Notes

On the Average Molecular Weights of Complex Macromolecular Architectures Made from Different Precursors

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Recently the synthesis and characterization of macromolecules of complex architectures, with the constituent segments made from the same or different species, the so-called miktoarm stars from the Greek word μικτος meaning mixed, has been advanced and stars of the type A_2B, A_2B_2, ABC, and ABCD have already been prepared by anionic polymerization.[1,2] In the synthesis procedure of these macromolecules appropriate chlorosilanes link together linear precursors which form the parts of the complex macromolecule. The linear precursor chains of the i type ($i = 1, 2, 3, ..., n$), depending on the route of their formation, have certain number-average molecular weight distributions $P_i(m)$ which determine both their number- and weight-average molecular weights m_{ni} and m_{wi}. In the limit of large molecular weights where the real summations can be replaced with integrations, they can be written as:

$$m_{ni} = \frac{\int_0^\infty dm\, m\, P_i(m)}{\int_0^\infty dm\, P_i(m)} = -\left.\frac{\dot{\bar{P}}_i(s)}{\bar{P}_i(s)}\right|_{s=0}$$

$$m_{wi} = \frac{\int_0^\infty dm\, m^2\, P_i(m)}{\int_0^\infty dm\, m\, P_i(m)} = -\left.\frac{\ddot{\bar{P}}_i(s)}{\dot{\bar{P}}_i(s)}\right|_{s=0},$$

$$\bar{P}_i(s) = \int_0^\infty dm\, e^{-ms} P_i(m) \quad (1)$$

where $P_i(s)$ is the Laplace transform of $P_i(m)$ with respect to m, and the dot and double dot denote first and second derivatives with respect to s.

In this paper we extend our previous investigation of stars made from the same kind of precursor arms[3] to macromolecules of more complex architecture made from more than one different precursor. We relate the number- and weight-average molecular weights M_n and M_w of the complex macromolecule to those of the different precursor parts. Though the synthetic procedure's aim is well-defined model macromolecules, only nearly monodisperse products are possible. Not only does uncertainty exist in the molecular weights of the polymers, but there is difficulty in controlling precisely even the number of arms. Theoretical relations therefore between the molecular weights of the precursors and the final complex architectures are useful guide in the detection and characterization of the final products. They can also be useful in the determination of the molecular weight of a part of a complex macromolecule if the molecular weights of the whole macromolecule and those of the other parts are known. The complex macromolecule is made from a total number f of precursors and contains f_i precursors of the ith kind ($i = 1, 2, ..., n$) so that $f = \sum_i f_i$. If m_{ij} is the molecular weight of the jth precursor of the ith kind ($j = 1, 2, ..., f_i$), then the total molecular weight of a specific macromolecule is equal to $M = \sum_i \sum_j m_{ij}$. If we neglect steric interactions which differentiate the probability of linkage depending on the order of attack, we can assume that all precursor chains have equal probabilities to be connected to the link agents. The probability then of a specific complex macromolecule is equal to the product of the probabilities of its constituent precursors, and in order to find the probability $P_c(M)$ that the complex macromolecule has the specific molecular weight M, the sum of the probabilities $P_{ij}(m_{ij})$ which yield the molecular weight M has to be taken into account.

$$P_c(M) = \prod_{ij} \int_0^\infty dm_{ij}\, P_{ij}(m_{ij})\, \delta(M - \sum_i \sum_j m_{ij}) \quad (2)$$

where the Dirac delta function insures the equality of M with the sum of the corresponding m_{ij} of the constituent parts. Using the Laplace transform $\bar{P}_c(s) = \int_0^\infty dM\, e^{-Ms} P_c(M)$ of this distribution and the fact that precursors of the same kind have the same initial probability distributions, we can take from eq 2 a simple relation in terms of the Laplace transforms of the probabilities of the constituent species and their numbers f_i:

$$\bar{P}_c(s) = \sum_i (\bar{P}_i(s))^{f_i} \quad (3)$$

The average molecular weights of the complex macromolecule are equal to

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

$$M_w = \frac{\int_0^\infty dM\, M^2 P_c(M)}{\int_0^\infty dM\, M P_c(M)} = -\left.\frac{\ddot{\bar{P}}_c(s)}{\dot{\bar{P}}_c(s)}\right|_{s=0} \quad (4)$$

respectively, and by means of eq 3 we can find M_n and M_w in terms of $\bar{P}_i(s)$ and its derivatives as

$$M_n = -\left.\frac{\frac{\partial}{\partial s}\sum_i (\bar{P}_i(s))^{f_i}}{\sum_i (\bar{P}_i(s))^{f_i}}\right|_{s=0} = -\sum_i f_i \frac{\dot{\bar{P}}_i(0)}{\bar{P}_i(0)}$$

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Table 1. Experimental Values (in 10^{-3}) of the Average Molecular Weights of the Precursors (First Columns) as Well as the Experimental Value $\underline{M}_w$ of the Complex Macromolecule[a]

	m_{nA}	m_{wA}	m_{nB}	m_{wB}	$\underline{M}_w$	M_w	M_n	ref
A_2B								
$(PS)_2PBd$	13.0	14.2	22.0	22.9	47.8	49.1	48.0	4
$(PBd)_2PS$	9.5	9.9	21.7	23.7	41.1	42.0	40.7	4
$(PI)_2PS$	15.9	16.5	21.7	23.7	53.4	54.7	53.5	2
$(PS)_2PI$	25.9	28.2	15.9	16.5	59.9	69.6	67.7	2
$(PS)_2PBd$	23.7	25.8	14.8	15.7	62.1	64.0	62.2	4
$(PI)_2PS$	8.0	8.3	7.3	7.4	25.5	23.3	23.0	4
$(PS)_2PI$	20.8	21.7	33.8	35.2	75.3	76.1	75.4	4
$(PI)_2PS$	34.0	35.7	79.1	83.1	147	150.0	147.1	4
$(PI)_2PS$	25.4	26.6	45.0	47.2	105	97.5	95.8	4
$(PS)_2PI$	36.2	38.0	42.0	43.7	114	116.2	114.4	4
A_2B_2								
$(PS)_2(PBd)_2$	12.2	12.8	29.3	30.8	89.8	84.2	83.0	1b

	m_{nA}	m_{wA}	m_{nB}	m_{wB}	m_{nC}	m_{wC}	$\underline{M}_w$	M_w	M_n	
ABC										
(PS)(PI)(PBd)	20.7	21.9	15.6	16.2	12.2	12.7	46.4	49.3	48.5	1a
$(PS)(PI)(PBd)_2$	7.9	8.3	8.2	8.5	7.7	8.0	24.7	24.1	23.8	5

	m_{nA}	m_{wA}	m_{nB}	m_{wB}	m_{nC}	m_{wC}	m_{nD}	m_{wD}	$\underline{M}_w$	M_w	M_n	
ABCD												
(PS)(P4MeS)(PI)(Pbd)	15.9	16.7	15.4	16.7	14.5	15.4	16.2	16.5	65.5	62.8	62.0	1b

[a] The theoretical values M_w and M_n (columns 7 and 8) are taken from eq 6. PS = polystyrene, PI = polyisoprene, Pbd = polybutadiene, and P4MeS = poly(4-methylstyrene).

$$M_w = -\left.\frac{\dfrac{\partial^2}{\partial s^2}\left[\prod_i (\bar{P}_i(s))^{f_i}\right]}{\dfrac{\partial}{\partial s}\left[\prod_i (\bar{P}_i(s))^{f_i}\right]}\right|_{s=0} =$$

$$-\sum_i f_i \frac{\dot{\bar{P}}_i(0)}{\bar{P}_i(0)} - \frac{\bar{P}_c(0)}{\dot{\bar{P}}_c(0)} \sum_i f_i \left[\frac{\ddot{\bar{P}}_i(0)}{\dot{\bar{P}}_i(0)} \frac{\dot{\bar{P}}_i(0)}{\bar{P}_i(0)} - \left(\frac{\dot{\bar{P}}_i(0)}{\bar{P}_i(0)}\right)^2\right] \quad (5)$$

But $\dot{\bar{P}}_i(0)$ and $\ddot{\bar{P}}_i(0)$ can be written in terms of m_{ni} and m_{wi} as $\dot{\bar{P}}_i(0) = -m_{ni}\bar{P}_i(0)$ and $\ddot{\bar{P}}_i(0) = m_{wi}m_{ni}\bar{P}_i(0)$, and replacing them in eq 5 we end up with the relations

$$M_n = \sum_i f_i m_{ni} \qquad M_w = M_n + \frac{\sum_i f_i m_{ni}(m_{wi} - m_{ni})}{M_n} \quad (6)$$

which connect the average molecular weights of the precursors and those of the final complex macromolecule. Notice that these relations are true for any distributions of the molecular weights of the precursors, yielding a first insight even for the cases of broader distributions.

A comparison with experimental findings for four different categories of macromolecules is presented in the Table 1. The first columns contain the experimental results, while columns 7 and 8 contain the theoretical values M_n and M_w based on eq 6. The last column contains the references where the synthesis of these macromolecules is reported. The experimental conclusions were based on a combination of low-angle laser light scattering and membrane osmometry with size-exclusion chromatography analysis. The complex polymer chromatograms exhibit narrow and symmetrical distributions which do not change after elimination of excess of linear precursor by fractionation. We see that the experimental values of $\underline{M}_w$ are close to the theoretical values, confirming the high uniformity of the prepared polymers.

References and Notes

(1) (a) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649; (b) **1993**, *26*, 2479.
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(3) Kosmas, M.; Vlahos, C.; Hadjichristidis, N. *Macromolecules* **1991**, *24*, 5727.
(4) Iatrou, H.; Kioulafa, E.; Hadjichristidis, N.; Roovers, J.; Mays, J., to be published.
(5) Unpublished results.