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RAPID DETERMINATION OF THE MOLECULAR-WEIGHT DISTRIBUTION OF ETHYLENE GLYCOL OLIGOMERS BY THIN-LAYER CHROMATOGRAPHY AND THEIR PHOTOMETRIC EVALUATION*

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SUMMARY

Thin-layer chromatography, coupled with the direct photometric measurement of the spots visualized with iodine vapour, offers a suitable means of estimating the molecular-weight distribution of oligomeric polyethylene glycol derivatives. The present work is restricted to the lower oligomers in order to permit a comparison with gas chromatographic data, but more interest is attached to the resolution of higher oligomers, for which gas–liquid chromatography is unsuitable.

INTRODUCTION

The use of programmed-temperature gas chromatography is restricted to volatile derivatives in the determination of the molecular-weight distribution (MWD) of polyethylene glycol compounds having the general formula $RO(CH_2CH_2O)_nR'$, where R and R' are e.g. hydrogen atoms, alkyl groups, or alkylaryl groups and n is the degree of polymerization. Admittedly, the substitution of trimethylsilyl groups for the OH groups raises the volatility of some derivatives and permits the resolution of oligomers with molecular weights of nearly 1000 under suitable conditions[1]. However, with less volatile derivatives, such as those in which R and R' represent p-(1,1,3,3-tetramethylbutyl)phenyl groups, progressively poorer results are obtained as the molecular weight exceeds 700–800. This emerges from a comparison with the corresponding molecular-weight distribution obtained by column chromatography[2].

For the determination of the MWD of less volatile higher members, one must resort to liquid–solid chromatography, and very good results have in fact been obtained by thin-layer chromatography in the fractionation of derivatives with R = p-n-nonylphenyl and R' = H, with n values of up to 16 (see ref. 3), and in the determination of the MWD of compounds with n values of up to 14 by the circular technique and the densitometric evaluation of a photograph of a suitably visualized chromatogram[4]. Furthermore, compounds with n values of up to 27 have been separated in the case of the series $RS(CH_2CH_2O)_nCH_2CH_2SR$ with R = R' = tert-hexyl[5].

The aim of the present study was to examine the accuracy of TLC, coupled with direct photometric evaluation in the determination of the MWD of ethylene glycol oligomers. The visualizing agent was iodine vapour which has been used recent-

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* Translated by Express Translation Service.

ly for the paper chromatographic detection of these compounds[6]. The advantages of iodine vapour over the usual sprays are as follows:

(a) no damage to the plate and no spot enlargement;

(b) inextensive and transient adsorption on the silica, giving a uniform surface, with little difference from the initial one;

(c) the generally pale brown spots on a white background are easy to measure photometrically;

(d) iodine vapour is often non-destructive, because it can be removed under reduced pressure.

The main disadvantage of iodine vapour is that the fading time of the spots varies with the nature of the substance. However, the problems of accuracy introduced by this fact into the photometric evaluation can be minimized by optimizing the geometry and the saturation of the tank, the time of exposure, and the "fixation" of the visualized plate.

The work was done on two types of compounds having the formula $RO(CH_2CH_2O)_nR'$, one type with $R = R' =$ phenyl, and the other type with $R = p\text{-}tert.$-nonylphenyl and $R' = H$, the value of n ranging up to 17. The results were checked against gas chromatographic data.

EXPERIMENTAL

The diphenyl derivatives, whose mean degree of polymerization $\bar{n}$ was about 7.3 and 10.3, were prepared as described before[1]. Single oligomers with $n = 6, 8$, and 9 with purities of 99.5, 98.8, and 98.0%, respectively, determined by gas chromatography, were synthesized in the laboratory, while the derivatives with $R = p\text{-}tert.$-nonylphenyl and $R' = H$, with $\bar{n} = 5.4$ and 6.4 were commercial products (ex Chemische Werke Hüls). The compound with $n = 3$ (93.0%) was obtained by fractionation of a mixture with $\bar{n} = 3.3$ (see ref. 7) by column chromatography.

The silica adsorbent (Merck, type G) was applied in 40–20-μ thick layers to glass plates measuring 15×5 cm and 15×2.5 cm. This was done by means of an applicator with a fixed slit of 200 μ. A photometric check on the resulting plates was found to be essential and the more irregular ones were rejected. The plates were dried by raising the temperature to 180° in 1 h and by maintaining this temperature for $\frac{1}{2}$ h. This was done to avoid blister formation in the silica layer.

40 μg samples were applied to the plates as a 1% solution in acetone with a 10-μl Hamilton microsyringe, so as to form a spot with a diameter not exceeding 3 mm. The spots were eluted to a distance of 12.5 cm by the ascending technique with various solvents (chromatographic grade, C. Erba, Milan) and their mixtures, the plates having been placed in cylindrical Desaga tanks (20×5 cm) equilibrated with solvent vapour.

The spots were then visualized in similar tanks in a horizontal position; the atmosphere in these was saturated with iodine vapour by placing a few iodine crystals at the bottom. The plates were kept in the tanks for at least 15 min. Each plate was then immediately covered with a glass plate of the same size, and an adhesive tape was stuck around the edge to minimize evaporation of the iodine in order to preserve the colour of the spots.

The plates were then evaluated photometrically with a Joyce Chromoscan, the

TABLE I

DATA OBTAINED FROM THE THIN-LAYER CHROMATOGRAPHIC AND THE GAS CHROMATOGRAPHIC ANALYSIS OF AN ARTIFICIAL BINARY AND A TERNARY MIXTURE OF OLIGOMERS OF THE TYPE $RO(CH_2CH_2O)_n R'$, R = R' = PHENYL

$\bar{x}_n$ is the mean molar fraction in %, and s_n is the corresponding mean square deviation, based on three determinations.

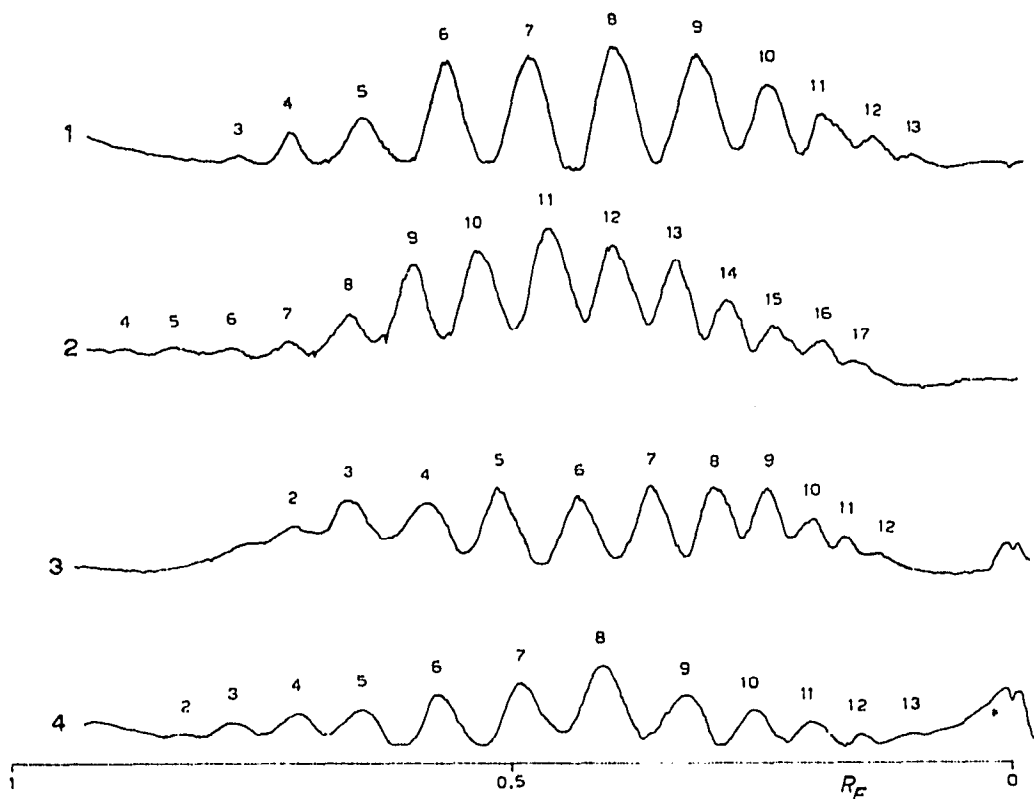| n	Composition of the mixture by		
	Gravimetry x_n	GLC x_n	TLC $\bar{x}_n \pm s_n$
8	52	54.0	50.5 ± 2.1
9	48	46.0	49.5 ± 2.1
6	33	37.3	25.3 ± 1.5
8	36	34.0	37.2 ± 1.8
9	31	28.7	37.5 ± 2.0

Fig. 1. Tracings obtained for the thin-layer chromatograms of polyethylene glycol derivatives of the type $RO(CH_2CH_2O)_n R'$. Temperature 25°. The numbers over the peaks give the n values. Curve 1: R = R' = phenyl; $\bar{n}$ = 7.3; solvent–butanone. Curve 2: R = R' = phenyl; $\bar{n}$ = 10.5; solvent:butanone–water (90:10). Curve 3: R = p-tert.-nonylphenyl, R' = H; $\bar{n}$ = 5.4; solvent: butanone–water (95:5). Curve 4: R = p-tert.-nonylphenyl, R' = H; $\bar{n}$ = 6.5; solvent:butanone saturated with water.

TABLE II

COMPARISON OF DATA OBTAINED BY THE THIN-LAYER CHROMATOGRAPHIC AND BY THE GAS CHROMATOGRAPH ANALYSIS OF POLYETHYLENE GLYCOL DERIVATIVES

n is the degree of polymerization; $\bar{n}$(calc.) is the number average degree of polymerization found from the molcular-weight distribution; $\bar{x}_n$ is the mean molar fraction in %; and s_n is the corresponding mean square deviation, based on four determinations.

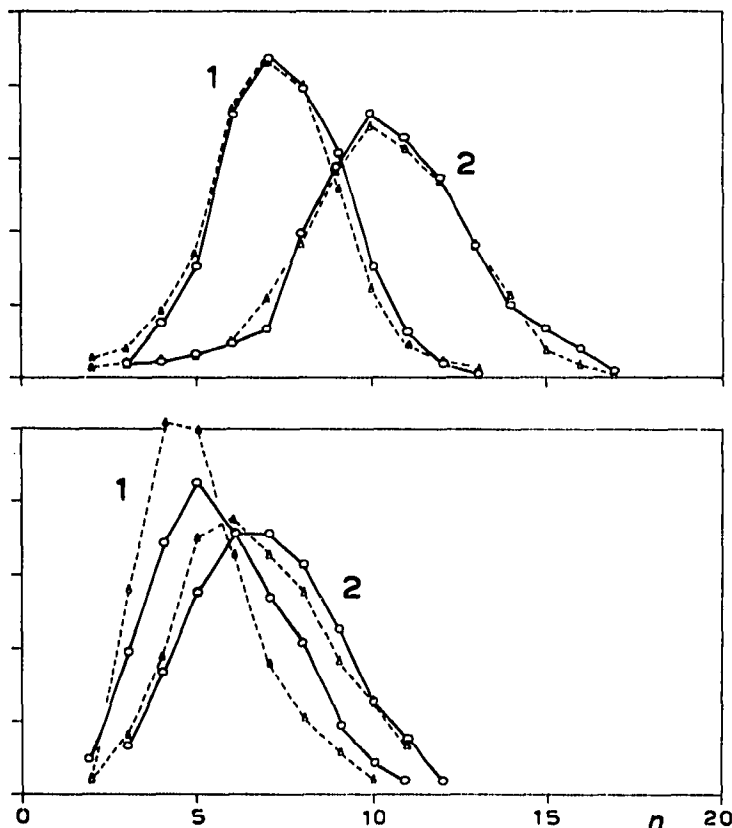| n	$RO(CH_2CH_2O)_nR'$, $R = R' = phenyl$				$RO(CH_2CH_2O)_nR'$, $R = p\text{-}tert.\text{-}nonylphenyl$			
	$\bar{n} = 7.3$		$\bar{n} = 10.5$		$\bar{n} = 5.4$		$\bar{n} = 6.5$	
	GLC x_n	TLC $\bar{x}_n \pm s_n$	GLC x_n	TLC $\bar{x}_n \pm s_n$	GLC ($R' = TMS$) x_n	TLC ($R' = H$) $\bar{x}_n \pm s_n$	GLC ($R' = TMS$) x_n	TLC ($R' = H$) $\bar{x}_n \pm s_n$
1	—	—	—	—	traces	—	—	—
2	1.30	—	0.93	—	0.99	2.41 ± 0.90	0.99	traces
3	2.00	1.02 ± 0.21	1.05	—	14.02	9.69 ± 0.28	4.11	3.12 ± 0.82
4	4.44	3.85 ± 0.26	1.18	1.07 ± 0.48	25.60	17.04 ± 0.70	9.46	8.37 ± 0.12
5	8.56	7.78 ± 0.49	1.30	1.62 ± 0.21	23.76	21.21 ± 0.64	17.54	13.99 ± 1.23
6	18.46	18.09 ± 0.92	2.33	2.32 ± 0.31	15.07	17.75 ± 1.00	18.78	17.72 ± 0.39
7	21.93	21.84 ± 0.62	5.59	3.39 ± 1.27	9.59	13.41 ± 0.11	16.39	17.83 ± 1.18
8	20.08	19.85 ± 0.43	9.30	9.81 ± 0.61	5.77	10.45 ± 0.59	13.98	16.71 ± 0.54
9	13.04	15.48 ± 0.33	14.26	14.45 ± 1.23	3.17	4.79 ± 0.68	9.21	11.36 ± 0.53
10	6.20	7.73 ± 0.45	17.16	18.07 ± 1.79	1.68	2.17 ± 0.10	6.39	6.32 ± 0.74
11	2.38	3.11 ± 0.34	15.68	16.40 ± 1.42	0.35	1.08 ± 0.26	3.15	3.70 ± 0.25
12	0.99	1.03 ± 0.27	13.49	13.68 ± 1.29	—	traces	—	0.88 ± 0.17
13	0.62	0.22 ± 0.05	9.08	8.92 ± 0.86	—	—	—	traces
14	—	—	5.63	4.92 ± 0.74	—	—	—	—
15	—	—	1.98	3.33 ± 0.15	—	—	—	—
16	—	—	0.86	1.84 ± 0.20	—	—	—	—
17	—	—	0.18	0.18 ± 0.06	—	—	—	—
$\bar{n}$(calc.)	7.20	7.44	10.21	10.51	5.18	5.69	6.61	6.75

light absorption of the plates being recorded by an apparatus capable of measuring the transmission. The maximum sensitivity was found at 430 nm (obtained with a glass filter) and a slit of 5×0.5 mm. The linear response of the recorder in the absorption was in the range 0–1.5 and the symmetry of the triangular peaks permitted the amount of each component of the mixture to be estimated by measuring the areas.

The samples were also subjected to programmed-temperature gas chromatographic analysis under the same conditions as used before[1]. The compounds with $R = p\text{-}tert.$-nonylphenyl and $R' = H$ were first converted into their trimethylsilyl (TMS) derivatives.

RESULTS AND DISCUSSION

The relative error in the MWD was determined by analyzing known mixtures of diphenyl derivatives with $n = 6$, 8, and 9, after finding a linear relationship between the amount adsorbed on the plate and the light absorption of the resulting spot, rendered visible with iodine vapour. The linearity of this relationship extended up to 40-μg samples, with a 5% accuracy (relative mean square deviation of the slope). Table I shows the results obtained by TLC and GLC for a binary and a ternary

2. Molecular-weight distributions as determined by TLC (circles and full line) and by GLC igles and broken line) for polyethylene glycol derivatives of the type $RO(CH_2CH_2O)_nR'$ $R = R' = $ phenyl (upper figure) and $\bar{n} = 7.3$ (1), $\bar{n} = 10.5$ (2); and with $R = p\text{-}tert.\text{-}$ lphenyl, $R' = H$ (lower figure) and $\bar{n} = 5.4$ (1) and $\bar{n} = 6.5$ (2). n is the degree of polymeri- n, and x_n is the molar fraction in % (cf. Table II).

ure; the molar fractions are expressed in %. For the binary mixture, the values omparable with the actual composition, but indicate a distortion in favour of the er oligomer (the reactivity of iodine seems to be proportional to n). For the ternary ure, on the other hand, systematic errors, particularly for $n = 6$, were caused by the that light absorption of the spot decreased with time (15–20% in the first 10 min, ompared to a 1–2% decrease for the $n = 9$ compound in the same period). This liarity leads to low values for those members of the mixture with a low or a medium cular weight, but this can be minimized by doing the photometric scanning in 2–3 min after visualization.

Fig. 1 shows some thin-layer chromatograms obtained for derivatives of both s. The spot at the start line in the case of the monononylphenyl derivatives is due termediates and by-products of the industrial synthesis.

The data listed in Table II indicate good agreement between TLC and GLC gards the molecular-weight distribution of the two series of compounds. This es particularly to the distribution at higher degrees of polymerization, where istortion at lower n values is less apparent (cf. Fig. 2). Furthermore, the precision nost always lower (in %) for compounds at the beginning of the distribution e than for those at its end.

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