Comments

Polydispersity Index: How Accurately Does It Measure the Breadth of the Molecular Weight Distribution?

It is well-known that both average molecular weight and molecular weight distribution are the two key characteristics that determine properties of polymers and that polydispersity index (PDI) is used as a measure of the breadth of the molecular weight distribution. PDI is defined as M_w/M_n where M_w and M_n are the weight average and number average molecular weight, respectively, and it is related to the standard deviation of M_n(s_n) by the following equation:[1]

$$\frac{{s_n}^2}{{M_n}^2} = \frac{M_w}{M_n} - 1 \qquad (1)$$

The general belief is that a polymer sample with higher PDI would have a "broader" molecular weight distribution, interpreted by a larger s_n. However, it is clear from the above equation that PDI yields information on s_n/M_n but not on s_n, which is a better measure of the breadth of a distribution curve. Consider two polymer samples having the same PDI, say 2, but with different M_n values 10 000 and 100 000. Here, s_n of the two samples are 10 000 and 100 000, respectively. It is obvious that although the above two polymer samples have the same PDI, their standard deviations are completely different. By analogy, with two samples having different M_n, the sample with higher PDI may not have larger s_n. This problem is compounded by the fact that in many introductory polymer science textbooks such as refs 2−4, it is not explained explicitly that the PDI is a measure of s_n/M_n, not that of s_n The above clarification of what PDI represents is commonly overlooked and we believe it is important to point out.

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