Rheokinetics of Thermal-Induced Gelation of Waterborne Polyurethane Dispersions

Samy A. Madbouly[†] **and Joshua U. Otaigbe***

School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received May 30, 2005; Revised Manuscript Received August 8, 2005

ABSTRACT: Thermal-induced gelation for waterborne polyurethane dispersion has been studied rheologically under isothermal condition over a wide range of frequencies at different constant temperatures (55, 60, 65, and 70 °C). The elastic storage modulus, G', at a constant temperature in the vicinity of the gel point increases abruptly, and the magnitude of the elevation in G' was found to be temperature dependent. Similar behavior has been observed for both the viscous loss modulus, G'', and the complex dynamic viscosity, η^*. The gel point, t_{gel}, was determined from the point of intersection in tan δ vs gelation time for different constant shear frequencies, where tan δ is frequency independent and all curves cross over, indicating the validity of the Winter−Chambon criterion. The value of t_{gel} obtained from the coincidence of G' and G'' was in excellent agreement with that obtained from tan δ vs t. At the gel point, G' and G'' showed a power law with shear frequency, i.e., $G' \sim G'' \sim \omega^n$ with critical exponents n' and n'' for G' and G'', respectively. The values of n' and n'' are identical at t_{gel} (n' and $n'' \sim 0.58$), and both decreased exponentially with gelation time at 70 °C. The exponent values n' and n'' are in good agreement with that predicted from the percolation theory (i.e., $n = 2/3$). In addition, the temperature dependence of n' and n'' was investigated in the vicinity of the gel point. Both n' and n'' decreased with temperature and intersected at the gel temperature, i.e., $n' = n''$ at $T_{\mathrm{gel}} = 67$ °C. The value of $T_{\mathrm{gel}} = 67$ °C was in good agreement with that obtained previously from the temperature at which tan δ is frequency independent and also from the temperature at which G' and G'' coincided. The zero shear viscosity, η_0, and the equilibrium shear modulus, G_{eq}, conformed well with power law scaling functions of the relative distance from the gel point, ϵ, i.e., $\eta_0 \sim \epsilon^{-k}$ and $G_{\mathrm{eq}} \sim \epsilon^{z}$ (where k and z are scaling parameters).

Introduction

Waterborne polyurethane dispersions belong to an important class of polymer dispersions used in many industrial applications such as coatings for wood finishing, glass fiber sizing, textiles, adhesives, automotive topcoats and primers, films for packaging, gloves, and other applications. Pure polyurethane polymers with desirable properties for a number of applications can also be recovered from these dispersions, making them versatile and widely applicable. In recent years, significant emphasis has been placed on the use of waterborne polyurethane dispersions (PUD) due to their health and environmental safety.[1−7] Design and control of these systems have been traditionally undertaken by trial and error methods due to their inherent complexity. These environmentally friendly products are used to reduce the VOC (volatile organic compounds) released into the atmosphere by solventborne systems and are expected to exhibit the same performance as that of conventional solventborne systems. However, control of rheology and physical properties via rational synthesis of waterborne polyurethane dispersions is difficult.

Rheological properties and gelation of concentrated PUDs are little studied and are therefore fertile ground of fundamental science research due to the industrial importance of these materials. Rheological behavior of colloidal gels has been studied extensively both practically and theoretically.[8−11] Chemical gels are known to be typically formed via gradual branching of linear chains into a cluster that are interconnected via covalent bonds, leading to a 3-dimensional polymer network structure. The network structure can also be formed physically (physical gels), where the polymer chains are connected together to form the networks by different kinds of physical forces, such as hydrogen bonds, electrostatic attraction, and van der Waals forces.

Dynamic rheology is a powerful tool to monitor gelation (or cross-linking) and microstructural changes in a material, as it allows properties to be probed in at-rest conditions without disruption of the microstructure. In addition, it is quite an effective method for studying the curing process of thermosetting polymers and for the examination of the viscoelastic properties and transition temperatures of the cured products. The viscoelastic behavior of polymer gels near the sol−gel transition has been studied experimentally[12−19] and theoretically.[20−24] The main focus of these studies was to find the relationship between linear viscoelastic properties and the structure of gels at the gel point. The experimental determination and prediction of gelation are important for the processing of cross-linking polymers, whereas the criticality of the phenomenon and the universality of the properties on the gelation threshold make gelation interesting from a fundamental point of view.[25,26] The formation of polymer gels can be monitored from the time evolution of viscoelastic material functions at the gel point, where the entire network process can be divided into two parts separated by the gel point. The gel point is one of the most important

---

[†] Permanent address: Cairo University, Faculty of Science, Department of Chemistry, Orman-Giza 12613, Egypt.

* To whom all correspondence should be addressed: Tel 601-266-5596; e-mail Joshua.Otaigbe@usm.edu.

10.1021/ma0511088 CCC: $30.25

parameters of gelation that is characterized by the appearance in the reactive system of a macromolecule with infinitely large molecular weight. The sol−gel transition point can be determined by a sudden change of a range of physical properties.[27] In theory, the criterion for gel formation is the existence of one long chain running through the whole system. In practice, a sudden loss of flow is the most common and conventional fingerprint to determine the sol−gel transition point. This is facilitated by the fact that at the gelation point the viscoelastic properties change abruptly from an initially liquidlike state to a solidlike state.[28−34] Several models for gelation have been proposed and the most well-known is percolation theory.[35,36] The percolation theory was generalized to predict how the viscoelastic properties, such as dynamic shear moduli and viscosity, are expected to scale with time or frequency.[37]

The frequency dependence of complex viscosity for PUDs of different compositions has been reported in our previous publication.[38] The viscosity of PUDs was dramatically changed as a function of PU concentration. At $PU \leq 40$ wt %, the viscosity was slightly increased with concentration and almost constant regardless of the value of frequency. At $PU = 46$ wt %, the viscosity increased dramatically (4 orders of magnitude) and becomes no longer frequency dependent. The critical concentration at which the viscosity of the dispersions increased dramatically was evaluated on the basis of the Krieger−Dougherty equation[39] and was found to be equal to 0.43 volume fraction.[38,39] Furthermore, the frequency dependence of dynamic shear moduli, G' and G'', for different PU concentrations was also studied for this dispersion. It has been found that at $PU \leq 40$ wt % the PUDs behave as liquidlike materials; i.e., G' is much lower than G'', and both of them are frequency dependent. At $PU = 46$ wt %, G' and G'' were increased strongly and became frequency independent, indicating the formation of fractal gel.

As previously reported,[40] we found the linear viscoelastic properties of polyurethane dispersions with 40 and 42 wt % polyurethane to be greatly changed by the onset of the gelation process. The viscoelastic material functions, such as dynamic shear moduli, G' and G'', complex shear viscosity, η^*, and loss tangent, tan δ, were found to be very sensitive to the structure changes during the gelation process and the formation of a fractal polymer gel. At the onset temperature of the gelation process, an abrupt increase in G', G'', and η^* (several orders of magnitude) was observed during the dynamic temperature ramps (2 °C/min heating rate) over a wide range of angular frequency. The temperature dependence of tan δ was found to be frequency independent at the gel point, T_{gel}; i.e., the crossover in tan δ regardless of the value of frequency can be taken as an accurate method for determination of T_{gel}. The coincidence of G' and G'' at the gel point was also found to be frequency independent similar to the behavior of tan δ vs T. Furthermore, a dramatic increase in η_0 (v-shape) was observed at $T = T_{\mathrm{gel}}$ and found to be in good agreement with the value obtained from tan δ vs T behavior. The time−temperature−superposition principle was found to be only valid for temperatures lower than the T_{gel}; the principle failed at $T \geq 70$ °C, as expected. The morphology of the dispersions after annealing in tightly glass bottles at 70 °C for 2 h in water bath showed for certain PU concentrations (36, 38, and 40 wt %) a network structure with a unique periodicity and phase connectivity. A lower critical solution temperature (LCST) type phase diagram was estimated on the basis of the different morphology of the dispersions. The co-occurrence of liquid−liquid and liquid−solid transitions at the same temperature range reflected the complex behavior of this dispersion.

The present study described in this article is part of our long-range research program that is aimed at providing critical fundamental insights into the rational synthesis and control of structure and properties of polyurethane dispersions and films and other reactive polymer dispersions. This article considers in details time evolution measurements of the viscoelastic properties at different constant temperatures and shear frequencies near the gel temperature. The gel point will be evaluated and shown to be consistent with the criterion of Winter−Chambon.[41,42] The apparent activation energy of the gelation process will be investigated in future proposed research. In addition, some of the viscoelastic material functions, such as G', G'', and η_0, will be expressed in power law scaling functions with critical exponents that may be useful in predicting the behavior of the PUDs studied. The analytical approach adopted should be widely applicable to polyurethanes and other reactive polymer systems, making an important contribution to the literature on critical macromolecular gels and reacting complex fluids.

Experimental Section

Materials. Polyester polyol (Desmophen 1019-55) and isophorone diisocyanate (Desmodur-I) were supplied by Bayer MaterialScience, Pittsburgh, PA. Dimethylolpropionic acid (DMPA), dibutyltin dilaurate (DBTDL), 1-methylpyrrolidinone (NMP), triethylamine (TEA), hexamethylenediamine (HMDA), diethylamine (DEA), and tetrahydrofuran (THF) were received from Aldrich Chemical Co. Ethoxylated nonylphenol ammonium sulfate (Abex EP-110, Rhodia Chemicals, Cranbury, NJ) was used as a surfactant. Defoamer (Foamstar-111) was received from Cognis Co., Cincinnati, OH. All the materials were used as received.

Prepolymer Synthesis. A 250 mL round-bottom, four-necked flask with a mechanical stirrer, thermometer, condenser with nitrogen in/outlet, and a pipet outlet was used as a reactor. The polymerization was carried out in a constant temperature oil bath. Desmophen 1019-55 and DMPA were charged into the dried flask at 70 °C. While stirring, NMP (10 wt % based on total feed) was added and stirring was continued until a homogenized mixture was obtained. Desmodur-I and DBTL were added and stirring was continued for 30 min at this temperature. The mixture was heated to 80 °C for about 3 h to afford an NCO-terminated prepolymer. The NCO content during the reaction was determined using a standard dibutylamine back-titration method. Upon obtaining a theoretical NCO value, the prepolymers were cooled to 60 °C, and the neutralizing solution, i.e., TEA (DMPA equiv) dissolved in NMP (2 wt %), was added and stirred for 30 min while maintaining the temperature at 60 °C.

Dispersion and Chain Extension. Dispersion of PU was accomplished by adding the prepolymer to the mixture of water and surfactant (4 wt % based on total solid). Agitation was maintained at 750 rpm. After 20 min, 20 wt % solution of HMDA in water was added over a period of 30 min, and chain extension was carried out for the next 1 h. Subsequently, defoamer (Foamstar-I) was added, and stirring was continued for 5 min at a speed of 250 rpm. For experiments requiring control of the polymer molecular weight, diethylamine was included in the chain extension step. In the preparation of all polymers the ratio of isocyanate groups/amine groups (from chain extension/termination) was 1.1/1.

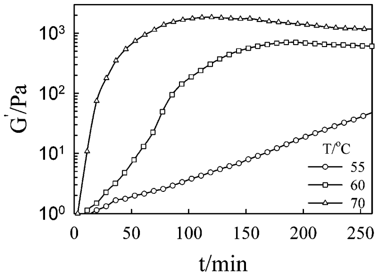

Figure 1. Time dependence of dynamic storage modulus, G', of PUDs (40 wt % PU) at constant shear frequency ($\omega = 1$ rad s^{-1}) for different constant temperatures.

Rheological Measurements. The viscoelastic measurements were done using an Advanced Rheometerics Expansion System (ARES, Rheometrics Inc.) equipped with two 25 and 40 mm parallel plates diameter. To prevent dehydration of the PUD, a thin layer of low-viscosity silicone oil was applied to the air/sample interface. In this study, the following rheological experiments were performed: (1) Strain sweep at a constant temperature and frequency range of 0.1−100 rad s^{-1} was used to obtain the linear viscoelastic range of the sample. (2) A time sweep at different constant temperatures (55, 60, 65, and 70 °C) and constant shear frequency ($\omega = 1$ rad s^{-1}) in the linear viscoelastic regime (strain amplitude ≤10%) was used to determine the influence of the gelation process on the visoelastic characteristic functions (G', G'', η^*, and tan δ). (3) A frequency sweep at fixed constant temperatures (55, 60, 65, and 70 °C) for different gelation time in the linear viscoelastic regime (strain amplitude ≤10%) was used to obtain the visoelastic characteristic functions (G', G'', η^*, and tan δ) over a wide range of frequency and time. These measurements allow us to test the validity of expressing G', G'', and η_0 in power law forms with critical exponents based on the percolation theory.

Results and Discussion

Effect of Temperature. Monitoring the variation of viscoelastic material functions, such as G', G'', η^*, and tan δ, as a function of curing time at different constant temperatures and shear frequencies can be used for investigating the kinetics of thermal-induced gelation rheologically. To do this, it is imperative to accurately determine the gel temperature, T_{gel}, which is the temperature at which the fractal gel of waterborne polyurethane dispersion takes place. The exact value of T_{gel} for 40 wt % PU was previously determined from the temperature dependence of tan δ at different constant shear frequencies as reported in a prior publication.[40] At 67 °C all curves of tan δ at different constant shear frequencies coincided and became no longer frequency dependent, indicating that $T_{\text{gel}} = 67$ °C. For this reason, we will investigate in this section the time evolution of the viscoelastic properties of gelation process around this temperature. Isothermal time dependence of elastic stored modulus, G', at different temperatures and constant shear frequency ($\omega = 1$ rad s^{-1}) is shown in Figure 1. A dramatic increase in G' at all temperatures was clearly observed as a result of formation of an elastic fractal gel. At long times the value of G' levels off and becomes time independent. The magnitudes of the elevation in G' and the time at which G' levels off, t_{lo}, were found to be strongly temperature-dependent; i.e., the magnitude of the elevation in G' increases and t_{lo} decreases with increasing temperature. The fact that the magnitude of the elevation in G' increases greatly with increasing time and temperature is attributed to the gelation process and the significant increase in branching (formation of fractal gel). The G' reaches a plateau value at long times particularly at 60 and 70 °C. The plateau value is related to an equilibrium modulus, G_{eq} (a typical criterion for the formation of an elastic, fractal gel). At 55 °C the gelation process is significantly slower than that at 60 and 70 °C, implying that a longer curing time than the one observed at higher temperatures is needed to reach the plateau region.

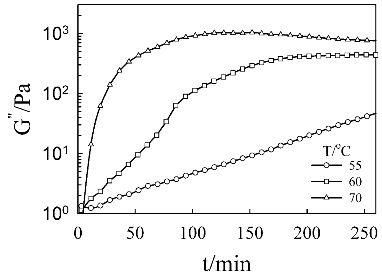

Figure 2. Time dependence of dynamic loss modulus, G'', of PUDs (40 wt % PU) at constant shear frequency ($\omega = 1$ rad s^{-1}) for different constant temperatures.

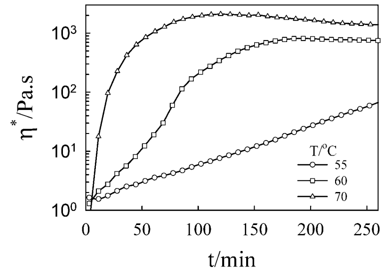

Figure 3. Time dependence of dynamic complex viscosity, η^*, of PUDs (40 wt % PU) at constant shear frequency ($\omega = 1$ rad s^{-1}) for different constant temperatures.

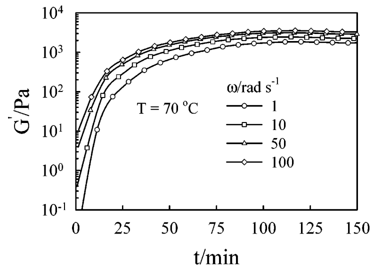

Figure 4. Variation of G' as a function of time at 70 °C for different constant shear frequencies.

Similar behavior can be obtained for the other viscoelastic material functions, such as the viscous loss modulus, G'', and the complex dynamic viscosity, η^*. The time dependence of G'' and η^* at $\omega = 1$ rad s^{-1} and different constant temperatures are demonstrated in Figures 2 and 3, respectively. Like the behavior of G' with time and temperature already discussed, G'' and η^* increase with gelation time and reach equilibrium values (time independent) at long times. The values of G'' and η^* at 55 °C are also increased slightly with increasing curing time but did not reach equilibrium values because the gelation process is very slow at low temperature.

Effect of Shear Frequency. In this section, the thermal-induced gelation of PUDs is examined over a wide range of frequency under isothermal conditions. Figure 4 shows the time dependence of G' at 70 °C for different constant shear frequencies. Clearly, the variation of G' with time and frequency can be divided into two different regimes. At $t \leq 50$ min (regime I), G'

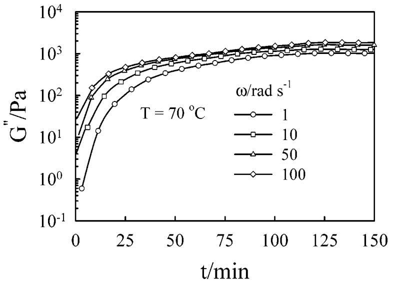

Figure 5. Variation of G'' as a function of time at 70 °C for different constant shear frequencies.

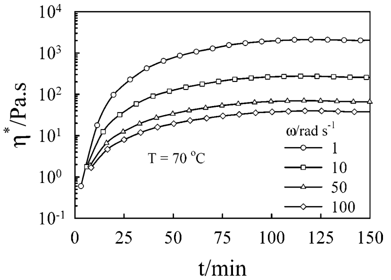

Figure 6. Variation of η^* as a function of time at 70 °C for different constant shear frequencies.

increases rapidly with time, and the magnitude of the elevation in G' is shear frequency dependent. (The magnitude of the elevation at low frequency is higher than that at high frequency.) This regime (regime I) includes the gel point at which the chain branching of polymer becomes significant and the fractal gel starts to form. At $t > 50$ min (regime II), G' is no longer time dependent and only slightly frequency dependent as a result of the formation of an equilibrium modulus, G_{eq}, which is a typical criterion for the formation of an elastic, fractal gel. Similar behavior can be obtained for the variation of G'' with gelation time at different shear frequency, as seen in Figure 5. The only difference between Figures 4 and 5 is that the magnitude of the elevation in G' at a given gelation time and shear frequency is higher than the elevation in G'' at the same experimental conditions. This slight change in the behavior of G' and G'' during the gelation process is attributed to the higher sensitivity of G' than G'' to the structure change accompanying the formation of fractal gel. This higher sensitivity of G' to the gelation process is attributed to the fact that the stress induced in the system by the branching and the formation of fractal gel is primarily elastic in origin. The time dependence of the complex viscosity, η^*, at 70 °C for different shear frequencies shows similar behavior as that obtained for G' and G'', as shown in Figure 6. At the beginning of the measurement, η^* is almost frequency independent over the wide range of frequencies used. At long times, η^* increases dramatically, reaching equilibrium values that are strongly frequency dependent.

Determination of t_{gel}. One can determine t_{gel} from rheological data based on the Winter–Chambon criterion.[41,42] According to this criterion, the gel point is identified as the instant in time when the moduli scale in an identical fashion with time; i.e., storage and loss moduli show the following power law behavior:

$$G' \sim G'' \sim \omega^n \tag{1}$$

The exponent n is called the relaxation exponent and can be linked to microstructural parameters. According to this relation, if the power law holds in a sufficiently wide range of shear frequency, the loss tangent, $\tan \delta = G''/G'$, can be written as

$$\tan \delta = \tan\left(\frac{n\pi}{2}\right) \tag{2}$$

This equation implies that $\tan \delta$ is independent of ω at the gel point. The validity of this theory has been extended to a variety of chemically and physically cross-linking systems. Figure 7 shows the time dependence of $\tan \delta$ at 70 °C and different constant shear frequencies. One can see from this figure that $\tan \delta$ is frequency independent at $t_{gel} = 17$ min, indicating that the system has reached the gel point and the cluster of the fractal structure is macroscopically percolated. At a time longer than the gel point, $\tan \delta$ decreases gradually with time due to the fact that the magnitude of elevation in G' is higher than that in G'' as a result of the formation of an elastic fractal gel. On the basis of this experimental fact, it is apparent that the Winter–Chambon theory is applicable to this system over a wide range of frequency (as shown in Figure 7), suggesting that there is a self-similar structure (or critical gel) at the gel point. Beyond the gel point, elastic effects dominate, since the fractal gel is capable of storing energy. This is why G' increases at a more rapid rate than G'' at long times.

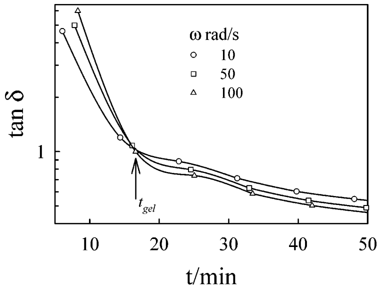

Figure 7. Loss tangent, $\tan \delta$, as a function of time at 70 °C for different constant shear frequencies. The gel point, t_{gel}, is determined from the intersection point.

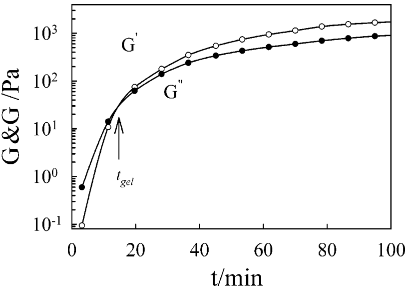

Figure 8. Time dependence of $G'$and G'' at 70 °C and 1 rad s^{-1}. The arrows show the t_{gel} obtained from intersection point of G' and G''.

Figure 8 shows the time dependence of G' and G'' at 70 °C and $\omega = 1$ rad s^{-1}. At the beginning of the measurement and before the occurrence of gelation process, the value of G'' is about 1 order of magnitude greater than G'. Both G' and G'' increase strongly with time toward equilibrium values (gelation time independent) at long times. The value of G' which was lower in magnitude than G'' increased more sharply than G'', and G' becomes greater than G'' at $t > t_{gel}$. This method gives $t_{gel} = 17$ min, which is identical to the value that was obtained from $\tan \delta$ vs t (Figure 7) already discussed. As previously reported, we found that the gel temperature, T_{gel}, determined from the crossover of G'

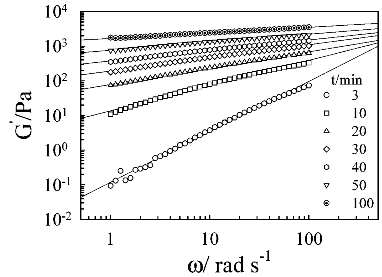

Figure 9. Variation of G' as a function of shear frequency for different constant gelation times at 70 °C.

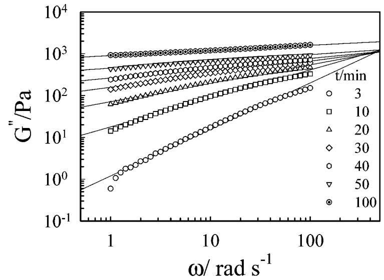

Figure 10. Dependence of G'' on shear frequency for different constant gelation times at 70 °C.

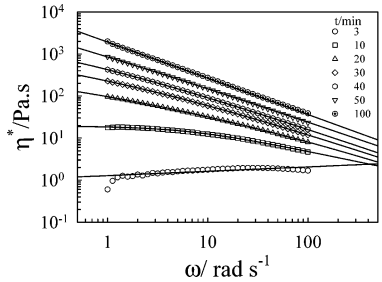

Figure 11. Variation of η^* as a function of shear frequency for different constant gelation times at 70 °C. The solid lines are calculated from the Carreau–Yasuda model (eq 6).

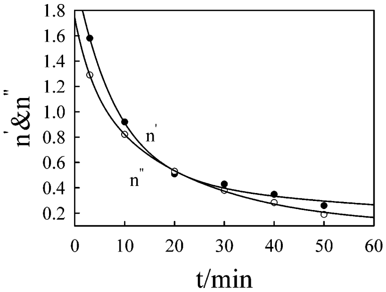

Figure 12. Time dependence of exponents n' and n'' obtained from G' and G'' data at 70 °C, respectively, according to eq 1.

and G'' was shear frequency independent and also equal to the value obtained from tan δ vs T at different shear frequency.[40] However, it is known for other systems that the crossover of G' and G'' is not a general criterion for determination of t_{gel} and T_{gel} due to its significant frequency dependence. Previously, we have reported that the T_{gel} of thermally cross-linked poly(vinyl methyl ether) determined at 100 rad s^{-1} was found to be about 20 °C higher than that obtained at 1 rad s^{-1}.[43] An analogous behavior was recently reported by Zhao et al.,[44] who found that the temperature at which the G' and G'' intersect was shear stress and frequency dependent for the sol–gel transition of a hybrid gel. Winter et al.[12,13] reported that when the gelation point cannot be evaluated from the crossover of G' and G'', it could be related to the critical conversion point of cross-linking reaction. At this point both G' and G'' were found to follow a power law as described in eq 1.[12,13]

Critical Phenomena at Gel Point. Figure 9 shows the frequency dependence of G' at different time intervals at 70 °C. One can see from this figure that at t = 3 min the value of G' increases with increasing frequency with a slope of about 2, indicating a classical liquid behavior. The value of G' increases with both frequency and gelation time. At a very long time, G' becomes no longer frequency dependent and reaches an equilibrium value (G_{eq}) due to the formation of an elastic fractal gel. Similar behavior was obtained for the frequency dependence of G'' for different gelation times; i.e., G'' increases rapidly with time and frequency and attains an equilibrium value (time and frequency independent) (Figure 10).

The frequency dependence of η^* for different gelation times is depicted in Figure 11. Obviously, η^* is almost frequency independent at $t = 3$ min; after that the value of η^* increases abruptly with increasing gelation time, and the entire curve becomes strongly frequency dependent. It must be stated here that the measurements depicted in Figure 11 were made over a relatively narrow frequency range (ω = 1–100 rad/s) to obtain a systematic change in the viscosity within the time scale of the gelation process of the system. The relatively long times involved in measurements performed over a wider frequency range (especially in the low-frequency regime) will preclude detection of the desired gradual change in the viscosity. Only the observation of the dramatic increase in the viscosity of the system is feasible under the conditions just mentioned.

It is apparent that Figures 9 and 10 demonstrate the variations of G' and G'' as a function of shear frequency in accordance with the power law of eq 1, respectively. This behavior is applicable over the entire range of frequency. The values of the exponents n' and n'' for G' and G'', respectively, are gelation time dependent. Figure 12 shows the time dependence of n' and n'' at 70 °C for 40 wt % PU. The values of the two exponents decrease exponentially with time and become identical at the gel point; i.e., at t_{gel}, n' and $n'' = 0.58$. The values of the exponents are very close to those obtained for different systems reported in the literature and found to be in good agreement with that predicted theoretically from the percolation theory ($n \sim 2/3$).[45–49] At very long times the values of the two exponents decrease and become as low as 0.2, indicating the formation of an elastic or rigid fractal gel.

The values of the exponents n' and n'' should be temperature dependent due to the different degrees of gelation accomplished at different temperatures. For this reason the frequency dependence of G' and G'' at different constant temperatures in the vicinity of gel point was investigated, as shown in Figure 13. The values of G' and G'' are shifted horizontally by a factor of a which is temperature dependent to avoid overlap between the data and to give a clear comparison of the data over a wide range of temperatures. Clearly, at $T \leq 66$ °C, G' is lower than G'', and both of them are strongly frequency dependent (liquidlike behavior). At $T = 68$ °C, G' and G'' overlap, and at higher temperatures G' increases more rapidly than G'' and both of them become less temperature dependent (solidlike behavior or gel formation). The values of the exponents n' and n'' can be obtained from the slopes of each curves

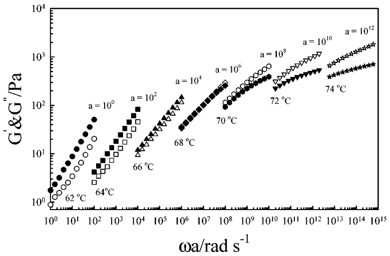

Figure 13. Dynamic shear moduli, G' (open symbols) and G'' (solid symbols), as a function of shear frequency at different constant temperatures. The x-axis is extended by a factor a ranging from 1 to 10^{12} to obtain a valid comparison.

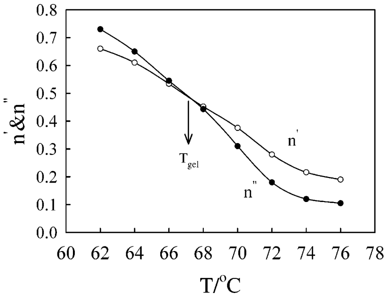

Figure 14. Temperature dependence of the exponents n' and n'' obtained from the slopes of G' and G'' vs ω, respectively, according to eq 1.

of G' and G'' vs ω at different constant temperatures. Figure 14 shows the temperature dependence of n' and n'' for 40 wt % PUD. One can see that the exponents n' and n'' decrease strongly with temperature and cross over at the T_{gel}. The value of $T_{gel} = 67$ °C is identical with that obtained previously from the temperature at which tan δ is frequency independent and also from the temperature at which G' and G'' cross over.[40] At T_{gel}, the exponents $n' = n'' = 0.49$, which is in close agreement with that obtained from the above analysis at 70 °C (i.e., at t_{gel} $n' = n'' = 0.58$) and with those obtained experimentally for different systems and predicted theoretically from the percolation theory ($n \sim 2/3$).[45−49]

The zero shear viscosity, η_0, and the equilibrium shear modulus, G_{eq}, are also expressed in power law scaling functions near the gel point:

$$\eta_0 \sim \epsilon^{-k} \quad (p < p_c) \tag{3}$$

$$G_{eq} \sim \epsilon^{z} \quad (p > p_c) \tag{4}$$

where p and p_c are the reaction extents at time t and t_{gel}, respectively. The relative distance from the gel point, ϵ, can be defined as

$$\epsilon = \frac{|p - p_c|}{p_c} \tag{5}$$

The values of η_0 at different times can be determined from fitting the classical frequency dependence of η^* for different times (Figure 11) to the Carreau−Yasuda model:

$$\eta^* = \eta_0\left[1 + \left(\frac{\eta_0\dot{\gamma}}{\tau^*}\right)^a\right]^{(n-1)/a} \tag{6}$$

where n, a, and τ^* are material constants. By using eq 6, we can calculate η_0 as a fitting parameter to the experimental results using the nonlinear regression technique. An excellent description of the data was obtained as shown in Figure 11. In this figure the lines are computed from eq 6 while the points are experimental.

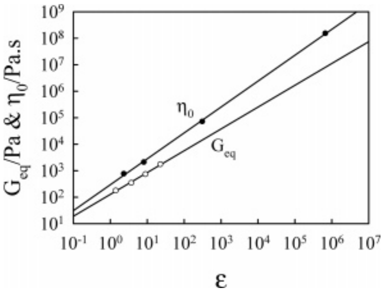

Figure 15. Dependence of zero shear viscosity, η_0, and equilibrium shear modulus, G_{eq}, on the relative distance from the gel point, ϵ, in a double-logarithmic scale at 70 °C.

The values of G_{eq} can be obtained from the frequency-independent values of G' from Figure 9. Figure 15 shows the ϵ dependence of G_{eq} and η_0 in a double-logarithmic scale; the slopes of the two linear curves directly determine the values of z and k, respectively. The exponent n can be predicted from the critical exponent values of k and z, as reported by Martin et al.[50]

$$n = \frac{z}{k + z} \tag{7}$$

The values of z and k obtained from the slopes of the two curves of Figure 15 are 0.85 and 0.95, respectively, which yields a value of $n = 0.47$. This value is in good agreement with the values obtained from the power law of G' and G'' at T_{gel} (Figure 14).

On the basis of the discussion in the preceding sections, it is apparent that the viscoelastic properties of PUDs are very sensitive to the structure changes accompanying the formation of an elastic fractal polymer gel. In addition, the critical phenomenon near the gel point can be well described by the scaling power laws based on percolation theory and Winter−Chambion approaches.

Conclusions

The thermal-induced formation of an elastic fractal gel in PUDs of 40 wt % PU was investigated rheologically from the time evolution measurements of viscoelastic material functions, such as (G', G'', η^*, and tan δ) over a wide range of frequency under isothermal conditions at constant different temperatures (55, 60, 65, and 70 °C). The viscoelastic material functions abruptly changed at the onset of gelation process. The Winter−Chambon method for determination of t_{gel} from the time dependence of tan δ (the point at which all curves of tan δ are coincided and no longer frequency dependent) was found to be applicable over a wide range of frequency. The value of t_{gel} at different constant temperatures obtained from the time at which tan δ is frequency independent was found to be identical to the value obtained from the crossover of G' and G''. In addition, G' and G'' were found to follow a power law behavior as a function of frequency ($G'' \sim G'' \sim \omega^n$) with exponents n' and n'' that are strongly dependent on gelation time and temperature. The exponent values are very close to the value obtained for other different cross-linking systems and in good agreement with that predicted theoretically based on the percolation theory ($n \sim 2/3$). The zero shear viscosity, η_0, and the equilibrium shear modulus, G_{eq}, could be expressed in power law scaling functions with the relative distance from the gel point, ϵ, i.e., $\eta_0 \sim \epsilon^{-k}$ and $G_{eq} \sim \epsilon^{z}$ with $k = 0.95$ and $z = 0.85$, in close agreement with the predicted value based on the percolation theory.

Acknowledgment. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award DMR 0213883. Partial support of this work from the Bayer MaterialScience, Pittsburgh, PA, is gratefully acknowledged. We thank Anton Paar USA for providing us with direct access to their new MCR 501 rheometer.

References and Notes

(1) Markusch, P. H.; Tirpak, R. E. Symposium, New Orleans, LA, 1990.
(2) Kim, B. Y.; Kim, T. K. *J. Appl. Polym. Sci.* **1991**, *43*, 393–398.
(3) Kim, C. K.; Kim, B. K. *J. Appl. Polym. Sci.* **1991**, *43*, 2295–2301.
(4) Chan, W. C.; Chen, S. A. *Polymer* **1993**, *43*, 1265–1270.
(5) Dreja, M.; Heine, B.; Tieke, B.; Junkers, G. *J. Colloid Interface Sci.* **1997**, *181*, 131–140.
(6) Wicks, Z. W.; Wicks, D. A.; Rosthauser, J. W. *Prog. Org. Coat.* **2002**, *44*, 161–183.
(7) Howarth, G. A. Polyurethanes, polyurethane dispersions and polyureas: Past, present and future. *Surf. Coat. Int., Part B: Coat. Trans.* **2003**, *86* (B2), 111.
(8) Queslel, J. P.; Mark, J. E. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: Oxford, 1988; Vol. 2, pp 271–309.
(9) Dušek, K.; Dušková-Smrčková, M. *Prog. Polym. Sci.* **2000**, *25*, 1215–1 260.
(10) Guenet, J.-M. *Thermoreversible Gelation of Polymers and Biopolymers*; Academic Press: New York, 1992.
(11) Larson, R. G. In *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, 1999; Chapter 5.
(12) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683–697.
(13) Winter, H. H.; Morganelli, P.; Chambon, F. *Macromolecules* **1988**, *21*, 532–535.
(14) Scanlan, J. C.; Winter, H. H. *Macromolecules* **1991**, *24*, 47–54.
(15) Izuka, A.; Winter, H. H.; Hashimoto, T. *Macromolecules* **1992**, *25*, 2422–2428.
(16) Adolf, D.; Martin, J. E.; Wilcoxon, J. P. *Macromolecules* **1990**, *23*, 527–531.
(17) Hodgson, D. F.; Amis, E. J. *Macromolecules* **1990**, *23*, 2512–2519.
(18) Muller, R.; Gerard, E.; Dugand, P.; Rempp, P.; Gnanou, Y. *Macromolecules* **1991**, *24*, 1321–1326.
(19) Takahashi, M.; Yokoyama, K.; Masuda, T.; Takigawa, T. *J. Chem. Phys.* **1994**, *101*, 798–804.
(20) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. A* **1989**, *39*, 1325–1332.
(21) Muthukumar, M. J. *Chem. Phys.* **1985**, *83*, 3162–3168.
(22) Takigawa, T.; Takahashi, M.; Urayama, K.; Masuda, T. *Chem. Phys. Lett.* **1992**, *195*, 509–512.
(23) Hess, W.; Vilgis, T. A.; Winter, H. H. *Macromolecules* **1988**, *21*, 2536–2542.
(24) Muthukumar, M. *Macromolecules* **1989**, *22*, 4656–4658.
(25) Lairez, D.; Adam, M.; Emery, J. R.; Durand, D. *Macromolecules* **1992**, *25*, 286–289.
(26) Adolf, D.; Martin, J. R. E. *Macromolecules* **1991**, *24*, 6721–6724.
(27) Zhao, Y.; Cao, Y.; Yang, Y.; Wu, C. *Macromolecules* **2003**, *36*, 855–859.
(28) Grisel, M.; Muller, G. *Macromolecules* **1998**, *31*, 4277–4281.
(29) Hone, J. H. E.; Howe, A. M.; Cosgrove, T. A *Macromolecules* **2000**, *33*, 1199–1205.
(30) Balan, C.; Völger, K. W.; Kroke, E.; Riedel, R. *Macromolecules* **2000**, *33*, 3404–3408.
(31) Daoud, M. *Macromolecules* **2000**, *33*, 3019–3022.
(32) Yoon, P. J.; Han, C. D. *Macromolecules* **2000**, *33*, 2171–2183.
(33) Tanaka, F. *Macromolecules* **1998**, *31*, 384–393.
(34) Matricardi, P.; Dentini, M.; Crescenzi, V. *Macromolecules* **1993**, *26*, 4386–4387.
(35) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.
(36) De Gennes, P.-J. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(37) Schiessel, H.; Blument, A. *Macromolecules* **1995**, *28*, 4013–4019.
(38) Madbouly, S. A.; Otaigbe, J. U.; Nanda, A. K.; Wicks, D. A. *Macromolecules* **2005**, *38*, 4014–4023.
(39) Krieger, I. M.; Dougherty, T. J. *Trans. Soc. Rheol III* **1959**, 137–152.
(40) Madbouly, S. A.; Otaigbe, J. U.; Nanda, A. K.; Wicks, D. A. *Polymer*, in press.
(41) Winter, H. H. In *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1989.
(42) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367–382.
(43) Madbouly, S. A.; Ougizawa, T. *J. Macromol. Sci., Phys.* **2004**, *B43*, 655–670.
(44) Zhao, Y.; Cao, Y.; Yang, Y.; Wu, C. *Macromolecules* **2003**, *36*, 855–859.
(45) Takenaka, M.; Kobayashi, T.; Hashimoto, T.; Takahashi, M. *Phys. Rev. E* **2002**, *65*, 041401–041407.
(46) Takenaka, M.; Kobayashi, T.; Saijo, K.; Tanaka, H.; Iwase, N.; Hashimoto, T.; Takahashi, M. *J. Chem. Phys.* **2004**, *121*, 3323–3328.
(47) Groot, R. D.; Agterof, W. G. M. *Macromolecules* **1995**, *28*, 6284–6295.
(48) Kioniksen, A.-L.; Nystrom, B. *Macromolecules* **1996**, *29*, 5215–5222.
(49) Choi, J. H.; Ko, S.-W.; Kim, B. C.; Blackwell, J.; Lyoo, W. S. *Macromolecules* **2001**, *34*, 2964–2972.
(50) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. A* **1989**, *39*, 1325–1332.

MA0511088