

## NOTES

*GPC Calibration for Water-Soluble Polymers*

In a recent investigation of the free-radical polymerization of acrylamide in aqueous solution,<sup>1</sup> it was found that classical kinetics accurately predict the molecular weight distribution (MWD) of the synthesized polymer. Transfer to monomer controls molecular weights giving a linear polymer having the most probable distribution. This presents a convenient method of synthesizing water-soluble standards for GPC calibration. The linear polyacrylamide has a very broad MWD which is the most probable distribution. This broad MWD standard can be used to determine the GPC molecular weight calibration over a wide range of molecular weights. Mark-Houwink constants are available for polyacrylamide in water,<sup>1</sup> and these can then be used to construct a universal calibration curve for GPC. The universal calibration curve may then be used to construct molecular weight calibration curves for other water-soluble polymer. This statement should be qualified somewhat. To date, Benoit's universal calibration curve concept has not been proven valid for water-soluble polymers. It is likely, however, that the wide applicability of the universal calibration curve for water-soluble polymers will be experimentally verified in the near future.

This note reports the synthesis of two linear broad-MWD polyacrylamide standards having most probable distributions. In addition, a commercial polyacrylamide (Polyhall 402 manufactured by Stein-Hall Ltd.) has been characterized and may now also be used for GPC calibration.

## POLYMER SYNTHESIS

Two broad-MWD polyacrylamides, standards A and B, were synthesized in aqueous solution using a free-radical initiator, 4,4'-azobis-4-cyanovaleric acid (ACV) and isothermal polymerization.<sup>1</sup> The synthesis conditions were:

*Standard A:*  $T = 40^{\circ}\text{C}$ , monomer concentration = 0.281 moles/l., ACV concentration =  $7.14 \times 10^{-4}$  moles/l.

*Standard B:*  $T = 50^{\circ}\text{C}$ , monomer concentration = 0.563 moles/l., ACV concentration =  $1.43 \times 10^{-3}$  moles/l.

*Standard C:* Polyhall 402, a commercially available linear polyacrylamide manufactured by Stein-Hall Ltd. We were not supplied with any molecular weight information on this polyacrylamide.

## POLYMER CHARACTERIZATION

## Gel Permeation Chromatography

A Waters ALC/GPC Model 301 with five 4-foot columns of the following specifications was used: Bio-Glass, 2500 Å; CPG-10, 2000 Å; Porasil DX, 400-800 Å; Porasil CX, 200-400 Å; CPG, 125-240-370 Å. Carrier solvent, water and room temperature; sample concentration, 0.01 wt-%; flow rate, 3 ml/min.

Standard A, with theoretical differential MWD,

$$W(M) = \frac{M}{\bar{M}_n^2} \exp\left(-\frac{M}{\bar{M}_n}\right) \quad (1)$$

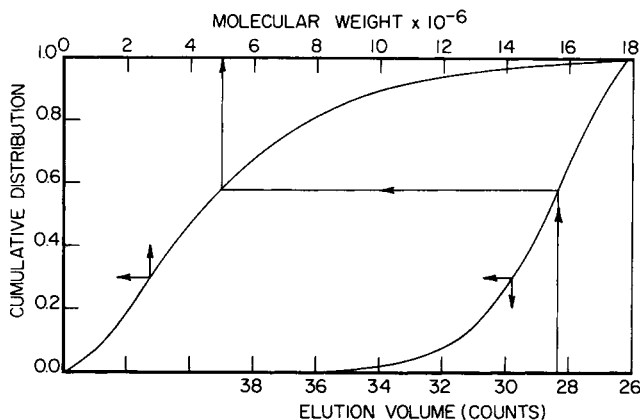


Fig. 1. Cumulative molecular weight distributions for standard A: theoretical and measured by gel permeation chromatography.

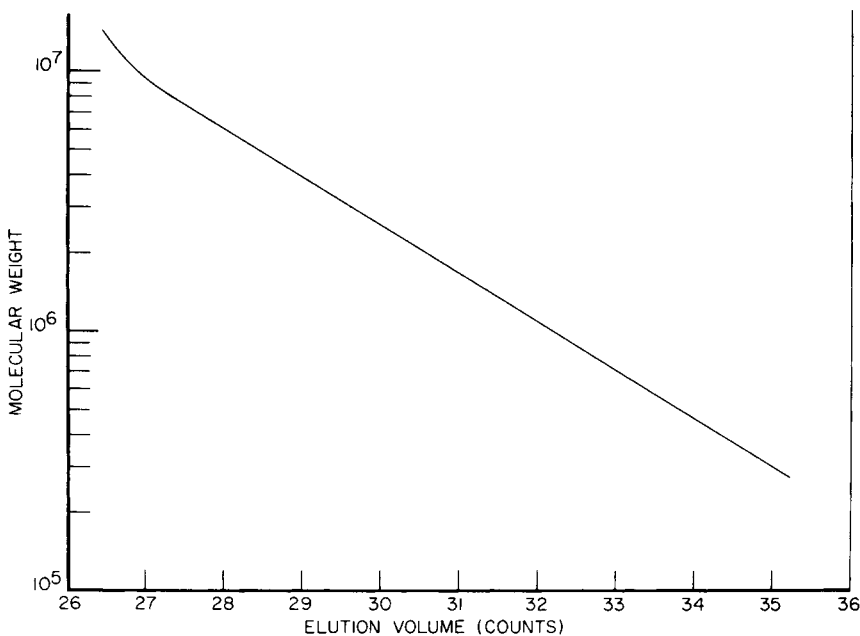


Fig. 2. Molecular weight calibration curve found using information in Fig. 1.

where  $M$  is molecular weight and  $W(M)$  is weight fraction, and  $\bar{M}_n = 2.52 \times 10^6$ ,  $\bar{M}_w = 5.04 \times 10^6$ ,  $\bar{M}_z = 7.56 \times 10^6$  was used to find the GPC molecular weight calibration curve. Figure 1 shows the cumulative most probable distribution and cumulative GPC chromatogram for standard A. The use of these curves as shown provided the molecular weight calibration in Figure 2. This technique of using a broad-MWD standard to obtain a molecular weight calibration curve which adequately corrects for axial dispersion was recently successfully applied by Swartz, Bly, and Edwards<sup>2</sup> and was first suggested by Cantow, Porter, and Johnson.<sup>3</sup>

The calibration curve in Figure 2 was then used to determine the MWD and molecular weight averages of standards B and C. Figure 3 shows a comparison of the MWD mea-

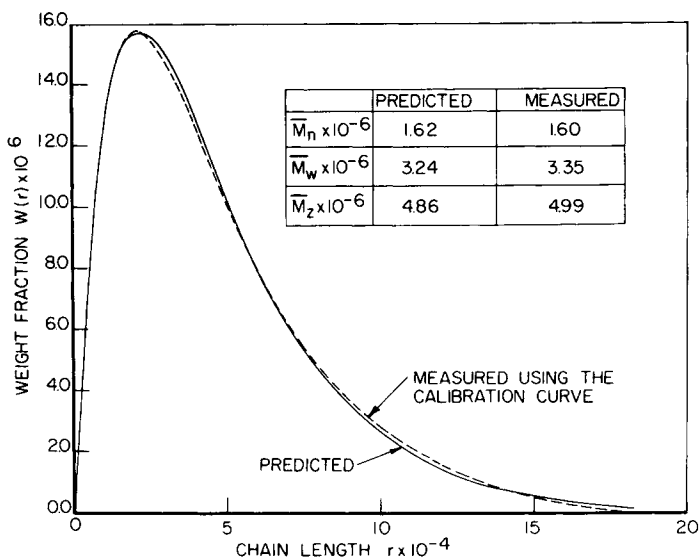


Fig. 3. Differential molecular weight distributions and averages for standard B: theoretical and measured by gel permeation chromatography. (Chain length  $r$  is equal to the polymer molecular weight divided by the monomer molecular weight.)

sured by GPC and eq. (1) with  $\bar{M}_n = 1.620 \times 10^6$ . Also shown is a comparison of molecular weight averages,  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ . The good agreement gives validity to the molecular weight calibration curve in Figure 2. The MWD by GPC for standard C is tabulated in Table I.

### Viscometry

Mark-Houwink equations for linear polyacrylamide in aqueous solution at  $T = 25^\circ\text{C}$  follow<sup>1</sup>:

$$[\eta] = 6.80 \times 10^{-4} \bar{M}_n^{0.66} \quad (2)$$

$$[\eta] = 4.54 \times 10^{-4} M^{0.66} \quad (3)$$

where

$$4.54 \times 10^{-4} = \frac{6.80 \times 10^{-4}}{\Gamma(2 + a)} \text{ and } a = 0.66$$

Equation (2) was proven valid for polyacrylamide having the most probable distribution,<sup>1</sup> and accordingly eq. (3) can be derived from eq. (2).

To further test the validity of our GPC molecular weight calibration curve in Figure 2, standard B was characterized by viscometry. Its intrinsic viscosity at  $25^\circ\text{C}$  in water was measured to be 8.17. The intrinsic viscosity of standard B measured by GPC was found to be

$$[\eta]_{\text{GPC}} = 4.54 \times 10^{-4} \int_0^\infty F(v)M(v)^{0.66} dv = 8.21$$

where  $F(v)$  is the normalized GPC detector response and  $v$  is the retention volume. The basis for this calculation may be found in Flory's text.<sup>4</sup> Finally, using eq. (2),

$$[\eta]_{\text{eq. (2)}} = (6.80 \times 10^{-4})(1.60 \times 10^6)^{0.66} = 8.45$$

TABLE I  
Molecular Weight Distribution and Averages for Standard C Measured by GPC Using  
Calibration Curve in Figure 2<sup>a</sup>

Molecular wt. $M \times 10^{-4}$	Differential MWD $W(M) \times 10^8$	Cumulative MWD
10.	2.22	
20.	4.19	0.0032
40.	7.43	0.0149
60.	9.90	0.0323
80.	11.73	0.0541
90.	12.45	0.0662
100.	13.05	0.0789
150.	14.68	0.1490
200.	14.77	0.2231
250.	14.05	0.2954
300.	12.93	0.3629
400.	10.44	0.4797
500.	8.25	0.5728
600.	6.54	0.6464
700.	5.26	0.7050
800.	4.29	0.7526
1000.	2.98	0.8243
1500.	1.301	0.9254
2000.	0.549	0.9692
2500.	0.220	0.9873

<sup>a</sup>  $\bar{M}_n = 2.40 \times 10^6$ ;  $\bar{M}_w = 5.83 \times 10^6$ ;  $\bar{M}_w/\bar{M}_n = 2.43$ .

This excellent agreement confirms the validity of the GPC calibration curve in Figure 2.

Standards A, B, and C may be obtained by contacting one of us (A.E.H.).

#### References

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Received May 10, 1973

Revised June 4, 1973