Polymers and oligomers with transverse aromatic groups and tightly controlled chain conformations

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Anionic ring-opening polymerisation of spiro[cyclopropane-1,9′-fluorene] with fluorenyl anion as initiator yields polymers **1** with chains which are essentially all-*anti* and have transversely-oriented fluorenyl groups, as shown by strong upfield shifts for the mid-chain methylene and 1,8-fluorenyl protons; synthetic routes to some specific oligomers are also reported.

Controlling the secondary structure of acyclic molecules and polymers is important for many applications. We have shown that quaternary centres exert extensive conformational effects on adjacent chains.[1,2] Combining these effects with the rigid side groups provided by transversely-oriented fluorene rings should lead to a polymer **1** with a highly-constrained all-*anti* (extended chain) secondary structure; any *gauche* bonds in the chain create strong interactions between CH_2 groups in the chain and the 1,8-CH groups on the fluorene rings. Calculations on oligomers using the MM3 force field[3,4] predict that all-*anti* structures are 9–10 kJ mol^{-1} more stable than the next best conformation, which has one *gauche* bond in the terminal section of the chain. Introduction of *gauche* bonds in the interior parts of these oligomers costs 13.5–14 kJ mol^{-1}, corresponding to a >200:1 preference for all-*anti* conformations at ambient temperature in these parts of the chain. In structures like **1**, *anti* conformations can be readily recognised from the upfield shifts

in ¹H NMR spectra due to aromatic ring current effects. Thus the CH_2OH protons in diol **2** ($n = 1$, R = H), whose X-ray structure‡ is shown in Fig. 1, resonate at δ 2.85, whereas in acetal **3** the corresponding protons occur at δ 3.95.

Anionic ring-opening polymerisation is a common process for heterocyclic monomers like epoxides, but it has barely been explored for hydrocarbon monomers like cyclopropanes. [1.1.1]Propellane[5] and some bicyclobutanes[6] (which have much higher strain energies) and a few vinylcyclopropanes[7] have been polymerised by this process. Simple 1,1-disubstituted cyclopropanes with two anion-stabilising groups appear good candidates, but the only example in the literature is with CO_2Me as the stabilising group.[8]

We find that polymerisation of spiro[cyclopropane-1,9′-fluorene][9] **4** can indeed be initiated by an S_N2 reaction with fluorenyllithium. Temperatures > 100 °C are required; we have used DMPU as solvent, but HMPA is also effective. During polymerisation reactions with monomer:initiator ratios > 3:1, a precipitate appears after about 10 min at 150 °C, raising concern that chain growth may be limited by the insolubility of the product. This insolubility precludes any simple determination of the degree of polymerisation (DP), but NMR data (see below) indicate that oligomers below the octamer **1** ($n = 8$) are almost absent in products from reactions with monomer:initiator ratios > 12:1, so polymerisation probably continues in spite of the precipitation. Further optimisation of this polymerisation will be undertaken and we intend making modified monomers with flexible chains on the periphery of the aromatic rings to improve solubility.

We found a much improved synthesis of **4** in > 90% yield from fluorene, BuLi and ethylene sulfate.[10] Ethylene sulfate is much more efficient in this reaction than 1,2-dibromoethane, which gives mixtures of dimer **1** ($n = 2$),[11] **4** and cyclohexane derivative **5**,§ even when fluorenyllithium is added slowly to excess dibromide. Ethane-1,2-diyl dimesylate only gives **4**, without **1** ($n = 2$) or **5**, but is relatively unreactive. We are investigating the reasons for the effectiveness of ethylene
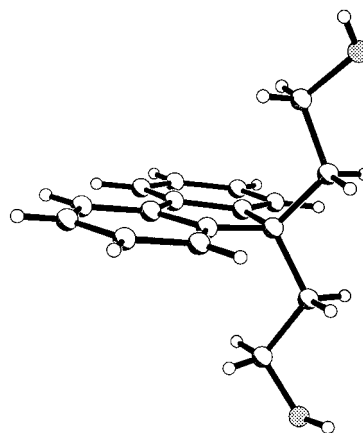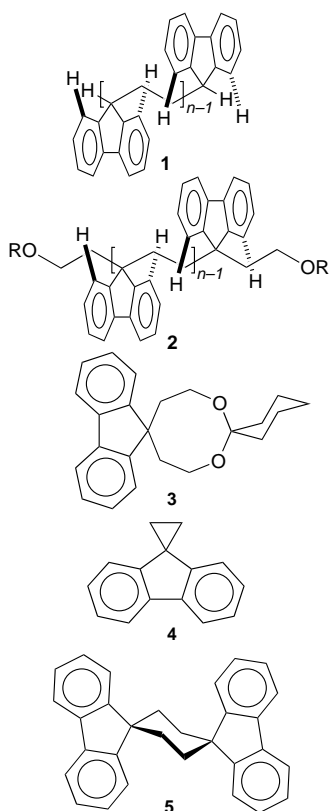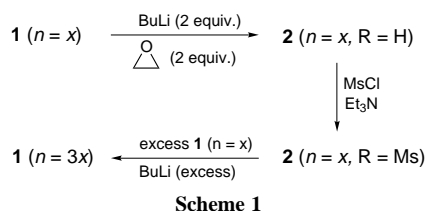

1

2

3

4

5

Fig. 1 X-Ray structure of diol **2** ($n = 1$, R = H) showing the all-*anti* aliphatic chain

sulfate in this cyclisation, and whether this observation has more general implications.

In order to examine the physical properties of the novel structure represented by **1**, we have prepared some specific oligomers by a general route. Thus reaction of an excess of the monoanion of dimer **1** ($n = 2$) (prepared using BuLi) with dimesylate **2** ($n = 1$, R = OMs) gives the pentamer **1** ($n = 5$), along with small amounts of the octamer from reaction of 3 equiv. of **1** ($n = 2$) with 2 equiv. of **2** ($n = 1$, R = OMs). Similarly, reaction of excess fluorenyl anion with dimesylate **2** ($n = 2$, R = OMs) gives the tetramer **1** ($n = 4$) and reaction of an excess of the monoanion of dimer **1** ($n = 2$) with dimesylate **2** ($n = 2$, R = OMs) gives the hexamer **1** ($n = 6$). Since mesylates **2** (R = OMs) are readily prepared from the hydrocarbons **1**, this route can potentially be used repetitively with a rapid growth in DP, as shown in Scheme 1, so long as starting oligomer can be separated from the product. Reaction of excess fluorenyl anion with dimesylate **2** ($n = 1$, R = OMs) only gives **5**, with no observable trimer formation, but trimer can be isolated by preparative TLC from polymerisation runs with 2 : 1 ratios of **4** : fluorenyllithium. These oligomers can be capped at both ends by double deprotonation with BuLi, and reaction with electrophiles [*e.g.* MeI, MEMCl, oxirane and (PhS)₂], and many of these derivatives show improved solubility.

Somewhat surprisingly, the best solvent for **1** is CHCl₃, the solubility of the tetramer, pentamer and hexamer are >45, 31 and 26 mg ml⁻¹ respectively; the heptamer is very insoluble. In the ¹H NMR spectra of oligomers **1** ($n = 2$–6) in CDCl₃, CH₂ groups and some aromatic protons are shifted upfield substantially, with shifts increasing towards the middle of the molecule and with increasing chain length. The shifts for CH₂ groups range from δ 1.75 for the dimer to δ 0.42 for the central CH₂CH₂ in the hexamer. As might be expected, the largest upfield shifts for the aromatic protons are observed for the 1,8-fluorenyl protons (Table 1), with progressively smaller shifts for the 2,7-, 3,6- and 4,5-protons. Upfield shifts for the 1,8-fluorenyl protons are predictable to within 0.02 ppm from a simple additivity scheme based on the number of fluorene units which are α (adjacent), $\Delta\delta$ −0.38, β (next to adjacent) $\Delta\delta$ −0.26, γ $\Delta\delta$ −0.11, δ $\Delta\delta$ −0.04, ϵ $\Delta\delta$ −0.02 and ϕ $\Delta\delta$ −0.01; this scheme allows us to identify the heptamer from polymerisation reactions and the octamer as a by-product of the preparation of the pentamer. It predicts that the 1,8-fluorenyl protons in the middle of the polymer should resonate at δ 6.04, and we believe that it provides excellent evidence for a strong preference for the all-*anti* conformation in solution. These polymers and oligomers therefore possess a novel architecture (flexible, but possessing many of the attributes of a rigid rod). They could be useful as molecular spacers, and the regular array of aligned aromatic rings is an intriguing feature. The distance between two aromatic rings on the same side of the polymer chain, calculated to be 7.71 Å, gives enough room to intercalate another aromatic ring between them. Furthermore, the intervening chains, while saturated, are perfectly aligned for maximum through-bond coupling,[12] and electron- and energy-transfer down these chains may well be rapid. Finally, we point out that anionic ring-opening polymerisation of 1,1-disubstituted cyclopropanes has now been observed for cases where the growing anion is a malonic ester derivative[8] (pK_a ~ 13) and where it is a fluorenyl anion (pK_a ~ 22). We are exploring the limits for this process, but we believe that many novel polymeric structures might be made this way.

Notes and References

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‡ *Crystal data* for **2**: C₁₇H₁₈O₂, M = 254.31, monoclinic, space group $P2_1/c$, a = 7.391(1), b = 24.846(4), c = 7.898(1) Å, β = 103.50(1)°, V = 1410.3(3) Å³, Z = 4, D_c = 1.198 g cm⁻³, λ = 0.71073 Å, graphite monochromated Mo-Kα X-radiation, μ = 0.38 mm⁻¹, $F(000)$ = 544, T = 293 K. Data were collected on a Siemens P4 four circle diffractometer for a quadrant of reciprocal space for 2.78 > 2θ > 40.00. The structure was solved by direct methods and refined by full-matrix least-squares methods (175 parameters) against all 1292 unique intensity data with I > 2$\sigma(I)$ to final R1 = 0.0628 for the 723 reflections with I > 2$\sigma(I)$. CCDC 182/714.

§ Dispiro[9*H*-fluorene-9,1′-cyclohexane-4′,9″-9*H*-fluorene] **5**, a new compound, shows a broadened absorption in its ¹H NMR spectrum for the methylene protons at room temperature; the variable temperature behaviour of this compound will be discussed elsewhere.

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Table 1 ¹H NMR chemical shifts in CDCl₃ for 1,8-fluorenyl protons in oligomers **1**

	δ_H(ppm)			
	Ar¹ (Terminal rings)	Ar²	Ar³	Ar⁴
Dimer	7.28			
Trimer	7.01	6.89		
Tetramer	6.90	6.63		
Pentamer	6.86	6.53	6.39	
Hexamer	6.84	6.48	6.28	
Heptamer	6.83	6.46	6.24	6.18
Octamer	6.83	6.45	6.22	6.14