Preparation of large cyclic poly(oxyethylene)s

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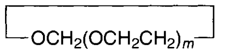
A preparation is described which affords good yields of cyclic poly(oxyethylene)s with narrow chain length distributions and number-average molar masses in the range 1000–20 000 g mol^{-1}.

Unsubstituted crown ethers, *i.e.* uniform cyclic oligo(oxyethylene)s, have been of interest since Pedersen's first report.[1] In recent times several authors[2–4] have described methods for synthesis of crown ethers as large as 60-crown-20. However, the interest in polymer chemistry is in cyclic polymers with chain lengths long enough to generate characteristic 'polymer' properties, say 100–200 chain atoms or more.[5] Moreover samples of cyclic polymers with narrow chain length distributions are most suitable for comparison with linear polymers, since the linear polymers themselves will not be uniform in composition. Linear poly(oxyethylene)s with narrow chain length distributions are readily prepared by anionic polymerisation, and are available over a wide molar mass range from a number of commercial sources. Recent reports[6,7] from this laboratory have demonstrated the efficient preparation of low-molar-mass cyclic poly(oxyethylene)s ($M_n \leqslant 3000$ g mol^{-1}) from such linear precursors with little or no change in their molar mass distributions.

One of the methods used[6] was reaction of a glycol with CH_2Cl_2 under Williamson conditions and at high dilution (concentration maintained below 10^{-5} mol dm^{-3}) to attain ring closure *via* an acetal linkage, *i.e.* reaction of polyethylene glycol [PEG, $H(OCH_2CH_2)_mOH$] with CH_2Cl_2 to obtain **I**.



I

Here m is a number-average value over a narrow chain length distribution, typically $M_w/M_n < 1.1$. The reactions of Scheme 1 were involved.

Yields as high as 80% of the required cyclic polymer were reported[6] for cyclisation of PEG1000 ($m \approx 23$ E units) by this route, with a somewhat lower yield of 60% for PEG3000 ($m \approx 68$ E units). The efficiency of the reaction reflects the extremely high reactivity of the chloroether formed in step (ii), which ensures rapid reaction under the conditions of high dilution necessary to obtain efficient cyclisation in competition with chain extension. Even so, a proportion of chain extension could not be avoided, but this fraction was much reduced in products by a simple fractional precipitation.[6]

We now report development of this chemistry which (*a*) promotes higher yields of cyclics (up to 95%) and (*b*) enables cyclisation of poly(oxyethylene)s with number-average molar masses as high as $M_n = 20\,000$ g mol^{-1}. We denote the cyclic polymers by their nominal number-average molar mass and the suffix RA (R for ring, A for acetal closure). Thus sample 3000RA is cyclic poly(oxyethylene) prepared from PEG3000.

(i) $—OCH_2CH_2OH + CH_2Cl_2 \longrightarrow —OCH_2CH_2OCH_2Cl + HCl$

(ii) $—OCH_2CH_2OCH_2Cl + HOCH_2CH_2O—$
$\longrightarrow —OCH_2CH_2OCH_2OCH_2CH_2O— + HCl$

Scheme 1

The polyethylene glycols were used as received from commercial sources. The basic procedure was as follows. A solution of PEG (5 g) in CH_2Cl_2 (100 cm^3) in a pressure-equalising funnel or syringe pump was slowly added (48 h) to a stirred suspension of powdered KOH (85%, 7 g) in CH_2Cl_2 (100 cm^3) at 30 °C. The solution was then stirred for a further 48 h to ensure complete reaction of all hydroxy groups.

One improvement was the use of a poor solvent, the intention being to facilitate ring closure by reducing (on average) the end-to-end distance of the linear polymer coil whilst maintaining solubility. For preparation of the medium cyclics ($3000 \leqslant M_n \leqslant 6000$ g mol^{-1}) this was achieved by replacing CH_2Cl_2 with a mixture of CH_2Cl_2 and hexane (non-solvent). The method was optimised for PEG3000, and a 93% yield of the required cyclic material was achieved with CH_2Cl_2–hexane (65 : 35 *v*/*v*), the residue being chain extended polymer which was readily removed by precipitation fractionation (see below). For cyclisation of the longer chains ($M_n \geqslant 10\,000$ g mol^{-1}) it was found advantageous to use mixtures of CH_2Cl_2 and chlorobenzene.

The reaction was monitored by analytical GPC, as illustrated for the cyclisation of PEG10000 in Fig. 1. The GPC curve of the starting material [Fig. 1(*a*)] contained a single narrow peak. After cyclisation, the major peak was found at higher elution volume (as expected for a cyclised polymer of the same molar mass distribution[8]) and signals assigned to chain extended polymer were found at lower elution volumes [Fig. 1(*b*)]. The yields quoted in Table 1 were estimated from the area under the deconvoluted major peak relative to the total area.

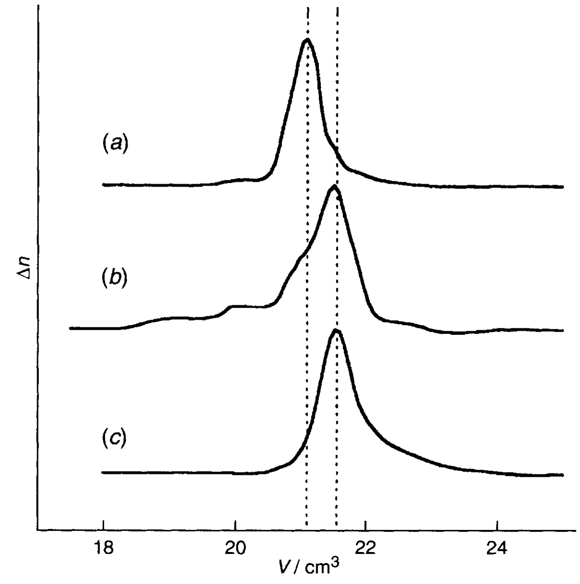


Fig. 1 GPC curves (refractive index difference, Δn, *vs.* elution volume, V) obtained during the cyclisation of PEG10000: (*a*) original linear PEG10000; (*b*) product before purification by precipitation fractionation; (*c*) purified cyclic poly(oxyethylene) 10000RA

Since chain extended polymer (cyclic or linear) was less soluble than the required product, it could be separated by a simple precipitation–fractionation procedure. The reaction product (*ca.* 5 g) was dissolved in toluene (250 cm^3) at 25 °C. Heptane was slowly added until the stirred solution became cloudy. Equilibrium phase separation was ensured by heating the cloudy solution until it cleared, and then cooling it slowly with gentle stirring to 25 °C. A clear concentrated phase separated from a clear dilute phase and was removed. GPC served to show that the dilute phase contained predominantly cyclic polymer. If necessary, the separation procedure could be repeated until essentially all extended chain polymer was removed. The required product was isolated by evaporating the solvent.

^{13}C NMR spectra of the purified product showed resonances from internal oxyethylene carbons (δ 70.3–70.7), CH_2 adjacent to the acetal link (δ 72.5), and CH_2 of the acetal link (δ 95.5), with no signals attributable to end groups (δ 61.5). Within experimental error, the relative integrals confirmed chain lengths equivalent to those of the starting materials. The quality of 10000RA obtained in this way can be judged from the GPC curve shown in Fig. 1(*c*). The shift in the elution volume between curve (*a*) and (*c*) corresponds, as expected, to a ratio of molar mass of linear polymer to apparent molar mass of cyclic polymer of 1.3.[8]

Loss of the required cyclic polymers in the purification procedure reduced the recovered yields to about 75% of those listed in Table 1. For a cyclic polymer prepared from 5 g of precursor with a yield (*via* GPC) of 90%, the final recovery was *ca.* 3 g of purified product. For the most difficult preparation (*e.g.* 20000RA, yield *via* GPC = 35%) a recovery in excess of 1 g can be expected.

The longest cyclic polymer prepared as described above (20000RA) contains in excess of 1350 chain atoms. For comparison, the chain lengths of the samples of cyclic poly(dimethylsiloxane)s prepared in sufficient quantity for study reach about 800 chain atoms.[5,9] Cyclic poly(styrene)s have been prepared with chain lengths up to 40 000 chain atoms.[10,11] Considered as materials for research and development, the cyclic poly(oxyethylene)s have certain advantages over other preparations. They are water soluble and so have potential for novel interaction with water-compatible systems of interest in chemistry, colloid chemistry and biochemistry. They provide a range of cyclic poly(oxyethylene)s above the present upper limit of the large uniform crown ethers (*i.e.* $M \approx 1000$ g mol^{-1}). They crystallise at temperatures just above ambient, allowing convenient investigation of crystallisation rates and morphologies, and of chain folding in normally helical chains.

Table 1 Cyclisation of polyethylene glycol

Sample	Precursor	Solvent(s) (*v*/*v*)	Yield/mass% (GPC)
1000RA	PEG1000	CH_2Cl_2	85
1500RA	PEG1500	CH_2Cl_2	85
2000RA	PEG2000	CH_2Cl_2	85
3000RA	PEG3000	CH_2Cl_2–hexane (65/35)	93
4000RA	PEG4000	CH_2Cl_2–hexane (65/35)	80
6000RA	PEG6000	CH_2Cl_2–hexane (65/35)	82
10000RA	PEG10000	CH_2Cl_2–chlorobenzene (50/50)	63
20000RA	PEG20000	CH_2Cl_2–chlorobenzene (50/50)	35

At the present time the physical properties of the cyclic poly(oxyethylene)s are under investigation in a number of laboratories. This work includes comparative studies of the crystallinity of cyclic and linear poly(oxyethylene)s of molar mass 3000 g mol^{-1} or less[7,12] which, *via* measurements of lamellar spacings by X-ray scattering and LAM-1 frequencies by Raman spectroscopy, provides excellent proof of the success of the cyclisation procedure.

Chain folding in lamellae of the higher-molar-mass polymers (*e.g.* 10000RA) complicates this method of characterisation, but measurement of the self-diffusion coefficients of cyclic and linear poly(oxyethylene)s ($M_n = 10\,000$ g mol^{-1}) in aqueous solution by pulse-gradient spin-echo NMR spectroscopy has yielded results consistent with the two architectures.[13]

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