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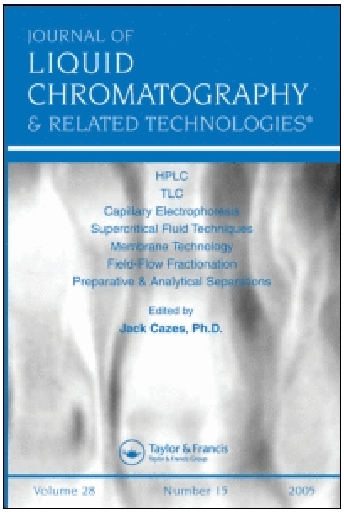

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# BIMODAL GEL PERMEATION CHROMATOGRAM OF ACRYLONITRILE-STYRENE COPOLYMERS

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## ABSTRACT

Gel permeation chromatograms were recorded for an acrylonitrile-styrene copolymer in both dimethylformamide (DMF) and DMF-LiBr-$H_2O$ as solvents. In the DMF solvent, a bimodal chromatogram was observed, while in the DMF-LiBr-$H_2O$ solvent, monomodal behavior was observed for the same sample. In order to investigate the cause for such behavior, the molecular weight averages of the copolymer were determined in these solvents. Further, the chromatogram in the former solvent was corrected for observed nonlinearity of the calibration curve. We concluded that apparent differences in the chromatograms are due, at best in part, to the nonlinearity. General conditions for the appearance of bimodal chromatograms were examined **based on this idea, using simulation techniques.**

## INTRODUCTION

Several studies have been reported concerning the determination of the molecular weight distribution (MWD) of acrylonitrile-styrene (AS) copolymers using precipitational and solution fractionation techniques.[1-4]

On the other hand, gel permeation chromatography (GPC) is more convenient for determining the molecular weight distributions of polymers, especially for homopolymers. However, GPC can often provide valuable information concerning the MWD of copolymers such as AS-copolymers.

An appropriate solvent had to be selected that would dissolve the copolymer and yet not degrade the column packing. A column set was selected that would provide resolution over the molecular weight range of interest. N,N-dimethylformamide was selected as eluent because AS-copolymers are soluble at all comonomer ratios. When we used this solvent in practice, however, bimodal curves appeared in the chromatograms similar to those that have been reported for acrylonitrile-vinyl ether copolymers.[5] However, addition of small amounts of $LiBr-H_2O$ to the DMF led to a smooth unimodal chromatogram for a sample that exhibited a bimodal distribution in DMF alone.

Some investigators consider that this may be due to the association of copolymer molecules to form large agglomerates.[3-6] However, there is no evidence to support this idea. We studied this phenomenon experimentally and analytically, and reached a conclusion that is different from that of previous investigators. This will be described in detail.

## EXPERIMENTAL

### Gel permeation chromatography

A Shimadzu GPC Model-1A was employed with a series of four columns: cross-linked polystyrene gels (Toyosoda TSK-Gel) of 1 x $10^6$, 1 x $10^6$, 1 x $10^5$ and 1 x $10^4$A permeability limits, operated at ambient temperature; flow rate was 1.0 ml/min.; polymer concentration 0.2 g/dl; solvent: DMF and DMF-0.2M $LiBr-H_2O$. The bimodal chromatogram recorded in DMF became unimodal by addition of at least 0.02M $LiBr-H_2O$. However, at higher concentrations the chromatograms were erratic. Therefore, the DMF-0.02 M $LiBr-H_2O$ solvent was adopted for obtaining unimodal chromatograms. Calibration curves were constructed with narrow distribution polystyrene standards (Pressure Chemical Corp. Pittsburgh, PA, USA). As shown in Figure 1, the calibration curves were shifted to higher elution counts with increasing amounts of $LiBr-H_2O$ in the solvent, and resolution was eventually degraded to the point where valid MWD's could not be obtained. Here the elution count means the number of lines marked in each 5 ml elution on chromatogram.

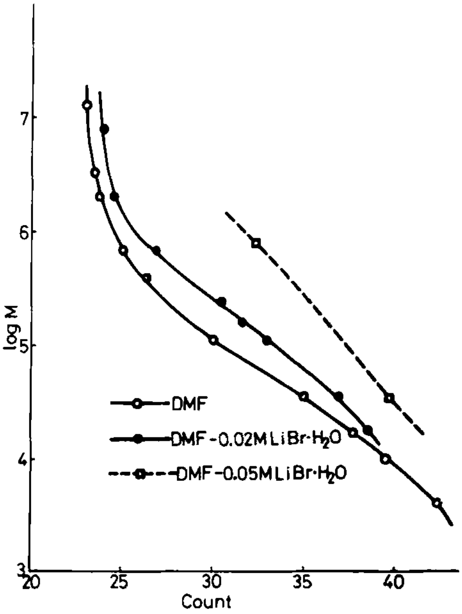

FIGURE 1. Calibration curves for polystyrene in different solvents.

## Viscometry and Osmometry

The intrinsic viscosities of the AS-copolymer were determined in the above two solvent systems at 30°C, with a Ubbelohde viscometer. To eliminate the effects of dust, intrinsic viscosity measurements were made after filtering solutions through two pieces of Alpha-6 filters, the pore size of which is 0.45μ (Gelman Instrument Co.). Particular attention was given to minimizing the effect of atmospheric moisture upon the measurements. The efflux time was measured using a viscometer Model-303B (Hewlett Packard Co.) with a repeatability of 0.01sec.

The number-average molecular weights were determined at 30°C with a Hewlett Packard Model-502 high speed membrane osmometer with an Allerfeinst grade of Ultracellafilter (Sartrius Co.). For example, when DMF was used as solvent, the membrane was pretreated by immersing it successively in water, water-isopropanol (50 : 50 vol.), isopropanol: DMF (75 : 25, 50 : 50, 25 : 75) and, finally, DMF. The same procedure, i.e., was applied to the other solvents, i.e., DMF-LiBr-$H_2O$ and methyl ethyl ketone (MEK).

## AS-copolymer

An experimentally polymerized AS-copolymer was used after washing with methanol. The acrylonitrile content, was determined by nitrogen analysis, is 27.8 ± 0.3wt.%. This value suggests that the polymer would be obtained in azeotropic copolymerization, that is, the sample was expected to be compositionally homogeneous and to have a smoothed molecular weight distribution. In fact, these were confirmed by solution fractionation.[7]

## RESULTS AND DISCUSSION

A GPC chromatogram was recorded for the AS-copolymer with DMF as solvent. Figure 2 shows that the chromatogram thus obtained has two peaks, whereas only a unimodal curve is observed when the DMF-LiBr-$H_2O$ is used. Kenyon and Mottus suggest that the cause of the bimodal character in acrylonitrile copolymers is related to association between polymer molecules and solvent.[5] Cazes, on the other hand, postulates that the phenomenon is due to aggregation of polymer molecules.[6] If the behavior is based on the association, some evidence should be afforded for the occurence of an equilibrium between monomolecular species and aggregated species or associated species. For example, the ratio of peak heights in the bimodal curve might change as

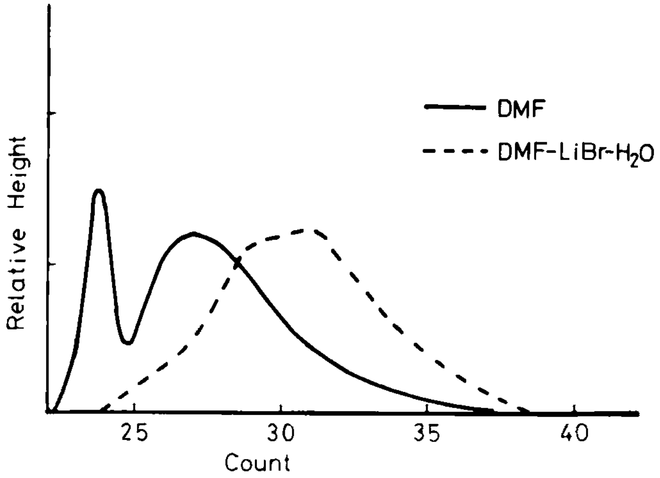

FIGURE 2. Chromatograms of a AS-copolymer in DMF and DMF-LiBr-$H_2O$.

the temperature of GPC operation is varied. However, no change was observed, even over a 90°C temperature range. Next, the number-average molecular weight for the copolymer was determined by osmometry in DMF, in DMF-LiBr-$H_2O$, and in MEK as a reference point. As shown in Table 1, no significant difference was observed among these solvents. Furthermore, the addition of LiBr-$H_2O$ to DMF did not lead to any appreciable difference in the intrinsic viscosities. These results suggest that the solution properties of the copolymer in DMF are almost the same as in DMF-LiBr-$H_2O$ and that neither association nor aggregation occurs in DMF.

As shown in Figure 3, the relative height of the earlier eluting peak in the bimodal curve increased with decreasing polymer concentrations. This fact supports the theory that the early eluting peak is not due to aggregation or association. Furthermore, this peak occurs at 23.5 counts, which just corresponds to that of an abrupt change in slope of the calibration curve. Therefore, it is considered that the early eluting peak may be due to this nonlinearity of the calibration curve. To prove this theory, the chromatogram must be corrected for that molecular weight distribution, which would be calculated by assuming a linear calibration. This procedure is as follows. Generally, the chroma-

TABLE 1 Number-average molecular weights and intrinsic viscosities of a AS-copolymer in different solvents.

| | DMF | SMF-LiBr-$H_2O$ | MEK |
|---|---|---|---|
| $\bar{M}_n$ | 67200 | 68800 | 66700 |
| $[\eta]$ (dl/g) | 0.756 | 0.748 | ----- |

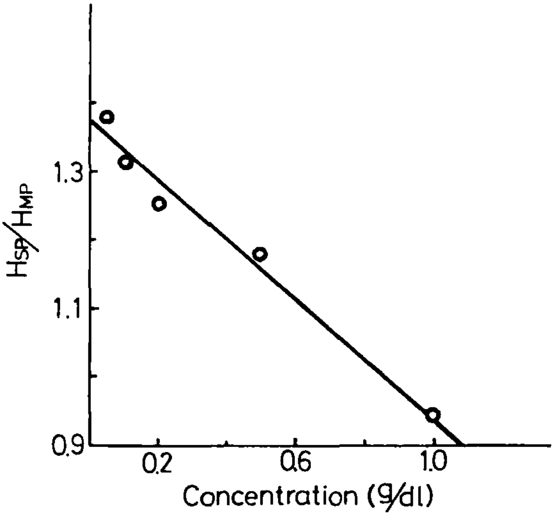

FIGURE 3. Concentration dependence of peak height ratio in bimodal chromatogram.
$H_{sp}$: height of early eluting peak, $H_{mp}$: that of later eluting peak.

togram $f(V)$ is related to the molecular weight distribution curve $f(\log M)$ by eq.(1).

$$f(V)\,dV = -f(\log M)\,d\log M \qquad (1)$$

The chromatogram $f_c(V)$ for linear calibration is derived from that for the observed one by eq.(2). This is hereafter called the corrected chromatogram.

$$f_c(V) = f_o(V)\left(\frac{dV}{d\log M}\right)\left(\frac{d\log M}{dV}\right)_c \qquad (2)$$

where $f_o(V)$ is the observed chromatogram, $dV/d\log M$ is the slope of the observed calibration curve, and $(d\log M/dV)_c$ that of linear calibration curve: a value of $-0.10$ is used for practical calculations.

The elution counts also must be converted to corrected ones with the following equation.

$$V = (\log M - \log M_o)\left(\frac{d\,v}{d \log M}\right)_c + V_o \qquad (3)$$

where $\log M_o$ and $V_o$ are the co-ordinates of an adequately fixed point; we use the values of 4.808 and 35.0, respectively, in the following calculation. The corrected chromatogram is obtained using eqs.(2) and (3), and is shown in Figure 4. Obviously the early eluting peak disappears with this correction. Consequently, we propose that of the early peak in DMF is due to the abrupt increase in the slope of the calibration in the lower count region. In other words, early eluting higher molecular weight copolymer species are inadequately resolved as a result of the shape of the calibration curve in this region of the chromatogram.

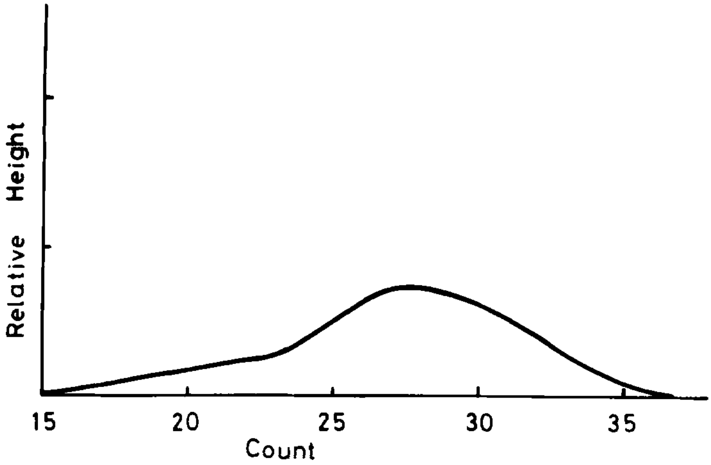

FIGURE 4. Corrected chromatogram obtained from bimodal one shown in Figure 1.

General conditions for the appearance of bimodal curve will be examined by assuming log-normal distribution functions for the molecular weight distribution. The chromatogram $f_o(V)$ for a curved calibration is given by eq.(4).

$$f_o(V) = f_c(V)\left(\frac{d \log M}{d V}\right)\left(\frac{d V}{d \log M}\right)_c \tag{4}$$

In this study, we assume that $f_c(V)$ is expressed by the following normal distribution function.

$$f_c(V) = \frac{1}{\sqrt{2\pi}\,\beta_s} \exp\left[-\frac{1}{2\beta_s^2}(V - V_o)^2\right] \tag{5}$$

where $\beta_s$ is the standard deviation, $V_o$ is the peak count, i.e., the elution count showing the maximum height in chromatogram. Eq.(5) shows that the molecular weight distribution is expressed by a log-noraml distribution function if the calbration curve is linear. This is expressed by eq.(6).

$$\log M = A V + B \tag{6}$$

where A and B are constants. Accordingly, $\beta_s$ can be correlated with the standard devitaiton $\beta_o$ of log-normal distribution function.

$$\beta_s^2 = \frac{\beta_o^2}{5.304 A^2} \tag{7}$$

Therefore,

$$\frac{\bar{M}_w}{\bar{M}_n} = \exp(\beta_s^2) = \exp\left(\frac{\beta_o^2}{5.304 A^2}\right) \tag{8}$$

We can easily obtain $\bar{M}_w/\bar{M}_n$ for the original distribution curves from eq.(8). The chromatogram for the curved calibration will be calculated using eqs.(3) and (4), and the effects of various factors on the shape of chromatograms will be clarified. An example is shown in Figure 5, in which 5.0 and 27.0 are adopted for $\beta_s$ and $V_o$, respectively. In this case, the chromatogram is obviously bimodal. Generally the broader the distribution, the larger the early eluting peak is. The height of the earlier peak decreases as the chromatogram shifts higher elution counts. Also, we should note that the corrected chromatogram, which is shown in Figure 4, is not symmetrical. The chromatogram for a curved calbration was calculated after combining two distribution functions in the proper ratio:

$$f_b(V) = f_1(V) + R\, f_2(V) \qquad (9)$$

where $f_b(V)$ is the combined distribution curve, $f_1(V)$

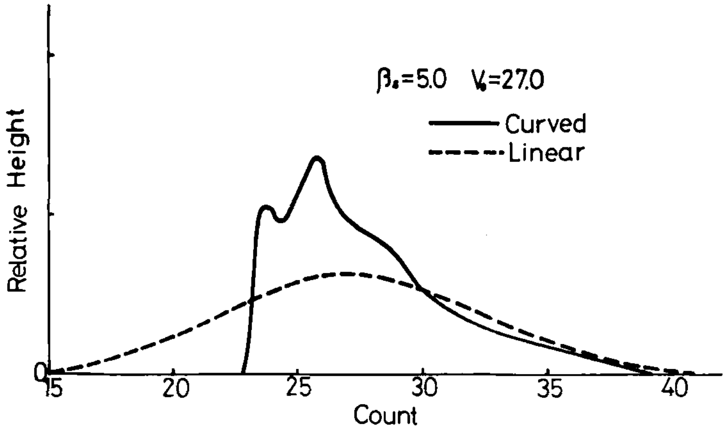

FIGURE 5. Chromatograms for linear and curved calibrations (calculated).

and $f_2(V)$ are the distribution curves expressed by eq. (5) with different values of $\beta_s$ and $V_o$, and R is the ratio of the areas of the two distribution curves. Figure 6 shows that the calculated distribution curve for a curved calibration is very similar in shape to the observed chromatogram (Fig.2) in DMF. Accordingly, it is believed that the observed chromatogram is a composite of two distribution curves.

When we use the DMF-LiBr-$H_2O$ solvent instead of DMF as eluent, the chromatogram changed from a bimodal to a unimodal curve. This phenomonon can be explained as follows. The chromatogram in the DMF-LiBr-$H_2O$ solvent is shifted, by 3.5 counts, towards higher elution counts. On the other hands, as shown in Figure 1, the

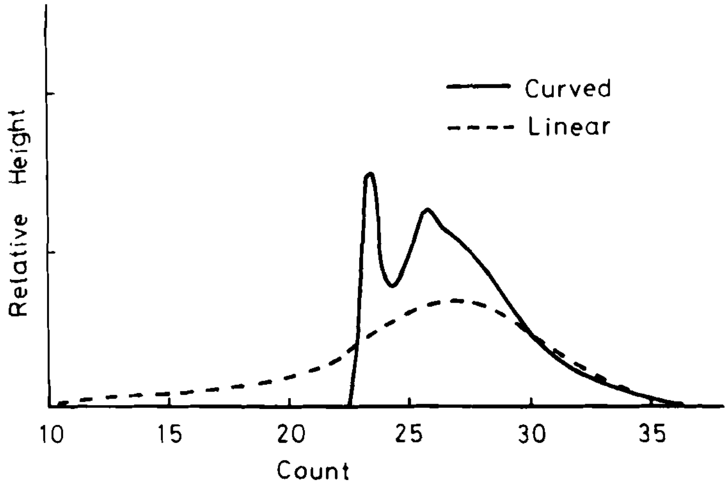

FIGURE 6. Chromatograms obtained by combining different two distribution curves with $\beta_1 = 3.5$, $V_1 = 27.0$, $\beta_2 = 4.0$, $V_2 = 18.0$ and $R = 0.15$, where $\beta_1$ and $\beta_2$ correspond to $\beta_s$, and $V_1$ and $V_2$ correspond to $V_o$ in eq.(5).

permeation limit of columns in GPC could not be expected to be appreciably changed even if LiBr was added to DMF. Accordingly, the chromatogram is located at a relatively distant position from the elution count where the slope of calibration abruptly changes and thus, it remains unimodal.

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