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PREPARATION OF ETHYLENE GLYCOL OLIGOMERS

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Abstract—Procedures are described for the preparation of pure nonaethylene glycol and practically pure pentadecaethylene glycol from the monosodium salt and the ditosylate of triethylene glycol, using both toluene and tetrahydrofuran as diluents. The much faster reaction in the latter makes this the preferred reaction medium.

INTRODUCTION

The anionic polymerization of ethylene oxide [1] yields low molecular weight polymers of narrow molecular weight distribution, which have proved most useful in studies on chain folding during crystallization [2–4]. It is possible that more useful information would result from studies of monodisperse ethylene oxide oligomers, particularly if their preparation is such that all end-groups are identical.

Fractional distillation of polydisperse polyethylene glycol has been used [1] to separate individual oligomers up to the hexamer, but the decreased volatility of the higher homologues makes extension of this process impractical.

The preparation of Hibbert *et al.*, and many subsequent preparations, were carried out before gel permeation chromatography (GPC) and gas-liquid chromatography (GLC) were available. Consequently reliable estimates of purity are not available. It is known [10] that products completely free from halogen and vinyl end-groups cannot be obtained by repeated fractional crystallization. The purity of oligomers so obtained, other than those separated by distillation, is in doubt.

Bömer *et al.* [13] have used the reaction between the α,ω-ditosylate of a given glycol and the monosodium salt of the same glycol, with elimination of sodium tosylate. The general "triplication" reaction is written

$$\mathrm{TosO}\left[\mathrm{CH_2CH_2O}\right]_n\mathrm{Tos} + 2\mathrm{NaO}\left[\mathrm{CH_2CH_2O}\right]_n\mathrm{H} \rightarrow \mathrm{HO}\left[\mathrm{CH_2CH_2O}\right]_{3n}\mathrm{H} + 2\mathrm{NaOTos}$$

This reaction takes place at room temperature; at the end of the reaction, residual tosylate groups can be readily hydrolysed so that the product contains only oligomers with hydroxy end-groups.

Step-wise synthesis of individual oligomers was first reported by Perry and Hibbert [5]. They replaced the hydroxy groups on a given glycol by chlorine, and then reacted 1 mol of the resultant α,ω-dichloro derivative with 2 mol of the monosodium salt of the given glycol, in a Williamson synthesis carried out in the range 70–170°C. Preparations of ethylene glycol oligomers containing as many as 186 monomer units have been described [6, 7]. These products were isolated by repeated low-temperature crystallization and purity was checked by time-temperature cooling curves. Others have used this method [8–12] and some [8, 10] have described its limitations with respect to the formation of by-products and their ease of removal. The by-products are oligomers of more than $3n$ monomer units, arising from equilibration between sodium salts of the original and resultant glycols, and also oligomers with unsaturated end-groups, arising from elimination of hydrogen chloride. An excess of starting glycol can be used to minimise the yield of higher homologues [10] but the strongly alkaline conditions and the high temperatures which favour the formation of unsaturated end-groups are inherent in the method.

Melting and freezing points of various ethylene glycol oligomers, taken from the literature [6–9, 11, 13–15] are plotted against degree of polymerization (x) in Fig. 1. The melting points of the oligomers prepared by the method of Hibbert *et al.* are seen to be generally lower than those prepared by the method of Bömer *et al.* This may be attributable to the effect of non-hydroxy end-groups. For example, it is known that the melting points of ethylene glycol oligomers are substantially reduced when hydroxy end-groups are replaced by chloro groups [14, 16]. Oligomers prepared by the method of Bömer *et al* which have an even number of chain units ($x = 18$ or 36 in Fig. 1) have low melting points relative to oligomers prepared in the same way which have x odd. This has been attributed [13] to the presence of by-products formed by elimination or cyclization reactions which can occur only in products formed by linking an even number of units.

Here we describe the synthesis of nonaethylene gly-

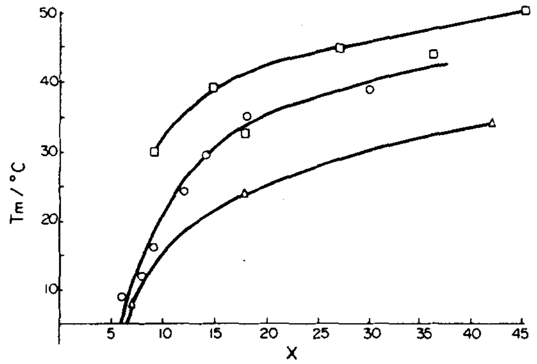

Fig. 1. Melting point (T_m) vs degree of polymerization (x) for ethylene glycol oligomers: (□) Bömer *et al.* [13] or (○) other workers [8, 9, 11, 14] for oligomers synthesized by the method of Hibbert *et al.* Freezing points measured by Hibbert *et al.* [6, 7, 15] are indicated (△).

col and pentadecaethylene glycol by the tosylate method starting from triethylene glycol. The procedures of Bömer *et al.* [13] have been considerably modified. Our methods are described in some detail, since only a brief account has been published earlier [13].

EXPERIMENTAL

Materials

Analar pyridine (BDH) was left overnight over calcium hydride, then boiled under reflux over calcium hydride (1 hr) and finally distilled through a 30 cm Vigreux column, collecting distillate b.p. 113–114°C. Toulene-*p*-sulphonyl chloride (BDH, > 98%) was used without further purification from a fresh batch. Analar toluene was allowed to stand overnight over calcium hydride and then distilled on to, and stored over, type 4A molecular sieve (Union Carbide).

Triethylene glycol (BDH, > 99% by GLC) was stood for several days over anhydrous magnesium sulphate, and then fractionally distilled through a 35 × 2.5 cm Vigreux column at reduced pressure, collecting material b.p. 94–100°C/~0.1 mm Hg. Fractions which by GLC (1.8 m column at 175°C packed with 3% polyethylene glycol adipate) showed only one peak were united and used.

Analar methanol (BDH) was distilled from magnesium methoxide onto Type 4A molecular sieve (Union Carbide). Tetrahydrofuran (BDH) was left overnight over calcium hydride, and then boiled under reflux (1.5 hr) before being distilled directly onto the solid to be dissolved. Sodium metal (BDH) was used without further purification. Diethylene glycol and ethylene glycol (Shell Chemical Co. Ltd, commercial grades) were used as received.

Procedures

Triethylene glycol ditosylate (**I**)

A solution of toluene-*p*-sulphonyl chloride (12.83 g, 0.067 mol) and triethylene glycol (4.96 g, 0.033 mol) in dry pyridine (15 cm^3) under dry N_2 was stirred at 0°C (2 hr), becoming semi-solid. Addition of this to ice and water (400 cm^3) precipitated **I** (11.68 g, 78% yield), m.p. 80.5–82°C. Recrystallization twice from ethanol gave pure **I**, m.p. 81.5–82°C. The infrared (i.r.) spectrum (NaCl) showed bands at 1175, 1190 cm^{-1} ($—O_3SC_6H_4CH_3$) [17]) and no bands at 3200–3600 cm^{-1} (—OH). The proton magnetic resonance (PMR) spectrum ($CDCl_3$) showed resonances at 7.5–7.6τ ($—CH_3$), 5.8–6.5τ ($—CH_2—$) and 2.2–2.7τ (Ar-H) with associated integrals in complete accord with the expected structure. (Anal. Calc for $C_{20}H_{26}O_8S_2$: C, 52.39%; H, 5.71%; S, 13.98%. Found: C, 52.3%; H, 5.9%; S, 13.9%). Subsequent preparations on a larger scale gave material for "triplication" in similar yields.

Nonaethylene glycol (*II*) *and pentadecaethylene glycol* (*III*)

(A) *Preparation in toluene*. A solution of sodium methoxide in methanol was prepared by the addition of dry methanol (47.5 g, 1.49 mol) to Na (4.57 g, 0.20 g atom) under dry N_2. Redistilled triethylene glycol (75.2 g, 0.5 mol) was then poured rapidly (1 min) into the vigorously stirred methoxide solution cooled in ice. The solution was stirred at room temperature (0.5 hr) before the methanol was evaporated off in a fast stream of N_2 leaving a pale yellow liquid. To this vigorously stirred liquid was added rapidly (3 min) a solution of triethylene glycol ditosylate (45.9 g, 0.1 mol) in toluene (500 cm^3). The flask was shielded from light and the two phase mixture was stirred (8 hr per day, 5 days per week).

From time to time solids were washed down the flask walls into the bulk and samples of the mixture were withdrawn for analysis by GPC. After 6 weeks the mixture was rotary evaporated to remove toluene. Addition of water (300 cm^3) to the residue gave a cloudy solution which was filtered, made up to 1 dm^3, and boiled under reflux (2 hr), becoming almost neutral. This solution was rotary evaporated to yield a solid suspended in an oily liquid, which was extracted with dichloromethane (500 cm^3) leaving a residue of sodium tosylate (23.65 g, 61% yield). The dichloromethane solution was washed with aqueous Na_2Co_3 (10% w/v, 50 cm^3) and the aqueous washings re-extracted with dichloromethane (8 × 300 cm^3). The bulked dichloromethane extracts were dried ($CaSO_4$). Filtration of the solution followed by rotary evaporation yielded an oil (58 g) which contained some sodium tosylate. This was removed by dissolving the oil in dichloromethane (150 cm^3) and washing with 10% w/v aqueous Na_2Co_3 (20 cm^3, aqueous phase re-extracted with dichloromethane, 8 × 120 cm^3). The bulked dichloromethane extracts were concentrated (150 cm^3) and washed with water (20 cm^3, aqueous phase re-extracted with dichloromethane, 9 × 120 cm^3). Rotary evaporation of the bulked dried ($CaSO_4$) dichloromethane solution yielded a yellow oil (43.8 g), from which was distilled triethylene glycol (18.6 g). The residue (22.1 g) was a mixture of oligomeric ethylene glycols ($HO[CH_2CH_2O]_xH$, $x = 3, 6, 9, 12, 15, 18, 21$).

A simple retort-shaped short-path still, with a pot volume of 50 cm^3 was used to distill the residue. The still was heated in an electric furnace and could be evacuated to pressures less than 0.001 mm Hg. Pre-dried glass wool packed into the still pot served to prevent bumping. By slowly raising the temperature (noted on a thermometer with its bulb clamped to the still pot) and noting carefully the rate of distillation and the ease of solidification of the distillate, it was possible to separate almost pure nonamer and pentadecamer. For example, 7.20 g residue gave combined fractions as follows: (i) 1.51 g, b.p. 140–159°C/ ~ 0.005 mm Hg, mainly $x = 6$; (ii) 4.27 g, b.p. 177–215°C/ ~ 0.001 mm Hg, mainly $x = 9$; (iii) 0.27 g, b.p. 228–244°C/ ~ 0.001 mm Hg, $x = 9, 12, 15$; (iv) 0.64 g, b.p. 246°–257°C/ ~ 0.001 mm Hg, mainly $x = 15$; (v) 0.50 g, residue. Three such distillations (total charge 20.48 g) yielded almost pure nonamer (12.04 g) and pentadecamer (1.55 g). Repeated redistillation of the nonamer fraction yielded pure **II** (9.21 g, 22.3% yield*, b.p. 186–192°C/ ~ 0.001 mm Hg) as a white hygroscopic solid, m.p. 29.1–29.6°C (sealed tube). The pentadecamer (1.55 g, 4.6% yield, b.p. 246–257°C/ ~ 0.001 mm Hg) was not redistilled, and was a pale yellow, slightly hygroscopic solid, m.p. 38.4–39.7°C (sealed tube). Attempts to remove the colour by precipitation from toluene solution using isooctane, or by treatment with active carbon, were unsuccessful.

(B) Preparation in tetrahydrofuran

The monosodium salt of triethylene glycol was prepared, as previously described, from methanolic sodium methoxide (0.31 mol sodium methoxide) and triethylene glycol (133.8 g, 0.89 mol). An attempt was made to remove last traces of methanol by heating the viscous mixture at 90–100°C/ ~ 1 mm Hg until bubbling ceased. To the cooled stirred liquid was added (0.5 hr) a solution of triethylene glycol ditosylate (70.1 g, 0.15 mol) in dry tetrahydrofuran (680 cm^3). As addition proceeded the solution deepened in colour (yellow) and a faint cloudiness appeared. The reaction mixture was shielded from light and stirred continuously at room temperature for 124 hr. The white solid precipitate of sodium tosylate (54.99 g, 94% yield) was filtered off. The filtrate was heated *in vacuo* to evaporate most of the tetrahydrofuran. Water (300 cm^3) was added, and the mixture boiled (2.5 hr) and concentrated (~200 cm^3) before extracting with dichloromethane (8 × 200 cm^3). The combined extracts were washed with 10% w/v aqueous Na_2CO_3 (50 cm^3) and the aqueous phase re-extracted with dichloromethane (6 × 50 cm^3). Finally the combined organic extracts were washed with water (25 cm^3). Continuous extraction (82 hr) of the combined aqueous extracts with dichloromethane yielded practically pure triethylene glycol (49.6 g). Evaporation of solvent from the combined dichloromethane extracts gave a crude product from which triethylene glycol (36.0 g) was distilled. The residue (33.7 g) contained a mixture of higher oligomers, similar in composition to that obtained in (A).

A single short-path distillation of this residue, as described in (A) but with a larger apparatus, gave fractions as follows: (i) 3.48 g, b.p. 168–175°C/ ~ 0.005 mm Hg, $x = 3$, 6, 9; (ii) 0.81 g, b.p. 180–200°C/ ~ 0.001 mm Hg, $x = 6$, 9; (iii) 22.95 g, b.p. 200–210°C/ ~ 0.001 mm Hg, mainly $x = 9$; (iv) 0.83 g, b.p. 220–250°C/ ~ 0.001 mm Hg, $x = 9$, 12, 15; (v) 2.86 g, b.p. 250–270°C/ ~ 0.001 mm Hg, mainly $x = 15$; (vi) 0.74 g, residue. Redistillation of fraction (iii) gave pure **II** (18.9 g, 29.8% yield, m.p. 29.6°C). The pentadecamer fraction (2.86 g, 5.5% yield) was not redistilled.

RESULTS AND DISCUSSION

Bömer *et al.* [13] have described the "triplication" of triethylene glycol in an excess of glycol as diluent. The reaction time at room temperature was 50 days. They have also described a "triplication" of nonaethylene glycol with toluene as diluent, for which the reaction time at room temperature was 8 days.

In our first preparation toluene was used as diluent. The excess of glycol was not soluble in this system, and vigorous stirring was employed. Substantial conversion was obtained in 14 days at room temperature, although we allowed the reaction to run for a longer period of time. At the end of the reaction, after hydrolysing any unreacted tosylate groups, the glycols were separated from sodium tosylate by extraction of a concentrated aqueous solution with dichloromethane. We found this procedure more convenient than the use of ion-exchange resin [13]. The yield of crude oligomers ($x = 6$, 9, 12, 15, 18, 21; see Fig. 2) was about 50% of the theoretical nonamer yield. The minor products with $x > 12$ arise from equilibration between sodium salts of the original and resultant glycols. An attempt was made to separate the nonamer by fractional crystallization from toluene solution at 0°C using isooctane as precipitant. A similar solvent has been used [18] to fractionate high molecular weight poly(ethylene oxide). It proved difficult to separate substantial quantities of nonamer and pentadecamer in this way. Repeated molecular distillation from a retort-shaped still gave pure nonaethylene glycol which crystallized as a white solid (about 20% yield) and practically pure pentadecaethylene glycol which crystallized as a pale yellow solid (about 5% yield).

Tetrahydrofuran was then found to be a much better diluent. In this system triethylene glycol, its ditosylate and its monosodium salt are all soluble, whilst sodium tosylate is insoluble. The sodium tosylate can be removed by filtration, and its weight can be used to estimate the conversion. High conversions were obtained at room temperature in 4–5 days. The yields and compositions of the crude oligomer mixture were similar to those obtained with toluene as diluent; e.g. molecular distillation gave nonamer in about 30% yield and pentadecamer in about 6% yield.

Mass spectroscopy

Samples of distilled nonamer from each preparation were examined by mass spectroscopy (AEI Model MS12). Within the limits of reproducibility, the spectra were identical with a repeat pattern of fragments arising from successive loss of ethoxy units readily discernible. No fragments nor patterns of fragments arising from loss of tetramethyleneoxy units were seen: such chain units might have been found in the product of preparation (B) if fission of an ether bond in tetrahydrofuran had led to its incorporation in the product. No molecular ion was observed at *m/e* 414, but a small peak at *m/e* 415 may have arisen from a route:

$$M + {}^{+}CH_2CH_2OH \rightarrow MH^{+} + CH_2CH_2O$$

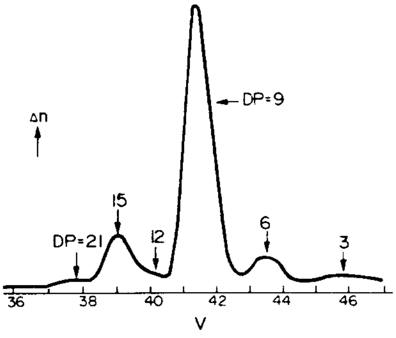

Fig. 2. Differential refractive index (Δ*n*, arbitrary scale) against elution volume (V) for GPC of the oligomer mixture prior to distillation. The peaks corresponding to the various oligomers are indicated.

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* The yield of nonamer is based on the incorporation of one ditosylate residue in the product; that of pentadecamer on the incorporation of two ditosylate residues.

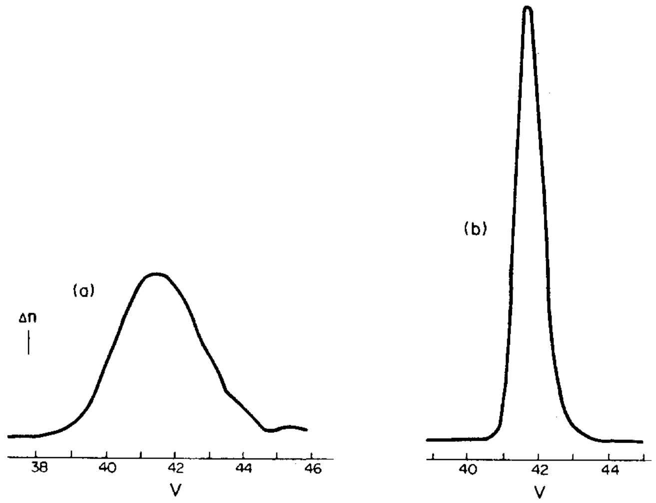

Fig. 3. Differential refractive index (Δn, arbitrary scale) against elution volume (V) for GPC of (a) PEO-400 ($x_n \sim 9$; 2 cm^3 injection of 1.7 g dm^{-3} solution) and (b) pure nonaethylene glycol (2 cm^3 injection of 1.5 g dm^{-3} solution).

Infrared spectroscopy

Spectra were recorded on a Perkin–Elmer Model 237 spectrometer. Samples were studied as thin films between NaCl plates: precautions were taken to minimise uptake of moisture. The spectra of the melts were almost identical to those of samples of commercial polyethylene glycol of similar molecular weight (PEO-400 and -600, dried by melt evacuation at 30–60°C/ ~ 0.001 mm Hg, 15–20 hr). There was no evidence of unsaturated or carbonyl groups: such impurities have been reported in other ethylene oxide oligomers [19]. The spectra of the solids (room temperature, −76°C) were recorded and are discussed elsewhere [20].

Nuclear magnetic resonance spectroscopy

Spectra (CDCl$_3$) were recorded on a Perkin–Elmer R12B spectrometer. Resonances were found at 6.3τ (—CH$_2$—) and 7.0–7.4τ (—OH). The ratio of integrals CH$_2$/OH was variable from sample to sample, and probably reflected the effects of moisture on the broad and weak —OH resonance. Methoxy end-groups (resonance at 6.6τ), which were detected in the lower oligomeric products of the preparative reaction $x = 3$, 6), were not detected in the nonamer and the pentadecamer. These arise from competitive reactions of sodium methoxide and the sodium salt of triethylene glycol with triethylene glycol ditosylate, which lead to the formation of the dimethyl ether of triethylene glycol and the methyl ether of hexaethylene glycol.

Gel permeation chromatography (*GPC*)

Six Styragel columns (length 1.2 m, diameter 0.94 cm, nominal pore sizes 5–8, 10, 15–35, 20–50, 50–200 and 70–200 nm) were used with tetrahydrofuran at 25° and 1 cm^3/min flow rate and a differential refractometer (Optilab Multiref 901) as detector. Samples were injected at a concentration of 1–2 g dm^3 via a 2 cm^3 loop. The system was calibrated for molecular weight by use of commercial polyethylene glycols (PEO–400, -600 and -1000 supplied by Shell Chemical Co.; PEO–2000 and -3000 supplied by Fluka A.G.) and triethylene glycol.

A chromatogram of the oligomer mixture prior to distillation is illustrated in Fig. 2. A chromatogram of the nonaethylene glycol purified by distillation is shown in Fig. 3, where it is compared with a chromatogram of PEO–400 ($\bar{x}_n \sim 9$). The nonamer peak was sufficiently well resolved from the peaks of its immediate neighbours ($x = 6$, 12) to establish that the distilled nonamer is better than 99% pure. The pentadecamer peak was not so readily resolved from those of its neighbours ($x = 12$, 18, 21). Accordingly the chromatograph was used in recycle mode, using the alternate pumping method [21], to show that the pentadecamer fraction [preparation (A)] is about 98% pure, the impurity being dodecamer.

Vapour pressure osmometry

A vapour pressure osmometer (Mechrolab Model 301) was used at 25°C with distilled toluene as solvent. The instrument was calibrated with recrystallized benzil. The nonaethylene glycol had M = 393 (calculated 414) and the pentadecaethylene glycol (preparation A) had M = 626 (calculated 678). The experimental uncertainty in the method is ±10%.

Melting point

Melting points were measured for small samples (5–10 mg) sealed into capillary tubes in a dry box. The oil bath temperature was raised at 0.1 K min^{-1} from a temperature 4–5 K below the melting point. Melting was observed through a telescope. The thermometer was calibrated against National Physical Laboratory standards. The melting points found compare well with those reported by Bömer *et al.* [13] (purest nonamer sample 29.6°C, cf. 29.8–30.0°C; pentadecamer 39.1 ± 0.6°C, cf. 38.6–38.8°C).

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