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Kinetic Analysis of Fractal Gel Formation in Waterborne Polyurethane Dispersions Undergoing High Deformation Flows

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ABSTRACT: Isothermal and nonisothermal kinetics studies of thermal-induced gelation for waterborne polyurethane dispersions have been investigated rheologically. The change in the viscoelastic material functions such as elastic storage modulus, G', viscous loss modulus, G'' and complex dynamic viscosity, η^* during the gelation process was evaluated accurately for the first time. The isothermal kinetics reaction was described using a phenomenological equation based on the Malkin and Kulichikhin model that was originally developed for predicting isothermal curing kinetics of thermosetting polymers from differential scanning calorimetery (DSC) data. The Malkin and Kulichikhin model was found to conform excellently well for the rheokinetics data presented here. The rate of the gelation process was found to be a second-order reaction regardless of the temperature and shear frequency, and to be in good agreement with literature data. The isothermal gelation kinetics was also analyzed using a standard isoconversional method that is based on replicated experimental data and model-free kinetics calculations. This isoconversional method evaluates an effective activation energy that is independent of the degree of conversion, indicating that the rate of gelation is controlled by a single step (homogeneous) process with no change in the fractal gel formation mechanism at different degree of conversions. The temperature dependence of the gelation rate constant was well described by an Arrhenius plot with an average apparent activation energy equal to 127 ± 2 kJ/mol, in reasonable agreement with the value obtained from the temperature dependence of gel time, t_{gel}. The nonisothermal kinetics reaction rate was interpreted using the classical rate equation, the Arrhenius equation and the time−temperature relationships. A frequency-independent apparent activation energy was evaluated nonisothermally and found to be similar to that obtained from isothermal kinetics data. The high value of activation energy is thought to be due to the strong interaction between the PU-dispersed particles during the gelation process, making a significant contribution to the rate of structure formation. It is noteworthy that, in some respects, these results resemble those from other cross-linking polymer networks and gels measured by DSC, yet in very important ways the aqueous PUDs of the present study is quite unique.

Introduction

Aqueous polyurethane dispersions (PUDs) have recently emerged as important alternatives to their solvent-based counterparts for various applications due to increasing health and environmental awareness. These aqueous PUDs provide unique physical, chemical and mechanical properties compared to other aqueous polymer dispersions like styrene−butadiene and acrylics. Waterborne polyurethane dispersion is an important class of polymer dispersion that can be used in many industrial applications such as coatings for wood finishing, glass fiber sizing, adhesives, automotive topcoats, and other applications. It can also be used to obtain polyurethane films that can themselves be useful in various applications, such as textiles and medical and automotive applications. The PU films are generally optically transparent and have found a variety of uses in the protection of articles in both interior and exterior applications. 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. The aqueous PUDs are applied with high solids content, compared to the solvent-based PUDs, because their viscosity does not depend on the molecular weight of polyurethane, as we recently reported.[1] Design and control of these systems has been traditionally undertaken in industry by costly trial and error methods due to their inherent complexity.

Rheological properties of concentrated polyurethane dispersions and gels are subjects of current research interests due to the industrial importance of these materials. Rheological behavior of colloidal gels has been studied extensively both practically and theoretically.[2−5] Chemical gels normally take place by gradual branching of linear chains into a cluster that are interconnected via covalent bonds to form a three-dimensional polymer network structure. The network structure can also be formed physically (i.e., 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.

Fundamental investigation of the kinetics of polymer cross-linking reactions is an attractive area for research studies to obtain better understanding of the cure behavior and mechanism of macroscopic gelation, as well as, for controlling the production process and final performance of the systems. A variety of experimental techniques have been employed to study the kinetics of cross-linking reactions in polymers. The most popular techniques are FTIR[6−8] (Fourier transform infrared spectroscopy), ^{13}C NMR (nuclear magnetic resonance),[9−12] SEC (size exclusion chromatography),[13,14] and DSC (differential scanning calorimetry).[15−18] In most studies reported in the literature, the samples are cured isothermally for different time intervals before being tested and analyzed.

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Dynamic rheology is a powerful tool for monitoring gelation and microstructural changes in a material, because 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 gelation process of polymer dispersions and for the examination of the viscoelastic properties and transition temperatures of the polymer fractal gels. The viscoelastic behavior of polymer gels near the sol−gel transition have been studied experimentally[19−26] and theoretically.[27−31] The main emphasis 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 is important for the processing of polymer gels and dispersions, 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.[32,33] 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 parameter of gelation, that is characterized by the appearance in the reactive system of a macromolecule with infinitely large molecular weight.

The frequency dependence of complex viscosity for PUDs of different compositions has been investigated and reported in our previous publication.[1] The critical concentration at which the viscosity of the dispersions increased dramatically was evaluated based on the Krieger−Dougherty equation[34] and was found to be equal to 0.43 volume fraction. The frequency dependence of dynamic shear moduli, G' and G'' for different PU concentration was also studied for this dispersion. It has been found that at PU $\leq$ 40 wt %, the PUDs behave as liquid-like 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. In addition,[35] the linear viscoelastic properties of PUDs with 40 and 42 wt % PU were found 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. The temperature dependence of tan δ was found to be frequency independent at the gel-point, T_{gel}, and the frequency-independent crossover in tan δ was found to be an accurate method for determination of T_{gel}, like other researchers have found for other cross-linking systems. Furthermore, we observed a dramatic increase in η_0 (v − shape) at $T = T_{gel}$ that was found to be in good agreement with the T_{gel} value obtained from tan δ vs T. 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. A lower-critical solution temperature (LCST) type phase diagram was estimated based on 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.

Furthermore, 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.[36] 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.

The aim of the present work is to study the kinetics of the special thermal-activated gelation reaction of PUD with 40 wt % PU by evaluating the viscoelastic material functions (elastic storage modulus, G', viscous loss modulus, $G''$and complex dynamic viscosity, η^*) during the gelation process both isothermally and nonisothermally. The isothermal kinetics reaction will be interpreted using a phenomenological equation based on the Malkin and Kulichikhin model,[37] which was predicted originally for the isothermal curing kinetics of thermosetting polymers studied by DSC. The nonisothermal kinetics reaction rate will be shown to be consistent with a model that incorporates the classical rate equation, the Arrhenius equation and time−temperature relationships.[38] The apparent activation energy will be determined isothermally and nonisothermally, and the values obtained will be compared with that obtained from the temperature dependence of gel time, t_{gel}. To the best of our knowledge, this study represent the first reported attempt to couple the rate of gel structure formation with the gelation concept for aqueous PUDs undergoing deformation and flow under isothermal and nonisothermal conditions, making an important contribution to the literature. In addition, the results of the present study may stimulate a better understanding of the rheokinetics and morphological evolution in aqueous PUDs and related systems. Furthermore, the combination of the experimental and analytical method used in the present study is thought to be a powerful and reliable approach in the fundamental study of the role of changes in the chemical and rheological conversion during the thermal-induced gelation of aqueous PUDs.

Experimental Section

Materials. Polyester polyol (Desmophen 1019−55), and isophorone diisocyanate (Desmodur-I) were supplied by Bayer MaterialScience, Pittsburgh, PA. Dimethylol propionic 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 the reaction was being stirred, NMP (10 wt % based on total feed) was added, and stirring was continued until a homogenized mixture was obtained. Desmodur-I and DBTDL 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. Once the theoretical NCO value was obtained, 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.

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} 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 range (strain amplitude $\leq 10\%$) in order to determine the influence of the gelation process on the visoelastic characteristic functions (G', G'', η^* and tan δ).
3. A frequency sweep at a given constant temperatures (55, 60, 65, and 70 °C) for different gelation times in the linear viscoelastic region (strain amplitude $\leq 10\%$) to obtain the visoelastic characteristic functions (G', G'', η^*, and tan δ) over a wide range of frequency and time.
4. A temperature sweep (2 °C/min) at different constant shear frequencies and a certain strain rate in the linear viscoelastic range (strain amplitude $\leq 10\%$) in order to determine the temperature dependence of the linear viscoelastic properties.

This last measurement enables us to study the kinetics of the gelation reaction by following the change in the viscoelastic material functions during the nonisothermal gelation process.

Results and Discussion

Effect of Gelation on Rheological Behavior. Previously[1,35] we have found that thermal-induced gel formation is governed by the particle size and particle−particle interaction. For samples of low concentration of PU (PU ≤ 34 wt %) the particle size is very small (less than 50 nm) and the particles are far apart and do not significantly interact with each other. Therefore, these samples with low PU concentration did not show any evidence of thermal-induced gelation. By contrast, samples with high PU concentration (PU ≥ 36 wt %) contained relatively large particle sizes (more than 70 nm) and showed evidence of strong interactions with each other that subsequently led to thermal-induced gelation. It is noteworthy that all the samples of low PU concentration (PU ≤ 34 wt %) did not show any significant increase in the magnitudes of the viscoelastic material functions (G' or G'' or η^*) even at high temperatures, indicating that any thermal-induced increase in the viscoelastic material functions is due to a typical gelation process with no water evaporation.[1,35] More extensive details of thermal-induced gelation and related effects in the PUDs of this study have been described and reported in our recent publications.[1,35]

Knowledge of gelation temperature, T_{gel} is very essential for accurate determination of kinetics of thermal-induced gelation in physical or chemical gels. Previously, the exact value of T_{gel} for 40 wt % PU was determined from the temperature dependence of tan δ at different constant shear frequencies.[35] At $T_{gel} = 67$ °C all curves of tan δ at different constant shear frequencies coincided and became no longer frequency dependent. For this reason, we will investigate in this section the time evolution of the viscoelastic properties of the 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 and $T \leq 70$ °C 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 experimental fact that the magnitude of the elevation in G' increases greatly with increasing time and temperature is attributed to the evolution of 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) that is related to the formation of 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, and a significantly longer gelation time is needed to reach the plateau region.

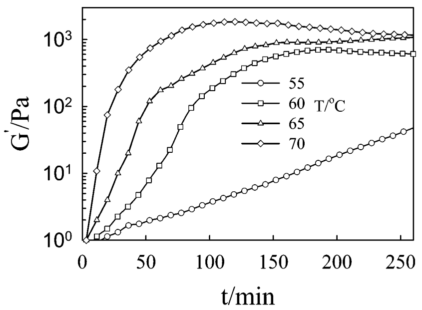

Figure 1. Time dependence of dynamic storage modulus, G', for PUD (40 wt % PU) at constant shear frequency ($\omega = 1$ rad s^{-1}) for different constant temperatures.

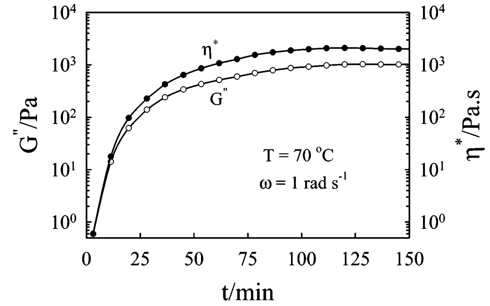

Figure 2. Dynamic loss modulus, G'', and dynamic shear viscosity, η^*, for PUD (40 wt % PU) as a function of gelation time at 70 °C and 1 rad s^{-1}.

Similar behavior was 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 70 °C is depicted in Figure 2. As was observed for the variation of G' with time and temperature, G'' and η^* increase with gelation time and reach equilibrium values (time-independent) at longer time. However, both G'' and η^* reached a plateau almost at the same gelation time; the elevation in η^* is considerably higher than G'' and gives a comparable elevation to that obtained for G' at the same frequency and time (Figure 1). This is attributed to the fact that the stress induced in the system by the formation of fractal gel is mostly elastic in nature.

The rate of change of G' with time at a given temperature, $(dG'/dt)_T$, is directly related to the extent of the gelation reaction. Figure 3 shows the time dependence of $(dG'/dt)_T$ for different constant temperatures. Clearly, dG'/dt initially increases to a maximum value and then decreases again. The inflection point (or maximum point) shifts to longer time with decreasing temperature. The initial increase in dG'/dt is related to the very quick rate of gelation corresponding to the initial time period

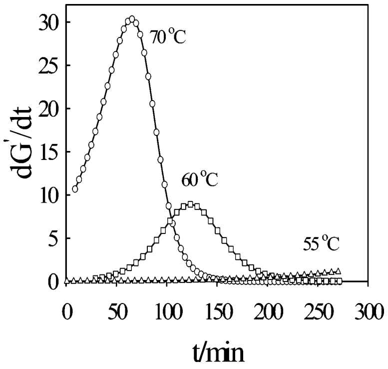

Figure 3. Time dependence of dG'/dt at different constant temperatures and 1 rad s^{-1} for PUD (40 wt % PU).

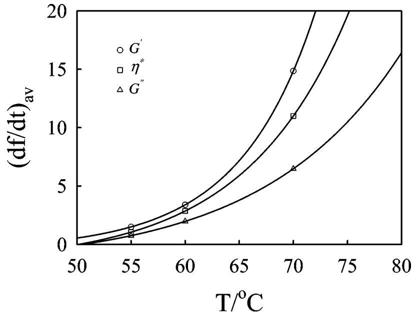

Figure 4. Temperature dependence of the average rate change of G', G'', and η^*.

of the measurement, as seen in the rapid increase of G' with time once the gel is formed (see Figure 1). The decrease in dG'/dt at long times is attributed to a decrease in the number of interactions between the PU-dispersed particles as the gelation process evolves. The shift of the inflection point to longer time at a lower temperature is directly related to the longer time needed for gelation, particularly at 55 °C. Similar behavior has been reported by Zlatanic et al.[39] in the literature; i.e., dG'/dt was found to increase with curing time in the early stage of curing process and then decreased at the late stage in the rheological study of the copolymerization reaction of acrylate-terminated unsaturated copolyesters with styrene. The authors ascribed this behavior to not only the change of cross-linking reaction rate with time but also to the autocatalytic effect of the cross-linking process related to the microphase separation that occurs in the initial time before the inflection point for the specific system studied. Similar behavior is reported elsewhere for the thermal-induced cross-linking of poly(vinyl methyl ether).[40]

The effect of temperature on the gelation kinetics can be quantified by calculating the average rate of change of the viscoelastic material functions (G', G'', and η^*) with time from the following equation:

$$\left(\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{\mathrm{av}} = \frac{1}{t_1 - t_2}\int_{t_1}^{t_2} \frac{\mathrm{d}f}{\mathrm{d}t} \qquad (1)$$

where f is the viscoelastic material function (G' or G'' or η^*) and t_1 and t_2 are the times at the beginning and ending of gelation process, respectively. This equation has been used previously by Lopes et al.[38] for the rheological data of the storage modulus only to evaluate the temperature dependence of structure development of gelation for high-methoxy pectin/sucrose system.[38] Figure 4 shows the change of (df/dt)$_{\mathrm{av}}$ as a function of temperature; (df/dt)$_{\mathrm{av}}$ increases exponentially with temperature for the three different viscoelastic material functions, indicating that the reaction rate increases with temperature as expected. The average rate of change of G' is higher than that of η^*, and much higher than the corresponding value for G''. This behavior again indicates that G' has the highest sensitivity to the structure change occurring in the gelation process compared to the sensitivity of η^* and G''. The low sensitivity of G'' to structure change of a material has also been previously observed in the viscoelastic behavior of block copolymers near the order−disorder transition[41] and in some polymer blends near the phase separation temperature.[42]

Isothermal Gelation Kinetics. The kinetics of the thermal-induced gelation of PUDs can be evaluated rheologically by applying fundamental rate laws with traditional model-fitting methods.[44] Such kind of analysis requires a knowledge of the best model that can fit the experimental data followed by a simple evaluation of the kinetics parameters such as the activation energy (E_a) and preexponential factor using Arrhenius equation.[44−48] This method is reported in the literature to afford a single value of activation energy for an overall process.[44−48] The E_a value obtained in this manner is in fact an average value that does not reflect the effect of changes in the reaction mechanism and kinetics with the degree of conversion and temperature.[44−48] Another approach used in the literature to evaluate the activation energy as a function of the degree of conversion is the so-called isoconversional method that is based on replicated experimental data and model-free kinetics calculations, i.e., no assumptions model.[49−52] In the next two-sections the isothermal gelation kinetics of PUD (40 wt % PU) will be studied using the two analysis methods just mentioned above (i.e., model-fitting and isoconversional methods).

Model-Fitting Method. The Malkin and Kulichikhin[37] model was found to be an excellent model to describe the experimental rheological data of the gelation process based on the following phenomenological equation:

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = (k_1 + k_2\beta^m)(1 - \beta)^n \qquad (2)$$

where β is the rheological degree of conversion, n and m are empirical constants, the sum of which gives the order of reaction; and k_1 and k_2 are the temperature-dependent rate constants for the early and late stages of the gelation reaction. This model (eq 2) was predicted originally for the isothermal curing kinetics of thermosetting polymers studied by differential scanning calorimetery (DSC) and was used recently to interpret the rheological kinetics data of similar systems.[39,40,43] Equation 2 describes the overall kinetics in both the early and late stages of a reaction. The rheological degree of conversion, β, can be evaluated at different constant temperatures from the time dependence of G' (Figure 1) using the following relation:

$$\beta = \frac{(G'_t - G'_0)}{(G'_\infty - G'_0)} \qquad (3)$$

where G'_t is the value of the storage modulus at time t; and G'_0 and G'_∞ are the values of storage modulus at the beginning of the experiment and at the maximum gelation time, respectively. Figure 5 shows the rheological degree of conversion (calculated from eq 3) as a function of gelation time at different constant temperatures. Obviously, the degree of conversion is almost zero before the onset of gelation process and then increased strongly with gelation time. The maximum degree of conversion is almost unity at 70 and 60 °C, however it is very small or experimentally inaccessible at 55 °C due to the very slow gelation process at

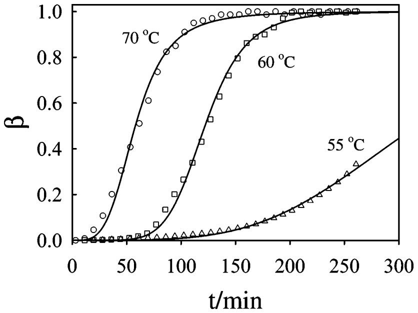

Figure 5. Rheological degree of conversion, β, as a function of gelation time for different constant temperatures. The symbols are experimental data calculated from eq 3, while the lines are calculated from eq 4.

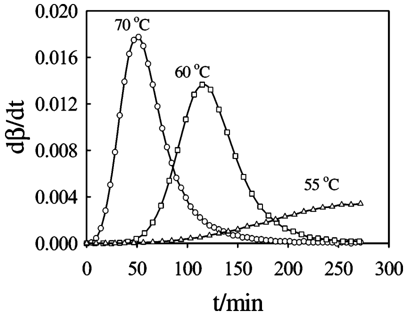

Figure 6. Variation of dβ/dt as a function of gelation time for different constant temperatures.

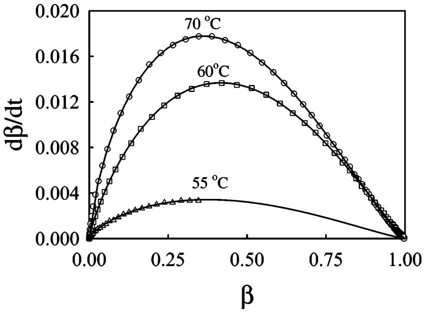

Figure 7. Variation of dβ/dt as a function of β for different constant temperatures. The symbols are experimental data while the lines are calculated from eq 2.

this temperature over the time scale of the measurements reported here (see Figure 5).

Figure 6 shows the rate of rheological degree of conversion, dβ/dt, as a function of gelation time for different constant temperatures. Again, at 70 and 60 °C, the gelation rate proceeds rapidly; however, on the other hand, it is very slow at 55 °C, requiring and needing a very long gelation time (outside the experimental time scale) to reach the inflection point. Similar to Figure 3, the inflection point shifts to longer time with decreasing temperature since the reaction at low temperature needs very long time in order to kinetically proceed to completion.

Figure 7 shows the rate of rheological degree of conversion (dβ/dt) as a function of β for different isothermal temperatures. One can obtain the kinetic parameters of eq 2 (m, n, k_1, and k_2) by fitting the experimental data of Figure 7 to eq 2 using standard nonlinear regression analysis. Here, the symbols are experimental data while the lines are computed from the equation using m, n, k_1 and k_2 as fitting parameters. The obtained parameters are listed in Table 1 with correlation coefficient or R^2 better than 99%. One can see that an excellent representation of the data was obtained using this model, giving a value of $m + n \sim 2$ that is independent of the change in the temperature and in good agreement with reported data in the literature. As already mentioned, this kinetic model depicted in eq 2 was originally used for interpreting the curing kinetics in a number of investigations of thermosetting polymers monitored by DSC reported in the literature; in many of these cases the curing reaction was found to be second order ($m + n = 2$).[53−56] On the basis of the above, it is apparent that the rheological kinetics of thermally activated gelation reaction of PUD can be well described by the Malkin and Kulichikhin model, in good agreement with reported studies in the literature.[39,40,43] Very recently, a second-order aggregation rate has been calculated theoretically for the gelation kinetics of moderately concentrated colloidal dispersions of fluorinated polymer particles.[57] To our knowledge, the present study is the first reported attempt to use and validate the Malkin and Kulichikhin model for aqueous PUDs and other polymer fractal gels and dispersions, making it possible to reliably and accurately extract the kinetics parameters that can be used to understand and control the gelation process.

Table 1. Kinetic Parameters of Thermal-Induced Gelation of PUD (40 wt % PU) Given by Equation 2

temp/°C	k_1/min^{-1}	K_2/min^{-1}	m	n
70	1.00×10^{-3}	0.0646	0.75	1.25
60	5.00×10^{-4}	0.0302	0.82	1.158
55	3.35×10^{-4}	0.0183	0.711	1.259

The temperature dependence of the apparent rate constants, k_1 and k_2, of eq 2 obtained from the above regression (Table 1) can be described by the Arrhenius relationship:

$$k = k_o \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where k_o is the preexponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute isothermal cure temperature. One can determine the value of E_a from the slope of the linear relationship between ln(k) and the inverse of absolute temperature as demonstrated in Figure 8. It was found that $E_a = 125$ and 129 kJ/mol for the temperature dependence of k_1 and k_2, respectively. This value of E_a is higher than the value obtained for the gelation process of other different cross-linking systems reported in the literature.[40,58,59] For example, we previously determined the value of $E_a = 74$ kJ/mol for thermal-induced cross-linking of PVME.[40] In addition, the values of rheological E_a determined by Fernandez et al.[59] for tetrafunctional epoxy resin and its blends with poly(methyl methacrylate) and poly(ethersulfone) were 71, 73, and 69 kJ/mol, respectively. The high value of E_a for the present system (PUDs) ascribed is due to the very strong physical interaction between the PU-dispersed particles which in turn leads to formation of a very strong elastic gel.[1,35]

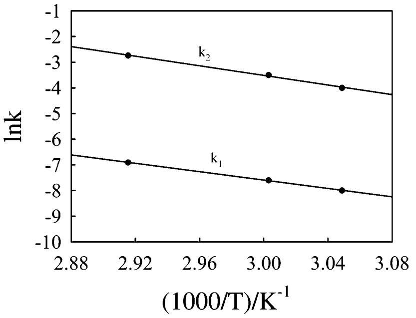

Figure 8. Arrhenius treatment of the temperature dependence of the rate constants, k_1 and k_2 of eq 2.

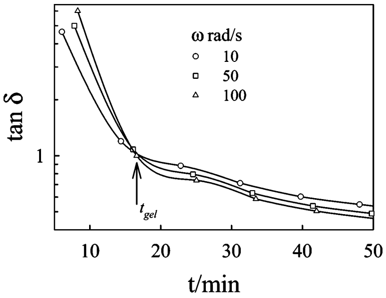

Figure 9. Time dependence of tan δ at different constant shear frequencies. The arrow shows the value of $t_{\rm gel}$.

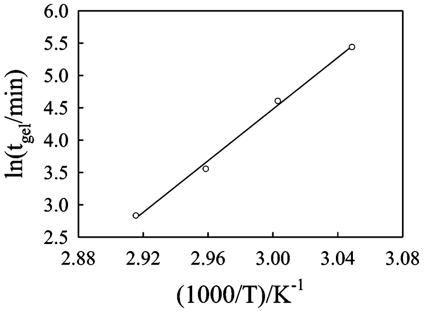

Figure 10. Dependence of $t_{\rm gel}$ on the absolute inverse temperature, *1/T* of the gelation process.

Figure 9 shows time dependence of tan δ at 70 °C and different constant shear frequencies. One can see that tan δ is frequency independent at $t_{\rm gel} = 17$ min, indicating that the system has reached the gel point and the cluster of the fractal gel is macroscopically percolated in good agreement with Winter−Chambon criterion.[19−21] To confirm the validity and accuracy of the $E_{\rm a}$ of the gelation process already discussed, we evaluated $E_{\rm a}$ of the gelation using the following equation:

$$\ln(t_{\rm gel}) = {\rm constant} + \frac{E_{\rm a}}{RT} \qquad (5)$$

From the slope of the linear relationship between $\ln(t_{\rm gel})$ and the inverse of absolute temperature (Figure 10) we found the apparent activation energy of the gelation process to be $E_{\rm a} =$ 125 kJ/mol and in good agreement with the values obtained earlier.

Isoconversional Method. On the basis of the isoconversional or *model-free* method, the gelation kinetics can be described by the following equation:[49−52]

$$g(\beta) = A \exp(-E_\beta/RT)t_\beta \qquad (6)$$

where $g(\beta)$ is the integral reaction model, E_β is the activation energy at constant value of conversion and A is the preexponential factor. Taking the natural logarithm of the above equation yields

$$-\ln t_\beta = \ln\left(\frac{A}{g(\beta)}\right) - \frac{E_\beta}{RT} \qquad (7)$$

From the slope of the linear relationship of $-\ln t_\beta$ vs $1/T$ one can evaluate E_β at different values of β as shown in Figure 11. Clearly, all curves have approximately constant slope and the calculated value of activation energy is approximately constant regardless of the degree of conversion; i.e., $E_\beta = 120 \pm 3$ kJ/mol, indicating that the rate of gelation is controlled by a single step (homogeneous) process with no change in the fractal gel or aggregation mechanism at different degree of conversions.

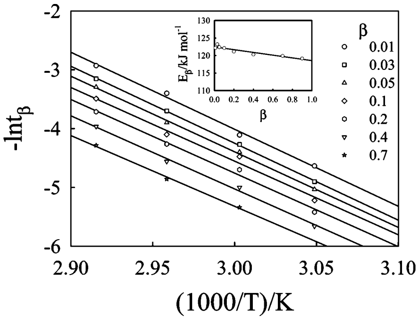

Figure 11. Isoconversional plots for the gelation process of PUD (40 wt % PU) as functions of the degree of conversion. The inset-plot shows the variation of the activation energy with the degree of conversion.

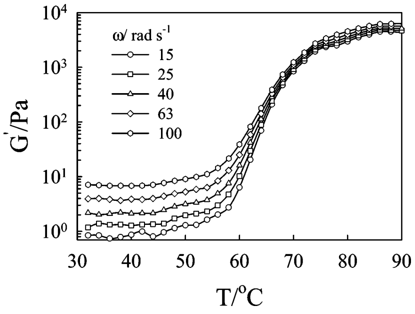

Figure 12. Temperature dependence of dynamic storage modulus, G', at different constant shear frequencies and 2 °C/min heating rate.

This is an interesting result that is in good agreement with the curing kinetics of diglycidyl ether of bisphenol A with *m*-phenylenediamine with nonstoichiometeric ratio studied recently using DSC by Sbirrazzuoli et al.[50] The authors just mentioned reported that the variation of the activation energy with degree of conversion is mainly dependent on the stoichiometeric ratio of the reactants. For nonstoichiometeric system they showed that the activation energy is almost constant and independent of the extent of conversion as in the present PUD system.[50] However, the activation energy decreased strongly with increasing degree of conversion for stoichiometeric system.[50] Very recently, Khawam et al.[52] reported that the variation of activation energy with degree of conversion could be real or artifactual. A true variation in activation energy is one that occurs because of the inherent complexity of the solid sample, which includes different reactivity of individual particles due to the particle size variations or crystal imperfections. Artifactual variations arise from the kinetics calculation methods employed. Khawam et al. suggested that care should be taken when interpreting kinetic results from isoconversional methods, if the variation in activation energy is artifactual, this variation can lead to a false mechanistic conclusion about a reaction being complex while, in fact it is not.[52] To avoid this problem in our study, we performed our analysis on results obtained from carefully controlled replicated experiments, allowing reliable averaged kinetic parameters to be obtained with correlation coefficient better than 98% as already discussed.

Non-Isothermal Gelation Kinetics. By heating the PUD, the viscoelastic material functions dramatically changed as a result of the formation of fractal gel. Figure 12 demonstrates the temperature dependence of the dynamic storage modulus, G', for 40 wt % PUD at 2 °C/min heating-rate and different constant shear frequencies. Clearly, the value of G' is almost constant with increasing temperature at a temperature range lower than the gel temperature (i.e., $T < 60$ °*C*). A sudden increase in the G' (several orders of magnitude, dependent on the values of applied shear frequency) at about 60 °C (onset

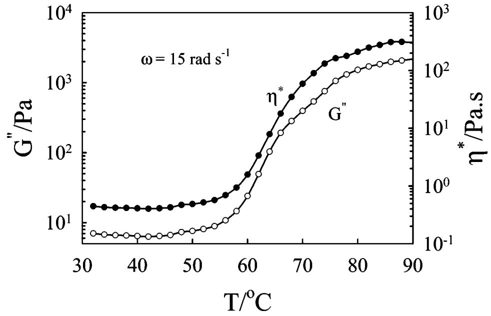

Figure 13. Dynamic loss modulus, G'', and dynamic shear viscosity, η^*, as a function of temperature (2 °C/min) and 15 rad s^{-1} shear frequency.

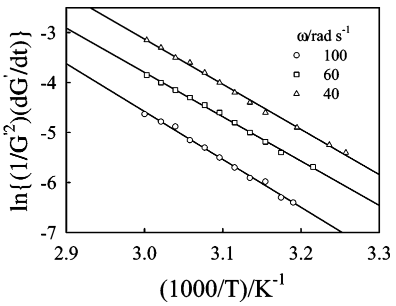

Figure 14. Arrhenius-type plot for the change of G' during the nonisothermal gelation of PUD, assuming a second-order reaction kinetics.

temperature for gelation, T_{onset}) was observed at all values of frequencies due to the onset of the formation of fractal gel. The magnitude of the elevation in G' increases greatly with increasing temperature due to the evolution of the gelation process and the significant increase in branching (formation of fractal gel). In addition G' is no longer frequency dependent at the high-temperature range due to the formation of an equilibrium storage modulus, G_{eq}', which is a typical criterion for the formation of an elastic fractal gel. An abrupt increase in the loss modulus, G'', and dynamic shear viscosity, η^* , was also detected at the onset of the gelation process, as shown in Figure 13.

Nonisothermal reaction kinetics was described as functions of time, temperature and concentration by a model proposed by Swartzel et al.[60,61] This model was developed to include the classical rate equation, the Arrhenius equation, and the time−temperature relationships according to the following equation:[38,62]

$$\ln\left(\frac{1}{G'^n}\frac{\mathrm{d}G'}{\mathrm{d}t}\right) = \ln k_o - \left(\frac{E_a}{RT}\right) \tag{8}$$

The gelation process is a second-order reaction as we found in the previous section ($n+m = 2$); therefore we replaced n in eq 8 by 2, and consequently the apparent activation energy can be obtained from the following relationship:

$$\ln\left(\frac{1}{G'^2}\frac{\mathrm{d}G'}{\mathrm{d}t}\right) vs \frac{1}{T} \tag{9}$$

The E_a determined from the slope of this relation was found to be frequency independent and equal to 125 kJ/mol, in very good agreement with the value obtained isothermally from the temperature dependence of t_{gel}; and also in reasonable agreement with the values obtained from the slopes of the two plots in Figure 8 (i.e., $E_a = 129$ and 125 kJ/mol). Figure 14 shows clear straight lines with identical slopes regardless of the values of shear frequency.

Conclusions

Isothermal and nonisothermal kinetics of thermally activated gelation reaction of PUD was investigated for the first time rheologically over a wide range of temperatures and gelation time. The viscoelastic material functions, G', G'' and η^* were evaluated isothermally at several constant temperatures (70, 65, 60, and 55 °C) and nonisothermally at 2 °C/min heating rate in the temperature range of 30−90 °C. These material functions abruptly changed at the onset of the gelation process, i.e., a dramatic increase in G', G'', and η^*. The model of Malkin and Kulichikhin, which was proposed originally for the isothermal curing kinetics of thermosetting polymers measured by differential scanning calorimetery (DSC), worked very well in describing the isothermal rheological kinetics of the present polyurethane dispersion system. The reaction rate was found to be second-order regardless of the change in temperature, in good agreement with literature data. In addition, the isothermal kinetics analysis of the gelation process was studied based on the *model-free* isoconversional method. The activation energy was found to be constant regardless of the extent of the degree of conversion, indicating that the gelation process is controlled by a single step (homogeneous) process with no change in the fractal gel formation or aggregation mechanism. The temperature dependence of the rate constants was found to be well described by the Arrhenius relationship with an apparent activation energy equal to 127 ± 2 kJ/mol, in reasonable agreement with the value (125 kJ/mol) obtained from the temperature dependence of the gel time, t_{gel}. The nonisothermal kinetics reaction rate was well described by a model proposed by Swartzel et al. that was originally developed to include the classical rate equation, the Arrhenius equation and the time−temperature relationships. Under nonisothermal condition, the apparent activation energy was found to be frequency independent and equal to 125 kJ/mol, in excellent agreement with the value obtained isothermally from the temperature dependence of t_{gel}. In some aspects, the foregoing results are similar to those from other cross-linking polymer networks and gels, yet in very important ways the present aqueous PUD system is quite unique and little studied. Therefore, this work may stimulate development of a new theory that explicitly takes into account direct coupling of the rate of gel structure formation with gelation concept for aqueous PUDs and other related water-soluble polymers undergoing high deformation flows under both isothermal and nonisothermal condition.

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