the reaction. a) the target homopolymer MMA after the first step (Mn = 6622, Mw = 12682, Polydispersity = 1.9), and b) the target block copolymers MMA-BA after the second step (Mn = 7541, Mw = 17331, Polydispersity = 2.3).

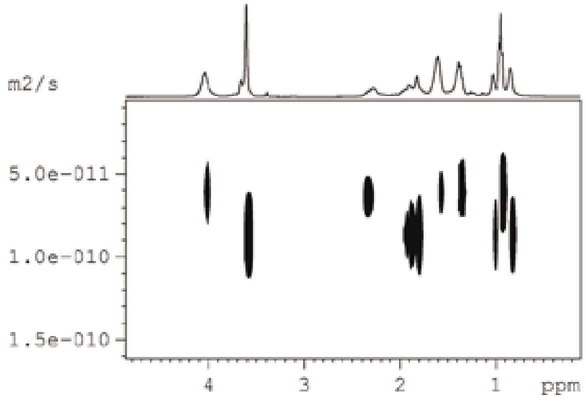

Fig. 3. DOSY ^{1}H spectrum (400 MHz, 298 K) of the sample of the target polymerized block copolymers dissolved in $CDCl_3$. The 1D spectrum of the sample is shown at the top. The DOSY spectrum shows two diffusion species characterized by two different diffusion coefficients (8.36×10^{-11} m^2s^{-1} and 5.82×10^{-11} m^2s^{-1}). The signals of the MMA have higher diffusion coefficient than the signals of the BA. The rapidly diffusing $CDCl_3$ solvent peak is outside this region.

Many authors have used diffusion coefficient measurements to predict the Mw of similar molecules with different molecular weights. They have observed a power law relationship between diffusion coefficient **D** and the Mw described by $\mathbf{D} \propto \mathrm{Mw}^{-\alpha}$ [15]. The plot of **D** vs. Mw is a straight line where α is the slope, and the *y*-intercept a scaling factor. Our calculations used the α value reported by Augé *et. al.* [18] for a family of PMMA in $CDCl_3$ below 30 kD ($\alpha = 0.48$), assuming that both MMA and BA homopolymers behave similarly in this respect. Considering that in the second step of the reaction there is unreacted MMA homopolymer from the first step (Mw = 12682 according to the first SEC chromatogram), a Mw of 15090 for the BA homopolymer can be estimated from the DOSY spectra using the relation $\mathbf{D}_{MMA}/\mathbf{D}_{BA} = (M_{BA}/M_{MMA})^{-\alpha}$. In SEC experiments, species with Mw values that differ only 16% of each other cannot be distinguished and behave as a single entity. Because of this, the SEC result obtained for the second step of the reaction shows no significant difference compared to the initial value.

It is important to mention that the DOSY experiment presented here does not have overlapping signals and no special processing is required to separate each contribution. Nowadays, many strategies have been developed to overcome the difficulties in processing spectra with overlapping signals [10, 19-23], and future progress in this area is expected to turn DOSY into a general analytical tool for polymer characterization.

Conclusion

Although the basic separation mechanism involved in DOSY and SEC is essentially the same in the sense that both techniques distinguish the polymers according to the difference in their respective hydrodynamic size, the absence of a stationary phase is an advantage of DOSY over SEC since adverse adsorption effects are essentially avoided. In this work, DOSY has been used as a fast and efficient way to determine the compositional analysis of a mixture of two homopolymers that appear to be a single species as judged by the presence of a single peak in SEC. Diffusion NMR is a faster method (14 min of experimental time required) compared to SEC that is a time-and solvent-consuming technique.

Experimental

Size-Exclusion Chromatography (SEC)

SEC was used to measure molecular weights and molecular weight distributions, Mw/Mn, with respect to polystyrene (PS) standards (TOSOH Corporation). The SEC experiments were carried out at 308 K in THF using a Waters 515 pump and a Waters 410 differential refractometer as detector (flow rate: 1mL/min, columns: Shodex, dimension 8.0 × 300.0 mm i.d. and particle size 6 μm).

NMR spectroscopy (^{1}H and DOSY experiments)

All NMR experiments described in this work were carried out on a Bruker 400 MHz AVANCE spectrometer equipped with a 5-mm broadband observe (BBO) z-axis gradient probe capable of generating nominal maximum field strengths of 50 G cm^{-1}. The target block copolymer (10 mg) was dissolved in ca. 0.7 ml. of $CDCl_3$ for NMR analysis.

The measurement of **D** was performed using the widely-accepted bipolar-gradient LED (BPLED) [24] pulse sequences, using a diffusion time of 400 ms and a LED delay of 50 ms. For each experiment, rectangular PFGs, with a duration of 1 ms (δ/2) followed by a recovery delay of 100μs were applied with increases from 5% to 95% of the maximum strength in 16 equally spaced steps. The strength of the gradient was first calibrated by measuring the self-diffusion coefficient of the residual HDO signal in a 100% D_2O sample at 298 K. A value of $1.90 * 10^{-9}$ m^2s^{-1} was used for back calculation of the gradient strength.

Experiments were carried out with active temperature regulation, at 298 K. Sample spinning at 20 Hz was used to reduce the effects of convection currents during the diffusion experiment [25]. After Fourier Transformation and baseline correction, the DOSY spectrum was processed by the Bruker Topspin software package (version 3.1) selecting a monoexponential function.

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