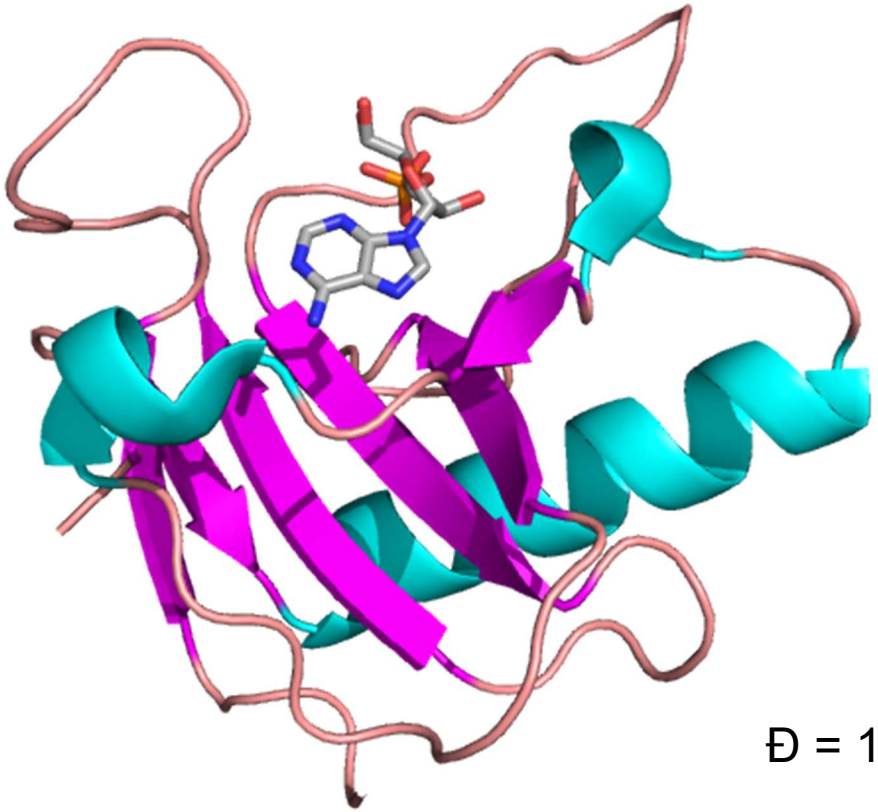
Controlling Dispersity

Questions

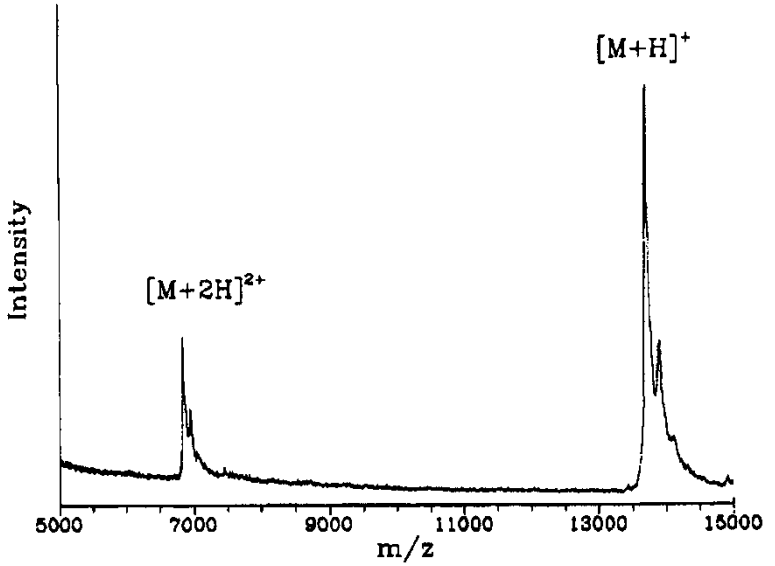
- Is dispersity alone sufficient as single parameter to describe the width of a molecular weight distribution ?
- Is narrower always better ?
- How can we control dispersity ?

The Quest for One

Proteins: Perfect control of chain length and sequence



Đ = 1.0



(Anal. Chem. **1990**, 62, 1836)

Ribonuclease A: molecular weight = 13 690,29 gr/mol
124 amino acids (degree of polymerization = 124)

Synthetic Polymers are Mixtures!

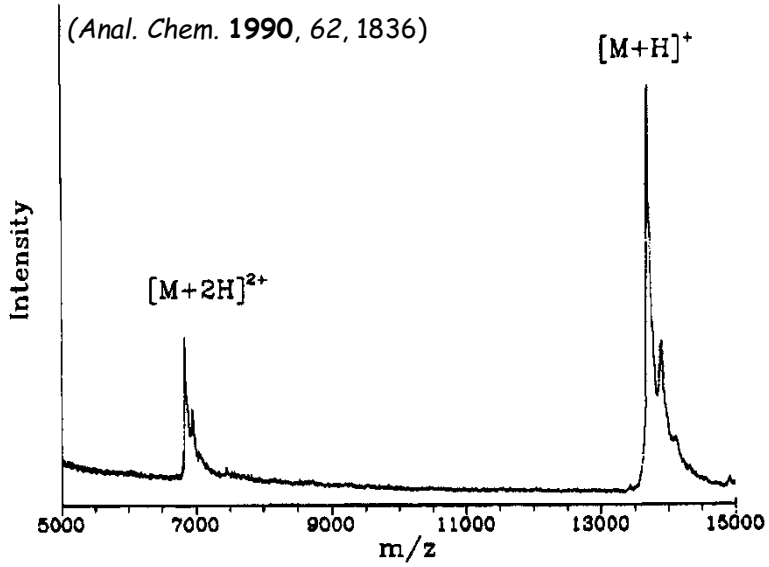
- Due to statistical variations in the polymerization process, polymers even in their purest form, are usually mixtures of molecules of different molecular weights
- Both the average molecular weight and the molecular weight distribution are needed to fully characterize a polymer

---

MALDI TOF mass spectra of a natural polymer (protein) vs. that of a synthetic polymer

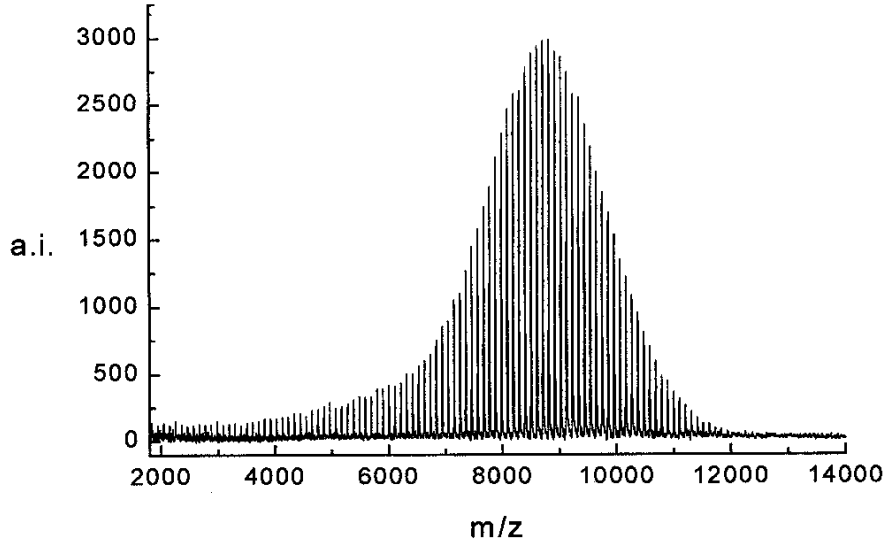
Ribonuclease A:

(Anal. Chem. **1990**, *62*, 1836)



Polystyrene (M_n = 9000 Da):

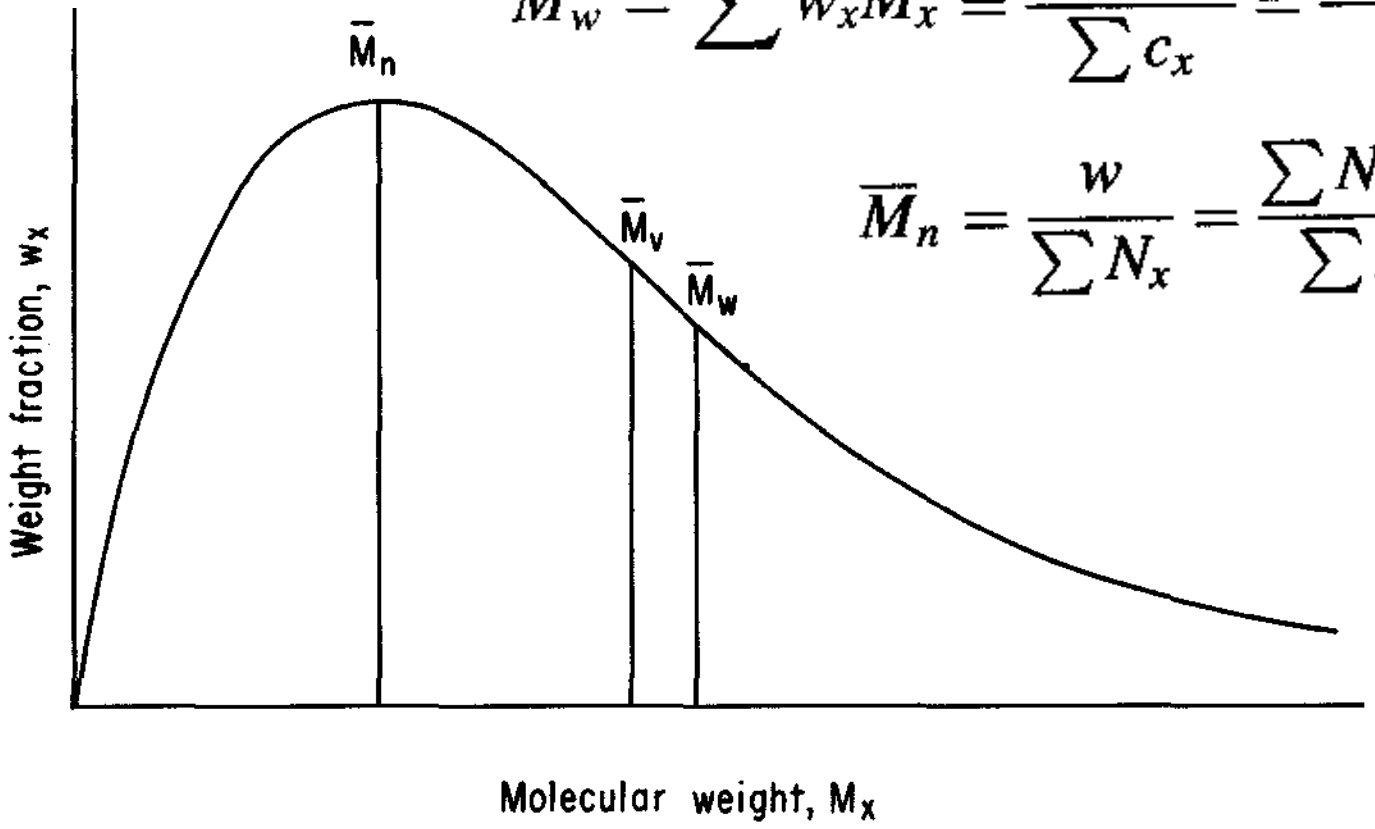
(Acta Polymer. **1998**, *49*, 272)



Polymer Molecular Weight

$$\overline{M}_w = \sum w_x M_x = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

$$\overline{M}_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x} = \sum \underline{N}_x M_x$$



- M_n is biased towards the low molecular weight fraction
- M_w is biased towards the higher molecular weight fraction
- M_w/M_n (= Đ = *dispersity*) depends on the breadth of the distribution curve and is used as a measure of chain length heterogeneity

Beyond Dispersity

Asymmetry factor (A_s), skewness (α_3), kurtosis (α_4)

The asymmetry factors (A_s) of our MWDs were calculated using the ECOSEC Analysis program. A_s is defined as the ratio of the distance from the peak maximum to the right edge of the peak and the distance from the peak maximum to the left edge of the peak at 10 % peak height. A graphical description is provided in figure S1.

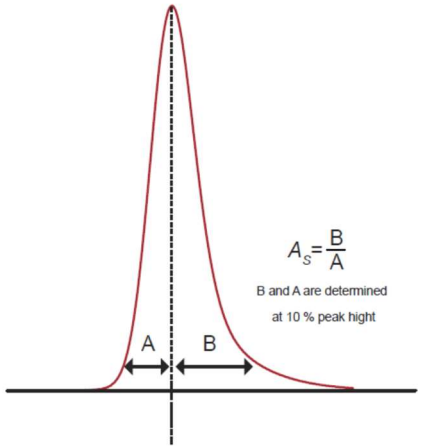


Figure S1. Graphical Illustration of the Calculation of Asymmetry Factor A_S

The third and fourth moments about the mean, skewness (α_3) and kurtosis (α_4), respectively, were calculated according to the method described by Rudin.[1] The equations are shown below.

$$\alpha_3 = \frac{M_z M_w M_n - 3M_n^2 M_w + 2M_n^3}{(M_w M_n - M_n^2)^{3/2}}$$

$$\alpha_4 = \frac{M_{z+1} M_z M_w M_n - 4M_n^2 M_z M_w + 6M_n^3 M_w - 3M_n^4}{(M_w M_n - M_n^2)^2}$$

α_3 is positive if the distribution is skewed toward high molecular weights, zero if it is symmetrical about the mean and negative if it is skewed to low molecular weights.

ACS Macro Lett. **2016**, 5, 7, 796–800
https://doi.org/10.1021/acsmacrolett.6b00392

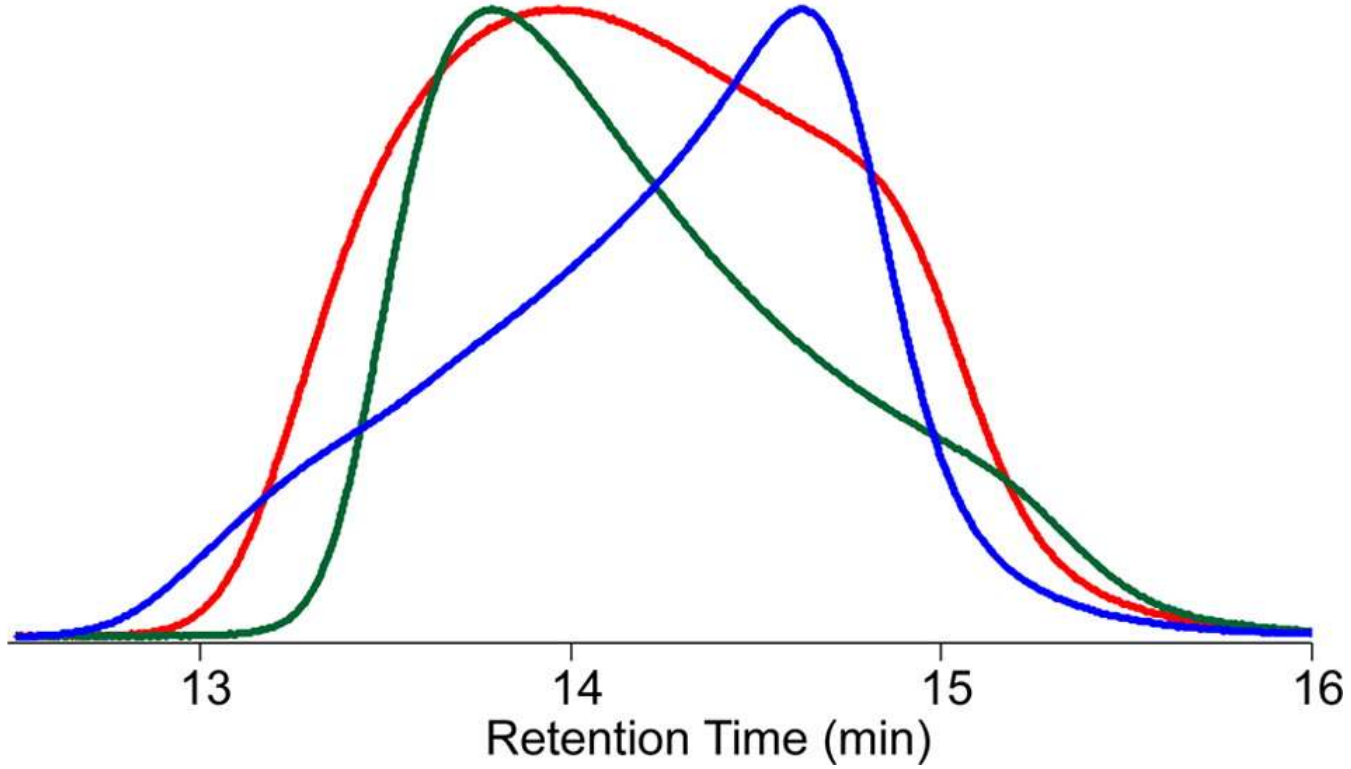
Asymmetry factors *(A_s) > 1 describe polymer MWDs tailing into low molecular weights, A_s < 1 describes polymer MWDs tailing into high molecular weights; A_s = 1 indicates a symmetric distribution.*

MWDs can be further described by going beyond Mn and Đ values to the third (skewness, α3) and fourth (kurtosis, α4) moments of the distribution function. ***Skewness*** *describes the symmetry of the curve, whereas* ***kurtosis*** *indicates the amount of tailing on either side of the MWD around Mp.*

See also: Rudin, A. *J. Chem. Educ.* **1969**, *46*, 595

Beyond Dispersity

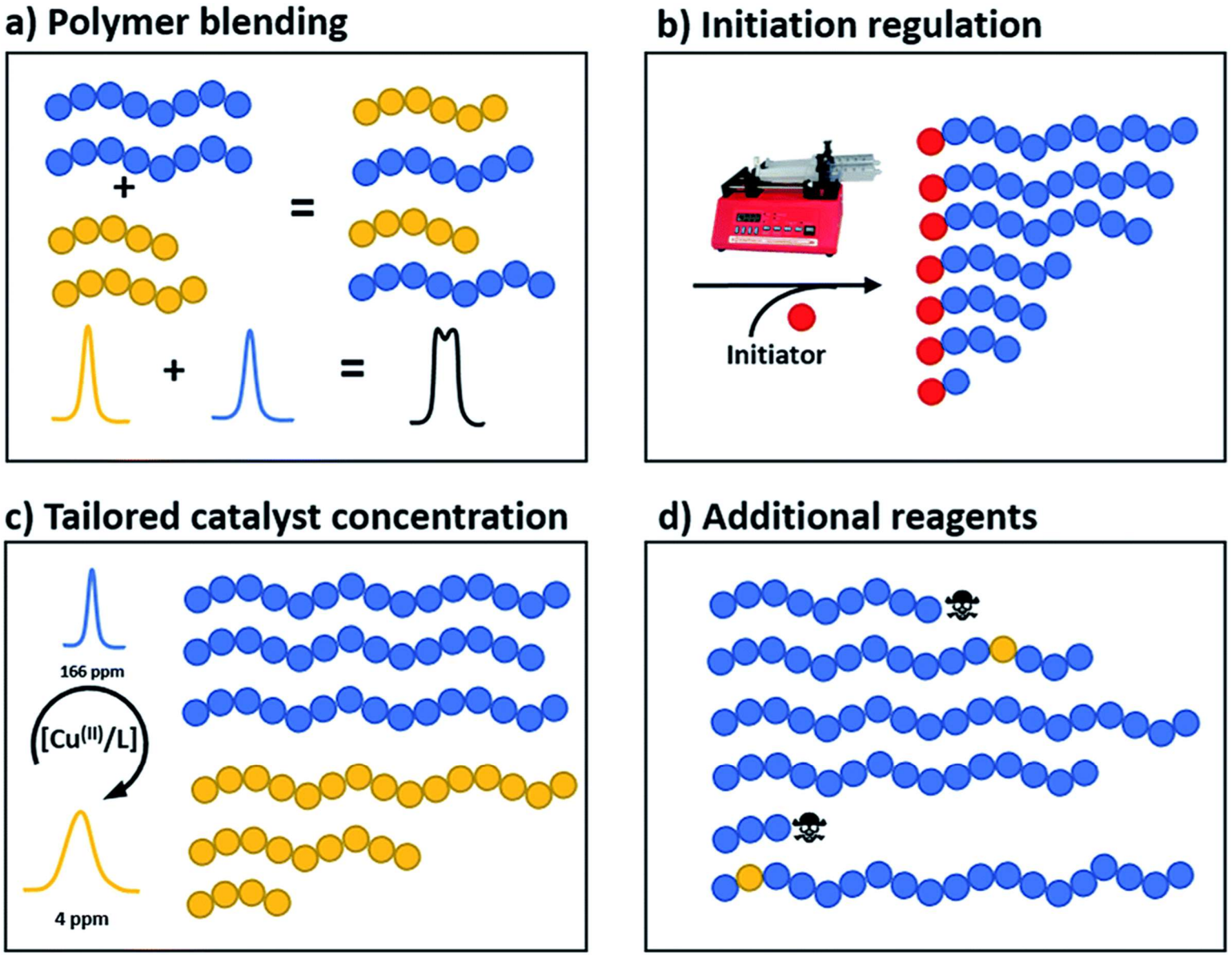
Addition Time (min)	Addition Type	M_n (kg/mol)	$Đ$	A_s	α_3	α_4
40	Constant	14.3	1.40	3.58	0.94	3.27
40	Linear Ramp	14.7	1.43	1.57	1.54	5.59
60	Exponential Ramp	14.1	1.43	0.34	2.52	11.93



ACS Macro Lett. **2016**, *5*, 796–800

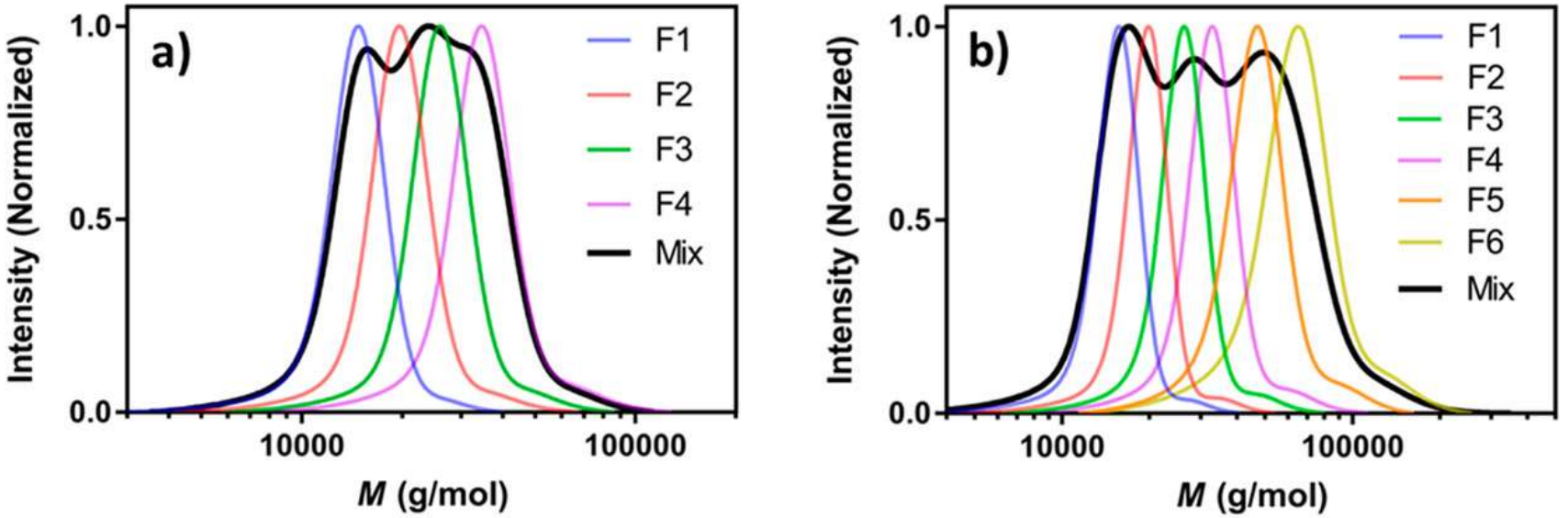
https://doi.org/10.1021/acsmacrolett.6b00392

Strategies to Control Dispersity



Chem. Sci., 2019, **10**, 8724-8734 https://doi.org/10.1039/C9SC03546J

Polymer Blending



c)

#[a]	Fraction	α (%)[b]	M_p (kg/mol)[c]	M_n (kg/mol)[c]	Đ[c]	Skewness[d]	Kurtosis[d]	FWQM/ FWTQM[e]
1	1	92.5	14.8	13.9	1.07	0.137	5.886	2.34
2	2	94.8	19.6	18.6	1.08	1.075	7.979	2.34
3	3	94.8	26.0	24.6	1.08	0.949	6.829	2.35
4	4	95.2	34.6	32.3	1.10	1.190	7.921	2.38
5	Tailored MWD 1	-	23.9	20.3	1.21	1.472	6.518	1.51
6	Tailored MWD 2	-	17.0	24.6	1.44	2.326	12.72	1.55

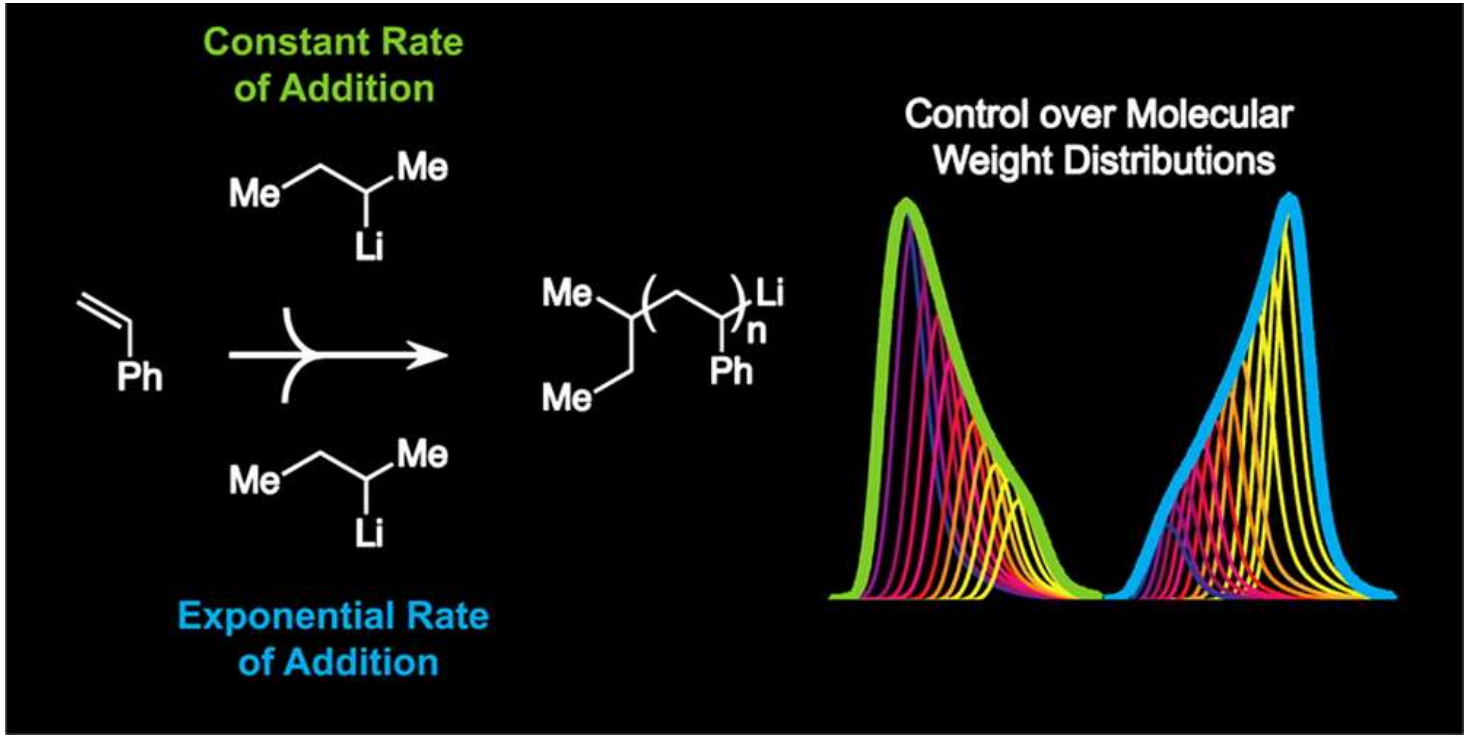
Macromolecules **2018**, *51*, 4553–4563

Initiation Regulation

Anionic Polymerization(*)

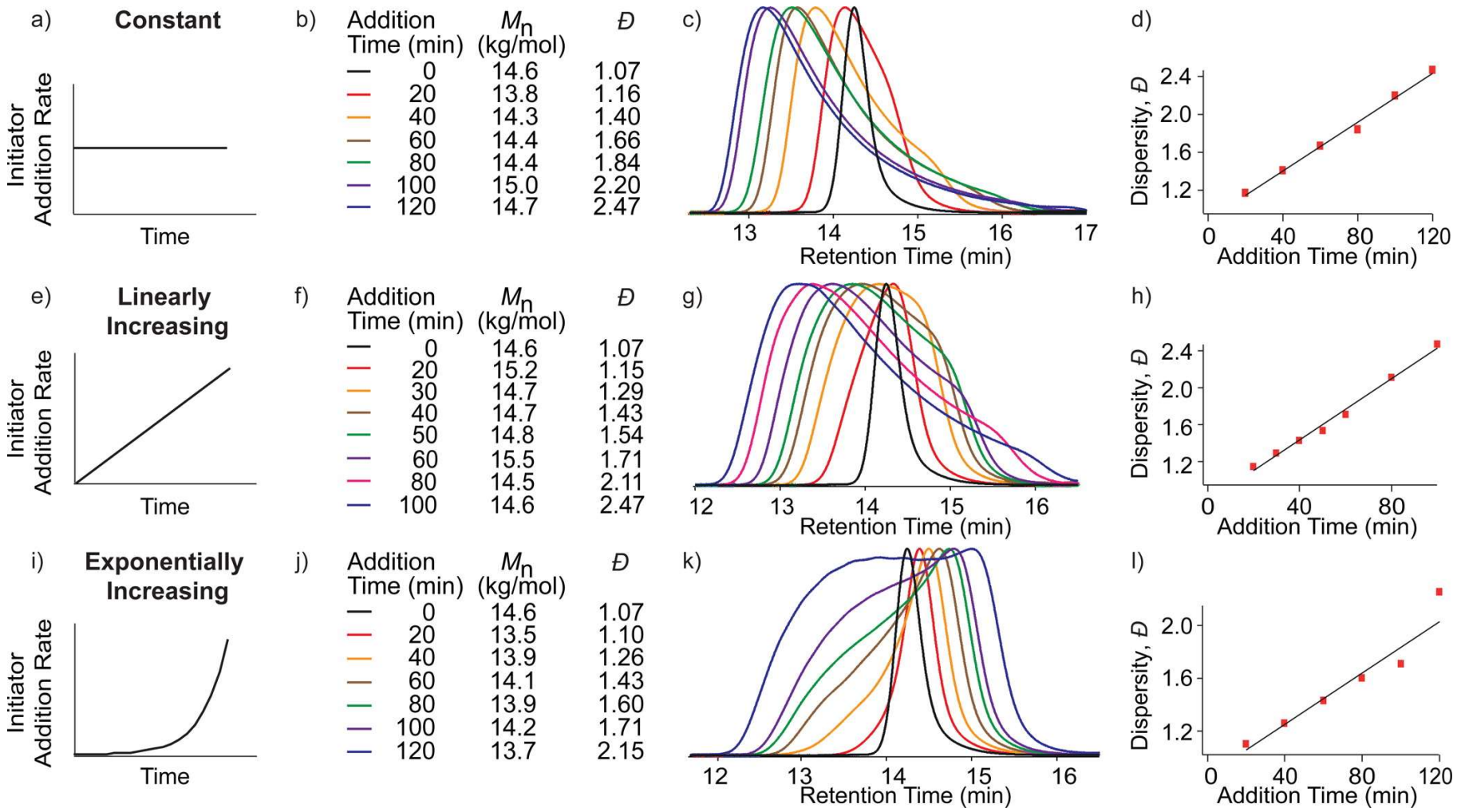
- **Normally: all initiator is added at once**
- **All chains start to growth at the same time -> narrow dispersity polymers**

(*) will be discussed in more detail later, see "*ionic chain polymerization*"



ACS Macro Lett. **2016**, *5*, 796–800
https://doi.org/10.1021/acsmacrolett.6b00392

Initiation Regulation



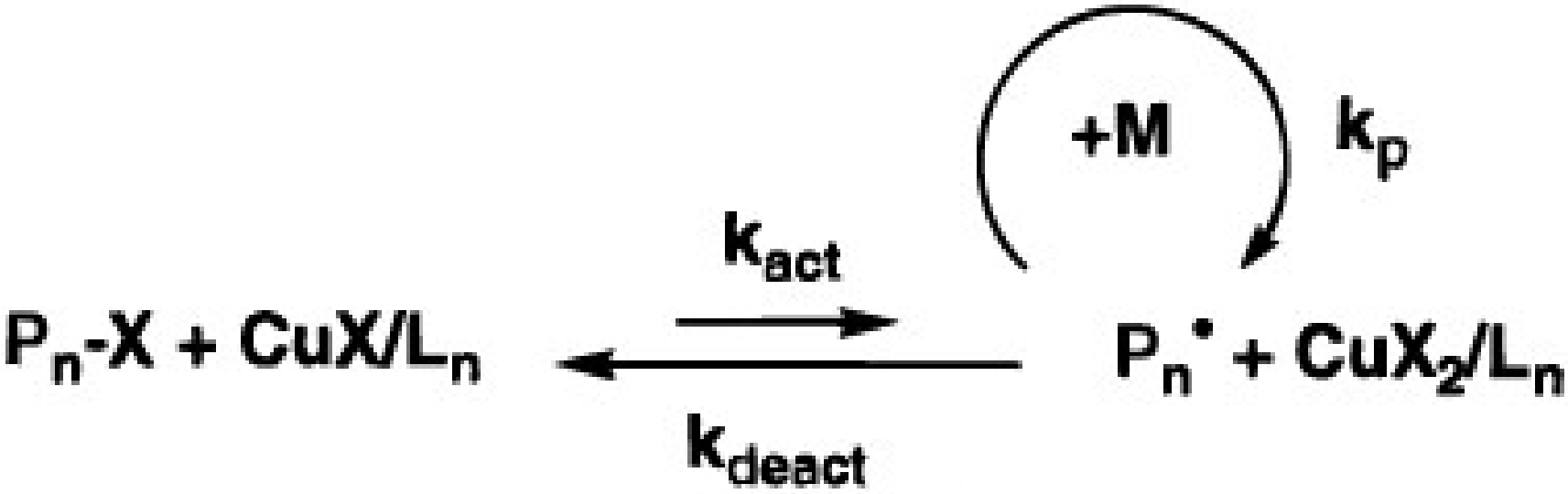
ACS Macro Lett. **2016**, *5*, 796–800
https://doi.org/10.1021/acsmacrolett.6b00392

Tailored Catalyst Concentration

Controlled / "living" radical polymerization

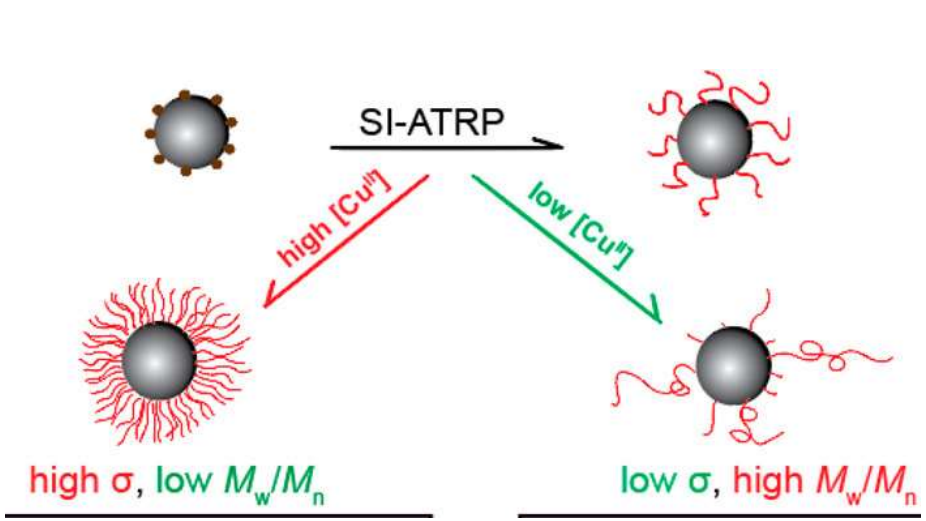
- **Atom transfer radical polymerization (ATRP)**

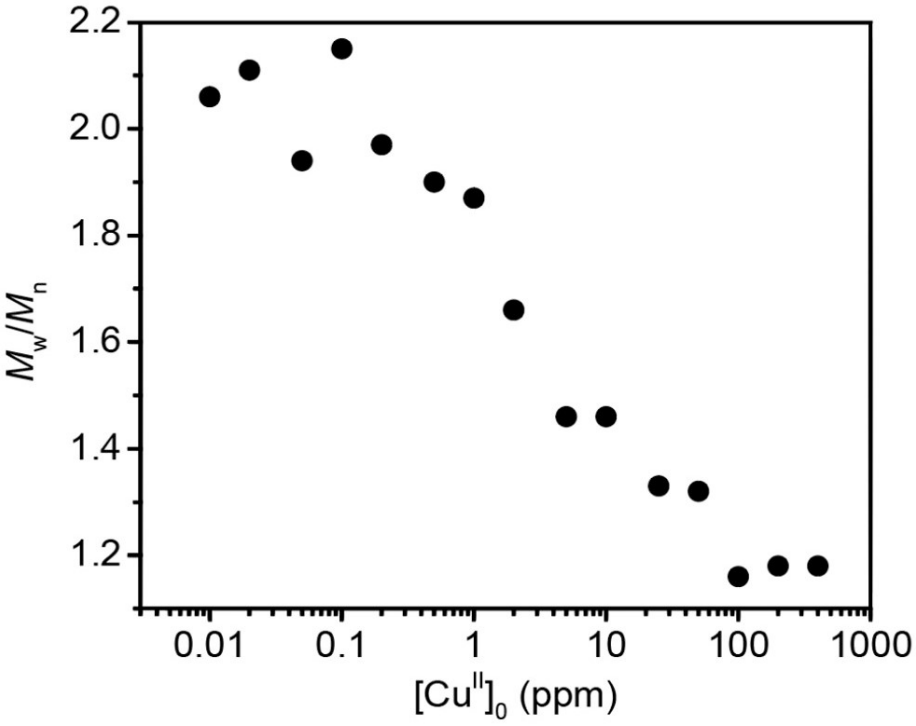
(*) will be discussed in more detail later, see "*controlled free radical polymerization*"



ACS Macro Lett. **2019**, *8*, 859–864
https://doi.org/10.1021/acsmacrolett.9b00405

Tailored Catalyst Concentration in ATRP





ACS Macro Lett. **2019**, *8*, 859–864
https://doi.org/10.1021/acsmacrolett.9b00405

Additional Reagents

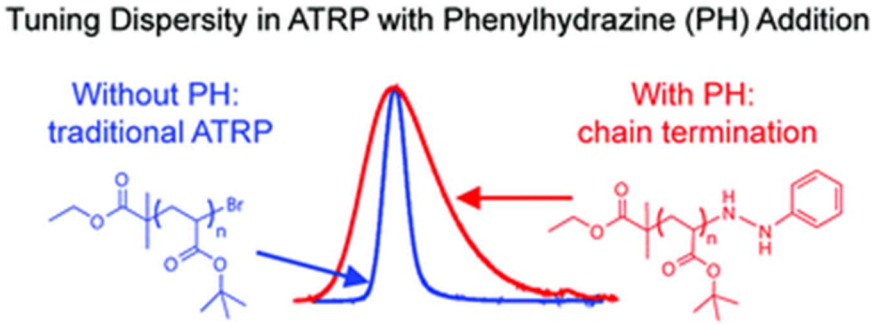
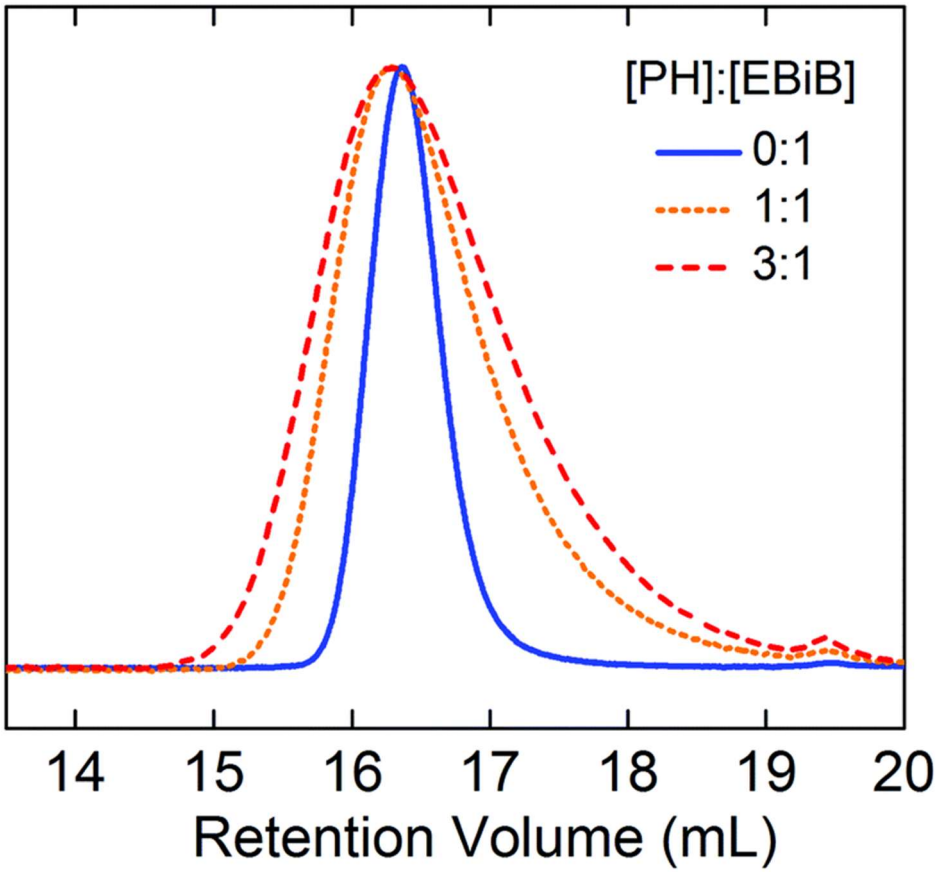
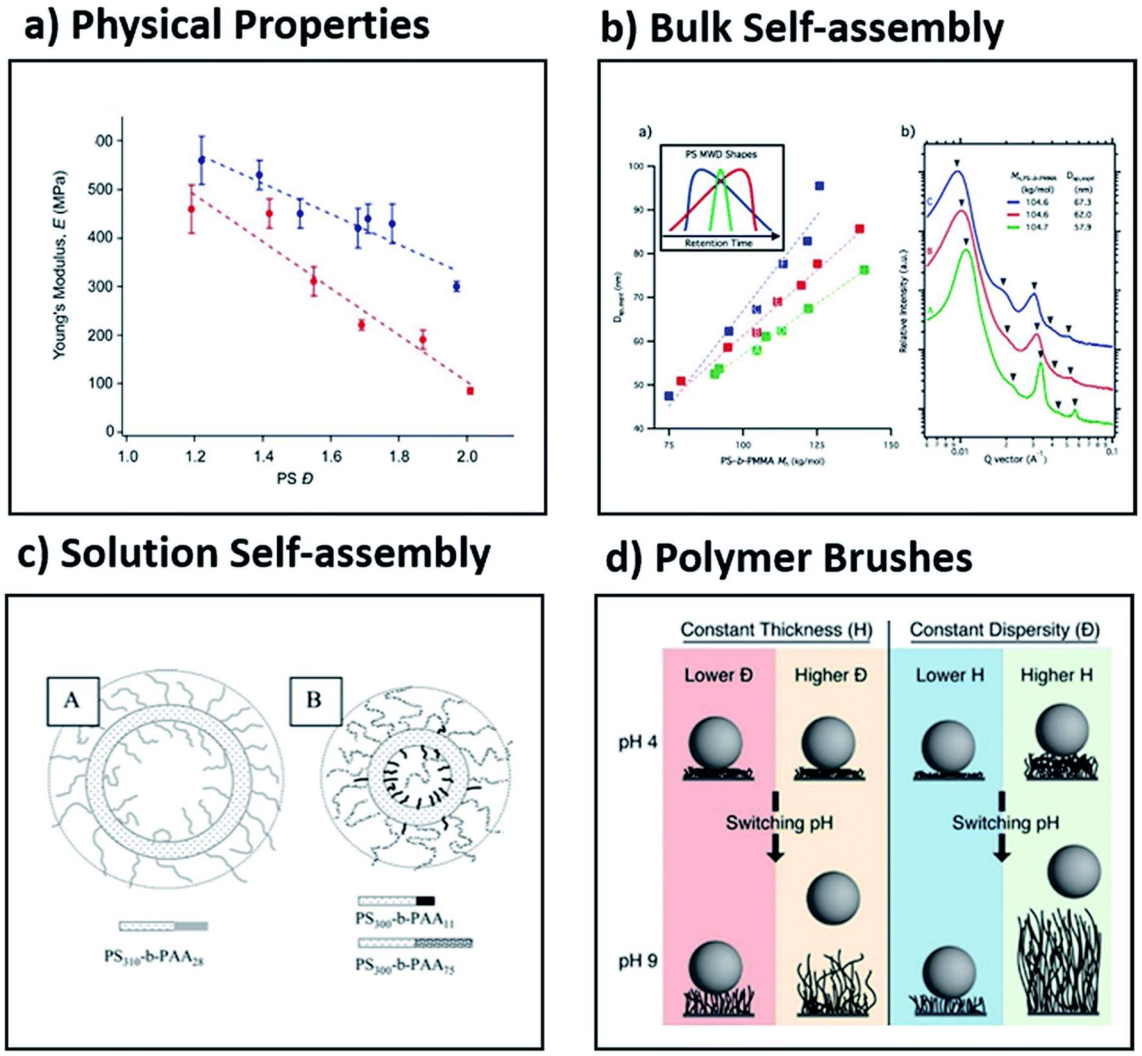


Fig. 2 Variation in molecular weight distribution (shown as GPC traces) with phenyl hydrazine content for three polymers of similar M_n. The following reaction conditions were used: [EBiB] : [CuBr] : [PMDETA] : [*t*BA] = 1 : 1 : 1 : 120, 50 °C, DMF. [PH] : [EBiB] = 0 : 1 (blue solid curve, $Đ$ = 1.07, $M_{n,NMR}$ = 6.2 kg mol^{-1}, 40 min reaction time); 1 : 1 (orange dotted curve, $Đ$ = 1.47, $M_{n,NMR}$ = 5.8 kg mol^{-1}, 8 min reaction time); 3 : 1 (red dashed curve, $Đ$ = 1.71, $M_{n,NMR}$ = 6.5 kg mol^{-1}, 120 min reaction time).



DOI: 10.1039/C8PY00033F
Polym. Chem., 2018, **9**, 4332-4342

Impact of Dispersity on Structure & Properties



Examples of the effect of dispersity on four different application areas, namely (a) the Young's modulus as determined by dynamic mechanical analysis, (b) the effect of skew on self-assembly in bulk, (c) the formation of vesicles in solution and (d) the release of adherent bacteria by polymer brushes. This figure is adapted from ref. 56, 59, 108 and 116 with permission from ACS publications.

Chem. Sci., 2019, **10**, 8724-8734 https://doi.org/10.1039/C9SC03546J

Diblock Copolymer Phase Behavior

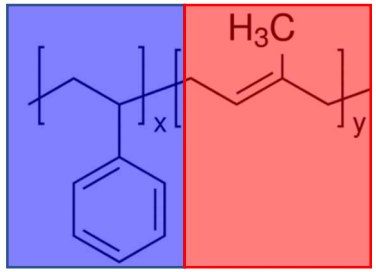
Table 1. Molecular Characteristics of PI–PS Diblock Copolymers

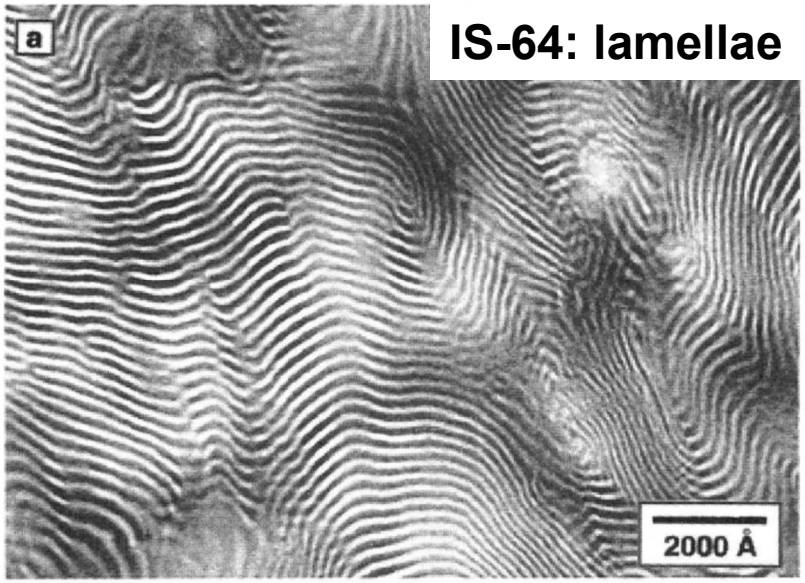
sample	f_{PI}	$10^{-4}M_n$	phase transitions[a,b]
IS-24[c]	0.24_2	5.44	$C \xrightarrow{293} E \xrightarrow{309} Dis$
IS-54[d]	0.54_0	1.70	$A \xrightarrow{124} Dis$
IS-63	0.62_6	3.46	$A \xrightarrow{247} Dis$
IS-64	0.64_2	3.98	$A \xrightarrow{267} Dis$
IS-65	0.65_1	3.95	$A \xrightarrow{190} D \xrightarrow{221} B \xrightarrow{279} Dis$
IS-66	0.66_4	3.97	$A \xrightarrow{159} D \xrightarrow{210} B \xrightarrow{268} Dis$
IS-68	0.67_5	3.99	$A \xrightarrow{134} D \xrightarrow{198} B \xrightarrow{252} C \xrightarrow{267} Dis$
IS-69	0.69_2	3.98	$B \xrightarrow{166} C \xrightarrow{265} Dis$
IS-70	0.70_4	3.47	$C \xrightarrow{177} Dis$
IS-82	0.82_0	7.91	$C \xrightarrow{300} Dis$

Macromolecules **1995,** *28,* 8796–8806

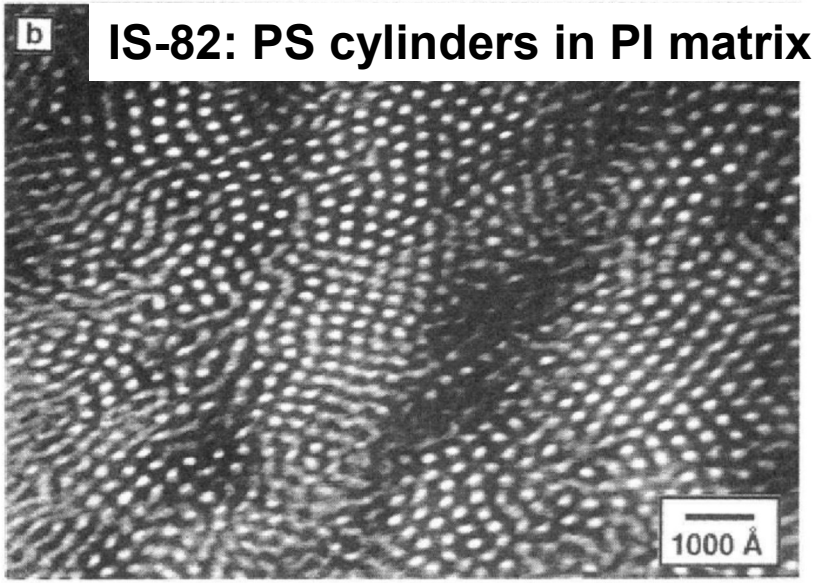
Polyisoprene–Polystyrene Diblock Copolymer Phase Diagram near the Order–Disorder Transition

ABSTRACT: The phase behavior of ten polyisoprene–polystyrene (PI–PS) diblock copolymers, spanning the composition range from 0.24 to 0.82 polyisoprene volume fraction (f_{PI}), has been studied near the order–disorder transition (ODT). Dynamic mechanical spectroscopy, transmission electron microscopy, and neutron and X-ray scattering have been used to characterize phase transition temperatures and ordered state symmetries. Five distinct microstructures were observed for this chemical system: spheres, hexagonally packed cylinders (HEX), lamellae (LAM), hexagonally perforated layers (HPL), and a bicontinuous cubic phase having an $Ia\bar{3}d$ space group symmetry. The bicontinuous $Ia\bar{3}d$ phase only occurs in the vicinity of the ODT between the HEX and LAM states at compositions of $0.65 \lesssim f_{PI} \lesssim 0.68$ and $0.36 \lesssim f_{PI} \lesssim 0.39$ (prior report). Farther from the ODT, within these composition ranges, the HPL phase occurs. We did not find the ordered bicontinuous double diamond (OBDD) morphology at any composition or temperature studied, and the overall phase diagram is qualitatively different from those reported previously for PI–PS block copolymers.





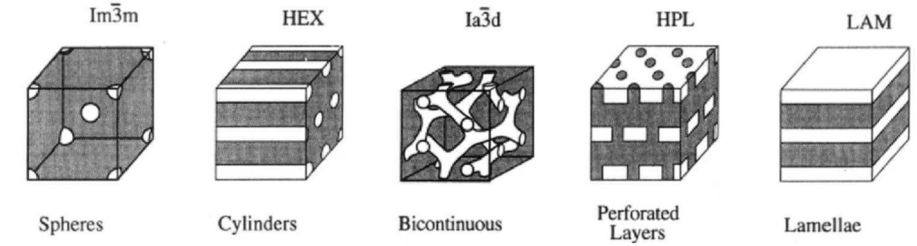
IS-64: lamellae



IS-82: PS cylinders in PI matrix

Compare the length scale of the phase separated structures with those observed in polymer blends

Experimental PS-PI Diblock Copolymer «Phase Diagram»



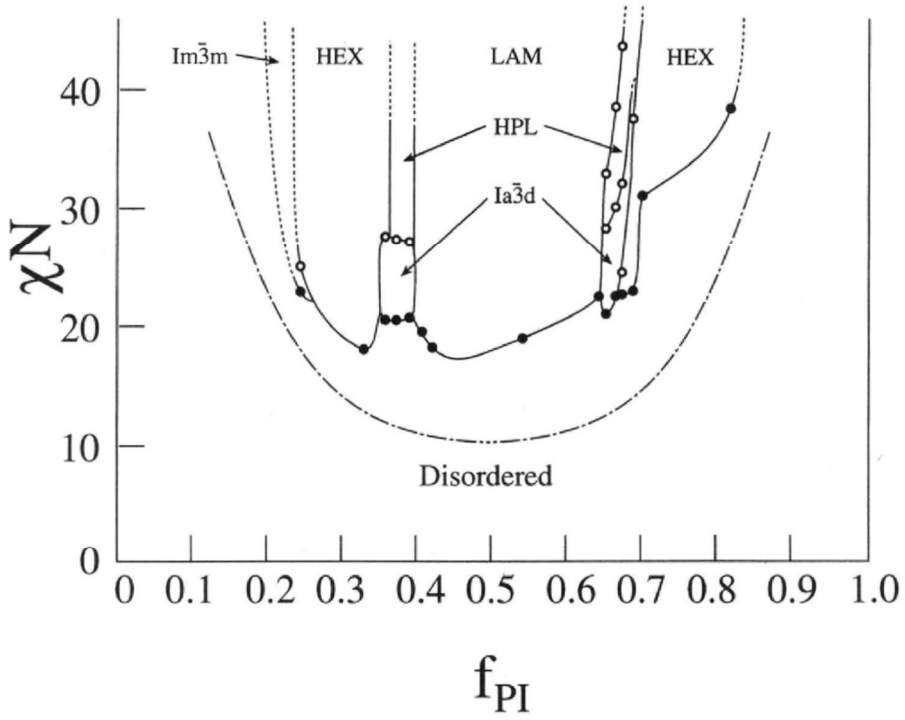


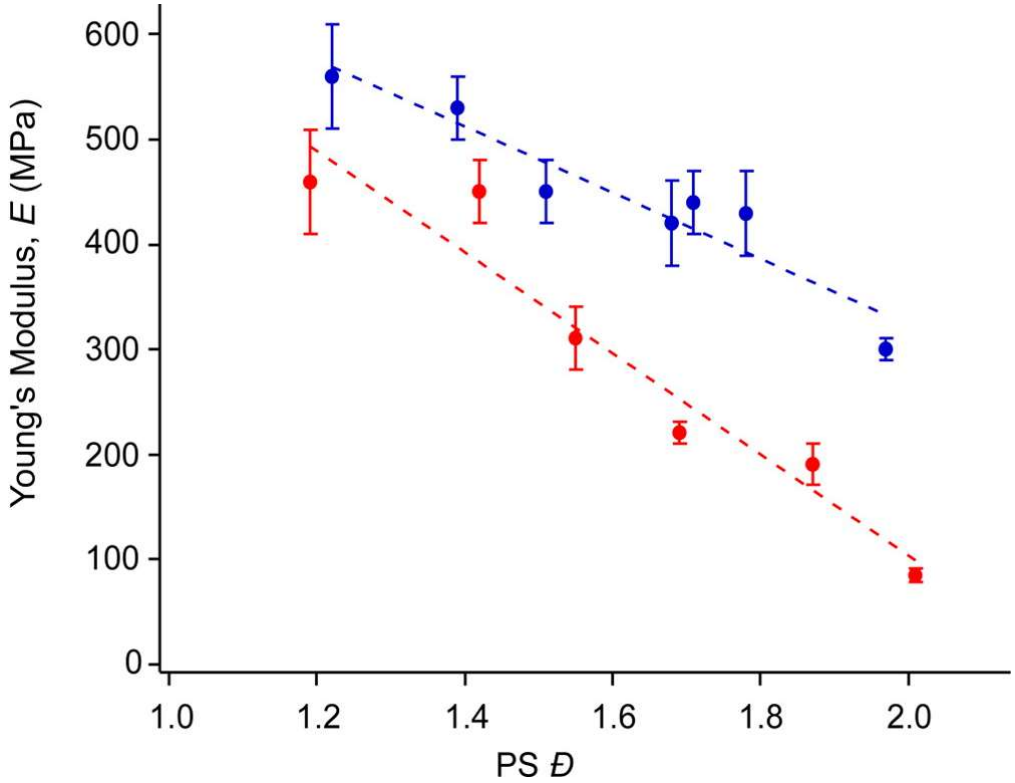
Figure 13. χN versus f_{PI} diagram for PI–PS diblock copolymers. Open and filled circles represent the order–order (OOT) and order–disorder (ODT) transitions, respectively, calculated using eq 1 and the rheologically determined transition temperatures (see Table 1). The dash–dot curve is the mean field prediction[5] for the ODT. Solid curves have been drawn to delineate the different phases observed but might not correspond to precise phase boundaries. Five different ordered microstructures (shown schematically) have been observed by us for this chemical system.

Diblock copolymers would like to phase separate in the same way as oil – water mixtures and polymer blends. Due to the fact that the two blocks are chemically linked together, phase separation, however, occurs at much smaller length scales

Dispersity Effects on Physical Properties

Young's moduli of poly(styrene-*block*-isoprene) block copolymers

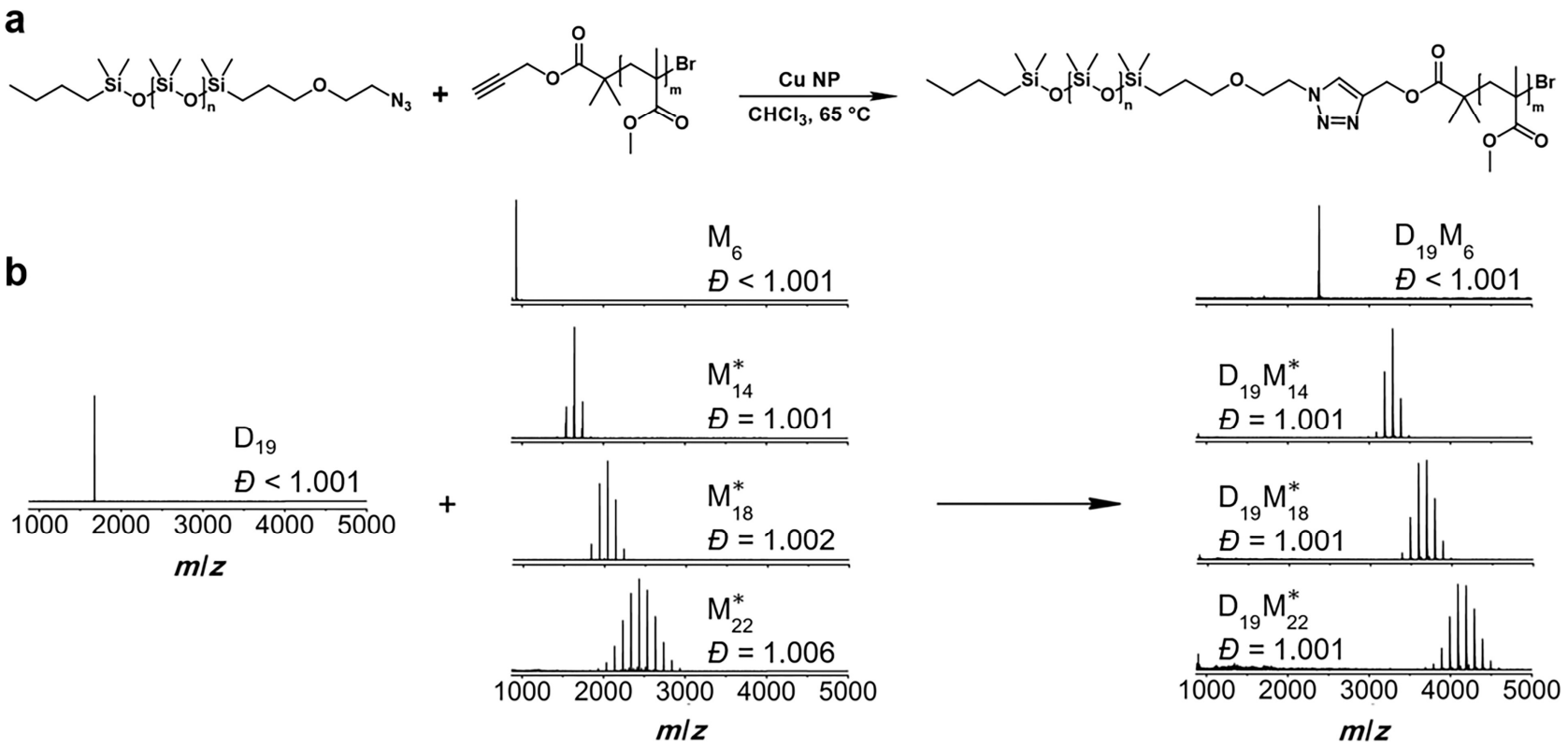
Entry	M_n (S) (kg/mol)	$Đ$ (S)	A_s	M_n (SI) (kg/mol)	$Đ$ (SI)	E (MPa)
1a	14.1	1.19	1.85	35.6	1.14	460
1b	14.2	1.22	0.52	35.1	1.16	560
2a	14.9	1.42	3.52	36.8	1.21	450
2b	14.1	1.39	0.37	33.6	1.22	530
3a	15.2	1.69	4.48	36.3	1.25	220
3b	14.1	1.71	0.31	36.5	1.28	440
4a	14.4	2.01	4.97	37.2	1.28	85
4b	13.8	1.97	0.26	34.4	1.29	300



Poly(styrene-*block*-isoprene) block copolymers with varying polystyrene (PS) MWD shapes and Young's moduli (E) determined with dynamic mechanical analysis. (b) Plot of PS $Đ$ vs E (MPa): blue circles indicate PS blocks with asymmetry factor (A_s) values of <1; red circles indicate PS blocks with A_s values of > 1; S = PS; SI = poly(styrene-*block*-isoprene). Each E value is an average of at least four measurements.

ACS Macro Lett. **2016**, *5*, 796–800 https://doi.org/10.1021/acsmacrolett.6b00392

Effects of Dispersity on Self-Assembly

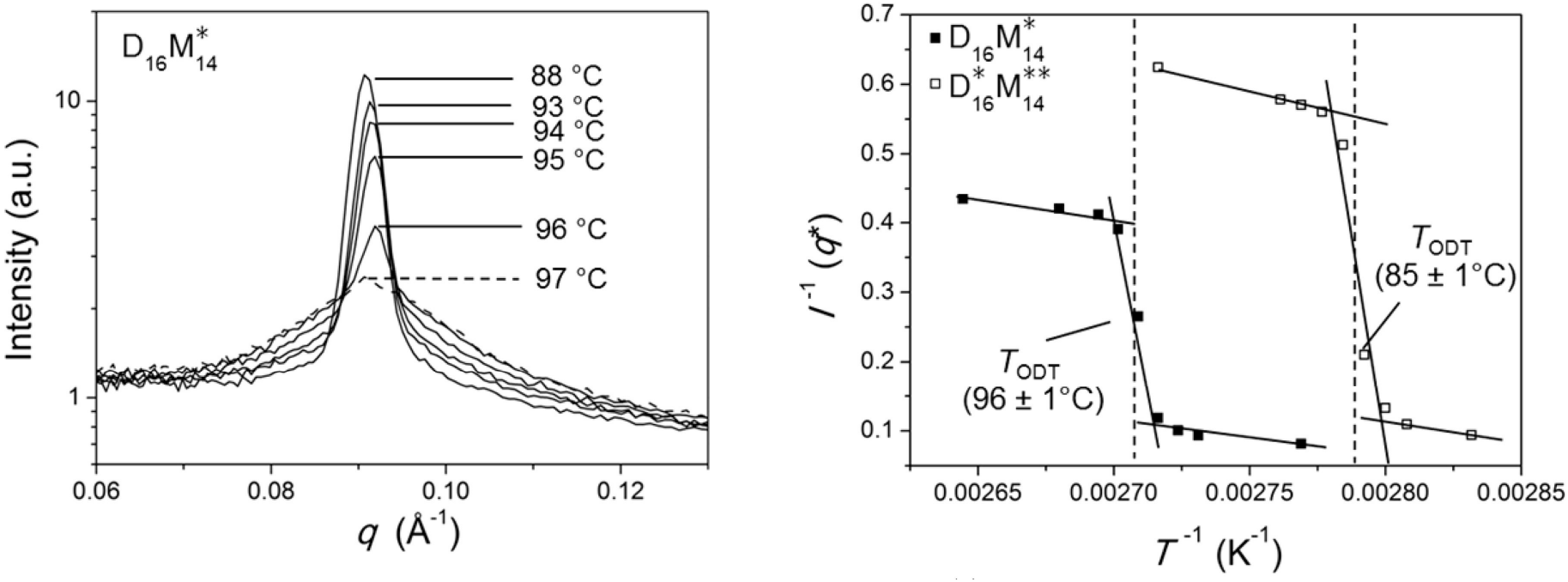


(a) Synthesis of block co-oligomers via click chemistry using α-alkynyl-oligoMMA (M) and ω-azido-oligoDMS (D) as building blocks. (b) Left: MALDI-MS analysis of discrete (no asterisk) and semidiscrete (*) oligomers obtained after chromatographic separation. Right: corresponding MALDI-MS data of the resulting block co-oligomers.

ACS Macro Lett. **2017**, *6*, 668–673 https://doi.org/10.1021/acsmacrolett.7b00262

For another related example: *ACS Macro Lett.* **2017**, *6*, 674–678 https://doi.org/10.1021/acsmacrolett.7b00266

Effects of Dispersity on Self-Assembly



Left: Temperature-dependent SAXS profiles of $D_{16}M_{14}^{*}$. Right: Inverse intensity at q^* as a function of inverse temperature for samples $D_{16}M_{14}^{*}$ and $D_{16}^{*}M_{14}^{**}$.

ACS Macro Lett. **2017**, *6*, 668–673 https://doi.org/10.1021/acsmacrolett.7b00262

Effects of Dispersity on Self-Assembly

Table 1. Summary of Oligo(DMS–MMA) Samples

entry	sample[a]	$M_{n,NMR}$[b]	$Đ_{D,MS}$[c]	$Đ_{M,MS}$[c]	f_D[d]	morphology[e]	d (nm)[e]	T_{ODT} (°C)[f]
				Disperse** Samples				
1	$D^{*}_{16}M^{**}_{14}$	3.0	1.031	1.132	0.51	ordered	7.4	85
2	$D_{16}M^{**}_{14}$	3.0	<1.001	1.132	0.51	lamellar	7.3	90
3	$D_{16}M^{**}_{19}$	3.5	<1.001	1.141	0.44	ordered	7.7	96
4	$D_{19}M^{**}_{14}$	3.2	<1.001	1.132	0.56	lamellar	7.9	99
5	$D_{19}M^{**}_{19}$	3.7	<1.001	1.141	0.48	lamellar	8.4	127
				Discrete and Semidiscrete* Samples				
6	$D_{10}M_{7}$	1.9	<1.001	<1.001	0.57	disordered	5.2	-
7	$D_{13}M^{*}_{12}$	2.6	<1.001	1.004	0.50	ordered	6.4	57
8	$D^{*}_{16}M^{*}_{14}$	3.0	1.031	1.001	0.51	lamellar	7.2	90
9	$D_{16}M^{*}_{14}$	3.0	<1.001	1.001	0.51	lamellar	7.1	96
10	$D_{16}M^{*}_{18}$	3.4	<1.001	1.002	0.45	lamellar	7.3	99
11	$D_{19}M_{6}$	2.4	<1.001	<1.001	0.75	disordered	6.0	-
12	$D_{19}M^{*}_{14}$	3.2	<1.001	1.001	0.56	lamellar	7.4	113
13	$D_{19}M^{*}_{18}$	3.6	<1.001	1.002	0.49	lamellar	7.6	129
14	$D_{19}M^{*}_{22}$	4.0	<1.001	1.006	0.45	lamellar	8.1	129

[a]Samples are referred to as D_XM_Y where "X" and "Y" specify the chemical degree of polymerization of the oligoDMS and oligoMMA blocks, respectively; dispersity is distinguished by no asterisk (discrete), * (semidiscrete), and ** (disperse). [b]Number-average molar mass reported in (kg/mol) from ^{1}H NMR end-group analysis. [c]Molar mass dispersity of each precursor determined with MALDI-MS. [d]Volume fraction of D based on reported homopolymer densities[22] at 140 °C (0.895 and 1.13 g/cm^3 for D and M, respectively) and ^{1}H NMR. [e]Determined from SAXS analysis performed at room temperature. [f]Order–disorder transition temperature determined from SAXS performed on heating.

DOI: 10.1021/acsmacrolett.7b00262
ACS Macro Lett. 2017, 6, 668–673

Learning Objectives

- Be familiar with the parameters asymmetry factor (As), skewness (α3) and kurtosis (α4) to describe molecular weight distributions.
- Be able to discuss different strategies to control dispersity.
- Understand the effects of dispersity on some materials properties of polymers.