

CHROM 4967

PREPARATION OF MONODISPERSE POLYETHYLENE OXIDES BY GEL PERMEATION CHROMATOGRAPHY OF DISCONTINUOUS POLYMER-HOMOLOGOUS SERIES

B. BÖMER, W. HEITZ AND W. KERN

Institute of Organic Chemistry, University of Mainz (G.F.R.)

SUMMARY

Starting from triethylene glycol, monodisperse polyethylene oxides of a molecular weight (MW) up to 2000 (degree of polymerisation (DP) ≤ 45) were synthesised in a two-step process.

During the first step the ditosylate of triethylene glycol is reacted with the sodium alkoxide of the same diol at room temperature. The condensation product (polymer homologues of triethylene glycol) was separated by molecular distillation and yielded the pure oligomers nonaethylene glycol (DP = 9, MW = 414) and pentadecaethylene glycol (DP = 15, MW = 678), as proved by gel chromatography.

During the next step the polymer homologues of nonaethylene glycol were synthesised in a similar way. The pure oligomers heptecosa (DP = 27, MW = 1207) and pentatetracontaethylene glycol (DP = 45, MW = 2000) were isolated by preparative gel permeation chromatography on a polystyrene gel cross-linked with 2% divinylbenzene. Using a column, 200 \times 5 cm, samples of up to 5 g could be separated.

The separation of technical polyethylene oxides prepared by polymerisation indicated that up to a DP of approximately 27 adjacent oligomers are still resolved.

INTRODUCTION

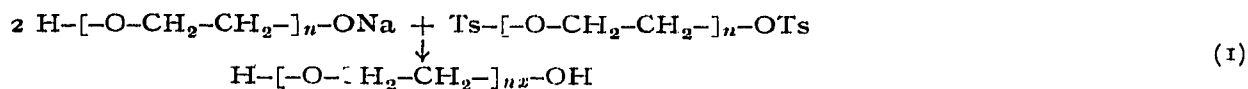
Oligomers have hitherto been prepared mainly either by separation of polymers of low molecular weight with the aid of efficient separation methods or by specific syntheses. In order to prepare monodisperse polyethylene oxides we have combined these two methods and have thus been able to obtain in a few stages absolutely uniform products of relatively high molecular weight.

We have chosen the Williamson ether synthesis for the construction of the polymer chain. This reaction has the advantage that both condensation components (ditosylate and sodium alcoholate) can be prepared from the corresponding diol under conditions where the ether bonds are fully stable. After termination of the condensation the unconverted reactive groups may easily be hydrolysed back to the hydroxyl groups, so that a reaction mixture with only one type of the end group is obtained.

In each stage of the synthesis, the alcoholate of an oligoethylene glycol reacts with the ditosylate of the same oligomer. Because of the influence of the dialcoholate

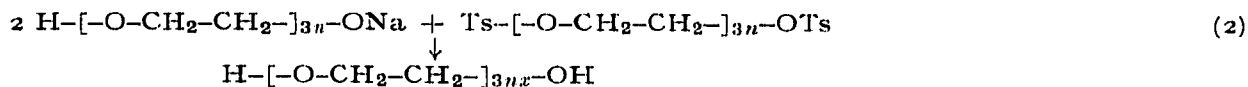
molecules, present in the equilibrium, the polymer homologues of the original oligomer are obtained after hydrolysis of the unreacted tosylate groups.

The synthesis can be written thus:



Ts = tosyl group

$n = 1, 2, 3, 4, 5 \dots$



$n = 1, 2, 3, 4, 5 \dots$

Using gel chromatography, which provides a method of separation according to molecular size, it should be possible to separate completely at least the first members of such a discontinuous polymer homologous series. By using an excess of diol, the main reaction product is the oligomer with a DP three times higher, which can be used as the starting material for the next synthesis stage.

We suggest the name "triplication process" for this type of synthesis.

It is especially important to have high purity triethylene glycol as the starting material. It can be shown by gas chromatography of the bis-(trimethylsilyl) ethers that the triethylene glycol used for the synthesis contains less than 0.1 % each of neighbouring oligomers, di- and tetraethylene glycol.

In the first stage we let sodium alcoholate of triethylene glycol react with the ditosylate of the same compound in an excess of triethylene glycol, in the dark and in a nitrogen atmosphere. After 50 days at room temperature over 90 % of the alcoholate had reacted. The sodium tosylate formed, in aqueous solution, was removed by ion-exchange chromatography and the excess triethylene glycol was distilled off under vacuum.

From the remaining mixture of polymer homologues of triethylene glycol, the oligomers nonaethylene glycol ($n = 9$) and pentadecaethylene glycol ($n = 15$) were isolated by repeated molecular distillations, and can be shown to be pure by gel chromatography. The crude yield of the condensation products was 74 % based on the ditosylate.

In the next triplication step the polymer homologues of nonaethylene glycol were prepared. The oily ditosylate of nonaethylene glycol was purified by column chromatography over silica gel and was obtained in a 72 % yield. The condensation was carried out in toluene and, after 8 days reaction at room temperature, 90 % of the alcoholate had been used. In order to hydrolyse unreacted tosylate groups, water was added and the reaction mixture refluxed. The excess nonaethylene glycol was removed by molecular distillation. The yield of condensation products was 81 % of the theoretical.

The mixture of polymer homologues of nonaethylene glycol, obtained in this way, was separated by gel chromatography on a polystyrene gel cross-linked with 2 % divinyl benzene. Tetrahydrofuran (THF) was used as eluant. The column dimensions were 200 × 5 cm which corresponds to a total volume of 3.9 l. We have already des-

cribed a reproducible method for filling a column of these dimensions¹. The average particle diameter of the swollen gel is about $65 \mu\text{m}$ and a theoretical plate count of 13,500 is obtained for benzene at an elution rate of 200 ml/h.

Fig. 1 shows an analytical gel chromatogram of polymer homologues of nonaethylene glycol. Although the molar ratio of diol to sodium was 2:1, a considerable amount of higher condensation products is formed. These are resolved up to $n = 63$.

Samples of up to 5 g in 50 ml THF could be roughly separated. The fractions thus obtained were then rechromatographed in amounts of 0.5–1 g and thus monodisperse substances were obtained.

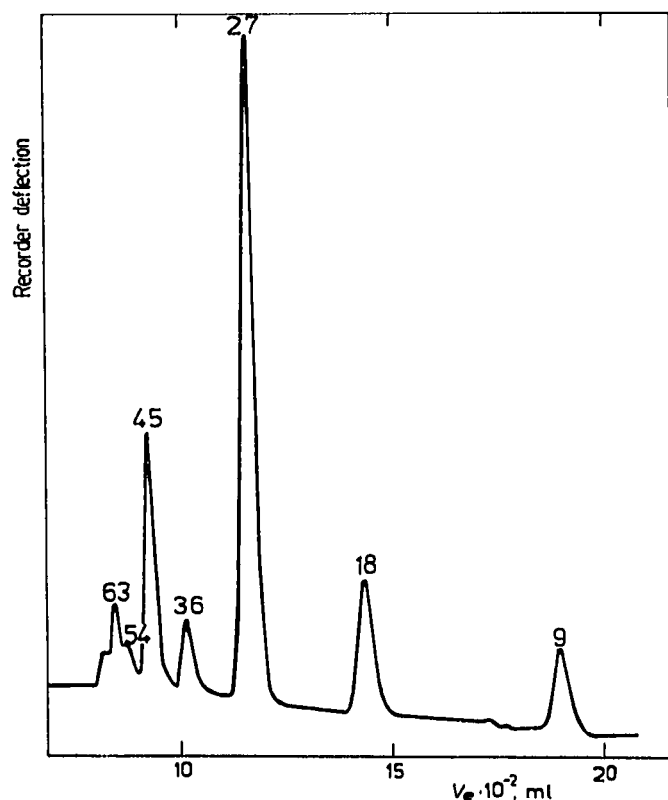


Fig. 1. Analytical gel chromatogram of a discontinuous polymer homologous series of oligoethylene glycols. $\text{HO}-[\text{CH}_2-\text{CH}_2-\text{O}]_n-\text{H}$ ($n = 9x$; $x = 1, 2, 3 \dots$). The numbers above the peaks correspond to the degree of polymerisation n .

Since the uniformity of the molecular weight was tested by gel chromatography, it was important to know the resolving efficiency under the separation conditions used. For this purpose we separated commercial polyethylene oxides prepared by polymerisation and forming a continuous polymer homologous series². In this way it was found that the resolving efficiency was adequate up to about $n = 27$ when comparable amounts of the homologues are present.

Alongside the dispersivity test by gel chromatography, molecular weight determinations were also carried out by vapour pressure osmometry. The values obtained agree very well with the formula weights.

Table I shows a comparison of the melting points of oligoethylene glycols. We determined the melting points in a thermostated vessel, the temperature of which was

raised about 0.2° every 10 min. The melting points of our oligomers lie significantly above the literature values.

From the theoretical considerations of the possibility of the formation of side products and of the ease with which they may be removed, it follows that only the products which are formed by linking an even number of units can include side prod-

TABLE I
MELTING POINTS OF OLIGOETHYLENE GLYCOLS
 $\text{H}-[\text{-O-CH}_2\text{-CH}_2\text{-}]_n\text{-OH}$

<i>n</i>	<i>M.p.</i> ($^\circ\text{C}$) <i>our values</i>	<i>M.p.</i> ($^\circ\text{C}$) <i>lit. values</i>
9	29.8-30.0	only b.p.
14	—	29.5
15	38.6-38.8	—
18	32.0-32.4	24 35
27	44.6-44.8	—
30	—	38.6
36	43.0-43.4	—
42	—	33.8
45	49.9-50.1	—
90	—	40.6
186	—	44.1

ucts, formed by elimination or cyclisation in appreciable amounts. In agreement with this the polyethylene oxides with $n = 18$ (2×9) and $n = 36$ (4×9) show relatively lower melting points and broader melting ranges than the absolutely pure substance with $n = 9, 15, 27$ and 45 .

Polyethylene oxides of higher molecular weight are not very soluble in THF. Preparative scale separations of the polymer homologues of heptecosaethylene glycol ($n = 27$) may be carried out on Merckogel OR 20000, a poly(vinyl acetate) gel with methanol as solvent. We filled two columns each 100×2.4 cm (total volume of each 450 ml) with a quantity of this gel with a narrow particle size distribution methanol being used as eluant. At an average particle diameter of $24 \mu\text{m}$ in the swollen state we obtained for diethylene glycol a theoretical plate count of 20000 for a 2 m column length at an elution rate of about 40 ml/h. In methanol this gel has a M_{lim} for polyethylene oxides of about 9000. This arrangement allows a good separation of the polymer homologues of nonaethylene glycol up to $\text{DP} = 72$.

The reaction mixture of a preliminary condensation of heptecosaethylene glycol ($n = 27$) was resolved up to $\text{DP} = 135$ (5×27), corresponding to a molecular weight of about 6000.

REFERENCES

- 1 W. HEITZ AND H. ULLNER, *Makromol. Chem.*, 120 (1968) 58.
- 2 W. HEITZ, B. BÖMER AND H. ULLNER, *Makromol. Chem.*, 121 (1969) 102.

J. Chromatog., 53 (1970) 51-54