Novel spiro-polymers with enhanced solubility

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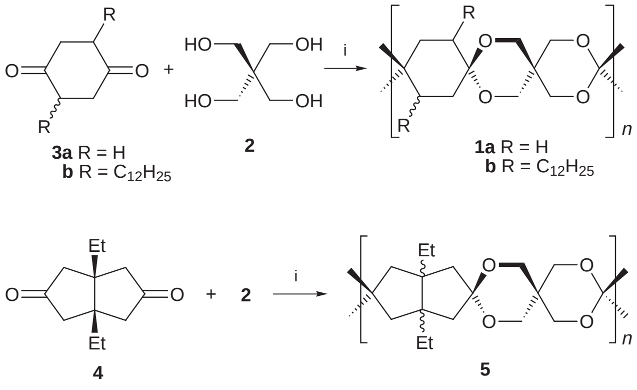
Well-defined spiro-polymers which are freely soluble in organic solvents can be prepared from the ketal-forming reaction between pentaerythritol and either a diketone bearing alkyl solubilising groups or a diketone which generates a contorted polymeric structure.

Ladder polymers are of interest as high performance materials due to their great rigidity, lack of rotational freedom and high thermal stability which arises because mass deterioration requires the scission of two covalent bonds within the same cyclic subunit.[1] However, they are difficult materials to make due to the need for an efficient polymerisation reaction that forms cyclic inter-monomer linkages. Spiro-polymers are a subclass of ladder polymers in which adjacent rings share a common atom.[1,2] Spiro-polyketals such as **1a**, readily prepared from pentaerythritol **2** and cyclohexane-1,4-dione **3a** (Scheme 1), are particularly attractive synthetic targets because the two bonds of the cyclic ketal-linking group form almost simultaneously during polymerisation. In addition, ketal formation is an efficient equilibrium process which can be driven to completion by the removal of water. Unfortunately, the regular structure of **1a** results in a highly crystalline material which has poor solubility in all solvents, including refluxing toluene. This leads to the formation of low molar mass products due to precipitation at an early stage of the polymerisation and prohibits molecular mass determination of the resulting material.[3,4] In addition, the possibility that **1a** is cross-linked by non-cyclic acetal linkages cannot be disproved by solution-based structural characterisation.

Our interests lie in the utilisation of spiro-polyketals as molecular-scale scaffolding for the assembly of rigid polymeric networks. However, soluble materials are required in order to assess the efficiency of ketal formation for macromolecule construction and to facilitate solution-based molecular mass determination. There are two common strategies for the improvement of the solubility of rigid polymers; decorating the polymer with solubilising groups (*e.g.* alkyl groups)[5] or introduction of structural irregularities which reduce the linearity of the polymer.[6] Here we describe the use of both of these approaches for obtaining soluble spiro-polyketals.



Scheme 1 *Reagents and conditions*: i, TsOH, toluene, reflux, 48 h.

The replacement of **3a** with 2,5-didodecylcyclohexane-1,4-dione **3b**, prepared by the base catalysed dialkylation of dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate followed by ester hydrolysis and decarboxylation,[7] in the spiro-polymerisation with **2** gives **1b** in good yield. This material is soluble in aprotic solvents (*e.g.* THF, CH_2Cl_2) and has ^1H and ^{13}C NMR spectra which are consistent with the proposed structure. Analysis using gel permeation chromatography (GPC) of a THF solution of **1b** (Table 1), using a calibration based on polystyrene standards, and NMR end-group analysis indicates only a modest degree of polymerisation ($\langle DP \rangle \approx 8$–10), however, even this figure represents at least 24 spirocycles per molecule, on average.

It is known that alkyl chains adjacent to the ketone group have an adverse steric effect on ketal formation.[8] Therefore, we sought a diketone which could accommodate alkyl solubilising groups at sites where they would not interfere with ketal formation. The readily prepared 1,5-dialkylbicyclo[3.3.0]-octane-3,7-diones satisfy this criteria. It was found that 1,5-diethylbicyclo[3.3.0]octane-3,7-dione **4**, prepared from dimethyl 3-oxopentane-1,5-dioate and hexane-3,4-dione using the Weiss–Cook reaction,[9,10] undergoes ketalisation with **2** to give polymer **5** in good yield (Scheme 1). Despite the absence of long alkyl solubilising groups, polymer **5** is freely soluble in aprotic organic solvents (*e.g.* toluene, THF, CH_2Cl_2, DMSO). This solubility must arise from the non-linearity of the dione precursor **4** which results in a randomly contorted structure similar to the dynamic random coil configuration adopted by flexible polymers in solution (Fig. 1).

Both GPC and ^{13}C NMR end-group analysis (Table 1) indicates that **5** has a reasonable average molecular mass for a polymer derived from small-scale step-growth polymerisation ($\langle DP \rangle \approx 28$–30). End groups give rise to clear signals corresponding to the carbonyl group (δ 215), the methylene groups adjacent to the carbonyl (δ 47.2; Fig. 2) and the methylene groups on the terminal pentaerythritol (δ 70.1). Calculation of average molecular mass was based on comparing the sum of the intensities of the two types of end-group methylene carbon signals with the combined intensity of the two types of methylene units within the main body of the polymer at δ 43.0–45.5 (Fig. 2) and 63.5–65.0. The apparent

Table 1 Yield, molecular mass data and glass transition temperatures for polymers **1b** and **5**. Molecular mass data is a range obtained for several samples

Polymer	Yield (%)	$\langle M_n \rangle$ (gpc)	$\langle M_w \rangle / \langle M_n \rangle$	$\langle M_n \rangle$ (NMR)	T_g/°C
1b	85	$(5–6) \times 10^3$	1.6–1.8	$(4–5) \times 10^3$	45[a]
5	88	$(12–14) \times 10^3$	1.8–2.5	$(8–9) \times 10^3$	180

[a] Sample appears to be partially crystalline (m.p. = 120 °C).

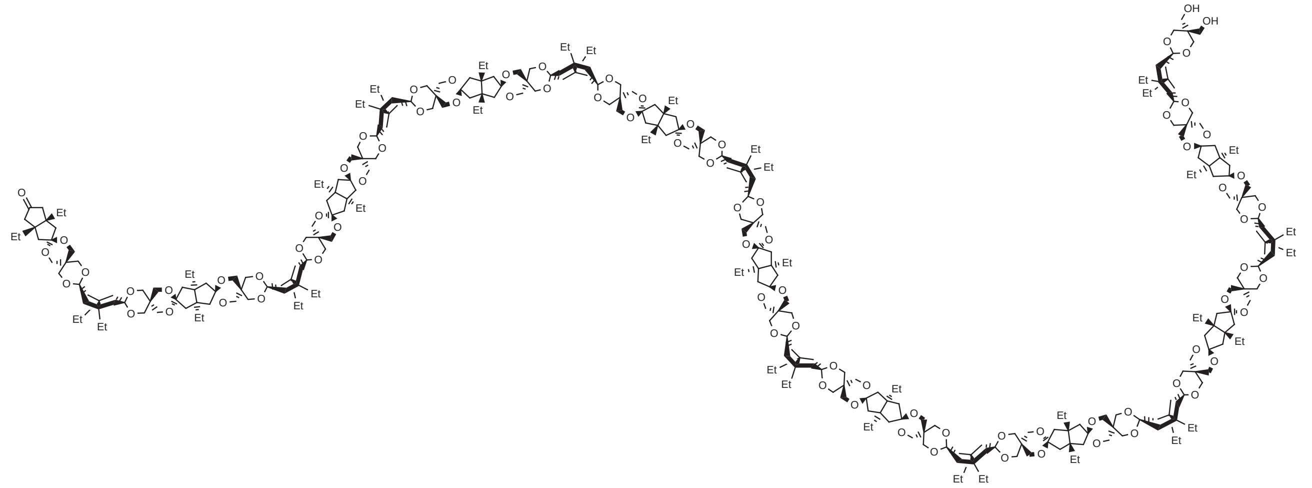


Fig. 1 A two-dimensional representation of the contorted configuration of polyketal **5** resulting from the bent shape of diketone **4**.

overestimation of the molecular mass by GPC, with respect to the absolute value estimated from end-group analysis, is attributable to the greater hydrodynamic volume per unit mass of rigid polymer **5** as compared to the polystyrene standards used for calibration. The observation of both ketone and alcohol end-groups in the ^{13}C NMR spectrum suggests that reaction conditions (*e.g.* higher concentration, longer reaction time) could be found for obtaining polymer **5** with greater molecular mass.

The irregular structure and low flexibility of polymer **5** results in it being a glassy solid with a high glass transition temperature (Table 1). Thermogravimetric analysis indicates that this material is stable up to 280 °C and it appears indefinitely stable in the solid phase but, unless suitable precautions are taken, it possesses only limited stability in solution towards hydrolysis. This study confirms that spiro-polymers of reasonable molecular mass can be achieved by ketal formation. In particular, the use of unhindered but non-linear diketones such as **4** gives well-defined (*i.e.* not cross-linked) soluble polyketals which possess an unusual combination of rigidity and structural irregularity.

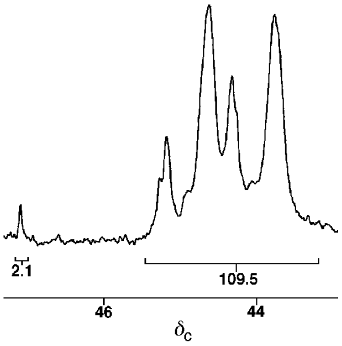


Fig. 2 Detail from the ^{13}C NMR spectrum of polyketal **5** showing the signal due to the methylene group adjacent to the terminal carbonyl (δ 47.2) and the methylene units derived from diketone **4** in the main body of the polymer (δ 43.0–45.5). Average molecular mass calculations used the stated intensities of these peaks together with those derived from the terminal pentaerythritol methylene signal (δ 70.1) and another well-defined group of signals at δ 63.5–65.0 from the pentaerythritol methylene signals in the main body of the polymer.

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