LETTER TO THE EDITORS

*On the Effect of Branching and Polydispersity on the Angular Distribution of the Light Scattered by Gaussian Coils**

It is well known that for a monodisperse system of Gaussian coils of degree of polymerization N, the angular distribution of the scattered light is given by the following expression:[1]

$$P(\theta) = \frac{2}{N^2u^2}\left[Nu - 1 + \exp\{-Nu\}\right] \tag{1}$$

where $u = \mu^2b^2/6$, b is the length of the statistical element of the chain and $\mu = (4\pi/\lambda)\sin(\theta/2)$, ($\theta$ being the angle between the incident and scattered beams).

If $P^{-1}(\theta)$ is plotted against Nu, this function has an asymptote[2] $y = Nu/2 + 1/2$ and, when the molecules are large enough (end-to-end distance of 2000 A. under the usual experimental conditions), one should be able to observe this asymptotic behavior. Now it is well known that either branching or polydispersity changes this ideal behavior, and we want to show what general information can be obtained on branching and polydispersity when $P(\theta)$ is known in a large range of values of Nu.

1. Effect of Polydispersity

Zimm[2] has shown that, for a polydisperse system characterized by its normalized weight distribution $f(N)$, $P(\theta)$ is given by the following expression:

$$P(\theta) = \frac{1}{\int Nf(N)dN}\int Nf(N)P_N(\theta)dN \tag{2}$$

If, as usual, we write:

$$\langle N_n\rangle = \frac{1}{\int \frac{f(N)}{N}dN} \tag{3}$$

$$\langle N_w\rangle = \int Nf(N)dN \tag{3'}$$

$$\langle N_z\rangle = \frac{1}{\langle N_w\rangle}\int N^2f(N)dN \tag{3''}$$

the first terms of the expansion of $P(\theta)$ as a function of u are:

$$P(\theta) = 1 - \langle N_z\rangle u/3 + \ldots \tag{4}$$

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Therefore the initial slope of the curve $P^{-1}(\theta)$ as a function of $\sin^2 \theta/2$ gives, as is well known, the radius of gyration or the end-to-end distance of a chain having a z-average molecular weight.

On the other hand, for large values of u, $P_N(\theta)$ reduces to its asymptotic value $2/Nu - 2/N^2u^2$ and the use of equation (2) gives:

$$P(\theta) = \frac{1}{\langle N_w \rangle} \frac{2}{u} \int f(N)dN - \frac{2}{\langle N_w \rangle u^2} \int \frac{f(N)}{N} dN \tag{5}$$

$$P^{-1}(\theta) = \langle N_w \rangle u/2 + \langle N_w \rangle / 2\langle N_n \rangle \tag{5'}$$

This expression shows that the use of the slope of the asymptote for the determination of the size of the molecules would give a dimension corresponding to molecules having the weight-average molecular weight. This shows also that, if $P^{-1}(\theta)$ is plotted as a function of u or any quantity proportional to $\sin^2 \theta/2$, the ratio of the initial slope, s_0, to the slope of the asymptote, s_∞, has the following value:

$$\frac{s_0}{s_\infty} = \frac{2}{3} \frac{\langle N_z \rangle}{\langle N_w \rangle} \tag{6}$$

and characterizes the breadth of the molecular weight distribution. Since $\langle N_z \rangle$ is always equal or larger than $\langle N_w \rangle$, s_∞/s_0 can have values between 0 and 3/2. Other useful information can also be obtained by considering the second term of the preceding expansion. This term represents the value of the intercept of the asymptote of the curve with the axis $u = 0$. It is also a quantity experimentally available, and gives us the ratio $\langle N_w \rangle / \langle N_n \rangle$. Since $\langle N_w \rangle$ is always equal to or larger than $\langle N_n \rangle$, this ordinate is always larger than 1/2. One sees too that if, instead of plotting $P^{-1}(\theta)$, one plots Hc/τ with the usual notation this intercept gives us directly the number average molecular weight.

To summarize, the determination of $P(\theta)$ over the whole range gives $\langle M_n \rangle$, $\langle M_w \rangle$, $\langle M_z \rangle$ and the characteristic dimension.

If $P^{-1}(\theta)$ is plotted as function of $\mu^2\langle \rho^2 \rangle$, all the curves have the same initial slope and their shape is only a function of polydispersity. Since it has been shown that the initial curvature is always smaller for a polydisperse system than for a monodisperse one[3] and since we know the position of the asymptote, it appears that the curve for a polydisperse case lies below that for a monodisperse one. The general curvature can change its sign and in extreme cases the whole curve can lie below the curve for a rod. It is interesting to note that a similar procedure can be applied to a polydisperse suspension of rods.

2. Effect of Branching

In order to evaluate the effect of branching, we assume that the distances between every pair of monomeric elements have a Gaussian distribution and therefore we can write:

$$P(\theta) = \frac{1}{N^2} \sum_i \sum_j \exp\{-up\} \tag{7}$$

In this expression the summation is extended to all pairs of elements of the chain and p is the number of links between elements i and j. (Since we assume that we have no cyclic structures, p is known without ambiguity.) Let us suppose now that the chain is formed with q branches having, respectively, $N_1, N_2 \ldots N_q$ elements:

$$N = N_1 + N_2 \ldots N_l + \ldots N_m + \ldots N_q$$

(We define a branch as a part of the chain lying between two branching points or one branching point and one end.) With these notations equation (7) can be written:

$$P(\theta) = \frac{1}{N^2}\left[\sum_{l=1}^{q} \sum_{i=1}^{N_l} \sum_{j=1}^{N_l} \exp\{-u|i-j|\} + \sum_{l \neq m} \sum_{i=1}^{N_l} \sum_{j=1}^{N_m} \exp\{-u(i+j+\lambda_{lm})\}\right] \tag{8}$$

where λ_{lm} is the number of links between the nearest elements of the branches l and m. Assuming that N is large, we can change the summation for i and j into integrations which gives:

$$P(\theta) = \frac{2}{Nu} + \frac{2}{N^2u^2}\left[-\sum_{l=0}^{q}(1 - \exp\{-uN_l\}) + \sum_{l<m}\sum \exp\{-u\lambda_{lm}\}(1 - \exp\{-uN_l\})(1 - \exp\{-uN_m\})\right] \tag{8'}$$

The complete evaluation of this sum is now possible when the exact structure of the chain is known. For instance for the Stockmayer's chain,[4] with four equal branches:

$$P(\theta) = \frac{2}{Nu} + \frac{4}{N^2u^2}[1 + 3\exp\{-Nu/2\} - 4\exp\{-Nu/4\}] \tag{9}$$

The first term of the expansion of equation (9) as a function of u gives the known value of the radius of gyration of this chain.[5] Equation (8') shows that the asymptotic behavior of $P(\theta)$ or $P^{-1}(\theta)$ is not modified by the branching and that $s_0/s_\infty = {}^2/_3(\rho^2/\rho_0^2)$, where ρ^2 is the actual radius of gyration and ρ_0^2 the radius of gyration of the same chain with N elements but without branching. The parameter ρ^2/ρ_0^2 has been introduced by Zimm and Stockmayer and has a very simple experimental meaning.

If, as usual, we plot $P^{-1}(\theta)$ as a function of $\mu^2\rho^2$, ρ^2/ρ_0^2 being always less than or equal to unity, it is seen that the branching will increase the general upward curvature. As an example, we have plotted in Figure 1 $P^{-1}(\theta)$ as a function of $\mu^2\rho^2$ for the three following cases: (*1*) Monodisperse coils; (2) polydisperse coils:

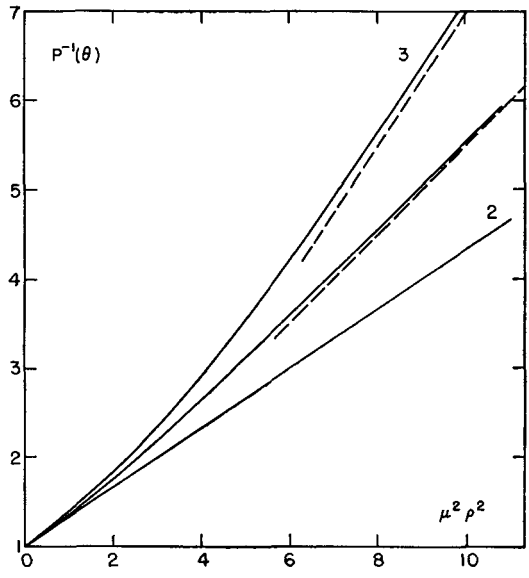

Fig. 1. Monodisperse coils (curve 1, middle curve), polydisperse coils (curve 2), cruciform molecules (curve 3).

$$f(N) = \frac{4N}{\langle N_w \rangle^2} \exp \{ - 2N/\langle N_w \rangle \}$$

following Zimm[2]; and (*3*) cruciform coil with four equal branches.

These considerations show that the precise determination, not only of the initial slope but of the whole $P(\theta)$ curve, is now highly desirable since it can give useful informations about branching or polydispersity providing only one of these two effects is present. If the two effects are present, we can only conclude that the asymptote permits the determination of the size of unbranched molecules with molecular weight $\langle M_w \rangle$.

References

1. P. Debye, *J. Phys. & Coll. Chem.*, **51**, 18 (1947).
2. B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
3. M. Goldstein, *J. Chem. Phys.*, in press.
4. W. H. Stockmayer and M. Fixman, Symposium on Branched Molecules, New York Academy of Sciences, 1953.
5. B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

H. BENOIT*

Gibbs Memorial Laboratory
Harvard University
Cambridge, Mass.

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* Permanent address: Strasbourg, France.