Salt Effect on Gel Permeation Chromatography of Partially Charged Polymers

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Synopsis

The effect of the addition of $0.1M$ LiBr to dimethylformamide (DMF) solutions of charged and uncharged polymers has been studied by GPC and $[\eta]$ measurements. LiBr has a salting-out effect on polyacrylonitrile (with (PAN-S) and without (PAN) sulfonate sulfur), polystyrene (PS), and poly (vinyl acetate) (PVAc), which is seen by a decrease in $[\eta]$ and an increase in the GPC retention time. The increase in retention time is, however, abnormally high for charged polymers. Association in PAN and PAN-S solutions in DMF can explain the experimental observations.

INTRODUCTION

The existence of charged groups in a polymer coil poses some special problems in interpreting the results of gel permeation chromatography (GPC). Following the idea of Benoit et al.,[1] the quantity which is measured in GPC is a hydrodynamic volume, given by the product $[\eta] \times M$. By measuring the count C at which the main portion of a polymer leaves the column and by using a calibration plot of log $([\eta] \times M)$ versus C, it is possible to calculate the product $[\eta] \times M$ of the unknown polymer. Any factor affecting the intrinsic viscosity $[\eta]$ is therefore going to change the hydrodynamic volume and the count at which a particular polymer appears.

Cha[2] has recently reported some results on the GPC analysis of polyacrylonitrile bearing some sulfonated groups (PAN-S), performed both in pure dimethylformamide (DMF) and in $0.1M$ LiBr in DMF. The electrolyte was added to reduce the dissociation of ionic groups on the polymer, thus passing from a charged to an almost uncharged coil. The addition of the salt produced[2] a tremendous effect on the retention time, which was increased by an amount corresponding to about 4 counts (1 count = 5 cm^3; flow rate = 1 cm^3/min). This effect was interpreted by an impressive decrease in coil size as a result of charge neutralization. Whereas a decrease in molecular dimension is the normal effect to be expected, the amount of coil contraction which is required to explain the delay of 4 counts leaves serious doubts on this being the only effect of salt addition.

We have tried to estimate the effect of a change $d[\eta]$ in intrinsic viscosity of a polymer fraction on the count C on the appearance of the peak in the chromatogram. On GPC calibration curves of plot of log ($[\eta] \times M$) versus C, a linear behavior was found, extended to a rather wide range of $[\eta] \times M$ values (see Fig. 1). We can therefore write

$$\log ([\eta] \times M) = A - KC$$

where K is the absolute slope of the calibration plot. If a change in hydrodynamic volume is due to a change in $[\eta]$ only, we have

$$d \log ([\eta] \times M) = -K \, dC$$
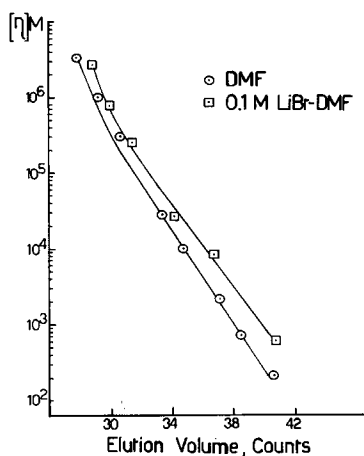
from which:

$$\frac{d[\eta]}{[\eta]} = -2.3 \, K \, dC \qquad (1)$$

Fig. 1. GPC calibration plot based on PS fractions in DMF at 80°C. ($\odot$) in DMF; ($\square$) in 0.1M LiBr–DMF.

which shows the effect on C of a relative change $d[\eta]/[\eta]$. For standard operational conditions (1 count = 5 cm³; flow rate = 1 cm³/min), K has a value between 0.2 and 0.3, which gives $d[\eta]/[\eta] = 0.5 \, dC$.

This means that a change of only 1 count is associated with a rather drastic (50%) change in intrinsic viscosity.

The change of 4 counts, reported as a result of salt addition to PAN-S, would therefore imply a dramatic salt effect on $[\eta]$.

We have therefore studied the effect of LiBr at one concentration (0.1M) in DMF, both on GPC and $[\eta]$ measurements for some polymers, charged and uncharged.

EXPERIMENTAL

Materials

The following polymers were examined:

1. Polyacrylonitrile, with (PAN-S) and without (PAN) sulfonate sulfur; all samples were obtained by radical polymerization.

2. A copolymer from acrylonitrile and methyl acrylate (AN–AM) with 1% sodium allylsulfonate (ASNa). All these samples were dissolved at 35°C in dimethyl sulfoxide and fractionated by precipitation with toluene.

3. Polystyrene (PS) fractions were obtained from Waters Associates as polymer standards.

4. Poly(vinyl acetate) (PVAc) fractions were obtained by dissolving some commercial products in benzene and by adding cyclohexane as non-solvent at 25°C.

Intrinsic Viscosity

All $[\eta]$ measurements were performed at 80°C (the operational temperature of GPC) in DMF, pure and with $0.1M$ LiBr. Bischoff suspended-level viscometers were used.

Gel Permeation Chromatography

We used a Waters Model 200 GPC, equipped with four standard Styragel columns (10^3, 10^4, 10^5, and 10^6 Å) at a flow rate of 1 cm³/min at 80°C. GPC sample injection concentration was 0.2% by weight, and time was 5 min. All samples studied were analyzed in pure DMF and then in $0.1M$ LiBr-DMF. PS fractions, of known $[\eta]$ and M, have been used to construct the calibration plot, both with and without salt. Figure 1 shows salt effect on the calibration curves.

RESULTS AND DISCUSSION

It is of interest to look first at the salt effect on $[\eta]$ for PS fractions in DMF at 80°C. Table I shows the results of our viscosity measurements. $[\eta]$ and $[\eta]'$ are the intrinsic viscosities in DMF and in $0.1M$ LiBr–DMF, respectively. As one can see, LiBr has a salting-out effect even on an uncharged polymer like polystyrene. This result is in agreement with some previous work on the salt effect on various uncharged chains[3]: invariably, salts tend to reduce coil dimensions with a decrease in $[\eta]$. A discussion of thermodynamic implications has been reported.[3] Here, we note that, for a salt concentration of $0.1M$, the decrease in $[\eta]$ is of the order of 20–30% and is not bound to the existence of a charge on the polymer.

These results were confirmed for two PVAc and one PAN fractions (see Table II). LiBr produces a salting-out effect with coil contraction similar to that of PS.

Decrease in $[\eta]$ is, of course, responsible for the shifting in the calibration curve of Figure 1. On salt addition, PS chains contract and the GPC peak

TABLE I
Intrinsic Viscosities and Counts of Appearance of PS Fractions in DMF at 80°C[a]

M_n	$[\eta]$	$[\eta]'$	C	C'	$C' - C$
1,780,000	1.90	1.55	27.8	28.8	1.0
773,000	1.30	1.00	29.2	29.9	0.7
392,000	0.77	0.64	30.6	31.4	0.8
96,200	0.29	0.27	33.4	34.1	0.7
49,000	0.20	0.17	34.7	36.7	2.0
19,650	0.11	—	37.2	—	—
9,700	0.075	0.06	38.6	40.7	2.1
4,600	0.045	—	40.80	—	—

[a] $[\eta]$ = Intrinsic viscosity in DMF (100 cm³/g); $[\eta]'$ = intrinsic viscosity in DMF + 0.1M LiBr; C = peak count in DMF (1 count = 5 cm³); C' = peak count in DMF + 0.1M LiBr.

TABLE II
Intrinsic Viscosities and Counts of Appearance of PVAc and PAN Fractions[a]

Sample	$[\eta]$	$[\eta]'$	C	C'	$C - C'$
PVAc	2.20	1.80	29	28.8	0.2
	0.102	0.076	36.8	36.2	0.6
PAN	2.92	2.62	28.2	30.3	2.1

[a] Symbols same as in Table I.

TABLE III
Intrinsic Viscosities and Counts of Appearance of PAN-S and AN–AM Fractions[a]

Sample	$[\eta]$	$[\eta]'$	C	C'	$C' - C$
PAN-S	2.05	1.89	27.4	31.3	3.9
	1.31	1.13	27.4	32.2	4.8
	0.51	0.47	28.8	33.7	4.9
AN–AM	1.13	0.99	28.4	32.4	4
With 1% ASNa	0.93	0.79	28.8	33.1	4.3

[a] Symbols same as in Table I.

shows up at a later time, the new count of appearance C' being larger. The difference $C' - C$ between the counts of peak appearance with and without salt is small and of the order expected from eq. (1).

The situation is entirely different when polymers with a few sulfonic groups are studied. Table III shows the results for PAN-S and AN–AM copolymer.

In agreement with the results previously obtained by Cha,[2] addition of 0.1M LiBr causes a shift of 4 or more counts; on the other hand, changes in $[\eta]$ are small and of the same order of magnitude as with uncharged polymers.

Figure 2 shows some of the gel permeation chromatograms obtained with AN–AM fractions. GPC and $[\eta]$ measurements for PAN-S and AN–AM appear therefore to be inconsistent. On the one hand, the measured de-
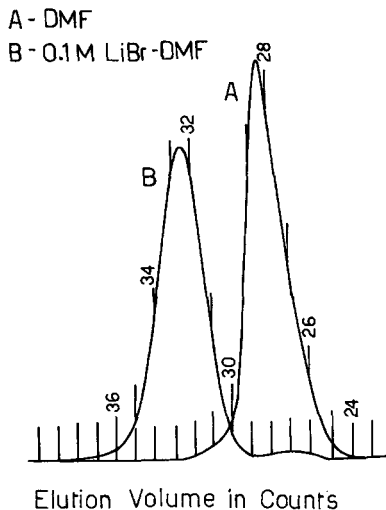
A - DMF

B - 0.1 M LiBr -DMF

Fig. 2. GPC chromatograms for an AN–AM copolymer fraction with (curve B) and without (curve A) salt.

crease in $[\eta]$ due to salt addition is far too small to explain the experimentally observed count shifts $C' - C$. On the other hand, the count of appearance C in the absence of LiBr is anomalous in the sense that, transferred on a polystyrene-based calibration plot, it gives a hydrodynamic volume $[\eta] \times M$ far too large.

Only the addition of LiBr makes the count of appearance C' reasonable and in agreement with the hydrodynamic volume estimated from $[\eta]$ and M values measured independently.

Chiang and Stauffer[4] have studied the association of PAN (uncharged) in various solvents, DMF included. One of the most striking results was that the intrinsic viscosity was only slightly affected by association, whereas weight-average molecular weight changes were very large. For example, one fraction gave in the associated form $M_w = 4.8 \times 10^5$ and $[\eta] = 2.15$ (100 cm^3/g), whereas after breaking of the supermolecular structure it gave $M_w = 2.25 \times 10^5$ and $[\eta] = 2.05$. It must be said that Chiang and Stauffer found this effect for PAN polymers prepared by an organometallic catalyst, whereas no evidence was found for a similar behavior for free-radical polymers.

Nevertheless, in the absence of more information on the effect played by charges on the association of free radical-produced PAN, we note that an effect similar to that described by Chiang and Stauffer would be consistent with our experimental observations. Association in PAN-S, AN–AM, and PAN samples would not be "seen" by $[\eta]$ measurements; on salt addition, a relatively small intramolecular contraction takes place, with a resulting decrease in $[\eta]$.

Gel permeation, on the other hand, would reveal the formation of a supermolecular structure as an increase in molecular weight, by letting the poly-

mer leave the column much earlier than expected on the basis of its true molecular weight.   Salt addition destroys all superstructures and the count of appearance of the polymer becomes normal.

We note that our analysis is, at this point, quite different from that given by Cha, the difference $C' - C$ being due mainly to an intermolecular effect (association) rather than to an intramolecular effect (coil contraction).   All this raises an interesting question on how an association can indeed be detected by GPC and not by $[\eta]$ measurements.   This is a problem on which further work is needed.

References

1. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B,* **5** 753 (1967).

2. C. Y. Cha, *J. Polym. Sci. B,* **7** × 343 (1969).

3. E. Bianchi, U. Bianchi, G. Tealdi, and B. Testa, presented at the Leiden International Symposium on Macromolecules, Leiden, 1970, to be published.

4. R. Chiang and J. C. Stauffer, *J. Polym. Sci. A-2,* **5,** 101 (1967).