A Novel Gelator of Organic Liquids and the Properties of Its Gels[1]

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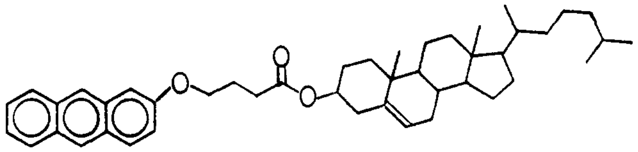
Received July 25, 1986

ABSTRACT: The properties of a new class of gels formed between ca. 1% by weight of cholesteryl 4-(2-anthryloxy)butyrate and a wide variety of organic solvents are described. Spectroscopic measurements indicate that the gelator molecules are stacked helically with the anthracenyl groups overlapping one another.

Introduction

In the course of other investigations, we observed serendipitously that small amounts (usually ca. 1% by weight) of cholesteryl 4-(2-anthryloxy)butyrate (CAB) cause reversible gelation of a wide variety of organic liquids (including alkanes, alkenes, alcohols, aldehydes, carboxylic acids, esters, amines, and aromatic molecules). These gels and those created by several analogues of CAB[2] are elastic solids and nearly translucent. They can be inverted without apparent flow and they exhibit a Tyndall-type effect. Their macroscopic properties fit any of the several definitions applied to "gels".[3]

The microscopic forces responsible for gelation appear to be unique in these systems since CAB is a relatively small molecule of low polarity which contains only carbon, hydrogen, and oxygen. Most organic gels require either a polymeric gelator, a large concentration of gelator, and/or a gelator with functional groups capable of acting as hydrogen bond donors.[3-13] Recently, partially fluorinated *n*-alkanes in relatively large concentrations were found to gel saturated linear hydrocarbons.[14] To our knowledge, this is the only reported example in which weak van der Waals type interactions are sufficient to allow gelation.



CAB

Results and Discussion

In a typical procedure, a mixture of CAB (ca. 1% by weight) and a solvent is heated until a solution is obtained. Cooling to ambient temperatures results in gel formation as witnessed visually by a rapid increase in viscosity and a decrease in translucence. Gel formation was followed quantitatively by ultraviolet absorption spectroscopy or, more conveniently, by fluorescence from the anthracenyl lumophore. A large (ca. 10-fold) increase in emission intensity and a significant change in emission spectral shape are observed as the gel forms. No band ascribable to a CAB excimer[15] was detected in either the isotropic or gel phase. Representative spectra of 0.72% CAB in *n*-dodecane are presented in Figure 1. The change in the wavelength of emission maximum is not thermally induced since emission spectra of both high temperature and very dilute ambient temperature solutions of CAB (which do not gel) exhibit λ_{max} 417 and 432 nm. The gel maximum is near 422 nm. The source of the large increase in fluorescence intensity upon gelation is unclear at this time. At least in part, it must arise from Tyndall scattering: similar effects have been observed in liquid-crystalline phases.[16] However, colloidal dispersions of anthracene in water do not exhibit enhanced emission intensities.[17]

The excitation spectra for the same solution used in Figure 1 showed maxima that correspond to the vibronic progression of the anthracenyl chromophore. In the isotropic phase, the 0–0 and 0–1 bands of the ^1L_a absorption (short–axis polarization)[18] appear at 390 and 370 nm, respectively. The excitation and absorption spectra in the gel phase are more complex. The absorption spectra show new bands at 396 and 376 nm in addition to those observed in the isotropic spectrum. However, the high-energy ^1B_b transition at 258 nm (long-axis polarization)[18] is almost unchanged in the gel and isotropic phases of heptane. The excitation spectra of the gel display the 396- and 376-nm bands much more prominently than the 390- and 370-nm bands. Order and proximity among CAB molecules appear to be necessary to observe the new bands: 0.81% of CAB in a 30/70 (w/w) cholesteryl chloride/cholesteryl nonanoate mixture at 40 °C (cholesteric liquid-crystalline phase) and at >80 °C (isotropic phase) gave absorption spectra in which the 396- and 376-nm bands were absent. From the above data, from the lack of excimer emission, and by analogy to studies with anthracene,[19] we ascribe the new bands to vibronic coupling of aggregated anthracenes (stacked but with their long molecular axes nonparallel).

The intense circular dichroism of guest molecules in cholesteric liquid crystals (observed by us[20] and others[21]) has been related to the helical arrangement of the solvent matrix.[21] The presence of strong circular dichroism in CAB gels is further evidence for aggregation and for a helical stacking of anthracenyl units. As seen in Figure 2, the magnitude of dichroic absorption, like emission, increases enormously upon gelation. The bands at 396 and 376 nm are present, with the former being the more intense.

Attempts to detect helicity and crystal-like order of CAB molecules in an *n*-dodecane gel by X-ray diffraction[22] were unsuccessful. Only a broad hump centered near a Bragg distance of 5–6 Å (and ascribable to hydrocarbon–hydrocarbon chain separations) was recorded. The hump was not shifted in the isotropic phase. Proton NMR spectra (300 MHz) of the same mixture displayed no differences between the gel and isotropic phase signals of *n*-dodecane. However, clear changes in the aromatic absorptions of CAB were detected as the sample passed from the isotropic to gel phase. These results indicate that the microscopic mobility of solvent molecules is not decreased upon gelation.

The gel structure can be seen by optical microscopy performed with polarized light on thin samples between microslides. Figure 3 shows that the extent of gel structure depends upon CAB concentration. Branching of the fan-like structures and the overlap between them increase with the weight percent of CAB. At the early stages of gel

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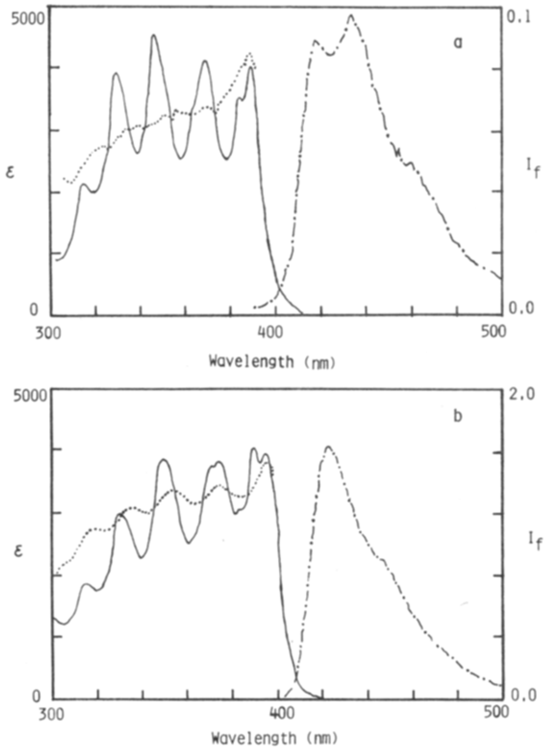

Figure 1. Isotropic (a; 67 °C) and gel (b; 25 °C) absorption (—), fluorescence (λexit 346 nm; -·-), and excitation (λemis 433 (a) and 422 nm (b); ···) spectra from 0.72% CAB in *n*-dodecane. The sample was not degassed. The fluorescence intensities between (a) and (b) are shown to observed scale.

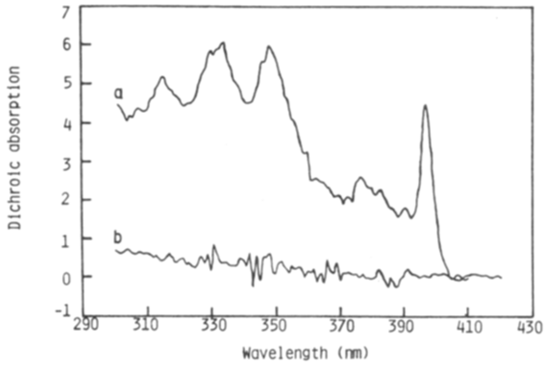

Figure 2. Induced circular dichroism spectra of 0.72% CAB in *n*-dodecane in the gel (a; 18 °C) and isotropic (b; 63 °C) phases.

formation, a faint Maltese cross pattern is visible. With time, the pattern disintegrates, disappears, and is superceded by growth of the fan-like structures. A possible explanation for the observation of the Maltese cross is that the gelator initially experiences a metastable liquid-crystal-like organization[23] that is well-aligned with respect to the glass surfaces.

Some manifestations of the gel structure should be and are found in the photochemistry of CAB. Irradiation (>300 nm) of CAB under a variety of conditions results in formation of the four conceivable photodimers which are linked at the 9 and 10 positions of the anthracenyl groups.[2] They were separated analytically into two pure fractions (A and B) and a mixture of two isomers (C). All irradiations were taken to <20% conversion (i.e., where the gel and liquid-crystalline phase appeared unchanged by macroscopic observation). At higher percentage conversion (>40%), crystals and phase separations were apparent. Prolonged irradiation of neat solid CAB at room temperature led no dimer formation.

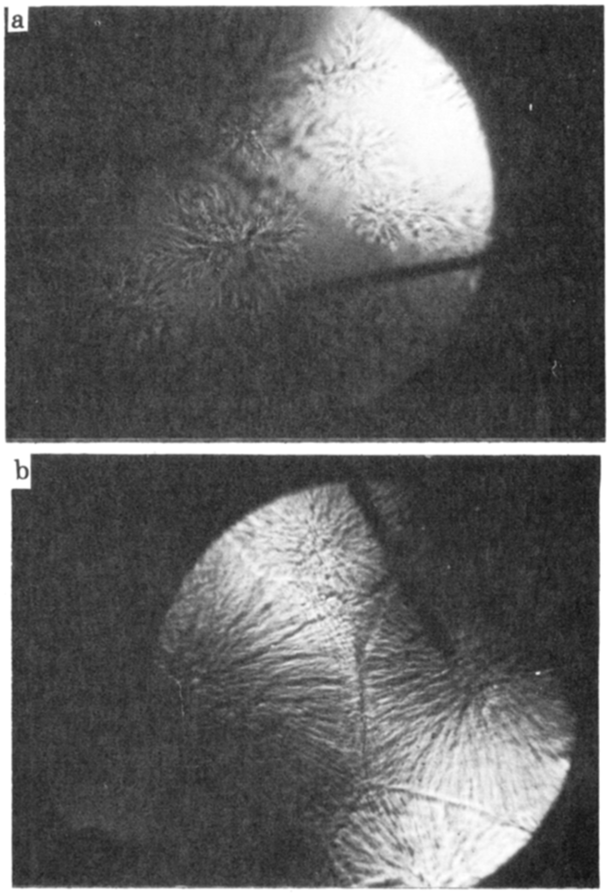

Figure 3. Textures of CAB–*n*-dodecane gels viewed through crossed polarizers (65×) at ambient room temperature: (a) 0.80% CAB; (b) 2.2% CAB.

Table I
Distribution of Photodimers from CAB

sample	phase	temp, °C	dimers, % A	B	C
1.12% CAB/dodecane	gel	26.0	29	19	53
1.47% CAB/dodecane	gel	25.5	28	16	56
1.47% CAB/toluene	isotropic	25.5	37	17	46
CAB	liquid crystalline	184.4	33	12	56
CAB	liquid crystalline	183.5	33	13	55
CAB	liquid crystalline	178.0	34	14	53
CAB	isotropic	204.4	31	20	50

Although the stereochemical assignments of the four dimers have not been completed, it is clear from their distributions (Table I) that the photochemistry of the gel phase is very similar to that of the neat liquid-crystalline and neat isotropic phases. Both of these differ especially from the A/C dimer ratio observed in isotropic toluene solutions. The fact that the (A + B)/C ratios are nearly constant except for the toluene solution may be fortuitous or indicative of similar alignment of CAB molecules in the gel, neat liquid-crystalline, and neat isotropic phases (all of which must differ from the molecular packing arrangement of the neat solid). Comparisons among these data suffer several limitations (differing temperatures, concentrations, and percents of CAB conversion). Yet, the fact that photodimers arise from very short-lived singlet states (<15 ns)[24] requires that the dimer distributions reflect in some ways the orientations of CAB molecules in the unirradiated bulk. To the extent that this is so, the photodimers indicate that the stacking of CAB in the gel and in the liquid crystal is not very different. In fact, all of the evidence obtained thus far is consistent with gelated

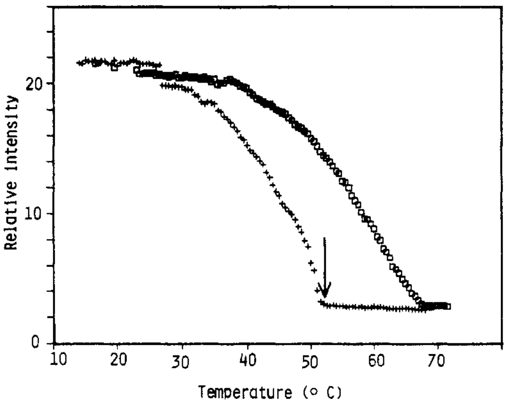

Figure 4. Fluorescence intensity at 422 nm (λex 355 nm) of 1.43% CAB in *n*-dodecane vs. temperature. Cooling (+) and heating (□) cycles are shown. The arrow indicates the gelation temperature.

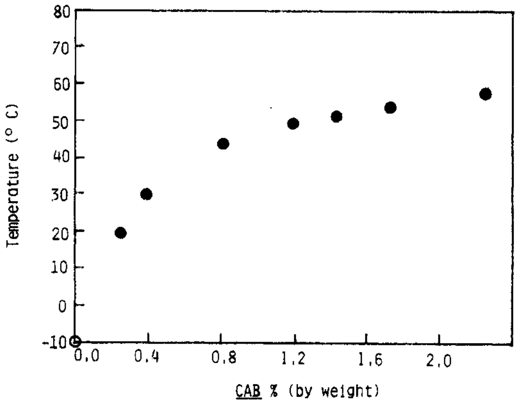

Figure 5. Gelation temperatures of CAB–*n*-dodecane gels vs. CAB concentrations. The crystallization temperature of *n*-dodecane is shown as an unfilled circle.

CAB being arranged in helically stacked threads.

The gelation point is somewhat broad and subjective. We define it to be the temperature at which the onset of emission intensity increase is observed during a cooling cycle of an isotropic solution. It appears to be independent of cooling rate, at least for *n*-alkane solutions. A representative plot of fluorescence intensity for 1.43% CAB in *n*-dodecane vs. temperature is presented in Figure 4.

Gelation temperature vs. CAB concentration profiles, as exemplified by *n*-dodecane in Figure 5, have an initial rise region followed by a plateau. In the plateau region, *n*-alkanes (*n*-heptane, *n*-octane, *n*-dodecane, and *n*-hexadecane) exhibit gelation temperatures that depend upon the concentration of CAB but not upon the alkane chain length. At 0.8% CAB by weight, the *n*-alkanes exhibit a gelation temperature of 43 ± 2 °C. Cyclohexane does not behave similarly, and the stability of its gel is much lower than that of the *n*-alkanes.

The initial rise portion of Figure 5 appears to include sol-gel formation. We believe that at all concentrations of CAB, a small amount (the solubility limit, analogous to the critical micelle concentration of surfactants) remains free in solution. CAB above this concentration aggregates to construct the gel network.

The stability of the gels, as measured by their lifetimes at ambient temperatures, depends upon the concentration of CAB and the nature of the solvent. For instance, at 3–4% CAB by weight in *n*-dodecane, the gels are very unstable. They rapidly become cloudy and then form crystals with attendant loss of their nonflowing characteristics. The most stable gels of CAB that we have observed employ 4-heptanol or heptanal as solvent. A mixture of 1.53% CAB in heptanal in a closed vessel has remained a gel at ambient temperatures for more than a year. Gels with other solvents are stable for a few hours to a few weeks.

Table II
Solvents That Do and Do Not Form Gels with CAB

gel formation observed		gel formation not observed
n-pentane	1-propanol	benzene
n-hexane	1-octanol	1-bromopropane
n-heptane	1-dodecanol	valeric acid
n-octane	benzyl alcohol	di-*n*-hexyl ketone
n-decane	4-heptanol	2-octanone
n-tetradecane	heptanal	2-undecanone
n-hexadecane	nonanoic acid	2-butene-1,4-diol
n-eicosane	*n*-pentyl acetate	1,3-propanediol
cyclohexane	*n*-butylamine[a]	toluene
decalin	benzylamine[a]	
1,3-pentadiene[a]	*N*-benzylmethylamine[a]	
α-methylbenzylamine[a]		
1-tetradecene		

[a] Gels formed by quenching the isotropic solutions at ca. 5 °C.

The position and types of functional groups on the solvents allow each of them to interact with CAB differently. Only with normal alkanes were the intermolecular forces weak enough to demonstrate that specific solvent–CAB interactions are not required for gel formation. Undoubtedly, where strong interactions exist, they have a major influence on gel formation. Qualitative results with several solvents that do and do not form CAB gels are summarized in Table II.

More detailed work to determine the structural features of the gelator and the solvent which are responsible for stable gel formation is in progress.

Experimental Section

Absorption spectra were obtained on a Perkin-Elmer UV–vis spectrophotometer. Fluorescence spectra were recorded front-face or right angle on a Spex Fluorolog spectrofluorimeter (150 W/1 XBO high-pressure xenon lamp) equipped with a Datamate computer. Gel solutions were sealed under reduced pressure in 0.8-mm (i.d.) Kimax cells. Optical microscopy was viewed through a Kofler hot-stage microscope with plane polarizers above and below the sample stage. Circular dichroism spectra were recorded on a Jasco ORD/UV 5 spectrophotometer with a CD attachment. NMR spectra were obtained on a 90-MHz Bruker FHX-10 or a 300-MHz Bruker AM-300WB spectrometer.

All solvents were reagent grade or better. 2-Methoxyanthracene was synthesized from phthalic anhydride and anisole by modification of a procedure described in the literature.[25] 2-Hydroxyanthracene was unstable and was made, as needed, from 2-methoxyanthracene.[26] It was converted to ethyl 4-(2-anthryloxy)butanoate by treatment with sodium hydride in dimethylformamide and then ethyl 4-bromobutanoate. Alkaline hydrolysis of the ester, followed by reaction with oxalyl chloride in benzene yielded 4-(2-anthryloxy)butanoyl chloride. CAB was obtained by adding the acid chloride to a solution of cholesterol in benzene. After recrystallization from *tert*-amyl alcohol (3×) and from ethanol/chloroform (3×), white needle crystals, mp 204–206 °C, were obtained. They displayed a monotropic cholesteric mesophase from 196–160 °C. ^{1}H NMR (90 MHz, $CDCl_3/Me_4Si$): δ 8.32 (1 H, s, ArH), 8.24 (1 H, s, ArH), 7.83–8.00 (3 H, m, ArH), 7.35–7.46 (2 H, m, ArH), 7.10–7.46 (2 H, ArH), 5.36 (1 H, s, alkenyl), 4.60–4.70 (1 H, m, oxycyclohexyl), 4.17 (2 H, t, J = 5.9 Hz, ArOCH_2), 2.56 (2 H, t, J = 6.9 Hz, CH_2COO), 0.67, 0.82, 0.90–2.2 (51 H, m, methylene and cholesteryl protons).

A Pyrex-filtered Hanovia 450-W medium mercury arc was employed in the preparative irradiations. Samples were degassed and sealed (three freeze–pump–thaw cycles at $<10^{-4}$ Torr) and then thermostated in an aluminum block with a window to the lamp. Analyses of products were performed on a Waters high-performance liquid chromatograph (254-nm UV detection) using a Waters Radial Pak silica column and an 80/20 hexane/chloroform (Aldrich, ethanol stabilized) mixture as eluent.

Acknowledgment. We acknowledge the National Science Foundation (Grants CHE83-01776 and CHE85-17632) for financial support of this work. Dr. Jerry Liu is thanked for several helpful discussions concerning the synthesis of CAB.

Registry No. CAB, 105900-20-7; CAB dimer, 105900-21-8; 2-methoxyanthracene, 42298-28-2; phthalic anhydride, 85-44-9; anisole, 100-66-3; 2-hydroxyanthracene, 613-14-9; ethyl 4-(2-anthryloxy)butanoate, 105930-59-4; ethyl 4-bromobutanoate, 2969-81-5; 4-(2-anthryloxy)butanoic acid, 105930-60-7; 4-(2-anthryloxy)butanoyl chloride, 105930-61-8; cholesterol, 57-88-5.

References and Notes

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Dual-Mode Transport of Molecular Oxygen in a Membrane Containing a Cobalt Porphyrin Complex as a Fixed Carrier

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Received May 5, 1986

ABSTRACT: Molecular oxygen transport through a polymeric membrane is found to be augmented by the addition of [$\alpha,\alpha',\alpha'',\alpha'''$-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt(II)–1-methylimidazole (CoPIm) complex, which forms an oxygen adduct rapidly and reversibly. The oxygen-binding rate and equilibrium constants for the Co complex in the membrane, i.e., a fixed carrier, were measured spectroscopically in situ. The oxygen permeability of the membrane containing CoPIm increased with decreasing upstream oxygen pressure, which is in accordance with a dual-mode transport model. The oxygen-binding parameters, determined spectroscopically, were adequate for an approximate analysis in terms of this model. The permeability ratio (P_{O_2}/P_{N_2}) was greater than 10 in the membrane containing a large amount of CoPIm.

Introduction

Much effort has been expended in studying the selective transport of gases through polymeric membranes.[1] One method that has been reported to find oxygen permselective membrane is the syntheses of polymers in which the solubility coefficient of oxygen is greater than that of nitrogen.[2,3] However, it is difficult to prepare a polymer in which only the oxygen solubility coefficient is substantially enhanced. This is easily understood from the fact that there is only a small difference between the solubilities of oxygen and nitrogen in organic solvents. In fact, no permselective membrane has been successfully prepared by this approach.

A polymer containing a carrier that interacts specifically and reversibly with oxygen would be an interesting possibility as an oxygen permselective membrane. Metal complexes such as iron porphyrin derivatives and cobalt–Schiff base complexes form oxygen adducts reversibly and bind oxygen according to a Langmuir isotherm. This approach has been successfully applied as an oxygen-transporting fluid[4] and as oxygen-separating liquid membranes.[5] Oxygen exhibited a high permeability in the latter. However, for the liquid membrane the membrane itself cannot be used under a differential gas pressure, and the liquid medium containing the metal complex is vaporized in use. Thus, it is not feasible to employ an oxygen-enriching membrane to separate oxygen from air.

We preliminarily reported the preparation of a polymer membrane containing a cobalt porphyrin complex as a fixed carrier in the membrane that sorbs and transports

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