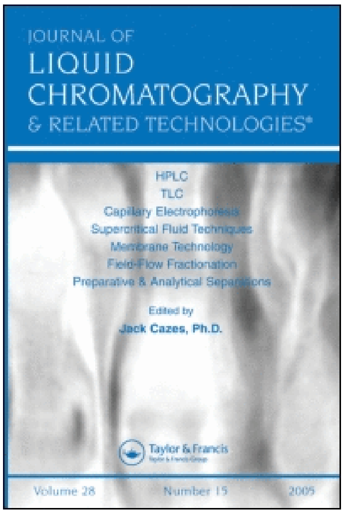

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GPC OF POLY(N-VINYLACETAMIDE) ON SILANIZED POROUS GLASS IN DMF AND DMF/LiBr

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ABSTRACT

Samples of poly(N-vinylacetamide) were characterized by exclusion chromatography on silanized porous glass columns in DMF and DMF + 0.01M LiBr. Chromatograms obtained in pure DMF were very different in appearance from those observed using DMF + 0.01M LiBr. It is proposed that solutions of the polymer in the pure solvent form stable microcrystalline aggregates leading to the appearance of exclusion limit peaks for the higher MW samples. Strong ion-dipole interactions between the polymer and LiBr prevent the formation of such aggregates, resulting in more normal chromatographic behavior.

INTRODUCTION

A number of important synthetic polymers--e.g., acrylonitrile homo- and co-polymers, polyamides, polyimides, and certain polyurethanes--are soluble in polar organic solvents but not in the more common GPC solvents, such as THF, $CHCl_3$ and toluene. Among the polar solvents previously reported for GPC are N,N-dimethylacetamide(1), hexamethylphosphotriamide(2), m-cresol(3), hexafluoroisopropanol(4) and N-methylpyrrolidone; but the most commonly used is N,N-dimethylformamide (DMF)(5-12) which has the advantages of relatively low toxicity, viscosity, and cost as well as good solvent power for a wide range of polymers. However, all of the forementioned polymers reportedly may display unexpected chromatographic behavior when eluted from GPC columns with DMF, namely very broad or bimodal chromatograms, with apparent molecular weight averages and distributions discordant with expectations based on synthesis conditions or with values obtained by other methods(5,7,8,10). The same accounts also report more "reasonable" chromatography when LiBr is added to the solvent, but no compelling explanation of this effect has been advanced. Especially tenuous are those arguments that ascribe "polyelectrolyte" behavior to non-ionizable polymers(9,10). On the other hand, more plausible explanations based on aggregation(7) fail to derive support from viscosity data which show only modest dependence on the presence of the salt(5,7,8,11).

One factor complicating the results cited above is the influence of solvophobic partitioning effects in the DMF/Styragel systems used, resulting in the excess retention of the polystyrene calibration standards themselves(13). This interaction results in anomalously high apparent molecular weights for polar polymers that are not as strongly retained(14). LiBr amplifies this effect, as is evident from the shift of polystyrene calibration curves to higher retention volumes in the presence of the salt(7,10,11). For this reason, we have chosen as a DMF GPC stationary phase porous silanized glass on which adsorption and partition effects are substantially reduced(13).

The present report describes the exclusion chromatography of poly(N-vinylacetamide), a compound of considerable interest as a precursor to polymeric dyes(15) or other functional macromolecules(16). In common with the polymers mentioned above, it is soluble only in highly polar solvents and exhibits similarly complex GPC behavior in DMF.

EXPERIMENTAL

Poly(N-vinylacetamide) samples with a range of molecular weights were prepared by free-radical polymerization of N-vinylacetamide(15) under varying conditions of initiator and monomer concentrations. "Distilled-in-glass" DMF was from Burdick and Jackson. LiBr was MCB Reagent Grade. GPC was carried out on four 44 cm x 0.88 cm ID stainless columns, packed with nominal 493Å, 327Å, 172Å and 89Å porous glass (Electronucleonics) silanized with chlorotrimethylsilane(13). The plate count, obtained with toluene at 2.0 ml min^{-1}, was 330 tpf. All samples were applied with a Valco 500 μl loop injector and monitored by differential refractive index. Except where noted, the solutions injected were 10 mg/ml in polymer. Viscosities were measured at 30.0°C with a Sofica Viscomat automatic viscometer.

RESULTS

Polystyrene calibration curves obtained in pure DMF and with 0.01M LiBr are shown in Figure 1. The effect of LiBr on polystyrene elution is to increase its retention by less than 1%, which may be contrasted with the ca. 3-5% increase in polystyrene retention found with Styragel mobile phase(7,10). This is evidence of the diminished role of partitioning on silanized glass. Also shown in Figure 1 is the primary calibration curve for poly(N-vinylacetamide) based on membrane and vapor phase osmometry data(17). (Since this curve is generated by an iterative procedure that fits its shape to the chromatograms and $\bar{M}_n$ values of polydisperse fractions, the elution volumes of the data points correspond to the "number-average position" of the chromatograms and not the peaks.) The divergence of polystyrene and poly(N-vinylacetamide) curves below 10^5 MW is partly a consequence of partitioning of the former, but also reflects the greater contour length per unit mass and solvent affinity of poly(N-vinlyacetamide). Both of these factors lead to greater chain expansion and hence earlier elution relative to polystyrene at equal MW's.

The influence of 0.01M LiBr on the chromatographic behavior of poly(N-vinlyacetamide) is demonstrated in Figure 2 in which chromatograms obtained in the presence and absence of salt are superimposed for polymers A-D, representing a range of MW's.

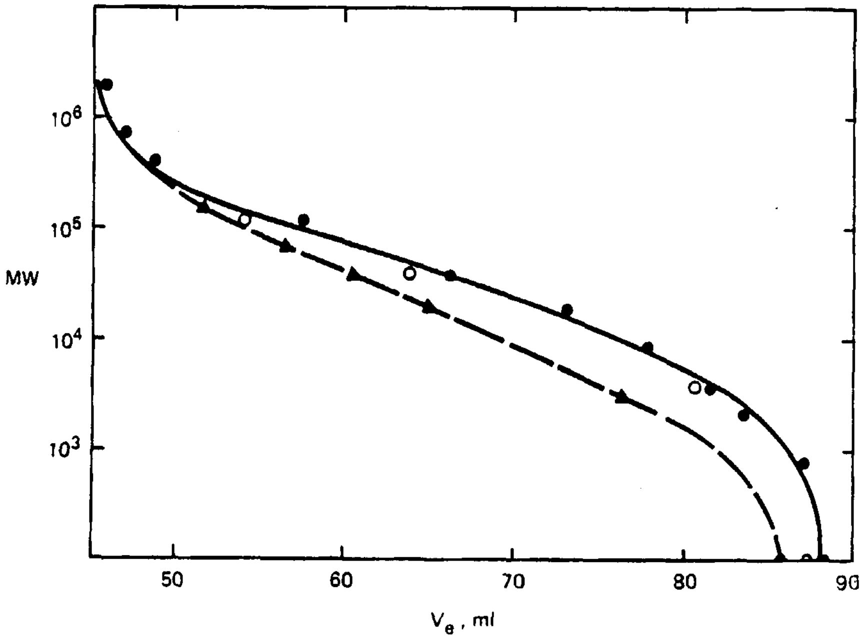

Figure 1. Calibration curves for polystyrene in pure DMF (○) and DMF + 0.01M LiBr (●). Broken line: poly(N-vinylacetamide)/0.01M LiBr "primary calibration curve" (see text).

Polymer A and a high-MW sample E were studied in more detail. GPC and viscosity data for the two samples, with and without LiBr, are summarized in Table 1.

The influences of both polymer and salt concentrations (C_p and C_s, respectively) on chromatographic behavior were further examined for Sample E with the results shown in Figures 3 and 4. While polymer concentration has little effect on the chromatogram shape, LiBr strongly alters the elution pattern in the range of $0<C_s<0.01M$, but has no visible effect between $C_s = 0.01$ and 0.10M. It was of interest to see whether this discontinuity was also reflected in viscosity behavior; in Figure 5 is shown the dependence of intrinsic viscosity on C_s at 30°C.

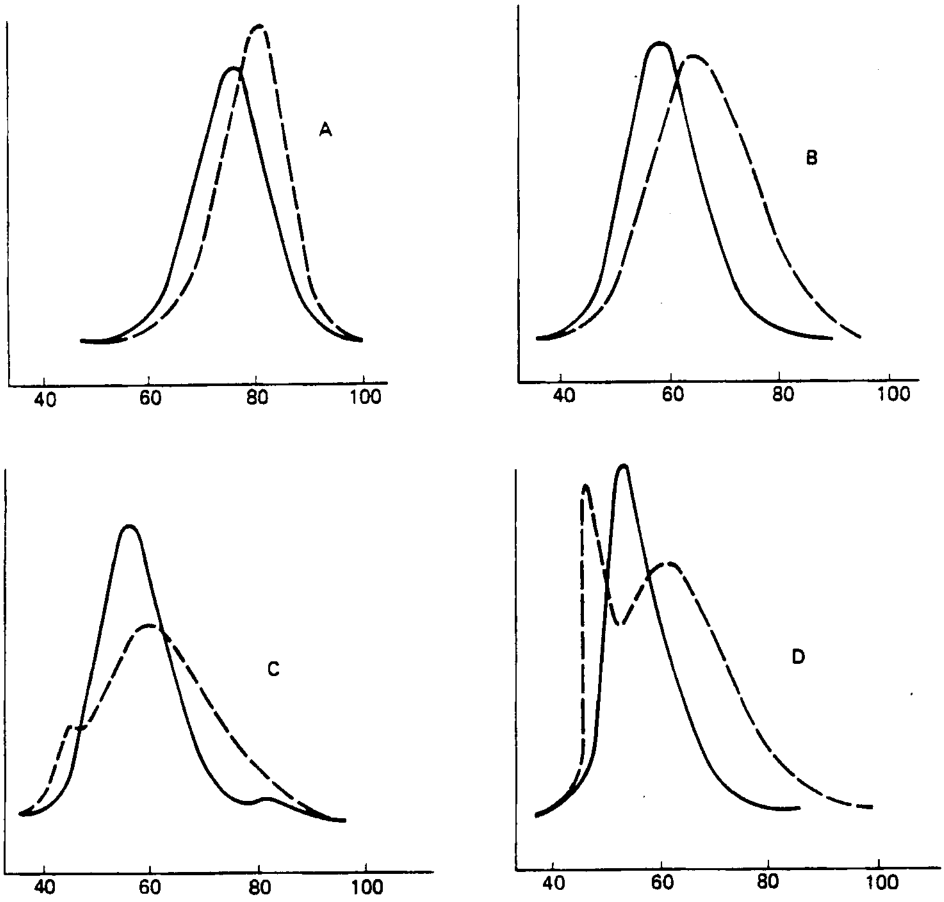

Figure 2. Chromatograms of poly(N-vinylacetamide) samples of varying MW's (A<B<C<D). Broken lines, pure DMF; solid lines, 0.01M LiBr.

DISCUSSION

The chromatographic behavior of poly(N-vinylacetamide) in the presence of LiBr is normal and poses no problems. As shown in Table 1 and Figure 1, MW values obtained through a polystyrene calibration curve are reasonably accurate above $5x10^4$; at lower MW's, the solvophobic retention of the standards result in a positive error of 200-300%. Results obtained in pure DMF are more

TABLE 1

Chromatographic and Viscometric Behavior for Poly(N-Vinylacetamide) Samples A and E

Sample	Solvent	PS M_p (a)	M_p (b)	$[\eta]$	K_H (c)	$\bar{M}_v$ (d)
A	DMF	$4x10^3$	—	.10	.29	—
"	0.01M LiBr	$2x10^4$	$5x10^3$	.083	.37	$6x10^3$
E	DMF	$2x10^{4(e)}$	—	.48	.52	—
"	0.01M LiBr	$2x10^5$	$1.5x10^5$	.45	.52	$2x10^5$

(a) Peak MW based on polystyrene calibration curve.
(b) Peak MW based on poly(N-vinylacetamide) calibration curve (0.01M LiBr).
(c) Huggins Constant.
(d) MW based on $[\eta]$-M relationship obtained from osmometry and viscometry data on polydisperse samples(17).
(e) MW of major peak; chromatogram bimodal.

complex. In the MW range below about $5x10^4$ (i.e., samples A and B), the chromatogram is shifted towards higher elution volumes in the absence of LiBr. At higher MW's, the chromatogram is broadened in both directions in pure DMF, and with sufficient broadening towards low retention volumes--i.e., the column void volume--an exclusion limit peak appears (e.g., samples C, D or E).

These results resemble those obtained by Kenyon and Mottus(8) for MW fractions of an 82:18 acrylonitrile: ethyl vinyl ether copolymer. As shown in Figure 6, these authors found that the higher polymers (MW>$4x10^4$) exhibited "high MW tails" which developed into the dominant peak in the MW range >10^5. Kenyon and Mottus discussed their results in terms of "association between polymer molecules and solvent." A more intelligible explanation for the unusual behavior of polyacrylonitrile polymers in pure DMF was offered by Coppola et al.(7) who cited studies by Chiang and Stauffer(18) that demonstrated clearly the presence of

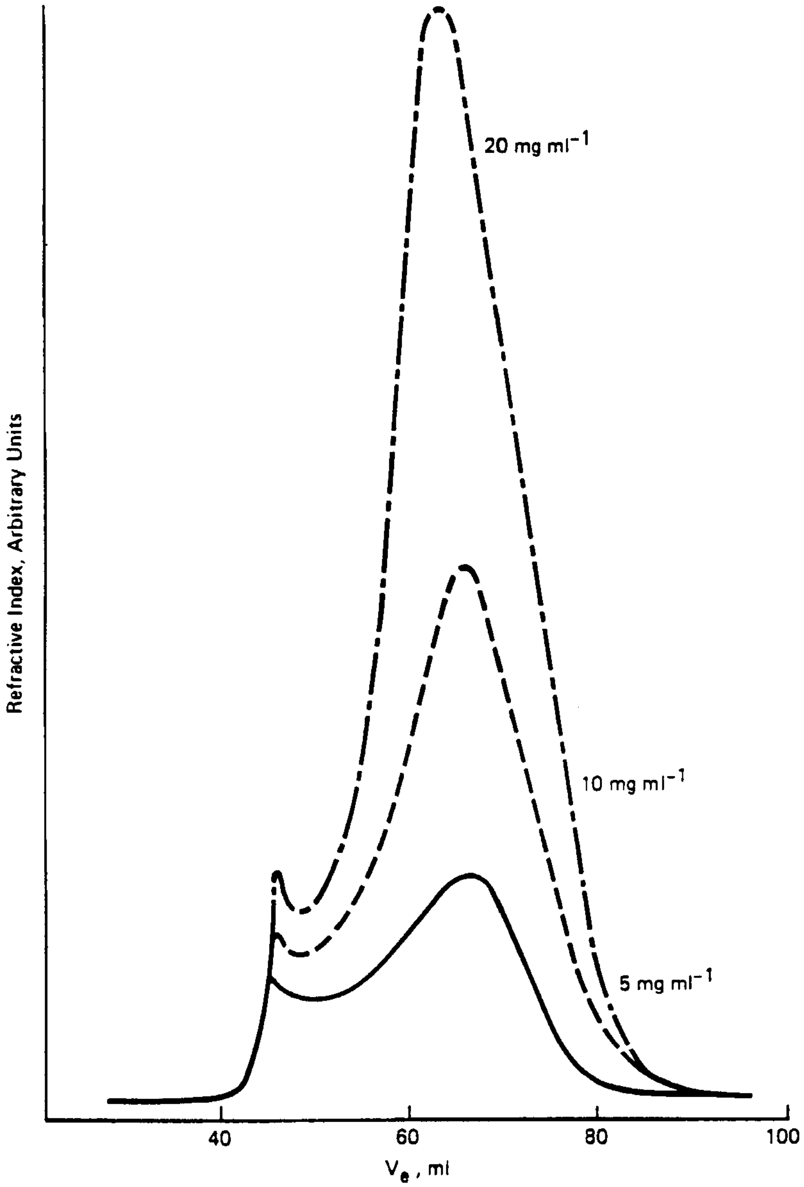

Figure 3. Effect of polymer concentration on chromatography. Value shown is mass of polymer applied to column.

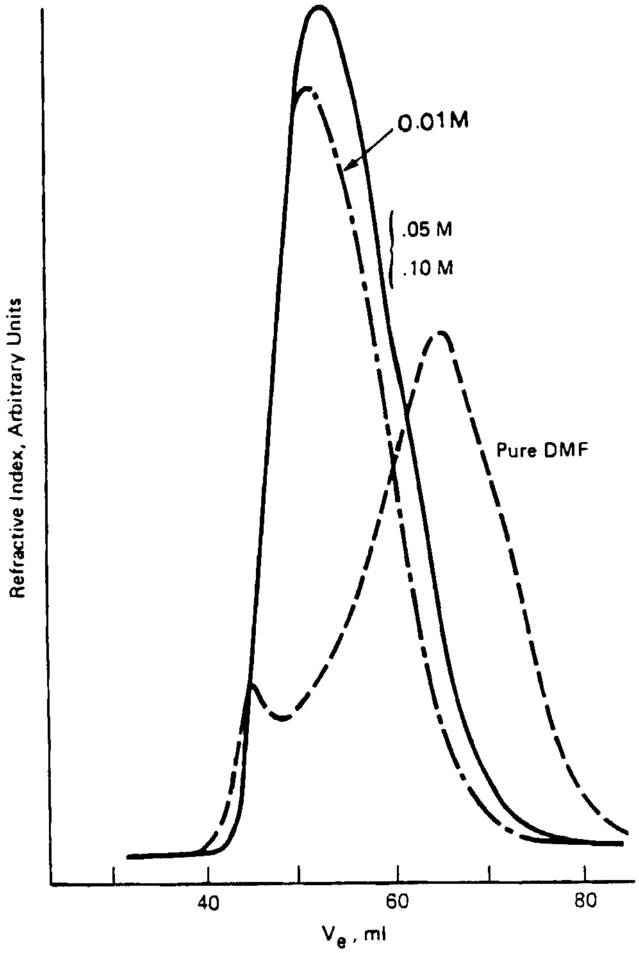

Figure 4. Effect of LiBr concentration in eluant on chromatogram shape.

polymer aggregates in such solutions. However, the influence of LiBr on intermolecular association of this type was not explicitly discussed.

Three findings reported by Chiang and Stauffer are particularly germane to the present study: (1) Those samples of polyacrylonitrile that dissolve in DMF only upon heating tend to form

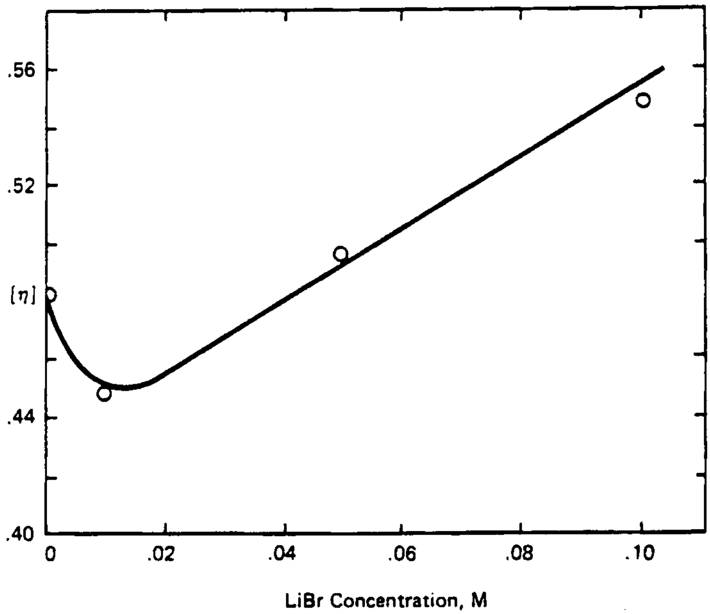

Figure 5. Dependence of intrinsic viscosity (Sample "E") on LiBr concentration.

stable aggregates; these solutions yield light-scattering molecular weights typically twice as big as the values obtained in DMSO at 140°C (in which medium there is no aggregation). (2) This increase in $\bar{M}_w$ is accompanied by an increase in $[\eta]$ of less than 20%. (3) The discrepancy between $\bar{M}_w$ measured in ambient DMF vs. hot DMSO was least for the lowest MW polymer. Chiang and Stauffer concluded that intermolecular dipole-dipole interactions lead to the formation of stable polyacrylonitrile aggregates in which microcrystalline regions act as physical crosslinks.

Like Chiang and Stauffer's semicrystalline polyacrylonitrile, poly(N-vinylacetamide) samples with MW's over ca. 2×10^4 dissolve perceptibly in DMF only above 50°C. Also in common with the former polymer, high MW poly(N-vinylacetamide) exhibits gradual phase separation on standing at room temperature. Both of these observations provide evidence for crystallization phenomena. The

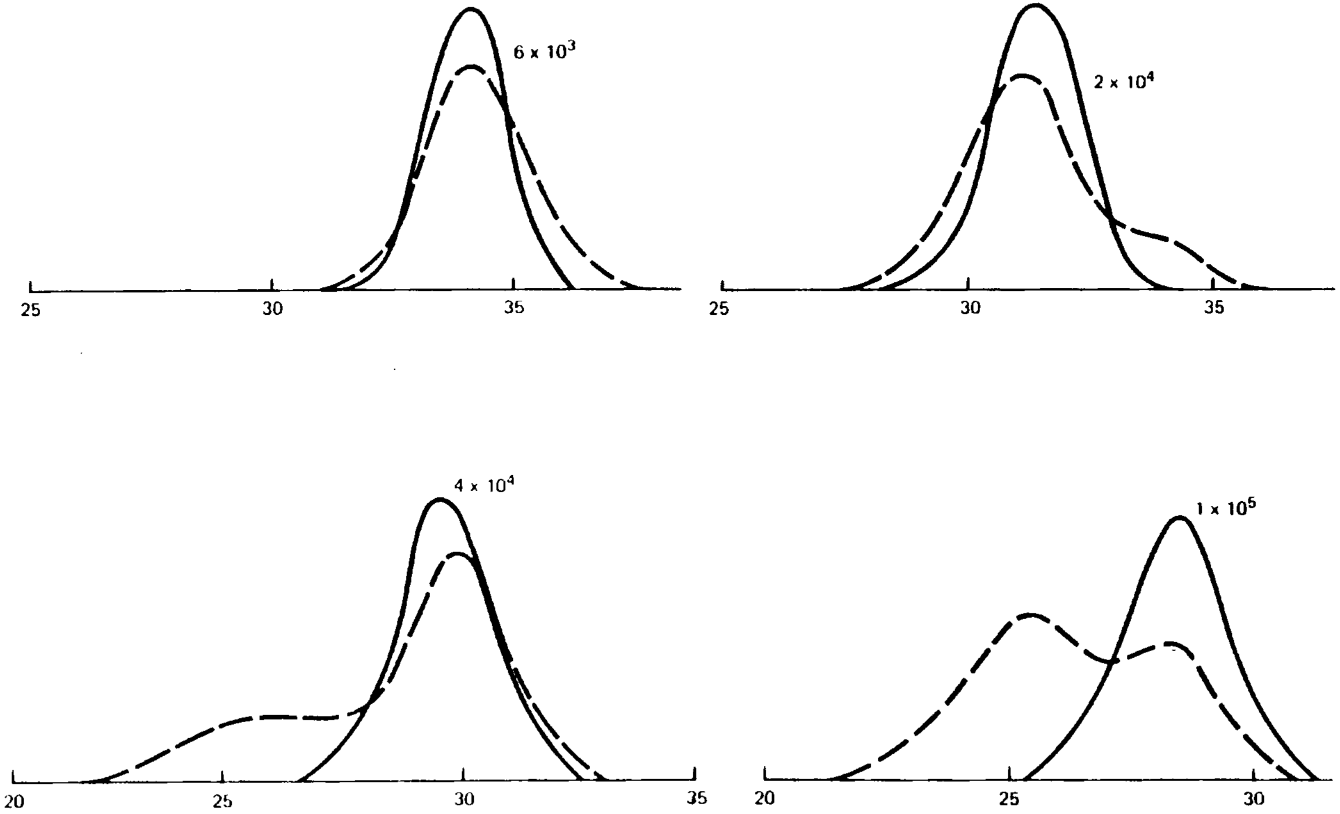

Figure 6. Chromatograms of MW fractions of acrylonitrile: ethyl vinyl ether copolymers. Broken lines, pure DMF; solid lines, 0.05M LiBr (redrawn from reference 8).

presence of a high MW shoulder or exclusion limit peak for the higher MW samples in pure DMF (see Figures 2C, 2D, 3 and 4) may then be ascribed to the formation of stable aggregates analogous to those found by Chiang and Stauffer. Should the higher MW species preferentially aggregate, one result would be a broadening of the GPC chromatogram. This is illustrated by Figures 2C and 2D if the "LiBr" chromatogram is assumed to correspond to the non-associating distribution.

It has been observed in numerous reports that lithium halides may lower the melting point or enhance the solubility of semicrystalline polyamides(19-23). These observations suggest that an ion-dipole complex is formed between salt and polymer. On the basis of infrared and nmr data for the system poly(1,4-benzamide)/LiCl/N,N-dimethlyacetamide, Panar and Beste(24) concluded that the affinity of chloride ion for polymeric N-H groups leads to an association polyanion. Solvated Li^+ (the metal ion associated with the carbonyl oxygen of N,N-dimethylacetamide) then forms the corresponding positive counterion. Such strong interactions between polymer and salt should interfere with intermolecular polymer association, especially if the latter process involves the slow formation of microcrystalline molecular aggregates. Consequently, the presence of LiBr prevents aggregation and yields the "normal" chromatographic behavior. Since the association process is very slow, simply increasing the concentration of polymer applied to the column--as shown in Figure 3--has no immediate effect on the chromatogram.

The addition of LiBr may generate an association polyelectrolyte, but simultaneously also raises the concentration of simple electrolyte, thus "screening out" intramolecular electrostatic repulsive forces. Consequently, a drastic increase in reduced viscosity at diminishing polymer concentrations and low salt content --so typical of polyelectrolytes--cannot be observed, and normal Huggins plots are obtained at all LiBr concentrations. On the other hand, we note two forms of discontinuous behavior as the quantity of salt varies. As shown in Figure 4, the effect of increasing LiBr content on GPC elution ceases when LiBr concentration exceeds 0.01M; and this same solvent composition also corresponds to a minimum in the dependence of polymer intrinsic viscosity on C_s. Since the molar concentration of polymeric amide groups declines from 0.06M to about 0.006M as the sample is eluted through the columns, the discontinuities observed at 0.01M LiBr are consistent with the formation of a stoichiometric complex between salt and polymer.

The basis of the reduction in $[\eta]$ upon addition of 0.01M LiBr is unclear as is the subsequent viscosity increase at higher C_s. We note that the relevant works on acrylonitrile homo- and copolymers all report viscosity changes of similar magnitude and direction--i.e., 5-20% decrease on addition of salt(5,7,8). One could speculate that this reduction in $[\eta]$ corresponds to the dissolution of aggregates: Chiang and Stauffer observed viscosities 4-18% higher for associated vs. nonassociated polyacrylonitrile solutions(18). In the present case, such dissolution is attained at relatively low C_s, and higher LiBr concentration increases the viscosity, possibly through modifying the solvent structure.

In conclusion, the anomalous GPC behavior of poly(N-vinylacetamide) in pure DMF may be ascribed to the formation of stable aggregates whose existence derives from the tendency of the polymer to crystallize below ca. 50°C. LiBr prevents the formation of such aggregates by generating an association polyelectrolyte via ion-dipole interactions with both polymer and solvent. DMF is most typically employed as a GPC solvent for polymers that are insoluble in THF or MEK because of strong polar interpolymer forces. Since these types of interactions often form the basis of crystallization phenomena, "anomalous" chromatographic behavior of the kind observed here might seem to go hand in hand with the use of DMF as a solvent for GPC.

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