

Phase Equilibria and Fractionation of Linear Homopolymers in Solution: A Thermodynamic Numerical Interpretation

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Synopsis

A numerical procedure is described for the quantitative interpretation of experimental fractionations by successive precipitations. The analysis is based on a thermodynamic relationship ($mp''/mp' = A \cdot B^p$) between the masses of a polymeric component with degree of polymerization, p , distributed between two liquid phases in equilibrium (mp'' and mp') and the parameters A and B , which are independent of the degree of polymerization but functions of the thermodynamic variables. An individual pair of A and B parameters corresponds to every individual fraction. The numerical procedure, which is iterative in nature, provides the means for calculating the molecular-weight distribution of the individual fractions. The procedure requires data from the experimental fractionation (number-average degree of polymerization and total mass fraction of each fraction) and knowledge of the molecular-weight distribution function of the whole, starting polymer. The procedure was applied to the analysis of the results of two experimental fractionations of polyamide 11, whereby convergence was quickly reached after a few iterations in the calculations of every set of A and B parameters.

INTRODUCTION

The experimental study of relationships between properties and molecular weight of linear homopolymers constitutes the basis for their physical and physicochemical characterization. Most synthetic polymers, because of the mechanistic nature of the methods of preparation, exhibit varying degrees of polydispersity in regard to molecular weight, whereby the above-mentioned studies must be carried out on samples of different molecular weights obtained by fractionation procedures. To this end, the fractionation method employed must fulfill the following conditions:

1. It must produce samples that span a convenient range of molecular weight.
2. The fractions must exhibit a narrow distribution of molecular weights.
3. The yield of polymer on each step of the fractionation must be sufficiently large as to allow for the application of analytical techniques to the individual fractions.

These conditions, especially the last two, are mutually contradictory, and the literature shows a large variety of fractionation methods that undertake to fulfill them simultaneously.

One of the procedures most widely employed, because it requires only a

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solvent and a nonsolvent for the polymer, is the one based on successive precipitation of fractions.

The aim of this communication is to describe a numerical procedure for the quantitative interpretation of the results of fractionations by successive precipitation. The method provides the means for calculating the molecular weight distribution of the individual fractions, and for judging to what extent the above-mentioned second condition is met. In order to illustrate the performance of the procedure, it will be applied to the analysis of two fractionation-by-precipitation processes carried out on two different samples of polyamide 11, with *m*-cresol and ethyl alcohol as solvent and precipitant, respectively.¹

FOUNDATION OF THE METHOD

The numerical analysis is based on the thermodynamic relationship expressed by eq. (1), which was first derived by Schulz² and later confirmed, theoretically, by Flory³ and, experimentally, by Breitenbach and Wolf⁴ and Kamide et al.⁵

$$\frac{m''_p}{m'_p} = A \cdot B^p$$

where m''_p and m'_p are the masses of the polymeric components with degree of polymerization, p , distributed between the liquid phases in equilibrium (gel, double primed; and sol, primed, respectively). To each step of the fractionation (denoted by a subindex, j) there corresponds a pair of parameters, A and B . They are independent of the degree of polymerizations but are functions of the thermodynamic variables (composition, pressure, and temperature).

A direct derivation of the analytical expressions for the A and B parameters based on the Flory-Huggins theory, however, is impaired by the inherent limitations of the theory, and by the pseudoternary nature of the system (solvent, nonsolvent, polymer) which would require the use of a large number of semiempirical constants.

In this paper, therefore, we present a method for the numerical evaluation of the whole set of A and B parameters, which requires only data from the experimental fractionation (m''_j = total mass of polymer in the j th fraction, and $P''_{n,j}$ the number-average degree of polymerization of the j th fraction) and the knowledge of the molecular-weight distribution function of the starting polymer.

The whole procedure is based on the quantities m''_j and $P''_{n,j}$, which can be directly obtained from the experimental fractionation, or, alternatively, can be analytically set forth after the relationship expressed in eq. (1), according to the scheme of the fractionation method. Furthermore, although the analytical expression (eq. 2 and 3) cannot be solved for A and B by direct inversion, it is still possible to obtain calculated values of the quantities m''_j and $P''_{n,j}$, postulating arbitrary, initial values of A and B , and assuming a distribution function for the molecular weight of the whole polymer. Evaluation of the differences between the experimental and the calculated values of these quantities leads to better approximated parameters A and B and provides the foundation for the iterative procedure.

THE ITERATIVE PROCEDURE PROPER

Equations (2) and (3) show functional relationships between the m_j'' and $P_{n,j}''$ quantities with the parameters A_j and B_j

$$(m_j'')_{\text{calc.}} = \int_0^\infty m_{p,j}'' dP \quad (2)$$

$$(u_j'')_{\text{calc.}} = \frac{m_j''}{P_{n,j}''} = \int_0^\infty m_{p,j}'' \cdot P^{-1} dP \quad (3)$$

where

$$m_{p,j}'' = Q_{p,j} \frac{A_j \cdot B_j^p}{1 + A_j \cdot B_j^p} \cdot m_p$$

is the total mass of p-mers in the gel phase of the j th equilibrium, and

$$Q_{p,j} = \prod_{k=1}^{j-1} \frac{1}{1 + A_k \cdot B_k^p}$$

is the fraction of p-mers in the sol phase of the $(j - 1)$ th equilibrium.

The mass fraction of polymers in the initial polymer (m_p), required to carry out the calculations, follows immediately from the molecular-weight distribution function of the whole polymer. It becomes necessary then to postulate a function for the unknown distribution. In the case of polyamides, because they are produced by means of polycondensation processes, it is reasonable to assume a "most-probable" or Flory-Schulz distribution.⁶

$$m_p = \frac{P}{DP_n^2} \exp - \frac{P}{DP_n}$$

It will be shown later that the convergence of the iterations seems to provide an empirical criterion in regard to the proper choice of the distribution function.

The procedure then starts with a pair of initial, reasonable values (A_j^0 ; B_j^0) for the A and B parameters of the first fraction ($j = 1$) to calculate the first, approximated values of m_j'' and u_j'' .

The differences $\Delta m_j'' = (m_j'')_{\text{exp.}} - (m_j'')_{\text{calc.}}$ and $\Delta u_j'' = (u_j'')_{\text{exp.}} - (u_j'')_{\text{calc.}}$ between the experimental and calculated values of m_j'' and u_j'' are now attributed to the errors on the values of the initial, arbitrary parameters A_j^0 and B_j^0 , whereby the following system of equations can be set up:

$$\Delta m_j'' = \frac{\partial m_j''}{\partial A_j} \delta A_j + \frac{\partial m_j''}{\partial B_j} \delta B_j \quad (4)$$

$$\Delta u_j'' = \frac{\partial u_j''}{\partial A_j} \delta A_j + \frac{\partial u_j''}{\partial B_j} \delta B_j \quad (5)$$

Because the differences $\Delta m_j''$ and $\Delta u_j''$ are known, and the partial derivatives can be analytically obtained from eqs. (2) and (3), the system is immediately solvable for δA_j and δB_j , providing a new pair of better approximated A_j and B_j values, i.e., $A_j^1 = A_j^0 + \delta A_j$ and $B_j^1 = B_j^0 + \delta B_j$. The cycle is then repeated until the differences $\Delta m_j''$ and $\Delta u_j''$ are smaller than some pre-established limits. In our case, it required between 5 and 10 iterations to reach values of the differences comparable to or smaller than the respective experimental errors. From a practical point of view, and in order to smooth the convergence of the process, it is usually convenient to divide the calculated increments by a number between 1 and 10.

RESULTS AND DISCUSSION

Table I illustrates the performance of the numerical method in interpreting the results of actual experimental fractionations. The experimental work¹ was carried out on two different samples of polyamide 11, and the data related to number-average degree of polymerization (\overline{DP}_n), intrinsic viscosity, and relative mass of each individual fraction are indicated in Table 5 of the preceding paper.¹

With the help of the whole set of calculated pairs A_j and B_j , it is possible to estimate the weight-average molecular weight (\overline{M}_w) and the ratio $\overline{M}_w/\overline{M}_n$ for each individual fraction of polyamide (Table I). The latter provides an index on the fractions³ polydispersity, and it is immediately apparent that they all display a distribution of molecular weights comparable to that of the original, unfractionated polymer. Clearly, then, the employed¹ sol-

TABLE I
Calculated A_j and B_j Parameters for the Experimental Fractionation of Commercial (Cl) and Postpolymerized (PPI) Samples of Polyamide 11, Together with the Corresponding Experimental \overline{M}_n and Calculated \overline{M}_w

Fraction	Mass Fraction	\overline{M}_n	A_j	B_j	\overline{M}_w	$\overline{M}_w/\overline{M}_n$
Cl-1	0.020	18500	0.00963	1.00471	36600	1.98
Cl-2	0.069	18300	0.03360	1.00510	35500	1.94
Cl-3	0.069	16500	0.04317	1.00432	31800	1.93
Cl-4	0.064	15400	0.04801	1.00381	29600	1.93
Cl-5	0.198	14000	0.21173	1.00362	27084	1.93
Cl-6	0.124	12600	0.19788	1.00255	24300	1.92
Cl-7	0.149	12200	0.33890	1.00307	23400	1.92
Cl-8	0.081	11200	0.28288	1.00210	21400	1.91
Cl-9	0.041	10300	0.21080	1.00060	19800	1.92
Cl-10	0.083	10000	0.78735	1.00054	19400	1.94
Cl-11	0.044	9100	0.99760	0.99742	17800	1.95
Cl-12	0.056	8400	—	—	—	—
PPI-1	0.255	37600	0.25517	0.10077	89700	2.38
PPI-2	0.315	33900	0.60447	1.00052	80154	2.36
PPI-3	0.127	31800	0.37241	1.00037	75000	2.36
PPI-4	0.233	29700	3.45160	1.00019	69700	2.35
PPI-5	0.070	22700	—	—	—	—

vent/nonsolvent system possesses a limited fractionating capability, and does not fulfill the above-mentioned condition concerning the polydispersity of the fractions. However, because the numerical method is capable of calculating the molecular-weight distributions of the individual fractions, the measurements of properties that depend on degree of polymerization could be corrected for polydispersity, thus avoiding the difficulties encountered with fractions having broad distribution of molecular weights. In addition to the results presented in Table I, the behavior of the iterations in regard to convergence constitutes an important criterion to judge the feasibility of the method. A typical example is shown in Table II, which displays the evolution of all parameters involved in the application of the method to the first fraction of commercial nylon 11. The data in the table make it clear that, with properly chosen initial parameters and dividers of the increments, the best-approximated values of A and B are quickly approached, and that further iterations do not produce any further appreciable changes.

Also, in order to assess how the assumed distribution of molecular weights affects the outcome of the calculation, the numerical procedure has been carried out with the experimental data corresponding to the fractionation of commercial nylon 11, but assuming distributions with degrees of polydispersity U ($U = (\overline{DP}_w/\overline{DP}_n) - 1 = k^{-1}$) of 0.5, 1.03, and 1.5. The mass fraction of polymers (m_p) in the initial polymer is then calculated with the general equation:⁶

$$m_p = \frac{k^{k+1}}{\overline{DP}_n \cdot k_i} (p/\overline{DP}_n)^k \exp(-k \cdot p/\overline{DP}_n)$$

The results of the calculation, quoted in Table III, seem to suggest that the convergence of the iterations is achieved for an ever decreasing number of fractions, as the assumed polydispersity deviates from the actual value of sample.

TABLE II
Calculation of the Parameters A_j and B_j for the First Fraction ($j = 1$)
of Commercial Nylon 11

Steps	$-\Delta m_j'' \times 10^6$	$-\Delta u_j'' \times 10^8$	$-\delta A_j \times 10^6$	$\delta B_j \times 10^7$	A_j	B_j
1	30,000	10,000	200,000	69300	0.589	0.9970
2	20,000	5,000	60,000	42600	0.0300	1.0012
3	10,000	3,000	20,000	20900	0.0190	1.0033
4	10,000	1,000	10,000	9420	0.0142	1.0042
5	7,000	800	5,000	3580	0.0119	1.0045
6	4,000	400	2,000	1020	0.0107	1.0047
7	2,000	200	1,000	205	0.0102	1.0047
8	1,000	100	600	30	0.0099	1.0047
9	600	60	300	5	0.0098	1.0047
10	300	30	100	1	0.0097	1.0047
11	100	10	70	1	0.0096	1.0047
16	3	1	1	1	0.0096	1.0047

^a Experimental $m_j'' = 0.0205$ g, experimental $u_j'' = 0.203 \times 10^{-3}$. Limits of the integrations $P_1 = 1$ to $P_2 = 1600$. The iterations were started with $A^0 = 0.15$ and $B^0 = 0.99$.

TABLE III
 Numerical Calculations of the A_j and B_j Parameters for the Fractionation of the Commercial Sample CI, Assuming Different Values of the Polydispersity Factor U

Fraction	A_j			B_j		
	$U = 0.5$	$U = 1.03$	$U = 1.5$	$U = 0.5$	$U = 1.03$	$U = 1.5$
1	0.009	0.009	0.011	1.0056	1.0047	1.0023
2	0.035	0.033	0.048	1.0059	1.0051	1.0019
3	0.050	0.043	0.062	1.0039	1.0043	1.0011
4	0.061	0.048	0.071	1.0025	1.0038	1.0006
5	0.327	0.211	0.343	1.0004	1.0036	1.0000
6	0.395	0.198	0.431	0.9965	1.0025	0.9779
7	1.021	0.339	0.888	0.9933	1.0030	0.9964
8	1.854	0.238	1.264	0.9850	1.0021	0.9929
9	5.776	0.210	—	0.9695	1.0006	—
10	—	0.787	—	—	1.0005	—
11	—	0.997	—	—	0.9774	—
12	—	—	—	—	—	—

Finally, it has not escaped our attention that this numerical analysis of the fractionation constitutes a genuine alternative procedure to the absolute methods for measuring \bar{M}_w . This is a remarkable accomplishment, especially useful within the range of molecular weights discussed in this paper where absolute methods, like light scattering, are faced with operational difficulties.

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