Pyrenyl-Linker-Glucono Gelators. Correlations of Gel Properties with Gelator Structures and Characterization of Solvent Effects

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ABSTRACT: A series of glucono-appended 1-pyrenesulfonyl derivatives containing α,ω-diaminoalkane spacers (Pn, where n, the number of methylene units separating the amino groups, is 2, 3, 4, 6, 7, and 8) have been prepared. Careful analyses of correlations between the structures of these molecules and their gels have provided important insights into the factors responsible for one-dimensional aggregation of small molecules containing both lipophilic and hydrophilic parts. The gelation behavior has been examined in 30 liquids of diverse structure and polarity, and the properties of their gels and the gelation mechanisms have been investigated using a variety of techniques. Possible reasons are discussed regarding why the Pn are better gelators than the corresponding naphthyl analogues (Nn) which had been investigated previously. P2 and P3 are ambidextrous gelators (i.e., they gelate both water and some organic liquids), and P4–P8 gelate some organic liquids which are protic and aprotic, but not water. In at least one of the liquids examined, P3, P4, P6, P7, and P8 form gels at less than 1 w/v % concentrations, and some of the gels in 1-decanol are thixotropic. Analyses of the gelation abilities using Hansen solubility parameters yield both qualitative and quantitative insights into the role of liquid-gelator interactions. For example, the critical gelation concentrations increase generally with increasing polar and hydrogen bonding interactions between the gelators and their liquid components. As revealed by FT-IR, 1H NMR, UV−vis, and fluorescence spectra, hydrogen-bonding between glucono units and π−π stacking between pyrenyl groups are important in the formation and maintenance of the gel networks. The results from this study, especially those relating the aggregation modes and liquid properties, offer insights for the design of new surfactant-containing low-molecular-mass gelators with predefined gelating abilities.

INTRODUCTION

Gels consisting of a low concentration of a low-molecular-mass gelator (LMOG) and a liquid, as well as the mechanisms of their formation, are receiving increased attention because of the many realized and potential applications of these materials and because of the insights into one-dimensional (1D) aggregation and self-assembly modes that they provide. Solutions/sols of LMOGs can self-assemble into 1D fibers, rods, ribbons, and nanotubes, as well as two-dimensional (2D) objects (i.e., platelets) or other aggregate morphologies through hydrogen bonding, π−π stacking, London dispersion forces, and other types of van der Waals interactions. A key requirement for these objects to make gels is their additional organization into three-dimensional (3D) networks which can immobilize the liquid component. Because the noncovalent forces responsible for the 1D objects and their 3D networks are intrinsically weaker than the covalent bonds associated with gels based on cross-linked polymeric networks, LMOG-based gels are, in general, more responsive to stimuli such as heat, light, ultrasound, shearing, pH, host−guest complexes, added metallic ions, and oxidative/reductive reactions. Examples of each of these have been documented to influence the strengths of LMOG gels and their sol−gel transitions.

Gelation of liquids by LMOGs requires a fine balance between dissolution and aggregation. Many LMOG molecules contain functional groups which promote both tendencies in a given liquid. For example, we and others have explored the gelating abilities of LMOGs, which consist of an aromatic group (A), a linker (L), and a steroidal (S) group. Even when very intriguing differences in the modes of aggregation and gelation of the ALS molecules have been identified to be a consequence of subtle changes in the liquid component, the underlying physical causes have been difficult to separate.

Some members of another class of LMOGs, amphiphiles in which the A (or a long alkyl chain) and L parts are
hydrogelators, ambidextrous with somewhat longer spacers, and organogelators with the longest spacers. An advantage of such LMOGs is that changes in the fluorescence spectra and intensities from the aromatic groups can be diagnostic for gelation and LMOGs is that changes in the organization within the assembled objects.

Previously, we employed 2-naphthyl as a hydrophobic group and glucono as a hydrophilic moiety, separated by \( \alpha, \omega \)-diamine spacers of different lengths, to prepare a series of fluorescent LMOGs (\( \text{Nn} \), Chart 1). The \( \text{Nn} \) with shorter spacers were extended the comparisons among LMOGs of similar structures and to quantify further the interactions among them with different liquids, we examine here: (1) the gelating ability of a series of \( \text{Pn} \) LMOGs in which the spacers between the pyrenyl and glucono groups have been varied; (2) the properties of their gels in a wide range of liquids; and (3) correlations between the Hansen solubility parameters and the gelation trends of the \( \text{Pn} \).

Substitution of 1-pyrenyl for 2-naphthyl is not a trivial structural modification because the area and volume occupied by pyrene (187.04 Å\(^2\) and 181.13 Å\(^3\), respectively), being significantly larger than that of naphthalene (139.87 Å\(^2\) and 123.99 Å\(^3\), respectively), can affect in a significant way how the gelator molecules pack into the objects that evolve into the 3D gelator networks. Furthermore, pyrenyl moieties have much higher fluorescence quantum yields than their naphthyl counterparts and they are more prone to form detectable excimers. These attributes allow more detailed insights into the molecular packing arrangements within the gel matrices than are available with the \( \text{Nn} \). In fact, the results presented here demonstrate that the \( \text{Pn} \) are much more efficient LMOGs than the \( \text{Nn} \) (as measured by several experimental criteria) and their gels behave in very different ways. The insights derived from those results have led to a deeper understanding of the LMOG structure—gelation and LMOG—liquid relationships.

### EXPERIMENTAL SECTION

#### Syntheses and Purifications of \( \text{Pn} \).

Details concerning the syntheses and purification of the \( \text{Pn} \) are included in Supporting Information. The initially purified material, referred to as Series A, was used in all experiments except as noted in the text. In some experiments, Series A material was purified further to yield \( \text{Pn} \) denoted as Series B.

#### Gelation Tests.

All concentrations are expressed in % as 100 \( \times \) the ratio of gelator weight (g) to liquid volume (mL). A known weight of a \( \text{Pn} \) and a measured volume of selected liquid were placed into a flame-sealed tube (5 mm i.d.), and the tube was heated in an oil bath until the solid was dissolved. After the solution/sol had cooled to room temperature in air, the tube was inverted to determine whether the sample flowed perceptibly. If none was observed over a period of ca. 10 s, the sample was given a preliminary designation of a gel (G). Samples with both a liquid and gel-like material are referred to as partial gels (PG). Samples in which the \( \text{Pn} \) remained dissolved are solutions or sols (S). When a solid appeared after the \( \text{Pn} \) dissolved in a hot liquid, the designation given is precipitate (P). If a \( \text{Pn} \) could not be dissolved even at the boiling point of a liquid, the sample is designated as insoluble (I). Samples with microcrystalline \( \text{Pn} \), and which flowed when inverted, are designated as suspensions (Sus). Critical gelator concentrations (CGCs) are the lowest \( \text{Pn} \) concentrations which produced gels (as prepared by the method above). Gelation temperatures (\( T_{gel} \)) are the ranges over which gels, inverted in flame-sealed tubes, fell under the influence of gravity when heated at ca. 2 °C/min in a water bath.

#### Calculation of HSPs.

HSP values for the liquids examined were taken from the literature. Hansen space was calculated using version 1.3 of the Hansen Solubility Data Fitting Software from UMD Complex Fluids and Nanomaterials Lab. For the purpose of this analysis, the samples of the \( \text{Pn} \) in liquids are separated into soluble (S), gel (G), and insoluble (I) categories; suspensions, partial gels, and precipitates were treated as “insoluble”. Gels and partial gels formed only under sonication (G* and PG*) were treated as “insoluble” because their mixtures could not be dissolved by heating. HSP values for each gelator were determined using data fitting of each Hansen space. The distances (\( R_\alpha \)) between the gelator \( \delta_g \) and the \( \delta_p \) and those of a liquid \( \delta_m \) in Hansen space were calculated using eq 2.

$$ R_\alpha = \sqrt{4(\delta_g - \delta_m)^2 + (\delta_p - \delta_m)^2 + (\delta_h - \delta_m)^2} \tag{2} $$

<table>
<thead>
<tr>
<th>Chart 1. Molecular Structures of the Glucono-Based 1-Pyrenyl Derivatives (( \text{Pn} ) where ( n = 2, 3, 4, 6, 7, 8 )) and 2-Naphthyl Derivatives (( \text{Nn} ) where ( n = 0, 2, 3, 4, 6 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chart 1" /></td>
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</table>
Table 1. Appearances, a T_gel Values (°C) of Gels of 2.5% Pn, and Critical Gelator Concentrations (CGCs, %) in Different Liquids As Determined in 5 mm (i.d.) Sealed Tubes b

<table>
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<tr>
<th>liquid</th>
<th>P2</th>
<th>P3c</th>
<th>P4</th>
<th>P6</th>
<th>P7</th>
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<td>S</td>
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<td>methanol</td>
<td>P</td>
<td>OG</td>
<td>55–56, 0.83</td>
<td>OG</td>
<td>50–51, 1.25</td>
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<tr>
<td>ethanol</td>
<td>P</td>
<td>OG</td>
<td>68–69, 0.83</td>
<td>OG</td>
<td>66–67, 0.5</td>
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<td>1-propanol</td>
<td>P</td>
<td>OG</td>
<td>69–70, 0.5</td>
<td>OG</td>
<td>74–75, 0.42</td>
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<td>OG</td>
<td>77–78</td>
<td>0.09</td>
<td>OG</td>
<td>73–74, 0.31</td>
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<td>1-pentanol</td>
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<td>80</td>
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<td>58–59, 0.62</td>
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<td>59–60, 0.62</td>
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<tr>
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<td>P</td>
<td>Sus</td>
<td>Sus</td>
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<td>OG</td>
<td>PG</td>
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<td>cyclohexane</td>
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<td>diethyl ether</td>
<td>I</td>
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</table>

a OG = opaque gel, TG = transparent gel, PG = partial gel, Sus = suspension, P = precipitate, I = insoluble. b Gel formation after sonication at room temperature. c Thixotropic gel. The same appearances were noted for samples in 1 cm (i.d.) tubes. d Appearances cited from ref 27.

**Scanning Electron Microscopy (SEM), Transmission Electronic Microscopy (TEM), and Polarizing Optical Microscopy (POM).** SEM pictures of xerogels were taken on a Quanta 200 scanning electron microscopy spectrometer (Philips-FEI) at 20 kV and 10 mA. Xerogels were prepared by freeze–drying 2.0% gels. Prior to examination, the xerogel was attached to a copper holder with conductive adhesive tape, and then it was sputter-coated with a thin layer of gold using a SCD 005 cool sputter coater (Bal-Tec) at 30 mA and ~10 Pa for 80 s. In the following measurements, “freeze–dried” means that samples were prepared in an Alpha1−2 freeze–dryer (Christ) at −80 °C and ~4 Pa for 24 h.

Samples for TEM measurements were prepared by placing one drop of a 0.02% or 0.05% solution/sol of P7 in acetonitrile onto a carbon-coated copper grid (400 mesh) and then allowing the liquid to evaporate in air at room temperature. After drying of the grid, the sample was stained with a solution of 2% phosphotungstic acid in ethanol for 1 min and then dried in air. Measurements were made on a JEM-2100 (JEOL) microscope at 200 keV.

POMs were recorded on a Leitz S85 SM-LUX-POL microscope equipped with crossed polaris, a Leitz 350 heating stage, a Photometrics CCD camera interface connected to a computer, and an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. Samples were flame-sealed in 0.4 or 0.5 mm pathlength, flattened Pyrex capillary tubes (VitroCom, Inc.).

**Contact Angles.** Static contact angle measurements were performed on an OCA 20 video-based contact angle measuring device (Data-Physics). A drop of a hot solution/sol was placed onto a mica sheet, cooled to room temperature (to form a gel), and freeze–dried. Water droplets were placed on the freeze–dried surface via a microsyringe, and images were captured to measure the angle of the liquid–solid interface. Each sample was recorded at six different points on a surface.

**Steady-State Fluorescence.** Steady-state emission spectra of the gel and sol phases of N2-saturated 1.5% P7 (Series B) in acetonitrile in flame-sealed 4 mm (width) × 7 mm (length) Pyrex flattened capillaries (VitroCom, Inc.) were recorded in a front-face mode at an angle of ~45° with respect to the incident beam of a Photon Technology International Fluorometer (SYS 2459). In order to compare the change in the fluorescence spectra with gelation, a sample was heated and cooled using a Quantumwest temperature controller and an Omega temperature probe at ca. 10 °C/min, allowing 20 min equilibration time before recording spectra. The sample was not moved between recording spectra at different temperatures, and the instrumental parameters were unchanged.

**NMR.** 1H and 13C NMR spectra were recorded on an AVANCE 300 MHz spectrometer (Bruker). Data processing and analyses were performed using MestRe-C 2.3a software. Chemical shifts were referenced to an internal standard, tetramethylsilane (TMS). 4

**FTIR.** Spectra of sols and gels were recorded in transmission mode using a Bruker Equinox 55 infrared spectrometer. The gel samples were coated onto a KBr plate as a smooth film and then freeze–dried. Drops of hot sol samples were dropped onto a KBr plate and then freeze–dried as described above.

**Elemental Analyses.** Analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer using acetonitrile as a calibration standard.
X-ray Diffraction (XRD) and Calculated Molecular Lengths. The XRD diffractogram of a xerogel from 2% P7 (Series B) in acetonitrile was collected on a D/Max-2550/PC diffractometer with Cu Kα (λ = 0.154 nm) radiation generated at 40 kV and 40 mA. The scan rate was 1°/min. The xerogel was prepared by placing an aliquot of a gel directly onto a glass sample holder which was then freeze-dried as described above. XRD diffractograms of neat powders, neat liquids, and gels (using Pn of Series B) were conducted on a Rigaku R-Axis image plate system with Cu Kα X-rays (λ = 0.154 nm) generated by a Rigaku generator operating at 40 kV and 30 mA with the collimator at 0.5 mm (to obtain 0.5-mm-diameter beams). Data processing and analyses used Materials Data JADE (v 5.0.35) XRD pattern processing software. Samples were sealed in 0.5 mm glass capillaries (W. Müller, Schönewalde, Germany), and diffraction data were collected for 2 (neat powder) or 10 h (gel and liquid). The extended molecular lengths of the Pn were calculated using Materials Studio 4.3 software with the addition of the van der Waals radii^{31} of terminal atoms. The energy minimization of gelator conformations was made using the Discover module.

UV−vis and CD. Spectra were recorded on a Chirascan circular dichroism spectrometer starting at 25 °C. A hot sol of P7 was poured into a 1 mm path length quartz cell, which was sealed with a Teflon cap to avoid loss of liquid and cooled to room temperature to form a stable gel. The temperature-dependent spectra were recorded from low to high temperature in increments of 5 °C, allowing 10 min equilibration times after each increase, to a maximum of 55 °C. P7 samples at very low concentrations (0.1%) were placed in thin path length cells (vide infra) for UV−vis and CD measurements. They were visually transparent.

Rheology. Measurements were performed using a stress-controlled rheometer (TA ARG2 instrument) equipped with stainless steel parallel plates (20 mm diameter, 1 mm gap). A liquid trap device was placed above the top plate to minimize evaporation. Before data were recorded, a hot aliquot of Pn in 1-decanol was placed between the parallel plates of the rheometer and heated to 80 °C to ensure that a solution/sol was present. The sample was cooled to 20 °C at ~10 °C/min and incubated there for 15 min to reform the gel. Linear viscoelastic regions of the gel samples were determined by measuring the storage modulus, G′ (associated with energy storage), and the loss modulus, G″ (associated with the loss of energy), as a function of the stress amplitude. Thereafter, the moduli were measured from 0.1 to 100 Hz at a constant shear stress in the linear region (12 Pa). The stress sweeps of each Pn were measured 3 times and averaged using new samples for each run. Reported error limits are the difference between the value in one run and the average value. Also, recovery experiments at a constant frequency were performed by applying a constant oscillatory shear stress which was sufficient to destroy the gel structure (i.e., well beyond the linear viscoelastic region) for 2 min followed by a very small, constant oscillatory shear stress (1 Hz, 1 Pa) in the linear viscoelastic region while recording G′ and G″ as a function of time.

RESULTS AND DISCUSSION

Purification and Purity of Pn. The purification of Pn was very difficult due to the presence of glucono groups. The initially purified material, referred to as Series A, was purified further to yield Pn denoted as Series B. The melting points of the Series B Pn are ~0.5 °C higher than those of Series A, and their melting ranges are somewhat narrower (Supporting Information Table S1). In addition, elemental analyses of Series B Pn are closer to the values expected for a half-hydrate than those of Series A; although a common method to purify glucono-containing compounds is to wash the crude product with 32,33 or crystallize it from 34 methanol, P4−P8 form very viscous suspensions in methanol without heating, or (as noted) gelate methanol with heating and cooling. Because the procedure for obtaining the Series B products is laborious and entails a significant loss of the product, and the difference between the elemental analyses for the two series is relatively small, < 2%, we have used the series A material except where noted in the text; series B material was employed only where greater purity was deemed necessary.

Gelation Properties. The results from attempts to gelate 30 different liquids in the presence of 2.5% of the Pn by heating and then cooling the mixtures, and the critical gelation concentrations (CGCs) of those that led to gels are summarized in Table 1. At this concentration, all of the Pn dissolved in dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), pyridine, and n-butylamine without heating, and no gels were formed even when the solutions/sols were cooled to ~3 °C in a refrigerator for several hours. Also, the Pn could not be dissolved in benzene, toluene, cyclohexane, n-nonane, diethyl ether, triethylamine, CH3Cl, CH2Cl2, and CCl4 even when heated to the boiling points of these liquids. Both P2 and P3 are ambidextrous—they can gelate both water and some organic liquids. P4, P6, P7, and P8 were able to gelate the 10 alcohols tested (i.e., protic liquids), as well as acetonitrile, THF, acetone, ethyl acetate, and other relatively polar organic liquids, which are aprotic. However, they were unable to gelate water. The inability of the Pn with longer linkers between the saccharide and pyrenyl groups to gelate water is most easily attributed to their greater hydrophobicity. The increasing number of methylene units also enhances the solubility of the Pn in organic liquids, thereby altering the balance between aggregation and dissolution.39 In addition, some gels marked with “b”, such as P4 in methanol, could be formed when their mixtures were sonicated at room temperature.8 Gels such as P3 in 1-decanol were thixotropic36 at room temperature (i.e., these gels flowed immediately after being spun in a closed container on a spin coater for about 15 s and ceased to flow upon standing about 1 min without mechanical perturbation.

As mentioned, P2 and P3 gelate water, and so do the corresponding naphthyl analogues with short spacers, N0 and N2. However, the comportment of the molecules with longer spacers are somewhat different: whereas P4−P8 form homogeneous suspensions in water after the heating−cooling process, N3−N6 dissolve in water only upon being heated and then precipitate when cooled to room temperature.38 More importantly, the Pn can gelate not only the protic liquids gelated by Nn, but also a wider variety of aprotic liquids. From a structural standpoint, the origin of the improved gelating ability of the Pn series may be related to their increased solubility in organic liquids and their enhanced π−π stacking.37 Both factors are known to be important contributors to the ability of many other molecules to be effective LMOGs.4,14 However, molecular packing considerations, to be discussed below, may play an important role as well.

Because gels of P2 became precipitates after one day, their CGCs could not be determined with confidence and they are not reported. Of the gels present at 2.5% of Pn, all except P2 were stable in sealed vessels at room temperature for at least one month. The $T_{gel}$ values of gels of 2.5% Pn in the same liquid are near each other as a result of the similar structures and CGCs of the Pn. In some cases at 2.5%, such as P3 in 1-decanol and P7 in acetone, the $T_{gel}$ values are much higher than those of other Pn gels; this result follows from P3 and P7 exhibiting the lowest CGCs in these liquids. The data in Figure S1 show that the $T_{gel}$ of gels of P7 increase with increasing concentration up to ~1.5% and then reach a “plateau” value.

Many of the CGCs are less than 1%, so that the Pn are “supergelators.”38 In fact, the CGCs of P3 in 1-butanol, 1-
heptanol, and 1-decanol, P6 in acetonitrile, P7 in acetonitrile and ethyl acetate, and P8 in ethyl acetate are less than 0.1%! These concentrations translate to an ability of one molecule of P3 to immobilize ∼3850 molecules of 1-decanol, and one molecule of P7 to immobilize ∼7300 molecules of ethyl acetate. By contrast, the CGC of only N6 in acetonitrile is <0.1%.19 By this criterion, the Pₙ are again more efficient gelators than their Nₙ analogues.

Gelation and Hansen Solubility Parameters (HSPs). In an attempt to understand better the relationship between the gelator structures and the range of liquids that they are (and are not!) able to gelate, we have employed an analysis using HSPs. Table S2 summarized the HSPs of the liquids.23 The Hansen spaces25 are shown in Figure 1 for P3 and in Figures S2–S6 for the other Pₙ. As a result of the extremely high δₜ value of water and the obvious inability of current Hansen theory to provide reasonable results for the Pₙ samples in water—they skewed the plots—data from these samples were not included in the analyses. The polar interaction parameter, δₚ, and hydrogen bonding interaction parameter, δₕ, of the 30 liquids examined here cover a large portion of Hansen space, while the dispersive interaction parameter, δ₅, falls within a narrow range (14.5 < δ₅ < 19 MPa⁰.₅). In all of the graphs, the point for water is an outlier; current theory does not take into full account the properties of some of the liquids, at least as they apply to gelation by LMOGs. Furthermore, δₜ for the gelated liquids of P2 (Figure S2) and P3 (Figure 1) span a larger range of values (from 10 to 42 MPa⁰.₅) than those of P₄—P₈ (from 6.1 to 22.3 MPa⁰.₅). The ranges are consistent with P2 and P3 being ambidextrous and P₄—P₈ being only gelators of organic

Figure 1. Solubility data for 2.5% P₃ in neat liquids represented in Hansen space. Blue (soluble), red (gel), and yellow (insoluble).

Figure 2. Critical gelation concentrations (CGCs) of P₃ in some liquids as a function of (a) δₚ, (b) δₕ, (c) δₜ, (d) overall Hansen solubility parameter (δ), and (e) Rₕ in Hansen space from P₃.
liquids. In addition, the Hansen spaces of $P_4$–$P_8$ are almost the same as a consequence of their similar gelation behavior in the liquids. However, the difference between Hansen spaces of $P_3$ and $N_3$ is obvious: there are more gel points in the Hansen space of $P_3$ but more soluble points in that of $N_3$ (Figure S7). For example, whereas $P_3$ is an ambidextrous gelator, $N_3$ is only an organo-gelator, and methanol is gelated by $P_3$ while $N_3$ dissolves in it.

Figure 2 shows correlations of the individual HSPs, the overall HSPs, and the distances in Hansen space from $P_3$ with its CGCs in the gelated liquids. Although $\delta_d$ (Figure 2c) does not appear to have a clear effect on the gelating ability of $P_3$, the CGCs increase roughly with increasing $\delta_p$, $\delta_h$, overall $\delta$, and $R_a$ (Figure 2a,b,d,e, respectively); the gelating ability of $P_3$ decreases in liquids with higher polarity and more hydrogen-bonding interactions. Similar correlations are found for the other $P_n$ (Figures S8–S11). However, there is no trend that we can discern between the Hansen parameters and the CGCs of the $P_n$ as a function of the linker length, $n$. Regardless, it is clear that the changes in the gelating abilities of the LMOG homologues are a result of primarily polar and H-bonding interactions between the gelator molecules and the liquid components.

**Morphology Studies.** SEM images of the immobilizing networks of xerogels from gels with one liquid and different $P_n$ homologues were compared (Figure 3). The xerogel samples were homogeneous, and SEM images taken at different parts of each sample were like the ones shown. The results demonstrate, as expected, that the morphologies of the xerogels depend upon both the structures of the gelator and the nature of the liquid. The aggregates of $P_2$ from its hydrogel appear like a beehive, and differ from those of $P_3$. The SEM images of the xerogels from gels of $P_4$–$P_8$ in acetonitrile were also compared. The xerogel from $P_4$ in acetonitrile has a fibrous network structure, while those of $P_6$, $P_7$, and $P_8$ in acetonitrile, although similar to each other, display belt-like structures. If the xerogel networks are like those in the actual gels (and this is not
always the case\textsuperscript{22,39}), the images suggest that aggregation increases with increasing spacer length $n$.

In an attempt to reveal the nature of the aggregates in greater detail, both TEM and SEM images were recorded for samples starting from sols and xerogels of P7 in acetonitrile. Careful inspection of TEM images of fibrils made from a 0.02% sol of P7 (Figure S12) appear to contain left-handed twisted fibrils with ca. 4.5 nm width. Increasing the concentration of P7 to 0.05% resulted in a large amount of thread-like fibrils with an average diameter of 14.5 nm (Figure 4a) and without apparent twisting (although some are bent). At still higher concentrations (Figure 4b–f), the fibrils become thicker and integrate into networks (Figure 4b), and finally fuse into lamellar-like structures (Figure 4f).

The static contact angle of a water droplet on a film of the xerogel made from 1.5% P7 in acetonitrile, 116.5 $\pm$ 3.0° (Figure S13), was larger than that on a film of the xerogel from 1.5% N2 in acetonitrile, 105.1 $\pm$ 1.0°\textsuperscript{19}. The more hydrophobic surface of the xerogel from P7 is consistent with the aforementioned larger aromatic surface areas of pyrenyl than naphthyl and the longer spacer length.

**Packing Arrangements from XRD Studies.** Many diffraction peaks are detectable in the XRD diffractograms of neat P$_n$, especially P2 and P3 (Figure S14). The similarity among the diffractograms of P4–P8 is indicative of their packing arrangements being similar as well; all can be indexed to monoclinic lattices. In addition, the small incremental increases in the $d$ spacings calculated from the lowest angle peaks in the diffractograms and the similarity between the absolute $d$ values and the lengths calculated for the extended conformations of interdigitated pairs of P4–P8 molecules (e.g., for P7, the $d$ value is 4.16 nm and the calculated end-to-end distance of an interdigitated dimer is 4.36 nm) provide additional support for their packing arrangements being closely related. However, the morphologies of P2 and P3 are different from each other and from those of P4–P8 (Table S3). The $d$ value of the lowest angle peak of P2 is almost equal to the calculated length of an extended P2 molecule, and that of P3 is longer than the calculated length of an extended P3 molecule, but shorter than the calculated length of an interdigitated pair (Figure S15).

The XRD patterns of neat P7, a xerogel from a P7–acetonitrile gel, and a gel of P7 in acetonitrile are compared in Figure S16. The diffraction peaks of the P7 component in the gel were identified by subtracting empirically the amorphous scattering of the acetonitrile liquid from the total gel diffractogram.\textsuperscript{40} Unlike the monoclinic lattice of neat P7, the three reflection peaks of the P7 xerogel correspond to $d$ values of 4.16, 2.05, and 1.39 nm and follow a 1:(1/2):(1/3) progression ratio consistent with (but not definitive for, given the dearth of peaks) a lamellar organization.\textsuperscript{41} A lamellar packing arrangement is suggested as well by the TEM (Figures 4a and S12) and SEM (Figure 4b–f) images of fibers in the xerogel. However, the diffraction pattern of the P7 gel is less clear; it consists of one small peak with a $d$ value of 4.16 nm and another broad peak at higher angle (smaller distance). The differences between the XRD patterns and electron microscopy images of neat P7 and its xerogel demonstrate that the molecular packing arrangements of P7 in the two phases are not the same, and that P7 molecules in the xerogel adopt the more regular packing arrangement. Although the basis for the differences cannot be discerned from the information in hand, the three phases of P7 display the same lowest angle $d$ value, 4.16 nm. That distance is suggestive of lamellar arrangements for all and is close to the diameter of the smallest fibrils observed by TEM (Figure S12). Thus, we hypothesize that the packing arrangement of the P7 molecules in the strands, fibers, and sheets, of the xerogels involves an interdigitated head-to-tail orientation (Scheme S2).

**Spectroscopic Studies.** With increasing temperature, the peaks in the UV–vis absorption spectra of 0.1% P7 in acetonitrile at ~280, 350, and 380 nm increase and that at ~295 nm decreases (Figure 5). Such changes are expected if

\[ \pi-\pi \text{ stacking of pyrenyl moieties plays an important role in the gelation.} \]

Because the absorption band at 377 nm is red-shifted by about 3 nm as the sol cools to its gel state (where intermolecular association among P7 molecules increases), the pyrenyl groups appear to be in J-type aggregates (as do the N2 molecules in acetonitrile\textsuperscript{19}). Also, the presence of 5 isosbestic points indicates that the species in the sol and gel phases interconvert directly, without the presence of a significant amount of any new intermediates. We propose that an important driving force for J-type aggregation of the pyrenyl groups is related to H-bonding of the glucono units at the opposite end of the P7 molecules.

Circular dichroism (CD) spectra of P7 in its sol and gel phases (Figure 6) show a clear increase in intensity with increasing aggregation. The CD intensity frequently increases when chiral LMOG molecules self-assemble with appropriate orientations.\textsuperscript{13,43} The influence of increased aggregation on CD intensities is most apparent in Figure 6b where the very strong bands from 0.1% P7 in acetonitrile at 25 °C virtually disappear at 55 °C; as indicated in Figure S17, the intensity changes are completely reversible with temperature. Thus, the CD signals originate from the chirality of the supramolecular aggregates rather than from the inherent chirality of the LMOG molecules.\textsuperscript{44} Analogous results were obtained from N2 in acetonitrile.\textsuperscript{19} Taken together, these results support a model in which the P7 molecules are organized in helical arrangements within their fibrillar networks.

Fluorescence measurements have been used as well to probe the self-assembly of 1.5% P7 (Series B) in acetonitrile (Figure 7). Emissions from both phases include structured peaks from monomeric pyrenyl singlet states and a broad band from an excimeric emission (Figure 7a). Although the absorption and CD spectral studies show that the P7 molecules are more...
associated in the gel phase than in the sol phase, the relative intensity at the wavelength maximum of the excimeric emission is higher in the less aggregated sol phase. The same trend was found in the N2 system, but some others are known to behave differently. However, deconvoluting the spectra into their monomeric and excimeric components was not possible due to the multiple species present (as indicated by the excitation spectra in Figure S18). Regardless, the spectra in Figure 7a show a clear and marked difference between the positions and shapes of the excimeric components of emission in the gel and sol phases. As indicated by the inset of Figure 7a, the changes are reversible. Although the relative intensities of the monomer and excimer emissions in the sample cooled to room temperature from the sol phase change with time (increasing $I_{381\text{ nm}}/I_{473\text{ nm}}$ intensity ratio; Figure 7b), the shape and emission maximum of the excimer band change only slightly (Figure S19). Thus, over time, the P7 molecules within the initially formed gel network rearrange to environments less conducive to excimer formation. The change of the ratio with time may be due to Ostwald ripening and related phenomena. Similar phenomena have been reported by others in different gelator assemblies.

Note also that the maximum emission wavelength of the excimeric emission of the sol phase, 488 nm, is red-shifted by 10 nm with respect to that of the gel phase, and the red shift occurred with increasing temperature (inset of Figure 7a). This difference may arise from a change in the local polarity experienced by the pyrenyl units in the two phases or by an inability of the excimeric geometries to be achieved rapidly (leading to blue-shifted emissions). At the elevated temperatures of the melted gel (i.e., the sol phase), pyrenyl units are more exposed to acetonitrile molecules which provide a relatively polar microenvironment. In the gel phase, the polarity of the microenvironment of pyrenyl units may be lower due to $\pi-\pi$ stacking of pyrenyl units and exclusion of acetonitrile molecules from their immediate vicinity. In such a case, the emission wavelength maximum of the excimer would be blue-shifted in the gel phase with respect to the sol phase. A lower average polarity for the pyrenyl groups of P7 in the gel phase is indicated also by a decrease in $I_1/I_3$, the ratio between the intensities of the first and third monomer vibronic peaks, from 1.31 in the sol phase to 1.24 in the gel phase (the $I_1/I_3$ ratio of pyrene in acetonitrile is 1.79, and in less polar ethanol and benzene is 1.18 and 1.05, respectively).

Overall, these results indicate that the greater mobility of the P7 molecules in the sol phase allows facile reorientations within the excited singlet lifetimes of neighboring pyrenyl groups into the necessary excimeric geometry, and that the preferred orientations of neighboring pyrenyl groups in the networks of the gel phase are not very close to the optimal excimeric
geometry and are less able to form excimers due to more severe packing constraints.

As mentioned previously, glucono units have been introduced into the \textit{Pn} structures as a means to promote strong intermolecular H-bonding interactions and to enforce segregation among the structural units of the \textit{Pn} as they aggregate. The spectroscopic tools employed in the discussion above primarily the pyrenyl part of the \textit{Pn} molecules. FTIR spectra of the xerogels of \textit{P7} from acetone and ethanol, and of \textit{P7} in a DMF solution/sol have been used to investigate the expected H-bonding interactions of the glucono part (Figure S21). The spectrum of \textit{P7} in DMF contains bands at 3326, 1639, 1313 (1140), and 1540 cm\(^{-1}\) that can be attributed to the stretching vibrations of OH(NH), CO, and SO, and the bending vibration of NH, respectively.\(^{52}\) In the xerogels, these bands shift to 3274, 1624, 1304 (1128), and 1548 cm\(^{-1}\) (\textit{P7}/acetone) and to 3278, 1625, 1307 (1132), and 1548 cm\(^{-1}\) (\textit{P7}/acetone). These shifts are consistent with the formation of intermolecular H-bonds as aggregation of \textit{P7} occurs.\(^{6}\)

Additional information about the nature of the aggregation process for \textit{P7} was obtained from the temperature and concentration dependence of its \(^1\)H NMR spectra in DMSO-\(d_6\), a liquid in which the gelator is readily soluble (Figure S22). At 4.0\% (0.07 mol/L) \textit{P7}, the proton signals at room temperature can be assigned based on molecules with similar structures.\(^{53}\) Hydroxyl peaks from the glucono moiety shifted from 5.35 and 4.58–4.39 at 25 °C to 4.98 and 4.18–4.10 ppm at 85 °C. The NH signals shifted from 8.09 and 7.46 to 7.68 ppm over the same temperature range (Figure S22a). The observed shifts are attributed to decreased inter- and/or intra-molecular hydrogen-bonding interactions as the temperature is increased.\(^{54}\) To distinguish between the inter- and intra-molecular interactions, spectra at 25 °C were recorded at different concentrations (Figure S22b); as the concentration of the gelator increases, the relative contribution of intermolecular H-bonding interactions also increases. In the range of 1.0\% (0.02 mol/L) to 8.0\% (0.14 mol/L) \textit{P7}, signals of the hydroxyl and NH groups shifted slightly to lower field with increasing concentration. Given the large temperature dependence of the hydroxyl proton signals at 4.0\% (0.07 mol/L) \textit{P7} and the much smaller dependence as the concentration was doubled to 8\% (0.14 mol/L), we conclude that the perturbations caused by inter-molecular interactions are relatively small. The \textit{intra}-molecular H-bonding networks are largely retained as aggregation occurs and the influence of the glucono–glucono interactions on the nature of the aggregate structures is primarily from electrostatic forces (i.e., polarity). Of course, the balance between inter- and intra-molecular H-bonding interactions within aggregates of the \textit{Pn} will change with the characteristics of the liquid employed. However, the results in DMSO seem to point to the greater importance of effects more easily explained by Hansen-type parameters.

In Hansen space of \textit{P7} (Figure S23), DMSO is outside the soluble sphere but inside the gel shell (at 2.5\% concentration), and the distance \(R_{DMSO}\) of \textit{P7} is less than \(R_g\) in DMSO—\(R_{DMSO} < R_g\)—consistent with the proton shifts when changing the concentration of \textit{P7} in DMSO. However, because \(\delta_h (10.2 \text{ MPa}^{0.5})\) and \(\delta_d (18.4 \text{ MPa}^{0.5})\) of DMSO are very close to those of \textit{P7}, much of the \textit{P7} may remain dissociated even at the highest concentration investigated, 8\%.\(^{55}\) The relatively small dependence of the hydroxyl proton signals on concentration may be a consequence of the ease of intramolecular H-bonding that competes with intermolecular H-bonding even when significant aggregation of the \textit{P7} molecules occurs. Such a scenario also explains the small variations in chemical shifts of the NMR spectra when temperature or concentration is changed.

The pyrenyl signals provide additional information about \(\pi-\pi\) stacking.\(^{16}\) The chemical shift of the \(\alpha-H\) (\(\delta_h^\text{inset}\) of Figure S22a) of the pyrenyl ring at 4\% \textit{P7} is at 9.00–9.03 ppm at 25 °C and moves to 9.03–9.07 ppm at 85 °C (Figure S22a); the same signal is shifted slightly to lower field with increasing concentration (Figure S22b). These modest shifts are consistent with the UV-vis and fluorescence results which indicate that the pyrenyl units are not oriented well with respect to each other even in the gel phase. However, the change in the chemical shift of the \(\alpha-H\) (next to the sulphonyl group) in the naphthyl ring of \textit{N2} in DMSO-\(d_8\) is smaller than that of \(H_h\) in the pyrenyl analogues. This observation is suggestive of but not definitive proof of better \(\pi-\pi\) stacking in the gel networks of the \textit{Pn} series.

**Rheology of the Gels.** A strict definition of a gel must include specific mechanical behavior. For that reason and because some of the gels in Table 1 are anisotropic at room temperature, the rheological properties of several of the \textit{Pn} gels have been examined.

2.0\% \textit{P3-P8}/1-decanol gels were selected for investigation of the effect of spacer length on the mechanical properties of the gels. The rheology of the \textit{P2} gel was not examined due to its instability; as mentioned, it undergoes phase separation at room temperature after \(~1\ day). The storage modulus, \(G'\), and loss modulus, \(G''\), were measured as a function of shear stress at 20 °C. The shear stress sweeps of each \textit{Pn} in Figure 8 are the average of 3 measurements, and the \(G'\) and \(G''\) values at stress \(= 10 \text{ Pa}\) for \(G'/G''\) ratios, and yield stress are summarized in Table S4. From the results in Figure 8, the initial \(G'\) is higher than \(G''\) by about 1 order of magnitude in each sample and remains

**Figure 8.** Log–log shear stress sweeps (frequency = 1.0 Hz) for gels of 2.0\% (■) \textit{P3}, (red ○) \textit{P4}, (green ▲) \textit{P6}, (blue ▼) \textit{P7}, and (pink ★) \textit{P8} in 1-decanol at 20 °C. \(G'\), closed symbols; and \(G''\), open symbols.
higher over large ranges of shear stress. This is the comportment expected of a true gel phase.\textsuperscript{56} With a gradual increase in applied stress, both $G'$ and $G''$ remain almost invariant (i.e., in the linear viscoelastic region), and at a certain yield stress, they cross, indicating a mechanical breakup of the gels; beyond the yield stress, they deviate from linearity. From the results in Figure 9, both the value of $G'/G''$ at the initial

![Figure 9](image_url)

Figure 9. Yield stress and $G'/G''$ ratios of gels of 2\% P3–P8 in 1-decanol at 20 °C.

stress and yield stress decrease and then increase with increasing length of the spacer of $P_n$. Furthermore, the P4 gel is the most fragile as indicated by its lowest $G'/G''$ value (4.3 ± 0.1) and yield stress (30 ± 3 Pa). The P3 gel is the most stable mechanically; it possesses the largest $G'/G''$ ratio (11.1 ± 0.3) and yield stress (4460 ± 160 Pa). Because the CGCs of P3–P8 in 1-decanol are very low (<0.3%) and the concentrations employed in the rheological studies are 2\%, the large differences in the mechanical properties of the $P_n$ gels cannot be attributed to the small concentrations of the gelator molecules not incorporated within the networks. The $G'/G''$ values at the initial stress and the yield stresses (except P3) indicate that the mechanical properties of the gels improve with increasing spacer length of the $P_n$ (Figure 9).\textsuperscript{57}

X-ray diffractograms of even 10\% $P_n$ in 1-decanol (Figure S24 and Table S5) provide very little useful information about the molecular packing arrangements in these gel networks; they lack sharp diffraction peaks. The similar optical microscopy images of 2\% P3–P8 in 1-decanol (Figure S25) cannot supply any information about the different mechanical stabilities of these gels, either. However, because the $T_{gel}$ and $G'/G''$ values of 2\% $P_n$ in 1-decanol (Figure S26) follow similar trends, the mechanical strengths may be related to the energy needed to melt the networks.

P7 was chosen to investigate the role of gelator concentration on the rheological properties of the gels. As the P7 concentration in 1-decanol was increased from 0.5\% to 2.0\% (Table S6), $G'/G''$ at stress = 10 Pa increased drastically, from 0.9 ± 0.05 to 8.7 ± 0.15, and the yield stress changed from a very low value, 7.9 ± 1 Pa, to 1412 ± 80 Pa. Thus, both the elastic property (including thixotropy) of the gel and the stability of the gel network depend acutely on gelator concentration.\textsuperscript{57} Also, as expected of a true gel,\textsuperscript{56} $G'$ of a 2\% P7 in 1-decanol is nearly constant over a frequency range of 0.01 to 100 Hz and remains greater than the associated $G''$ (Figure S27). This is the typical behavior of a gel (albeit a weak one, given the absolute magnitude of $G'$).

Finally, as mentioned above, some of the gels in Table 1, including 2\% P7 in 1-decanol, show thixotropic properties at room temperature. In order to determine the magnitude and reproducibility of the thixotropic behavior, the shear–stress stimulus response was examined. A 2\% P7 in 1-decanol gel was sheared at a constant stress of 1680 Pa for 2 min, and then the evolution of the moduli as functions of time was monitored. During the recovery process, a shear stress of 1 Pa and a frequency of 1 Hz were applied to minimize perturbations to the gel reformation; the time axis was started as rapidly as the rheometer allowed (ca. 2 s delay) after the end of the destructive shear (Figure S28). The inset reveals that the gel network was destroyed partially by the high stress; it became more viscous than elastic as evidenced by $G' < G''$. However, the sample recovered 55\% of its elastic properties after cessation of the high stress.\textsuperscript{57,58}

**Model for Molecular Packing of $P_n$ Molecules in their Gel Networks.** On the basis of the data presented above, a

![Chart 2](image_url)

Chart 2. Schematic Representation of a Possible Aggregation Mechanism for P7 in Acetonitrile
possible formation process for the gel networks of P7 in acetonitrile (and, presumably, the other Pn to varying degrees) is proposed (Chart 2). It relies on the conclusions derived from several experimental observations:

1. Spectroscopic measurements indicate that π−π stacking of J-type aggregates and intermolecular H-bonding are important driving forces for the formation and maintenance of the gel networks. Synergistic operation of the forces enhances the probability that the gelator molecules will aggregate into fibrils whose diameter is equal to the length of an interdigitated pair of P7 molecules.
2. From contact angle measurements, the surfaces of the fibrils from the organogels are hydrophobic.
3. CD and TEM measurements indicate that the individual fibrils aggregate into twisted, thin fibers which subsequently aggregate into belts and then fuse into the lamellar structures implied by the XRD data.

**CONCLUSIONS**

In summary, a series of fluorescent Pn LMOGs, based on glucono and pyrenyl groups, has been synthesized and their abilities to gelate a wide variety of liquids have been examined empirically and by Hansen solubility parameters. The nature of the gels and their properties, determined by a variety of techniques, have allowed several conclusions about the importance of spacer lengths between the glucono and pyrenyl groups from internal comparisons of the Pn and external comparisons between the Pn and naphthyl analogues, NN, to be derived. The range of gelator behaviors among the Pn is extremely broad: some of the Pn are ambidextrous, some are "supergelators", and some of their gels are thixotropic. As expected, π−π stacking (in J-type aggregates) and intermolecular H-bonding interactions synergistically drive the formation of the gel networks. This series of LMOGs demonstrates how the addition or removal of even one methylene group in a fairly large molecule can alter dramatically its ability to self-assemble and to interact with a liquid.

The correlations between the gelation behaviors of the Pn and Hansen solubility parameters indicate that the changes among the LMOG homologues are primarily a result of polar and H-bonding interactions between the gelator molecules and the liquid components. Also, the morphologies and microstructures of the gel networks depend strongly upon the length of the spacer group in the Pn. Finally, the mechanical properties of the gels can be controlled to some extent by adjusting the spacer length or by changing the gelator concentration.

The results derived from these studies offer insights into how to design other surfactant-containing LMOGs. We intend to explore the extent to which the design criteria implied by the results with the Pn (as well as the comparisons made with the structurally similar NN) can be used to construct new classes of molecules with predefined gelating properties.

**ASSOCIATED CONTENT**

1. Supporting Information

Synthesis and characterization of Pn, Hansen spaces of Pn in 30 liquids, the correlation of Hansen solubility parameter and CGCs, contact angle figures of the xerogel from P7 in acetonitrile, X-ray diffraction patterns, rheological data, and additional spectra and images. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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Unexpectedly, the shape of the excitation spectra of 1.5% P7 in acetonitrile were somewhat different in flattened capillaries with 0.4, 0.85, and 84 mm pathlengths (Figure S20a); the corresponding emission spectra differ as well, but to a smaller extent (Figure S20b). Although we cannot offer a good explanation for this phenomenon, we hypothesize that it is related to instrumental factors, i.e., the depth of the focused excitation beam within the samples or even enhanced surface effects in the narrowest samples. Additional studies will be necessary to understand these differences.


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