3404 *Macromolecules* **2000,** *33,* 3404−3408

Viscoelastic Properties of Novel Silicon Carbodiimide Gels

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Received October 21, 1999; Revised Manuscript Received February 14, 2000

ABSTRACT: A novel non-oxide sol−gel system based on the reaction of bis(trimethylsilyl)carbodiimide with methyltrichlorosilanes has been examined quantitatively with regard to its viscoelastic properties. The chemistry and phenomenology of this process are completely analogous to the well-known oxide sol−gel process. The changes of the elastic modulus G' and the viscous modulus G'' have been measured with low strain amplitude and constant frequency versus time. At the crossover point, i.e., $G' = G''$, the gel point is reached. The gelation time is independent of the oscillatory frequency ω. The dynamic moduli G' and G'' have also been measured versus strain amplitude and shear stress amplitude. A relaxation exponent of $n = 0.65$, strength $S = 0.25$, and $G'_{(\text{end of reaction})} = 10^5$ Pa·s have been determined.

I. Introduction

The sol−gel process is well-known for the production of oxide ceramics and glasses.[1,2] Several authors have tried to extend this field of research in order to establish non-hydrolytic[3] and non-oxide[4] sol−gel routes. However, compared to the numerous studies about oxide sol−gel processes based on hydrolysis−condensation reactions of alkoxides and other metal compounds, only a few analogous systems have been found to prepare non-oxides. For example, Gabriel and Riedel[5,6] reported an anhydrous sol−gel process for the synthesis of oxygen-free polymeric gels. This non-oxide sol−gel chemistry with silicon carbodiimides opens a new area for the Si−C−N materials with a broad range of possible technological applications such as coatings, membranes, fibers, or bulk materials.[7]

The poly(silylcarbodiimides) are used as single-source precursors for the production of ceramic materials. The thermally induced decomposition produces amorphous or polycrystalline silicon carbonitrides, which are interesting materials because of their high hardness, strength, toughness, and high-temperature capability. The synthesis, physicochemical characterization, and thermal stability of silicon carbodiimides were recently investigated.[8] For several applications, such as fiber-spinning, dip-, spin-, and spray-coating, or infiltration methods, the rheology of the system is important. In this paper we report some of the first studies of the rheological properties of carbodiimide gels at constant temperature.

A gel is defined as a two- or multicomponent system of semisolid nature, rich in liquid and consisting of continuous solid and fluid phases of colloidal dimensions.[1,9] It contains a stable cross-linked or entangled network structure infiltrated with a liquid. The network structure is formed by chemical or physical gelation processes. Chemical gelation produces branched structures based on covalent bonds between the molecules and network subunits, whereas the physical gelation is determined by forces (van der Waals, electrostatic, hydrogen bonding) that generate reversible intermolecular associations;[10−12] regarding the definition of the term "gel" see also ref 13.

The gel point is usually defined as the time or the degree of reaction at which the solution no longer remains liquid. Originally qualitative rheological considerations were used to define the gel point. The gel point often was determined visually when no flow of the system was observed upon tilting the container. In the investigations on poly(dimethylsiloxane) by Winter and Chambon[23] in 1986 and on silica sol−gel materials by Sacks and Sheu[14] in 1987, they observed a rapid increase of storage modulus and loss modulus near the gel point during dynamic flow measurements. Sacks and Sheu interpretated this increase as condensation growth and agglomeration of polymeric species. Also, a rapid decrease in loss tangent was measured, which has been interpretated as an increase in the elastic character of the material as a three-dimensional network structure develops. Winter and Chambon associated the gel point with the point where both oscillatory moduli have the same variation with the frequency, and Sacks and Sheu defined the gel point as a specific value of the loss tangent, determined under well-defined measuring conditions.

The aim of this work is to characterize the viscoelastic properties of the novel carbodiimide gels and to determine the gel point quantitatively using the stress-controlled oscillatory technique.

II. Formulation of the Gels

1. Principles. The non-oxide sol−gel process is similar to oxide processes in many respects. Figure 1 shows a simplified scheme of the main chemical characteristics of the non-oxide compared to an oxide route. The starting material in both cases is a chlorosilane which reacts, first, to replace the chlorine atoms. As can be seen from the scheme, the bis(trimethylsilyl)carbodiimide molecule behaves in a similar way as water. This can be explained by the fact that the carbodiimide group is a typical pseudo-chalcogen[15] replacing the oxygen atom, while the Me_3Si units behave in a similar way to the hydrogen atoms. It has to be stressed that this analogy is based not only on chemical reaction equations but also on the phenomenology of the sol−

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10.1021/ma991756p CCC: $19.00

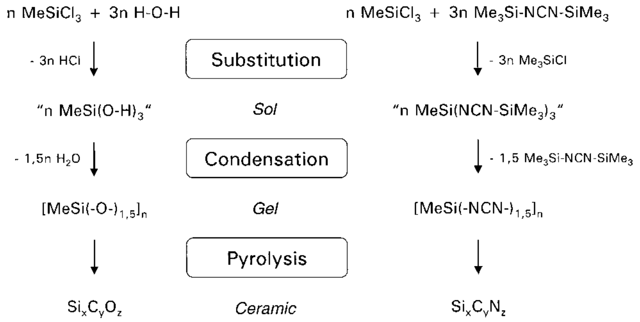

Figure 1. Comparison of the classic oxide process (left) with the novel non-oxide sol−gel process (right).

gel transition as well as the physical (spectroscopic) properties.[8]

The phenomenology of the carbodiimide system shows a continuous transition from a liquid mixture of starting materials to a solid gel, followed by an aging period which is characterized by shrinkage and syneresis. Concerning the spectroscopic properties, it has been found that the chemical shifts in NMR spectra and absorption energies in XANES spectra are very similar to the corresponding oxygen compounds. During the sol−gel process, substitution and condensation are occurring at the same time. The more substitution and condensation reactions take place, the higher the degree of cross-linking of the polymeric network. To produce ceramic materials, the dried gels have to be pyrolyzed.[4−6] In both systems, the oxide[1] as well as the non-oxide[16] the methyl groups can be replaced by many different substituents, e.g., H, Cl, allyl, or aryl, which lead to gels and ceramics with a wide variety of compositions.

2. Synthesis. The reaction of methyltrichlorosilane **1** with bis(trimethylsilyl)carbodiimide **2** and a catalytic amount of pyridine produces a transparent gel that consists of a polymeric network **3** and the liquid chlorosilane **4** (a). The reaction is irreversible, and the gel cannot be liquefied by increasing the temperature,[5,6] which is in contrast to gels otained from dichloromethylsilane.[17]

$$\underset{\mathbf{1}}{n\ \mathrm{MeSiCl_3}} + \underset{\mathbf{2}}{1.5n\ \mathrm{Me_3Si{-}NCN{-}SiMe_3}} \xrightarrow{\text{pyridine}} \underbrace{\underset{\mathbf{3}}{[\mathrm{MeSi(NCN)_{1.5}}]_n} + \underset{\mathbf{4}}{3n\ \mathrm{Me_3SiCl}}}_{\text{gel}} \qquad \text{(a)}$$

The reaction time to reach the gel point can be altered by varying the amount of pyridine and by changing the reaction temperature, as shown in Figure 2. A gel can also be obtained at room temperature and without pyridine after several weeks. By varying the substituents of the chlorosilane, i.e., replacing the methyl group in **1**, the properties can be adjusted, for example, the shrinking behavior. The gelation time in Figure 2 was estimated simply by the visual observation of the fluidity which is not very precise. However, it was possible to derive an apparent activation energy value of approximately 90 kJ/mol from an Arrhenius plot.[18]

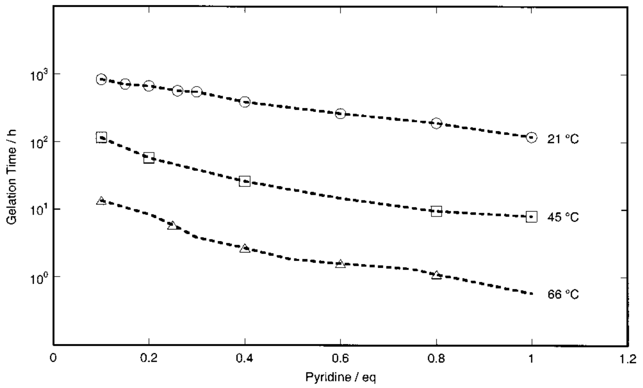

Figure 2. Influence of catalyst amount and reaction temperature on the gelation time, shown at different temperatures.

3. **Experimental Section.** The preparations of the gels were carried out in dried glass vessels under an inert gas atmosphere of dry argon. The measurements were made on a dynamic stress rheometer DSR 200 (Rheometric Scientific) with Searle double cylinders geometry. The outer cylinder was heated and maintained at 45 °C during the whole measurement. The liquid samples (ca. 15 mL) were poured into the cup under inert gas. Once in the inner cylinder the sol was protected from air contact by a thin layer of low viscous silicone oil, which does not react with the carbodiimide sols. A slight argon flow was continuously applied during the measurements at the surface between the oil and air. After the measurements, a gel body was observed in the gap between the cylinders.

Preparation: 10 mL (85.3 mmol) of methyltrichlorosilane **1**, 29.1 mL (127.95 mmol) of bis(trimethylsilyl)carbodiimide **2**, and 3.45 mL (42.59 mmol = 0.5 equiv) of pyridine were mixed in a 50 mL Schlenk flask. The solution was stored at 45 °C for 8 h before beginning the rheological measurements. **1** is a commercial product which was purified by distillation. **2** was synthesized from a mixture of cyanoguanidine (42 g), hexamethyldisilazane (177 g), and ammonium sulfate (0.2 g) by heating to reflux for 8 h and distillation over a Vigreux column at 164 °C.[19] The samples for all measurements were synthesized and treated the same way.

III. Quantitative Examination of Viscoelastic Properties during Gelation

Gels are viscoelastic materials which exhibit both solid and fluid rheological behavior, as a function of the evolution and strength of the internal network. Their fluid behavior is complex, with a transition between the two rheological states being a well-defined "yield state".

In a chemical sense, the dynamics of the gelation process are given by the extent of reaction $p(t)$, an intrinsic parameter of the reaction which defines the time evolution of the network formation. It is expected that $p(t)$ is a solution of a differential equation that models the reaction.[20] The reaction starts with $p = 0$, when the system is a liquid, and reaches the end at $p = 1$ (the system has a solid rheological behavior). At the critical value $p(t_c) = p_c$, $0 < p_c < 1$, the time derivative of the viscosity function $\eta(t)$ tends asymptotically to infinity, and the rheological behavior of the gels become dominated by elasticity, through the presence of the elastic modulus $G_e(t)$, $G_e(t) \approx 0$ for $t < t_c$. This critical level of reaction defines the yield state and implicit the transition from fluid to solid behavior. In our study, the yield state is very difficult to investigate

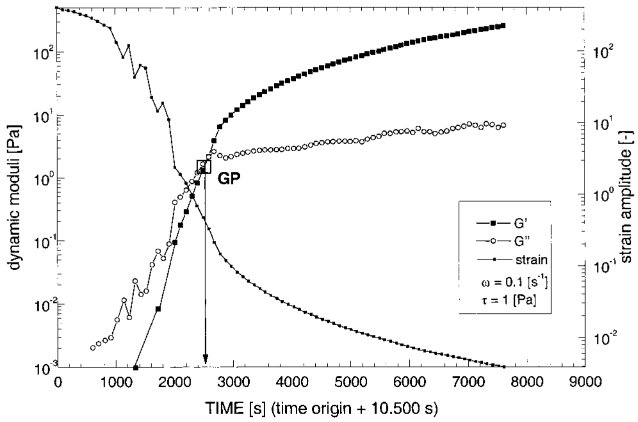

Figure 3. Dynamic moduli G' and G'' for the poly(methylsilsesquicarbodiimide) system at 45 °C (controlled stress oscillatory experiment: frequency $\omega = 0.1\ \text{s}^{-1}$, shear stress amplitude $\tau = 1$ Pa, double cylinder Searle geometry). The gel point GP corresponds at the absolute reaction time $t_c = 10500 + 2500 = 13000$ s.

in detail due to the fast reaction rates in carbodiimide gels.

The gel point "GP" is located in the vicinity of the yield state at the time $t = t_c + \Delta t$; it is defined in this paper as the intersection between the elastic (storage) modulus G' and the viscous (loss) modulus G'', measured in oscillatory viscometric motions with low strain amplitude, constant applied shear stress amplitude, and constant frequency ω. The gelation process is sometimes described by the time evolution of the loss tangent—$\tan\delta = G''/G'$, where $\tan\delta \to \infty$ at the onset of the process (fluid behavior) and $\tan\delta \to 0$ when the reaction is complete; the loss tangent takes the value 1 at the intersection where $G' = G''$.[14,21,22]

In Figure 3 are shown the time evolution of both dynamic moduli for the samples under investigation; the gel point is marked on the figure by the intersection point. Some authors, for example Winter,[12] have associated directly the concept of the gel point with the critical level of reaction $p = p_c$. In this case GP is not necessarily equal to the intersection.

A possible interpretation of the linear viscoelastic model of the gel[10,22,23] states that at $p = p_c$ the frequency dependence of the dynamic moduli is defined by the same power law, G' and G'' being proportional to ω^n. Accordingly with this model, the gel is described at the yield state by a relaxation modulus

$$G(t) = St^{-n} \tag{1}$$

where $0 < n < 1$ is the relaxation exponent and S is the strength of the gel.

The two moduli are related at $p = p_c$ by

$$G'(\omega) = G''/\tan\delta = S\Gamma(1 - n)\omega^n \cos\delta \tag{2}$$

with $\delta = n\pi/2$, where $\Gamma(n)$ is the gamma function.

Therefore, the yield state coincides with the cross point, i.e., GP, only if $n = 0.5$.

In the following section we investigated (i) the influence of the oscillatory frequency on the gelation process and GP and (ii) the material properties of the sample at the end of the reaction of the poly(methylsilsesquicarbodiimide) system.

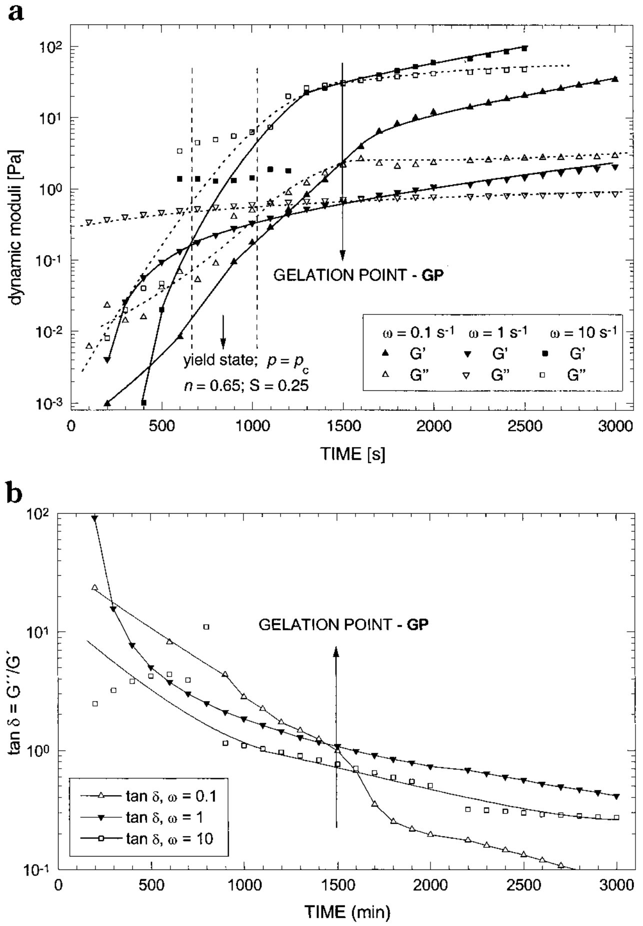

Figure 4. (a) The gelation process (G' and G'') as a function of frequency. The yield state ($p = p_c$) is installed previously to the gel point GP, defined as the crossover point ($G' = G''$). (b) The loss tangent as a function of time and frequency.

IV. Rheological Properties of Poly(methylsilsesquicarbodiimide) Gels

The major problem of the rheological investigation of chemical sol–gel systems is their double time dependencies. As has been mentioned in the Introduction, the dynamics of the network formation is a function of the extent of reaction $p(t)$. On the other hand, the gels are viscoelastic materials. Therefore, at a fixed time of reaction $p(t_0)$, the rheological properties are time-dependent (time variable ξ) due to the presence of elasticity, $\eta(p(t),\xi)$, $G_e(p(t),\xi)$. The superposition of these two effects makes the correlation between the experimental data and the formulation of a complete constitutive relation for the gels very difficult.

One way to study the viscoelastic properties of the gels independent of the transition of the network structure is "to freeze" the sample at different reaction times, prior to the onset of the rheological test. This principle was used in order to study UV-sensitive thiol–ene polymer gels.[23–25] Unfortunately, this procedure is not applicable to the sample under investigation here. As a consequence, we follow the rheological properties of the sample with continuous measurement of the storage and loss modulus in oscillatory experiments (Figure 3). The gelation process is determined by the formation of the network structure. And the response of the networks is better tested in stress-controlled experiments, since the shear stress amplitude is imposed and the amplitude of the deformation is measured

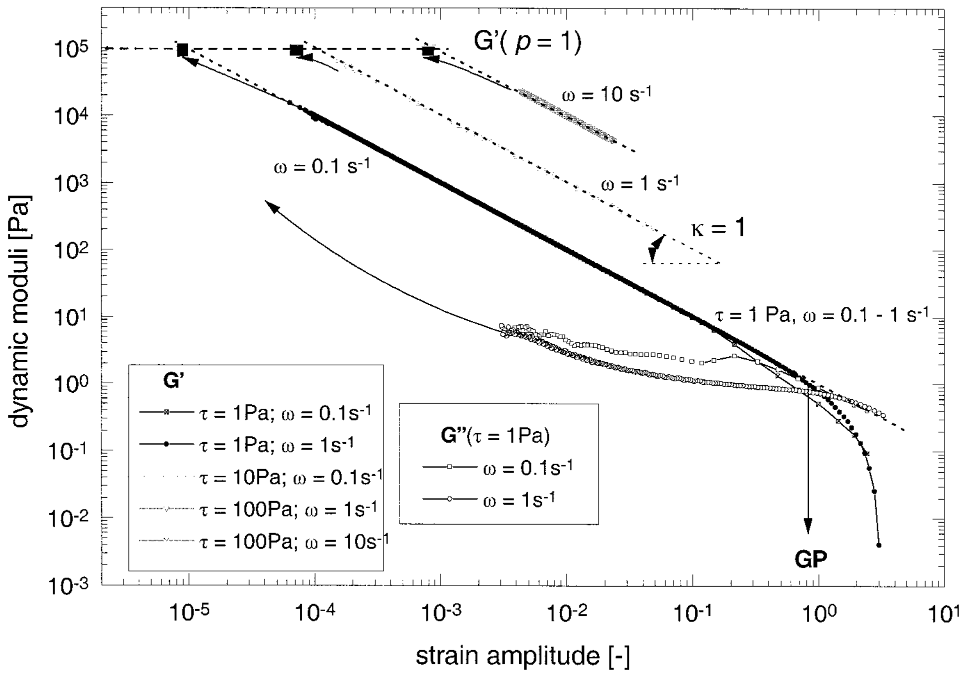

Figure 5. Dependence of the dynamic moduli on strain amplitude as a function of frequency and shear stress amplitude (the loss modulus is represented only for $\tau = 1$ Pa). The direction of the moduli evolution is represented by arrows.

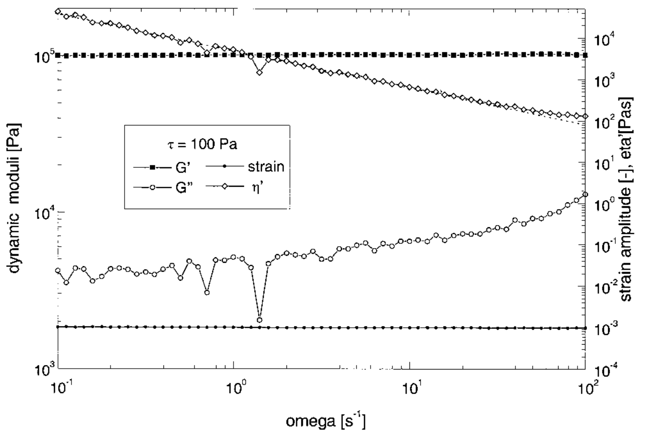

Figure 6. Dynamic moduli and viscosity η' as the function of oscillatory frequency at constant shear stress amplitude; G' is constant, and G'' shows a nearly linear increase with frequency. The shear thinning character (decrease of viscosity with ω) is also relevant.

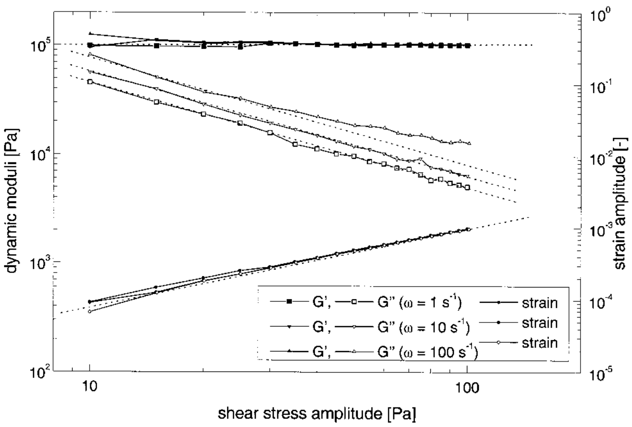

Figure 7. Dynamic moduli and strain amplitude as a function of shear stress amplitude at constant frequencies. At the end of reaction ($p = 1$) the stress τ varies linearly with the strain γ (accordingly with Hooke's law), and the loss modulus decreases linearly with the stress (the exception is at high values of the stress and frequency).

(therefore, the onset of the motion is properly investigated). Almost all the data presented in this paper have been repeated twice. Taking into account the very high air sensitivity of the samples, the repeatability of the data was acceptable. The differences between two identical tests result in the spreading of the G'' data, but not in its order of magnitude.

Figure 4a,b shows the time evolution of the dynamic moduli and the loss tangent in the vicinity of the gel point, at constant frequencies of the applied oscillatory shear stress (the data measured at $\omega = 10$ s^{-1} disclose the presence of material instabilities). The starting point $t = 0$ of time in Figure 4 has been chosen for all experiments as the reaction time when the elastic modulus G' reaches the measurable value of 10^{-3} Pa. Related to this relative time axis, the time location of the gelation point GP is independent of the frequency.

The absolute reaction time is different for each of the measurements (the starting point of the reaction time coincides with the moment when the sample was put in the gap of the rheometer); however, the differences between the absolute times corresponding to the measured gel points are spread around the medium reaction time of 267 min, within the interval of ±10% (a value which might be attributed to the experimental error).

According to our definition of the yield state and the generally accepted model for describing the frequency dependence of the gel structure at $p = p_c$ (see relations 1 and 2), material constants $n = 0.65$ and $S = 0.25$ have been obtained for the carbodiimide gel. Therefore, the yield state occurs prior to the GP with a time lag of $\Delta t \approx 600$ s. Its exact position is spread over a period of 300 s for the tested frequencies (Figure 4a).

Figure 5 shows the dependencies of the dynamic moduli on the strain amplitude γ at constant applied stress amplitude τ and frequency ω. The results are consistent with the previous ones; the formation of the network structure is independent of frequency. The slope of the storage modulus, beyond the gel point, equals 1 ($\kappa = 1$) in the double-logarithmic plot for all tested frequencies, $\omega \leq 10\ \mathrm{s}^{-1}$ (G' is increasing linearly with decreasing γ). It is also remarkable that there is little sensitivity of the evolution of the loss modulus to frequency at constant small stress amplitude.

As the reaction reaches the end $p \rightarrow 1$, the dependence $G'(\gamma)$ has a lower value of the slope κ. Finally, the elastic modulus becomes constant $G' \cong 10^5$ Pa, independent of ω and γ (Figures 6 and 7).

V. Conclusions

The present work reports the first quantitative determination of viscoelastic properties of carbodiimide gels. The results show that the gelation behavior of carbodiimide gels and the time of the gel point are independent of the oscillatory frequency. The gel point is identified with the intersection point of the elastic modulus G' and the viscous modulus G'', i.e., for $G' = G''$. Some materials properties of poly(methylsilsesquicarbodiimide) have been determined at the yield state ($p = p_c$) according to the Winter and Chambon interpretation:[23] (i) relaxation exponent: $n = 0.65$ and (ii) the strength $S = 0.25$.

At the end of the reaction, G' reached a value of 10^5 Pa·s. The yield state defines rheologically the phase transition (fluid−solid) of the gels.

Our future work will be focused on detailed time-resolved spectroscopic studies during the sol−gel transition in order to correlate the results with the rheology of the gels described in this paper.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. For offering a research fellowship to Prof. Corneliu Balan acknowledges the financial support of DAAD, Bonn. We also thank Rheometric Scientific, Aschaffenburg, for lending measurement devices.

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