

Notes

CHROM. 3847

Gas chromatographic determination of the molecular-weight distribution of polyethylene glycol products*

Temperature-programmed gas chromatography seems promising for the molecular-weight fractionation of polyethylene glycol (PEG) and its derivatives, because these substances can be made more volatile by replacing the two terminal OH groups by methoxy¹, acetyl², or trimethylsilyl³ groups. Under suitable conditions, one can thus fractionate such derivatives having molecular weights of up to about 900 (see ref. 3).

However, the molecular-weight distribution may be distorted during the conversion of the PEG into its derivative and during the analysis owing to incomplete volatilization in the evaporator, preferential condensation of the higher-molecular-weight members in the dead space between the column and the detector, and the irreversibility of the distribution equilibrium of the higher-molecular-weight members on the column. The chromatographic distortion can be minimized by adjusting the conditions, but it must be known if the true molecular-weight distribution is to be determined.

The present work was aimed at estimating this error by comparing the values obtained for the number-average molecular weight \bar{M}_N of low-volatility purified

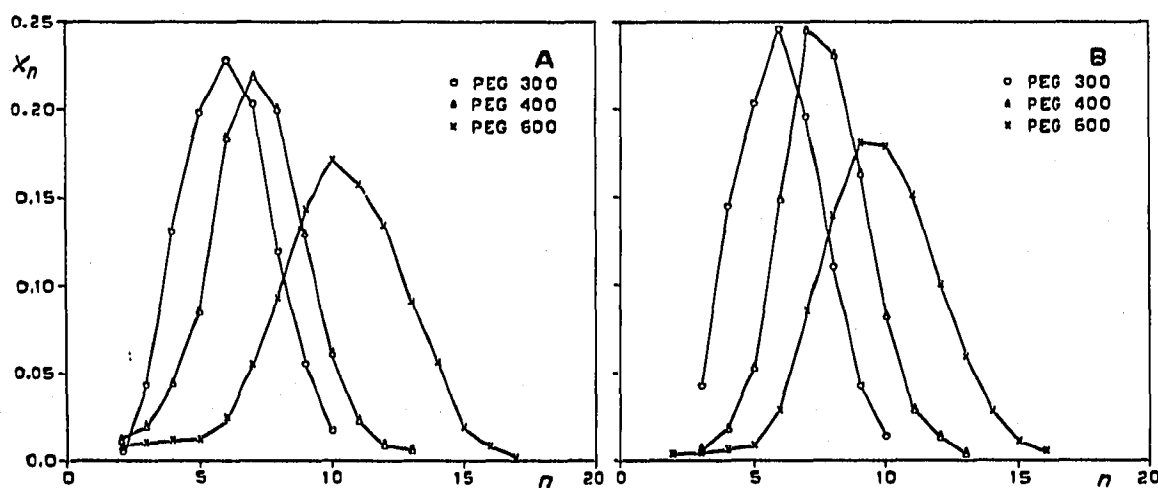


Fig. 1. Molecular-weight distribution of polyethylene glycol derivatives [X_n -mole fraction of a component with n -ethylene oxide units (in the starting PEG)]. (A) = $C_6H_5O(CH_2CH_2O)_nC_6H_5$; (B) = $C_6H_5S(CH_2CH_2O)_{n-1}CH_2CH_2SC_6H_5$.

* Translated by Express Translation Service, London S.W. 19.

TABLE I

COMPARISON BETWEEN THE VAPOUR-PRESSURE OSMOMETRIC (VPO) AND THE GAS-LIQUID CHROMATOGRAPHIC (GLC) VALUES OF THE NUMBER-AVERAGE MOLECULAR WEIGHT \bar{M}_N

$C_6H_5O(CH_2CH_2O)_n C_6H_5$		$C_6H_5S(CH_2CH_2O)_{n-1}CH_2CH_2SC_6H_5$	
\bar{M}_N (VPO)	\bar{M}_N (GLC)	\bar{M}_N (VPO)	\bar{M}_N (GLC)
436	438	472	492
481	487	545	511
699	621	735	631

polyethylene glycol derivatives by: (a) calculation from the gas chromatographic distribution pattern; and (b) measurement with a vapour-tension osmometer. The total error, incurred both in the chemical conversion and in the chromatographic analysis, was found by comparing the chromatographic \bar{M}_N for the derivatives [\bar{M}_N (GLC)] with the osmometric \bar{M}_N for the starting polyethylene glycols, [\bar{M}_N (VPO)]. This was done with more volatile derivatives in order to minimize the changes incurred during chromatographic analysis. Some of the gas chromatographic data have been published before³.

Experimental

The analysis was performed with a Wilkens Aerograph 1521-1 gas chromatograph fitted with a double column, a double flame ionization detector, and a temperature programming device. The columns and the working conditions were the same as before³. The osmometric determinations were carried out with a Hewlett-Packard 302 vapour-tension osmometer, the concentration being about $5 \times 10^{-3} M$ in toluene.

Commercial polyethylene glycols with stated mean molecular weights of 300, 400, and 600 were used to prepare³ the derivatives:

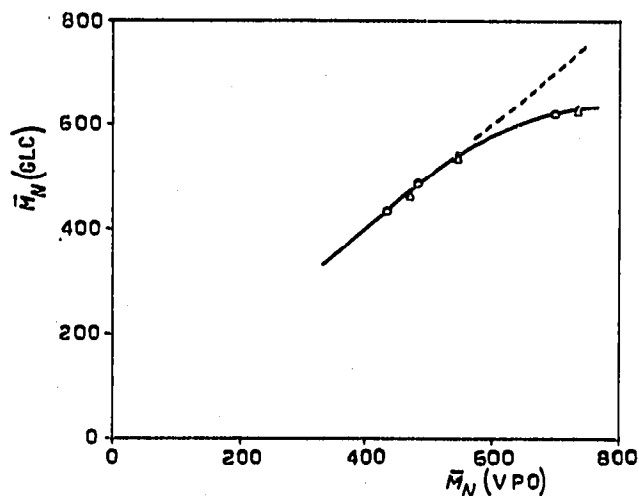


Fig. 2. Comparison between the osmometric (VPO) and the chromatographic (GLC) values of \bar{M}_N . ○ = $C_6H_5O(CH_2CH_2O)_n C_6H_5$; △ = $C_6H_5S(CH_2CH_2O)_{n-1}SC_6H_5$.

TABLE II

COMPARISON BETWEEN THE VAPOUR-PRESSURE OSMOMETRIC (VPO) VALUES OF \bar{M}_N FOR THE STARTING POLYETHYLENE GLYCOLS AND THE GAS-LIQUID CHROMATOGRAPHIC (GLC) \bar{M}_N OBTAINED FOR THE CHLORO AND THE TRIMETHYLSILYL DERIVATIVES³

\bar{M}_N (VPO)	\bar{M}_N (GLC)	
	$Cl(CH_2CH_2O)_{n-1}CH_2CH_2Cl$	$(CH_3)_3SiO(CH_2CH_2O)_nSi(CH_3)_3$
304	310	286
409	366	359
625	458	506

$RO(CH_2CH_2O)_nR$ where R = phenyl or trimethylsilyl

$RO(CH_2CH_2O)_{n-1}CH_2CH_2R$ where R = chloride or thiophenyl

The phenyl and the thiophenyl derivatives were purified by liquid-solid chromatography^{4,5}.

Results

Fig. 1 shows the gas chromatographic molecular-weight distribution curves found for the phenyl and the thiophenyl derivatives. The \bar{M}_N values calculated from these curves are compared in Fig. 2 and Table I with the corresponding vapour-pressure osmometric values. Up to about a molecular weight of 550, the discrepancy between the GLC and the VPO values is only 1-2% for these low-volatility derivatives. The PEG 400 sample that shows this error contains small amounts of compounds with mol. wt. \approx 700, and so—in view of the small error—the gas chromatographic analysis under the present conditions can be considered to give quantitative results up to a molecular weight of 700.

Fig. 3 shows the gas chromatographic molecular-weight distribution of the chloro and the trimethylsilyl derivatives. In order not to introduce new distortions,

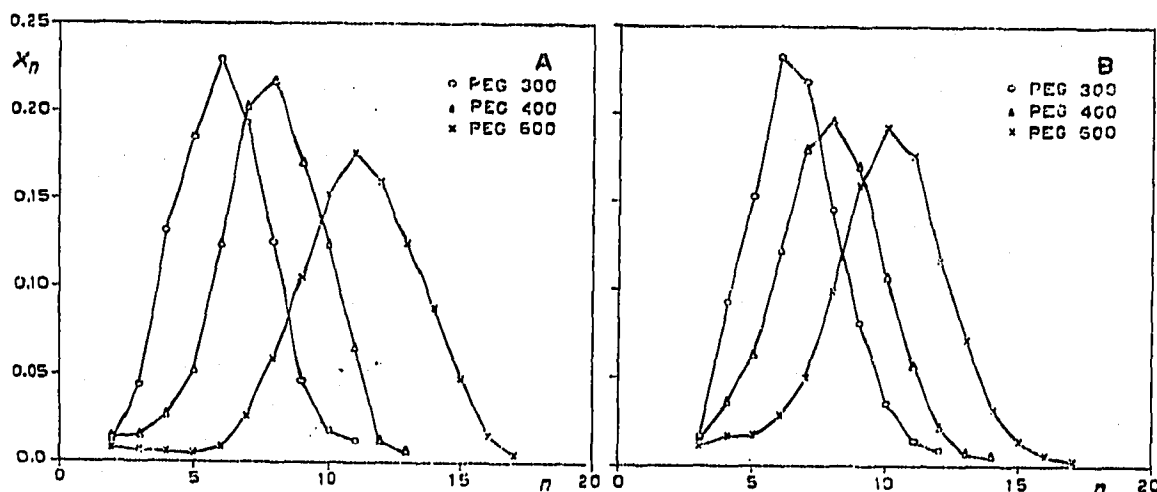


Fig. 3. Molecular-weight distribution of polyethylene glycol derivatives. (A) = $(CH_3)_3SiO(CH_2CH_2O)_nSi(CH_3)_3$; (B) = $Cl(CH_2CH_2O)_{n-1}CH_2CH_2Cl$.

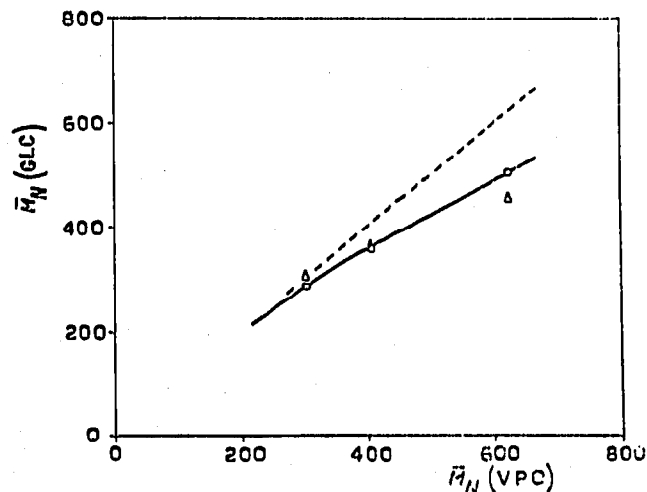


Fig. 4. Comparison between the osmometric values for the \bar{M}_N of the starting polyethylene glycols and the gas chromatographic values of \bar{M}_N of the chlorine and the TMS derivatives of these polyethylene glycols. ○ = $(\text{CH}_3)_3\text{SiO}(\text{CH}_2\text{CH}_2\text{O})_n\text{Si}(\text{CH}_3)_3$; △ = $\text{Cl}(\text{CH}_2\text{CH}_2\text{O})_{n-1}\text{CH}_2\text{CH}_2\text{Cl}$.

the derivatives were not purified. Table II compares the \bar{M}_N (VPO) values for the starting polyethylene glycols and the \bar{M}_N (GLC) values obtained with these derivatives. Showing the same comparison, Fig. 4 indicates that GLC tends to give values that are too low. This discrepancy, which can be considered negligible (a few percent) only in the case of PEG 300, is due mainly to the incomplete conversion of higher-molecular members into the derivatives. Investigations of the factors influencing this conversion are likely to lead to an increase in the yield, and thus in the range of molecular weights of polyethylene glycols in which GLC gives analytically acceptable results.

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