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GEL PERMEATION CHROMATOGRAPHIC SEPARATION CHARACTERISTICS OF LOW MOLECULAR MASS FURFURYL ALCOHOL OLIGOMERS

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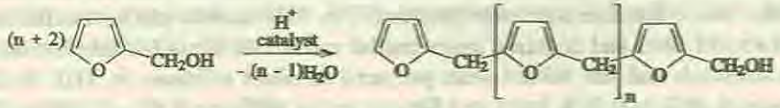
ABSTRACT. The gel permeation chromatographic (GPC) separation pattern of low molecular weight furfuryl alcohol oligomers has been determined on a 100 Å Ultrastyragel GPC column using tetrahydrofuran (THF) as the mobile phase. The alcohol oligomers, because of their stronger hydrogen bonding with THF, exhibit larger effective volumes than their molar masses would suggest and, therefore, elute at lower elution volumes (V_e) in comparison with their isomeric ethers. In contrast, the oligomers without any methylol substituents elute at higher elution volumes (V_e) than ethers of comparable molecular mass. The separation mechanism of each of the three oligomer homologous series can be accounted for by the general relationship: $V_e = A - B \log M$.

INTRODUCTION

Resins derived from furfuryl alcohol constitute the most important biomass-based polymers of the furan series [1,2]. In their fully cured state, these resins exhibit remarkable resistance to chemical attack and to heat [3]. These properties and the low cost of their production have promoted the wide industrial applications of these resins particularly as insulation materials [4] and in wood technology where they are used to enhance dimensional stability of wood and to improve chemical resistance [5].

High resolution NMR studies of not only the low molar mass oligomers formed in the early part of the reaction [6,7] but also of the subsequent cross-linking process [8], have contributed to a better understanding of the complex mechanism leading to the resinification of furfuryl alcohol. Gandini [9], in a review of the literature up to 1992, has provided a comprehensive summary of recent studies on the structure, properties, and cross-linking mechanisms [10] of these resins.

Furfural alcohol (1) is a bifunctional monomer for which, in the initial stages of its acid catalyzed resinification, three oligomeric homologs (a), (b) and (c) have been identified [6,7]. A chemically consistent reaction scheme for this initial stage involves either a head-to-tail self condensation leading predominantly to linear oligomers (Equation 1), or a head-to-head self condensation between methylol groups resulting in the formation of dimethylene ether linkages (Equation 2).



(1)

(2)

The ether bridges formed in this latter reaction convert, with the elimination of formaldehyde, to methylene moieties (Equation 3) by a process which is poorly understood.

(3)

The most plausible kinetic mechanism for the polycondensation reaction requires that lower molar mass oligomers resulting from simultaneous propagation and termination processes remain abundant even in the partially cured resins [11].

The significance of the GPC technique in this context is its inherent capacity to provide data which are qualitatively and quantitatively descriptive of the low molar mass oligomer distribution of a particular resin prepared under specific conditions. If a proper quantitative analysis of the kinetics of the polycondensation reaction is to be made, the qualitative information contained in the elution patterns of the oligomers must be subjected to a quantitative evaluation and analysis resulting in an accurate determination and assignment of the peaks in the GPC profiles. The results of our investigation of these separation characteristics are reported here.

EXPERIMENTAL

Chemicals. Analytical grade furfuryl alcohol and THF were obtained from May and Baker. The TKS A-300 (Batch TS-204) low molar mass polystyrene calibration standard with a degree of polymerisation of 3 was supplied by Millipore.

Low molar mass furfuryl alcohol oligomers. The details of the preparation and isolation of the oligomers (2-12) have been reported elsewhere [6,7]. Assessment of the purity of each oligomer was based on observation of a single GPC peak.

GPC chromatographic system, mobile phase, and sample preparation. The chromatographic system consisted of a Waters model M510 solvent delivery apparatus which was set at 500 psi for a flow rate of 0.8 $cm^3.min^{-1}$; a Waters model U6K injector, and a Waters model M401 differential refractometer detector. The refractometer sensitivity was set at 4x and 8x.

An Ultrastyragel (7.8 x 300 mm) GPC column of 100 Å designation was connected to the chromatographic system and calibrated at ambient temperature. On a daily basis, prior to elution, the system was flushed to introduce fresh solvent to the reference cell and thereafter equilibrated until a stable baseline trace was obtained. The THF mobile phase was filtered with a Waters 0.45 μM filter and degassed under partial vacuum to minimize baseline drift. The calibration standards and test solutes were prepared as dilute solutions in THF in the concentration range 0.04% to 0,02% (w/v) and filtered with a Millipore 0.45 μM Millex SR

filter cartridge before injection. Volume samples of up to 40 μL were injected immediately after loading into the sample loop.

RESULTS AND DISCUSSION

Figure 1 (d) depicts the calibration curve for the 100 Å Ultrastyragel column based on the elution behaviour to the TKS A-300 polystyrene standard, showing deviation from linearity from a molar mass of about 600 g.mol^{-1} - a phenomenon which may be attributed to incomplete column resolution. Use of the calibration plot provided an initial means of assigning the polystyrene-equivalent molar masses to each solute peak in the GPC profiles of the oligomers. A further means of identification was based on assignment of the GPC peaks assuming the normal oligomerization sequence of dimer, trimer, tetramer, pentamer, etc. The alcohol oligomers are individually capable of further polycondensation as is demonstrated by the behaviour of the dimer when used as initial reactant (Figure 2).

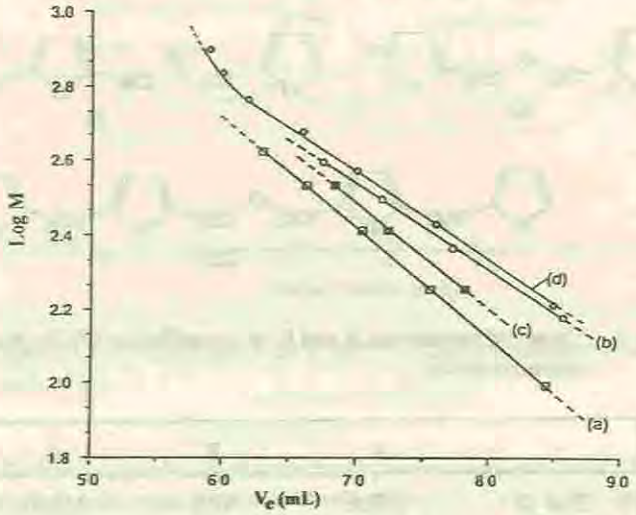


Figure 1. Plots of log M *vs* V_e for the oligomers [(a), (b) and (c)] and the TKS A-300 polystyrene standard (d).

Plots of log M *vs* V_e gave rise to three linear plots (Figure 1 a, b and c) corresponding to the three oligomerization routes of furfuryl alcohol. The best straight line (correlation coefficient, r = 0.9997) was obtained for alcohol homologous series (Figure 1a). Table 1 summarises the results of the linear regression analysis for the three plots of the three oligomer series (a), (b) and (c).

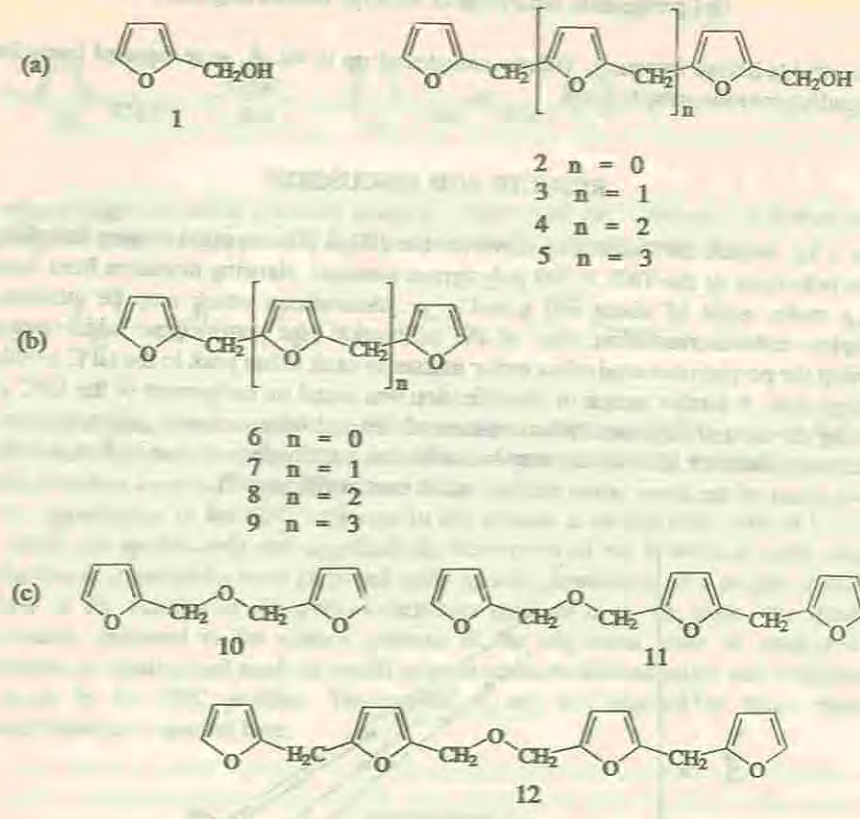


Table 1. Values of parameters A and B, and coefficient (r^2) for linear plots of three oligomer series.

	A	B	r^2
Plot 1a	179.6	43.3	0.9997
Plot 1b	157.5	35.2	0.9985
Plot 1c	151.9	33.9	0.9864

Notes:

1. Least squares fit of data to $V_e = A - B \log M$, where V_e is the peak elution volume, M is the molar mass, and A and B are constants.
2. All experiments were conducted at a flow rate of 0.8 cm^3 min^{-1}, sensitivity 4x.

In addition, it is noteworthy that on using the elution of the oligomers formed by the polycondensation of the dimeric alcohol (Figure 2) as a source of data for a corresponding plot of log M *vs* V_e, linearity was obtained up to the decamer (molar mass = 832 $g.mol^{-1}$). It is also observed that the linear portion of the polystyrene calibration curve is closely parallel

to the linear plot corresponding to the oligomer series with no methylol groups (Figure 1b). This may indicate a similarity in hydrodynamic behaviour of the two types of oligomers. Noting that for each of the three oligomer series, ΔM, the "repeat difference", in molar mass between successive oligomers is 80, it was observed that the corresponding difference in elution volume, ΔV_e, seemed to be largest for the linear plot for the oligomer series (b). The plot also had the lowest gradient of the three linear plots of log M *vs* V_e reflecting best peak centre resolution [12]. Furthermore, this plot for the oligomer series (b) was displaced to higher elution volumes than the ether (Figure 1c) and alcohol (Figure 1a) oligomer plots, respectively, indicating that members of this oligomer series were of smaller "effective size" than suggested by their molar masses due to a lesser degree of hydrogen bonding between THF and oligomer series (b). In contrast, because of more extensive hydrogen bonding with the THF mobile phase, the alcohol oligomer series exhibited larger effective molecular sizes as reflected in their lower elution volumes.

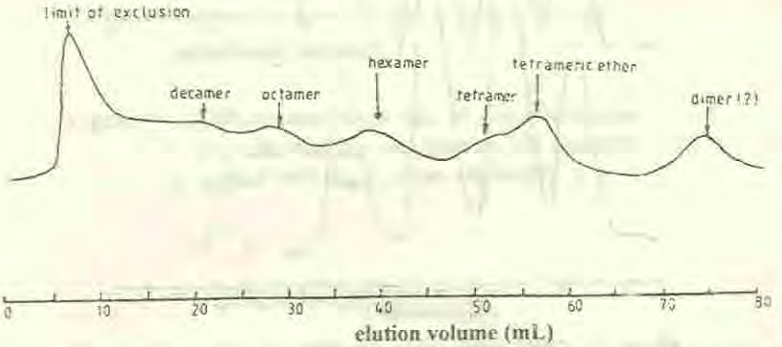


Figure 2. GPC separation profile of the dimeric alcohol polycondensation products after 6 h reaction time.

Figures 3a and 3b show, respectively, the chromatographic profiles of a simulated mixture of alcohol oligomers, and of the same mixture but with difuryl methane (**6**, molar mass = 148 g.mol^{-1}) added. Comparison of relative peak heights in the two profiles indicates that the addition of **6** causes the height of the monomer (**1**, molar mass = 98 g.mol^{-1}) peak to be enhanced and its width to be broadened towards higher elution volume, V_e. This is ascribed to only partial resolution of the peaks corresponding to the two compounds despite the sizeable difference in their molar masses. A similar pattern was observed for the dimer (**2**), trimer (**3**) and tetramer (**4**) alcohol peaks when samples of oligomers (**7**), (**8**) and (**9**) were separately added to the simulated alcohol mixture. On the other hand, the chromatogram for the mixture of monomer (**1**), dimer (**2**) and trimer (**3**) alcohols with the ether (**10**) (Figure 4) indicated that compounds (**2**) and (**10**), even though they have the same molar mass of 178 g.mol^{-1}, were separable because of the more effective hydrogen bonding of the alcohol with THF.

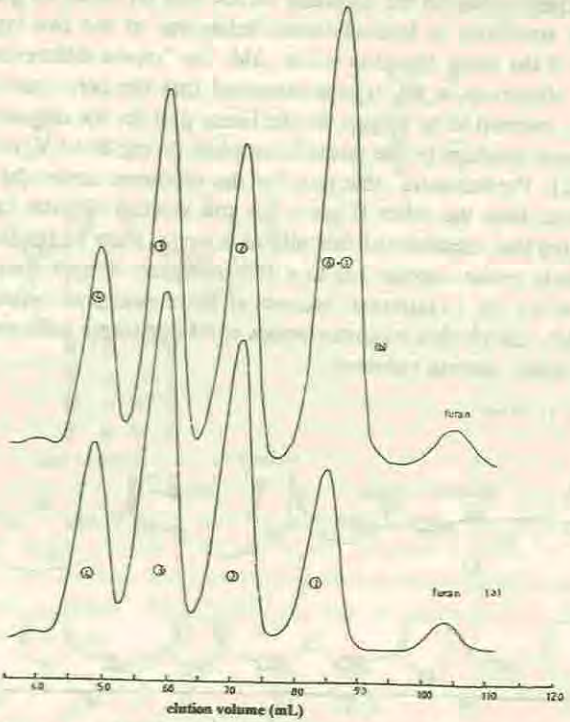


Figure 3. GPC separation profiles of (a) a simulated mixture of furan, the monomer, and alcohol oligomers, and, (b) the same mixture spiked with difuryl methane.

These observations on the GPC elution patterns of the furfuryl alcohol oligomers lead to the following conclusions:

a) For identical molar masses, displacement towards higher elution volume is observed if
   i) the oligomer contains no methylol group,
   ii) the oligomer contains an ether function rather than a methylol group.
b) For oligomers of the same homologous series, the separation mechanism is quantitatively accounted for by the general relationship:
   $V_e = A - B \log M$
c) Addition of a methylol group or of a furfuryl group causes almost the same decrease in the elution volume.

The results of our investigation point to the possibility of applying quantitative GPC analysis of the low molecular weight oligomers to the evaluation of the kinetics of the oligomerization process of furfuryl alcohol.

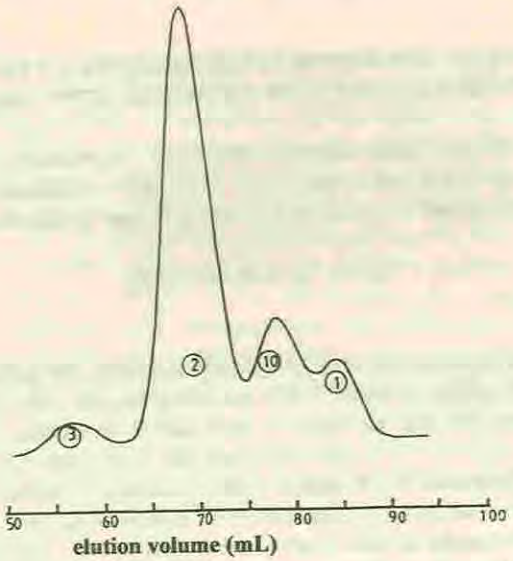


Figure 4. GPC separation profile of the monomeric (**1**), dimeric (**2**), and trimeric (**3**) alcohols spiked with the trimeric ether (**10**).

ACKNOWLEDGEMENT

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