A New Approach to the Determination of Distribution Functions, Especially for Polymers

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Inherent weaknesses in current methods for the determination of molecular weight distribution functions are pointed out and a new method based on liquid-liquid distribution at equilibrium conditions is outlined.

The object in characterisation of a sample by fractionation methods is to determine the distribution function of the sample under study in respect to a chosen parameter. The experimental method involves a series of physical or chemical processes, resulting in a number of fractions, the weights of which are determined. From the experimental data the distribution function can then be calculated. The mathematical treatment is a simple one provided that any fraction does not contain such parts of the original sample, which appear in other fractions. This is the case for instance at the fractionation of spheres of different sizes by a series of screens.

If, and this is the important case, each fraction contains all types of units represented in the unfractionated sample, the problems become more complicated.

Let us assume that the original sample has a weight frequency function which, in respect to the separation parameter, γ, is

$$y = f(\gamma)$$

then the quantity of substance in the fraction numbered p can be written

$$W_p = \int_0^\infty F(\gamma,\ p) \cdot f(\gamma) \mathrm{d}\gamma \tag{1}$$

where $F(\gamma,p)$ is a function determined by the program used in the fractionation and by the nature of the physical or chemical process used.

The first condition required to solve the integral equation given in (1) with respect to $f(\gamma)$ using the experimentally determined W_p values is that the functions $F(\gamma,p)$ are known. These functions may be derived from theoretical considerations or from independent experiments. It is true that even with this function unknown, it is possible to characterize the sample by a relation between W_p and p, provided that the fractionating process is completely standardized. The basic information which was sought for is, however, not reached.

In the determination of molecular weight distribution functions of high polymers (see e. g. Ref.[1]) it is customary to utilize methods with maximum selectivity. Even so the fractions are far from homogeneous in molecular weight. It may very well be so that the width of the frequency function of single fractions are comparable to that of the original sample. The reaction mechanism in such fractionation methods is incompletely understood which, in other terms, implies that the function $F(\gamma, p)$, where now γ stands for the molecular weight, is unknown.

It is customary in the mathematical treatment of the experimental results of the type discussed to make some assumptions concerning the shape of the distribution functions of the fractions. In the method described by Mark and Raff[2] it is supposed that the fractional frequency curves are symmetrical and narrow. Beall[3], working on the basis that the fractional frequency curves "must tend to be unimodal", worked out a time-consuming but probably more reliable method. Such methods may imply a gross oversimplification especially at low and high molecular weights. The chief weakness of these methods is that basic assumptions are introduced at early stages of the calculations.

What possibilities exist to surmount these difficulties? The possibilities to derive the function $F(\gamma, p)$ theoretically or from experimental data seem small. In precipitation or dissolution fractionation methods knowledge regarding the relation between the activities of the polymer in the solution and the precipitate have to be known. Although such relations have been worked out by Huggins[4] and Flory[5], they are still incomplete and their usefulness in this case at least debatable. Experimental determination of the function $F(\gamma, p)$ requires access to preparations with unique molecular weight or known distribution functions. Preparations of polymers of medium or high DP undisputably of this type are unknown.

The solution must consequently rest in a new method of fractionation, where the mechanism of reaction is known. As far as the authors know nobody has explicitly stated that the problem is composed of two parts. The first part is to determine the distribution function with respect to some suitable parameter. The second part is to determine a relation between this parameter and the molecular weight. Only then the molecular weight distribution function can be derived. The method should preferably be chosen in such a way that the function $F(\gamma, p)$ is theoretically known.

The reason why it is desirable to treat the problem in this way is that the relation between the parameter and the molecular weight is not necessarily a monotonous function. Thus Morey and Tamblyn[6] investigating the precipitation method report that low molecular weight material under certain conditions can precipitate before high molecular weight material.

Let us discuss the possibilities to solve the problem. It seems obvious that only a chemical equilibrium method can be useful. This implies that diffusion methods or chromatographic methods have to be ruled out.

The liquid distribution methods, closely related to the precipitation and dissolution methods, can, however, be expected to fulfill the requirements. Such a method has been used by Schulz and Nordt [7]. They concluded that the method is relatively ineffective in fractionation. These writers have, however, used different composition of the liquid system at different stages of the fractionation procedure. Such a procedure is certainly efficient if the object is to obtain fractions of as widely different molecular weights as possible, but if the object is to determine the molecular weight distribution function of the original sample it will result in the same difficulties as classical precipitation procedures.

It must be a pre-requisite that the fractionation parameter γ is kept constant for every type of molecules present at all steps of the fractionation.

If the partition coefficient is chosen as the parameter this implies that it is necessary to have constant composition of the liquid system at all steps in the procedure.

It is obvious that this will lead to a decreased fractionation effect, but this can be compensated by a method of multiplication. The Craig countercurrent system seems to lend itself admirably to investigations of this type. Countercurrent fractionation according to related principles for high polymers have been used successfully by Swenson and coworker [8,9] in this laboratory. His method did, however, not involve equilibrium conditions.

In a series of papers of one of the authors the possibilities to apply countercurrent methods to this problem will be analyzed theoretically and experimentally. It will be shown that if the polymer is distributed between two immiscible liquids in a counter current apparatus the quantity of polymer in each fraction can be written

$$W_p = \binom{n}{p} \int_0^\infty \frac{k^p}{(1+k)^n} f(k) \, \mathrm{d}k$$

where k is the partitition coefficient for a specific size of molecules and $f(k)$ denotes the weight frequency function for the polymer with respect to the parameter k. The number of the fractions is p $(p = 0,1,2\ldots\ldots n)$, the total number of fractions being $n + 1$. From this integral equation $f(k)$ can be derived by a properly chosen approximation method.

If the average molecular weight $\overline{M}_p$ in each fraction is determined experimentally one can write

$$\overline{M}_p^a = \frac{1}{W_p} \cdot \binom{n}{p} \int_0^\infty \frac{k^p}{(1+k)^n} \cdot f(k) \cdot M^a \, \mathrm{d}k$$

where a is a parameter fixed by the conditions of the method [10]. Because $f(k)$ is known it is possible to calculate M as a function of k. The molecular weight frequency function can be derived from the formula

$$g(M) = f(k) \cdot \frac{dk}{dM}$$

DISCUSSION

The principle for the determination of molecular weight distribution functions outlined has its merits in the possibilities of a more precise mathematical treatment than is theoretically possible with earlier used methods.

From a practical point of view it is first of all necessary to find a pair of immiscible liquids, both being solvents for the polymer to be studied. It seems probable that such systems are not easily found except in a few cases, but already the existence of one such system may allow studies leading to deeper insight into the laws of high polymers.

It is also necessary that a thermodynamic equilibrium is reached when the polymer is distributed between the liquids. Interaction between molecules of different size should be negligible, or in other words the partition coefficient shall be independent of the presence of reasonable quantities of other size molecules. From a mathematical point of view this means that the function $F(\gamma, p)$ shall be independent of the molecular frequency function of the sample.

Only experimental studies can ascertain whether the mentioned conditions can be realized. Preliminary experiments with polyglycols and two phase liquid systems composed of trichloroethylene, chloroform, ethanol and water are promising, and detailed results will be published.

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