Notes

On the Polydispersity of Star Macromolecules

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Received February 26, 1991;
Revised Manuscript Received May 29, 1991

In the synthesis procedure of star-branched macromolecules, molecular agents link together linear chains, which form the branches of the star.[1-4] The linear precursor chains, depending on the route of their formation, have a certain number-average molecular weight distribution $P_b(m)$ proportional to the number of the chains in the sample with molecular weight m. Characteristic properties of the initial sample that can be found from $P_b(m)$ are the number-average molecular weight m_n and the weight-average molecular weight m_w of the precursor branches. In the limit of large molecular weights where the real summations can be replaced with integrations, these two quantities are given by

$$m_n = \frac{\int_0^\infty dm\, mP_b(m)}{\int_0^\infty dm\, P_b(m)} = -\left.\frac{\dot{\bar{P}}_b(s)}{\bar{P}_b(s)}\right|_{s=0}$$

$$m_w = \frac{\int_0^\infty dm\, m^2P_b(m)}{\int_0^\infty dm\, mP_b(m)} = -\left.\frac{\ddot{\bar{P}}_b(s)}{\dot{\bar{P}}_b(s)}\right|_{s=0}$$

$$\bar{P}_b(s) = \int_0^\infty dm\, e^{-ms}P_b(m) \qquad (1)$$

where $\bar{P}_b(s)$ is the Laplace transform of $P_b(m)$ with respect to m, and the dot and double dot denote first and second derivatives with respect to s, respectively. m_w is larger than or equal to m_n, and the polydispersity factor $I_1 = m_w/m_n - 1$ increases with the width of the distribution $P_b(m)$. For a monodisperse sample $m_w = m_n$ and $I_1 = 0$.

An interesting question is how the polydispersity of the precursor arms influences the polydispersity of the larger complex macromolecules that may form. At least two factors are expected to influence the distribution of the molecular weights of the star macromolecules. The first is steric hindrance[5] arising for example from excluded-volume interactions,[6] which make the approach to the core more difficult for a larger chain than for a smaller chain. The second is the content of the final sample, depending strongly on the route of fractionation and purification. Does the final sample contain stars with the same number f of branches or are species with different f's present? The simplest problem, with the steric hindrance not taken into account and for samples with a single f, has first been studied by Morton et al.,[7] who employed a Gaussian form for $P_b(m)$ and proved approximately that the polydispersity factor of the star with f branches, $I_f = M_w/M_n - 1$ (with M_w and M_n the weight- and number-average molecular weights of the star), is equal to I_1/f where I_1 is the polydispersity factor of the precursor arm. We will show in this paper that the relation

$$I_f = I_1/f \qquad (2)$$

of Morton et al. is exactly valid for any form of $P_b(m)$ under the assumptions that the steric hindrances are not important so that all precursor chains have equal probabilities to be attached to the core agent and that stars of a unique f exist in the sample. Our results will be extended to samples with more than one f, and a comparison with experimental findings will be given.

If the star macromolecule has f branches with molecular weights $m_1, m_2, ..., m_f$, their probability distributions are $P_b(m_1), P_b(m_2), ..., P_b(m_f)$, respectively. The probability distribution $P_s(M)$ of the star with molecular weight $M = m_1 + m_2 + ... + m_f$ (the sum of the molecular weights of the arms) when the m's take all possible values is given by

$$P_s(M) = \int_0^\infty dm_1\, P_b(m_1) \int_0^\infty dm_2\, P_b(m_2) ... \int_0^\infty dm_f\, P_b(m_f)\, \delta(M-m_1-m_2-...m_f) \qquad (3)$$

where the δ function ensures the equality of M with the sum of the corresponding m's. It is convenient to use the Laplace transform of $P_s(M)$ with respect to M

$$\bar{P}_s(s) = \int_0^\infty dM\, e^{-Ms}P_s(M) \qquad (4)$$

since

$$M_n = \frac{\int_0^\infty dM\, MP_s(M)}{\int_0^\infty dM\, P_s(M)} = -\left.\frac{\dot{\bar{P}}_s(s)}{\bar{P}_s(s)}\right|_{s=0}$$

and

$$M_w = \frac{\int_0^\infty dM\, M^2P_s(M)}{\int_0^\infty dM\, MP_s(M)} = -\left.\frac{\ddot{\bar{P}}_s(s)}{\dot{\bar{P}}_s(s)}\right|_{s=0} \qquad (5)$$

With replacement of $P_s(M)$ of eq 3 in eq 4, a simple relation between the Laplace transforms of the distributions of the complex macromolecule and its precursor is taken:

$$\bar{P}_s(s) = [\bar{P}_b(s)]^f \qquad (6)$$

By means of eq 6, we can find M_n and M_w (eq 5) in terms of $\bar{P}_b(s)$ and its derivatives as

0024-9297/91/2224-5727$02.50/0

$$M_{\mathrm{n}} = -\left.\frac{\frac{\partial}{\partial s}[\bar{P}_{\mathrm{b}}(s)]^{f}}{[\bar{P}_{\mathrm{b}}(s)]^{f}}\right|_{s=0} = -\left.\frac{f[\bar{P}_{\mathrm{b}}(s)]^{f-1}\dot{\bar{P}}_{\mathrm{b}}(s)}{[\bar{P}_{\mathrm{b}}(s)]^{f}}\right|_{s=0} = -f\frac{\dot{\bar{P}}_{\mathrm{b}}(0)}{\bar{P}_{\mathrm{b}}(0)}$$

$$\begin{aligned} M_{\mathrm{w}} &= -\left.\frac{\frac{\partial^2}{\partial s^2}[\bar{P}_{\mathrm{b}}(s)]^{f}}{\frac{\partial}{\partial s}[\bar{P}_{\mathrm{b}}(s)]^{f}}\right|_{s=0} \\ &= -\left.\frac{f[\bar{P}_{\mathrm{b}}(s)]^{f-1}\ddot{\bar{P}}_{\mathrm{b}}(s) + f(f-1)[\bar{P}_{\mathrm{b}}(s)]^{f-2}\dot{\bar{P}}_{\mathrm{b}}(s)^2}{f[\bar{P}_{\mathrm{b}}(s)]^{f-1}[\dot{\bar{P}}_{\mathrm{b}}(s)]}\right|_{s=0} \\ &= -\frac{\ddot{\bar{P}}_{\mathrm{b}}(0)}{\dot{\bar{P}}_{\mathrm{b}}(0)} - (f-1)\frac{\dot{\bar{P}}_{\mathrm{b}}(0)}{\bar{P}_{\mathrm{b}}(0)} \end{aligned} \qquad (7)$$

But $\dot{\bar{P}}_{\mathrm{b}}(0)$ and $\ddot{\bar{P}}_{\mathrm{b}}(0)$ are given in eq 1 in terms of m_{n} and m_{w} and are equal to $\dot{\bar{P}}_{\mathrm{b}}(0) = -m_{\mathrm{n}}\bar{P}_{\mathrm{b}}(0)$ and $\ddot{\bar{P}}_{\mathrm{b}}(0) = m_{\mathrm{w}}m_{\mathrm{n}}\bar{P}_{\mathrm{b}}(0)$. Replacing them in eq 7, we finally take M_{n} and M_{w} as $M_{\mathrm{n}} = fm_{\mathrm{n}}$ and $M_{\mathrm{w}} = m_{\mathrm{w}} + (f-1)m_{\mathrm{n}}$, so that

$$M_{\mathrm{w}} = M_{\mathrm{n}} + m_{\mathrm{w}} - m_{\mathrm{n}} \text{ (sample of one } f\text{)} \qquad (8)$$

Equation 8 is valid for a sample with a unique f. Notice also that from this relation eq 2 of Morton et al. is obtainable, proving in this way that when the final sample includes only stars of the same f, $I_f = I_1/f$, for any distribution $P_{\mathrm{b}}(m)$.

For a distribution of f's a mean number of branches $\langle f\rangle$ has to be defined as

$$\langle f\rangle = \left.\frac{\sum f[\bar{P}_{\mathrm{b}}(s)]^{f}/f!}{\sum [\bar{P}_{\mathrm{b}}(s)]^{f}/f!}\right|_{s=0} \qquad (9)$$

where the summation applies over all f's in the sample and the f factorial in the denominator ensures the indistinguishability of macromolecules with the same number f of branches. M_{n} and M_{w} are then equal to

$$M_{\mathrm{n}} = -\frac{\sum f[\bar{P}_{\mathrm{b}}(0)]^{f-1}\dot{\bar{P}}_{\mathrm{b}}(0)/f!}{\sum [\bar{P}_{\mathrm{b}}(0)]^{f}/f!} = m_{\mathrm{n}}\langle f\rangle$$

and

$$\begin{aligned} M_{\mathrm{w}} &= -\frac{\sum \{f[\bar{P}_{\mathrm{b}}(0)]^{f-1}\ddot{\bar{P}}_{\mathrm{b}}(0) + f(f-1)[\bar{P}_{\mathrm{b}}(0)]^{f-2}\dot{\bar{P}}_{\mathrm{b}}(0)^2\}/f!}{\sum f[\bar{P}_{\mathrm{b}}(0)]^{f-1}[\dot{\bar{P}}_{\mathrm{b}}(0)]/f!} \\ &= m_{\mathrm{w}} + m_{\mathrm{n}}\frac{\sum f(f-1)[\bar{P}_{\mathrm{b}}(0)]^{f}/f!}{\sum f[\bar{P}_{\mathrm{b}}(0)]^{f}/f!} \end{aligned} \qquad (10)$$

where in eq 10 the relations $\dot{\bar{P}}_{\mathrm{b}}(0) = -m_{\mathrm{n}}\bar{P}_{\mathrm{b}}(0)$ and $\ddot{\bar{P}}_{\mathrm{b}}(0) = m_{\mathrm{w}}m_{\mathrm{n}}\bar{P}_{\mathrm{b}}(0)$ have been used. From eq 10 we see that, though M_{n} is always proportional to the mean number $\langle f\rangle$ of the branches, M_{w} depends on the distribution $P_{\mathrm{b}}(m)$ through the value $\bar{P}_{\mathrm{b}}(0) = \int_0^{\infty}\mathrm{d}m\, P_{\mathrm{b}}(m)$. Further manipulation of these two general expressions is possible when the distribution of the f's in the final sample is known. Relation 8 for a unique f for example is recovered from these general expressions, and when stars with more than one f are present in a known distribution, it is a simple matter of substitution to find the result. We give an example of the applicability of eq 10 by considering the other extreme situation where in the final sample stars with all f's are present. The summation of eq 10 up to infinity can then be done, and M_{n} and M_{w} are in this case equal to $M_{\mathrm{n}} = m_{\mathrm{n}}\langle f\rangle$ and $M_{\mathrm{w}} = m_{\mathrm{w}} + m_{\mathrm{n}}\langle f\rangle$ so that

$$M_{\mathrm{w}} = M_{\mathrm{n}} + m_{\mathrm{w}} \quad \text{(stars of all } f\text{'s present)} \qquad (11)$$

M_{w} for this broader distribution is larger, yielding also a larger polydispersity factor

$$I_f = \frac{I_1}{\langle f\rangle} + \frac{1}{\langle f\rangle} \quad \text{(stars of all } f\text{'s present)} \qquad (12)$$

Table I
Experimental Values (in g mol^{-1}) of the Average Molecular Weights of the Precursor Branches and the Stars (First Four Columns) and Theoretical Values (Last Two Columns) Describing the Two Extremes of a Sample with a Single f and Samples with All f's

				$M_{\mathrm{w}} \times 10^{-5}$	
$m_{\mathrm{n}} \times 10^{-4}$	$m_{\mathrm{w}} \times 10^{-4}$	$M_{\mathrm{n}} \times 10^{-5}$	$M_{\mathrm{w}} \times 10^{-5}$ (ref)	one f (eq 8)	all f's (eq 11)
3.74	3.90	2.70	2.76 (2)	2.72	3.09
8.80	9.20	5.90	6.04 (2)	5.94	6.82
3.56	3.70	4.10	4.15 (2)	4.11	4.47
2.10	2.18	2.47	2.50 (3)	2.48	2.69
1.88	1.97	3.40	3.44 (4)	3.41	3.60
1.20	1.31	2.16	2.18 (4)	2.17	2.29
1.07	1.12	1.93	1.97 (4)	1.94	2.04
0.34	0.36	0.61	0.62 (4)	0.61	0.65
0.51	0.54	0.92	0.93 (1)	0.92	0.97
1.99	2.57	1.17	1.22 (1)	1.23	1.43
3.69	4.01	2.23	2.26 (1)	2.26	2.63
7.80	8.30	4.62	4.78 (1)	4.67	5.45
4.82	5.48	1.95	2.15 (1)	2.02	2.50

A comparison with experimental findings is presented in the first four columns of Table I where the numbers in parentheses in column 4 denote the references. The conclusions were based on a combination of sedimentation ultracentrifugation analysis in θ-solvents and size-exclusion chromatography analysis where the star polymer chromatograms exhibit narrow and symmetrical distributions, which does not change after the elimination of the excess of linear precursor by fractionation. We quote also two theoretical values of M_{w}: those corresponding to a sample with a unique f (eq 8) and those of samples with all f's (eq 11). We see that the experimental values of M_{w} lie between these two extremes and are very close to the values of the fifth column, confirming the conclusions of Hadjichristidis, Fetters, Roovers et al. about the high uniformity of the star polymers they prepared.

References and Notes

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