Leibniz-Institut für Polymerforschung Dresden

Polymers in Solution

Dresden, 9th November 2022

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Bioactive and Responsive Polymers
Institute of Macromolecular Chemistry
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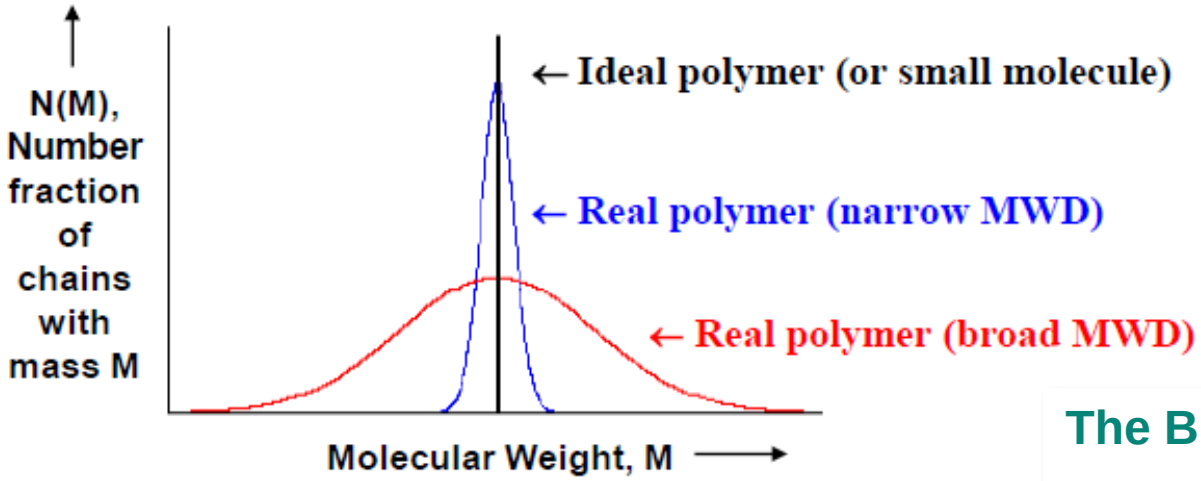
DRESDEN concept

Leibniz Gemeinschaft

4. The statistical character of macromolecules

1. Introduction



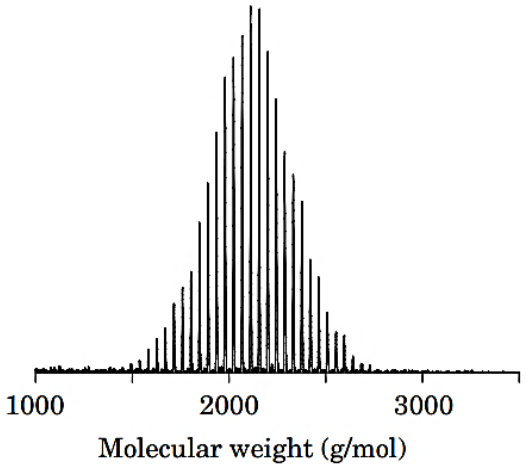


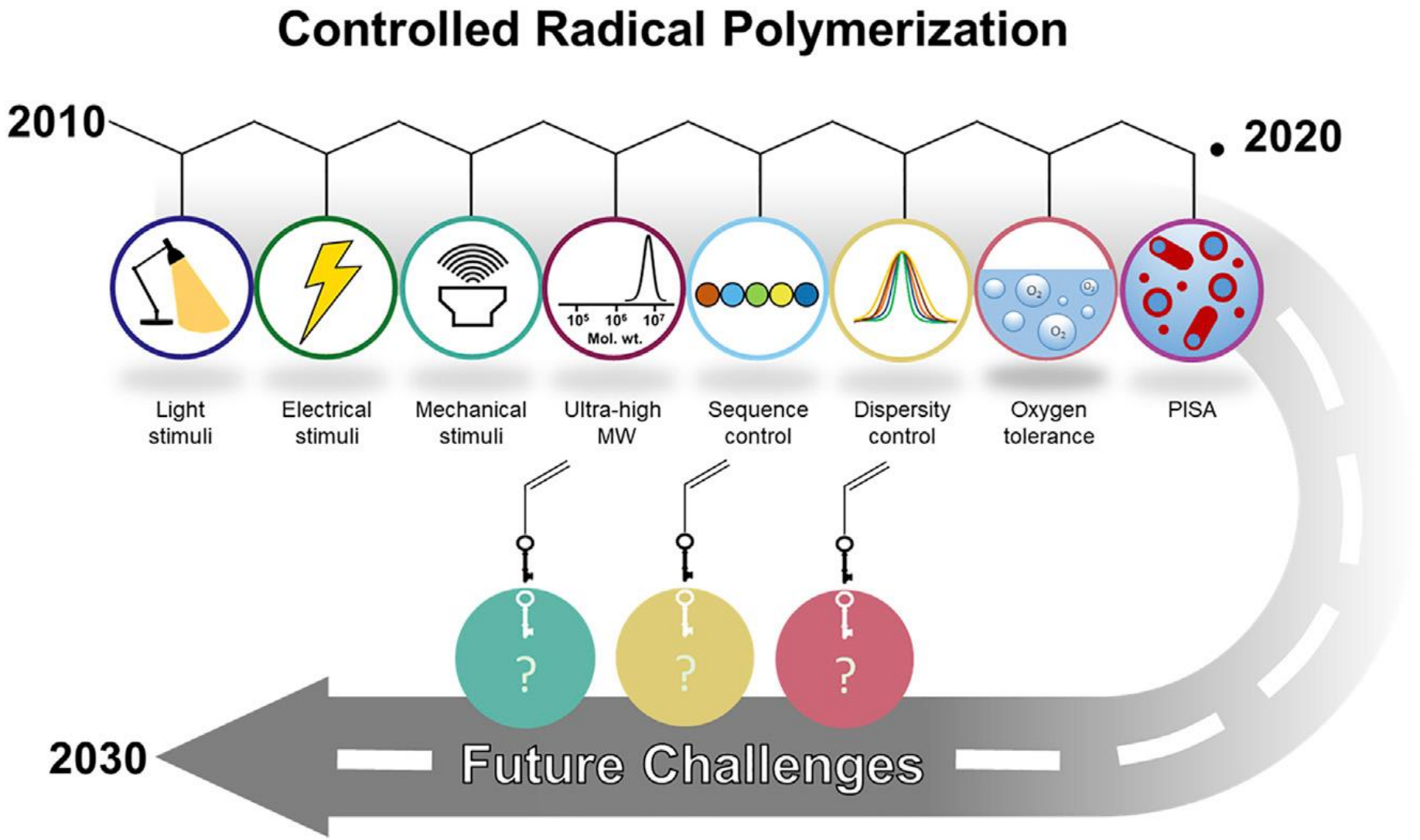
Figure 1.54. Example of a mass spectrum of a polymer obtained in MALDI-TOF mass spectrometry. Poly(ethylene glycol) of a nominal molecular weight of 2,000 g/mol is shown. (From Ref. 10.)

The Bigger Picture: Challenges and opportunities

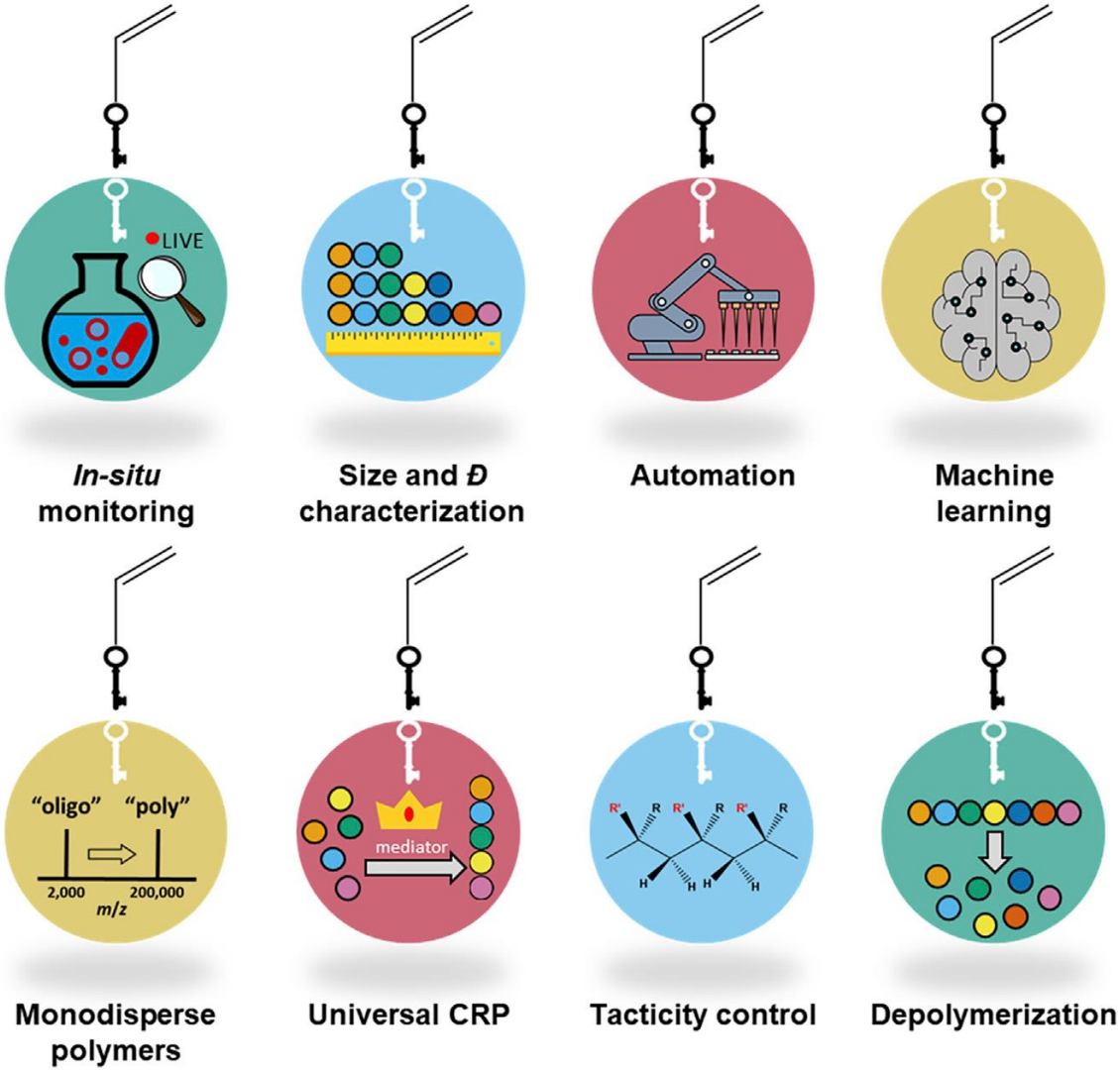
Universal catalysts compatible with a range of monomers and stimuli are urgently required to produce materials **with enhanced control over monomer sequence, dispersity,and tacticity**

New **depolymerization** and **degradations** for polymer recycling and bio-relevant applications should be the focus of future research

Advanced characterization methods, automation systems, and machine learning are currently undeveloped and could offer exciting new avenues



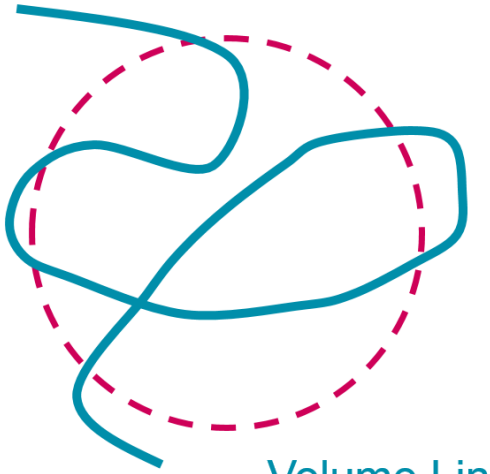
Chem, 1575–1588, July 9, 2020 2020 Elsevier Inc.1575



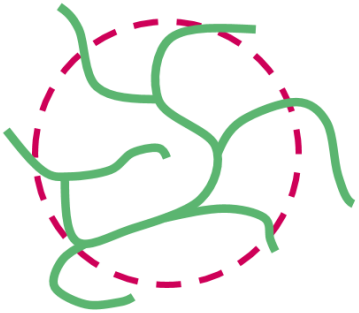
Chem, 1575–1588, July 9, 2020 2020 Elsevier Inc.1575

2. Polymers with different degree of branching

Linear Chain



Branched Chain

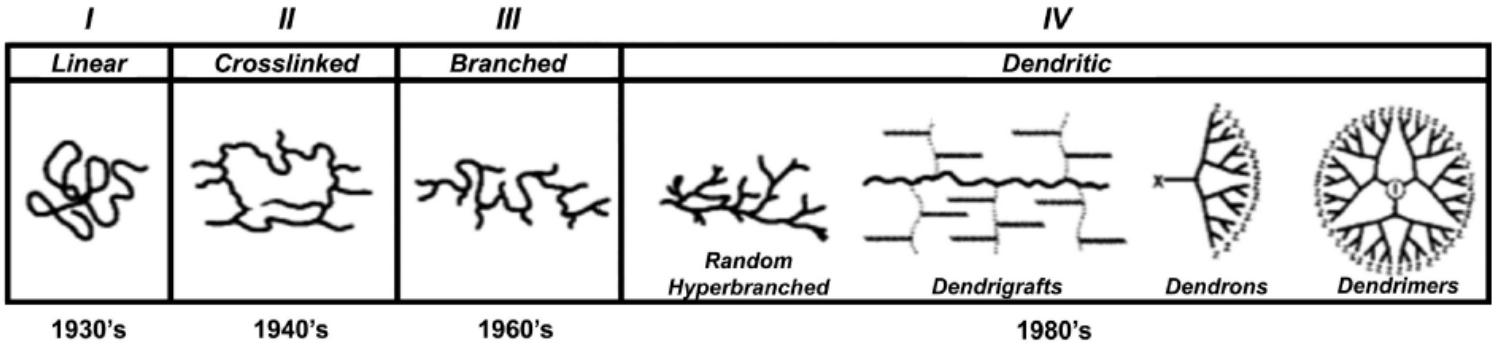


At Equal MW

Volume Linear > Volume Branched

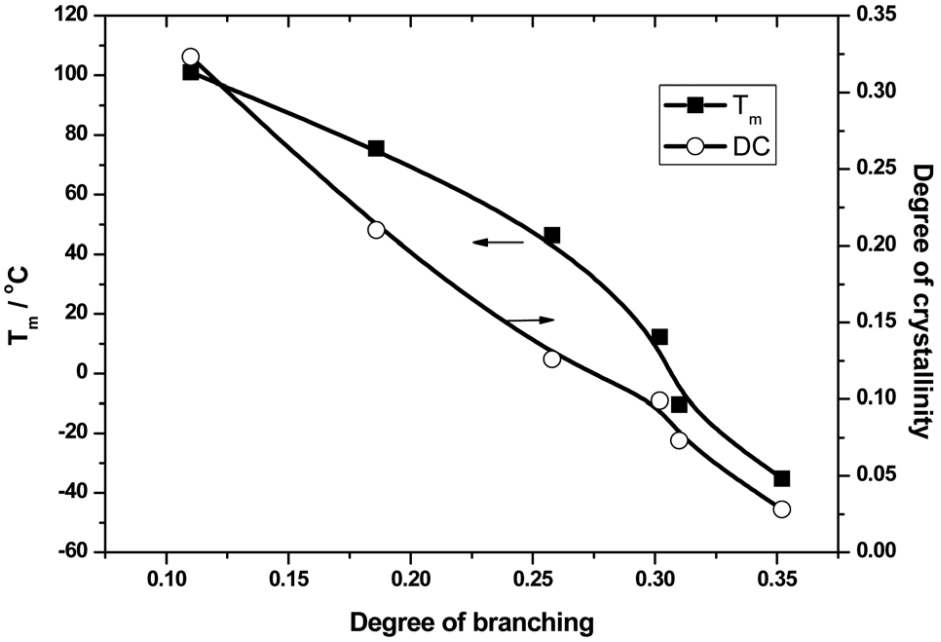
Molecular Density Linear < Molecular Density Branched

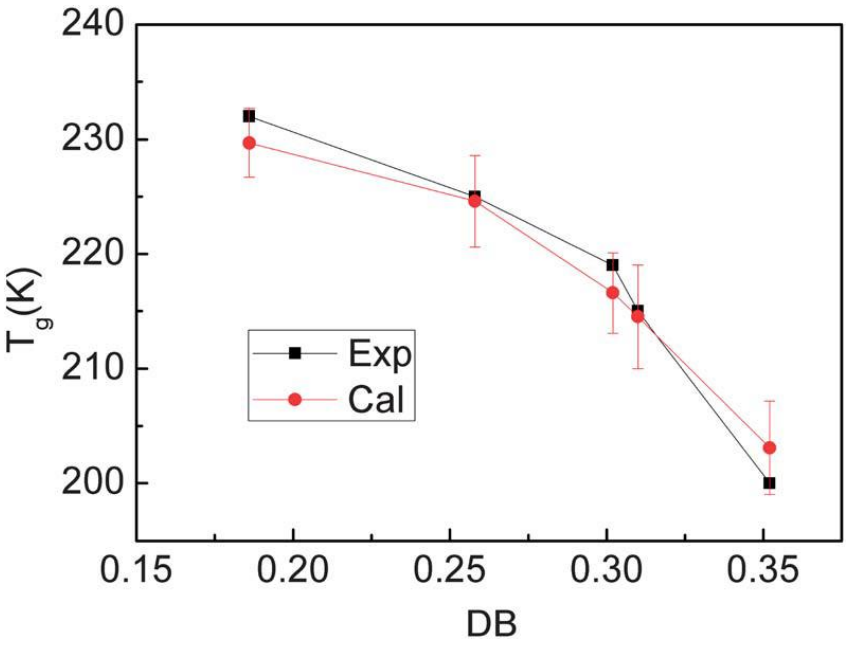
Intrinsic Viscosity Linear > Intrinsic Viscosity Branched



2. Polymers with different degree of branching

The relationship between the degree of branching and glass transition temperature of branched polyethylene:experiment and simulation



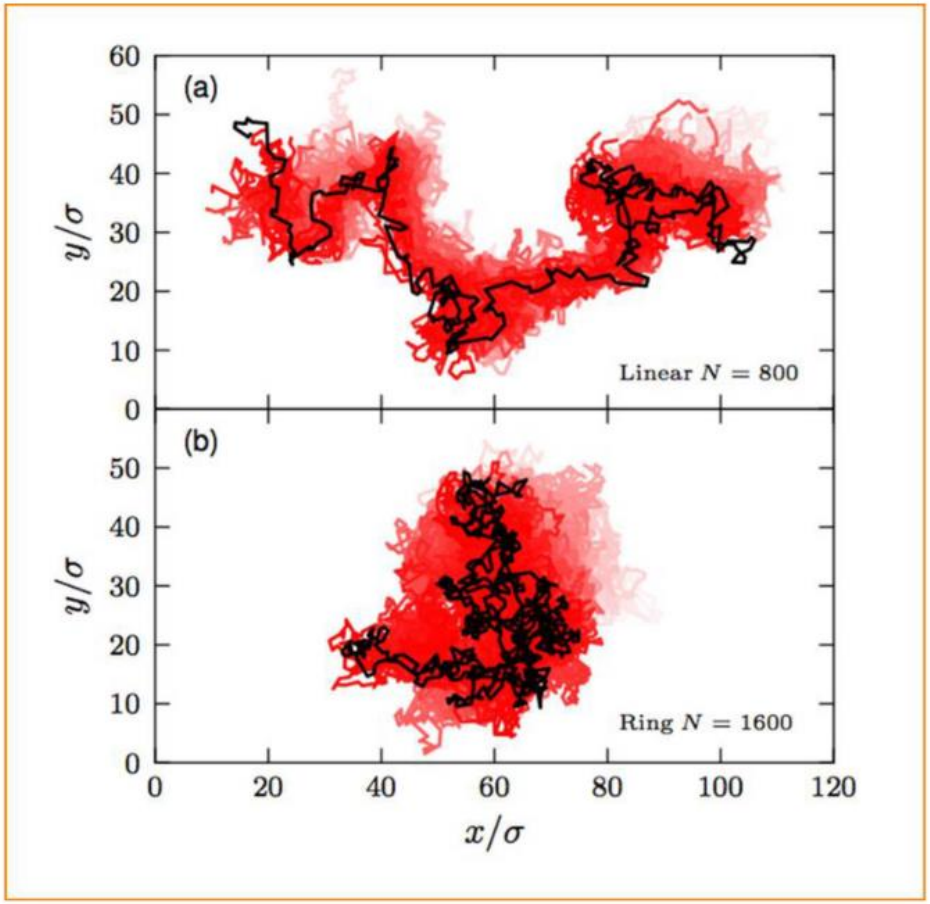


$$\mathrm{DB} = \frac{D + T}{D + T + L}$$

10.1039/c3py00896g

2. Polymers with different degree of branching

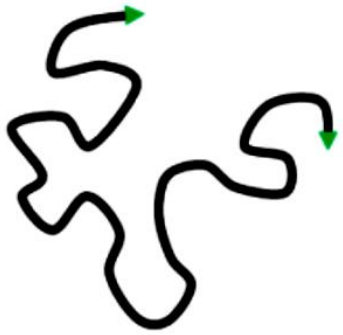
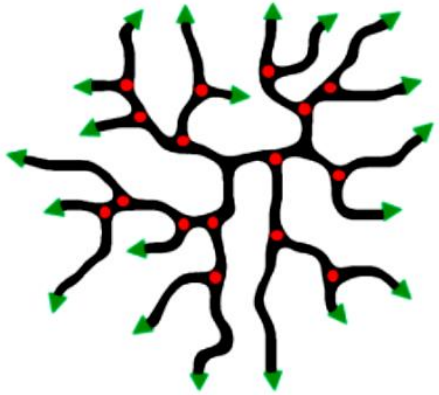
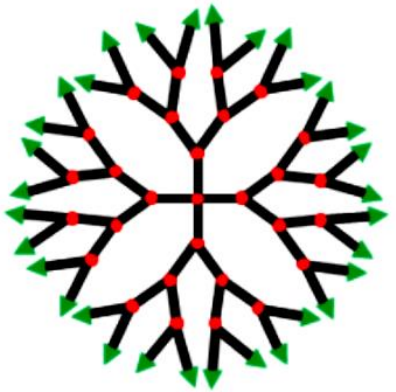
Polymer Topology Matters



- Linear chains move like a snake

- Rings move by an amoeba-like motion

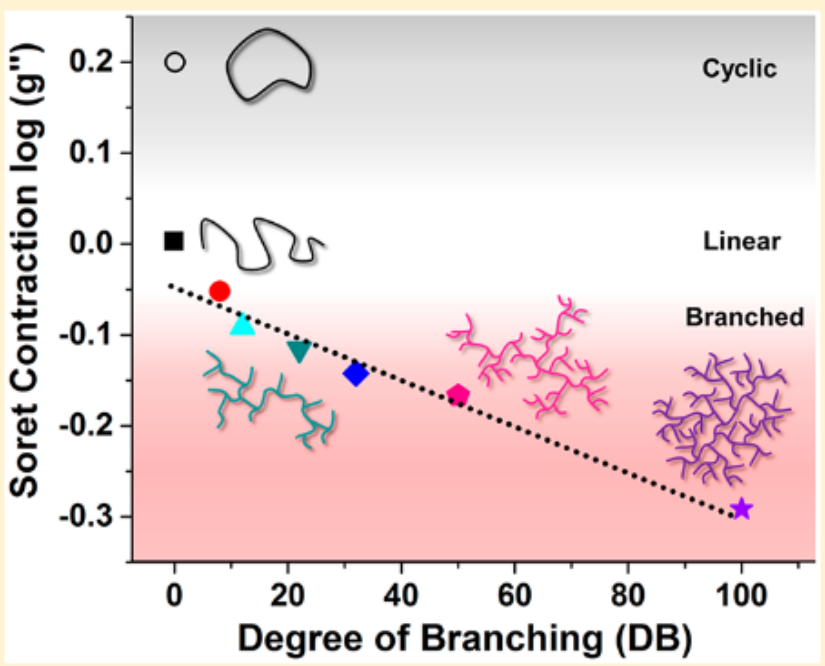
2. Polymers with different degree of branching

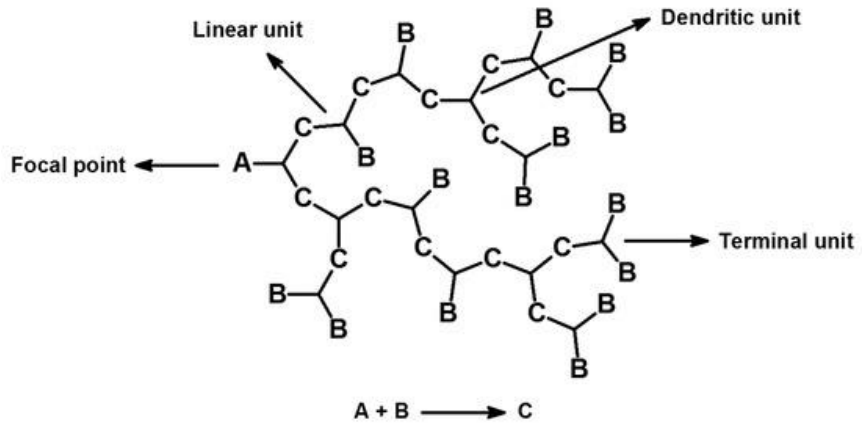
linear polymer	hyperbranched polymer	dendrimer
		
linear	three-dimensional, irregular	three-dimensional, regular
one-step synthesis	one-step synthesis	multi-step synthesis
easy purification by precipitation	easy purification by precipitation	purification by chromatography
easy scale-up	easy scale-up	difficult scale-up
dispersity (Đ) > 1.01	Đ > 1.1	Đ = 1.0
DB = 0	DB = 0.4-0.6	DB = 1.0
no cavity	presence of cavities	numerous cavities
2 end-groups	multiple end-groups	large number of end-groups
strong entanglements	weak entanglements	no entanglements
high viscosity	low viscosity	very low viscosity

Journal of Controlled Release, **2020**, 321, pp.285-311.
ff10.1016/j.jconrel.2020.02.019ff.

2. Polymers with different degree of branching

Thermal field-flow fractionation (ThFFF) was used to characterize the architecture of aromatic–aliphatic polyesters with varying degrees of branching





Thermophoretic force

$$S_T = D_T/D$$

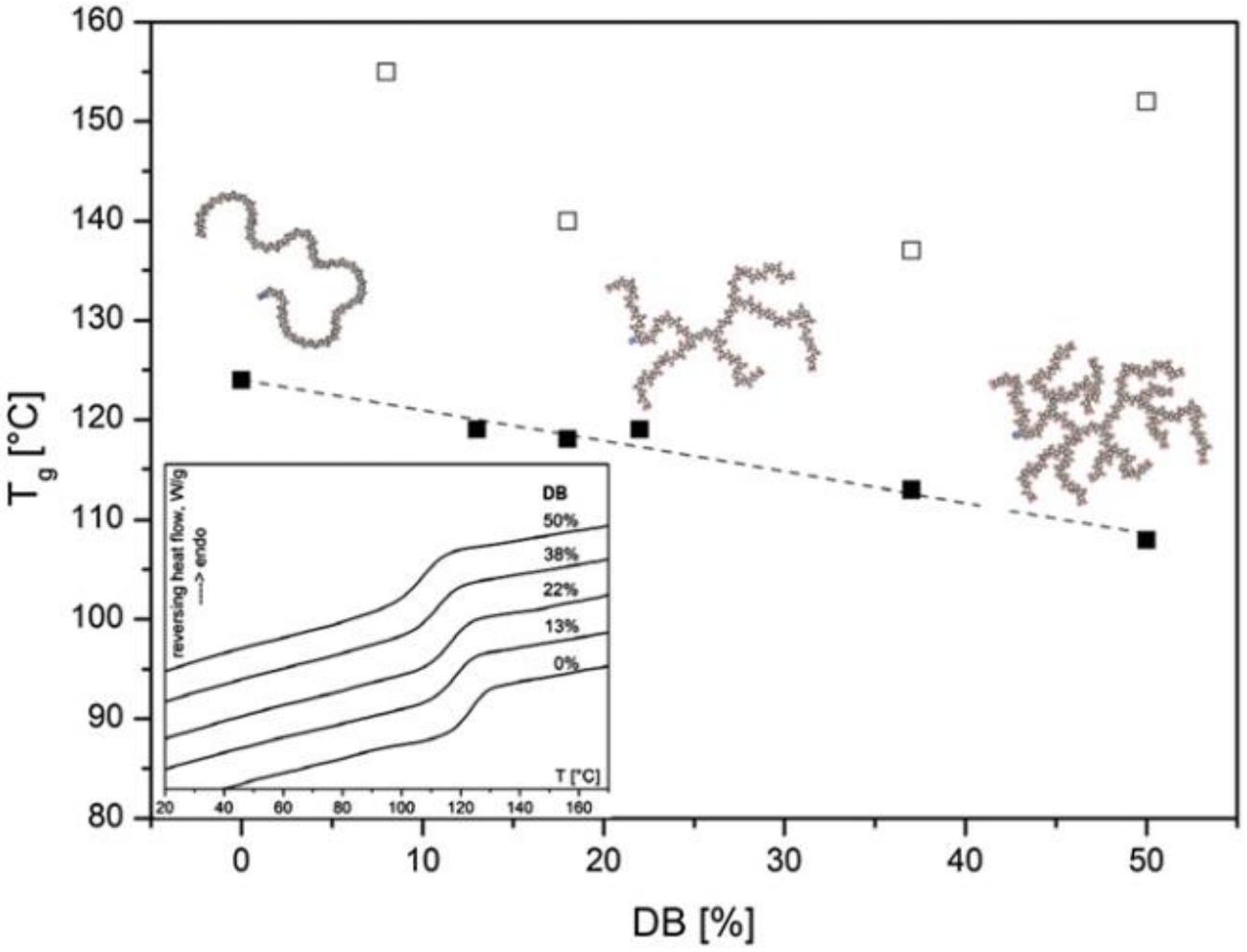
D, diffusion coefficient; $\mathbf{D_T}$ the thermodiffusion coefficient. The quotient of both coefficients is called **Soret coefficient (S_T).**

A **Soret contraction factor (g″)**, defined as the ratio of the ST of a branched polymer to the ST of a molecular weight equivalent linear analogue, is introduced **as a metric to indicate degree of branching (DB).**

Anal. Chem. **2019**, 91, 19, 12344–12351

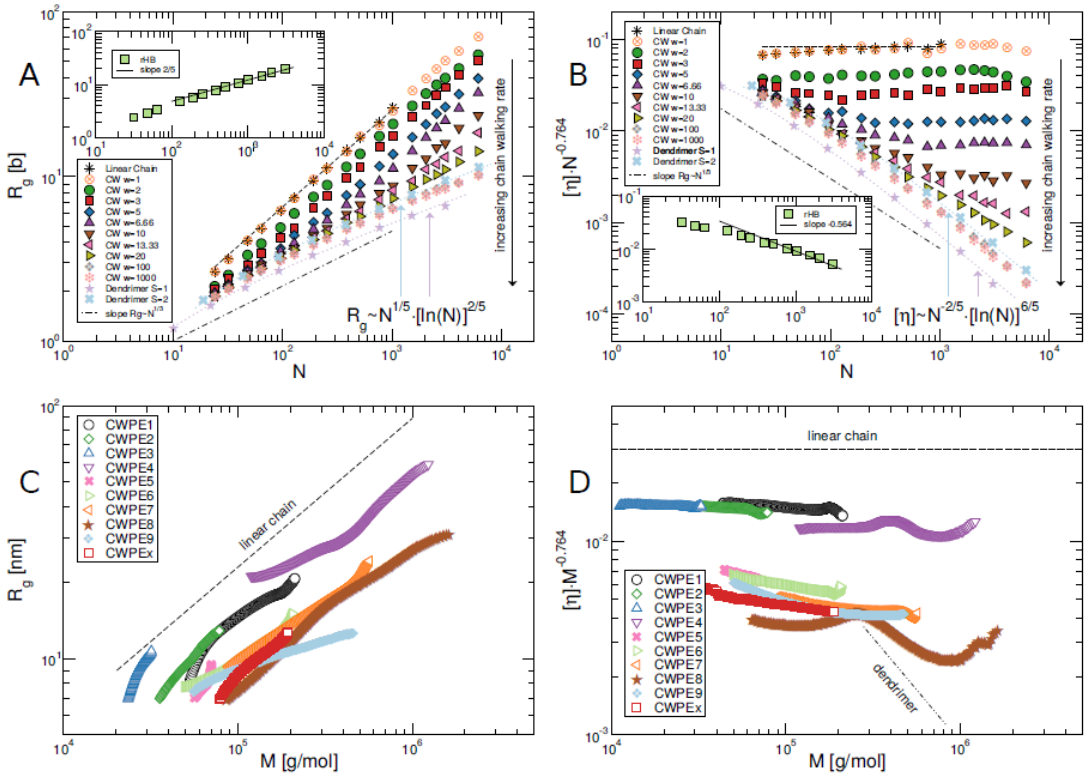
2. Polymers with different degree of branching

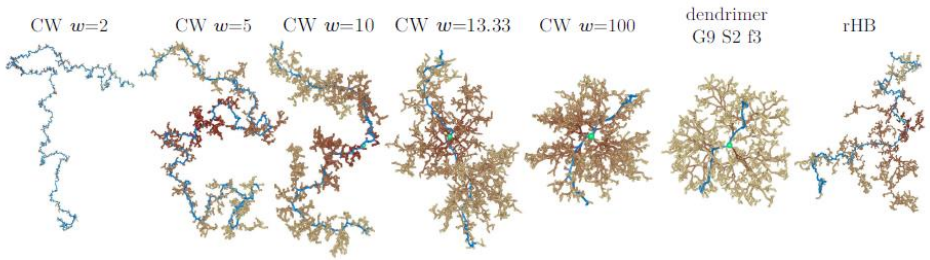
Effect of the degree of branching on the glass transition temperature of polyesters

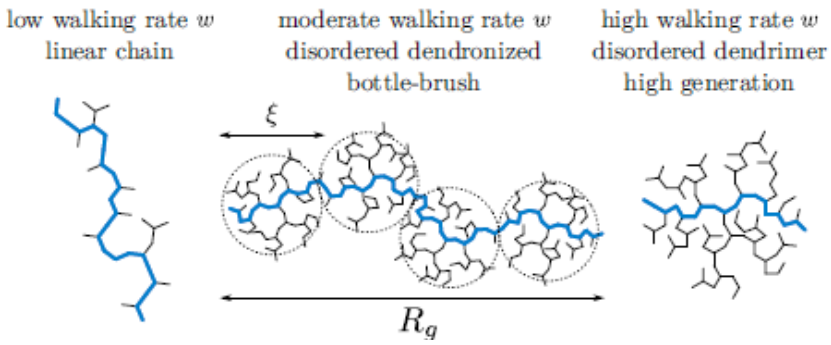


A. Khalyavina et al. / Polymer 53 (**2012**) 1049e1053

2. Polymers with different degree of branching



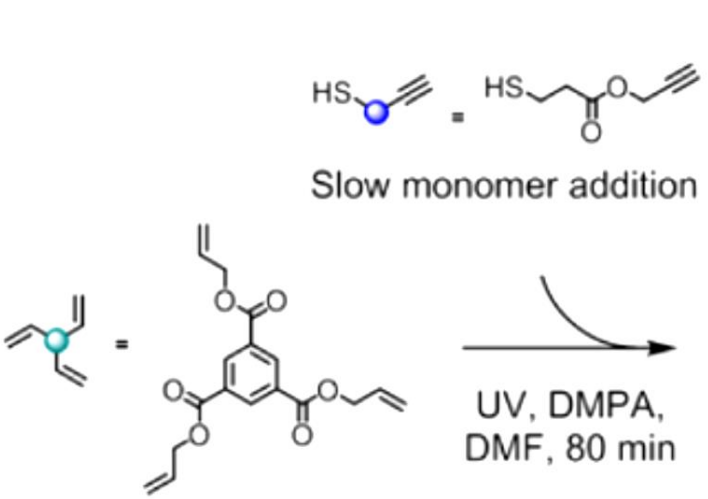


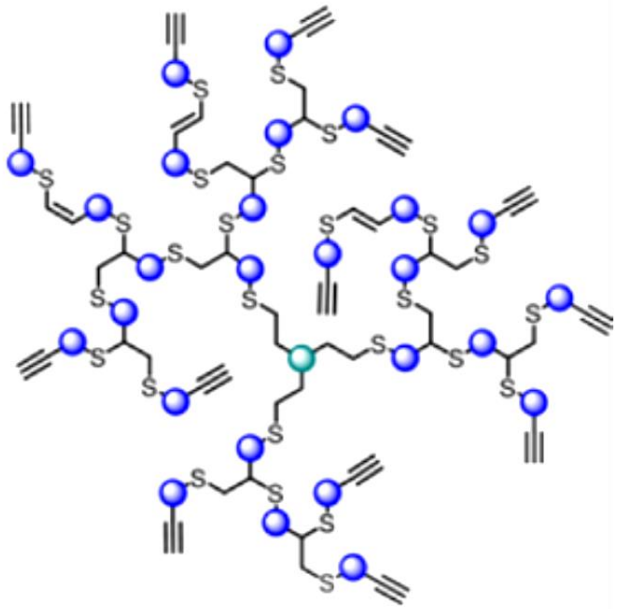


Ron Dockhorn *et al*, *J. Am. Chem. Soc.*, DOI: 10.1021/jacs.9b06785 **2019**

2. Polymers with different degree of branching

Hyperbranched Polymers with High Degrees of Branching and Low Dispersity Values: Pushing the Limits of Thiol–Yne Chemistry





✓ Fast, UV, one-pot

✓ High degrees of branching

✓ Low dispersity values

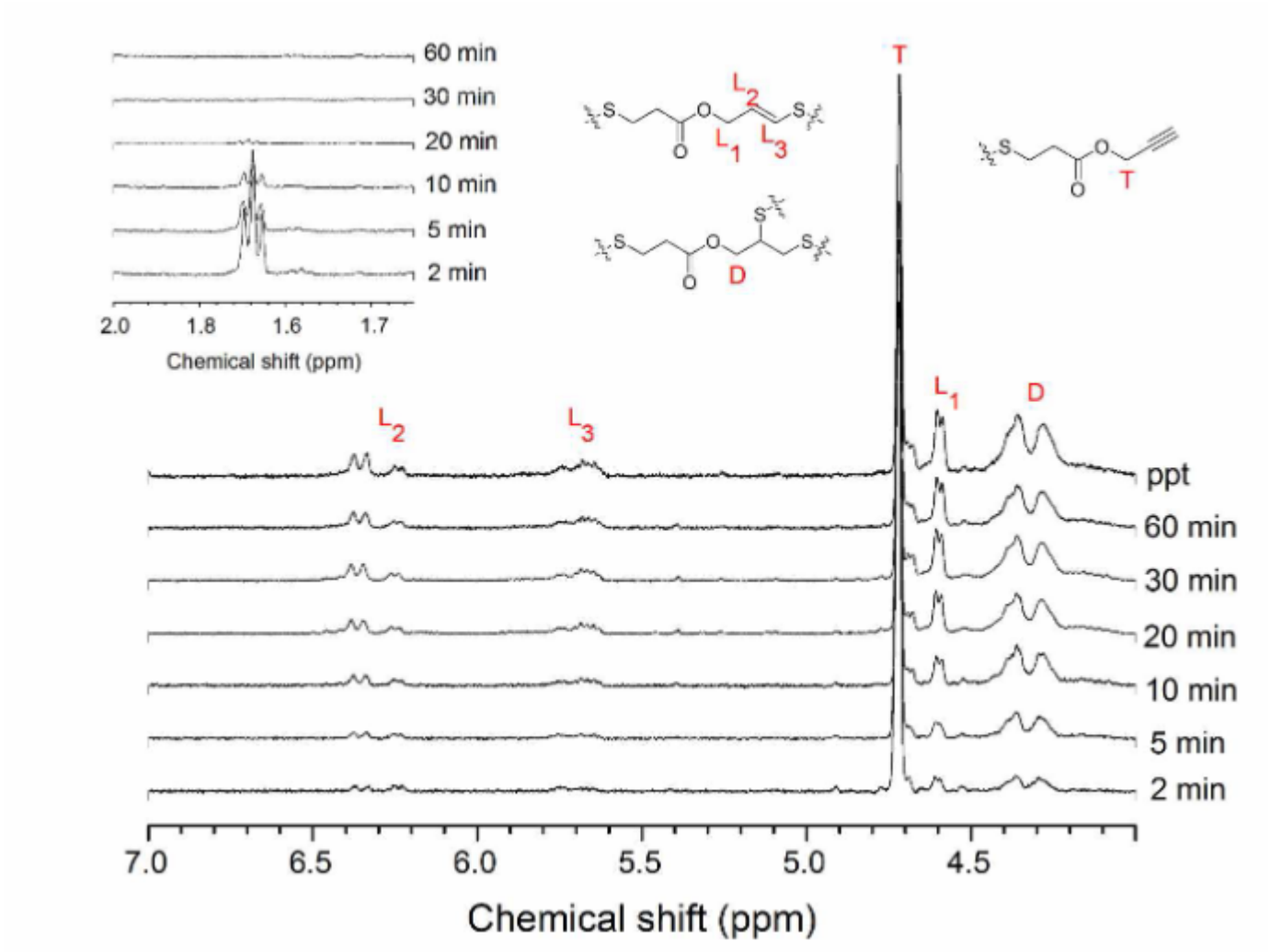
Degrees of branching were determined by ^{1}H NMR spectroscopy **to be greater than 0.8 in most cases.**

Increasing the fraction of core molecule was found to decrease dispersity to values as low as **1.26 and 1.38** for the alkene core and alkyne core.

Macromolecules 2016, 49, 4, 1296–1304

2. Polymers with different degree of branching

Hyperbranched Polymers with High Degrees of Branching and Low Dispersity Values: Pushing the Limits of Thiol–Yne Chemistry



$$DB = \frac{D + T}{D + T + L}$$

Macromolecules 2016, 49, 4, 1296–1304

3. Polydispersity and Mechanism of Polymerization

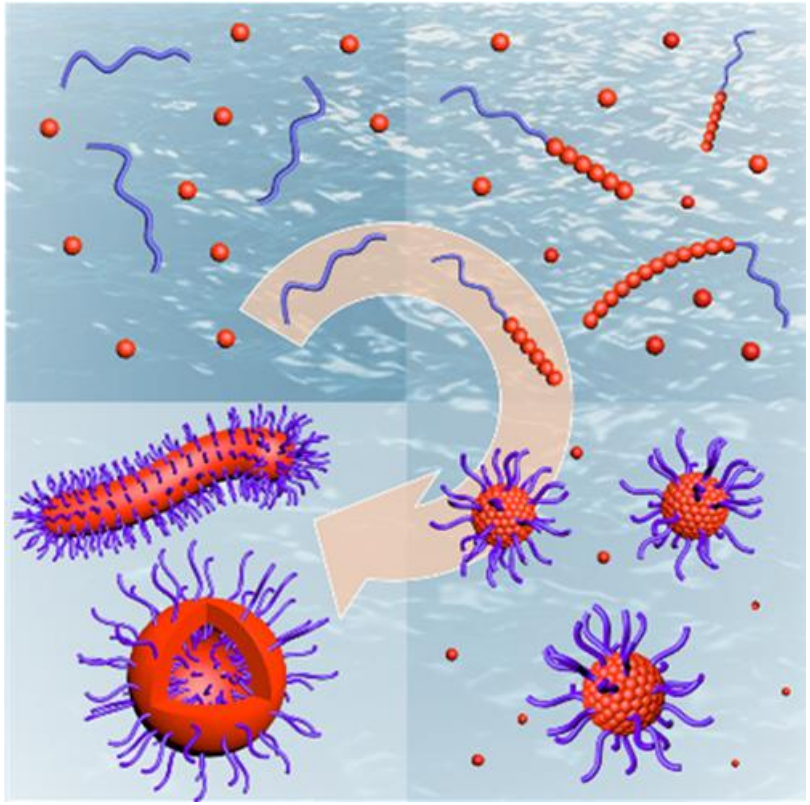
Depends on the reaction mechanism of the polymer formation reaction and the chosen conditions (e.g. p, T)

Kind of polymer	Reaction	M_W/M_N
Living Polymers	Anionic Group transfer	1.0...1.05
Condensation polymer	Step reaction Bifunctional Monomers	~ 2
Addition polymers	Radical addition Cationic addition Coordination polymerization (Organometallic complexes)	2-10 2-30
Branched Polymers	Radical	2-50
Networked Polymers	Step reaction of tri-, tetrafunctional Monomers	∞ at the gel point

Atom transfer radical polymerisation (ATRP), **reversible addition–fragmentation chain-transfer (RAFT) polymerisation and nitroxide-mediated radical polymerisation (NMP)** have enabled the synthesis of well-defined macromolecules with controlled molecular weight, architecture, end-group fidelity and dispersity. **Dispersities in the range of Đ = 1.01–1.20**

3. Polydispersity and Mechanism of Polymerization

Principles and Characteristics of Polymerization-Induced Self-Assembly (PISA) with Various Polymerization Techniques



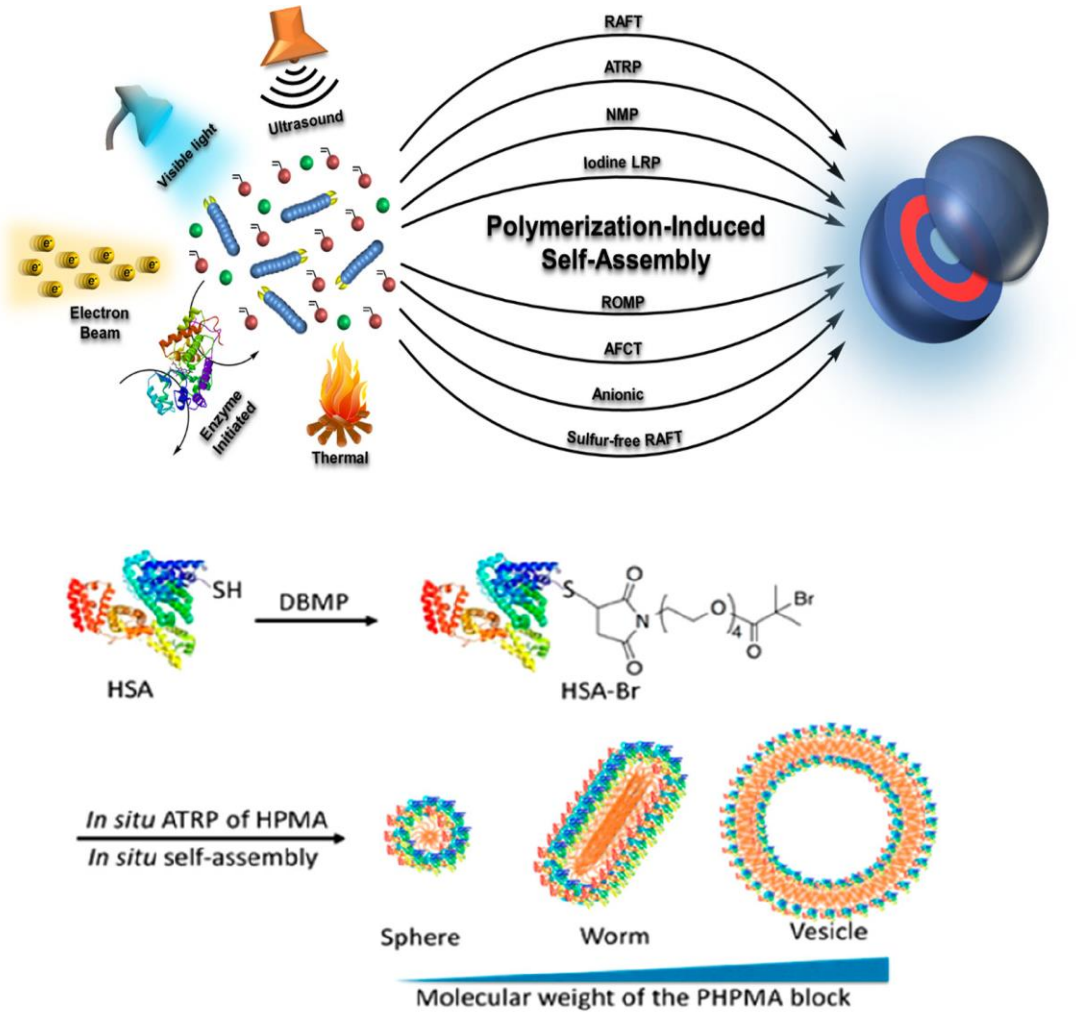
Preparation of a pre-defined polymer architecture is a key challenge to a researcher.

Polymerization Induced Self-Assembly (PISA) to synthesize polymeric nanoparticles with **pre-defined morphology and precise control over size and shape.** This methodology has become a potential strategy for the synthesis **of various block copolymer nano-objects.** The PISA strategy produces core–shell polymeric nanoparticles with a wide scope of morphologies **including spheres, worms, rods, and vesicles.**

A few parameters including the **degree of polymerization, core-forming monomers, macro-CTA and solid content of the final product are precisely employed for the PISA procedure to accomplish the ideal size and shape.**

3. Polydispersity and Mechanism of Polymerization

Principles and Characteristics of Polymerization-Induced Self-Assembly (PISA) with Various Polymerization Techniques



Alternative PISA protocols, which allow the preparation of nanoparticles with improved control over copolymer morphology and functionality.

For example, initiation based on visible light, redox chemistry, or enzymes enables the incorporation of sensitive monomers and fragile biomolecules into block copolymer nanoparticles.

ACS Macro Lett. **2019**, 8, 8, 1029–1054

4. Distributions. Statistical growth

The statistical growth of a constant number of chains in a living polymerization leads to the narrow Poisson distribution of the mole fraction as a function of the degree of polymerization N:

$$x(N) = \frac{\nu^{N-1} e^{-\nu}}{\Gamma(N)}$$

$\nu = \langle N \rangle_n - 1$ and $\Gamma(N)$ is the gamma function. The corresponding distribution in terms of mass fractions is

$$w(N) = \frac{N \nu^{N-1} e^{-\nu}}{\Gamma(N)(\nu + 1)}$$

The polydispersity decreases with increasing degree of polymerization and depends only on $\langle N \rangle_n$:

$$\frac{\langle N \rangle_w}{\langle N \rangle_n} = 1 + \langle N \rangle_n^{-1} - \langle N \rangle_n^{-2} \approx 1 + \langle N \rangle_n^{-1}$$

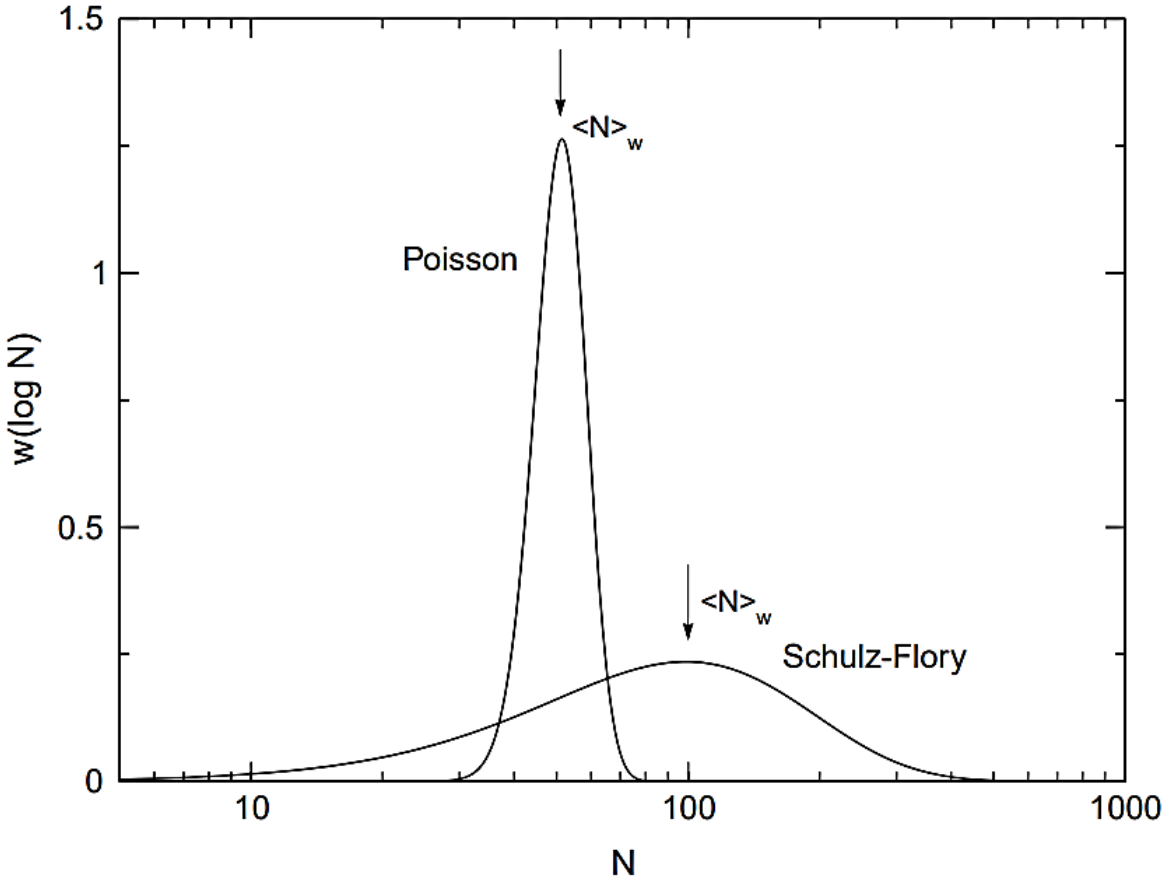
The much broader Schulz–Flory distribution

$$w(N) = \langle N \rangle_n^{-2} N (1 - \langle N \rangle_n^{-1})^{N-1}$$

with a constant polydispersity of $\langle N \rangle_w / \langle N \rangle_n = 2$ is known from radical polymerization [9].

4. Distributions. Statistical growth

Typical Distributions



Poisson and Schulz-Flory distribution with identical N = 50. The arrows indicate N_w = 51 (Poisson) and N_w = 100 (Schulz–Flory).

4. Distributions. Statistical growth

Step-growth Polymerization

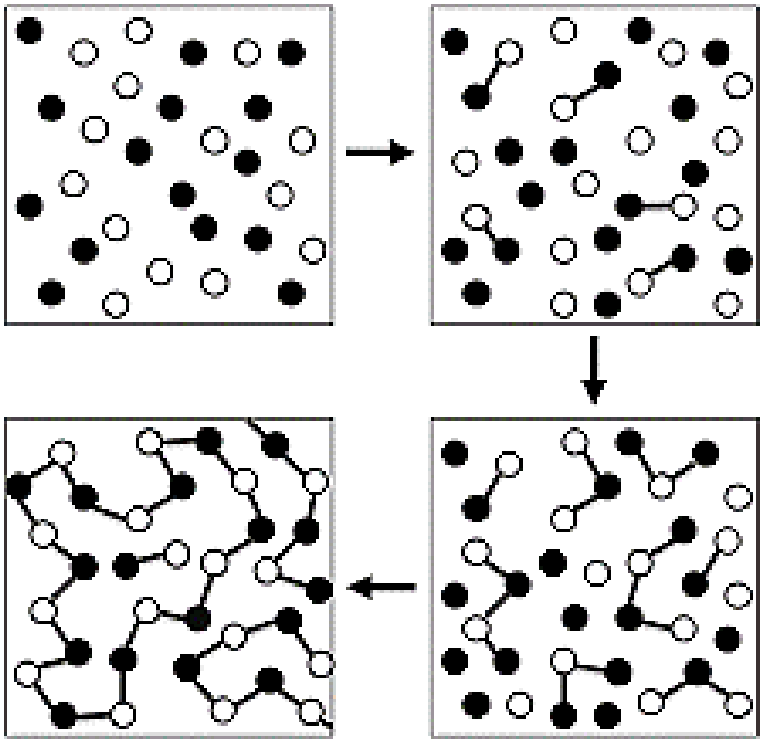
Step growth polymerization is the formation of a polymer from bi-functional or multifunctional monomers.

Self-condensation of A-B and the stoichiometric polymerization of A-A with B-B where A may react only with B and vice-versa.

Let p = probability that a B group has reacted (This is equivalent to the fraction of B groups reacted)

1 – p = probability that a B group is unreacted

In virtually all cases one can assume that the reaction events are independent. Thus, the probability that an x-mer has formed is given by $\mathbf{p^{x-1}(1-p)}$



4. Distributions. Statistical growth

Step-growth Polymerization

Most Probable Distribution: Number Fraction

$$N_x = p^{x-1}(1-p)$$

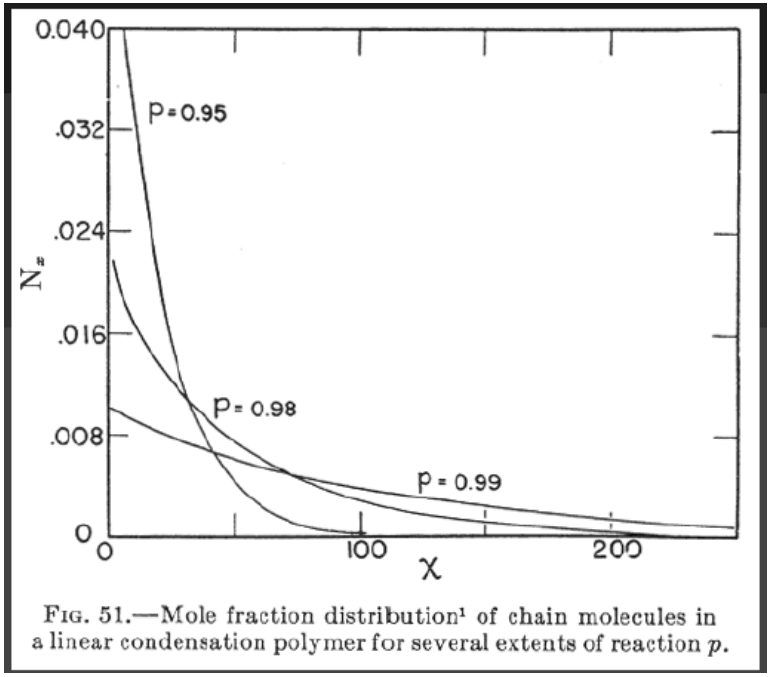


FIG. 51.—Mole fraction distribution[1] of chain molecules in a linear condensation polymer for several extents of reaction p.

Most Probable Distribution: Weight Fraction

$$W_x = xp^{x-1}(1-p)^2$$

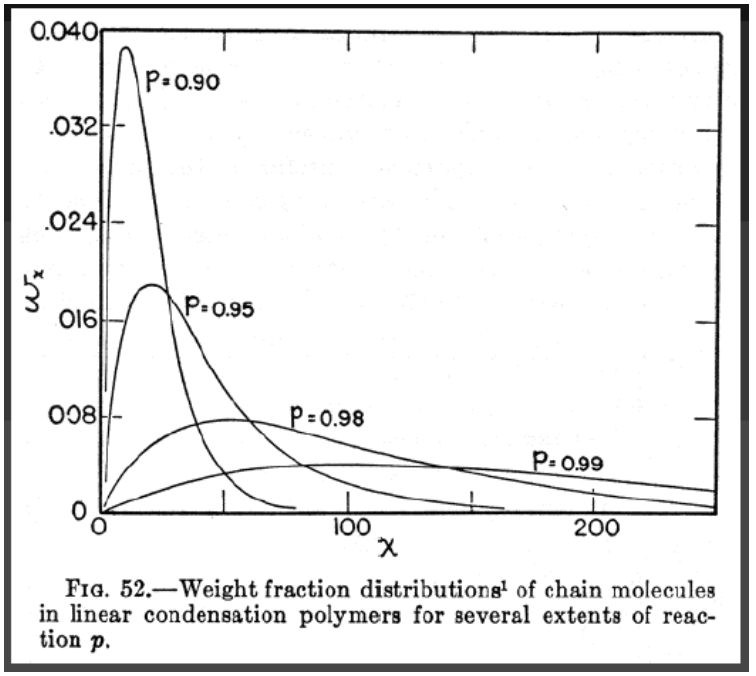


FIG. 52.—Weight fraction distributions[1] of chain molecules in linear condensation polymers for several extents of reaction p.

4. Distributions. Statistical growth

Chain-growth Polymerization

Chain growth polymerization is the formation of polymers from unsaturated monomers.

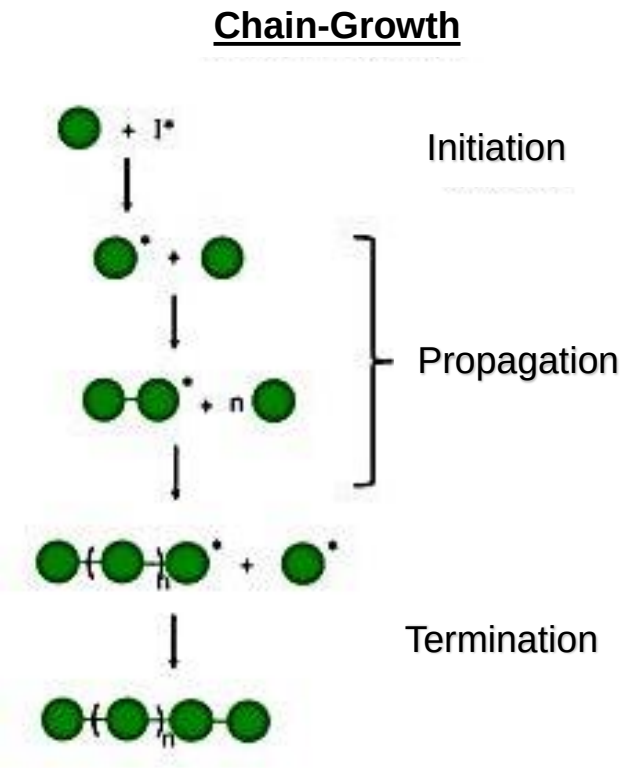
Consider a chain growing until random something stops it.

Let p = probability that it keeps on going.
1 – p = probability that it gets stopped

Thus, the probability that an x-mer formsS is given by $p^{x-1}(1-p)$

According to the initiator used in the chain growth polymerization process, there are three types of chain growth polymerization.

- Radical Polymerization – the initiator is a radical
- Cationic Polymerization – the initiator is an acid/cation
- Anionic Polymerization – the initiator is a nucleophile



4. Distributions. Statistical growth

Chain-growth Polymerization

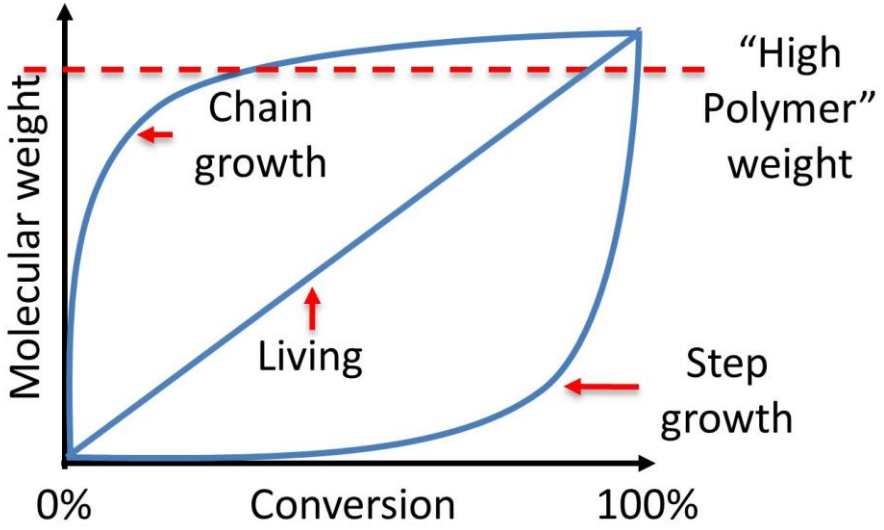
Most Probable Distribution: Number Fraction	$N_x = p^{x-1}(1-p)$
Number Average Molecular Weight, M_n	$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$
Most Probable Distribution: Weight Fraction	$W_x = xp^{x-1}(1-p)^2$
Weight Average Molecular Weight, M_w	$A = \sum_i w_i M_i = M_w$
the Polydispersity	M_w / M_n

It is the same as for step-growth polymerization. Other things can happen in chain growth polymerization: two growing chains can join their two active ends, etc., ➔ **it can give rise to different statistics.**

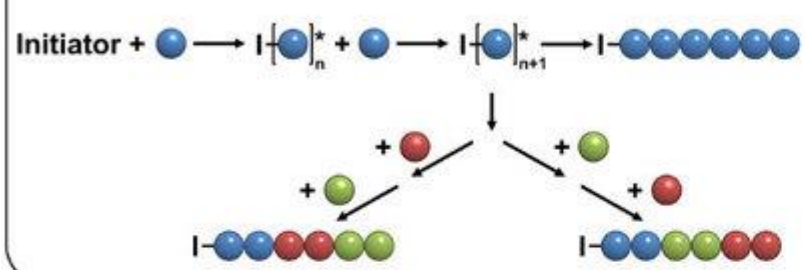
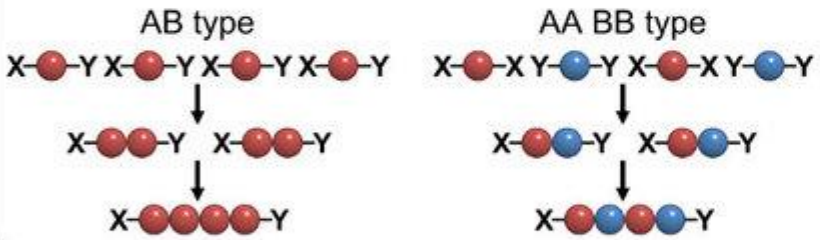
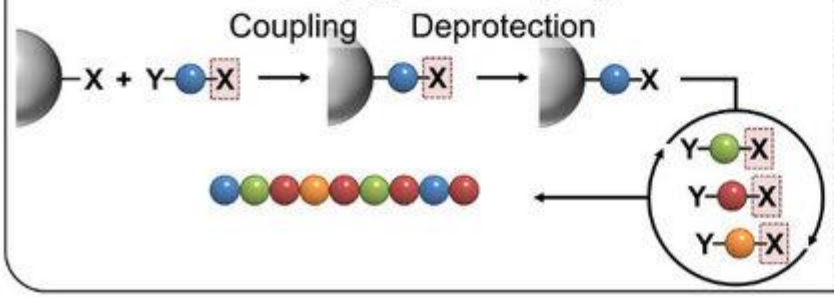
4. Distributions. Statistical growth

Differences from chain-growth polymerization

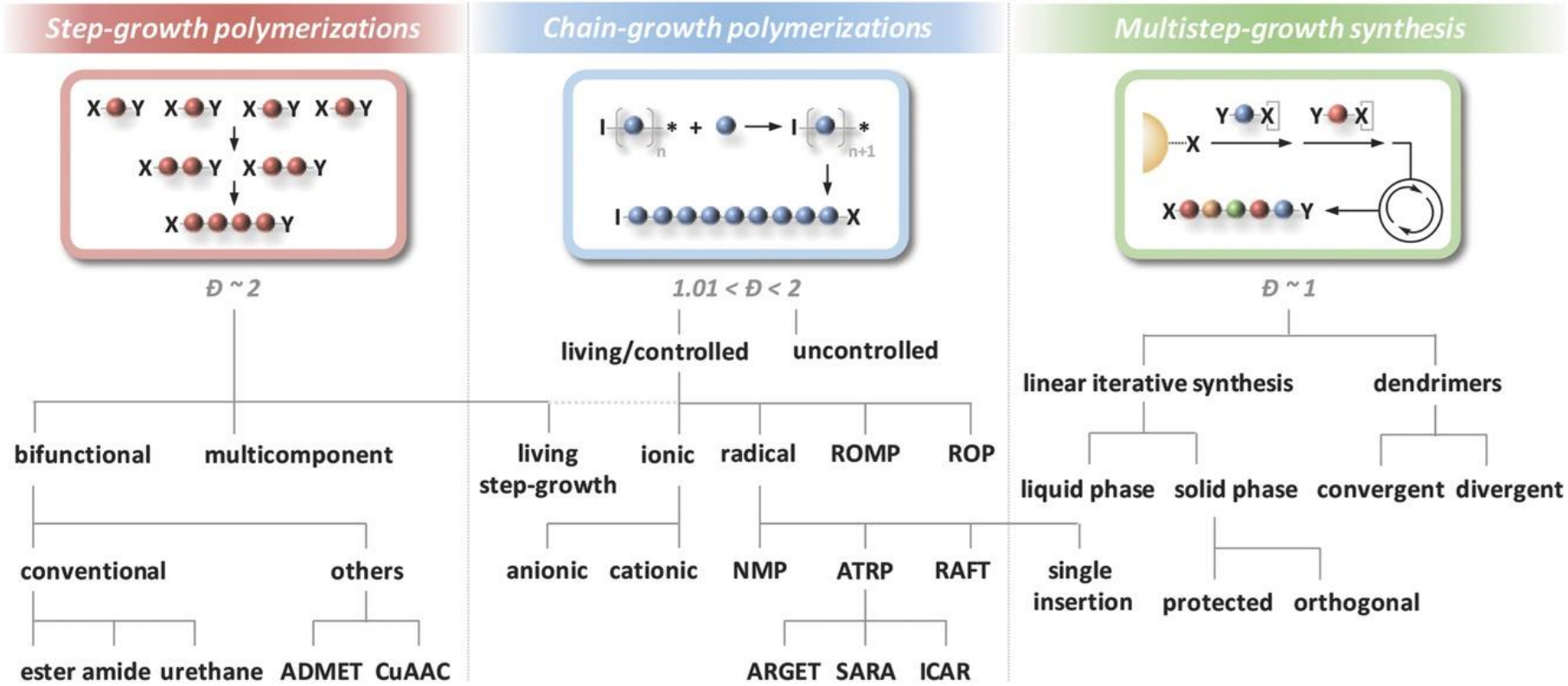
Step-growth polymerization	Chain-growth polymerization
Growth throughout matrix	Growth by addition of monomer only at one end or both ends of chain
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times
Similar steps repeated throughout reaction process	Different steps operate at different stages of mechanism (i.e. initiation, propagation, termination, and chain transfer)
Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length	Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization
Ends remain active (no termination)	Chains not active after termination
No initiator necessary	Initiator required



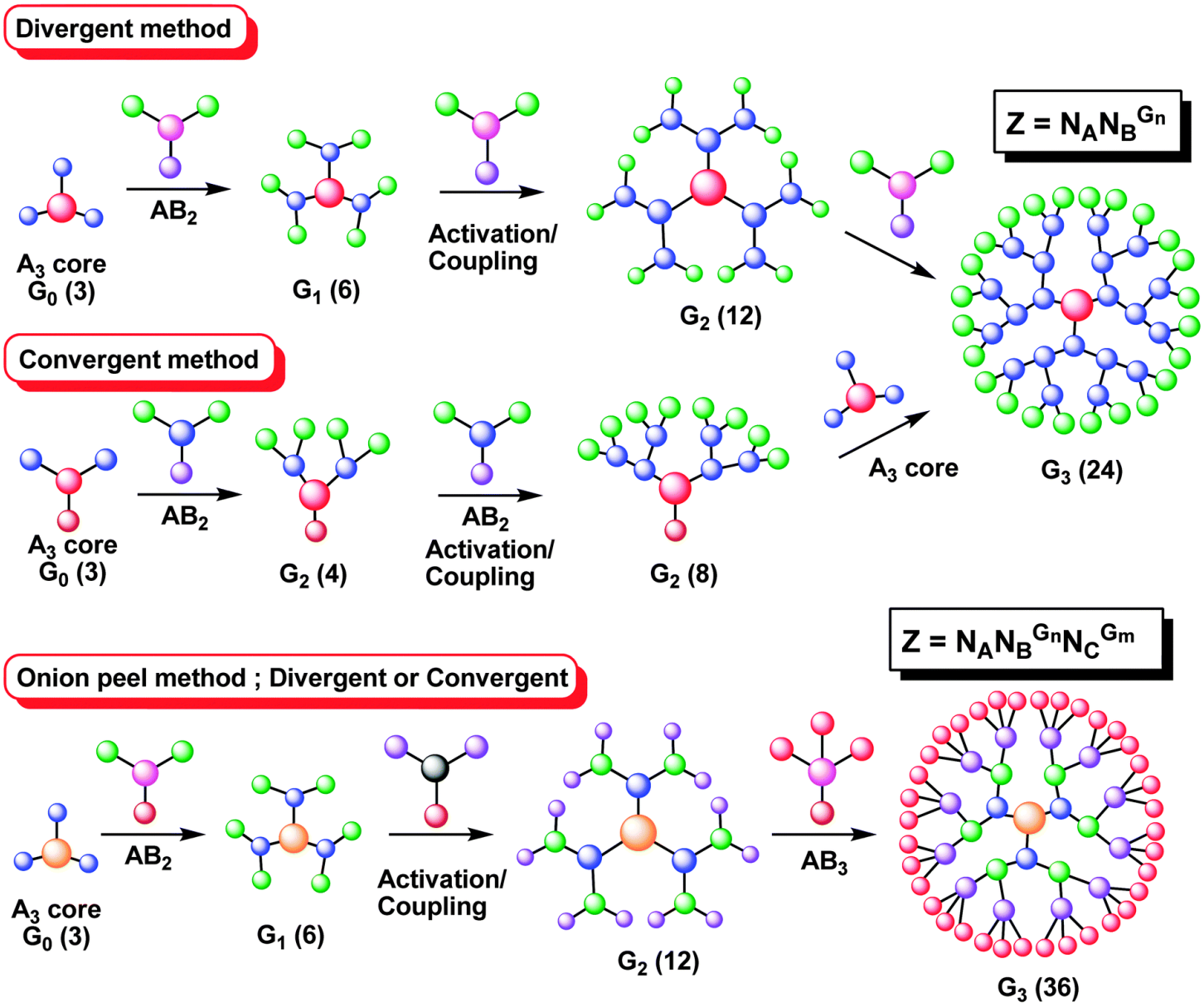
4. Distributions. Statistical growth

Polymerization method	Accessible molecular weight distribution	Accessible microstructure
Chain-growth polymerization methods 	Broad distribution with uncontrolled methods $\bar{M}_w/\bar{M}_n \sim 2$ Narrow distribution with controlled methods $\bar{M}_w/\bar{M}_n \sim 1.01$	Straightforward access of graft and multiblock copolymers Synthesis of gradient, periodic and alternating copolymers is challenging
Step-growth polymerization methods 	Generally broad distribution $\bar{M}_w/\bar{M}_n \sim 2$	Straightforward access of alternating, periodic and multiblock copolymers
Multistep-growth coupling 	Monodisperse structures $\bar{M}_w/\bar{M}_n \sim 1$	Complete control over the arrangement of monomers

4. Distributions. Statistical growth



4. Distributions. Statistical growth



5. Molar Distributions

Molar Mass in Polymers

Number average molar weight

$$M_n = \frac{\sum_i c_i}{\sum_i (c_i/Mi)} = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Weight average molar weight

$$M_w = \frac{\sum_i (ciM_i)}{\sum_i c_i}$$

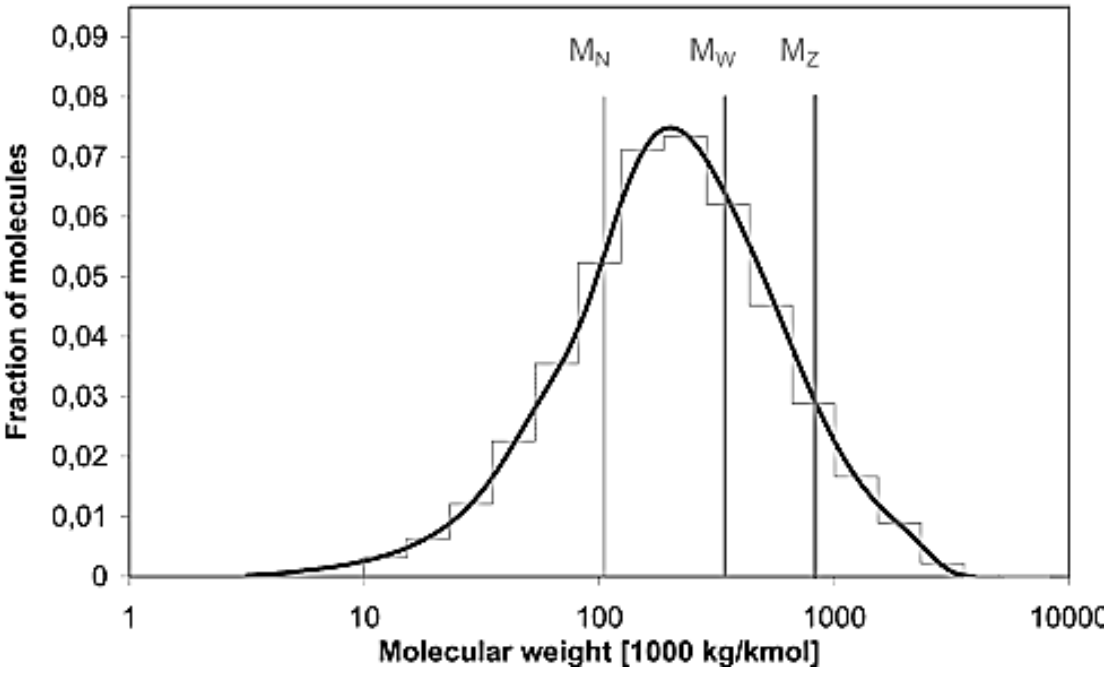
z-average molecular weight

$$M_z = \frac{\sum_i (ciM_i^2)}{\sum (c_i M_i)} = \frac{\sum_i z_i M_i}{\sum z_i}$$

MMD (polydispersity) is with $\mathbf{M_w/M_n}$

For **monodisperse** samples $\mathbf{M_w/M_n = 1}$

Polydisperse polymers have $\mathbf{M_w/M_n > 1}$

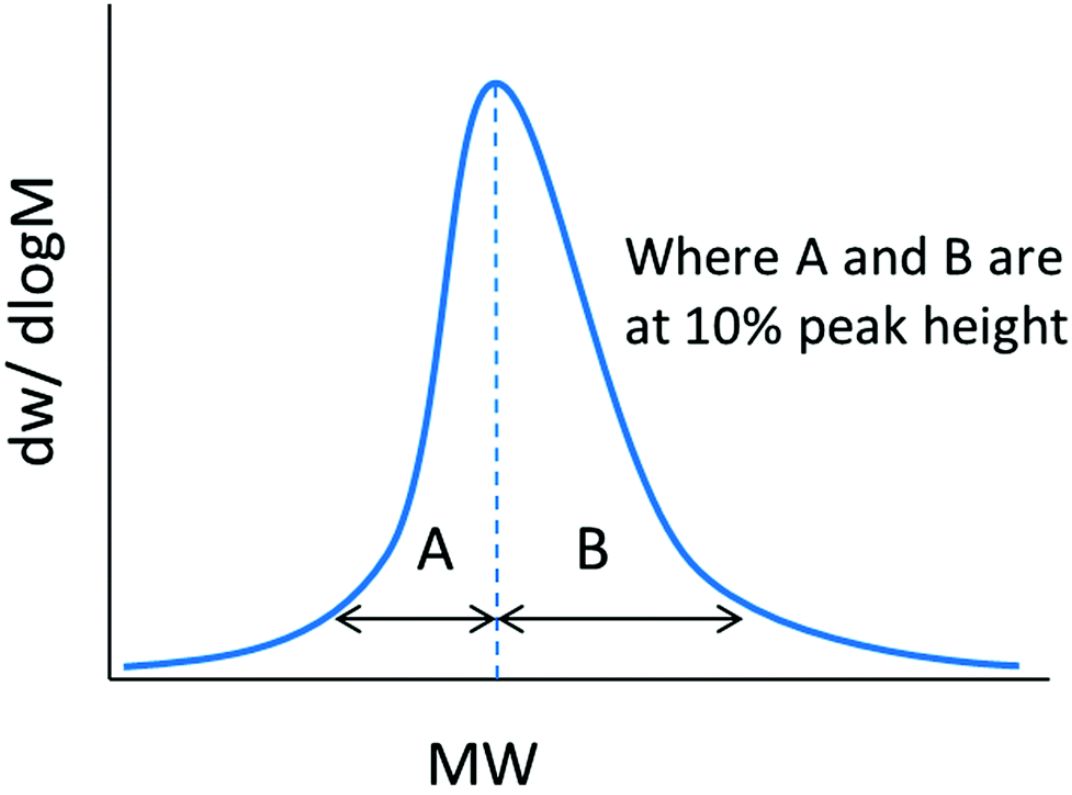


5. Molar Distributions

Symmetry of the shape of the distribution

Asymmetry factor (A_s) to describe the symmetry of the shape of the distribution, which gives a qualitative measure of the skew of a distribution. This factor is determined as the ratio of the distance from the peak maximum to the front of the peak over the distance from the peak maximum to the back of the peak at 10% of the peak height.

$$A_s = \frac{B}{A} = \left| \frac{\mathrm{MW}_{\mathrm{upper\,10\%}} - M_\mathrm{p}}{\mathrm{MW}_{\mathrm{lower\,10\%}} - M_\mathrm{p}} \right|$$

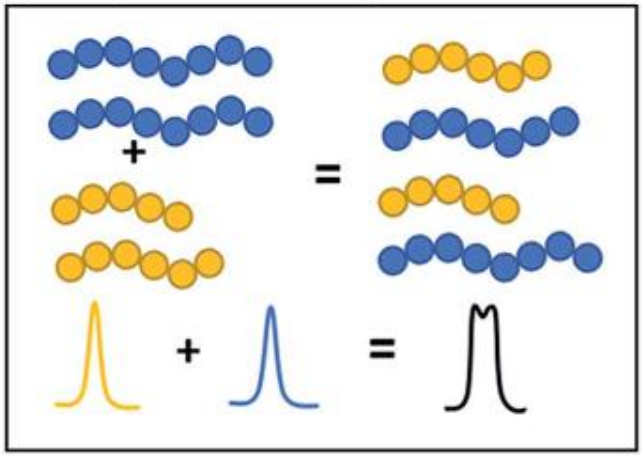


Chem. Soc. Rev., 2017, **46**, 4119-4134

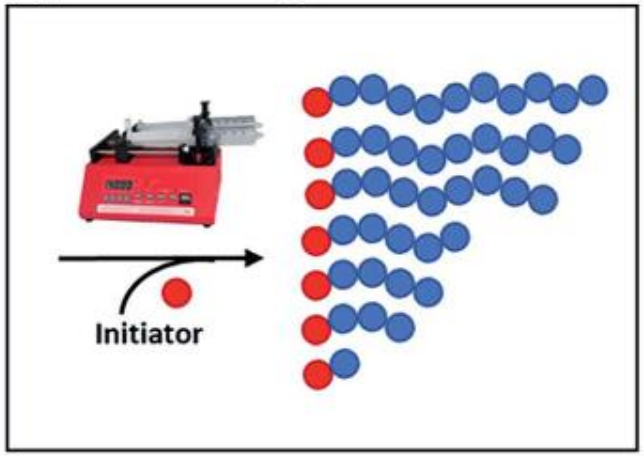
6. How can we tune some of this properties?

Methods to tune dispersity

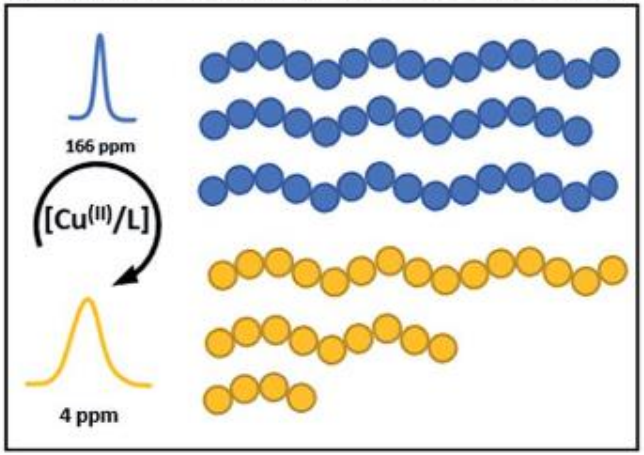
a) Polymer blending



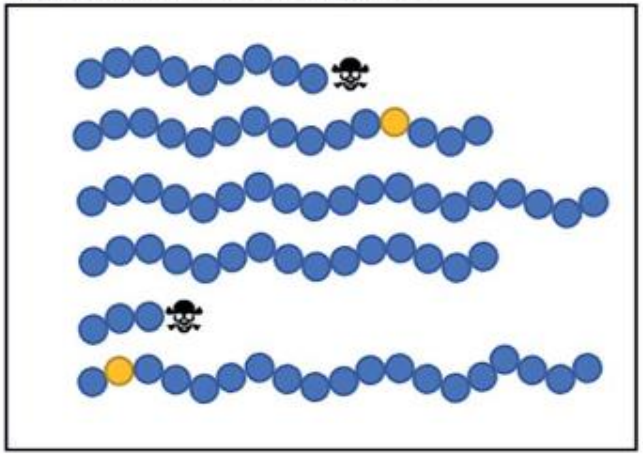
b) Initiation regulation



c) Tailored catalyst concentration



d) Additional reagents



Chem. Sci., 2019,**10**, 8724-8734

6. How can we tune some of this properties?

Methods to tune dispersity

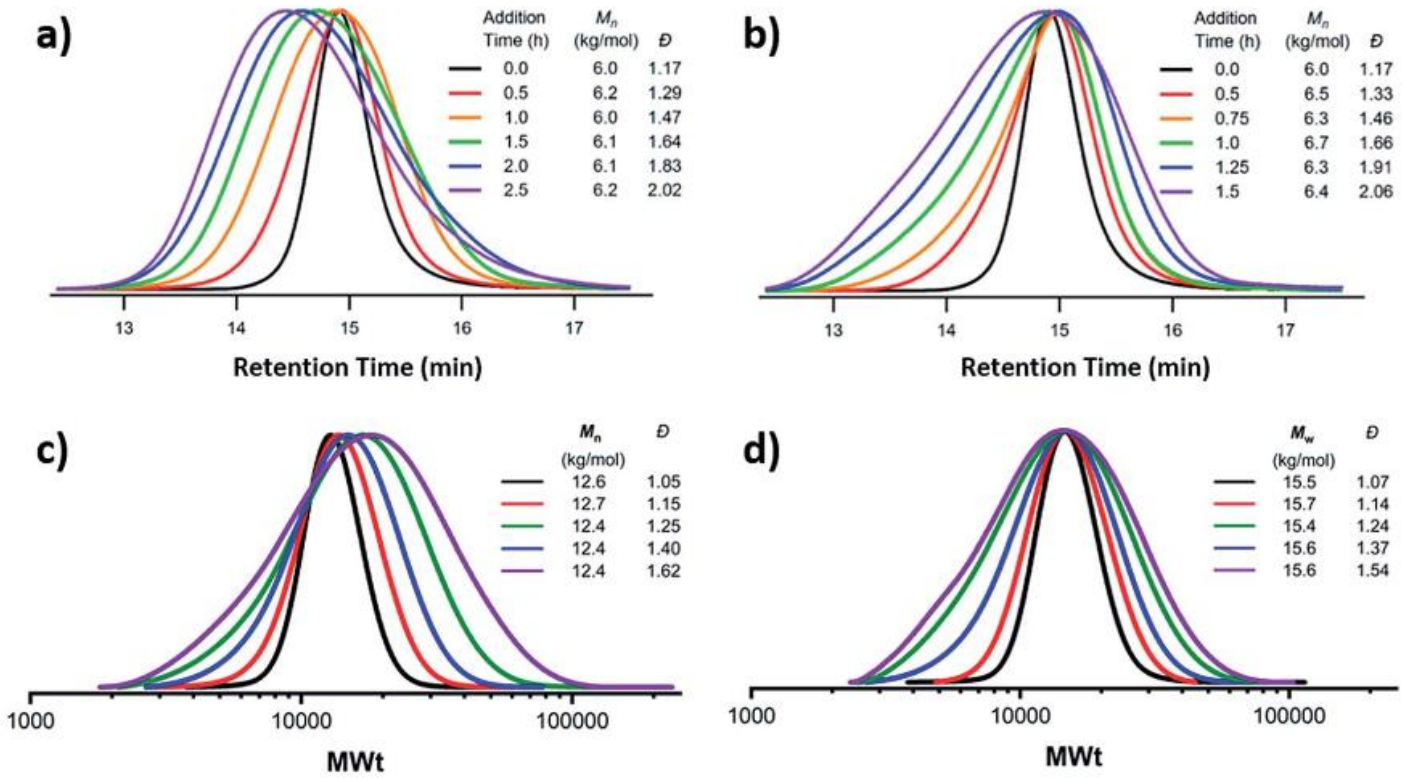
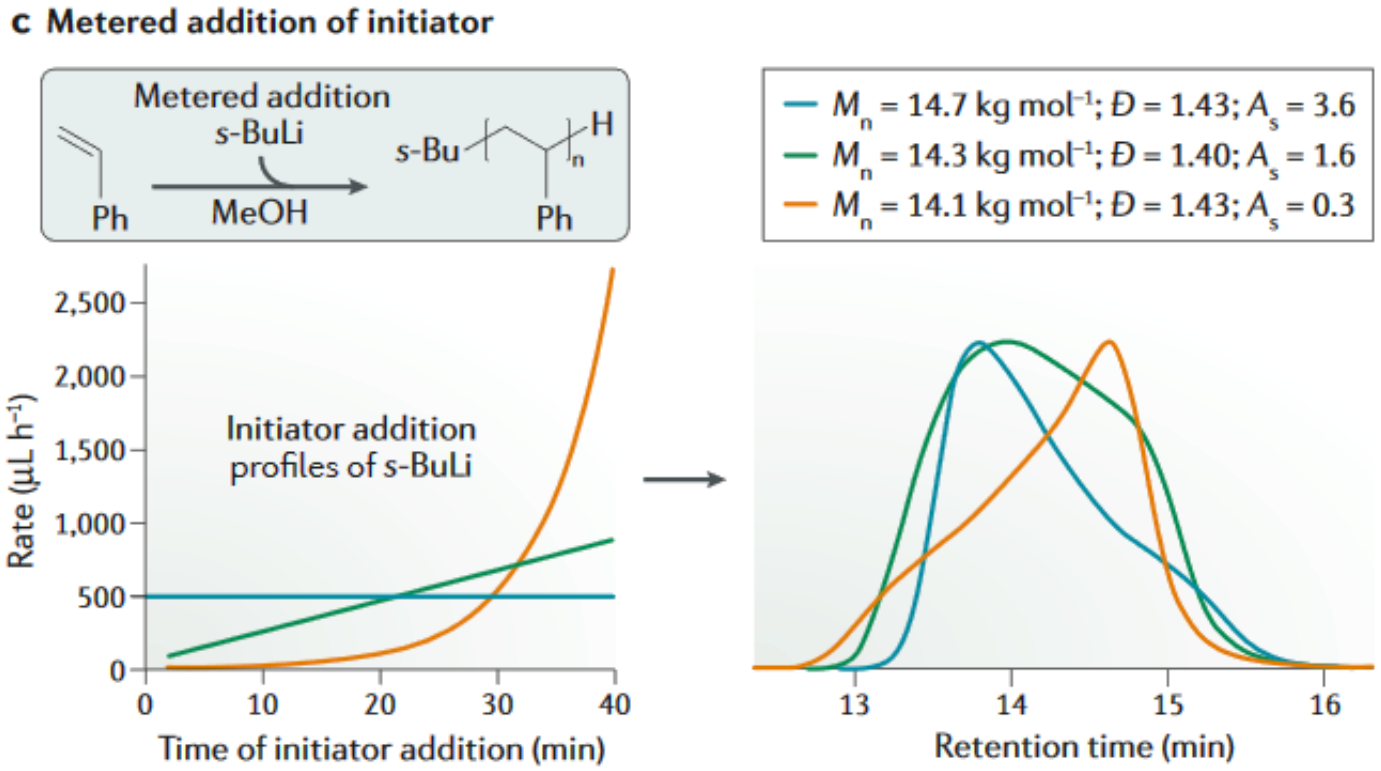


Fig. 4 Comparison of two methods by which the molecular weight distribution is tuned. Firstly, the metered addition of initiator to the NMP of styrene with (a) at a constant rate and (b) with varying rate and secondly *via* the reduction of catalyst concentration in photo-induced ATRP to maintain (c) M_n or (d) M_w constant. This figure is adapted from ref. 53 and 73, permission from ACS publications and Wiley respectively.

Chem. Sci., 2019,**10**, 8724-8734

6. How can we tune some of this properties?

Methods to tune the shape

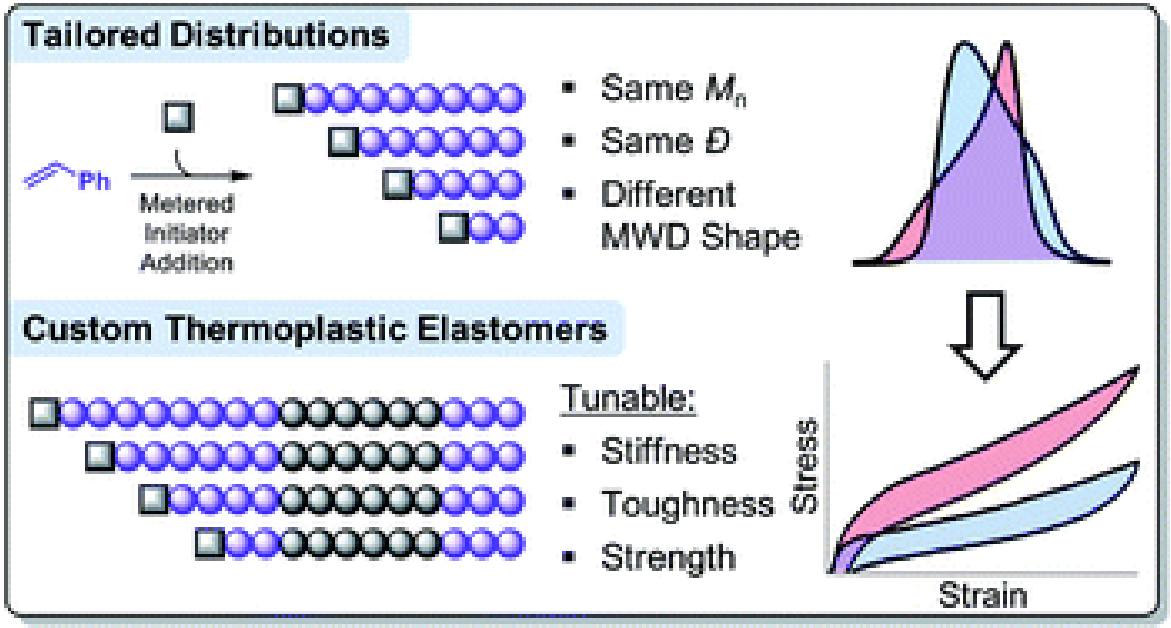


Gentekos, D.T., Sifri, R.J. & Fors, B.P. Controlling polymer properties through the shape of the molecular-weight distribution. *Nat Rev Mater* **4,** 761–774 (2019).

6. How can we tune some of this properties?

Methods to tune the shape

Tailor-made thermoplastic elastomers: customisable materials via modulation of molecular weight distributions



Chem. Sci., 2020,**11**, 1361-1367

7. Example Questions

- What is the difference between hyperbranched polymers and dendrimers? How can we determine the degree of branching?
- Define Asymmetry factor (A_s). What kind of properties can be influenced?
- Differences from chain-growth polymerization
- How can we tune the polydispersity?