Anthraquinone–Steroid based Gelators of Alcohols and Alkanes

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Gelation depends on key structural features of the gelator but not on specific gelator–liquid interactions other than those related to solubility.

Previously, we studied the properties of gels comprised of a variety of organic liquids and a family of molecules (ALS) whose 2-anthryl or 2-anthraquinonyl groups (A) are connected to steroids (S) *via* a linking group (L).[1–3] They and structurally dissimilar molecules[6–12] gel reversibly many organic fluids. It is known that minor structural modifications to molecules within one class of gelators may cause major changes in their gelation ability. Here, we report some correlations between the structures of ten new ALS molecules and their gelling abilities with selected liquids.

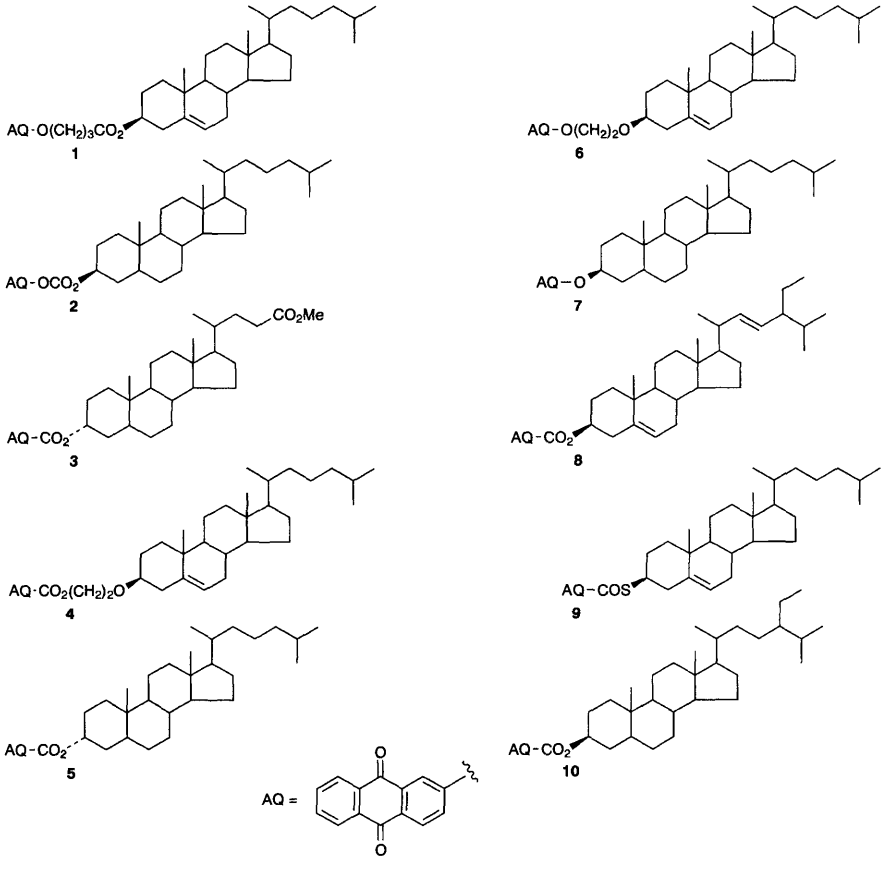
The ALS, **1–10**, were designed to probe the influence of specific structural features, such as the α/β stereochemistry at C-3 of S, the nature of the alkyl chains on C-17 of S, and the length and functionality of L, on gelation ability. The ALS were prepared using simple, standard reactions: **1** by *O*-alkylation of 2-hydroxyanthraquinone with cholesteryl 4-bromobutanoate in the presence of base; **2** by condensation of 2-hydroxyanthraquinone and cholestanyl chloroformate; **3–5** and **8–10** by esterification of anthraquinone-2-carboxylic acid chloride with steroids; **6** and **7** from 2-hydroxyanthraquinone and 3β-(2-hydroxyethoxy)-5-cholestene and 3α-cholestanol, respectively, under Mitsunobu etherification conditions.[4]

Compounds **1**, **6** and **8–10** (in *ca.* 0.5–3 mass% concentrations) gel a wide variety of linear and branched alcohols and alkanes. However, compounds **2–5** and **7** did not gel these or several other liquids. Since all of the ALS examined here were very soluble in chloroform, dichloromethane, benzene and toluene, no gels formed when their solutions were cooled. By contrast, a lack of adequate ALS solubility is at least partly responsible for the inability of methanol, ethanol and hexane to be gelled. In a typical experiment, an ALS and an organic liquid were heated in a sealed test tube until the solid dissolved. The hot solutions were cooled to room temperature in the air, to *ca.* 10 °C under cold tap water, to *ca.* 0 °C in ice, or to *ca.* −10 °C in a refrigerator. Gelation was considered successful if the sample became semi-transparent and solid-like with no apparent flow upon inversion of the test tube.

From the gelating abilities of **1–10** and other ALS,[2] the following observations concerning gelator structure can be made.

(*i*) Gelation is facilitated when the stereochemistry at C-3 of the S unit is β. The 3β isomer of **5** is known to be an effective gelator of several alcohols and alkanes;[2] neither **5** nor **3**, ALS with α stereochemistry at C-3 of the S unit, gels the same liquids. However, both the α and β epimers of related non-ALS molecules, cholesteryl diazobenzenecarboxylates, do act as gelators.[12]

(*ii*) Minor structural changes to a sterol chain at C-17, such as introduction of an unsaturated unit and/or an ethyl substituent, do not destroy gelling ability: cholesteryl anthraquinone-2-carboxylate,[2,5] **8** and **10** are efficient gelators. Previous work (as well as our present results with **3**) indicates that ALS molecules with grossly shortened or otherwise modified chains at C-17 do not gel *n*-alkanes and alcohols.[2] Some D-azahomosteroids with *gem* di-*n*-propyl groups at C-17 are known to be better gelators of cyclic alkanes than *n*-alkanes.[6]



The opposite trend is observed with ALS gelators that retain the C_8H_{17} *chain of cholesterol* at C-17.

(*iii*) Although the length and/or functionality of L may be important factors, we can discern no clear relationship between either one and gelation ability from the structures of the ALS studied here and those reported previously.[2] Although changes in L do have marked effects on ALS gels, the variations in the examples are not sufficiently systematic to allow creditable structure–stability relationships to be made.

Gels were found to persist for longer periods of time when ALS concentrations were increased and incubation temperatures were lowered. Rheological gelation temperatures (T_g) of mixtures of **1** or **9** and a variety of organic fluids were measured by the 'inverse-flow' and/or 'ball-drop' methods.[13] Upon being heated, the gels employing **1** melted over narrow temperature ranges (*ca.* 2°), while those containing **9** exhibited much broader (10–15°) melting transitions; only data with **1** will be discussed here. As previously observed,[2] initially T_g increased rapidly with gelator concentration before approaching a 'saturation' value (Fig. 1). From the collected results, several interesting empirical conclusions can be made.

(*i*) In spite of its chiral nature, **1** forms gels with DL-, D- or L-octan-2-ol whose T_g values are indistinguishable within experimental error (Fig. 1). The diastereoisomeric gelator–liquid interactions must be too small in magnitude to be detected by our methods.

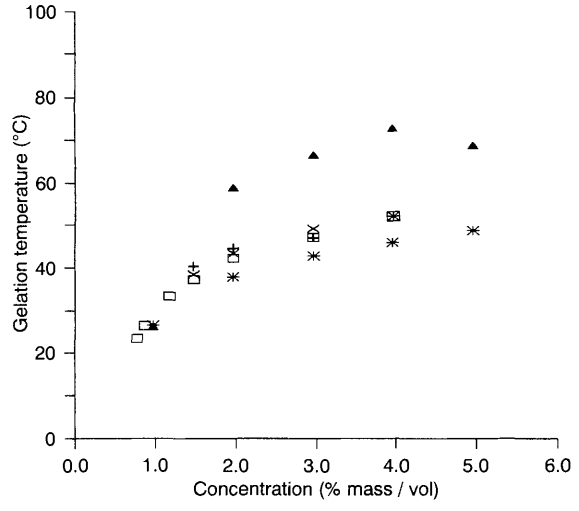


Fig. 1 Gelator concentration *versus* median gelation temperature for **1** in benzyl alcohol (*), dodecane (▲), DL-octan-2-ol (□), D-octan-2-ol (×), or L-octan-2-ol (+)

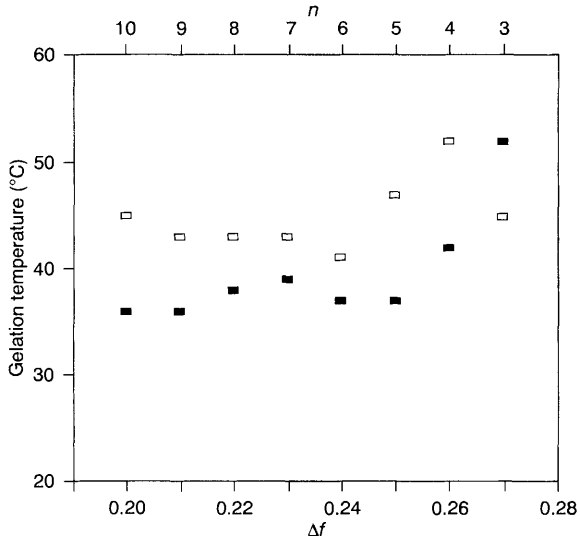


Fig. 2 Median gelation temperatures for gels from 1 mass% (■) or 1.5 mass% (□) of **1** in alkan-1-ols *versus* Δf(solvent polarity)[14] and n (number of carbon atoms in the alcohol molecules)

(*ii*) The virtual invariance of the T_g values of gels from **1** and alkan-1-ols with 5–10 carbon atoms (Fig. 2) suggests that specific gelator–liquid interactions do not contribute significantly to gel melting. The aberrant behaviour of the gel from 1.5% **1** and propanol is reproducible but not understood at this time. Since the polarity function, $\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$ (where ε is the liquid dielectric constant and n is the refractive index),[14] varies in a continuous fashion throughout the series of alcohols, T_g must not be responding to bulk polarity.

(*iii*) T_g values of gels from **1** and *n*-alkanes are considerably *higher* than those from **1** and alkan-1-ols. Gels from the anthryl analogue of **1**, cholesteryl 4-(2-anthryloxy)butanoate (CAB), exhibit much *lower* T_g values with alkanes than with alcohols.[3] Interestingly, CAB gels have the same (spectroscopically-measured) T_g value throughout a series of *n*- alkanes (hexane to hexadecane).[2] The source of differing trends between **1** and CAB is probably related to **1** being more soluble in alcohols than is CAB.

Gels from several concentrations of **1** and benzyl alcohol between cover slips were also examined by optical microscopy using crossed polars. The strand networks, characteristic of ALS gels,[2] melted when the samples were heated and reappeared when they were cooled at temperatures which correspond closely to the T_g from the 'ball-drop method'. Thus, the strand networks of **1** (and, by inference, **6**, **8–10**) must use surface tension[2] to immobilize the vast excess of the liquid component.

In conclusion, we have identified some of the key structural features that control gelation of alcohols and alkanes by ALS molecules: gelation is inhibited by α stereochemistry at C-3 of S; branching or unsaturation of the steroidal chain at C-17 has some influence on the efficiency of gelation, but truncation of the chain results in ineffective gelators; the length and the functionality of L play an important and complex role in gelator efficiency, but the number of examples is insufficient to derive firm conclusions. We also find no evidence to indicate that specific gelator–liquid molecular interactions, such as hydrogen bonding, play an important role in determining the melting temperatures of the gels.

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