Supporting information

A fast and efficient way of obtaining the average molecular weight of block copolymers via DOSY

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Contents

Materials

Chemicals

All components as well as reagents and solvents were used as received without further purifications, unless stated otherwise. Benzene-d6 (99.6%), CDCl3 (99.8%), D2O (99.9%) and are obtained from Merck. Acetone-d6 (99.9%), toluene-d8 (99.5%), tetrahydrofuran-d8 and are obtained from Cambridge Isotope Laboratories. Methyl methacrylate (MMA) standards are purchased from PSS. The following molecular weights were used: 1700 g/mol, 16900 g/mol, 60000 g/mol, 84900 g/mol and 106000 g/mol. The monomers methyl methacrylate (MMA, 99% Merck), butyl acrylate (BA, 99% Merck), methyl acrylate (MA, 99% Merck) and poly(ethylene glycol) methyl ether acrylate (PEGMEA, M_n 480, Sigma-Aldrich) were deinhibited over a column of activated basic alumina before use. 2-(Dodecylthiocarbonothioylthio)propionic acid (DOPAT) was synthesized according to the literature.[1] The reagents and chemicals used to synthesize DOPAT were purchased from Sigma Aldrich or VWR. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDP-TTC, 97% Boron Molecular) was used as received. 1,1'-azobis(isobutyronitrile) (AIBN, 98% Sigma-Aldrich) was recrystallized twice from methanol before use. Dimethyl sulfoxide (DMSO, Merck) and 2-butanol (Sigma-Aldrich) were used as received.

Characterization

NMR

All NMR tubes were dried in an oven at 130 °C overnight in advance. The polystyrene standards were prepared with 1 mg polystyrene and 1 mL of a deuterated solvent (benzene-d_6, chloroform-d, acetone-d_6, toluene-d_8 and tetrahydrofuran-d_8). All experiments were run without spinning to avoid convection. ^{1}H DOSY NMR spectra were recorded at 298 K with an air flow of 400 L h^{-1} on a Bruker Avance III nanobay NMR spectrometer equipped with a 9.4 T magnet, GAB/2 gradient amplifier and 5 mm BBFO probe with z-gradient coil with maximum gradient strength of 50 G cm^{-1}, operating at 400.20 MHz (^{1}H).

The standard Bruker pulse program, ledbpgp2s, employing a stimulated echo sequence with longitudinal eddy current delay and 2 spoil gradients was utilized. Pulse gradients were used with a total duration of 5-10 ms. Gradient recovery delays were 2 µs. The diffusion time is 200 ms. The number of gradient steps was set to be 12. Bruker software, TopSpin 4.1.3 and Dynamics Center 2.7.3, were used for data acquisition and processing.

SEC-MALLS

Size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) measurements were performed on an Agilent 1260 Infinity system coupled to a SLD2020 laser light scattering detector (PSS Polymer Standards Service GmbH) equipped with a vertically polarized temperature stabilized light source operating a wavelength of λ_0 = 660 nm and an Agilent refractive index detector as concentration detector. The mobile phase for the SEC experiments was tetrahydrofuran (THF) for all the BA and MA polymers, the mobile phase for the other polymers was N,N-dimethylformamide (DMF) with 1 g/L lithium bromide (LiBr).Chromatographic separation was performed by using a combination of 3 columns (8 x 300mm), all of 10µm particle size : PSS GRAM 1000, 1000, 30 A for DMF and PSS SDV 10^6, 10^{5}and 10^{3}A for THF, with separation ranges of 500 to 1 x 10^6 g mol^{-1}.. An injection volume of 100 µL and 25 µL of 0.25 wt % polymer solutions for conventional SEC and SEC-MALLS, respectively, and a flow rate of 1.0 ml min-1 was used for all measurements. All samples were

cleaned prior by filtration through PTFE membrane filters with a pore size of 0.45 μm (Millipore, Millex-FH). Measurements in DMF were carried out at 60 °C and those in THF at 30°CIn SEC-MALLS the refractive index increment of the samples was determined under the assumption of a nondissipative mass recovery. All data were recorded and evaluated by using PSS-WinGPC UniChrom (PSS).

Polymerization procedures

Thermal polymerization

In a typical procedure, the RAFT-agent DOPAT (0.5 mmol, 1 eq.), the thermal initiator AIBN (0.05 mmol, 0.1 eq), butyl acrylate (40 mmol, 50 eq.) and the solvent 2-butanol (4.27 mL) were added in a glass vial. The concentration of AIBN was set to 0.1 eq. The glass vial was sealed with a rubber septum, and the solution was purged with nitrogen (argon) for 20 minutes. Next, the reaction solution was transferred to a 10 mL gastight syringe, prepurged with argon (3x), and placed in the holder of the syringe pump. The flow reactor was manually flushed with 2-butanol before each new reaction. All reactions were performed at 90 ^{0}C.

Photoiniferter polymerization

The monomer MMA (3 M, 30 mmol, 3 g, 40 equiv.) and the photoRAFT agent CDP-TTC (0.75 mmol, 0.303 g, 1 equiv.) were dissolved in DMSO and passed N2 for 5 min. The solution was then transferred to a gastight syringe and placed in the syringe pump holder. The photo flow reactor has a volume of 0.9ml and is kept at 90 °C under illumination with blue light (450 nm), controlled by the variable power supply unit.
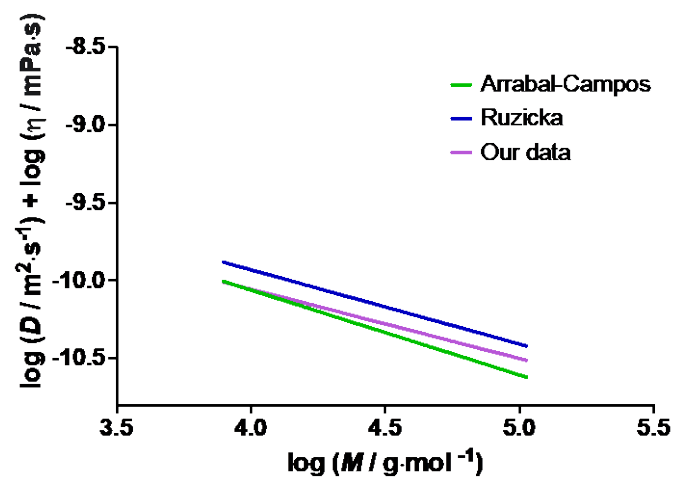
pMMA calibration - literature comparison

Figure S1: Viscosity-corrected DOSY calibrations for pMMA homopolymers derived at different laboratores. [2]
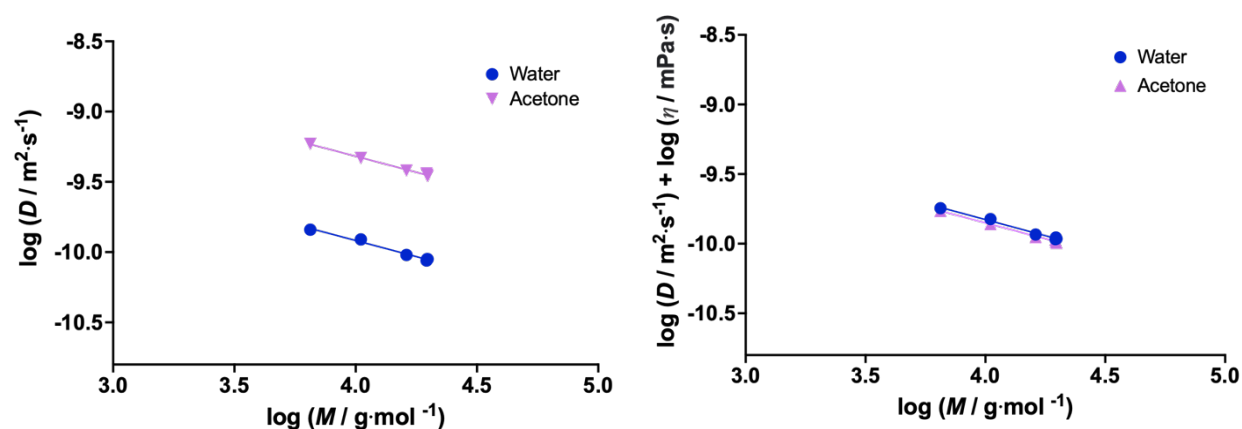
pPEGMEA homopolymer calibration

Figure S2: Diffusion calibration plots and viscosity-corrected calibration plots for RAFT-made pPEGMEA homopolymers.

Table S1: MALLS and DOSY results for the RAFT-made pPEGMEA homopolymers

Sample	MALLS M_w (g/mol)	Diffusion coefficient ($m^2 \cdot s^{-1}$) – D_2O	Diffusion coefficient ($m^2 \cdot s^{-1}$) – acetone-D6
pPEGMEA15	6500	8.08E-11	3.05E-10
pPEGMEA20	10500	6.31E-11	2.61E-10
pPEGMEA40	16200	5.41E-11	2.29E-10
pPEGMEA60	19700	4.60E-11	1.95E-10
pPEGMEA80	19600	4.90E-11	1.99E-10
pPEGMEA100	19800	4.92E-11	1.97E-10

Table S2: Viscosities of different deuterated solvents.

Sample	Viscosity (mPa·s)
benzene-d6	0.6076
$CDCl_3$	0.563
acetone-d6	0.295
toluene-d8	0.56
THF-d8	0.48

pBA-b-pMA data

Table S3: MALLS, DOSY and NMR results for pBA homopolymers and pBA-b-pMA block copolymers

| Sample	MALLS M_w (g/mol)	NMR conversion M_n (g/mol)	NMR conversion (%)	Diffusion coefficient (m²·s⁻¹) – benzene-D6
pBA35	6100	4210	86	2.07E-10
pBA55	8000	5850	78	1.76E-10
pBA75	8900	7940	79	1.40E-10
pBA35 – pMA30	9500	6250	68	1.72E-10
pBA35 – pMA60	7600	9130	82	1.52E-10
pBA35 – pMA90	8700	9980	64	1.46E-10
pBA35 – pMA120	9400	13710	48	1.43E-10
pBA55 – pMA30	10200	7950	70	1.56E-10
pBA55 – pMA60	11200	9210	56	1.45E-10
pBA55 – pMA90	13800	10530	52	1.41E-10
pBA55 – pMA120	14200	11860	50	1.37E-10
pBA75 – pMA60	6100	10770	47	1.27E-10
pBA75 – pMA90	8000	15240	81	1.15E-10
pBA75 – pMA120	8900	16960	75	1.13E-10
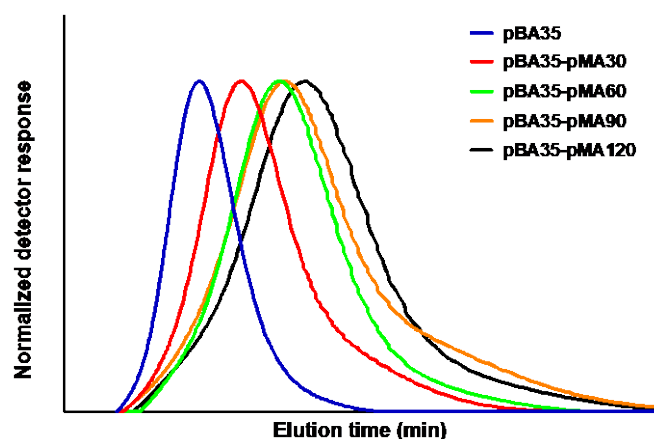
Figure S3: SEC chromatograms for the pBA35 homopolymer and its chain extensions as an example of the performed block extensions.
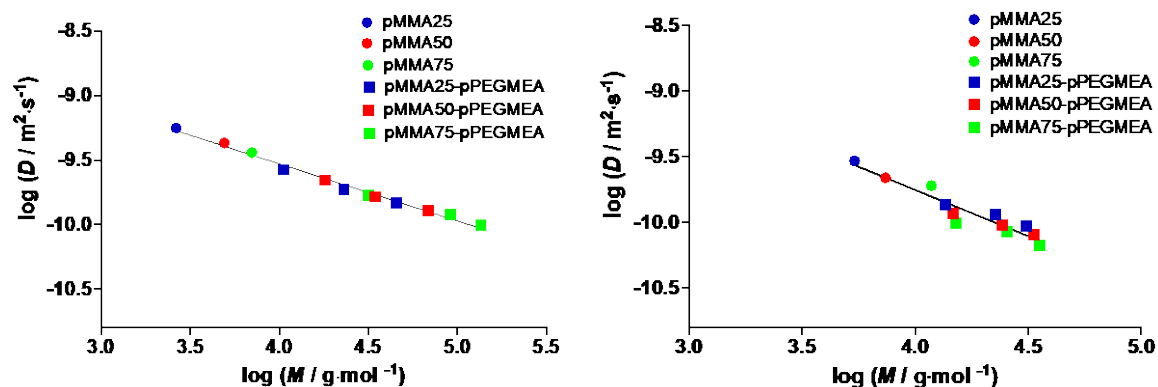
pMMA-b-pPEGMEA data

Figure S4: Joint DOSY calibration for pMMA homopolymers and pMMA-b-pPEGMEA block copolymers in acetone-d6 (left) and CDCl$_3$ (right).

Table S4: MALLS, DOSY and NMR results pMMA homopolymers and pMMA-b-pPEGMEA block copolymers.

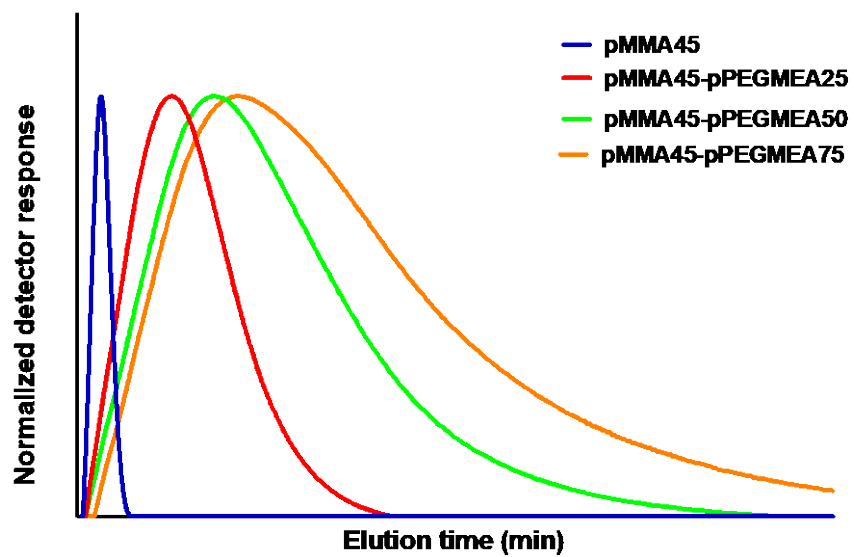| Sample	MALLS M_w (g/mol)	NMR conversion M_w (g/mol)	NMR conversion (%)	GPC M_w (g/mol)	GPC Đ	Diffusion coefficient (m²·s⁻¹) – acetone-D6	Diffusion coefficient (m²·s⁻¹) – chloroform-D
pMMA25	2630	2630	89	2660	1.16	5.59E-10	2.95E-10
pMMA45	4910	4910	90	3920	1.16	4.3E-10	2.19E-10
pMMA65	7010	7010	88	5750	1.03	3.61E-10	1.91E-10
pMMA25-pPEGMEA25	10600	11990	78	13400	1.27	2.67E-10	1.36E-10
pMMA25-pPEGMEA50	23000	17970	71	20400	1.45	1.88E-10	1.16E-10
pMMA25-pPEGMEA75	45400	22910	65	42500	1.76	1.48E-10	1.03E-10
pMMA45-pPEGMEA25	18000	15350	87	19500	1.60	2.21E-10	1.18E-10
pMMA45-pPEGMEA50	34500	21760	78	35200	1.74	1.65E-10	9.56E-11
pMMA45-pPEGMEA75	68400	31120	84	69400	1.79	1.28E-10	8.07E-11
pMMA65-pPEGMEA25	31500	17570	88	35800	1.62	1.69E-10	9.83E-11
pMMA65-pPEGMEA50	91100	25370	85	72100	1.79	1.20E-10	8.48E-11
pMMA65-pPEGMEA75	135000	35400	91	105000	2.01	9.91E-11	6.69E-11

Figure S5: SEC chromatograms for pMMA45 homopolymer and its chain extensions as an example of the performed block extensions.
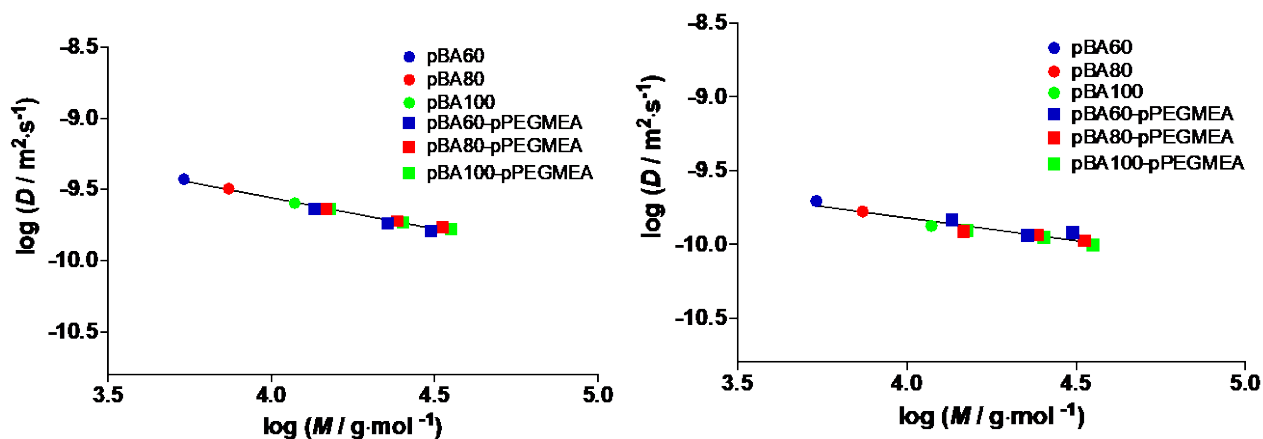
pBA-b-pPEGMEA calibration

Figure S6: Joint DOSY calibration for pBA homopolymers and pBA-b-pPEGMEA block copolymers in acetone-d6 (left) and CDCl$_3$ (right).

Table S5: MALLS, DOSY and NMR results pBA homopolymers and pBA-b-pPEGMEA block copolymers.

| Sample	MALLS M_w (g/mol)	NMR conversion M_w (g/mol)	NMR conversion (%)	Diffusion coefficient (m^2·s^{-1}) – acetone-D6	Diffusion coefficient (m^2·s^{-1}) – chloroform-D
pBA60	5400	7040	87	3.74E-10	1.96E-10
pBA80	7400	8760	82	3.21E-10	1.67E-10
pBA100	11800	11890	90	2.54E-10	1.33E-10
pBA60-pPEGMEA25	13600	8960	16	2.32E-10	1.46E-10
pBA60-pPEGMEA50	22700	10710	17	1.83E-10	1.15E-10
pBA60-pPEGMEA75	30900	12030	16	1.61E-10	1.2E-10
pBA80-pPEGMEA25	14700	12360	30	2.31E-10	1.22E-10
pBA80-pPEGMEA50	24300	15240	30	1.90E-10	1.16E-10
pBA80-pPEGMEA75	33400	19050	33	1.72E-10	1.06E-10
pBA100-pPEGMEA25	15100	17290	45	2.33E-10	1.24E-10
pBA100-pPEGMEA50	25400	25490	63	1.85E-10	1.11E-10
pBA100-pPEGMEA75	35500	31850	64	1.66E-10	9.88E-11

pBA homopolymer calibration
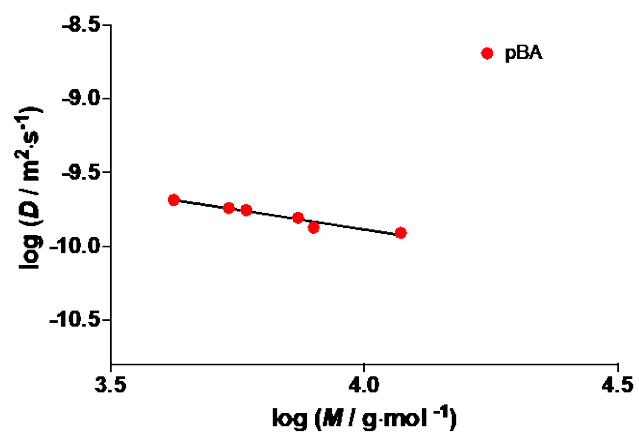
Figure S7: DOSY molecular weight calibration for RAFT-made pBA homopolymers in benzene-d6.
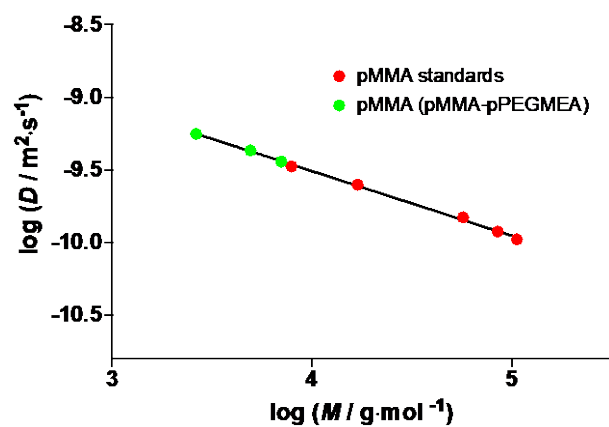
pMMA homopolymer calibration

Figure S8: DOSY molecular weight calibration for RAFT-made pMMA homopolymers (indicated in green, later used for chain extension) and commercial pMMA standards in deuterated acetone.

References

1. Ferguson, C.J., et al., Ab Initio Emulsion Polymerization by RAFT-Controlled Self-Assembly. Macromolecules, 2005. 38(6): p. 2191-2204.
2. Arrabal-Campos, F.M., P. Oña-Burgos, and I. Fernández, Molecular weight prediction with no dependence on solvent viscosity. A quantitative pulse field gradient diffusion NMR approach. Polymer Chemistry, 2016. 7(26): p. 4326-4329.