

Comments on Preparation of Broad-Distribution Poly(vinyl Chloride) Samples by Recombining Fractions

JOHN C. YINGST* and RICHARD P. CHARTOFF, *Department of Chemical and Nuclear Engineering, University of Cincinnati, Cincinnati, Ohio 45221*

INTRODUCTION

Whole polymer samples of poly(vinyl chloride) have reasonably narrow (\bar{M}_w/\bar{M}_n 2-4) molecular weight distributions (hereafter referred to as MWD). In order to prepare broad-distribution samples (\bar{M}_w/\bar{M}_n of 10 or more) for rheological studies, we have been working on recombining PVC fractions obtained by precipitation fractionation.^{1,2} The analysis that follows is used in the subsequent discussion of experimental results.

If a polymer is fractionated into n fractions, then the cumulative weight fraction $C(M_i)$ for the i th fraction can be computed by adding one half its weight fraction, w_i , to the weight fractions of all previous fractions, as shown in eq. (1). The cumulative weight fraction $C(M_i)$ is usually associated with the integral distribution function $I(M)$ where $C(M_i)$ represents a discrete set of experimental data points and $I(M)$ represents a smooth curve connecting the data points:

$$C(M_i) = \frac{1}{2} w_i + \sum_{j=1}^{i-1} w_j \quad (1)$$

where $C(M_i)$ = cumulative weight fraction for the i th fraction, M_i = average molecular weight of the i th fraction, and w_i = weight fraction of the i th fraction, i.e., weight of the i th fraction divided by the total polymer weight.

If the MWD of the whole polymer follows the Tung distribution function,³ it is described by

$$W(M) = yz e^{-yM^z} M^{z-1} \quad (2)$$

where $W(M)$ is related to the integral function $I(M)$ as follows:

$$W(M) = dI(M)/dM \quad (3)$$

Since experimentally $I(M)$ is equivalent to $C(M)$, a straight line may be obtained by plotting $\ln [1/1 - C(M)]$ versus M on log-log graph paper for the fractions. The slope of the line is z and the intercept is y .

The procedure described may be reversed to prepare a polymer with desired weight- and number-average molecular weights from a number of fractions of

* Present address: Monsanto Polymers & Petrochemicals Co., Addyston, Ohio, 45001.

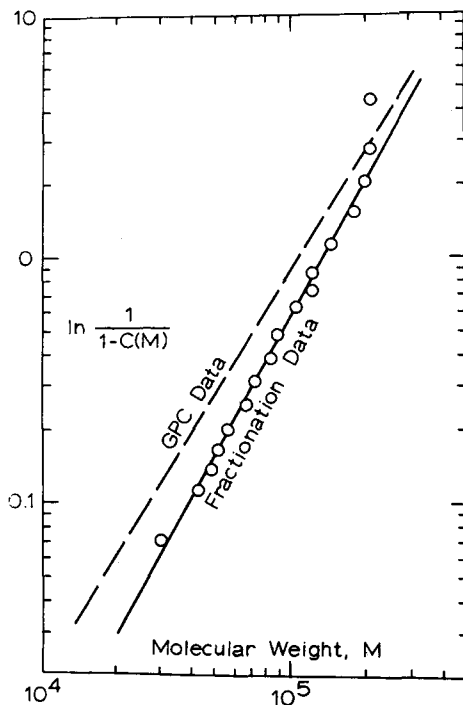


Fig. 1. PVC-1 fractionation data and GPC data plotted as $\ln [1/1 - C(M)]$ vs. M .

known average molecular weight. A plot of $\ln[1/1 - C(M)]$ versus M can be generated on log-log graph paper by using eq. (4)

$$\ln \frac{1}{1 - C(M)} = yM^z. \quad (4)$$

Here, the y and z values are calculated from the appropriate Tung function expressions relating \bar{M}_n and \bar{M}_w :

$$\bar{M}_w/\bar{M}_n = \Gamma\left[1 + \frac{1}{z}\right]\Gamma\left[1 - \frac{1}{z}\right] = \frac{\pi/z}{\sin \pi/z} \quad (5)$$

and

$$y = \left[\frac{\Gamma\left(1 + \frac{1}{z}\right)}{\bar{M}_w} \right]^z \quad (6)$$

where Γ is the gamma function.

Using values of M_i for the polymer fractions, values of $C(M_i)$ may be found from the appropriate Tung plot relating $C(M)$ to M for the modified MWD polymer. These values may in turn be used to find values of w_i by using eq. (7). Equation (7) is derived by rearranging eq. (1):

$$w_i = 2 \left[C(M_i) - \sum_{j=1}^{i-1} w_j \right]. \quad (7)$$

An objective of our experiments is to generate a broader MWD polymer while still retaining the weight-average molecular weight, \bar{M}_w , of the original polymer prior to fractionation. In order to do this, less of the "middle" molecular weight

fractions and more of the "high" molecular weight and "low" molecular weight fractions must be used in the recombination stage of the preparation. An example is given in the following narrative.

Before proceeding, however, some preliminary comments concerning the example are in order. First of all, we wish to emphasize that the ratio \bar{M}_w/\bar{M}_n does not uniquely define a MWD. For a given value of \bar{M}_w/\bar{M}_n , a polymer sample may have various distributions. The Tung function is only one of several empirical functions⁴ which are used to fit fractionation data. The value of a distribution such as Tung's depends on the actual polymer fitting it. In our work, this function was tested because of the success others have had with it in fitting PVC data.⁵ It is apparent from Figure 1 that it fits the data presented subsequently about as well as one could expect. Another two-parameter function, the most probable distribution, does not yield as good a fit to the data.¹ Thus, the presentation in this paper concentrates on fitting the Tung distribution to experimental data and preparing a Tung distribution of predetermined \bar{M}_w/\bar{M}_n from isolated fractions:

EXPERIMENTAL

Materials

In this paper, experimental data for three PVC samples are discussed: PVC-1, a commercial-grade material with \bar{M}_w 102,700 and \bar{M}_w/\bar{M}_n 2.15; PVC-2, a commercial-grade PVC with \bar{M}_w 73,900 and \bar{M}_w/\bar{M}_n 2.39; and PVC-3, a more crystallizable material, with \bar{M}_w 86,000 and \bar{M}_w/\bar{M}_n 2.80. All three were polymerized in suspension; PVC-1 and PVC-2 at 50°C; and the third, PVC-3, at -15°C.

Data and Discussion

A preparative fractionation was carried out on 44.4 g PVC-1 by precipitation fractionation using the THF-water solvent-nonsolvent system.^{1,2} Molecular weight data for the fractions were obtained by GPC and are listed in Table I along with the appropriate yield data. The data indicate good separation with respect to molecular weight, as shown by the low \bar{M}_w/\bar{M}_n values of fractions 6 through 17. A net yield of 96.11% for the fractionation indicates some polymer losses. These were due to low molecular weight material which could not be precipitated out at the end of the fractionation.

A log-log plot of $\ln [1/1 - C(M)]$ versus M for the data is shown in Figure 1. Both the straight line which best fits the data points and the straight line representing the GPC average molecular weights are drawn. Tung parameters for the fractionation data are listed in Table II along with the corresponding parameters calculated from GPC average molecular weights for the whole polymer. Values of \bar{M}_w and \bar{M}_w/\bar{M}_n for the Tung plot (Fig. 1) are listed in Table III along with the \bar{M}_w and \bar{M}_w/\bar{M}_n values calculated from the GPC data. Note that the Tung plot gives a higher \bar{M}_w but a narrower MWD than the GPC data. The major cause for this discrepancy is the poor data fit at the high molecular weight end of the distribution. Other contributing causes may be peak spreading in the GPC data, slight errors in the fractionation weight measurements, and the loss of 3.89% of low molecular weight material during fractionation (this unrecovered material is included in the GPC analysis of the whole polymer).

TABLE I
 PVC-1 Fractionation Data

Fraction	\bar{M}_w	\bar{M}_w/\bar{M}_n	Weight, g	Weight fraction	Cumulative wt. fraction ^a
1	206,900	2.09	1.535	0.0346	0.9827
2	201,300	2.00	2.449	0.0552	0.9378
3	191,200	1.59	3.221	0.0725	0.8740
4	181,400	1.49	5.164	0.1163	0.7796
5	146,000	1.41	3.975	0.0895	0.6767
6	121,400	1.36	4.303	0.0969	0.5835
7	120,800	1.39	1.540	0.0347	0.5177
8	104,700	1.33	3.379	0.0761	0.4623
9	88,900	1.30	3.770	0.0849	0.3818
10	83,200	1.29	1.302	0.0243	0.3247
11	72,500	1.26	2.682	0.0604	0.2798
12	66,700	1.26	1.905	0.0429	0.2282
13	56,000	1.23	1.720	0.0387	0.1874
14	51,000	1.22	1.131	0.0255	0.1553
15	44,400	1.22	1.056	0.0237	0.1307
16	43,100	1.25	0.933	0.0210	0.1083
17	30,300	1.30	2.608	0.0587	0.0685
			$\Sigma = 42.673$	$\Sigma = 0.9611$	

^a Calculated from eq. (1); original sample charge = 44.4 g; molecular weights determined by GPC.

 TABLE II
 Tung Parameters from PVC-1 Fractionation and GPC Data

	Tung parameters	
	Fractionation	GPC
z	1.84	1.59
y	3.395×10^{-10}	9.048×10^{-9}

 TABLE III
 PVC-1 Molecular Weight Averages from Fractionation and GPC Data

	\bar{M}_w	\bar{M}_w/\bar{M}_n
GPC	102,700	2.15
Tung	123,500	1.73

For the broad-distribution resins to be prepared by recombination, a weight-average molecular weight value of 100,000 was chosen, since it is close to that of the original PVC-1 whole polymer (102,000). Values of \bar{M}_w/\bar{M}_n were chosen to be 10 and 25. Log-log plots of $\ln [1/1 - C(M)]$ versus M corresponding to the above molecular weight averages were constructed on the same plot as the PVC-1 fractionation data (as shown in Fig. 2). Using the procedure described previously, values of $C(M)$ for each fraction were determined from Figure 2. In the figure, the procedure is illustrated graphically by arrows. For any desired broad-MWD polymer, a value of $\ln [1/1 - C(M)]$ corresponds to a polymer fraction with a certain molecular weight. From the $C(M)$ values obtained, w_i values were determined and the data listed in Table IV. As can be seen, very little "middle" molecular weight material is called for in the recombination.

TABLE IV
Weight Fraction Data for Broad-Distribution PVC Resins
Generated by Using the Tung Plot*

Fraction	$\bar{M}_w/\bar{M}_n = 10$			$\bar{M}_w/\bar{M}_n = 25$		
	$\ln \frac{1}{1-C(M)}$	$C(M)$	w_i	$\ln \frac{1}{1-C(M)}$	$C(M)$	w_i
1	2.20	0.889	0.222	2.14	0.882	0.236
2	2.20	0.889	—	2.14	0.882	—
3	2.04	0.870	—	2.04	0.870	—
4	1.81	0.836	0.006	1.81	0.836	—
5	1.48	0.772	0.052	1.48	0.772	0.042
6	1.22	0.705	—	1.25	0.713	0.018
7	1.20	0.699	0.042	1.21	0.701	0.006
8	1.02	0.639	0.078	1.05	0.650	0.096
9	0.84	0.568	—	0.86	0.577	—
10	0.80	0.551	0.098	0.83	0.564	0.076
11	0.68	0.493	0.018	0.70	0.503	0.046
12	0.62	0.462	0.044	0.64	0.474	—
13	0.50	0.393	—	0.533	0.413	—
14	0.455	0.366	—	0.482	0.382	—
15	0.421	0.345	—	0.458	0.367	—
16	0.370	0.309	—	0.400	0.330	—
17	0.249	0.220	0.440	0.275	0.240	0.480

* For both samples, $\bar{M}_w = 10^5$.

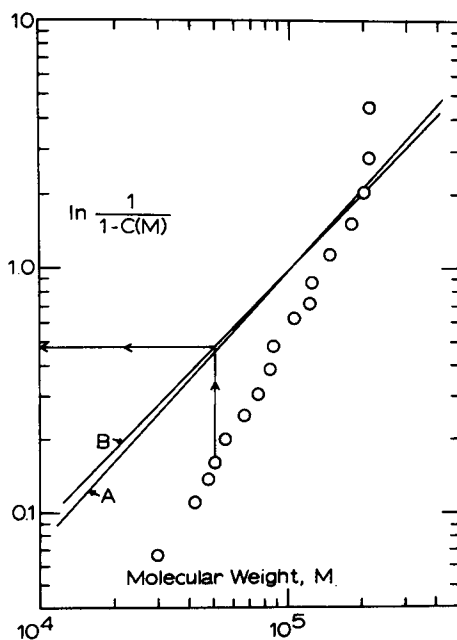


Fig. 2. Generation of $C(M)$ data for broad-distribution PVC samples from PVC-1 fractions using the Tung distribution function: (A) $\bar{M}_w = 10^5$, $\bar{M}_w/\bar{M}_n = 10$; (B) $\bar{M}_w = 10^5$, $\bar{M}_w/\bar{M}_n = 25$.

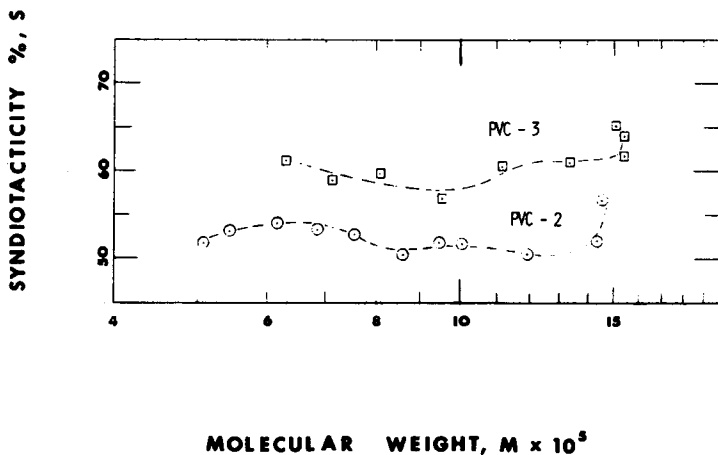


Fig. 3. Syndiotacticity index S vs. molecular weight for PVC-2 and PVC-3.

The recombination procedure was simulated by computer using the experimental GPC data for the fractions in the amounts shown in Table IV. The highest attainable \bar{M}_w/\bar{M}_n value was approximately 3.2, indicating a lack of sufficient high and low molecular weight material to broaden the \bar{M}_w/\bar{M}_n value to 10 or 25. The reasons for this are apparent if the $C(M)$ data in Tables I and IV are examined more closely.

The fact that the extremes of the \bar{M}_w/\bar{M}_n ratio are difficult to prepare by mixing is a consequence of the particular fractions available and has no direct relation to PVC itself. It is clear that both \bar{M}_w and \bar{M}_n must lie between the extremes of the fractions which comprise them. With the highest \bar{M}_w of 206,000 and lowest of 30,000, an \bar{M}_w/\bar{M}_n value as low as 3.2 is expected. According to the data for the $\bar{M}_w/\bar{M}_n = 10$ material, approximately 22% of the polymer must have molecular weight values lower than the lowest values found in the PVC-1 whole polymer; about 11% of the material must have molecular weights higher than the highest molecular weights found in the PVC-1 polymer. Since material is being called for on *both* ends of the PVC-1 molecular weight range, fractions from at least two other polymer samples, one with a moderately high average molecular weight and one with a low average molecular weight, are needed for an accurate preparation of the modified distribution. We are now carrying out preparative fractionations with other PVC samples in order to produce enough material of higher and lower molecular weights to prepare the specified broad-distribution PVC's.

It is important to note that the recombination procedure just described completely neglects the stereoregularity of the end product. The Tung plot (Fig. 1) shows that separation does not take place with respect to molecular weight at the beginning of the fractionation. This is the same behavior which is noted in the fractionations of two other PVC polymers reported elsewhere.^{1,2} Several authors⁶⁻⁹ have concluded that PVC molecules aggregate in solution so that the most highly syndiotactic portions of the whole polymer are associated. We have shown^{1,2} that during precipitation fractionation the high molecular weight aggregates come out of solution first. Thus, the syndiotacticity of the fractions varies.

Figure 3 illustrates the "syndiotacticity distributions" of PVC-2 and PVC-3. The index S represents the syndiotacticity values we obtained using the IR technique of Germar et al.¹⁰ These data indicate that the first fractions (high molecular weight) and the final fractions have greater S values than the central fractions.

For this reason it may be necessary to prepare a broad-distribution polymer with a given syndiotacticity distribution as well as a given MWD. To do so, at least two whole polymers with either different average stereoregularity values, different \bar{M}_w values, or both must be fractionated. At each value of M_i , fractions of equal (or nearly equal) molecular weight are blended such that

$$S_i = S_{i1} X_{i1} + S_{i2} X_{i2} \quad (8)$$

where S_i = syndiotacticity value of the i th fraction, S_{i1} = syndiotacticity value of the i th fraction from whole polymer 1, S_{i2} = syndiotacticity value of the i th fraction from whole polymer 2, X_{i1} = weight fraction of the i th fraction from whole polymer 1, and X_{i2} = weight fraction of the i th fraction from whole polymer 2. Note that

$$X_{i1} + X_{i2} = 1.0. \quad (9)$$

The average syndiotacticity values of the two whole polymers should be very far apart in order to provide a continuous range of syndiotacticity values to the desired polymer.

In this paper, we have introduced the new concept of fitting a modified molecular weight distribution polymer to a stereoregularity distribution as well. One of the problems in attempting to do this (as opposed to simply recombining the prepared fractions without regard to stereoregularity) is deciding what the stereoregularity distribution for a broad-MWD PVC should be. Before any further attempt to specify the stereoregularity distribution for a broad-MWD polymer can be made, much additional work must be done. Stereoregularity distributions for a number of commercial PVC samples should be determined, and these distributions should be examined for definite trends in syndiotacticity.

The data presented here also strongly suggest that much care must be taken to correctly interpret rheological data collected for PVC fractions. It is likely that the same precautions must be applied to studies done with fractions obtained from stereoregular polymers other than PVC.

References

1. J. C. Yingst, M. S. Thesis, University of Cincinnati, 1974.
2. J. C. Yingst and R. P. Chartoff, paper presented at Pittsburgh GPC Seminar, Pittsburgh, Pa., Oct. 1974.
3. L. H. Tung, *J. Polymer Sci.*, **20**, 495 (1956); *J. Appl. Polym. Sci.*, **10**, 375 (1966).
4. L. H. Peebles, Jr., *Molecular Weight Distributions in Polymers*, Interscience, New York 1971, Chap. 1.
5. L. H. Tung, in *Polymer Fractionation*, M. J. R. Cantow, Ed., Academic Press, New York 1967, Chap. E.
6. A. H. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 1093 (1972).
7. A. Crugnola and F. Danusso, *Polym. Lett.*, **6**, 535 (1968).
8. J. Lyngaae-Jorgensen, *J. Chromatogr. Sci.*, **9**, 331 (1971).
9. R. Salovey and R. C. Gebauer, *J. Appl. Polym. Sci.*, **17**, 2811 (1973).
10. V. H. Germar, K. H. Hellwege, and U. Johnsen, *Makromol. Chem.*, **95**, 52 (1966).

Received March 29, 1974

Revised May 22, 1974