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Synthesis and Characterization of Gels from Polyallylamine and Carbon Dioxide as Gellant

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Abstract: The synthesis and characterization of a novel series of polymer gels are reported. They are formed at ambient temperatures by bubbling CO_2 through solutions of polyallylamine (PAA; a latent gellant) in several organic liquids, including aliphatic alcohols and 1-methyl-2-pyrrolidone. The stabilities of the alcohol gels, as indicated by the (irreversible) degelation temperature, T_g^{dt}, were strongly dependent on the number of carbon atoms (C_n) in the alkyl chains of the alcohol liquids. The mechanism of formation and the microenvironmental properties of PAA-based gels containing a small amount of a pH-sensitive probe, 2,6-naphthalenedicarboxylic acid (2,6-NDCA), have been probed using static and dynamic fluorescence measurements. A measurable pH change and significant alterations to the fluorescence spectra were coincident with gelation of PAA solutions in 1-butanol as CO_2 was bubbled through, and the fluorescence spectra were monitored over several hours until no further changes were detected. Analyses of dynamic fluorescence decay histograms indicate the presence of three decay times due to different microenvironments where the 2,6-NDCA molecules are located.

Introduction

One of the most fascinating practical challenges in interfacial science is to develop new classes of dispersed systems that can be used as cleaning agents in cultural heritage conservation.[1] To this end, oil-in-water microemulsions have been formulated and successfully applied to remove polymeric coatings from surfaces of wall paintings.[2] During the past decade, some polymeric organogels have been used successfully in the restoration of easel paintings as well.[3] A significant advantage of the polymeric organogels over other topical applications is that they minimize penetration of the liquid components into the surface layers of the paintings and, thereby, reduce damage caused by swelling of the surface layers of paint.[4,5] Furthermore, a serious practical problem associated with the application of any cleaning formulation to a painting is its complete removal, and the problem is exacerbated when the formulation is very viscous.

Recently, we have developed a new family of organogels[6] based on "latent" low molecular-mass organic gelators (LMOGs) that are long-chained primary and secondary alkylamines.[7,8] Gelation occurs when a small, triatomic molecule (N.B., CO_2) is added to convert the uncharged amine into a salt (N.B., an alkylammonium alkylcarbamate) (eq 1). Primary *n*-alkylamines with between 8 and 18 carbon atoms (C_n) have been employed successfully for this purpose with CO_2 as the triatomic adduct.[7b] Most of these gels are very stable at room temperature in sealed vials (where the nonfixed CO_2 cannot escape into the atmosphere), but they can be reconverted to the initial amine solution by slightly elevating the temperature (to enhance the rate of carbamate dissociation) while bubbling nitrogen gas through (to remove the liberated CO_2 from the proximity of the amine molecules); all can be converted reversibly to gels and then back to solutions many times without evidence of degradation. The specific temperatures at which the gels are thermally converted to sols, T_g, depend on C_n, the concentration of the amine, and the polarity of the liquid component. In some cases, T_g is coincident with reversion of the alkylammonium alkylcarbamate to a solution of amine and gaseous CO_2. Carbamates can also be decomposed by dilute acid or base.[9]

$$R-NH-CO_2^{-}\,{}^{+}H_3N-R' \rightleftarrows R-NH_2 + R'-H_2N + CO_2 \quad (1)$$

Covalently bonded cross-linkers are known to convert polymer solutions into strong, highly porous gels.[10,11] If the

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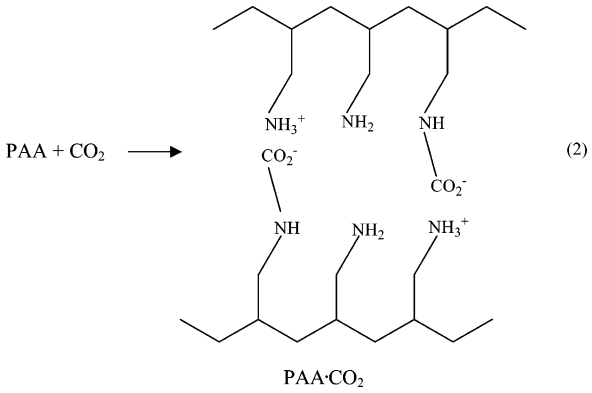
interactions between polymer chains and the cross-linking agent are electrostatic, gels with well-ordered structures are also possible.[10] Polyallylamine (PAA) has polymethylene chains with pendant aminomethyl groups on alternating carbon atoms. Even at high concentrations, PAA does not gel liquids in the absence of cross-linkers.[12] However, it can be transformed into a macroporous hydrogel when cross-linked.[13] Thus, we conjectured that PAA may be a "latent" gellant:[7,8] bubbling CO_2 through its solutions and formation of carbamate and ammonium centers might "cross-link" PAA chains through interchain ion-paired centers if they were present along with intrachain centers (eq 2). In this way, conversion of neutral PAA to a charged



(2)

polymer would set the three-dimensional network necessary for gel formation. We have found that this strategy does, in fact, lead to organogels, and we report here their properties and aspects of their formation based on fluorescence measurements of an added pH sensitive lumophore, 2,6-naphthalenedicarboxylic acid (2,6-NDCA).

Fluorescence has been a useful tool in several studies to investigate the mechanism of gelation and the microenvironments within gels.[14] In addition, lumophores such as pyrene[15] or benzene derivatives,[16] bound to polymer chains, have provided useful information concerning conformational transitions in many polymers, and 1- and 2-naphthalenesulfonyl derivatives are commonly employed as probes of PAA solutions.[17−19]

Results and Discussion

Detailed descriptions of sample preparations, experimental procedures, equipment employed, and analytical methods are included as Supporting Information.

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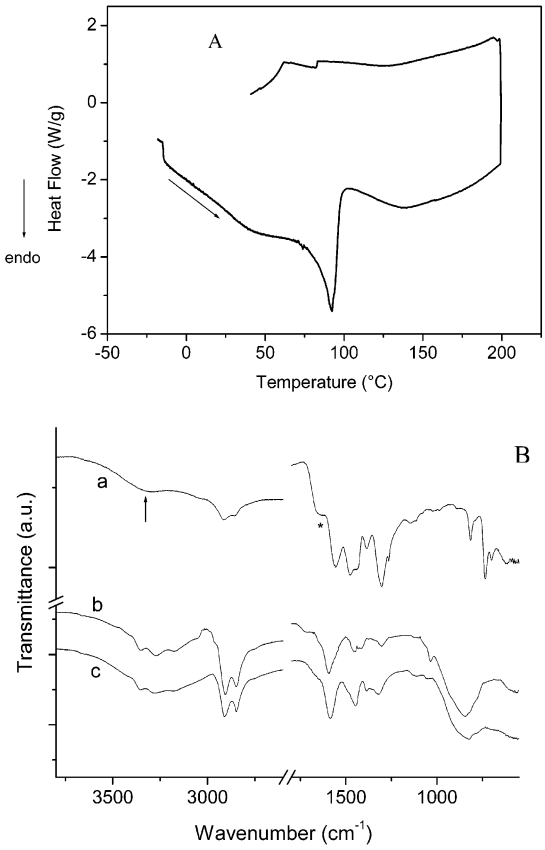

Figure 1. (A) DSC thermogram of neat PAA·CO_2. The arrow indicates the direction of heat change. (B) FTIR spectra of PAA·CO_2 before (spectrum a) and after (spectrum c) heating and cooling as shown in part A and of PAA before exposure to CO_2 (spectrum b). The arrow and star in spectrum a indicate the peaks from N—H and C═O stretches.

Characterization of Polyallylammonium Polyallylcarbamate (PAA·CO_2). A sample of PAA·CO_2 was obtained by bubbling CO_2 into a solution of 4 wt % PAA in CH_2Cl_2 for 5 min at 25 °C. Most of the solvent was evaporated by bubbling, and the remainder was removed by placing the sample under vacuum at 40 °C for 24 h. The DSC thermogram of the PAA·CO_2 (Figure 1A) includes an endotherm near 80 °C on first heating. Based on the absences of exotherms in the subsequent cooling DSC scan and an endotherm in the second heating DSC curve, the initial heating transformation is irreversible. In addition, no weight loss was detected by TGA during the second heating, but a 18.6 % weight loss, corresponding to 0.67 CO_2 molecules attached per pair of NH_2 groups of the PAA, was observed during the first heating from 25 to 130 °C. On this basis, the peak at ∼80 °C corresponds to the dissociation of PAA·CO_2 into CO_2 (that escapes into the atmosphere) and a polymer that is *primarily* PAA.

In our prior research on gelators comprised of low molecular-mass amines and CO_2, heating leads to amines that can be reconverted several times to ammonium carbamates upon bubbling CO_2 through the solutions.[7] However, heating the corresponding ammonium dithiocarbamates (made again in situ by exposing the amines to CS_2) produces *N*,*N*′-dialkylthioureas and H_2S; the amine → ammonium dithiocarbamate process is *not* thermally reversible.[8] Based on very small peaks near 180 ppm in ^{13}C NMR spectra of low molecular-mass amines that were exposed to CO_2 and heated,[8b] we suspect that a very small fraction (too low to be detected by our IR measurements below)

of the ammonium carbamate units of PAA·CO_2 suffer an analogous transformation on heating. Although a small amount of urea has no discernible effect on the ability of low molecular-mass amines to be cycled repeatedly through their nongelling (absence of CO_2) to gelling (presence of CO_2) forms, it can have serious consequences for the ability of PAA to be recycled as a gellant because the urea units can be cross-links between PAA chains.

FTIR spectra of the same sample were recorded (Figure 1B) before (top) and after (bottom) heating as indicated in Figure 1A. The shoulder at 1631 cm^{-1} (*) in the spectrum from the unheated sample is attributed to the stretching of the carbamate carbonyl group, and it is not well resolved due to the presence of another large peak. The broad peak at ~3330 cm^{-1} (arrow) is attributed to N−H stretches of ammonium and carbamate groups. Both peaks are diagnostic for PAA·CO_2. After the sample was heated, its spectrum includes peaks at 3351, 3272, and 3177 cm^{-1}, typical of a primary amine,[20] and the shoulder at 1631 cm^{-1} is absent; both changes are consistent with the expulsion of CO_2 and reversion of PAA·CO_2 to PAA. From the comparison of the pure PAA spectrum (spectrum b) and the one obtained after the heating of the polymer (spectrum c), it is possible to observe that the profile is about the same. The three peaks at 3351, 3272, and 3177 cm^{-1} are due to the N−H stretching in a primary amine. Another important datum is the absence of the peak at 1631 cm^{-1} due to the expulsion of CO_2.

From a comparison of the heats of decomposition of PAA·CO_2 and decylammonium decylcarbamate ($\Delta H = -88.8$ kJ mol^{-1} [7]) and with the assumption that the molar heats for loss of CO_2 from the two species are equal, 70% of the amino groups of PAA are estimated to participate as ammonium carbamates after CO_2 bubbling. This value is in excellent agreement with the (more precise) 67% calculated from TGA measurements mentioned previously.

Gel Formation and Stability. Samples were deemed to be gels when they showed no macroscopic phase separation and their liquid component did not flow when inverted for at least 3 min. Table 1 summarizes the stability of the gels from PAA·CO_2 as a function of the liquid and the gellant at 2 wt % and 4 wt % concentrations. Stability here is indicated by the period that the gel phase is retained when placed in a sealed glass tube at room temperature and the temperature, T_g, at which the gel becomes a solution/sol when heated (as determined by the "falling drop" method[18]).[21] To distinguish the irreversible transition temperatures measured here (N.B., when the CO_2 gas is allowed to escape to the atmosphere as shown in eq 1) from the reversible thermogelation transition temperatures frequently encountered in organogels,[22] T_g is designated T_g^{dt} (where dt indicates that loss of the gel phase is accompanied by decomposition of the gellant). At $T > T_g^{dt}$, the PAA·CO_2 gels undergo visible phase separation to form a liquid and a gummy white precipitate. Even in a closed glass vessel, where the liberated CO_2 gas is trapped, gels are not reformed when the systems are cooled, regardless of the cooling rate or if CO_2 is bubbled through again. Mild heating while bubbling N_2 gas through also leads to *irreversible* loss of the gel phase despite the fact that a similar treatment of gels from low molecular-mass amines and CO_2 leads to reversibility of gelation/degelation. The subtle structural changes in PAA leading to the irreversibility of its gelation are not understood completely at this time. As mentioned previously, we believe that they are related to small amounts of urea formation when PAA·CO_2 is heated (and water is lost instead of CO_2)[7,8] that would cross-link the polymer chains.

Table 1. Stability Parameters and Appearances[a] of PAA·CO_2 Gels in Various Liquids[b]

	[PAA·CO_2]	
liquid	2 wt %	4 wt %
methanol	TG[c] (55−70)	TG[e] (55−71)
ethanol	TG[d] (66−85)	TG[e] (67−88)
1-propanol	TG[f] (87−99)	TG[f] (88−99)
1-butanol	TG[f] (105−115)	TG[f] (105−115)
1-pentanol	TG[f] (105−118)	TG[f] (105−115)
1-hexanol	TG[f] (109−125)	TG[f] (110−128)
1-heptanol	TG[f] (115−129)	P
1-octanol	TG[f] (125−135)	P
benzyl alcohol	S	S
H_2O	S	S
xylenes	P	P
ethyl acetate	P	P
toluene	P	P
silicone oil	S	S
acetone	P	P
1-methyl-2-pyrrolidone	TG[f] (125−130)	TG[f] (128−135)
DMSO	TG[g]	TG[c]
dichloromethane	TG[g]	TG[g]

[a] S, P, and TG indicate solution, precipitate, and turbid gel, respectively. [b] Gelation temperature ranges, T_g^{dt} (°C), are in parentheses. [c] Stable < 1 week. [d] Stable < 2 weeks. [e] Stable < 2 months. [f] Stable > 2 months. [g] Stable < 1 day.

Otswald ripening,[23] in which the organization of the polymer chains in the network changes, causing the expulsion of a small amount of the liquid component, was observed for all the gels during the first two days after their preparation. The data in Table 1 demonstrate that PAA·CO_2 is a good gelant for alcohols. Most of the alcohols remain gelled for more than two months, even at 2 wt % polymer concentrations. Although the minimum amount of gellant necessary to gel the alcohols has not been determined, 1-butanol was gelled by 0.6 wt % PAA·CO_2 that persisted for less than one day. As shown in Figure 2, temporal stabilities and T_g^{dt} values increase with the chain length of the alcohol liquid component. This phenomenon can be attributed to the degree to which hydrophobic interactions between the polymer and liquid molecules allow dissociation of ion pairs (i.e., cross-linking points) within the gellant network.

In addition, PAA·CO_2 is also a good gellant for 1-methyl-2-pyrrolidone ($\mu_D = 4.09$ D[24]). Its gels are stable for more than two months at both 2 and 4 wt % gellant, and the T_g^{dt} values are comparable to those with 1-octanol as the liquid (Table 1).

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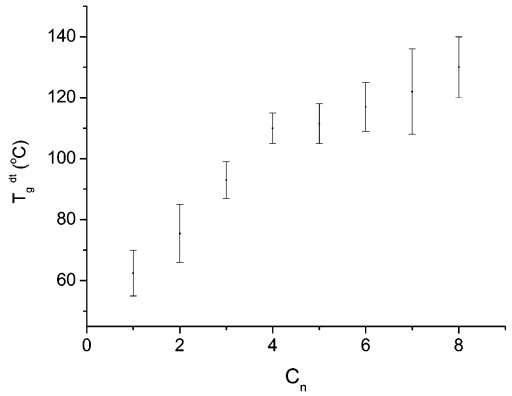

Figure 2. Dependence of T_g^{dt} as a function of the alkyl chain length of *n*-alkanols, C_n, in 2 wt % PAA·CO_2 gels.

Gels obtained from DMSO and dichloromethane are not very stable; they undergo phase separation less than one week after preparation.

Investigation of Temporal Changes in PAA·CO_2 Sols and Gels by Dynamic and Static Spectroscopic Measurements. To probe the microstructural changes that accompany gelation of solutions/sols of PAA·CO_2, fluorescence spectra and time-correlated single photon counting histograms of small quantities of an added probe molecule, naphthalene-2,6-dicarboxylic acid (2,6-NDCA), have been recorded as a function of time and temperature. Molecules of similar structure have been employed to monitor the behavior of other PAA solutions.[14] 2,6-NDCA can protonate amino groups of PAA and PAA·CO_2, thereby becoming ionically bound to one or two polymer chains. In addition, it is sensitive to the pH of its local environment. This property is very useful in our gelation studies due to the reduced basicity of the amino groups when they are converted to ammonium carbamate units: according to universal indicator paper, a 4 wt % PAA solution in water (pH ∼9.5) became acidic (pH 5.5) after bubbling through CO_2.

The system examined in greatest detail with this technique was composed of 4 wt % PAA in 1-butanol. It forms very stable gels, with $T_g^{dt} > 110$ °C, after CO_2 is added. As a result, temperature studies can be conducted to ∼100 °C in closed containers without alteration of the composition.

The absorption spectra of 2,6-NDCA in 1-butanol and water are very similar.[19] Since the concentration of amino groups in 4 wt % PAA is 0.43 M, the absorption spectra of a solution of 10^{-4} M 2,6-NDCA in 1-butanol with and without 0.43 M triethylamine were compared (Figure 3). The ∼3 nm batho-chromic shift of the peaks at 276, 286, and 296 nm upon addition of the base is a result of deprotonation of the 2,6-NDCA carboxylic groups.

Since the emission spectra of 2,6-NDCA in 1-butanol or in the presence of triethylamine (not shown) were independent of excitation wavelength (Figure 4), we conclude that only one species is emitting; no aggregates can be detected. As expected, the excitation spectra of the same samples were also independent of emission wavelength, and they are similar in shape and position to the absorption spectra.

As noted in Figure 5, the emission spectra from 2,6-NDCA in a solution of 4 wt % PAA in 1-butanol were very sensitive to λ_{ex}, and a similar trend was found after the solution in Figure 5 was gelled by bubbling through CO_2 (Figure 6a). As indicated

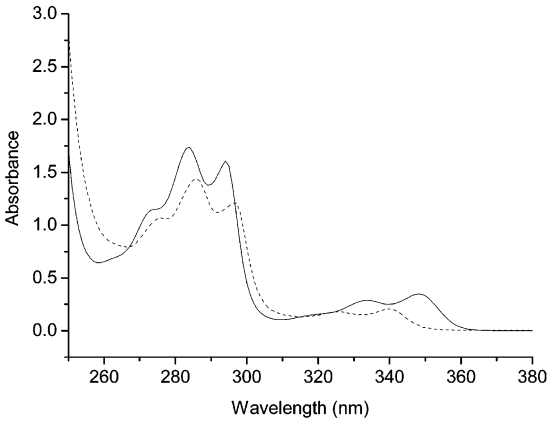

Figure 3. UV−vis absorption spectra of 10^{-4} M 2,6-NDCA in 1-butanol before (—) and after (- - -) the addition of 0.43 M triethylamine.

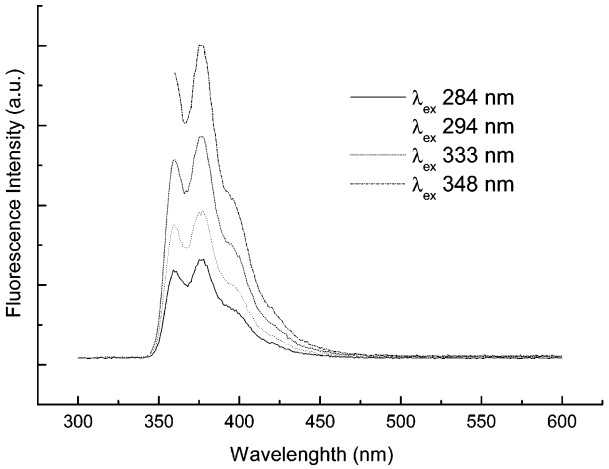

Figure 4. Fluorescence spectra of 10^{-4} M 2,6-NDCA in 1-butanol. The samples were deoxygenated by N_2 bubbling for 25 min at room temperature.

also by the wavelength dependence of the corresponding excitation spectra (Figure 5b), more than one emitting species is present. We believe that naphthyl groups are located in environments of different polarities, resulting in different degrees of deprotonation. Fluorescence of 2,6-NDCA was also studied as a function of time after gel preparation. The shapes evolved over 38 h from broad, featureless curves to highly structured ones that resemble the emission spectra in Figure 5. Only the spectra at the earliest and latest times are shown in Figure 6; note especially the emission spectra with λ_{ex} 286 and 296 nm.

A more comprehensive history of changes in the gel is displayed in the fluorescence spectra with λ_{ex} 296 nm (Figure 7). The first spectrum (indicated as $t = 0$) was recorded 3 min after the end of CO_2 bubbling, and the last was recorded 38.5 h thereafter. After ∼12 h, more vibronic structure was apparent (Figure 7 inset), indicating a significant change in the local environments experienced by a large fraction of the 2,6-NDCA molecules. It is probably associated with the probes being in sites within the gel that more closely resemble each other; immediately after CO_2 bubbling, probe molecules are probably in a more heterogeneous set of environments, and many may be like those in the PAA solutions (i.e., with 2,6-NDCA molecules ionically bound to amino groups of the PAA chains). We believe that addition of CO_2 initially forces the dissociation of 2,6-NDCA molecules from these sites, and they move slowly into regions richer in 1-butanol molecules.

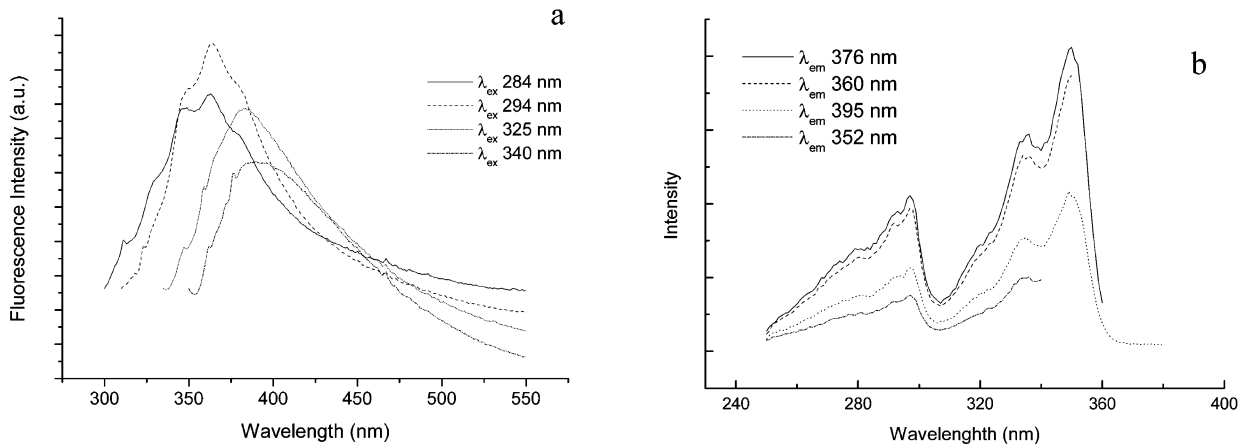

Figure 5. Emission (a) and excitation (b) spectra of 10^{-4} M 2,6-NDCA in 1-butanol in the presence of 4 wt % PAA. The samples were deoxygented by N_2 bubbling for 25 min at room temperature.

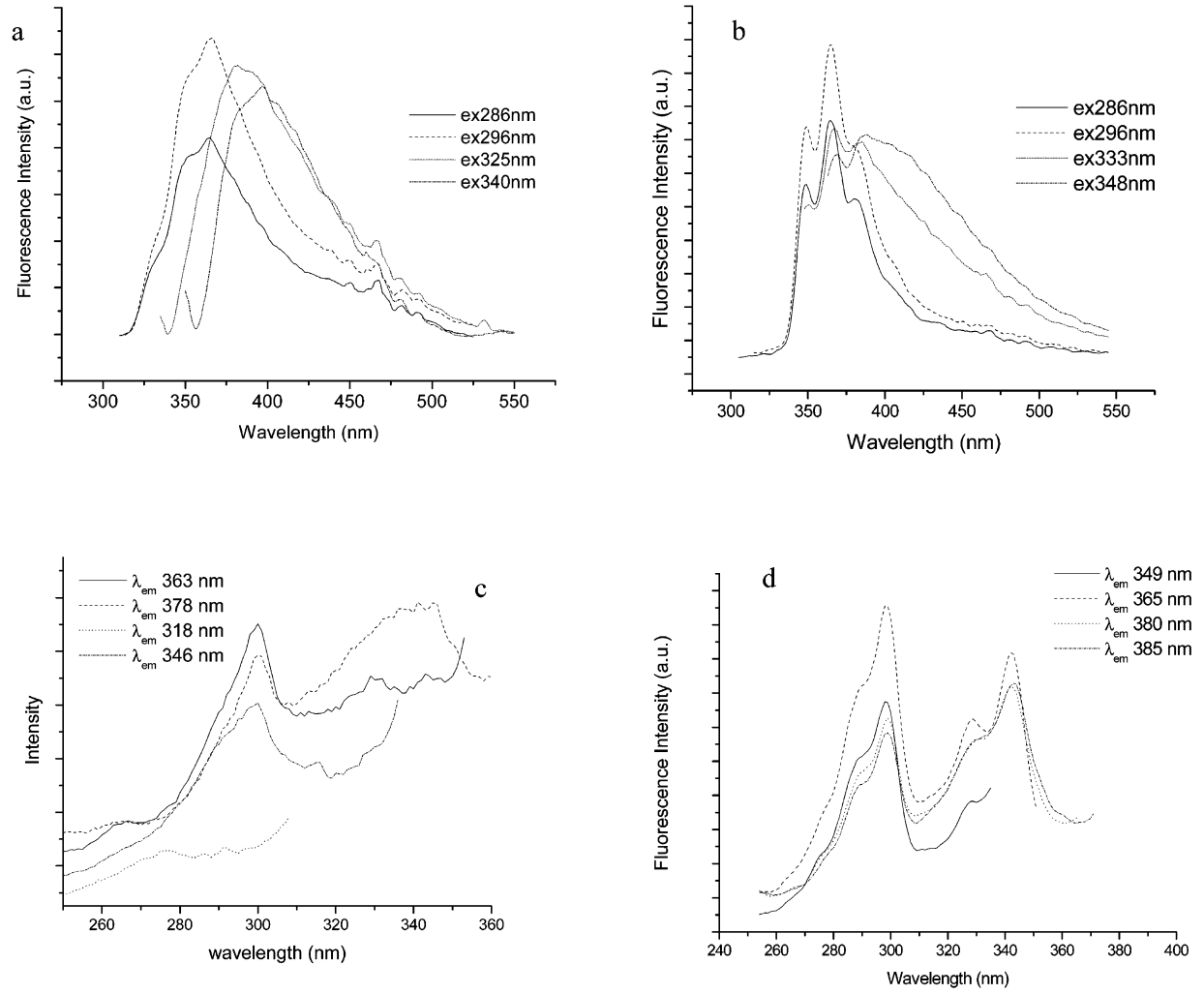

Figure 6. Emission (a,b) and excitation (c,d) spectra of 10^{-4} M 2,6-NDCA in 1-butanol containing 4 wt % PAA shortly after gelation by CO_2 bubbling (a,c) and 38 h thereafter (b,d). The samples were deoxygenated initially by N_2 bubbling for 25 min at room temperature.

Because the sample was not moved and the lamp remained lit throughout the entire period of spectral collection, the relative intensities are also an indicator of the changes occurring in the gel. The 35% increase in fluorescence intensity at 366 nm within the first 20 h may be a consequence of the increased acidity experienced by the 2,6-NDCA molecules after CO_2 is added and the time required for the system to equilibrate as a larger fraction of the 2,6-NDCA becomes protonated and is released from its electrostatic interactions with ammonium groups of PAA. This interpretation is supported by the large decreases in the fluorescence intensity at 366 nm of a solution of 2,6-NDCA in 1-butanol as triethylamine is added (Figure 8).

The time constant κ, derived from the fit to the data in Figure 9 to an exponential function, is 265 min^{-1}. At this time, it is

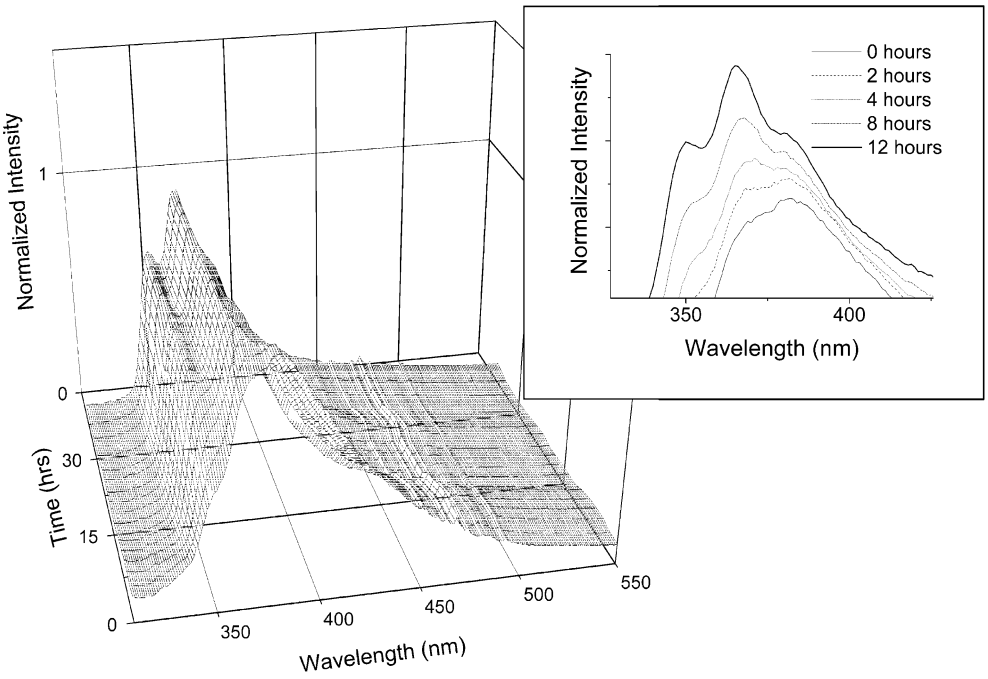

Figure 7. Temporal changes of the fluorescence spectra (λ_{ex} 296 nm) of 10^{-4} M 2,6-NDCA in a 4 wt % PAA·CO_2 in 1-butanol gel. The samples were deoxygenated by N_2 bubbling for 25 min at room temperature before bubbling with CO_2.

unclear whether relaxation of the gellant matrix and migration of the 2,6-NDCA molecules from their initial locations after the addition of CO_2 are concurrent in time or whether there is hysteresis. Although relaxation of the gel matrix may be faster than the equilibration of the 2,6-NDCA molecules among their residence sites, it is reasonable to assume that κ depends on the fraction of PAA amino groups involved in ammonium carbamate formation (i.e., the equivalents of CO_2 fixed per equivalent of amino groups in PAA); we have not explored this relationship.

We proceed assuming that the PAA·CO_2 gel is equilibrated when the ratio of the intensities of the emissions at 366 and 350 nm (I_r) no longer changes with time (Figure 9) and that the rates of changes in I_r and the relaxation of the gel network are the same. Then, I_r at any time $= t$ can be considered proportional to the amount of 2,6-NDCA in the 1-butanol part of the gel, and dI_r/dt is the rate of relaxation of the probes and their PAA·CO_2 matrix (eq 3).

$$\text{PAA} + \text{CO}_2 \rightarrow [\text{PAA}\cdot\text{CO}_2]^*_{\text{gel}} \rightarrow [\text{PAA}\cdot\text{CO}_2]^{\text{eq}}_{\text{gel}} \quad (3)$$

$[PAA·CO_2]^*_{gel}$ represents the state of the 2,6-NDCA molecules in the gel prior to reaching equilibrium, and $[PAA·CO_2]^{eq}_{gel}$ is their state in the equilibrated gel. Thus, we can relate $\alpha(t)$, the fraction of gel equilibrated at time $= t$ (eq 4), to I_r according to eq 5; note that I_r is ~1.75 at time $\rightarrow$ 0 and approaches 1.35 at time $\rightarrow \infty$ in Figure 9.

$$\alpha(t) = [\text{PAA}\cdot\text{CO}_2]^{\text{eq}}/\{[\text{PAA}\cdot\text{CO}_2]^{\text{eq}} + [\text{PAA}\cdot\text{CO}_2]^*\} \quad (4)$$

$$I_r(t) = I_r(0) - [I_r(0) - I_r(\infty)]\alpha = 1.75 - 0.4\alpha \quad (5)$$

According to our assumption about the equality of the relaxation rates of the matrix and the changes in the fluorescence spectra from 2,6-NDCA, the data in Figure 9 describe as well the temporal changes to α. Therefore, eq 5 can be expressed as eq 6 or, in terms of the fractional relaxation of the gel network, as eq 7.

$$I_r = 1.75 + 0.4\exp(-\kappa t) \quad (6)$$

$$\alpha = 1 - \exp(-\kappa t) \quad (7)$$

Fluorescence decay histograms of 2,6-NDCA within the PAA·CO_2 gels have been obtained by the time-correlated single photon counting method (Figure 10). The data are well fitted to triple exponential functions (reduced $\chi^2 < 1.2$),[25] suggesting either different locations or different emitting forms of the 2,6-NDCA molecules or a combination of these two factors. The reduced χ^2 were always >3 when single or double exponential functions were employed. The change of τ_1 with time in Figure 10 indicates that the natures of the 2,6-NDCA molecules are altered in ways that are reminiscent of the observations in Figure 9, but the asymptote value of τ_1 is reached after a much longer period, ~30 h (versus ~16 h for I_r). The relative amounts of each decay constant are indirectly proportional to the fraction, f_i, of the 2,6-NDCA molecules emitting in each environment. The data in Table 2 indicate that molecules in environments associated with τ_1 move to environments responsible for τ_2 and τ_3. As the gel ages, the average relaxation times $\langle\tau\rangle$ indicate that the average environment and state of the 2,6-NDCA molecules become more like those in PAA/1-butanol (presumably with a double negative charge) than those in 1-butanol alone (presumably uncharged): (1) the first and second pK_a's of 2,6-NDCA in water are 3.8 and 4.7,[26] and 1-butanol does not support autoprotolysis; (2) at a concentration of 0.43 M Et_3N (a base concentration and strength similar to those provided by 4 wt % PAA), the titration curve in Figure 8b and the blue-shifted

(25) (a) Ganguly, T.; Farmer, L.; Li, W.; Bergeron, J. Y.; Gravel, D.; Durocher, G. *Macromolecules* **1993**, *26*, 2315. (b) Nishimura, Y.; Yamazaki, I.; Ohta, N. *J. Luminescence* **2000**, *87*, 791.

(26) File n° NA/503; *National Industrial Chemicals Notification and Assessment Scheme*, Parramatta, Australia, April 1997.

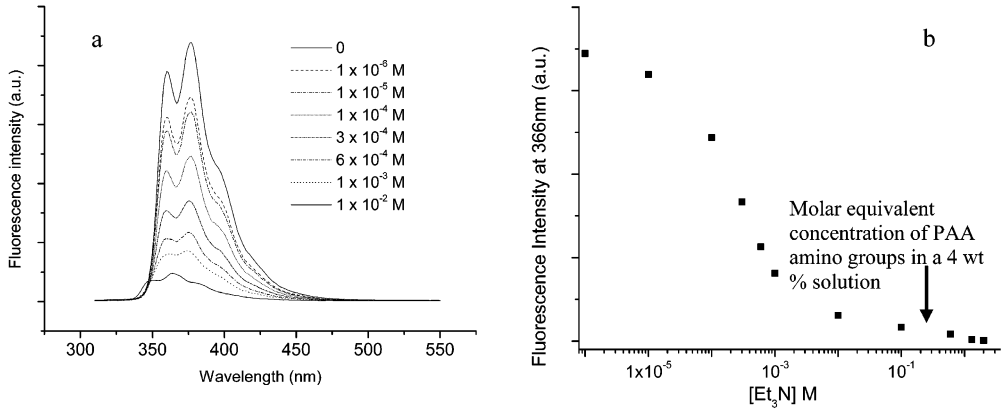

Figure 8. Dependence of fluorescence spectral shapes (a) and intensities at 366 nm (b) of 10^{-4} M 2,6-NDCA in 1-butanol as a function of the concentration of added triethylamine (Et_3N); λ_{ex} 296 nm. The samples were deoxygenated by N_2 bubbling for 25 min at room temperature.

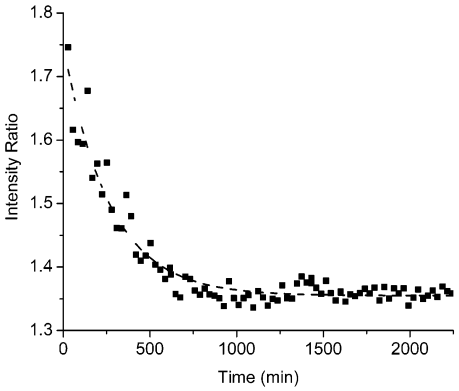

Figure 9. Ratio of the fluorescence intensities at 366 and 350 nm, I_r, from 10^{-4} M 2,6-NDCA in a 4 wt % PAA/1-butanol gel as a function of time after bubbling with CO_2 (λ_{ex} 296 nm). The best fit of the data to a monoexponential function (normal $\chi^2 = 4.6 \times 10^{-5}$) is shown as a dashed curve. The samples were deoxygenated by N_2 bubbling for 25 min at room temperature before bubbling with CO_2.

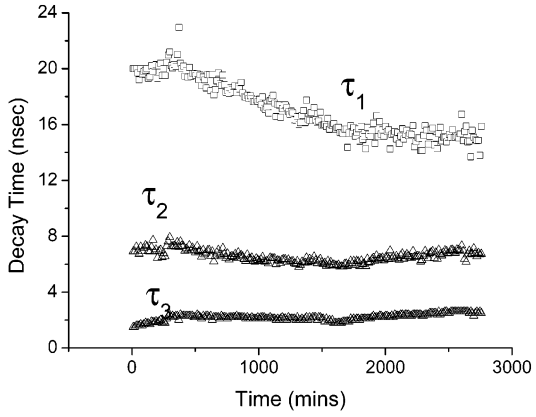

Figure 10. Decay constants (τ_i) of excited singlet states of 10^{-4} M 2,6-NDCA in 4 wt % PAA in 1-butanol as a function of time after bubbling with CO_2 to make the gel state; see text for details. λ_{ex} 296 nm; λ_{em} 365 nm.

emission spectrum in Figure 8a indicate that almost all of the 2,6-NDCA is doubly ionized.

Considering these observations and the data in Table 2, we can discuss the changes in the location and in the form of the 2,6-NDCA molecules in somewhat greater detail. In 1-butanol, the τ_2 value, 8.1 ns, can be attributed to the 2,6-NDCA molecules that are not ionized; the degree of deprotonation in this medium is very low. The longer decay constant τ_1 obtained

Table 2. Decay Constants (τ_i), Average Decay Constants ($\langle\tau\rangle$), and Fractional Contributions (f_i) to the Total Decay of Excited Singlet States of 10^{-4} M 2,6-NDCA in Deoxygenated 1-Butanol with and without 4 wt % PAA and before and after the Addition of CO_2[a]

medium	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	f_1	f_2	f_3	$\langle\tau\rangle$
1-butanol		8.1					
PAA in 1-butanol	18.7						
PAA·CO_2/1-butanol gel ($t = 0$)	20	6.9	1.5	0.6	0.35	0.05	14.5
PAA·CO_2/1-butanol gel ($t = 46$ h)	15.2	6.7	2.6	0.15	0.6	0.25	7.3

[a] λ_{ex} 296 nm; λ_{em} 365 nm.

upon addition of 4 wt % PAA, 18.7 ns, must be from the dicarboxylate form, and nearly all of the probes are associated with the polymer at ammoniated sites. Gelation increases the local dielectric near the PAA chains and the density of $-NH_3^+$ groups along the polymer backbones. Thus, the decrease of $\langle\tau\rangle$ with increasing time[27] in the gelled sample is associated with the net reprotonation of the carboxylate groups as the system equilibrates. The third component, τ_3, is found neither in 1-butanol nor in PAA solutions. Although the attribution of the τ_3 component is unclear, its low value and increasing importance as time passes indicate that it may be from either aggregated, singly ionized 2,6-NDCA molecules or doubly ionized 2,6-NDCA molecules that are trapped (perhaps physically) within the region of the ammonium carbamate groups.[26]

The fluorescence of 2,6-NDCA has also been examined as a function of temperature upon both heating and cooling between 25 and 100 °C. Prior to data collection, the samples were equilibrated at each temperature (±1 °C) for at least 30 min, the time found empirically necessary to reach a constant emission intensity. As expected from enhancement of nonradiative decay modes, a marked decrease in fluorescence intensity at 366 nm (λ_{ex} 296 nm) occurred as temperature was increased when the host matrix was 1-butanol, 1-butanol containing 4 wt % PAA, and a 4 wt % PAA·CO_2/1-butanol gel. However, the reversibility of the intensity changes on cooling the heated samples depended on the host and the highest temperature to which the sample was heated.

The fluorescence intensities at 366 nm from solutions of 10^{-4} M 2,6-NDCA in 1-butanol in the presence and absence of 4 wt

(27) Pradhan, A.; Pal, P.; Durocher, G.; Villeneuve, L.; Balassy, A.; Babai, F.; Gaboury, L.; Blanchard, L. *J. Photochem. Photobiol., B* **1995**, *31*, 101.

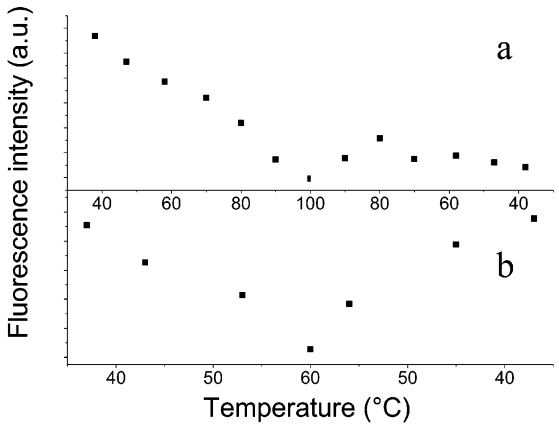

Figure 11. Temperature dependence of fluorescence intensity at 366 nm (λ_{ex} 296 nm) from 10^{-4} M 2,6-NDCA in two 4 wt % PAA·CO_2 in 1-butanol gels: (a) heating to 100 °C and cooling; (b) heating to 60 °C and cooling. The temperature changes were effected in time from left to right. The samples were deoxygenated by N_2 bubbling for 25 min at room temperature prior to bubbling with CO_2.

% PAA (without CO_2) return to their initial room-temperature values after being heated to 100 °C. Even in the presence of PAA, heating does not cause irreversible structural changes to the probe molecules or alter their emissive properties. Although heating a gelled sample to 60 °C and cooling to room temperature restores the original intensity (Figure 11b), heating to ca. 100 °C and cooling to room temperature does not (Figure 11a). In the latter case, the environments of the lumophores (or some of the lumophores, themselves!) have been altered irreversibly. As temperature is increased to ~100 °C, carbamate units of the gel undergo thermal decomposition. Manifestations of the loss of CO_2 include the lack of a T_g^{dt} during the second heating (as mentioned previoulsy) and visually detectable phase separation; in the sample heated to ~100 °C, ~30% of the volume in the upper part was liquid and the remainder appeared to be gel. As indicated by the data in Figure 11b, thermal decomposition occurs above 60 °C; from other experiments, the highest temperature to which the gels can be heated without irreversible changes is ~65°C.

Conclusions

Polyallylamine (PAA) itself is not a gellant of any of the liquids examined, but it is converted to an excellent one for alcohols and 1-methyl-2-pyrrolidone when CO_2 is bubbled through its solutions. Many other amine-containing polymers, including proteins, should be amenable to similar transformations in the presence of CO_2 (effecting potentially reversible "cross-linking" and three-dimensional network formation without the addition of strong acids or other reactive species). The chemical transformation from neutral amine functionalities to charged ammonium and carbamates groups increases the attractive interactions between polymer chains, since electrostatic attractions between the charged centers of the CO_2 adduct, PAA·CO_2, are stronger than the hydrogen bonding ones available to PAA itself. The added attraction force is sufficient to "cross-link" the polymer chains to an extent where their network is capable of immobilizing at least a 50-fold by weight excess of liquid; PAA, a "latent" gellant,[7,8] is transformed into PAA·CO_2, an excellent gellant. Unlike with low molecular-mass mono- and dialkylamine latent gelators (i.e., that also require addition of CO_2 to effect gelation[7]), the gelation process induced by bubbling CO_2 into PAA solutions is *thermally irreversible*. There is an interesting correlation between T_g^{dt}, the temperature at which CO_2 is liberated from PAA·CO_2, and the length of the chains of the alcohol liquids. The increase in temperature with increasing C_n is a clear indication that the electrostatic interactions between the charged centers are more localized and stronger in the media of lower polarity; dissociation is attenuated. Consistent with the more heterogeneous nature of the PAA·CO_2 gellant networks than the networks from the low molecular-mass amine/CO_2 adducts, the ranges of the T_g^{dt} values from the polymer are much larger than those from the low molecular-mass amines.

This heterogeneity is demonstrated spectroscopically by steady state and dynamic fluorescence from 2,6-NDCA. It allows us to follow the "annealing" of the polymeric gels after their initial formation over long periods and indicates that the probe molecules exist in three different environments within the gel networks. In addition, the fluorescence spectra indicate the nature of the alterations of the microenvironment surrounding the 2,6-NDCA molecules that occur when CO_2 is bubbled into the PAA-containing solutions. They include both local changes induced by the presence of charged centers on the polymer chains and movement of the probe molecules into regions rich in the liquid component. We demonstrate that the kinetics of these changes can be followed by monitoring the fluorescence intensity and suggest a model to link the fluorescence to the structural equilibration of the gellant network.

The temperature dependence on the fluorescence of the 2,6-NDCA has also been investigated. It indicates at the *microscopic* level what has been ascertained from DSC, TGA, and T_g^{dt} (by the falling drop method) measurements at the *macroscopic* level—that heating the gels above ~65 °C results in an irreversible loss of the gel structure but heating to lower temperatures does not alter the basic gel properties.

These gels may have several practical applications. During the last 10 years, one of the research goals in the field of art conservation and restoration has been to develop gels that can be applied as cleaning media on the surfaces of wood and canvas paintings.[1,3,28] In that regard, 1-methyl-2-pyrrolidone is one of the most commonly used cleaning agents in art conservation. The modes by which it is applied and, more importantly, how it is removed from a painted surface are factors that determine its ultimate utility. Applying it in a gel formulation like that afforded by PAA·CO_2 should limit the degree to which it penetrates surfaces and facilitate its removal after the cleaning stage. Any residual PAA·CO_2 polymer should be easily removed by treating the surface finally with a weak solution of aqueous acetic acid. Therefore, a future direction of this work is to test the gels described here and others based on similar concepts that can immobilize liquids such as 1-methyl-2-pyrrolidone, DMSO, and dichloromethane as cleaning agents in the cultural heritage conservation field. We hope to develop a repertoire of polymer-based gels that are very effective as cleaning agents

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for canvas and wood paintings but are also easily removed from the surfaces after application. A recent test of the cleaning ability of the PAA·CO_2/1-methy-2-pyrrolidone and PAA·CO_2/1-pentanol gels on a XIV century painting from Siena, Italy shows very promising results.

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Supporting Information Available: Detailed descriptions of sample preparations, experimental procedures, equipment employed, and analytical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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