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Distinct Kinetic Pathways Generate Organogel Networks with Contrasting Fractality and Thixotropic Properties

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Abstract: The kinetics of the isothermal transformation of sols, comprised of a low molecular-mass organogelator (LMOG) and an organic liquid, to their organogel phases have been followed by circular dichroism (CD), fluorescence, small angle neutron scattering (SANS), and rheological methods. The thixotropic properties (in the sense that severe shearing followed by rest lead to reestablishment of viscoelasticity) of the gels have been examined as well by rheological measurements. The compositions of the samples were either 5α-cholestan-3β-yl *N*-(2-naphthyl) carbamate (**CNC**) in an *n*-alkane (*n*-octane or *n*-dodecane) or 3β-cholesteryl *N*-(2-naphthyl) carbamate (**CeNC**) in ethyl acetate. Values of D_f, the mass fractal dimension of the microcrystalline self-assembled fibrillar networks (SAFINs) in the gels, have been extracted from the kinetic data using a model developed by Dickinson (*J. Chem. Soc., Faraday Trans.* **1997**, *93*, 111). The D_f values, 1.1−1.3 for the **CeNC** gels and 1.3−1.4 or 1.6−1.8 (depending on the temperature of incubation of the sol phase) for **CNC** gels, are consistent with the gel network structures observed by optical microscopy. In addition, comparison of the temperature dependence of both *n* (the Avrami component) and *K* (the Avrami "rate constant") for **CeNC**/ethyl acetate gelation with those reported previously for gelation of **CNC/***n*-alkane sols demonstrate that the very small change of a single bond in **CNC** to a double bond in **CeNC** causes significant differences in their gelation abilities and gel properties. The rheological measurements on **CNC**/*n*-alkane gels with spherulitic SAFIN units, formed by incubation of their sols at ≤28 °C, indicate that they are thixotropic. Gels with the same chemical composition but formed by incubation of their sols at ≥30 °C, leading to fiberlike SAFIN units, remain liquidlike after shearing regardless of the periods they are at rest. The time-dependent viscoelastic properties of the gel networks are treated according to a stretched exponential model. The observations from these studies provide detailed insights into the mechanisms of formation of molecular organogel phases and demonstrate the extreme sensitivity of the SAFINs and viscoelastic properties of such organogels to slight modifications in LMOG structure or sample history.

Introduction

Molecular organogels, a type of soft matter,[1] have experienced an enormous increase in interest during the past decade. They consist of a low concentration (usually ≤2 wt %) of a low-molecular-mass molecule (LMOG) and a liquid.[2] The self-assembled fibrillar networks (SAFINs) of most molecular organogels are formed thermoreversibly by cooling a solution or sol and are dissolved by heating the gel above a transition temperature (T_g).[2] Although fractal structures of polymer gels are more common and have been studied experimentally, theoretically, and by computer simulation for many years,[3,4] some SAFINs of LMOG gels are also fractal[5] and others are thixotropic (i.e., with time, they slowly recover their elasticity after experiencing intense shear).[6]

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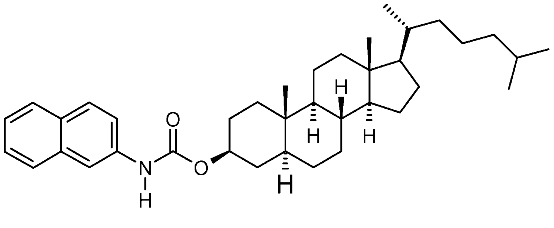
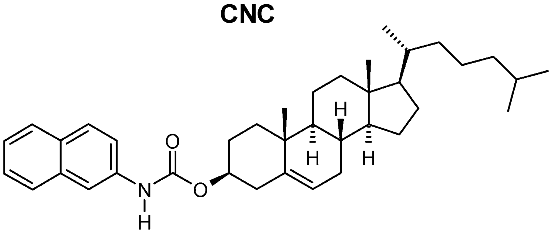
One of the most important defining parameters of a fractal object is its mass fractal dimension, D_f.[3] Several techniques have been developed to measure the D_f of gel-like materials. They include rheological measurements,[5a,b,7] light, neutron, and X-ray scattering methods,[3b,8] and adsorption−desorption experiments.[9] A real-space method, fractal analysis of digitized gel images, has been used recently[3,b10] to correlate measured variables and values of D_f based on physical models intended for application to polymer gels or porous materials such as zeolites.[3,a,11] Although those studies have yielded very useful information, the models employed may not be applicable directly to molecular organogels; the construction of three-dimensional SAFINs from polymer gellants begins with at least one dimension of the networks (N.B., the polymer chains) already in place, whereas those from LMOGs start with "zero" dimensional building blocks.[2d]

A fractal dimension provides direct information about the structures of gels but indirect information, if any, about the kinetics of their formation.[3] In principle, fractal dimensions should be obtainable from the kinetics of gelation, and they have been in a different context to describe self-similarities in the aggregation of some colloidal gels.[12] In that regard, Liu and co-workers[5c,d] have studied the formation of organogels comprised of *N*-lauroyl-L-glutamic acid di-*n*-butylamide as the LMOG and *iso*-stearyl alcohol as the liquid using the Avrami equations,[13] and they have correlated the so-called Avrami component *n*, which is related to the dimensionality of crystal growth, with D_f. We have also used the Avrami equations to study the gelation of *n*-alkanes by **CNC**[17] at different temperatures and have correlated *n* with D_f. However, it may be inappropriate to compare Avrami-derived D_f values from several systems in which different nucleation mechanisms for LMOGs are involved. For example, although both Liu and co-workers[5c,d] and we[17] studied one-dimensional aggregation processes, Liu found $D_f \approx 2$ in their homogeneous nucleating systems, while we calculated $D_f \approx 1$ in our heterogeneous nucleating ones. The D_f values calculated from the Avrami equations convolute information about the shapes of the objects formed and their mechanism of nucleation.[14] Their specific meaning must be confirmed by other information, such as autosimilarity relationships based on fiber branching.[5c,d]

Here, we calculate mass fractal dimensions (D_f) for the microcrystalline objects in SAFINs of molecular organogels (consisting of an **ALS**-type (**A**romatic-**L**inker-**S**teroid) LMOG, 5α-cholestan-3*β*-yl *N*-(2-naphthyl) carbamate (**CNC**),[15] or 3*β*-cholesteryl *N*-(2-naphthyl) carbamate (**CeNC**)) from kinetic data for the first time and investigate the thixotropic properties of the same gels. The fractal analyses are based on a physical model developed by Dickinson[16] and the time-dependent viscoelastic properties of the gel networks are treated according to a stretched exponential model to determine their thixotropic nature.



CNC



CeNC

Only those **CNC**/*n*-alkane gels prepared by incubation of their sols at temperatures ≤28 °C and, therefore, with spherulitic SAFINs,[17] have been found to be thixotropic; those formed by incubation at ≥30 °C (and with fiberlike SAFINs) remain liquidlike after shearing regardless of the period they are at rest. Both SAFINs rely on one-dimensional growth mechanisms.[18]

Throughout the −8 to 22 °C range of incubation temperatures explored, gels of **CeNC** in ethyl acetate remain liquidlike after shearing and exhibit only fibrous SAFINs by optical microscopy. From other experimental information and the Dickinson model, the D_f values remain 1.1−1.3. However, the Avrami component *n* changes from ca. ∼1 to ∼2 at an incubation temperature of the sol phase near 0.5 °C! These observations add evidence to our assertion that D_f values derived from *n* must be interpreted with caution.

The information provided here demonstrates the importance of controlling the history of molecular gels. Understanding the dynamics of their formation (i.e., history) provides insights into the nature of their aggregate structures and their thixotropic properties, as well as how to reproduce those structures and properties. Unfortunately, many publications have not mentioned the extent to which the properties of molecular gels depend on sample history. Here, we offer a blueprint for how to control and assess the dependence by offering methodologies for treating

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Table 1. Gelation Tests of Liquids with 1 wt % **CNC** and **CeNC** as LMOGs[a]

liquid	CNC[b]	CeNC[b]
methanol		P
ethanol	I	G (3 wt %, <1 week; 88.0−90.7 °C)
1-propanol	P	G (>1 week; 35.1−42.5 °C)
1-butanol	P	G (>1 week; 30.0−30.5 °C)
1-pentanol	P	G (>1 week; 38.0−38.8 °C)
1-octanol	P	G (3 wt %, >1 week; 59.1−71.5 °C)
n-octane	G (<1 week; 40.5−56.2 °C)	P
n-decane	G (<1 week; 46.7−63.8 °C)	P
n-dodecane	G (<1 week; 53.0−53.5 °C)	P
cyclohexane	G (3 wt %, >5 months; 47.1−74.2 °C)	P
benzene	S	S
acetonitrile	P	P
ethyl acetate	P	G (2 wt %, <1 week; 38.0−40.2 °C)
chloroform	S	S

[a] All sols were cooled to room temperature (22 °C) in air. [b] G, gel; P, precipitate; I, sample insoluble when the liquid was heated to boil; S, soluble. Values in parentheses are periods during which gels are stable in sealed vessels at room temperature and the T_g values determined by the inverse-flow method.[19]

the data and, from them, obtaining detailed insights into the self-assembly processes responsible for the construction of the SAFINs.

Results and Discussion

All experimental procedures and analyses, including syntheses and characterizations, are included in the Supporting Information.

Gelation Studies and Gel Structures from Optical Micrographs and Powder XRD. Table 1 summarizes results from gelation studies with **CNC** and **CeNC** as the LMOGs. Qualitatively, gelation was considered successful if no sample flow was observed upon inverting the container at room temperature (i.e., the "inverse flow" method[19]) after a third heating-and-cooling cycle. See Table 2 of Supporting Information and refs 17 and 15 for additional data. The gelation abilities of **CNC** and **CeNC** are very different although they are structurally very similar. The double bond at C5 forces the B-ring of the steroid part of **CeNC** to adopt a boat conformation, and that change affects the overall shape of the molecule (Figure 1).[20]

CNC/*n*-alkane sols, when cooled rapidly to 0 °C and incubated there, are known to yield gels with SAFINs in the form of highly branched, small fibers in spherulitic aggregates.[17] The diameters of the spherulitic assemblies of the gel become larger with increasing incubation temperature, and SAFINs of gels made by incubation of sols between ∼ 35 and 40 °C are nonspherulitic, long fibrous assemblies. With time, the gels with spherulitic (colloidal-type) SAFINs phase-separated into very long fibers whose diffraction pattern is the same as that of the fiberlike neat solid.

Powder XRD patterns of the spherulitic gel, the fiberlike gel, their xerogels, and the spherulitic and fiberlike neat solids are shown in Figure 2. **CNC** xerogels were prepared by drying fresh **CNC**/*n*-octane gels (defined as samples within 5 h of initial cooling) under a dynamic reduced pressure of 440 Torr for several days. This process yielded samples that were not thoroughly dried, as indicated by a broad peak around 20° in 2θ in XRD patterns and thermal gravimetric analyses (TGA). The needlelike **CNC** (Figure 3) crystallized from ethyl acetate exhibits mp 184.1−184.9 °C (lit.[15] mp: 178−180 °C) and a very sharp melting endotherm with a heat flow maximum at 185.4 °C by DSC (Figure 2 of the Supporting Information). Crystals of **CNC** obtained from acetonitrile are spherulitic, with mp 167.9−180.0 °C and a broader endotherm centered at 179.0 °C by DSC.

Various attempts to obtain single crystals of **CNC** (and **CeNC**) failed, so that the actual packing of the molecules within either morph is unknown. However, XRD studies demonstrate that the spherulitic SAFINs and the neat spherulitic solid have the same lamellar packing: the angle ratios of the second through sixth low angle peaks, with respect to the lowest angle one at 1.96°, are 1:1, 2.1:1, 3.0:1, 4.1:1, 5.1:1, and 6.0:1.[21] There may be some interdigitation, perhaps combined with molecular tilting with respect to the lamellar planes, because the estimated extended molecular length of a **CNC** molecule is 27 Å (based on the 3D models in Figure 1) and the lowest angle diffraction corresponds to a Bragg distance of 43.4 Å;[15] interdigitation of other **ALS** gelators within their SAFINs has been reported.[2a,c,d,22] The gels with fiberlike SAFINs have the same XRD diffraction patterns as the fiberlike solids. Although polymorphism is relatively common in LMOGs, there are few examples in which more than one morph leads to gels and, as is the case with **CNC**, where the morph of the SAFIN made from one sol can be changed simply by modifying the cooling protocols.[17,23]

CeNC crystallizes from 1/4 (v/v) ethyl acetate/hexane into tapelike objects (Figure 3c). Only fiberlike SAFINs were found when sols of **CeNC**/ethyl acetate were incubated at temperatures ranging from 0 to 22 °C. Macroscopic phase separation and crystallization into fibers whose molecular packing is the same as that in the gel SAFINs (Figure 4) occur when the incubation temperature is above 25 °C. Thus, there is no evidence of polymorphism in SAFINs of **CeNC**/ethyl acetate gels.

Spectral Studies of CNC and CeNC Aggregation Behavior. Dilute solutions of **CNC** and **CeNC** have similar UV−vis absorption spectra, as expected. Above 300 nm (where reliable data could be obtained over large concentration ranges), the shapes of the spectra remained almost unchanged as the concentration of the LMOG was increased, including at concentrations where gelation was observed (see Figure 5c and Figure 3 of the Supporting Information). The emission spectra are independent of excitation wavelength and remained similar in shape as the LMOG concentrations were increased (Figure 3 of Supporting Information). Although both the excitation and

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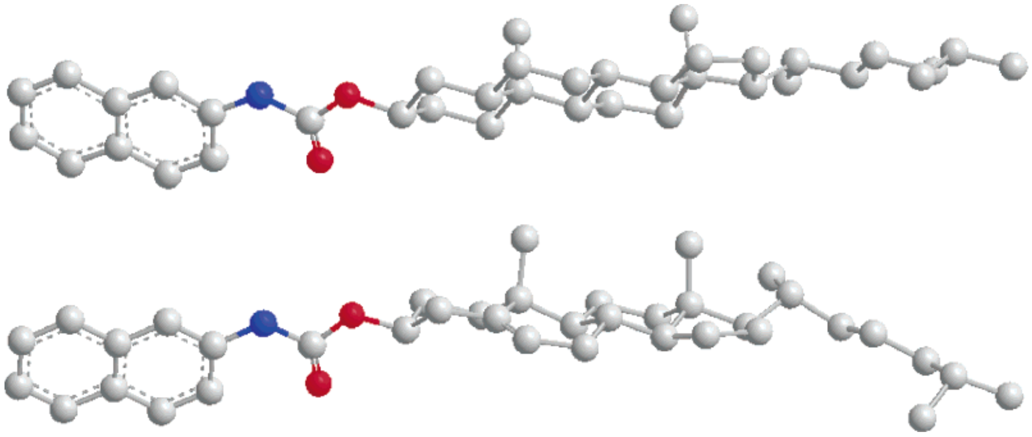

Figure 1. Structures of **CNC** (upper) and **CeNC** (lower), generated by Chem3D Ultra 8.0 (H atoms absent). Only steroidal (S) parts are shown in their lowest energy conformations (minimized by the MOPAC PM3 method); the other A and L parts are presented to emphasize the structural similarities and differences.

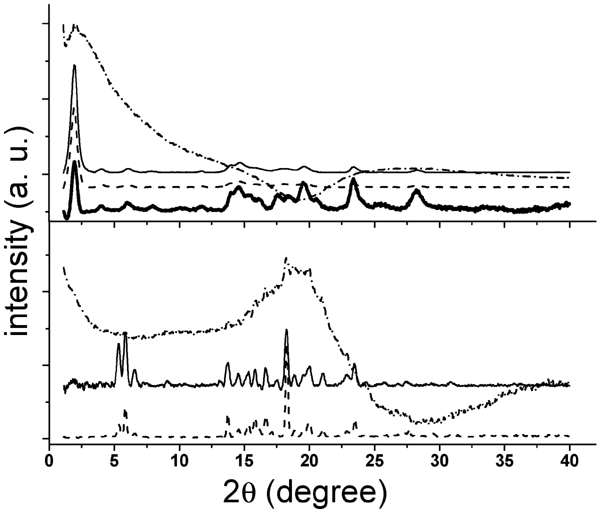

Figure 2. Powder XRD patterns of **CNC**. Upper: neat solid from acetonitrile (—), a 3.0 wt % in *n*-octane gel formed by incubation of a sol at 25 °C (— • — • —) and xerogels from a 3.0 wt % in *n*-octane gel formed at 25 (——) and 0 °C (— — —). Lower: neat solid from ethyl acetate (— — —), 1.0 wt % **CNC**/*n*-octane gel formed by incubation of a sol at 40 °C (— • — • —) and its corresponding xerogel (——). The approximate contributions of the liquids have been subtracted empirically[24] from the gel diffraction patterns.

emission spectra of the **CNC**/*n*-octane gel are red-shifted with respect to their solution spectra (by 10 and 7 nm, respectively), those of **CeNC**/ethyl acetate are not. The maxima of the latter remain at 336 nm (excitation) and 356 nm (emission).

However, significant changes in the shape and intensities of the CD spectra were observed as a consequence of the increased chiral organization that accompanied aggregation,[25] and several of these features were sensitive to the manner in which the gels were formed from their sols.

Figure 5a and 5b contain CD spectra of various phases of **CNC** with ethyl acetate or *n*-octane as the liquid. At very low concentrations, only very weak negative CD signals (near 330 nm) are observed because the molecules are not aggregated and their chromophores are far from the chiral centers on the steroidal parts; induced CD is inversely proportional to the third power of the distance between a chromophore and an optically active center.[26] With increasing concentration (and, thus, aggregation), significant increases in the CD signal are observed. In ethyl acetate, a nongelated liquid by **CNC**, the negative CD signals around 318 and 333 nm increase initially as **CNC** concentrations are increased to ca. 0.3 wt % and decrease thereafter (eventually becoming positive). In *n*-octane, a lower polarity and gelated liquid by **CNC**, the CD spectra of solutions below 0.25 wt % are similar to those in dilute (<0.3 wt %) ethyl acetate solutions. **CNC** precipitates from *n*-octane sols at concentrations above 0.3 wt % and forms gels above 0.9 wt %. As the concentration of **CNC** is increased in ethyl acetate or *n*-octane, its chiral aggregates produce much stronger CD spectra and different phases as well. In addition, CD spectra of **CNC**/*n*-octane gels are dependent on the temperature at which their sols were incubated. When 1.0 wt % sols are incubated at ∼35−40 °C, gels with fiberlike SAFINs are formed. Their CD spectra have stronger negative bands at 321 and 336 nm (∼3 nm red shift from 318 and 333 nm; ^1L_b bands of naphthyl groups[27]) than the corresponding gels formed by incubation at lower temperatures, and a new negative band appears at 303 nm. The origin of the CD band at 303 nm—it is also present, although less prominent, in absorption spectra (Figure 3a of Supporting Information)—is probably related to excitonic coupling by stacked naphthyl groups.[27] The spectrum of the gel with a spherulitic SAFIN, formed by incubation of a sol at 5.4 °C (Figure 5b), for example (see Figure 4 of the Supporting Information for spectra from gels incubated at temperatures in the range from 5.4 to 40.0 °C), shows a positive Cotton effect at ca. 340 nm, indicating the different packing arrangement of **CNC** molecules in the gels with fiberlike SAFINs. For a clearer comparison, molar ellipticities [θ][27] of the gels are plotted versus **CNC** concentration (Figure 5d).

The differences between both the gelation abilities of the two gelators and the way they organize within their SAFINs are apparent from their CD spectra. As noted in Figure 5a, the sign of the CD bands of **CNC** in ethyl acetate changes from negative to positive as the concentration (and aggregation) increases,

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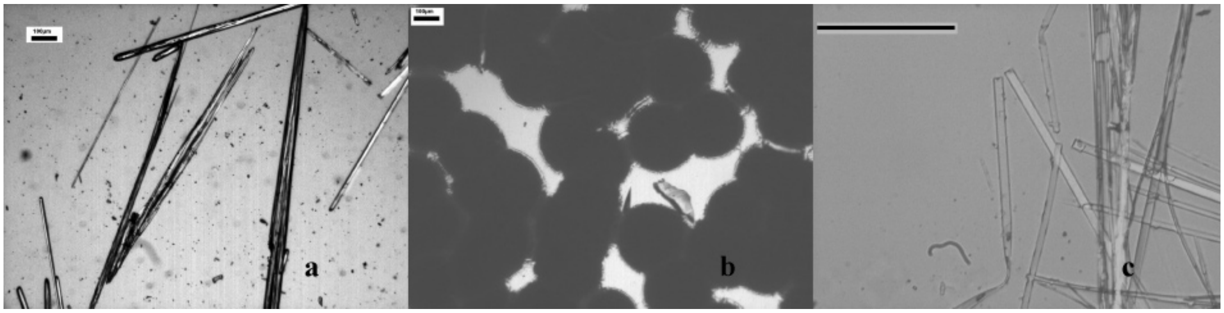

Figure 3. Optical micrographs of **CNC** neat solids recrystallized from (a) ethyl acetate and (b) acetonitrile solutions and (c) **CeNC** neat solids from 1/4 (v/v) ethyl acetate/hexane. Scale bars = 100 μm.

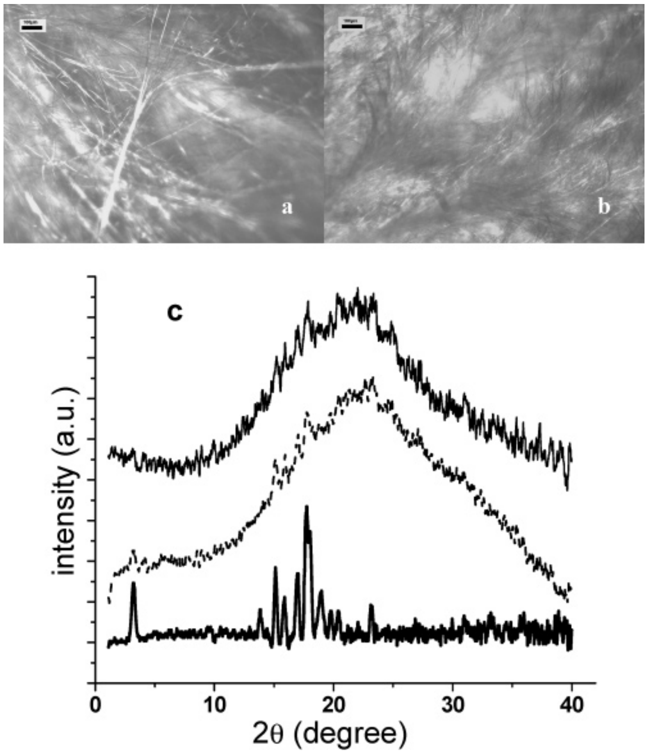

Figure 4. Optical micrographs of 2.0 wt % **CeNC**/ethyl acetate gels formed by cooling sols in air at 22 °C (a) and in an ice−water bath (b); scale bars = 100 μm. (c) Powder XRD patterns of **CeNC** neat crystals from 1/4 (v/v) ethyl acetate/hexane (—) and gels of 2.0 wt % **CeNC**/ethyl acetate formed from sols left at room temperature (− − −) and in an ice−water bath (−−) after subtracting empirically[24] the approximate contributions of the liquid.

without discernible changes in peak positions; **CeNC** precipitates from ethyl acetate sols at concentrations above 0.5 wt % and forms gels above 2.0 wt % at room temperature. Those peak positions correspond to the wavelengths of the band maxima in the absorption spectra. At equivalent dilute (0.05 wt %; 8.12×10^{-4} M) concentrations in ethyl acetate, the molar ellipticities of the 333 nm bands from both **CeNC** and **CNC** are comparable and negative (ca. −46 000 and ca. −34 000 mdeg $\mathrm{cm^{-2}\ mol^{-1}}$, respectively; Figure 5d), and the ellipticities become positive as the concentration is increased (Figure 5c). The molar ellipticities of the 318 nm bands from both **CNC**/*n*-octane and **CeNC**/ethyl acetate sols show similar trends. Thus, the change in sign of the CD bands does not depend on gelation because only **CeNC** forms a gel in ethyl acetate. However, there are significant wavelength shifts during the gelation of **CeNC** that are not very sensitive to the incubation temperature of its ethyl acetate sols (Figure 5c). These observations are consistent with the previously cited OM and powder XRD results indicating that the SAFINs of the **CeNC** gels are similar, regardless of the protocol used for their formation, and that the molecular packing within gel fibers is chiral (and probably helicoidal).[28] Because no gels are obtained from **CNC** in ethyl acetate, it is difficult to compare their CD spectra and those of **CeNC** at the same higher concentrations. However, it is interesting to note that the CD spectra of **CNC** in *n*-alkanes also exhibit strong positive features near 340 nm and large spectral shifts, but only when incubated at low temperatures (Figure 5b).[17] It is for that reason that the molar ellipticities for gels of **CNC**/*n*-octane were very different when their sols are incubated at 5 and 40 °C while the ellipticities for the gels of **CeNC**/ethyl acetate were nearly the same when their sols are incubated at 0 and 22 °C (Figure 5d).

Dickinson Model for Fractal Analyses and Its Adaptation to CNC/*n*-Alkane and CeNC/Ethyl Acetate Organogels. Analysis of the fractal nature of our molecular organogels is based upon a kinetic model developed by Dickinson.[16] A key feature of it is the time-dependent increase of excluded volume of the aggregates. The model requires that several conditions, which should apply to **CNC** and **CeNC** organogels, be met. They include the following: (1) the gels, once formed, have networks that persist in a steady state; (2) the LMOG aggregates act like hard, uncompressible particles; (3) the cross-sections of the LMOG aggregates are monodisperse or nearly so in size at each length scale and have similar shapes over several length scales; and (4) the kinetics of gelation follows the Smoluchowski model for diffusion.[29] More importantly, the model is based on the formation of two types of bonds, those that are "irreversible" fractal-type and those that are noncovalent and reversible. There may be different strengths of interactions which contribute to the stabilization of the aggregates in the percolating molecular organogel. Under these conditions mentioned above, eq 1 should be applicable to calculate the fractal dimensions of the SAFINs in our molecular organogels. For a derivation of eq 1, see Appendix 1 in the Supporting Information. C is a constant, and ϕ^{t}_{eff}, the effective volume fraction of aggregates at time = t, can be replaced by its corresponding bulk parameter, the volume fraction of the gel phase ϕ^{t}_{g}. In turn, ϕ^{t}_{g} can be expressed by other experimental parameters, such as scattering intensity, G', etc.

$$\ln \phi^{t}_{\mathrm{eff}} = C + (3 - D_{\mathrm{f}})/D_{\mathrm{f}} \ln t \qquad (1)$$

The equations used to analyze the temporal rheological data

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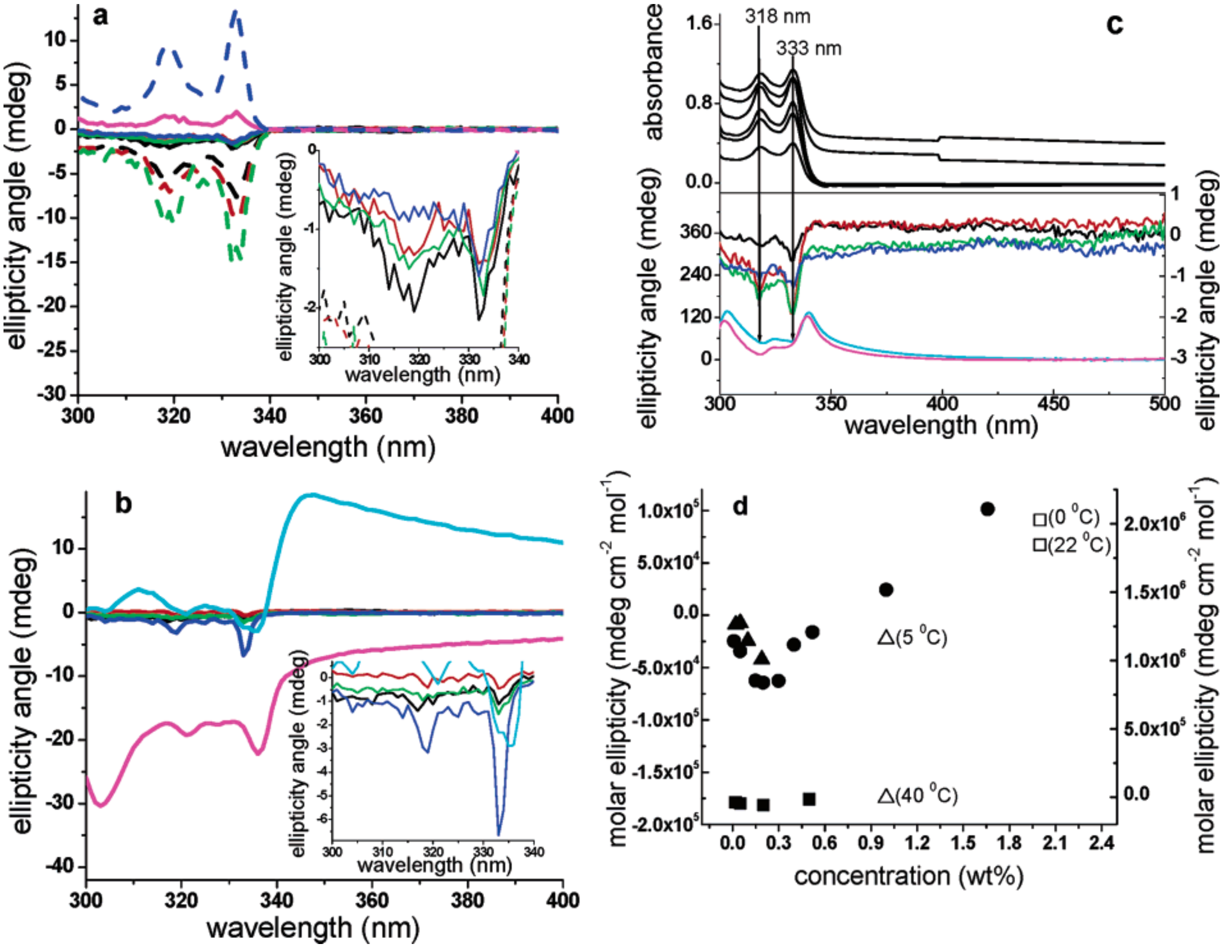

Figure 5. (a) Room-temperature CD spectra of **CNC**/ethyl acetate solutions/sols: 0.01 wt % in a 50 mm length cell and (black solid line), 0.05 (red solid line), 0.15 (black dashed line), 0.2 (red dashed line), 0.3 (green dashed line), 0.4 (green solid line), 0.52 (blue solid line), 1.0 (pink solid line), and 1.66 wt % (blue dashed line) in 5 mm length cells. (b) Room-temperature CD spectra of 0.02 (black solid line), 0.05 (red solid line), 0.1 (green solid line), and 0.25 (blue solid line) wt % **CNC**/*n*-octane solutions/sols and 1.0 wt % gels formed by incubating sols at 40 (pink solid line) or 5 °C (green solid line); cell lengths are 50, 10, 5, 5, 1, and 1 mm, respectively. The insets in (a) and (b) are expansions of the spectra near 0 mdeg. (c) Lower: Room-temperature CD spectra of 0.02 (black solid line), 0.05 (red solid line), 0.2 (green solid line), and 0.5 wt % (blue solid line) **CeNC**/ethyl acetate solutions/sols (right *Y*-axis) and 2.0 wt % gels (left *Y*-axis) formed by incubation of sols at 0 (pink solid line) and 20 °C (green solid line); cell lengths are 5, 5, 1, 0.2, 0.2, and 0.2 mm, respectively. Due to the opacity of the gel samples, the baselines of the recorded CD spectra were negative; they have been offset at the longest wavelengths to move the baselines to 0. Upper: Room-temperature absorption spectra (offset vertically) of 0.02, 0.05, 0.2, and 0.5 wt % **CeNC**/ethyl acetate solutions/sols and 2.0 wt % gels formed by incubation of sols at 0 and 20 °C (from bottom to top); cell thicknesses are 10, 10, 1, 1, 0.2, and 0.2 mm, respectively. (d) Molar ellipticities of **CNC**/ethyl acetate (●), **CNC**/*n*-octane (▲), and **CeNC**/ethyl acetate (■) sols at 333 nm and gels of **CNC**/*n*-octane (△) at 336 nm and **CeNC**/ethyl acetate (□) at 340 nm versus gelator concentration. Incubation temperatures for the gel samples are noted in parentheses.

are stretched exponentials, eqs 2 and 3, in which τ is a time constant representing the recovery speed and m is a dimensionless constant; The G' in eqs 2 and 3 can be other rheological parameters, such as G'', the complex viscosity η^*, etc.

$$G'(t) = G'(0) + [G'(\infty) - G'(0)](1 - e^{-(t/\tau)^m}) \qquad (2)$$

$$\ln\left[-\ln\frac{G'(\infty) - G'(t)}{G'(\infty) - G'(0)}\right] = m\ln t - m\ln\tau \qquad (3)$$

The kinetics of gelation of **CeNC**/ethyl acetate is also analyzed here using an Avrami equation (eq 4). It has been applied previously to explore the growth kinetics of SAFINs of molecular organogels.[6,17] In this equation, K is a temperature-dependent parameter, similar to a rate constant, and n is the so-called Avrami component that reflects the type of growth leading to phase separation. Note that eqs 2 and 3 are similar in form to eq 4. The parameter m in eq 3 and the Avrami component n are clearly related based on the similarity between the two equations.

$$\ln[-\ln(1 - \phi_g^t)] = n(\ln K + \ln t) \qquad (4)$$

Fractal Analyses Based on Kinetic Experiments. The time-dependence of the transformations of **CNC**/*n*-alkane sols to gels has been followed by SANS, rheology, CD, and fluorescence techniques. In each set of experiments, a different characteristic variable of the systems (X) was measured as a function of time: by SANS, the increase of total intensity of scatter collected in a solid angle over a 0.008−0.1 Å^{-1} range of Q; by rheology, the increase of the storage modulus G' (or, in some cases, the loss modulus G''); by CD, the increase of negative band intensities at 303 and 336 nm (incubation at 35.0 and 40.0 °C) or of positive band intensities at 343−347 nm (incubation below 30 °C); by fluorescence, the increase of emission intensity at 375 nm with excitation at 318 nm.

Since the fraction of the gel phase at time = t, $\phi_g^t = [X(t) - X(0)]/[X(\infty) - X(0)]$, can be expressed in terms of X at different

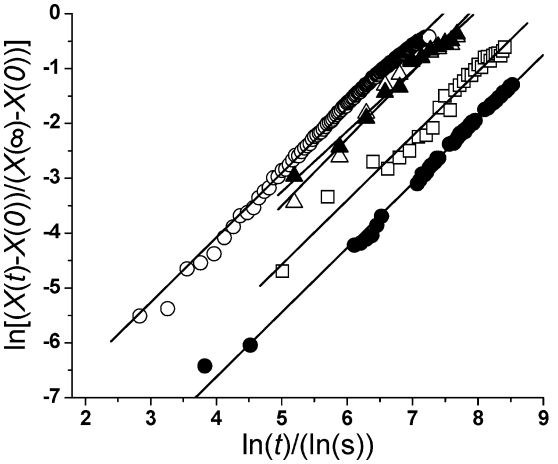

Figure 6. Plots of data according to eq 1 for gelation of sols of 1.0 wt % **CNC**/*n*-octane incubated at 40 °C: rheology G' (○, slope = 1.18, D_f = 1.38, R^2 = 0.997; *n*-dodecane as liquid), SANS (●, slope = 1.18, D_f = 1.38, R^2 = 0.996; *n*-dodecane-d_{26} as liquid), fluorescence (□, slope = 1.17, D_f = 1.38, R^2 = 0.988), and CD at 304 nm (△, slope = 1.22, D_f = 1.35, R^2 = 0.982) and at 336 nm (▲, slope = 1.11, D_f = 1.42, R^2 = 0.993). In the Y-axis, X is the variable quantity being plotted.

times as $X(0)$, $X(t)$, and $X(\infty)$, D_f can be extracted from eq 1 by plotting $\ln\{[X(t) - X(0)]/[X(\infty) - X(0)]\}$ versus $\ln t$ (Figure 6). $X(0)$ and $X(\infty)$ must be determined accurately in order to extract meaningful values of D_f. To do so, $X(\infty)$ has been calculated as the average of the last several data points at times after which no perceptible change could be discerned, at least over a time scale commensurate with the large changes; no attempt was made to include effects from hysteresis. Due to the stochastic nature of the initial nucleation, an irreproducible induction period, which is influenced by the incubation temperature (N.B., longer at higher temperatures) and the technique applied, is usually observed before intensities begin to change. Therefore, $t = 0$ for initial gel formation is considered to be when X begins to change rapidly from its initial value. As such, the exact $t = 0$ is somewhat subjective and has more error potentially than $t = \infty$. $X(0)$ is defined as either the average of X during the induction period or the value of X at the experimental zero time in the absence of a clear induction period. The uncertainty in both values probably contributes to the slight curvature in plots of the kinetic data. In order to determine the influence of these uncertainties on the calculated values of D_f, data treatments in which "zero time" was advanced or retarded by 10% were compared; the deviations from the reported values are small (Table 3 of the Supporting Information).

Data from SANS measurements taken at 40 °C on a sample consisting of 3 wt % **CNC** in *n*-dodecane-d_{26} are not shown in Figure 6 (see Supporting Information Table 7) because the rate of gelation is too rapid to allow a precise calculation of the slope; gelation was complete within <10 min according to the count intensities. Supporting Information Figure 10 shows plots of intensity versus Q counts collected for 10 s periods at different times after the 1.0 wt % sample as a sol had been incubated at 40 °C. The time range encompasses scattering curves from the very early stages to virtually full gel development. Although the signal-to-noise improves with time, the shapes of the curves are similar throughout. The plot at time ~9 h demonstrates the quality of the data; 2 oscillations are observable in spite of the very short collection period.

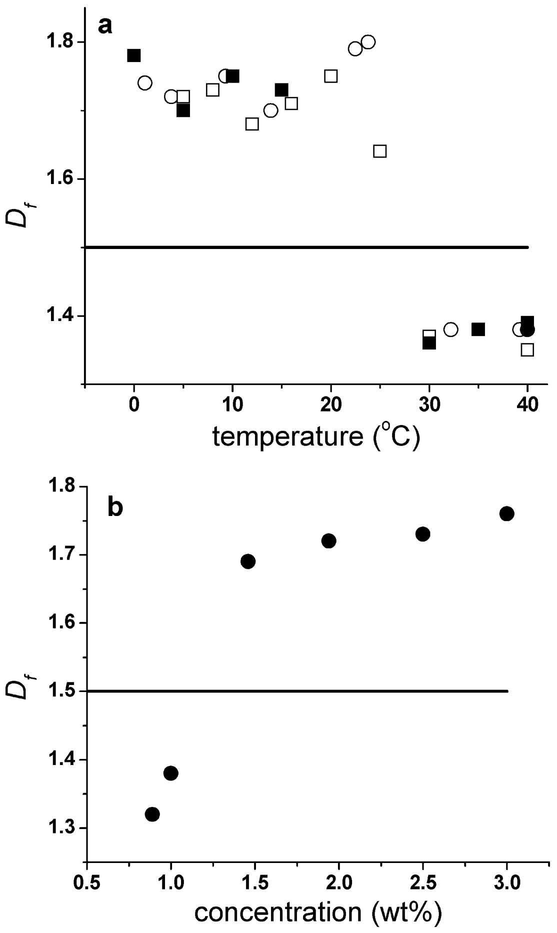

Figure 7. (a) D_f values versus sol incubation temperatures for 1.0 wt % **CNC**/*n*-alkane gels from fluorescence (○, *n*-octane), SANS (●, *n*-dodecane-d_{26}), CD (□, *n*-octane), and rheology G' (■, *n*-dodecane) data. (b) D_f values of **CNC**/*n*-octane gels versus gelator concentration from data obtained during fluorescence experiments on sols incubated at 32.2 °C.

At all temperatures investigated, D_f values are between 1 and 2 (Tables 3 and 4 of the Supporting Information), indicating that **CNC** molecules undergo one-dimensional aggregation and growth during gelation.[18] This conclusion is also reached by treating the data according to Avrami theory[17,13] and by the presence of fiber units, even for SAFINs whose micron-range aggregate units are spherulitic (Figure 6 of the Supporting Information). It is important to note that the existence of an autosimilarity relationship characterized by a fractal dimension is not apparent in treatments of the neutron scattering data from the **CNC** organogel. SANS measurements in the 0.004−0.3 Å^{-1} Q-range (not shown) contain scattering features typical only of the form factor of one-dimensional species with monodisperse cross-sections.[30] The absence of the characteristic fractality features suggests that they should be observed at much smaller Q-values (N. B., the large-Q cutoff is expected to be <0.001 Å^{-1} while the cutoff distance describing the pair correlation function at large distances, in the micron domain where optical viewing is possible, would be at Q < 0.0001 Å^{-1}) in an I versus $Q-D_f$ scattering function.[31]

Figure 7 contains plots of the temperature and concentration dependence of D_f values obtained from eq 1. For 1.0 wt % gels formed by incubation of sols above and below 30 °C, D_f is ca.

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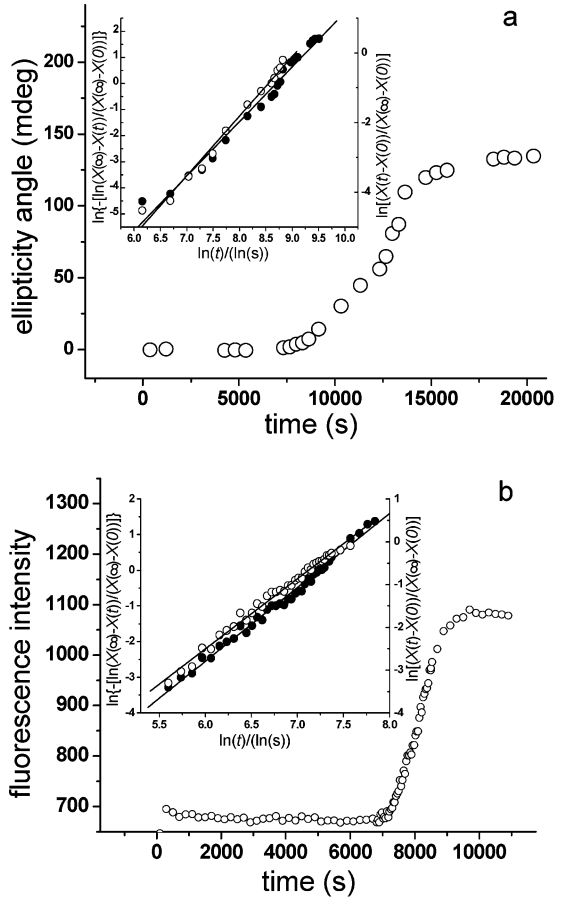

Figure 8. Kinetic studies of 2.0 wt % **CeNC**/ethyl acetate gel formation by following (a) CD intensity increases (340 nm) at 20.2 °C; the inset contains linear fits of the data based on the Avrami model (eq 4; ●, left *Y*-axis; $n = 2.09$, $R^2 = 0.990$) and fractal model (eq 1; ○, right *Y*-axis; slope = 1.71, $D_f = 1.10$, $R^2 = 0.992$) and (b) fluorescence intensity increases (358 nm) at 20.5 °C; the inset contains linear fits of the data based on the Avrami model (eq 4; ●, left *Y*-axis; $n = 2.07$, $R^2 = 0.996$) and fractal model (eq 1; ○, right *Y*-axis; slope = 1.64, $D_f = 1.14$, $R^2 = 0.995$).

1.3−1.4 and 1.6−1.8, respectively. Values of D_f between 1 and 1.5 indicate fiberlike SAFINs[18] while values between 1.5 and 2 predict spherulitic SAFIN structures (consisting of smaller fiber objects).[18] At 32.2 °C, D_f values are >1.5 at ≥1.5 wt % **CNC** and are <1.5 when CNC is <1.5 wt % (Figure 7b). As noted previously,[17] gels with fiberlike SAFINs are obtained only over very narrow **CNC** concentration ranges (below 1.5 wt %) and sol incubation temperature ranges (between 30 and 40 °C).

Kinetic Studies of CeNC/Ethyl Acetate Gel Formation Based on Avrami and Fractal Approaches. The transformations of 2.0 wt % **CeNC**/ethyl acetate sols to gels were followed by time-dependent intensity changes in CD (at 340 nm; Figure 8a) and fluorescence (λ_{ex} 333 nm; λ_{em} 358 nm; Figure 8b) signals. The data are treated according to fractal (eq 1) and Avrami models (eq 4). The approximate period required for temperature equilibration after sample transfer in these experiments was less than 30 s since a very small amount of sample was used. The shortest period to complete gelation was 10−15 min. Contributions from linear dichroism in the CD spectra are negligible since only slight changes in CD intensity were detected when samples were rotated by 90°. Data from both techniques produce Avrami components *n* near 2 and fractal dimensions D_f of 1.1−1.2. The temperature dependence of the Avrami parameters *n*, *K*, and D_f for 2.0 wt % **CeNC** in ethyl acetate samples are shown in Figure 9 (Table 5 of the Supporting Information). Very interestingly, a transition of *n* from ∼1 to ∼2 is observed around 2.5 °C as temperature is increased (Figure 9a). This is especially noteworthy because *n* is independent of temperature from 5 to 40 °C in **CNC**/*n*-alkane gel systems although there is a clear change in the SAFIN structure near 30 °C![17] The aforementioned OM and powder XRD data show no apparent differences in the SAFINs of the **CeNC**/ethyl acetate gels within the temperature range where the precipitous change in *n* is observed; it is a consequence of a change in the nucleation mechanism rather than in the growth and structure of the fibers. At incubation temperatures below ca. 0.5 °C, the gelation mechanism is based on *heterogeneous nucleation, interfacial control, and one-dimensional* growth; above ca. 0.5 °C, it is based on *homogeneous nucleation, interfacial control, and one-dimensional* growth.[14] The reason for the two regimes must, in part, depend on the degree of supersaturation which increases at lower incubation temperatures. However, heterogeneous nucleation is usually more important at low supersaturation, and it is difficult to distinguish between these two nucleation mechanisms.[32] Furthermore, since plots of ln *K* or 1/*K* versus temperature (Figure 9b) do not show an abrupt change in the

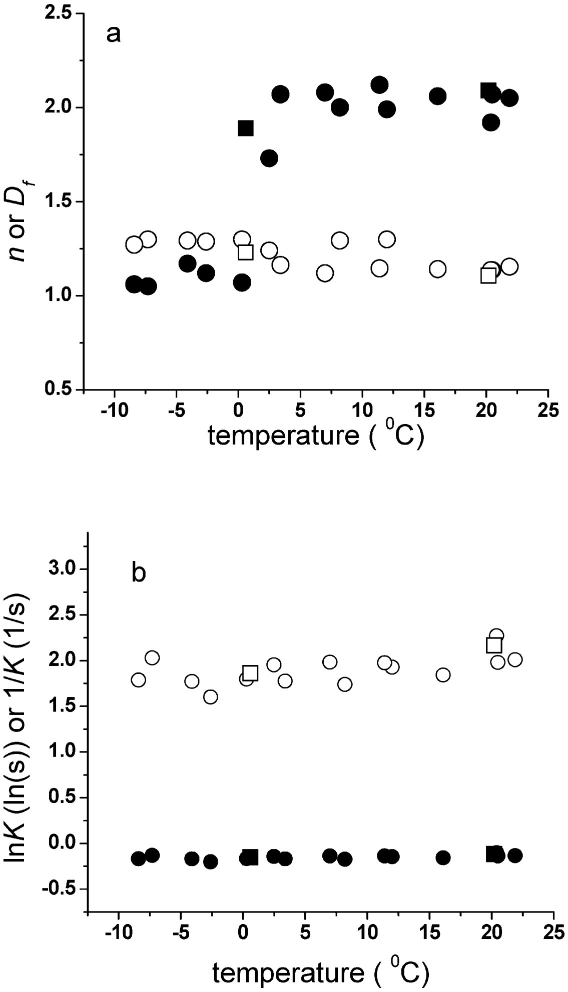

Figure 9. Analyses of data from 2.0 wt % **CeNC**/ethyl acetate samples. (a) Values of the Avrami component *n* (●,■) and D_f (○,□) versus temperature from fluorescence (●,○) and CD (■,□) data; (b) Values of the Avrami 1/*K* (●,■) and ln *K* (○,□) versus temperature from fluorescence (●,○) and CD (■,□) data.

temperature range investigated, it is reasonable to conclude that the same fiber growth mechanism is operative throughout.

Gels of 2.0 wt % **CeNC**/ethyl acetate are generally weak rheologically and not very stable at elevated temperatures or over long periods. However, they *do* form gels despite their D_f values being very low, 1.1−1.3 regardless of the incubation temperature. These D_f values indicate one-dimensional aggregation and fiberlike SAFINs[18] and are consistent with the OM observations, powder XRD patterns, and Avrami-based calculations.

We also observed that the CD and fluorescence intensities of the once-formed gels remained constant for hundreds to a few thousands of seconds, depending on temperature. However, the intensities decreased (see Figure 7a and 7b of the Supporting Information) thereafter without a corresponding discernible change in optical micrographs of the SAFIN. This behavior is indicative of an annealing process, such as syneresis.[2c]

Thixotropic Properties of CNC/*n*-Alkane Organogels. Previously,[17] we observed that **CNC**/*n*-alkane gels formed by cooling sols in an ice−water bath and at room temperature became fluid when shaken by hand and regelated when left at rest. Gels formed by incubation of sols at 40 °C had stronger networks that could not be destroyed when shaken by hand. Here, we examine the thixotropic properties of 1.0 wt % **CNC**/*n*-dodecane gels, formed by incubation of sols at various temperatures and sheared, using time-dependent rheological measurements, the recovery of G' and G''. **CeNC**/ethyl acetate gels undergo irreversible phase separation upon mechanical agitation.

Rheological experiments were conducted under oscillatory shear, and the storage modulus (G'), the loss modulus (G''), the ratio between G'' and G' (tan δ), and the complex viscosity (η^*) were measured as functions of frequency, ω. *n*-Dodecane, rather than *n*-octane, was the liquid to minimize evaporation from samples at superambient temperatures, and at a strain of 1% and a frequency of 10 rad/s, which are within the approximate linear viscoelastic (LVE) regime[33] (Figure 1 of the Supporting Information); at 40 °C, slightly below the sol−gel transition temperature, the frequency sweeps indicate that the sample behaves like a soft viscoelastic solid. The gap between the plates (0.3−0.5 mm) did not influence the rheological data, indicating that wall slip was not a factor. Samples were left undisturbed for 30 min to 4 h (based on the nature of the kinetic study) to complete gelation after the temperature, and the gap reached the desired values. The sample was then sheared at a constant shear rate of 2 s^{-1} for 600 s, and immediately afterward, the recovery of G' was monitored. A frequency-dependent sweep was also performed both before shearing and after recovery between 0.01 and 100 rad/s at 1% strain to ascertain whether a "true" gel was present.[34]

Figure 10 shows a typical plot of the increase of G' after shearing a **CNC**/*n*-dodecane gel. Treatment of the data according to eq 3 gives $m = 1$. The inset follows the recovery of G' from three consecutive runs and G'' during the first run, where a gel formed from the sol at 25 °C was mechanically disturbed. In each case, the data are fit to an exponential decay function according to eq 2. The similar values of G' and G'' immediately after shearing demonstrate that the gels were destroyed. With progressive shear-recovery cycles, the recovery time decreases, the plateau value G' becomes smaller, and macroscopic phase separation occurs eventually as the SAFINs of the gels become increasingly fatigued due to the cleavage of fibers and their "junction zones".[2] In addition, the spherulites of the original gel change their form to more and more fiberlike SAFIN structures as the number of shear-recovery cycles increases (Figure 11); shear also changes the nature of the SAFIN.[6,35]

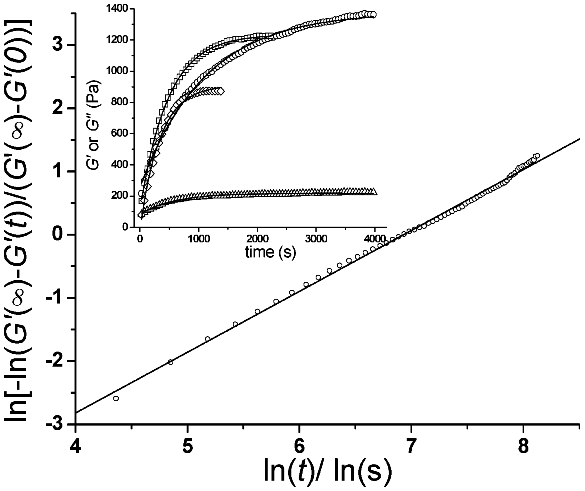

Figure 10. Recovery of G' at 25 °C of a sheared 1.0 wt % **CNC**/*n*-dodecane gel formed from its sol at 25 °C (first run, ○) and the linear best fit of the data according to eq 3 ($m = 1.0$, $R^2 = 0.998$). Inset: recovery of G' (○, first run, $\tau = 1107 \pm 20$ s, $R^2 = 0.997$; □, second run, $\tau = 478 \pm 3$ s, $R^2 = 1.000$; ◇, third run, $\tau = 341 \pm 11$ s, $R^2 = 0.996$) and G'' (△, first run, $\tau = 581 \pm 18$ s, $R^2 = 0.987$) after the gel was sheared and the corresponding single-exponential decay fits according to eq 2 as solid lines.

These trends are followed by other 1.0 wt % **CNC**/*n*-dodecane gels formed from sols incubated at temperatures ≤28 °C (Figure 8 in the Supporting Information). They are also thixotropic and have $m \approx 1$. The associated τ values are shown in Figure 12 (Table 6 of the Supporting Information). 1.0 wt % **CNC**/*n*-dodecane gels formed from sols incubated at temperatures ≥ 30 °C (Figure 8 of the Supporting Information) do not reestablish their gel states; in essence, they have infinite recovery times. The $1/\tau$ values, including those "assumed" to have zero (i.e., $1/\infty$) values, are plotted versus temperature in Figure 12. The recovery of the gel networks after shearing becomes faster as temperature increases up to 28 °C, and a sharp transition is observed thereafter (consistent with the temperature at which the change of spherulitic to fiberlike SAFINs is observed). The reproducibility of the absolute values of G', G'', and τ are not very good because they are sensitive to factors that are very difficult to control, such as the history of the sample, the presence of nucleating sites (e.g., microparticulates and small scratches on the rheometer plates). However, the trends are clear and reproducible. Since the chemical composition of the samples is the same, the thixotropy changes of the gels must be attributed only to differences in the rates and types of SAFIN formation.

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(34) (a) Almdal, K.; Dyre, J.; Hvidt, S.; Kramer, O. *Polym. Gels Networks* **1993**, *1*, 5−17. (b) Khan, S. A.; Royer, J. R.; Raghavan, S. R. *Aviation Fuels with Improved Fire Safety: A Proceeding*; National Academy Press: Washington, DC, 1997; pp 31−46.

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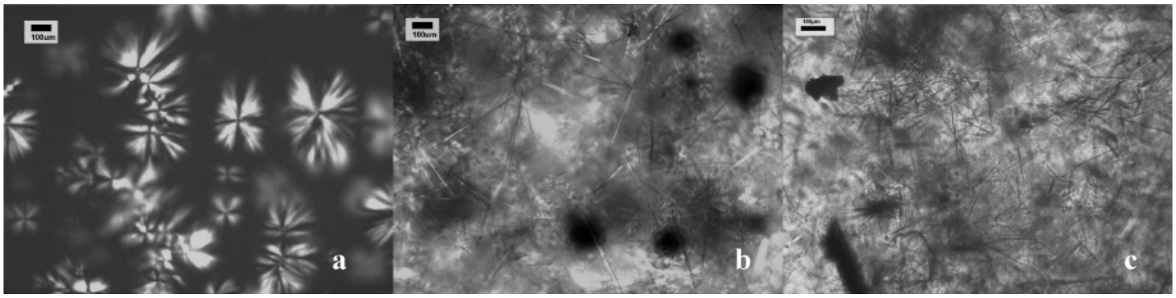

Figure 11. Optical micrographs of a 1.0 wt % **CNC**/*n*-dodecane gel freshly made by incubation of the sol at 25 °C (a) and after recovery from being sheared at 25 °C once (b) and twice (c). Space bars = 100 μm.

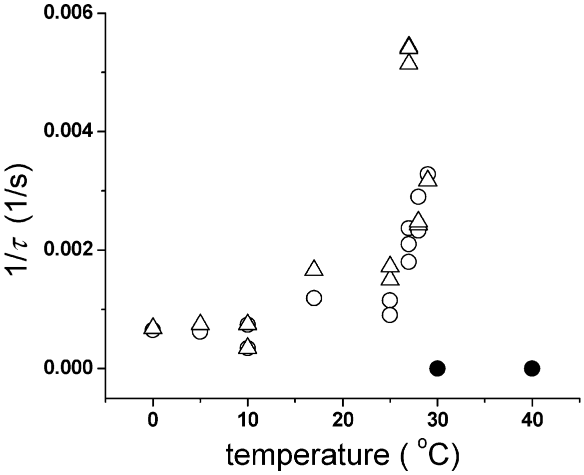

Figure 12. $1/\tau$ for recovery of sheared 1.0 wt % **CNC**/*n*-dodecane gels (first shearing) formed by incubation of their sols at the shear-recovery temperatures shown. The data are from G' (○) and G'' (△). The filled circles are for nongel samples, as indicated by G''/G' remaining >1 over long periods (Figure 8b and 8c of the Supporting Information) and visual phase separation.

Another feature of Figure 12 is that the τ values calculated from the changes in G'' are smaller than those from G'. We believe that the τ values from G' (which is more related with the solid characteristics of a material) are better reporters of the regelation processes than G'' (which is more associated with the liquid properties of a material).[6,42]

Similar shear-recovery experiments were also performed on 3.0 wt % **CNC**/*n*-dodecane gels from sols that had been incubated at 5, 15, and 30 °C. Although they were thixotropic, their recovery curves after shear could not be fitted to single-exponential decay functions, especially at early times (Supporting Information Figure 9). We conjecture that processes which are negligible at low concentrations, such as relaxation from aligned particles,[6] also contribute to the increase of G' and G''.

Based on analyses of more than 250 paints, Pryce-Jones concluded that thixotropy is more pronounced in systems containing nonspherical than spherical particles,[36] and the thixotropy of molecular organogels has been related to SAFINs of interwined and fused fibers[2a,43b,f] or ultrathin, extended, and stable fibers with low crystallinity.[43e,37] Here, the organogels with SAFINs consisting of entangled, long fibers are not thixotropic, while the gels with spherulitic aggregates are. Some form of interactions among the spherulites is necessary for gelation to occur. However, since interactions *among* neighboring spherulites should be weaker than the entanglement interactions *within* a single spherulite, the former is expected to be the primary reason why shear leads to loss of the gel properties as well as why those properties can be restored with time. For related reasons and as noted above, the fatigue observed after several shear-recovery cycles may be associated with the progressive destruction of the spherulites and their transformation into the more stable (but not thixotropic) fiber form of the SAFINs.

Conclusions

The fractal dimensions of SAFINs of molecular organogel systems consisting of **CNC**/*n*-alkane and **CeNC**/ethyl acetate mixtures have been extracted from kinetic data for the first time. The basic conclusions from those studies, especially the dependence of SAFIN structure on incubation temperature of the sol phases, have been confirmed by real space observations involving optical micrography. In addition, rheological experiments have been performed to determine the thixotropic nature of the gels. We note that although thixotropy is an important attribute of some paints, foods, and biological materials (such as actomyosin[38] and blood,[39] tooth enamel growth,[40] cell membrane function[41]),[42] it has been reported for few molecular organogels because of the experimental difficulties associated with obtaining reliable measurements.[43]

Several interesting observations, as well as several important conclusions concerning the gelation mechanisms of LMOG-based systems, have been reported here. Thus, by varying the incubation temperature of its sols and concentration in an *n*-alkane, **CNC** can be directed to either of two types of SAFINs which also correspond to two crystal morphs. At incubation temperatures ≤ 28 °C or **CNC** concentrations above 1.5 wt %, thixotropic gels with spherulitic SAFINs whose D_f values are 1.6−1.8 are formed. Their powder XRD patterns indicate

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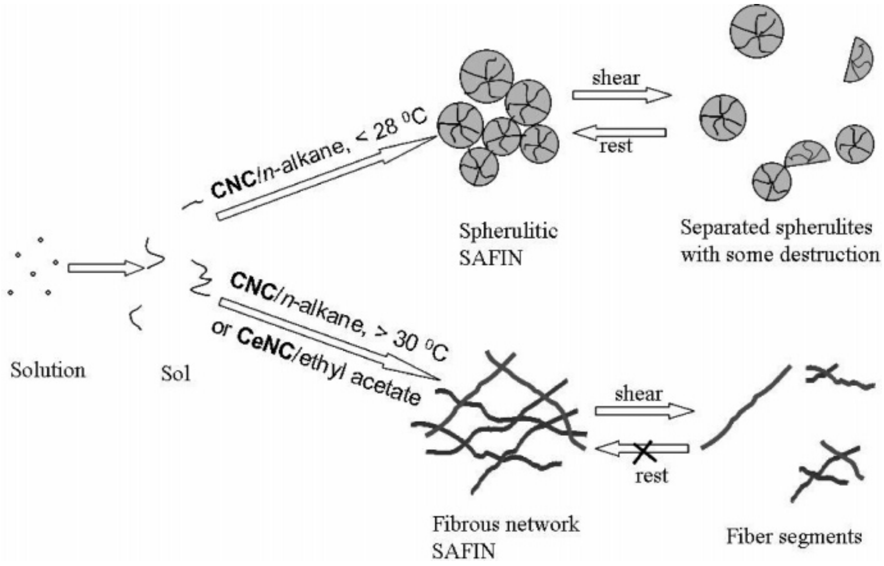
Scheme 1. Cartoon Representation of the Self-Assembly Processes Leading to Our LMOG Gels and the Consequences of Shear on the Spherulitic and Fibrillar SAFIN Morphs



lamellar packing of molecules within the fibers constituting the substructures that is the same as in crystals precipitated from ethyl acetate solutions. **CNC** concentrations of ca. 0.9−1.0 wt % and incubation temperatures of 30−40 °C produce gels with fiberlike SAFINs and D_f values of 1.3−1.4; once sheared beyond their structural limits, they do not recover their gelled states. The D_f values indicate one-dimensional aggregation and are consistent with microscopic observations and conclusions derived from Avrami-type studies.

At all temperatures where gels were formed, Avrami-type kinetic studies suggest "instantaneous nucleation" and one-dimensional growth of SAFINs in **CNC**/*n*-alkane gels.[17] However, these results do not explain why different SAFIN morphs derive from the same type of nucleation and growth mechanism; our fractal studies *do* differentiate the two processes. Thus, a combination of the results from Avrami and fractal treatments of the data reveals a deeper understanding of the processes responsible for SAFIN formation and gelation.

Under all of the experimental conditions employed to form **CeNC**/ethyl acetate gels, only one form of their SAFINs was observed, and fractal analyses yielded D_f values of 1.1−1.3, indicating one-dimensional assembly and fiberlike SAFINs. Surprisingly, the Avrami component *n*, which is normally temperature-independent, changes abruptly with incubation temperatures of **CeNC**/ethyl acetate samples. At 2 wt % **CeNC**, the increase in D_f from ca. 1 below 0.5 °C to ca. 2 above this temperature is probably due to a change in the nucleation mechanism from heterogeneous at lower temperatures to at homogeneous higher temperatures rather than structural changes in the SAFINs; *D_f values derived from the Avrami component n can lead to erroneous conclusions about SAFIN structures* unless they are confirmed by an independent observable.

The essence of these observations and conclusions are summarized in Scheme 1. Transformation of the sols is the critical point in the hierarchy of aggregation steps at which the SAFIN structure of the gels is determined:[44] the sols are dynamic structures which are able to interconvert rapidly with their unaggregated LMOG components. This model requires that the relationships between the rates for LMOG diffusion, nucleation of aggregated species, and growth along specific axes of SAFIN components determine which type of gel structure is eventually formed. Models for differential growth of anisotropic objects in very different systems have been developed[45] and polytropism in crystalline objects is well-established.[46] They can be parametrized to predict the formation of spherulitic or fibrillar objects like the ones obtained here. A future challenge will be to try to fit the empirical rates we have measured to models as a means of determining the form of the actual rate laws and the associated rate constants for gelation.

Regardless, the rheological measurements following the ability of a gel sheared beyond its stress limit to recover its viscoelastic properties have demonstrated the integral link between SAFIN structure and thixotropy in these systems. The correlation between the rheological changes and our real space observations of SAFIN objects before and after shearing lead us to the cartoon in Scheme 1. Gels with spherulitic SAFINs can be transformed into sols via shear without significant destruction of the building blocks of the SAFIN structure; their reassembly can then occur as the spherulites re-entangle.[47] However, shearing the gels with fibrous SAFINS must be accompanied by disassembly of the network and irreversible cleavage of fiber segments into shorter pieces. In the absence of an extraordinary force to "glue" the broken the segments together along the specific axes of the cleavage,[48] the SAFIN cannot be reformed and the viscoelastic properties of the original gel cannot be re-established. These conditions appear to be more

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stringent when the SAFINs of molecular organogels are crystalline, as here, than when they are not.[49]

There are already indications from careful studies with *N*-3-hydroxypropyl dodecanamide,[43d] 2,3-di-*n*-decyloxyanthracene,[43g] and a binary gelator of bis(2-ethylhexyl) sodium sulfosuccinate (AOT) and 4-chlorophenol[50] as the LMOGs that the phenomena reported here are more prevalent than generally appreciated. Regardless, it is clear that the dynamics of formation and history of molecular gels must be reported along with their composition. Without such information, it may not be possible for others to reproduce the SAFIN structures and other properties of molecular gels.

In general, gelation with **ALS** gelators depends on a delicate balance among $\pi-\pi$ stacking interactions of aromatic groups, dispersive interactions of steroidal groups, dipolar forces, and H-bonding where possible. Thus, the small differences between the molecular structures of **CNC** and **CeNC** have been shown to result in very different gelation abilities and behaviors. Clearly, the model and approach used here can be applied to many other self-assembling systems, including other molecular gels.[51] It will be interesting to determine whether the results from the fractal model applied here and from real space measurements of the SAFINs correlate in other systems. In that regard, future studies will employ structurally simpler LMOGs.

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Supporting Information Available: A detailed Experimental section, an Appendix with a derivation of the fractal equations used, and additional spectroscopic and kinetic data, including tables of D_f, n, and τ values for **CNC**/*n*-alkane and **CeNC**/ethyl acetate gels at several concentrations and temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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