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Quantitative Studies of Block Copolymers and Their Containing Homopolymer Components by Diffusion Ordered Spectroscopy

Wolf Hiller

Several polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) and polyisoprene-b-PMMA (PI-b-PMMA) block copolymers are studied with high-resolution diffusion ordered spectroscopy (DOSY) in order to quantify the amounts and molar masses of the copolymers and the containing homopolymers. These studies are particularly challenging because these homopolymers and one block of the copolymers consist of the same monomer type with different molar masses and compositions and cause a total overlap of these polymer components in the NMR spectra. However, DOSY can be proven as a powerful tool for separation and quantification of these moieties. Whereas exponential fittings only deliver averaged diffusion data, biexponential fittings of the individual magnetization curves can separate the overlapping polymer parts. This DOSY approach can be successfully tested for different blends of PS as well as PS and PS-b-PMMA of different molar masses and weighed compositions. The DOSY separation is also compared to size exclusion chromatography (SEC). In the case of the PS-b-PMMA and PI-b-PMMA block copolymers, DOSY identifies the contaminations with homopolymers, quantifies their individual amounts as well as determines the molar masses of both the copolymers and homopolymers. Two mathematical evaluations are used for quantifying these homopolymers with DOSY. These results are compared with the online coupling of SEC and NMR.

1. Introduction

Diffusion ordered spectroscopy (DOSY) was introduced by Morris and Johnson[1] and mainly used to study mixtures of smaller molecules in the past. However, it also has been extensively used for polymer characterizations. Johnson et al. showed already in 1995 the usage of DOSY for the determination of molar mass distributions.[2] Different mathematical functions for describing the molar mass distributions by NMR diffusion were discussed by Håkansson et al.,[3] Röding et al.,[4,5] and Williamson et al.[6] The determination of the polydispersity of polymers by DOSY was also described by Viéville et al.[7] and Jerschow and Müller[8] and with pulsed field gradient diffusion experiments already by Callaghan and Pinder.[9] Recent papers demonstrated the power of diffusion experiments for the determination of molar masses of poly(ethylene furanoate) polyesters,[10] polystyrene (PS),[11] poly(methyl methacrylate) (PMMA),[11,12] as well as polyethylene glycol.[12,13] Other DOSY applications presented by Li et al. described the determination of molar masses of polymers in diverse living/controlled polymerizations.[14] Furthermore, DOSY could even be applied to quantitatively determine threading in rotaxanated polymers.[15] Lewinski et al. showed the DOSY characterization of the L-lactide polymerization with respect to monomer conversion, structure, and molar masses[16] and Chamignon et al. studied both the molar mass and the solution properties of poly(*N*-acryloylmorpholine) in various organic and aqueous solvents.[17] Cherifi et al. studied the nitroxide-mediated polymerization of methyl methacrylate by DOSY.[18] DOSY can also be used to characterize block copolymers. Barrere et al. determined block lengths of copolymers,[19] Viel et al. performed the compositional analysis of block copolymers,[20] Natalello et al. studied amphiphilic block copolymers,[21] and Yu et al. determined the sizes of micelles by DOSY.[22]

The presented work will demonstrate the power of DOSY to separate and especially quantify mixtures of polymer components containing the same monomeric structures. The main focus is the quantitative DOSY study of block copolymers which can also contain homopolymers of the same monomer type as the blocks. In order to check the limits of DOSY for this task, blends of PS homopolymers as well as blends of PS-b-PMMA and PS homopolymers were analyzed by DOSY and also compared to size exclusion chromatography (SEC). Because of the total overlap of the ^{1}H NMR signals of the PS components, biexponential analyzing procedures were applied. Afterward, the individual amounts and the molar masses of the polymer components could be determined. Finally, several PS-b-PMMA and polyisoprene-b-PMMA (PI-b-PMMA) block copolymers were studied with this DOSY approach in order to determine both the

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molar masses and the contents of the copolymers as well as their contaminations by homopolymers. These DOSY data were compared to online SEC-NMR results.

2. Results and Discussion

2.1. DOSY Calculations

Diffusion coefficients will be determined by the signals attenuations due to varying gradient strengths according to the Stejskal–Tanner equation[23]

$$I = I_0 \exp\{-DQ\}$$
$$\text{with } Q = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) \quad (1)$$

where I is the measured NMR intensity, I_0 the unattenuated NMR intensity, D is the diffusion coefficient, γ the gyromagnetic ratio of the observe nucleus, g the gradient strength, δ the gradient duration, and Δ the diffusion delay. This equation will be slightly modified for the used DOSY pulse sequence for convection compensation including double stimulated echo and bipolar gradient pulses according to Jerschow and Müller,[24] where the δ is now twice the gradient pulse length and replaced by δ' and Δ is now the corrected diffusion delay taking into account the delays between the bipolar gradient pulses which will be replaced by Δ'.

The main focus of the paper is the investigation of DOSY for the quantification of polymer mixtures containing polymers with the same monomeric structure but different molar masses and different amounts. This problem can particularly occur in block copolymers which can also contain homopolymers as the precursor. The main challenge of such studies is the problem of the total overlap of the NMR signals of these polymer components in the ^{1}H NMR spectrum leading finally to average diffusion coefficients. The paper will first demonstrate, on blends of polystyrene of different molar masses as well as blends of PS and PS-b-PMMA block copolymers, how the different components can be quantified by DOSY. Then, the possibilities of DOSY to study also PS-b-PMMA and PI-b-PMMA block copolymers, with respect to their molar masses and contaminations, will be demonstrated. These data will be compared to online SEC-NMR results.

2.2. DOSY of Homopolymers

The first step of the analysis was the molar mass calibration of the diffusion coefficients of PS, PMMA, and PI. The diffusion coefficients were determined according to the convection compensation sequence with Equation (1) which also corresponds to the one-component 2D-DOSY processing presented in Figure S1, Supporting Information. **Figure 1** shows the calibration data.

It is clearly seen that two slopes are found for the three homopolymers. The diffusion coefficients of all homopolymers could be fitted to the simple power law equation

$$D = a\, M_w^b \quad (2)$$

for both slopes. The fitted parameters a and b are summarized in **Table 1**.

According to Figure 1 and Table 1, it is seen that the lower molar mass region up to about 32.000 g mol^{-1} provides almost identical diffusion behavior for the three polymers. These exponents are between −0.5 and −0.6 and thus correspond to the dilute-limit exponent. This is a clear indication for good-solvent behavior which is given by the Flory exponent of −0.6. The dilute-limit exponents are presented in many papers such as Barrere et al.,[19] Mazarin et al.,[12] Lewinski et al.,[16] and Li et al.[14] However, the higher molar mass regions are showing steeper slopes for the polymers due to the high concentration. The slopes are very similar for PS and PMMA. The molar mass dependence of PS and PMMA was also verified at the 400 MHz NMR system (see Figure S2A,B, Supporting Information). The dilution of the concentration provides finally a linear dependence of the diffusion coefficient versus molar mass as indicated in Figure S3, Supporting Information.

This paper is presenting higher concentrations of the polymer solutions which should correspond to the semidilute regime. The clear crossover of the characteristic exponent of −0.5 to higher negative values of the exponents of the

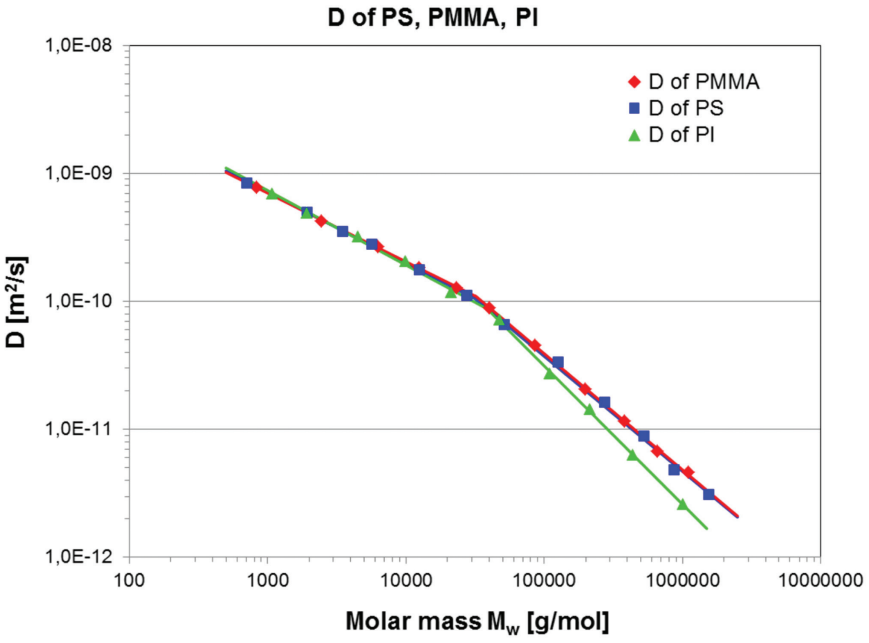

Figure 1. Molar mass dependence of the diffusion coefficients of PS (blue), PMMA (red), and PI (green) determined by DOSY (solid lines are the fitted molar mass dependences according to the parameters of Table 1).

Table 1. Fitted parameters *a* and *b* according to Equation (2) for the lower and higher molar mass regions of PS, PMMA, and PI (fitting of Equation (2) with a square error of $R^2 \geq 0.996$).

Homopolymer	*a* (Lower M_w)	*b* (Lower M_w)	*a* (Higher M_w)	*b* (Higher M_w)
PS	3.23×10^{-8}	−0.553	1.17×10^{-6}	−0.899
PMMA	2.85×10^{-8}	−0.536	1.34×10^{-6}	−0.907
PI	4.09×10^{-8}	−0.582	7.95×10^{-6}	−1.081

molar mass dependence of PS was also verified in refs. [25,26]. Whereas Beckert et al.[25] demonstrated pulsed field gradient measurements in semidilute solutions of PS in deuterated benzene, Zettl et al.[26] measured diffusion coefficients with fluorescence correlation spectroscopy of PS in toluene solutions. Beckert et al.[25] showed the molar mass dependences of PS at different concentrations in deuterated benzene and also obtained different slopes for molar masses below and above 30 000 g mol^{-1}. The slopes of their low molar region was also −0.5 and for the high molar mass regions the slopes are dependent on the concentration and vary between −1.2 and −1.9 with increasing concentration from 2 to 15 wt%. This is consistent with the results of Figure 1 where the transition also appears at about 32 000 g mol^{-1}. In particular, the slopes shown in Table 1 are in good agreement with the results presented by Beckert et al. in ref. [25].

2.3. DOSY of Blends of Polystyrene Homopolymers

In order to study the power of DOSY for the quantification of polymer mixtures, several blends of polystyrenes were prepared which consist of two different molar masses as well as different compositions. These blends provide ^{1}H NMR spectra with a complete overlap of the aromatic and aliphatic regions of the two polymers within the mixture. Therefore, the DOSY calculations need to be set up as a biexponential equation which allows for a separate calculation of the diffusion coefficients of the two molar masses in the mixture as well as the weighing factors presenting the weight percentage of each component. Accordingly, the following Equation (3) is used for the determination of the diffusion coefficients and the chemical compositions

$$I = I_0 \left[A \exp\left\{-D_1 Q\right\} + B \exp\left\{-D_2 Q\right\} \right] \quad (3)$$

The individual experimental parameters of the convection compensated pulse sequence are now given by $Q = \gamma^2 g^2 \delta'^2 \left(\Delta' - \frac{\delta'}{3}\right)$ where the gradient duration δ' and the corrected diffusion delay Δ' are summarized for the different molar masses in Table S3, Supporting Information. In particular, the gradient duration and the diffusion delay have to be increased with increasing molar masses due to the decreasing diffusion coefficients requesting larger gradient strengths and/or diffusion delays. The parameters *A* and *B* are reflecting the molar content of each polymer component (see Table S6, Supporting Information for independent fitting of *A* and *B* where the sum is very close to 1). In this case of molar quantification, Equation (3) can be simplified by using Equation (4)

$$I = I_0 \left[X_{wt} \exp\left\{-D_1 Q\right\} + (1 - X_{wt}) \exp\left\{-D_2 Q\right\} \right] \quad (4)$$

where X_{wt} and $(1 - X_{wt})$ correspond to the relative weight (or molar) percentage of the polymer components.

The DOSY experiments were performed on several polystyrene blends. The molar masses and chemical compositions of the blends are summarized in **Table 2**. This table shows blends where either the molar mass of only one PS is changing by keeping the chemical composition constant to the other PS (1:1) or both PS components keep their molar masses but the chemical compositions are continuously changing.

The 2D-DOSY experiment of the third sample of Table 2 using the one- and two-component DOSY processing of the TopSpin software is presented in **Figure 2**. It shows already that two components can be separated.

To obtain both the diffusion coefficients and the chemical compositions, Equation (4) was used for fitting the signal decays. **Figure 3** is showing the experimental and calculated curves for the third blend PS1920/PS27500 using a mono- and biexponential fitting of the signal intensities of the aromatics. It

Table 2. Molar masses and chemical compositions of the polystyrene blends: comparison of weighed compositions and molar masses of the manufacturer with the DOSY measurements processed via Equations (2) and (4) (biexponential fitting of D_1, D_2, $A = X_{wt}$, $B = 1 - X_{wt}$, and I_0 with a square error of $R^2 = 1$); M_{wi} are rounded to the nearest ten.

M_w/M_w [g mol^{-1}] Manufacturer	Composition (weighed)	Composition *A*/*B* (DOSY) Equation (4)	D_1/D_2 [$\times 10^{-10}$ m^2 s^{-1}] (DOSY) Equation (4)	M_{w1}/M_{w2} [g mol^{-1}] (DOSY) Equation (2)
1920/27500	0.25/0.75	0.26/0.74	4.67/1.15	2140/26 980
1920/27500	0.33/0.67	0.33/0.67	4.63/1.17	2170/26 250
1920/27500	0.49/0.51	0.49/0.51	4.72/1.20	2100/25 060
1920/27500	0.67/0.33	0.65/0.35	4.90/1.27	1960/22 520
1920/27500	0.75/0.25	0.75/0.25	4.86/1.24	1990/23 600
1920/51500	0.51/0.49	0.50/0.50	4.71/0.77	2100/44 640
5620/51500	0.49/0.51	0.51/0.49	2.69/0.74	5820/46 530
12500/51500	0.49/0.51	0.50/0.50	1.77/0.74	12 330/46 630
27500/51500	0.49/0.51	0.44/0.56	1.13/0.70	27 730/49 650

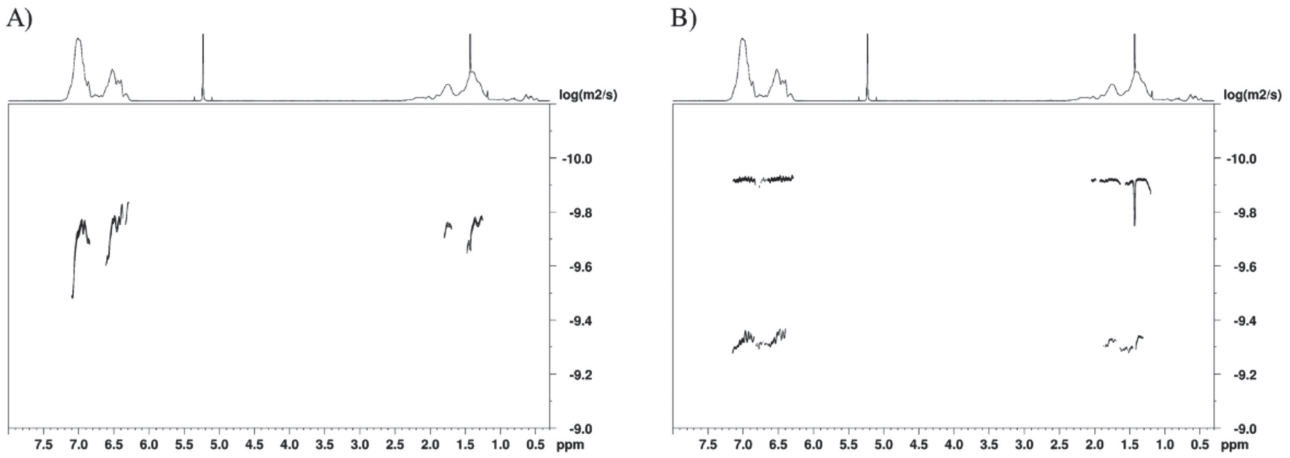

Figure 2. 2D-DOSY of the blend PS1920/PS27500 using the A) one- and B) two-component processing of Topspin.

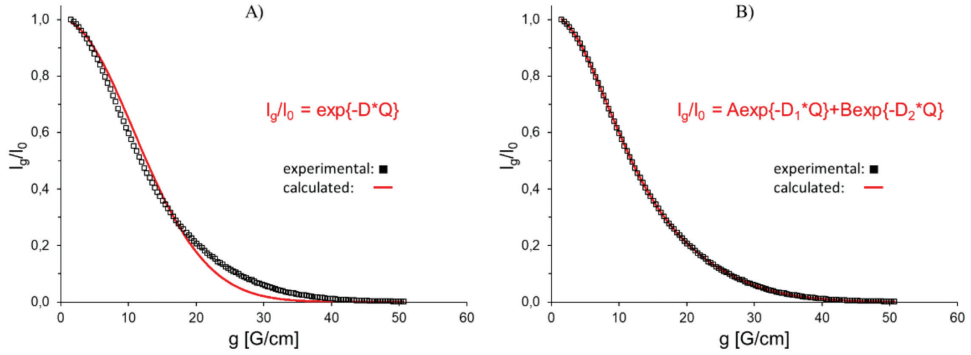

Figure 3. DOSY decays of the aromatic signal of the blend PS1920/PS27500 using the A) mono- and B) biexponential processing of Equations (1) and (3) ($R^2 = 0.99999$), respectively.

is evident from Figure 3B that a perfect match for the intensity decay is achieved by using the biexponential fitting. It turned out that all calculated curves perfectly match the experimental data (see also Figures S4A,B and S5A, Supporting Information). Therefore, all blends of Table 2 were now processed with Equation (4) where I_0 was also fitted. The fitted parameters D_1, D_2 and $A = X_{wt}$ and $B = 1 - X_{wt}$ are summarized in Table 2.

The 2D-DOSY spectra for the different chemical compositions of PS27500/PS1920 are shown as two-component processing in Figure S6, Supporting Information. The ^{1}H NMR spectra of the blends and their individual homopolymers are shown in Figures S4C and S5B–E, Supporting Information. These figures clearly illustrate the total overlap of all PS homopolymer signals within the blends.

In order to compare the separation of the PS mixtures with SEC and DOSY, **Figure 4** illustrates the UV chromatograms and the DOSY spectra of the two blends of PS51500 with PS1920 and PS51500 with PS27500. In case of the first blend (Figure 4A,B), a perfect separation is achieved for both methods and a quantification of the components is easy. The SEC quantification of the second blend (Figure 4C) is more difficult but can be achieved with deconvolution. However, the DOSY separation and quantification with Equation (4) is still more easy.

The 2D-DOSY spectra of all four blends for the different molar masses of PS51500 with PS1920, PS5610, PS12500, and PS27500 are presented for the aromatic regions in Figure S7, Supporting Information, respectively. This figure compares the 2D processing of the diffusion coefficients with the calculation of Equation (4) (blue dashed lines). The diffusion coefficients determined with Equation (4) and TopSpin are in very good agreement. It should be noted that the determination of the chemical compositions could be well performed with Equation (4).

Equation (3) was first used to fit the experimental signal decays of the aromatics in order to yield not only the diffusion coefficients D_1 and D_2 but also the parameters A and B independently. The following conclusions can be derived from Table 2, Figures 3 and 4, and Table S6, Figures S4A, S5A, S6, and S7, Supporting Information:

i. The biexponential fitting results of the blends using Equations (3) and (4) (with a regression square error of R^2 = 0.99999 to 1) are showing good agreements for both the chemical compositions as well as the calculated molar masses via the diffusion coefficients of both polymer components.
ii. Considering the chemical compositions, it can be concluded that Equation (3) delivers the sum of A and B of almost exactly 100% which verifies that A and B clearly represent the molar amounts of both homopolymers within the blend. This is particularly verified by the different weighed compositions of

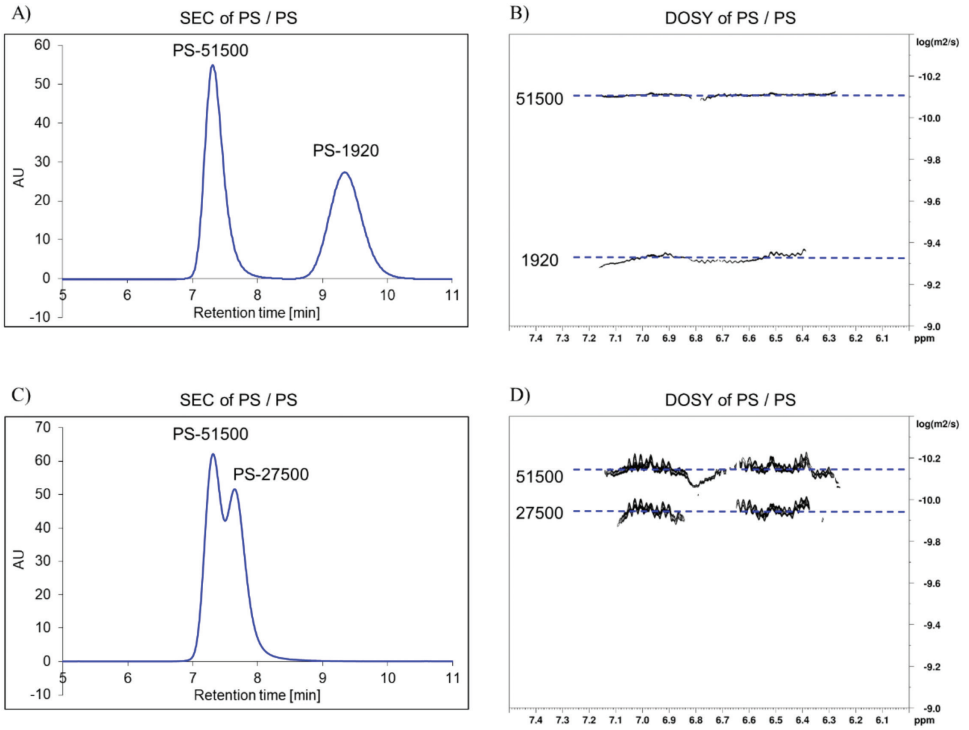

Figure 4. SEC and DOSY of the blends A,B) PS1920/PS51500 and C,D) PS27500/PS51500. The 2D-DOSY spectra were produced with the two-component processing and the blue dashed lines with the biexponential fit of Equation (4).

the blends PS1920/PS27500 where the DOSY fittings delivered the same compositions as the weighed ratios (see Table S6, Supporting Information). Therefore, Equation (4) could be used for the quantification of all mixtures which provided exactly the same quality of the fittings.

iii. In respect of determining molar masses, slightly higher precision was achieved for the component with the molar amount above 60%.

iv. Using the diffusion calibration parameters of Table 1 in combination with Equation (2), the molar masses M_{w1} and M_{w2} of both PS homopolymers can be calculated from the fitted diffusion coefficients D_1 and D_2 from Table 2. The lower molar masses agree well with the manufacturer data. In case of the higher molar masses, slightly smaller values are obtained.

v. In addition, it was also shown that the SEC and DOSY separation of similar molar masses of PS is problematic. If preparing a mixture of PS51500 with PS27500, even the SEC chromatogram provides an overlap of the two components. Only a separation of the peak maxima is visible. A correct quantification of the two components is already difficult, especially if the composition is not 1:1 anymore. The DOSY separation by using only 64 gradients between 3% and 95% will also provide only a monoexponential decay with Equation (3) which delivers an averaged diffusion coefficient of $D = 0.91 \times 10^{-10}$ m^2 s^{-1} corresponding to a molar mass of 37 200 g mol^{-1}. However, the DOSY separation of this mixture could be well achieved with minimum 128 gradient strengths varying between 3% and 100% of the maximum gradient strength causing signal decays clearly below 1% for the highest gradient strengths. In this case, even the quantitative analysis yields reasonable results for the molar amounts and the molar masses of PS. It should be noted, that the low intensities of the NMR spectra at high gradient strengths require still a good signal-to-noise in order to quantify the two exponential functions regarding diffusion coefficients and especially the amounts of these components. Biexponential fittings require high signal-to-noise for the identification of the two components as discussed by Morris et al.[27] Therefore, the high concentration of 10 mg per 0.6 mL was used.

2.4. DOSY of Blends of PS-b-PMMA Copolymers and Polystyrene Homopolymers

In the following, blends of the PS-b-PMMA block copolymer SM1-48900 and PS homopolymers will be studied by DOSY. The blends were weighed 1:1 in respect of the mass of copolymer to homopolymer.

First, the separation of the two mixtures of copolymer SM1-49500 with PS1920 as well as PS27500 will be compared with SEC and DOSY. **Figure 5** shows the UV chromatograms and the DOSY spectra of these two blends.

In case of the first blend (Figure 5A,B), again a perfect separation is achieved for both methods. However, the SEC quantification of the second blend (Figure 5C) with UV only is almost impossible due to the unknown tailing of the first eluting component. This would require a comprehensive multiple detection analysis. On the other hand, the DOSY separation and the quantification with Equation (4) is again possible.

The DOSY measurements and the biexponential fittings for all blends are demonstrated in Figure S8, Supporting Information. Figure S8, Supporting Information shows

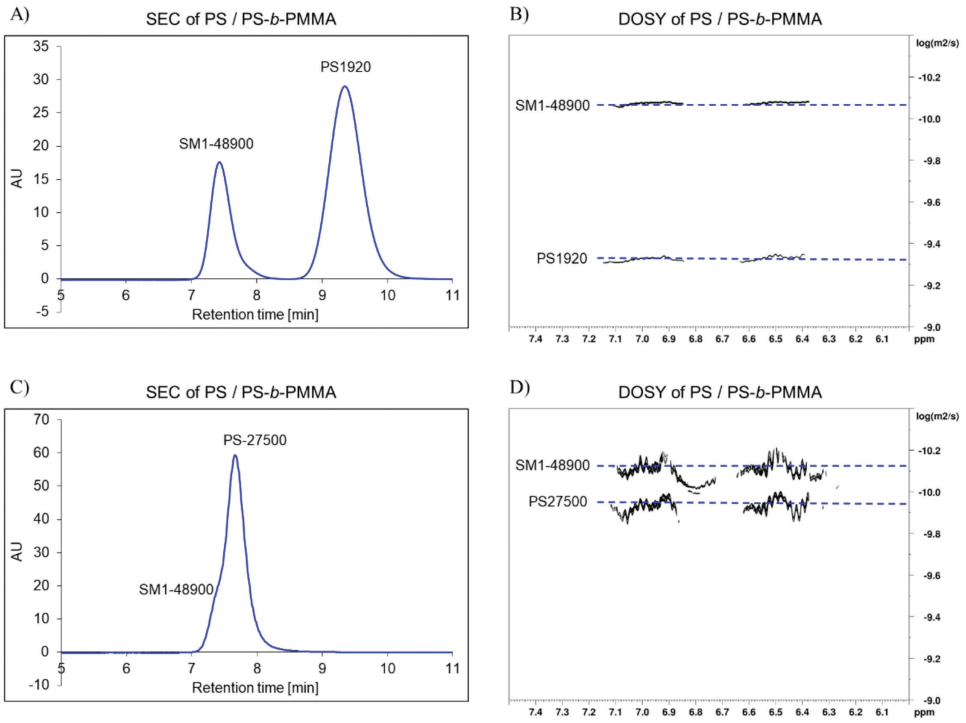

Figure 5. SEC and DOSY of the blends of PS and PS-b-PMMA [A,B) PS1920/SM1-48900 and C,D) PS27500/SM1-48900]. The 2D-DOSY spectra were produced with the two-component processing and the blue dashed lines with the biexponential fit of Equation (4).

well separated aromatic regions of the PS block and the PS homopolymers for all four mixtures. The diffusion coefficients of the fitting calculations are shown in **Table 3**. They deliver molar masses for both the copolymer and the homopolymers which are comparable to the data of the SEC-NMR and manufacturer, respectively.

The molar masses of the polystyrenes are almost perfectly matched, whereas the molar masses of SM1-48900 are smaller most likely due to the smaller aromatic content of this component in the mixture. Moreover, the fitted factors A and B again agree well with the weighed chemical compositions for at least three mixtures. This result again confirms that these factors represent the chemical composition.

It also should be noted that the separation of the PS-b-PMMA SM1-48900 with the PS 27500 could only be achieved with at least 128 gradient strengths as mentioned above for the PS blends. Otherwise, it is averaging the two magnetization curves to a monoexponential decay if less increments are used. The small differences of these molar masses and low contents can also cause the deviation for the quantification of the amounts within the mixture of these polymers.

2.5. DOSY of PS-b-PMMA and PI-b-PMMA Block Copolymers

2.5.1. Monoexponential Processing

Several diblock copolymers of PS-b-PMMA and PI-b-PMMA of different molar masses and different average chemical compositions were investigated with DOSY. The molar masses and chemical compositions of the copolymers are summarized in Table S2, Supporting Information.

The 2D-DOSY spectra of PS-b-PMMA are shown in **Figure 6** and the 2D-DOSY spectra of PI-b-PMMA are presented in **Figure 7**.

It is obvious from Figure 6 that the PMMA and PS blocks are not showing identical diffusion coefficients. This is not expected for a block copolymer. Most of them show smaller coefficients

Table 3. Molar masses and chemical compositions of the blends of PS-b-PMMA and PS: comparison of weighed PS compositions and molar masses of the manufacturer with the DOSY measurements processed via Equations (2) and (4) (biexponential fitting of D_1, D_2, $A = X_{wt}$, $B = 1 - X_{wt}$, and I_0 with a square error of $R^2 = 1$); M_{wi} are rounded to the nearest ten.

M_w/M_w [g mol^{-1}] PS/PSPMMA	Composition PS/PS block (weighed)	Composition A/B (DOSY) Equation (4)	D_1/D_2 [$\times 10^{-10}$ m^2 s^{-1}] (DOSY) Equation (4)	M_{w1}/M_{w2} [g mol^{-1}] (DOSY) Equation (2)
1920/48900	0.73/0.27	0.71/0.29	4.73/0.84	2090/40 680
5620/48900	0.71/0.29	0.69/0.31	2.74/0.82	5620/41 990
12500/48900	0.71/0.29	0.71/0.29	1.73/0.77	12 910/44 930
27500/48900	0.71/0.29	0.59/0.41	1.17/0.77	26 030/44 720

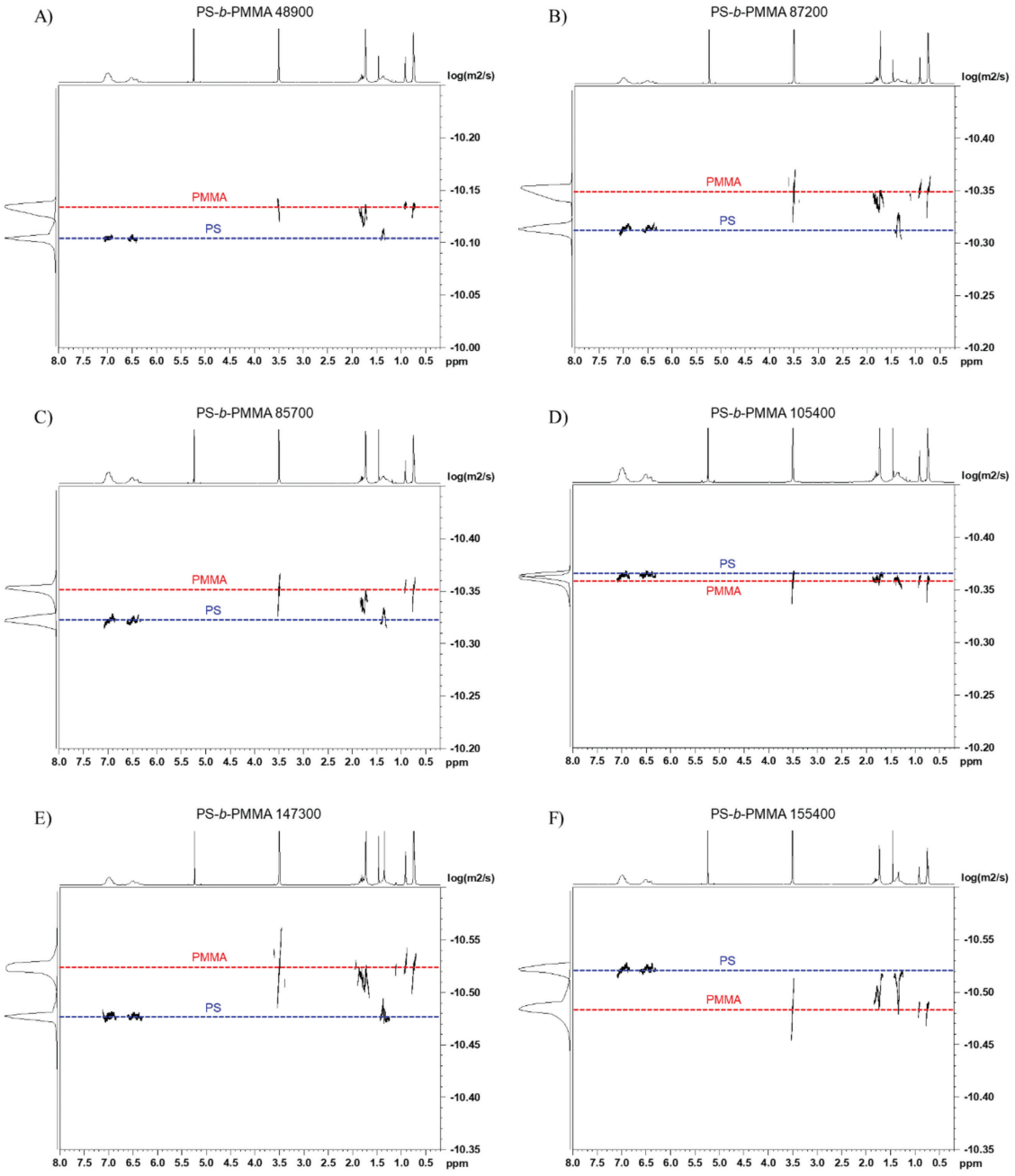

Figure 6. 2D-DOSY with one-component processing of the PS-b-PMMA block copolymers with the indicated maximum diffusion of the individual blocks shown by the vertical projections as well as the red and blue dashed lines for the PMMA and PS blocks, respectively. The PS-b-PMMA are labelled according to the different M_w [g mol^{-1}].

for PMMA (see Figure 6A–C,E), but two out of the six polymers also provide the opposite behavior (see Figure 6D,F).

These results can be interpreted as follows. These differences of the diffusion coefficients of the two blocks are an indication for a polymer mixture where the lower diffusion coefficient represents the entire block copolymer and the larger diffusion coefficient is an average of the coefficient of one block of the copolymer overlapped with a contamination of a polymer with the same structure as the block but having a lower molar mass as the copolymer. Especially, in case of the copolymers with the molar masses 48 900, 87 200, 85 700, and 147 300, the smaller diffusion coefficient of the PMMA part represents the copolymer diffusion and the larger diffusion coefficient of PS is caused by the mixture of the copolymer (represented by the PS block) with either polystyrene homopolymer of a lower molar mass as the copolymer or another low molar mass copolymer with a very high PS content. In case of the block copolymers 105400 and 155400, it is exactly the opposite situation of containing additional low molar mass PMMA or a low molar mass copolymer with a very high PMMA content. It should be noted

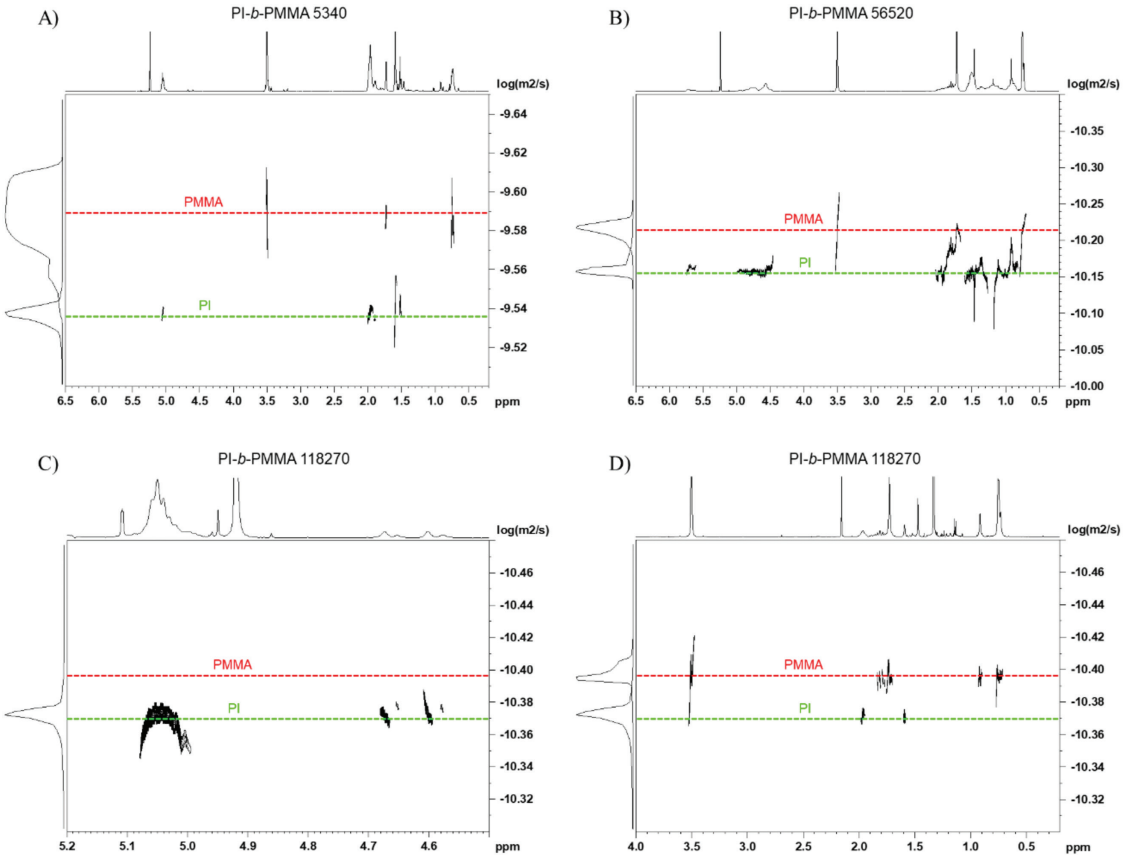

Figure 7. 2D-DOSY with one-component processing of the PI-b-PMMA block copolymers with the indicated maximum diffusion of the individual blocks shown by the vertical projections as well as the red and green dashed lines for the PMMA and PI blocks, respectively. The PI-b-PMMA are labelled according to the different M_w [g mol^{-1}].

that the data are processed with monoexponential fittings. A similar behavior of exponential DOSY processing was also observed by Viel et al.[20] for PS-b-PEO copolymers where the diffusion coefficients of the PS and PEO blocks were different due to overlapping PS homopolymer.

In order to prove this behavior further, PI-b-PMMA block copolymers were studied with DOSY. Figure 7 is demonstrating the 2D-DOSY spectra of PI-b-PMMA block copolymers of different molar masses and different average chemical compositions. These data are also shown in Table S2, Supporting Information.

The PI-b-PMMA block copolymers are showing the same behavior as the PS-b-PMMA copolymers. In case of Figure 7A,B, the PI regions are providing larger diffusion coefficients as PMMA which again suggests an overlap of the PI block with additional PI of a lower molar mass as the copolymer. The diffusion of the copolymer is represented by PMMA due to the smaller diffusion coefficients. Because of the very small content of PI for the high molar mass PI-b-PMMA IM3-118270 which causes very small DOSY cross peak intensities, the olefinic and aliphatic regions are separately presented with adjusted cross peak intensities (see Figure 7C,D). It also should be noted for all measurements that the DOSY plots were processed with monoexponential processing. The diffusion coefficients representing only the copolymer part of the samples are shown in the first column of Table S7, Supporting Information. Table S7, Supporting Information also shows the molar masses of the copolymers calculated via the diffusion coefficients by using the exponential fit. Most of the calculated values are comparable to the molar masses determined by SEC-NMR. The best results are obtained for copolymers with molar masses below 100 000 g mol^{-1}.

In order to prove the assumption that the copolymers contain additional polymer components of lower molar masses, results of the online SEC-NMR are used. Hiller et al. showed for the PS-b-PMMA copolymers SM1-48900[28] as well as SM2-87200, SM3-85700, and SM5-147300 that these block copolymers also contain PS homopolymer in the low molar mass SEC regions and the block copolymers SM4-105400 and SM6-155400 represent a low molar mass region of PMMA (see also Figure S10, Supporting Information).[29] This clearly supports the interpretation of the DOSY results. The same differentiation between the copolymer and the homopolymer is also possible for the PI-b-PMMA copolymers. Hiller et al. also showed SEC-NMR[30] as well as LCCC-NMR[31] results of PI-b-PMMA for the separation of these polymer components. For more details, see the next chapter.

2.5.2. Biexponential Processing

All block copolymers were measured with DOSY by varying 128 gradient strengths in order to increase the resolution and decay

the signal intensities to almost zero. Afterward, a biexponential processing using Equation (5) (corresponds completely to Equation (4)) in combination with Equation (2) was carried out.

$$I = I_0\left[X_{wt}^{copol}\exp\{-D_{copol}Q\} + X_{wt}^{homopol}\exp\{-D_{homopol}Q\}\right] \quad \text{with} \quad X_{wt}^{copol} + X_{wt}^{homopol} = 1 \tag{5}$$

The calculation of the amounts of copolymer and homopolymer was carried out by using the overlapping intensities of the homopolymer and the corresponding block of copolymer consisting of the same kind of monomer units.

In order to determine $D_{homopol}$ and $X_{homopol}$, two different ways will be proposed:

a. Equation (5) will be used for calculating both diffusion coefficients and both weight fractions.
b. Equation (5) will be used for calculating $D_{homopol}$ and both weight fractions by including a fixed D_{copol} parameter represented by the not overlapping monomer unit from the exponential fit.

Table 4 presents the calculation of both diffusion coefficients and the weight fractions (version a). **Table 5** shows the results for version (b) where $D_{homopol}$ and both weight fractions were determined by the fitting procedure. Equation (2) is used for calculating the molar mass via the diffusion coefficients.

The two different biexponential fittings methods delivered very good matching of the experimental data. In this respect, both methods are absolutely comparable. Differences between the results of Tables 4 and 5 could be found for the diffusion coefficients and the amounts of the polymers. It turned out that Table 4 provided in average slightly smaller diffusion coefficients and higher amounts of the homopolymers. Nevertheless, the calculated molar masses of the copolymers in Table 4 are comparable to SEC results. This is still remarkable because four unknown parameters were fitted in this approach.

In order to improve the accuracy of the molar masses and the amounts of the copolymer and the homopolymers, the fitting approach of version b was used. In this case, the diffusion coefficient of the copolymer component will be used as a fixed parameter which was taken from the monoexponential

Table 4. Diffusion coefficients, calculated molar masses, and amounts of the containing homopolymers and copolymers of the PS-b-PMMA (SM) and PI-b-PMMA (IM) block copolymers by using the biexponential fits of all parameters (fittings of $D_{homopol}$, D_{copol}, X_{wt}^{copol} (=1 − $X_{wt}^{homopol}$), and I_0 with square errors of $R^2 \geq 0.9999$).

Copolymer- M_w [g mol^{-1}] SEC-NMR	D_{copol} [×10^{-10} m^2 s^{-1}] (DOSY) Biexponential fit	$D_{homopol}$ [×10^{-10} m^2 s^{-1}] (DOSY) Biexponential fit	M_w^{copol} [g mol^{-1}] (DOSY) Biexponential fit	$M_w^{homopol}$ [g mol^{-1}] (DOSY) Biexponential fit	X_{wt}^{copol} (DOSY) Biexponential fit	$X_{wt}^{homopol}$ (DOSY) Biexponential fit
SM1-48900	0.698	1.189	52 830	25 450	0.746	0.254
SM2-87200	0.381	0.607	102 950	58 450	0.451	0.549
SM3-85700	0.356	0.524	111 100	68 790	0.233	0.767
SM4-105400 aromatics	0.371	0.537	105 890	66 870	0.566	0.434
SM4-105400 OCH_3	0.373	0.669	105 310	52 410	0.689	0.311
SM5-147300	0.262	0.426	155 780	86 550	0.475	0.525
SM6-155400 aromatics	0.295	0.685	136 520	51 050	0.829	0.171
SM6-155400 OCH_3	0.286	0.565	141 420	63 270	0.757	0.243
IM1-5430	2.674	4.534	6060	2300	0.816	0.184
IM2-56500	0.608	1.225	61 470	21 800	0.771	0.229
IM3-118300	0.393	2.266	99 500	7570	0.887	0.113

Table 5. Diffusion coefficients, calculated molar masses, and amounts of the containing homopolymers and copolymers of the PS-b-PMMA (SM) and PI-b-PMMA (IM) block copolymers by using the copolymer diffusion coefficients of the exponential fits (fittings of $D_{homopol}$, D_{copol}, X_{wt}^{copol} (= 1 − $X_{wt}^{homopol}$), and I_0 with square errors of $R^2 \geq 0.9999$).

Copolymer- M_w [g mol^{-1}]SEC-NMR	D_{copol} [×10^{-10} m^2 s^{-1}] (DOSY) Exponential fit	$D_{homopol}$ [×10^{-10} m^2 s^{-1}] (DOSY) Biexponential fit	M_w^{copol} [g mol^{-1}] (DOSY) Exponential fit	$M_w^{homopol}$ [g mol^{-1}] (DOSY) Biexponential fit	X_{wt}^{copol} (DOSY) Biexponential fit	$X_{wt}^{homopol}$ (DOSY) Biexponential fit
SM1-48900	0.735	1.554	49 900	15 680	0.885	0.115
SM2-87200	0.447	0.886	86 290	38 350	0.854	0.146
SM3-85700	0.445	0.703	86 790	49 600	0.835	0.165
SM4-105400[a)]	0.372	0.665	105 600	52 780	0.683	0.317
SM5-147300	0.299	0.562	134 410	63 590	0.800	0.200
SM6-155400[a)]	0.290	0.602	138 930	58 920	0.793	0.207
IM1-5430	2.612	4.126	6330	2700	0.738	0.262
IM2-56500	0.608	1.225	61 470	21 790	0.771	0.229
IM3-118300	0.400	2.882	97 460	5010	0.903	0.097

[a)] D_{copol} for SM4 and SM6 was averaged from the biexponential fits due to overlapping diffusions of both blocks with homopolymers.

fitting. It should be noted again that the PS-b-PMMA copolymers SM1, SM2, SM3, and SM5 contained only PS, and the PI-b-PMMA copolymers IM1, IM2, and IM3 contained only PI as the homopolymer. Therefore, the diffusion coefficients of these copolymer components are directly given by the diffusion of PMMA which is determined by a simple exponential fit. Thus, the corresponding diffusion coefficients can be directly taken from the exponential fit in Table S7, Supporting Information. According to Table 5, very good results for the molar masses and the weight fractions of these copolymers as well as their containing homopolymers could be obtained. The molar masses of the copolymers are matching the SEC results.

The copolymer SM4, however, seems to contain PMMA and PS as the homopolymer. In this case, the diffusions of PS and PMMA are overlapped by the corresponding block of the copolymer and the homopolymers. As the consequence, an exponential fit would always provide an averaged diffusion coefficient of the copolymer and the homopolymer for PS as well as PMMA. Therefore, the exponential fit of SM4 is not relevant and only shown in Table S7, Supporting Information. In case of SM6, it is also possible that it consists of a mixture of copolymer with PMMA and also a small part of PS homopolymer as indicated by the smaller molar mass of the copolymer as expected (see also Table S7, Supporting Information where D_{copol} of PS is related to M_w^{copol}). This will also affect the precision of $X_{wt}^{homopol}$ referring to PMMA. In order to get more details for these copolymers, the complete biexponential fitting of the PS and PMMA signals was performed. Table 4 shows these additional fittings for SM4 and SM6. These calculations delivered better accuracy of the molar masses for both copolymers. In addition, the biexponential fittings of the aromatics and the OCH_3 groups yielded consistent diffusion coefficients for these copolymers. In order to use also relevant copolymer data of SM4 and SM6 for Table 5, the averaged diffusion coefficients of the aromatic and the OCH_3 biexponential fittings of the copolymer part were included for the calculations of the PMMA homopolymer data for these two copolymers. Again, these results of Table 5 are matching well with the expected molar masses of the SEC.

The diffusion coefficients of all copolymers of PS-b-PMMA and PI-b-PMMA of Table 5 versus their nominal molar mass are shown in **Figure 8**. This figure also shows the comparison to the diffusion coefficients of the calibration standards represented by the solid lines. These data are in very good agreement which verifies the molar mass calculation via homopolymer standards.

The 2D-DOSY spectra of the block copolymers SM1, SM6, and IM2 with the biexponential processing of TopSpin in comparison to Equation (5) are presented in **Figure 9**. The remaining DOSY spectra of the copolymers with biexponential processing are shown in Figure S9, Supporting Information. It is visible in these figures that the copolymers also contain additional homopolymers. The PS-b-PMMA copolymers SM1 (see Figure 9A) as well as SM2, SM3, and SM5 (see Figure S9A,B,D, Supporting Information) contain PS homopolymer which is indicated by the two diffusion regions for the aromatics. The PS-b-PMMA copolymer SM6 contains PMMA homopolymer which is verified by the two diffusion regions for the OCH_3

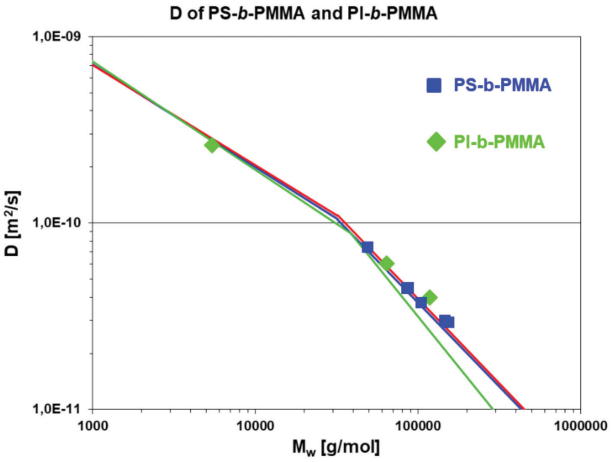

Figure 8. Diffusion coefficients of the PS-b-PMMA and PI-b-PMMA copolymers in dependence on the nominal molar mass. (*D* was calculated by using the relevant monomer units representing the copolymer, see also the first column of Table 5.) The solid lines are the molar mass dependences of *D* for the homopolymer standards from Figure 1 (blue line: PS, red line: PMMA, green line: PI).

and α-CH_3 (Figure 9B). SM4, however, presents both PS and PMMA homopolymer as indicated by the DOSY processing (see Figure S9C, Supporting Information). In case of the PI-b-PMMA copolymers, the additional homopolymer component was always PI as mainly seen by the two diffusion regions for the olefinic protons at 4.5–5.0 ppm (see Figure 9C for IM2 and Figure S9E,F, Supporting Information for IM1 and IM3, respectively).

The verification of the additional homopolymers and the calculated parameters M_w^{copol}, $M_w^{homopol}$, and $X_{wt}^{homopol}$ can only be performed with SEC or HPLC if the complete chromatographic separation of the precursor can be achieved. We demonstrated such possibility to quantify the PI precursor of PI-b-PMMA with SEC-NMR[30] and LCCC-NMR.[30,31] The proposed procedure requires at least a partial indication of the coeluting copolymer and homopolymer fractions which can be completely separated by using the simulated true chemical composition of the copolymer in dependence of the elution time. **Figure 10** demonstrates the separation of the homopolymer from the block copolymer fractions for the two block copolymers IM2 and SM6.

The true chemical composition of the copolymer region can be verified by a clear monomodal elution profile of both individual monomer units. In case of Figure 10A,B, this chemical composition is linearly changing and can be fitted by a simple linear regression. The total copolymer elution, however, is easily recognized by the PMMA elution for the PI-b-PMMA and by the PS elution for the PS-b-PMMA because these elution curves are monomodal. The other monomer units clearly show a bimodal elution. Therefore, it is possible to simulate the chemical composition for the entire copolymer elution and consequently simulate a monomodal elution curve out of the bimodal profile. As the result, one can obtain the entire homopolymer elution by subtracting the bimodal and the simulated monomodal elutions. Finally, these two separated elution curves allow for a complete quantification of the true molar

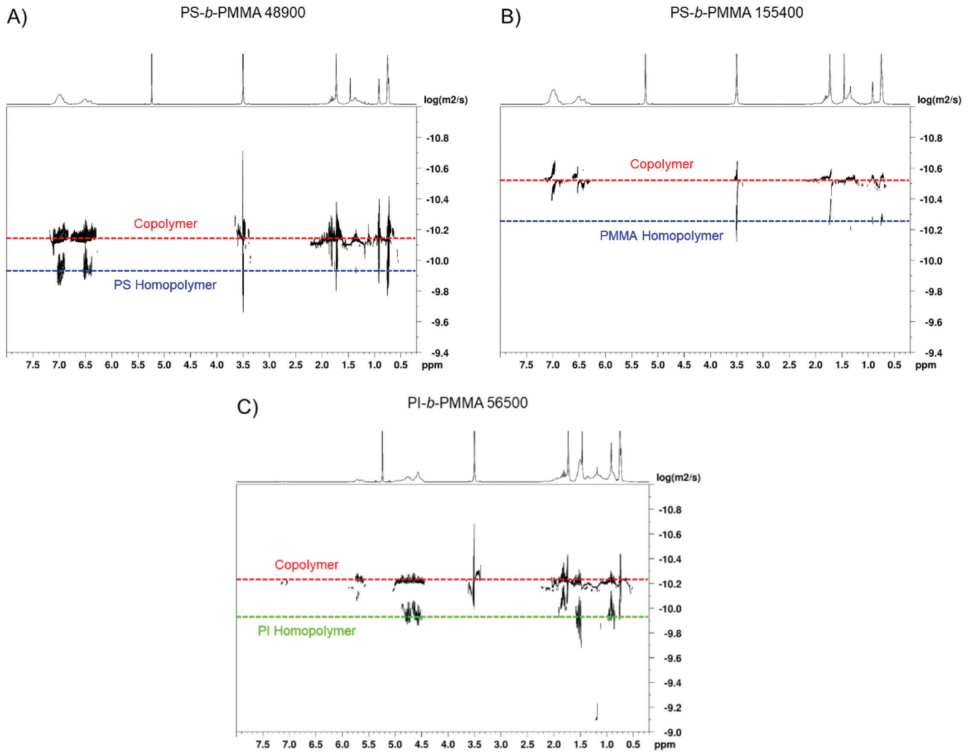

Figure 9. 2D-DOSY with two-component processing of the PS-b-PMMA SM1-48900, SM6-155400 and PI-b-PMMA IM2-56500 in comparison to the biexponential fit of Equation (5) indicated by the dashed lines.

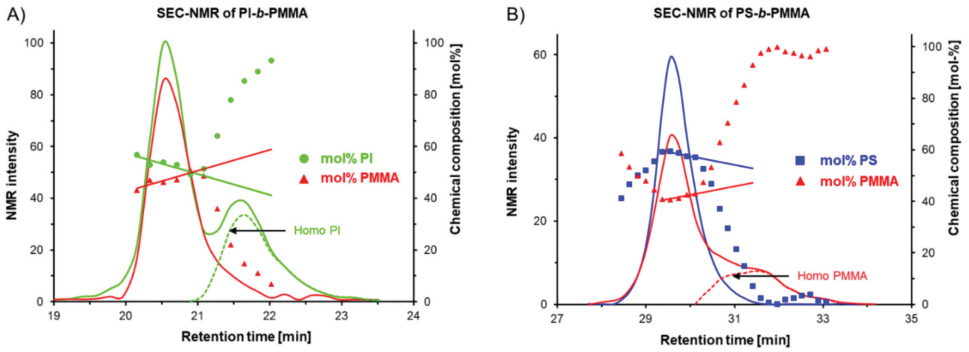

Figure 10. Online SEC-NMR of the block copolymers A) PI-b-PMMA IM2-56500 and B) PS-b-PMMA SM6-155400: the circles, triangles, and squares are presenting the chemical compositions. The solid lines are showing the NMR chromatograms of PI (green), PS (blue), and PMMA (red). The dashed lines are showing the calculated elution of the homopolymers. The straight lines are the regression lines referring to the simulated true chemical compositions of the copolymer region. (A) Adapted with permission.[30] Copyright 2012, Wiley-VCH. (B) Adapted with permission. Copyright 2013, American Chemical Society.

mass distributions as well as weight fractions of both the copolymer and homopolymer components.

In case of the PI-b-PMMA block copolymer IM2-56500, this comprehensive analysis was already successfully demonstrated in ref. [30] and also applied in Figure 10A. Both the molar mass and the amount of the containing PI homopolymer as well as the correct molar mass and the true chemical compositions of the copolymer could be quantified. We determined a molar mass of PI of M_w = 27 600 g mol^{-1} and $X_{wt}^{homopol}$ = 29.3% and a molar mass of the copolymer of 64 200 g mol^{-1} with SEC-NMR in ref. [30]. The DOSY data at the chemical shift region of 4.5–5.0 ppm delivered M_w = 21 790 g mol^{-1} and $X_{wt}^{homopol}$ = 22.9% for the homopolymer and 61 470 g mol^{-1} for the copolymer. The diffusion coefficient of the copolymer is the same as for the OCH_3 group determined by the exponential fit. Including also the other olefinic region of 5.5–6.0 ppm, M_w = 27 160 g mol^{-1} and $X_{wt}^{homopol}$ = 24.5% were determined. These results are in very good agreement with the SEC-NMR data.

The new analysis of PS-b-PMMA is presented in Figure 10B. In this case, slightly lower data for the molar masses and the content of PMMA homopolymer were determined with DOSY (see **Table 6**).

Table 6. Molar masses and molar amounts of the homopolymer precursors of the PI-b-PMMA (IM2) and PS-b-PMMA (SM6) block copolymers determined via Equations (2) and (5) and online SEC-NMR.

Copolymer	$M_w^{copolymer}$ [g mol^{-1}] (DOSY)	$M_w^{homopolymer}$ [g mol^{-1}] (DOSY)	$X_{wt}^{homopolymer}$ [rel. wt%] (DOSY)	$M_w^{copolymer}$ [g mol^{-1}] (SEC-NMR)	$M_w^{homopolymer}$ [g mol^{-1}] (SEC-NMR)	$X_{wt}^{homopolymer}$ [rel. wt%] (SEC-NMR)
PI-b-PMMA IM2	61 470	21 790	0.229	64 200[a)]	27 600[a)]	0.293[a)]
PS-b-PMMA SM6	138 930	58 920	0.207	164 100	75 900	0.253

[a)]Used with permission.[30] Copyright 2012, Wiley-VCH.

Consequently, this DOSY concept seems to be very useful for the characterization of block copolymers and especially in respect of determining molar masses and amounts of the polymer components. Moreover, the DOSY analysis requires much less efforts than the comprehensive SEC-NMR separation or SEC multi detector copolymer analysis. The other SEC-NMR diagrams are presented in Figure S10, Supporting Information. These copolymers are not providing such clear separation of the copolymer and homopolymer regions. Nevertheless, the molar mass distributions of the copolymers were delivered and could be used for comparison to DOSY.

3. Conclusion

It was shown that DOSY is a very powerful tool for the separation of polymer mixtures. In particular, it could be shown that mixtures of polymers of different molar masses containing the same structural monomer units can be separated and quantified if biexponential fittings are involved. It was possible to determine the molar masses as well as the amounts of each polymer component via the two-component fitting of the diffusion curves and the molar mass calibration of the diffusion coefficients. This separation problem is very similar to SEC if the same structural components are overlapping in the chromatogram. Whereas SEC showed problems for overlapping peaks, DOSY was still successful for the demonstrated blends. In particular, DOSY is very powerful if block copolymers are involved where DOSY can observe both blocks independently. Furthermore, DOSY was able to separate block copolymers regarding their additional parts of homopolymers. In this case, both the copolymers and homopolymers could be quantified in respect of their molar masses as well as their contents in the mixture. In particular, if the experimental diffusion coefficient of the copolymer part is known, the molar mass of the homopolymer as well as the amount of both polymers components can be well quantified. It can be concluded that the DOSY determination of the molar masses of PS-b-PMMA and PI-b-PMMA block copolymers can be well described by molar mass calibrations of homopolymers if the same kind of homopolymers as the blocks of the copolymers and the same concentrations as well as solvents are used for the DOSY measurements. To verify these investigations, online SEC-NMR studies were used in order to confirm the DOSY separation and quantifications. These SEC results also support the application of the DOSY homopolymer calibrations for the quantification of the block copolymers. However, it also would be very useful to find out a recipe for the separation limits of DOSY in respect of very similar molar masses and the minimum detectable contents of each polymer component.

4. Experimental Section

Materials and Solutions: The homopolymer standards of polystyrene, PMMA, and polyisoprene are from PSS GmbH (Mainz, Germany). The data of the different molar masses are presented in Table S1, Supporting Information. The PS-b-PMMA diblock copolymers were also produced by PSS GmbH. The PI-b-PMMA diblock copolymers are synthesized by the Max Planck Institute of Polymer Research in Mainz (Germany). The molar masses and average chemical compositions are summarized in Table S2, Supporting Information.

The polymer solutions of the homopolymers, blends, and copolymers were prepared by weighing 10 mg of the polymers in 0.6 mL CD_2Cl_2. This concentration was needed due to the necessary signal-to-noise of the individual DOSY spectra.

SEC Measurements: The UV chromatograms of the blends were recorded on an Agilent HPLC system 1100/1200 equipped with a ResiPore column by injecting 100 µL and a concentration of 1 mg mL^{-1} in THF.

NMR Experiments: The NMR experiments were performed with a 700 MHz spectrometer AVANCE-III HDX from Bruker BioSpin GmbH in Rheinstetten (Germany) equipped with a 5 mm helium cooled quadrupole resonance cryoprobe H(C,N,P). The 2D-DOSY measurements were carried with the pulse sequence for diffusion measurement using double stimulated echo for convection compensation and longitudinal eddy current delay (LED) (with bipolar gradient pulses for diffusion and three spoil gradient pulses)[24,32] due to the fact of convection in dichloromethane even at ambient temperature of 25 °C. The maximum gradient strength of the probe was calibrated to 57.5 G cm^{-1} corresponding to the diffusion coefficient of $1.91.10^{-9}$ m^2 s^{-1} at 25 °C for doped water.

The acquisition parameters for the DOSY experiments were 7.5 µs (90° pulse), relaxation delay of 3 s, and an acquisition time of 1.95 s (32 kB per FID). 128 gradient strengths varying linearly between 3% and 100% of the maximum gradient strength and 16 scans per increment were used for the polymer mixtures. The spectra of the polymer standards at 3% gradient amplitude provided a signal-to-noise of minimum 6000:1 for the aromatic protons of PS, 50 000:1 for the OCH_3 group of PMMA, and 15 000:1 for the olefinic protons of 1,4-PI. Sixty-four gradient strengths were used for the polymer calibrations. Depending on the molar mass, the duration of the gradient pulse was adjusted between 0.8 and 3.2 ms and the diffusion delay changed between 60 and 320 ms (for detailed parameters of the homopolymers and copolymers, see Tables S3 and S4, Supporting Information). The 2D-DOSY processing was performed with TopSpin 3.5 using one- and two-component exponential fittings. A line broadening of 2 Hz and zero-filling to 64 kB was applied to the F2 dimension and zero-filling to 1 kB in F1. The offline processing of the DOSY data was performed with the OriginPro software 2017 by using the integrals of the aromatic protons for PS, the OCH_3 integrals for PMMA, and the olefinic integrals for PI.

The standard deviation of the diffusion coefficients of the PS standards is given in Table S5, Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

block copolymers, diffusion ordered spectroscopy, homopolymers, molar mass

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