Size Exclusion Chromatography of Urea Formaldehyde Resins in Dimethylformamide Containing Lithium Chloride

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Synopsis

A rapid, reproducible method for investigating the molecular mass distribution of urea formaldehyde resins by size exclusion chromatography has been developed. By using concentrated lithium chloride solution to prepare the sample, materials of high viscosity and high molecular mass can be easily dissolved. Chromatography in dimethyl formamide containing lithium chloride eliminates hydrogen bonding and ensures that realistic values for molecular mass averages are obtained.

INTRODUCTION

During the past 15 years, a substantial effort has been made to study the molecular mass distribution of urea formaldehyde (UF) resins by size exclusion chromatography (SEC).[1-12] It seems, however, that a rapid, reproducible, and accurate procedure which will classify all UF resins including the most highly condensed types has yet to be reported.

Serious difficulties arise due to the poor solubility of high molecular mass material in any simple solvent or combination of solvents. Even the most effective solvent, i.e., dimethylsulfoxide will not dissolve completely a UF resin of high molecular mass.[10] Strong intermolecular hydrogen bonds form between the polar sites on the molecules, producing a supermolecular structure.

For many years it has been realized that strong aqueous solutions of lithium chloride will easily dissolve UF resins even when condensed to a high degree. Hope et al.[2] in an early article on the subject refer to this approach for sample preparation. It is clear that in some way lithium chloride eliminates the hydrogen bonds which are responsible for the association effect. The solutions obtained are clear, are of low viscosity, and can be infinitely diluted with solvents such as DMF and dimethylsulfoxide. The chemical nature of the resins is not altered, and the solute in solution remains unchanged for 24 h at room temperature.

It has been appreciated for some time that the addition of lithium halide to dimethylformamide (DMF) shows advantages over DMF alone when used as a solvent for the SEC of thermoplastic polymers. Cha[13] investigated the chromatography of polyacrylonitrile containing some sulfonate groups using lithium bromide in DMF as a solvent. He found that the salt caused an increase in the elution time of the polymer from the column and attributed this effect to charge neutralization and thus a reduction in the effective molecular size. However, Coppola et al.[14] working with uncharged

polyacrylonitrile considered that the effect on the solute molecular size was too great to be explained by this effect. They suggested that the lithium salt prevented the molecules associating together and allowed the polymer to elute at its true position.

DMF containing lithium salts has been used by a variety of other workers as a solvent for the SEC of polymers. Kenyon and Mottus[15] studied a variety of thermoplastic polymers while Hann[16] worked with polyurethanes and Connors et al.[17] found that the addition of LiBr to DMF simplified the chromatograms of lignins. Cathodic electrodipping primers were examined successfully by Nömayr et al.[18] These workers also studied the effect of varying the strength of the lithium salt in the solvent establishing that concentrations in excess of 0.5% produced essentially the same chromatogram.

In this study, evidence has been obtained which indicates that there is a strong association between some of the lithium salt used in the preparation of the solution and the dissolved solute. This occurs to such a degree that the salt will pass with the urea derivative through the chromatographic column.

Calibration of the chromatographic columns for the analysis of UF resins has caused problems for previous workers; however, when polyethylene glycol and urea–formaldehyde standards are used in a solvent containing a lithium salt, a logical relationship is apparent.

EXPERIMENTAL

Equipment

The chromatography system consisted of: a Waters 6000A pump; Rheodyne 70–10 injection valve fitted with a 100-μL loop and Model 70-11 filler port; Polymer Laboratories PL GEL 10-μm columns, porosities 10^4, 500, and 50 Å, all 300 × 7.7 mm, housed in a Waters column oven; a Waters R-401 Differential Refractometer; a Waters Model 730 Data Module with GPC integration option.

Reagents

Anhydrous lithium chloride (GPR grade from BDH); dimethyl formamide (reagent grade from BDH).

Calibration Standards

Polyethylene glycols were from Polymer Laboratories (Calibration Kit PEG-10); Urea (AR grade from BDH); Monomethylol urea (MMU), dimethylol urea (DMU), and methylene diurea (MDU) were prepared as described elsewhere.[19] Crude trimethylene tetraurea containing some hexa- and octaurea compounds was prepared as detailed below.

Preparation of Trimethylene Tetraurea

Methylene diurea (22.5 g, 0.17 mol) was dissolved in 250 mL water warmed to about 45°C. Formaldehyde solution (1 g of 50%, 0.017 mol) was added

followed by 1 drop of concentrated phosphoric acid. The solution was allowed to stand overnight, and the material which had precipitated out was filtered off and washed well with water. A chromatographic examination showed the material to be free from methylene diurea and to contain higher molecular mass oligomers (6 and 8 urea units), which could also be used for calibration.

Preparation of Samples

Many resin samples are only partially soluble in DMF unless a high initial concentration of lithium chloride is present. This causes the intermolecular hydrogen bonds to break, resulting in the resin dissolving completely. Once in solution the resin sample is infinitely dilutable with DMF. The salt concentration in the sample solution is adjusted to the same strength as that in the chromatographic solvent using one of two procedures. The first method, used with relatively low molecular mass resins, is to dissolve the sample (0.2 g) in molar lithium chloride solution in DMF (1 mL) and then dilute tenfold with DMF. The second method of sample preparation used with more difficult samples including semisolid materials is to add solid lithium chloride (0.04 g) to the sample (0.2 g) and mix vigorously with a small volume of DMF (up to 0.5 mL). After the sample has dissolved completely and sometimes warming to about 45°C may be necessary, DMF is added to give a final volume of 10 mL. To protect the columns, any extraneous particles which may be present are removed by passing the sample solution through a 0.5 μm filter.

Chromatographic Procedure

The SEC columns are thermostatted at 25 $\pm$ 1°C and equilibrated by passing the solvent (0.1M LiCl in DMF) at a flow rate of 1 mL min^{-1} until the retention times of a mixture of PEG standards is constant and identical with the retention times used in the calibration of the columns. If this cannot be achieved, the columns must be recalibrated.

With the sensitivity of the detector set to a suitable value (X16), 100 μL of sample solution is injected onto the columns via the sample loop.

Samples

Many samples of UF resins have been examined by this technique. Two typical resins illustrating the various aspects of the chromatography are considered in detail:

Resin A: A moderately condensed resin of high molar ratio (1:1.8) with no end urea addition.

Resin B: A moderately condensed resin with a very high initial molar ratio (1:2.0) but with a second urea addition to give a lower final molar ratio (1:1.4).

Both resins were tested when fresh and when considerably aged after storage at 21°C. These resins were further used to demonstrate the reproducibility of the method and to examine the effects of varying the salt concentration both in the sample solution and in the mobile phase.

RESULTS

Calibration Standards

Urea–formaldehyde condensation products and polyethylene glycols (PEG) of known molecular mass were chosen as calibration standards since the former can be directly related to the resins and the PEGs should behave similarly due to their polar nature. However, it was found that, although the plot of the PEG standards was linear over a large part of the range (see Fig. 1), there was poor resolution and nonlinearity at the low molecular mass end. Furthermore, the retention times of the urea derived standards did not correlate with the polymeric standards. Other polar materials such as sucrose, glucose, and water showed unexpectedly short retention times, i.e., they behaved in a similar manner to the urea compounds. Since SEC strictly separates by molecular size rather than molecular mass a possible explanation was that total solvation of the molecules was occurring at —OH and —NH groups. This would explain both the short retention times and the poor resolution as the difference between the effective masses would then be small.

There is indeed strong evidence that solvation does occur at all active hydrogen sites. A plot of the retention times of all materials so far considered against their molecular mass plus one associated solvent molecule per active
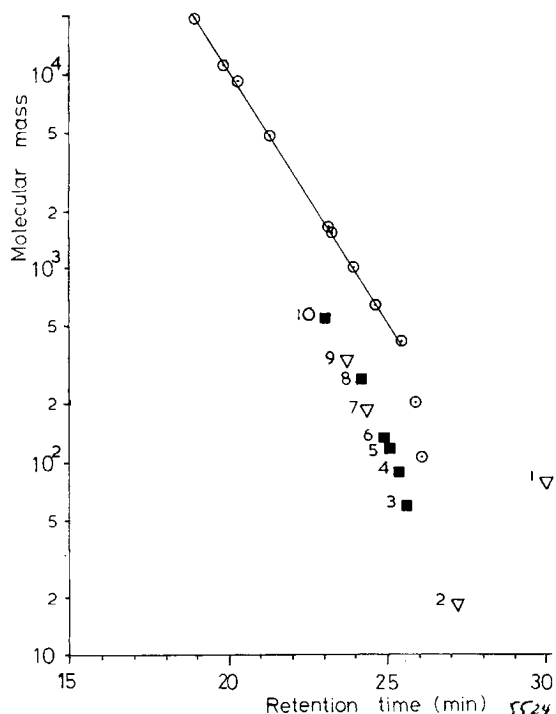

Fig. 1. Calibration plot of all standards using raw molecular masses: (○) poly(ethylene glycol) standards (full set from Polymer Laboratories); (■) urea derivatives; (3) urea; (4) MMU; (5) DMU; (6) MDU; (8) trimethylene tetraurea; (10) heptamethylene octaurea; (▽) other standards: (1) DMSO; (2) water; (7) glucose; (9) sucrose.

Fig. 2. (A) Calibration plot of all standards as their totally solvated masses: (●) PEG standards assuming terminal —OH groups solvated; (□) urea derivatives assuming all —NH groups and —OH groups solvated; (▼) other standards assuming all —OH groups solvated. (B) Calibration plot adopted for UF measurements: (■) urea derivatives as in Figure 1; (▽) other standards as in Figure 1; (○) UF points calculated using the structure and procedure described in the text.

hydrogen does fall on or very close to a straight line [Fig. 2(A)]. It seems justified therefore to base all calculations on the assumption that the molecules are fully solvated. To allow for the solvent molecules which are associated with the resin, an average structure has to be assumed. The most important factor governing this structure is the molecular ratio of urea to formaldehyde. Commercial products are normally manufactured with a ratio varying from 1:1.0 to 1:2.0, but a value of 1:1.5 would be considered a typical value. If chain branching, ether linkages, and cyclic structures can be ignored, then a very simplified structure such as

where S = possible sites for solvation.

can serve as a basis for calculating the contribution made by the solvent molecules to the molecular mass. Thus by assuming various values for n (the number of repeating units in the UF molecule) it is possible to replot the calibration curve [Fig. 2(A)] in terms of the unsolvated species. For example, taking a value for n of 30, the totally solvated molecule has an effective mass of 14,362. Using this mass, a retention time of 19.5 min is obtained from Figure 2(A). This retention time is then plotted against the corresponding mass of the unsolvated molecule (5310) to give a point on the new curve [Fig. 2(B)]. The calculated figures are in agreement with the experimentally determined points, and this calibration plot enables direct determination of the molecular mass averages of UF resins.

Effects of Lithium Chloride

When urea derivatives are dissolved in the mobile phase and chromatographed, a large negative peak is produced due to a deficiency of LiCl.

This indicates that some of the salt is carried through the chromatographic columns in a form that is closely associated with the urea derivative. Further examination of this phenomenum revealed that the addition of an equimolar amount of LiCl to urea and DMU solutions in the mobile phase was sufficient to exactly neutralize the negative peak, whereas with MDU 2 mol of LiCl were required to cancel out the negative peak.

The effect of altering the LiCl concentration in the sample solution was further examined, and it was found that variation over a large concentration range had very little effect on the molecular mass averages. However, samples prepared without LiCl and with a massive excess of LiCl did give significant variations in the values obtained (see Table I).

An exhaustive investigation of the effects of varying the lithium chloride concentration in the mobile phase was not made since this aspect has been examined previously by Nömayr et al.,[18] who demonstrated that increasing the concentration of LiCl above about 0.5% had little effect on the chromatogram obtained. However, if a sample is run in DMF without added LiCl but using dimethylsulfoxide to improve the sample solubility, there

TABLE I

Sample no.	Method of preparation	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	Dispersity
1	1 mL 1M LiCl–10 mL	146	1395	5559	9.53
2	1 mL 1M LiCl–10 mL	147	1419	5675	9.63
3	1 mL 1M LiCl–10 mL	144	1368	5456	9.48
4	1 mL 1M LiCl–10 mL	146	1397	5584	9.60
5	0.04 g LiCl–10 mL	144	1397	5620	9.68
6	No LiCl	163	1270	4451	7.80
7	0.5 mL 1M LiCl–10 mL	152	1464	5812	9.60
8	1.5 mL 1M LiCl–10 mL	145	1399	5525	9.65
9	2.0 mL 1M LiCl–10 mL	137	1347	5508	9.85
Standard deviation for samples 1–5		±1.2	±16	±73	±0.07
Coefficient of variation for samples 1–5		0.83%	1.15%	1.31%	0.73%

appears to be some very high molecular mass material which is excluded, and a somewhat variable pattern of peaks is produced, the position and intensity of which seem dependent on the method of sample preparation and the age of the solution. An example of this type of chromatogram is shown in Figure 3(a). Using LiCl in DMF as the eluting solvent for the analysis of about 50 UF samples, only one partially gelled sample showed any signs of exclusion.

Reproducibility

Five samples of resin were prepared for analysis using the methods described previously, four using 1M LiCl and diluting, the fifth using solid LiCl. The molecular mass figures obtained are given in Table I. The results obtained on samples prepared using different procedures are included for comparison purposes. The samples were prepared at the same time and were run one after another. Once in solution, samples were found to be stable for up to 24 h. After 3 days some distinct changes were noticeable.

Resin Samples

Two resin samples A and B were studied for changes in molecular mass distribution on storage for a period of about 6 months. Chromatograms of
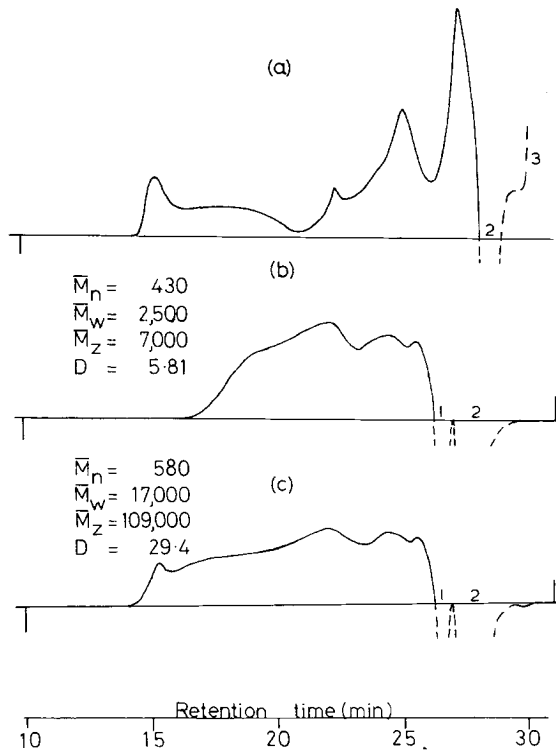

Fig. 3. Resin A: (a) fresh sample dissolved in DMSO/DMF (1/10) and run in a mobile phase of DMF alone; (b) fresh sample dissolved and run in 0.1M LiCl in DMF; (c) sample aged for about 6 months at 21°C dissolved and run in 0.1M LiCl in DMF. Peak identification: (1) lithium chloride; (2) water; (3) DMSO.

$\overline{M}_n =$ 160
$\overline{M}_w =$ 1,500
$\overline{M}_z =$ 6,000
D   =   9·37

(a)

1   2

$\overline{M}_n =$ 280
$\overline{M}_w =$ 2,700
$\overline{M}_z =$ 11,200
D   =   9·64

(b)

Retention time (min)

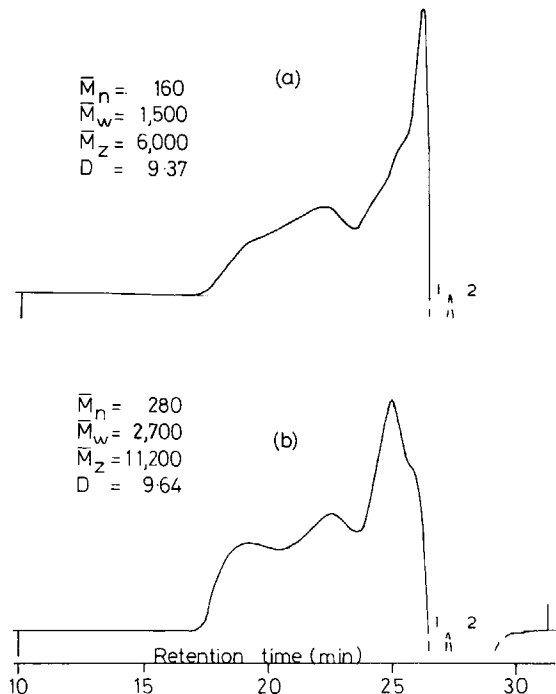10   15   20   25   30

1   2

Fig. 4.   Resin B: (a) fresh sample; (b) sample aged for about 6 months at 21°C. Both samples dissolved and run in 0.1M LiCl in DMF. Peak identification: (1) lithium chloride; (2) water.

fresh and old resins are shown in Figures 3(b), (c), and 4. It can be seen that resin A with no end urea addition shows a fairly even distribution when fresh, the low molecular mass end altering only slightly on aging while the medium to high molecular mass region becomes much more extended. Resin B containing the end urea shows a large low molecular mass peak when fresh which diminishes considerably on aging, producing a large increase in medium molecular mass materials while the high molecular mass end is relatively slow to change.

DISCUSSION

The objectives at the outset of this work were to develop a method of determining the molecular mass distribution of UF formulations which was rapid, reproducible, and applicable to all types of samples. Since the introduction of semirigid microparticulate crosslinked polystyrene gels, analysis times of 30 min or less have been commonplace. These columns therefore show a considerable advantage over the types previously used in this field, which were usually composed of large soft particles often based on a polysaccharide or a polyester.

The three-column set which was employed gives a separation time of about 30 min using a flow rate of 1 mL min^{-1} of DMF containing LiCl (0.1M). The columns were stored in this solvent when not in use and proved stable and reliable over a period of many months. There was no significant change in the calibration plot during this period.

The choice of the solvent has been crucial to the success of this investigation since it eliminates the hydrogen bonding in the solute and allows complete solvation of the molecules to occur. As a consequence, a rational calibration curve has been obtained leading to meaningful values for $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, and polydispersity. In the absence of lithium salt the degree of molecular association is variable, rendering all results thus obtained virtually meaningless.

Obviously some assumptions have had to be made about the structure of the polymer chain, but this is invariably the case when calibrating SEC columns for molecular mass determinations. These assumptions are only likely to cause significant errors in samples having final molecular ratios above about 1:2 (U:F) and commercial materials of this type are fairly rare.

The action of the lithium salt in rendering UF polymers soluble is not completely understood. However, it has been shown experimentally that lithium salt is transported through the SEC column with the urea derivative and that each urea group is associated with one molecule of LiCl probably via the carbonyl oxygen.

The lithium salt not only confers solubility on the polymer but also provides a secondary beneficial effect in that there is an increased detector response to the urea compounds compared with that observed in DMF alone. Since a lithium ion is associated with each urea unit, this effect is shown over the whole molecular mass range. On the other hand, the high degree of solvation of the urea derivatives means that there is very little relative difference in the molecular size of the low molecular mass components, causing poor resolution of these materials. However, the complete separation of these materials is not necessary for the purposes of determining average molecular masses, and they are better separated, using other techniques such as high performance liquid chromatography.

The actual values obtained for the molecular mass averages of commercial samples have varied widely. Typical figures found for freshly prepared materials were: $\overline{M}_n$ between 140 and 500; $\overline{M}_w$ between 800 and 3000; $\overline{M}_z$ between 3000 and 25,000; polydispersity between 5 and 20. These values can increase substantially on storage at 21°C for 6 months (see Figs. 3 and 4).

It can be concluded that this approach to the SEC of UF compositions is a viable method of quality control. It is also a powerful procedure for investigating the formation of the urea–formaldehyde polymers and not least their aging characteristics. Although only urea–formaldehyde polymers have been investigated in this study, it is likely that this technique could be useful in the analysis of similar materials such as melamine formaldehyde resins.

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