Ultrasonic Investigation of Polyurethane Gel Forming Systems

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Received August 24, 1998; Revised Manuscript Received January 29, 1999

ABSTRACT: Polyurethane systems corresponding to different reaction extents of the gelation process are investigated by ultrasonic methods in order to apprehend their high-frequency dynamical properties and their evolution during formation. The longitudinal moduli M calculated from the measurement of the longitudinal velocity and absorption exhibit a relaxation behavior which is attributed to the α process. The results are analyzed by comparison with low-frequency rheological data, allowing a more complete description of this relaxation by the Tamman−Vogel−Hesse−Fulcher equation. As moduli M are obtained versus temperature at a single frequency, data are treated by a transformed Havriliak−Negami function. The α relaxation process probed by ultrasonics is larger than the rheological one, which has been interpreted in terms of the influence of a secondary relaxation merging at high temperature.

I. Introduction

In gel forming systems, two main transitions can occur during the growth process: the sol−gel transition,[1] which is a transition of connectivity, and the vitrification[2] process associated with chain mobility. The gelation occurs through the growth of branched polymer units. As the reaction proceeds, the viscosity increases and diverges for a critical reaction extent at which an infinite cluster is formed and a static elastic modulus appears. The increase of connectivity leads also to a decrease in mobility and thus to an increase of the glass transition temperature. These two aspects have been studied using ultrasonic methods in some polymers.[3−6] While the vitrification process is clearly pointed out by ultrasonic measurement,[7] the sol−gel transition passes without any particular incidence on the velocity and absorption.

In the general frame of the study of the structure−mechanical properties relationships of polymers, polyurethane systems (PU) are of special interest because of their well-known chemistry and so can be considered as model systems. On the basis of trifunctional poly(propylene glycol)triol and difunctional hexamethylene diisocyanate, they lead to tridimensional networks. Four relaxation processes have already been reported in PU systems: the normal mode which characterizes the conformational relaxation of the molecular backbone, the α relaxation which characterizes segmental motion, and two sub-glass relaxation processes β and γ. These relaxations have been pointed out by different experimental techniques such as mechanical,[7] dielectrical,[8] and optical[9] methods in polyurethane. We focused in this paper on the dynamics of α relaxation, a phenomenon related to glass transition, involving polymer chain units and resulting in cooperative movements. In a previous work[9] it has been shown on a single system that ultrasonic methods associated with rheology allow a complete and a better description of the α relaxation. The relaxation times associated with this process follow a so-called Tamman−Vogel−Hesse−Fulcher (TVHF)[11] law. However, only relative values were determined, leading to some uncertainties. In the present study, both velocity and absorption obtained for all samples are absolute values, allowing a better comparison between low and high frequency. It is therefore interesting to study the evolution of these dynamics with the reaction extent from the starting materials to the fully cured polyurethane. It is further interesting to see how the prepolymer influences the dynamics of the final material. With this aim, several samples are prepared corresponding to different steps of the gel formation. The influence of cross-link density on α relaxation dynamics is investigated using different molecular masses of the prepolymer.

As these samples are very attenuative media, the measurements have been carried out at a single frequency but at a very large temperature range. To get information on the evolution of the relaxation time distribution, the data have been analyzed using the Havriliak−Negami empirical function in the temperature domain.

II. Experimental Section

Samples. Polyurethane (PU) systems were formed by condensation of a prepolymer poly(propylene glycol) triol with hexamethylene diisocyanate (HMDI). The reaction catalyzed by dibutyltin dilaurate leads to a tridimensionnal network. To study the system dynamics during its formation, quenched samples corresponding to different steps of the reaction were prepared at various initial stoichiometric ratios $r = 0$, 0.2, 0.4, 0.6, 0.8, and 1 defined as the initial relative concentration of NCO groups to OH groups:

$$r = [\mathrm{NCO}]_{\mathrm{initial}}/[\mathrm{OH}]_{\mathrm{initial}} \quad (1)$$

while the reaction extent p, representing the rate of formed links, is defined as

$$p = [\mathrm{NCO}]_{\mathrm{reacted}}/[\mathrm{NCO}]_{\mathrm{initial}} \quad (2)$$

For all samples, the reaction was carried out at 25 °C for 24 h until complete comsumption of NCO groups ($p = 1$). To understand the influence of molecular size on dynamics properties, three different molar masses are used for precursors: 260, 720, and 6000 g/mol. A gel is obtained for $r \geq 0.569$ in the case of systems based on triol 260 and 720 and $r \geq 0.76$ for the triol 6000. The critical stoichiometries have been

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10.1021/ma981324z CCC: $18.00

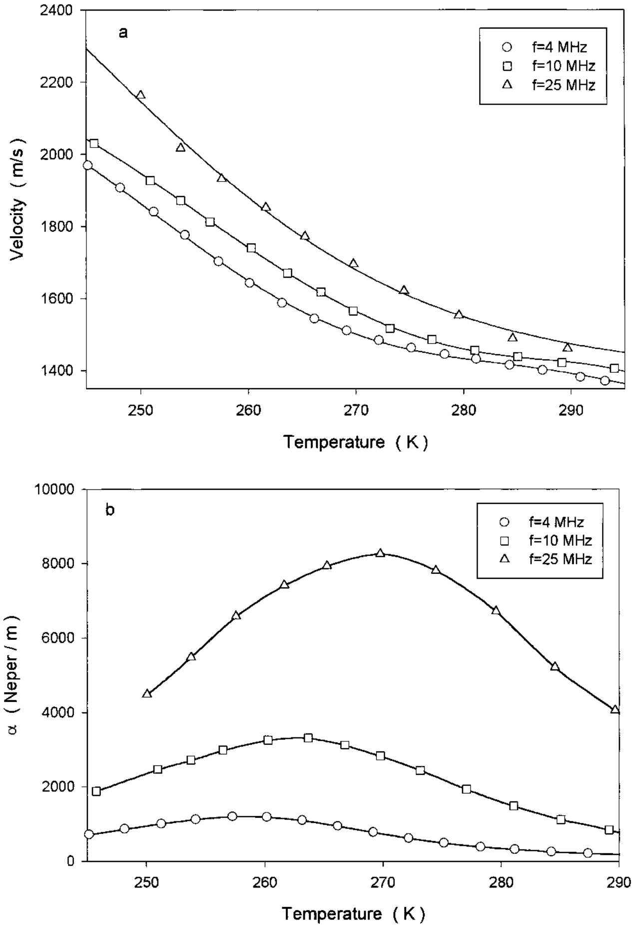

Figure 1. (a) Evolution of ultrasonic velocity versus temperature for different frequencies in pure triol720 system. (b) Evolution of absorption α versus temperature for different frequencies in pure triol720 system.

determined experimentally using the solubility criterion. The observed deviation from Flory–Stockmayer prediction is due to the average functionality of the triols, which is not exactly equal to 3, and also to the cyclization effect.

Ultrasonic Device. Ultrasonic measurements were done at fixed frequency using burst waves generated by a Matec MBS8000 system. Experiments were performed at 2.5 MHz for shear waves and at 4 and 2.5 MHz for longitudinal waves with Krautkramer transducers. The measurements were made using a signal transmission method: a PU sample of about 1.5 mm thickness was formed between two stainless steal buffers stuck to transducers. This setup allows a good acoustical coupling. The measurements were performed in the temperature range −60 to 80 °C using a thermostatic bath with an accuracy of ±0.1 °C. At each temperature velocity and absorption were determined by comparison of transit time and amplitude of the signal to those of a reference liquid (methanol) whose ultrasonic properties are well-known. This method enabled us to determine absolute values of velocity v and absorption α in the studied material.

III. Results and Discussion

A. Polyurethane Systems: Triol720/HMDI. The system triol720/HMDI has been first studied for $r = 0$ (pure triol) and $r = 1$ (stoichiometric ratio) and also during cure, that is to say, as a function of time from $p = 0$ to $p = 1$ at different temperatures.

For pure triol, the evolution of ultrasonic velocity and absorption coefficient α/f^2 versus temperature is given Figure 1a,b for three frequencies (4, 10, and 25 MHz). The absorption α increases with frequency and makes ultrasonic measurements difficult to perform. Hence, it is more convenient to realize low-frequency measurements as a function of temperature and to apply the temperature–frequency equivalence principle.

The relaxation behavior appears in the evolution of α_L/f^2 as a maximum while velocity increases nonlinearly. However, a comparison with low-frequency rheological data needs the determination of the high-frequency moduli (shear and longitudinal) which take into account both velocity and absorption:[12]

$$M' \approx \rho v_L^{\,2} \quad \text{and} \quad G' \approx \rho v_T^{\,2}$$

$$M'' \approx 2\rho v_L^{\,3}(\alpha_L/\omega) \quad \text{and} \quad G'' \approx 2\rho v_L^{\,3}(\alpha_T/\omega) \qquad (3)$$

assuming that $\alpha_L v_L/\omega \ll 1$ and $\alpha_T v_T/\omega \ll 1$, which is verified experimentally for PU.

For relaxation time determination, it has been established that it is not correct to take the maximum of α_L/f^2 peak versus T at different frequencies. Due to the nonnegligible velocity dispersion the peak of M'' is shifted to lower temperature by 9 K compared to α_L/f^2.

The longitudinal modulus M is related to the shear, G, and Young, E, moduli by[2]

$$M = K + {}^4/_3 G \qquad (4)$$

and[14]

$$E = \frac{9GK}{G + 3K} \qquad (5)$$

where K is the bulk modulus.

Do these moduli reveal the same relaxation process with identical relaxation time and distribution? The answer is not obvious. Experiments have been carried out on PU system at $r = 1$ using both rheological measurements giving shear modulus[7] and Young modulus[9,13] and ultrasonics at different temperatures. The imaginary part of the moduli exhibits a maximum. This behavior is characteristic of a relaxation that in the case of ultrasonic and rheology is attributed to α relaxation as it will be shown later. The temperature at which the maximum is reached is noticed T_α.

The determination of the shear velocity and absorption enables the calculation of G' and G''. However, shear waves do not propagate well in liquids, and the ultrasonic signal is very weak, especially in the rubbery state, in which case the detection of the maximum of α_T/f^2 is not possible as has been pointed out by Piché et al.[15] It is also difficult to find a reference liquid with well-known α_T and v_T so that only absolute values for velocity are obtained at a frequency of 2 MHz. Longitudinal and shear velocities are compared at the same frequency Figure 2. A vertical shift (Figure 2, inset) of 1100 m/s leads to the superposition of both v_L and v_T. As velocity is directly related to moduli M' and G' (4), one can conclude that the same relaxation process is probed by the two moduli. Knowing G' and M', the bulk modulus K' has been calculated assuming that G' and M' exhibit the same behavior. Figure 3 shows that out of the relaxational range, above T_α, G' vanishes, exhibiting a liquidlike behavior and $K' \sim M'$.

The comparison is also made between G and E moduli at low frequency. The first one is obtained with Rheometrics RDA II and the second using DMTA. Master curves at the same reference temperature are compared

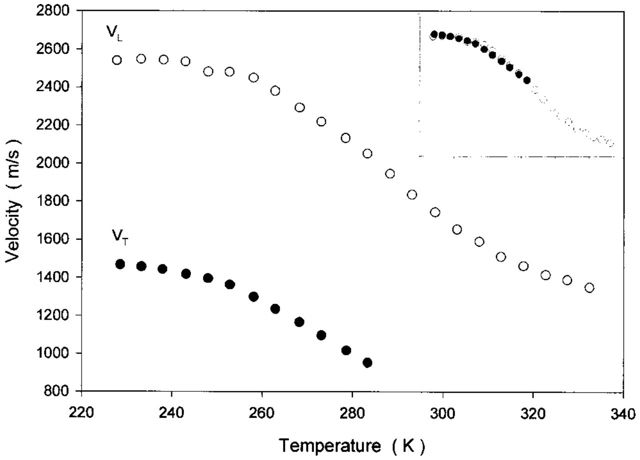

Figure 2. Longitudinal (open symbols) and shear (filled symbol) velocity versus temperature in the system triol-720/HMDI, $r = 1$ obtained at $f = 2.5$ MHz. A vertical shift of v_T on v_L is shown in the enclosed graph.

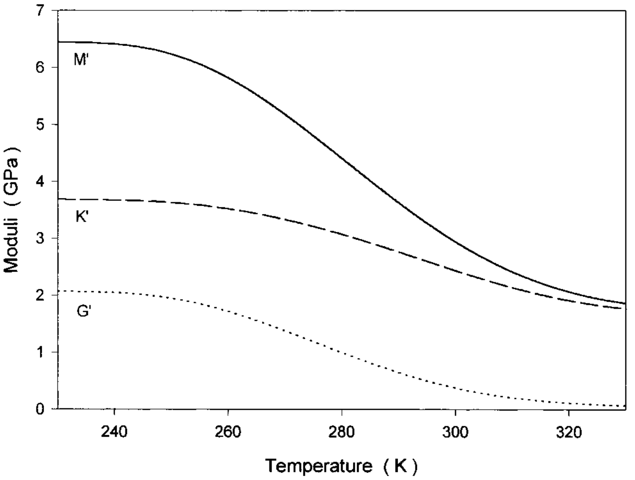

Figure 3. Evolution of the calculated longitudinal M', bulk K', and shear G' moduli versus temperature for the system triol720/HMDI, $r = 1$ at 2.5 MHz.

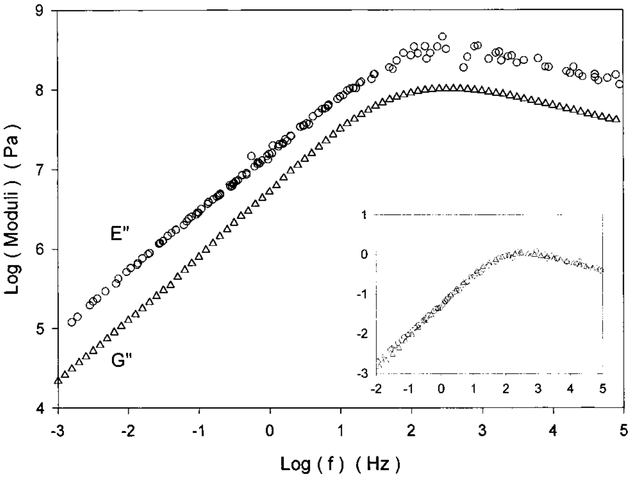

Figure 4. Frequency behavior (master plots) of rheological Young E'' and shear G'' moduli for the system triol720/HMDI ($r = 1$). The normalization by moduli maxima is shown in the enclosed graph.

in Figure 4. A vertical normalization (Figure 4, inset) shows that both moduli have the same relaxation process.

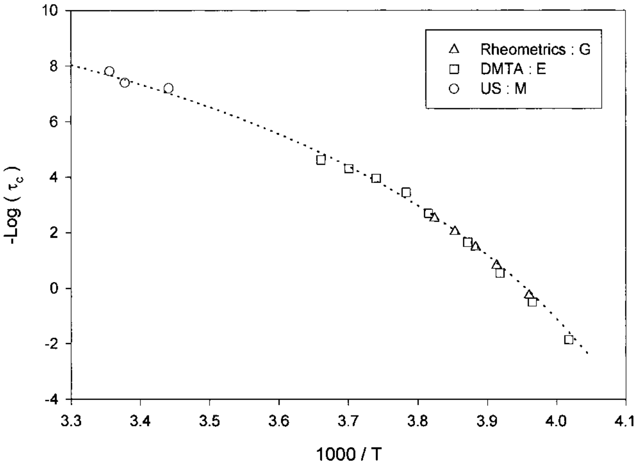

Figure 5. Arrhenius plot of characteristic relaxation times obtained from mechanical moduli M (longitudinal), E (Young), and G (shear) in $r = 1$ triol720/HMDI system. The dotted line represents a fit to TVHF equation.

For rheological data, the characteristic relaxation time corresponds to the maximum of the loss modulus versus frequency. However, ultrasonic measurements have been performed at a single frequency versus temperature, and then the relaxation time corresponding to T_α is defined by $\tau_c = 1/2\pi f$, where f is the experimental frequency.

Characteristic relaxation times obtained by rheology (G and E) and ultrasonics (M) are presented in an Arrhenius plot (Figure 5) for PU at $r = 1$. These times follow a Tamman–Vogel–Hesse–Fulcher law (TVHF) given by[11]

$$\tau = \tau_0 \exp\left[\frac{B}{T - T_0}\right] \tag{6}$$

In this expression, B represents an apparent activation energy, T_0 the temperature for which all movements are frozen, and τ_0 a relaxation time at very high temperature. This behavior is characteristic of α relaxation where the movements are not simply obtained by jump of energy barrier but are cooperative motions.[16] A fit of the experimental data gives $T_0 = 214$ K, $B = 1320$, and $\tau_0 = 2.4 \times 10^{-15}$ s. These results are quite different from those obtained in an earlier study[9] ($B = 1009$, $T_0 = 220$ K, and $\tau_0 = 8.3 \times 10^{-14}$ s) where only relative values of ultrasonic absorption were accessible, resulting in an uncertainty in the values of M_∞ and M_0.

B. Gel Formation of Polyurethane Based on Triol720. (*i*) *Kinetics of Cure.* The best way to study the evolution of the α relaxation during cure is to determine in a large frequency range the ultrasonic velocity and absorption at an appropriate temperature. An example obtained at frequency 2 MHz is presented Figure 6. Both parameters present a continuous increase with time of cure and a plateau when the gel is formed. No accident occurs at the sol–gel transition threshold, and then it is possible to say that the ultrasonic technique is only sensitive to molecular structure changes (hardening) related to gelation. However, when the material undergoes a vitrification process, the absorption α/f^2 exhibits a maximum[10] when the temperature T_α becomes greater than the temperature of cure.

An increase of v_L and α_L leads to an increase of M' and M''. Unfortunately, for all the reasons reported

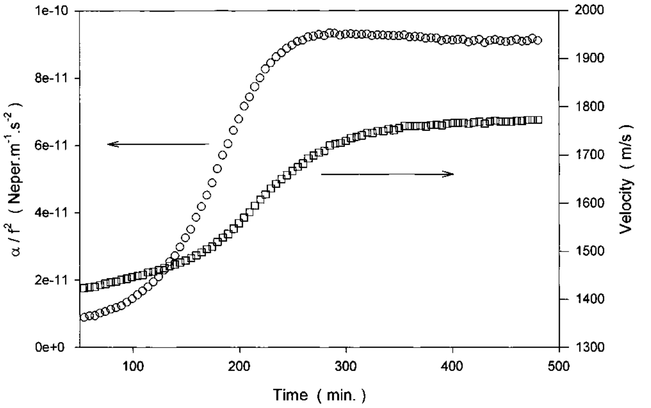

Figure 6. Evolution of ultrasonic absorption coefficient α/f^2 and velocity v_L during PU (triol720/HMDI) cure at $f = 2.5$ MHz.

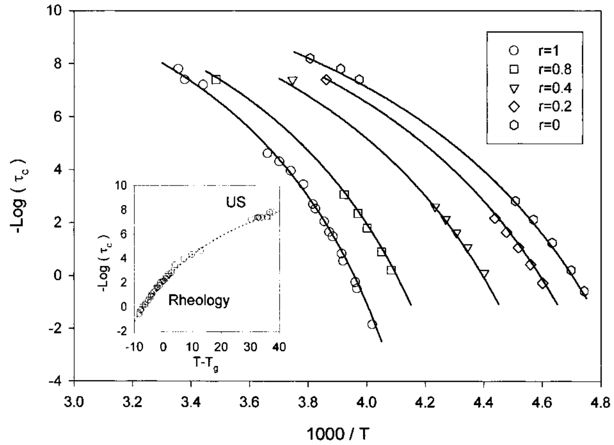

Figure 7. Arrhenius plot of the characteristic relaxation times obtained by rheological and ultrasonic measurements for triol720/HMDI systems at different stoichiometric ratios *r*. The solid lines represent a fit to TVHF equation. The enclosed graph represents a normalization by calorimetric T_g of the curves, and the dotted line represents a fit to the TVHF equation.

before, this cannot be done in a very large frequency range. An alternative is the study of nonstoichiometric systems representing different reaction extents of the gel formation. However, these quenched samples do not represent exactly the corresponding reaction extent. In the real system, at any stage of the reaction the concentration of the unreacted OH groups equals that of NCO groups whereas in the quenched samples no NCO groups remain. Nevertheless, in the mechanical point of view the difference is not obvious.[17]

(ii) Quenched Samples. To study the influence of connectivity on α relaxation, nonstoichiometric samples at $r = 0$, 0.2, 0.4, 0.6, 0.8, and 1 were studied as a function of temperature with ultrasonic techniques at a fixed frequency of 4 MHz using longitudinal waves. The values of M' and M'' are calculated from experimental velocity and absorption. Associated with rheological data G'' obtained in a previous work,[7] it is possible to plot TVHF curves for each value of *r* (Figure 7).

The only observed effect of connectivity on TVHF curves is the change in the value of T_0. A horizontal shift by a factor equal to the value of the calorimetric glass transition temperature (T_g) leads to the same TVHF law (Figure 7, inset). This have been verified for all values of *r*. An increase in *r* provokes an increase of T_g[18] and consequently of T_α, but the shape of $\log(\tau_c)$ versus $1000/T$ is not modified by sol–gel transition: this phenomenon appears at a higher length scale and can be probed by low-frequency measurements.[19]

In the case of PU systems the α relaxation probed can be described by a continuous distribution of relaxation times.[14] Some empirical relations exist which are used to fit more easily experimental data as the Havriliak–Negami (HN) equation[20] in the frequency domain and Kolraush–Williams–Watts in the time domain. Usually used for the analysis of dielectric data,[21] the first one has already been used in previous work[22] in the Cole–Cole form for ultrasonic frequency data and can be expressed for modulus M^* by

$$M^*(\omega) = M_0 + (M_\infty - M_0)\frac{1}{(1 + (i\omega\tau_{HN})^{\alpha})^{\beta}} \tag{7}$$

where M_0 and M_∞ are the limiting moduli at low and high frequency, respectively, and are given, in the case of ultrasonic experiments, by[2]

$$M_0 = \rho V_0^{\,2} \qquad M_\infty = \rho V_\infty^{\,2} \tag{8}$$

The HN parameters α and β represent respectively the symmetrical and asymmetrical distribution broadening of relaxation times: in a log–log frequency plot of M'', α and $-\alpha\beta$ represent respectively the low- and high-frequency slopes of the function. Ultrasonic experiments in most cases are not obtained versus frequency: in the better case a frequency study gives a maximum of 3 decades in highly attenuative medium which is not sufficient to describe a broad relaxation process. The HN function can then be adapted for the temperature domain:

$$M^*(T) = M_0(T) + [M_\infty(T) - M_0(T)]\frac{1}{(1 + (i\omega\tau_{HN})^{\alpha})^{\beta}} \tag{9}$$

The parameters α and $-\alpha\beta$ represent, in this expression, respectively the high- and low-temperature slopes of M'', centered on T_α where ω is the experimental frequency. $M_0(T)$ and $M_\infty(T)$ are obtained considering the linear evolution of the ultrasonic velocity at high and low temperature, respectively. τ_{HN} is a parameter of the HN function linked to the characteristic relaxation time by the following relation:[23]

$$\tau_{HN}(T) = \tau(T)\left[\frac{\pi}{2(\beta + 1)}\right]^{1/\alpha} \tag{10}$$

The dependence of τ with temperature is taken from the TVHF law seen below. Using the TVHF fit parameters obtained for each system, M' and M'' data have been fitted with HN function. The results are presented Figure 8a for normalized M'' and Figure 8b for M'. Only α and β are fit parameters, and the values obtained are presented in Figure 9 together with those from frequency HN analysis of rheological G'' data.[13] The distribution parameters α and αβ decrease linearly with *r*, which means a continuous broadening of the relaxation times distribution function. A difference in αβ values between rheological and ultrasonic data can be attributed to the fact that at highest frequencies (at lowest temperature) another relaxation process appears: the so-called β relaxation corresponding to polymer chain side groups motion. This process tends to merge on α process as can be seen in Figure 10, resulting in a

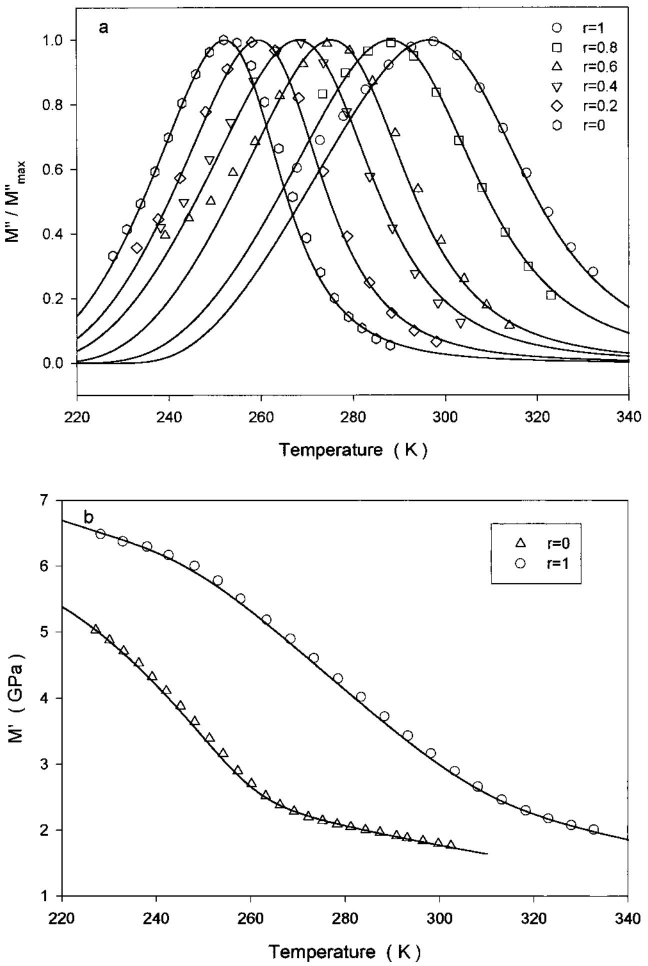

Figure 8. (a) Evolution of normalized modulus M'' versus temperature for studied polyurethane system at different stoichiometric ratios obtained by ultrasonic measurements at $f = 4$ MHz. The solid lines represent a fit to eq 9. (b) Evolution of modulus M' versus temperature for nonconnected ($r = 0$) and connected ($r = 1$) polyurethane systems triol720/HMDI obtained by ultrasonic measurements at $f = 4$ MHz. The solid lines represent a fit to eq 9.

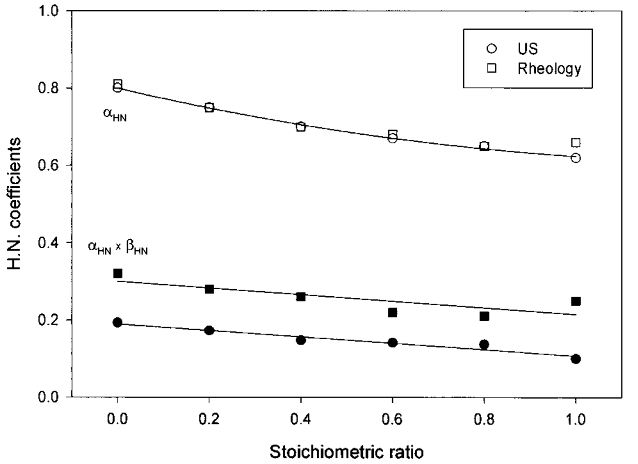

Figure 9. Havriliak–Negami coefficients α_{HN} (open symbols) and $\alpha_{HN}\beta_{HN}$ (filled symbol) versus stoichiometric ratio r, obtained by ultrasonic and rheology for triol720/HMDI systems.

less important value of the $\alpha\beta$ parameter obtained in ultrasonics compared to rheology. (In the latter case the two processes are well-separated.[9]) Rheological data have already been analyzed using the fragility concept by Böhmer et al.[24] in order to interpret the broadening, but in the case of PU gel forming system it did not give conclusive results.[7]

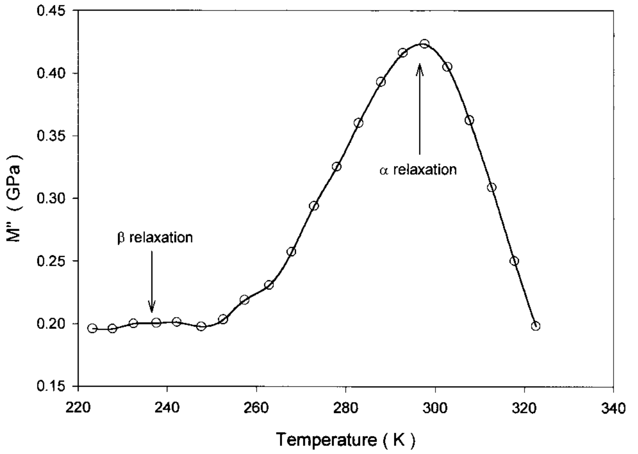

Figure 10. Evolution versus temperature of modulus M'' obtained from ultrasonic measurements at $f = 4$ MHz showing two relaxation regions in the system triol720/HMDI ($r = 1$).

Table 1

	system 260		system700		system 6000	
	α_{HN}	$\alpha_{HN}\beta_{HN}$	α_{HN}	$\alpha_{HN}\beta_{HN}$	α_{HN}	$\alpha_{HN}\beta_{HN}$
$r = 0$	0.84	0.20	0.80	0.19	0.80	0.26
$r = 0.6$	0.71	0.07	0.67	0.14	0.80	0.26

C. Influence of Prepolymer Molar Mass. Experiments has been made using ultrasonics on systems based on other triols of different molar masses—260 and 6000 g/mol—in order to apprehend the effects of chain length between cross-link points. Systems based on triol260 give similar results for characteristic relaxation times behavior than systems based on triol700 except a more important dependency of T_α on r. For systems based on triol6000, variation of r results in a weak variation of T_α which can be attributed to the low cross-link point density. However, when a correction by T_g is done, the same TVHF behavior is obtained for all systems. T_α follows then T_g variations. An interesting point is the variation of the distribution width. Figure 11 presents the normalized moduli M'' before and after the gel point. Data have been fitted using eq 9. The obtained HN coefficients are summarized in Table 1. It can be seen that the distribution width is almost the same for nonconnected systems (pure triols) but increases with r and in a more important way at low masses. For connected systems of high molar masses, the HN coefficients remain identical compared to those of $r = 0$. For system 260 and 700, the more the system is connected, the more the influence of secondary β relaxation process is important at low temperature as is shown in normalized M'' curves of Figure 11. The width value is maximum when the system is fully connected ($r = 1$). For the system based on triol6000 it can be said that the arm length is so large that connectivity has no effect on mobility and hence on the α relaxation process. When the mass of the prepolymer decreases, the cross-link density increases in connecting systems. This hypothesis can explain why the distribution width remains almost the same for the pure triols and increases weakly with connectivity for prepolymer of high molar mass.

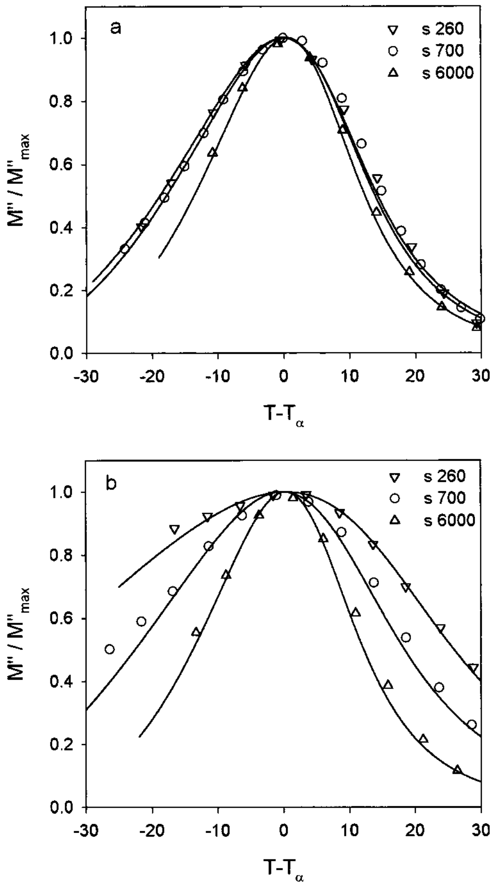

Figure 11. (a) Influence of prepolymer molecular mass (260, 700, and 6000 g/mol) on M″ width for nonconnected ($r = 0$) system. The solid lines represent a fit to eq 9. (b) Influence of prepolymer molecular mass (260, 700, and 6000 g/mol) on *M*″ width for the gelled ($r = 0.6$) system. The solid lines represent a fit to eq 9.

IV. Conclusion

Mechanical measurements at low (rheology) and high (ultrasonics) frequencies have been performed on polyurethane systems at different stoichiometric ratios representing different reaction extents in order to apprehend the evolution of the glass transition dynamics during gel formation. The longitudinal moduli *M*, calculated from the measurement of both ultrasonic velocity and absorption over a wide temperature range and at a single frequency (4 MHz), exhibit an α relaxation associated with glass transition dynamics and a β relaxation at lower temperature.

A comparison of the α relaxation of the longitudinal moduli at ultrasonic frequency with that of shear and Young moduli at low frequency shows that temperature dependence of the relaxation time is described by the same TVHF equation, implying that the same dynamics is probed in the case of polyurethane of interest. As the longitudinal moduli are obtained at a single frequency over a wide temperature range, the analysis of the relaxation time distribution is carried out using a transformed HN equation in temperature domain which is derived knowing the TVHF parameters. The distribution parameter α is found to be similar for all moduli while the parameter $\alpha\beta$ is smaller at ultrasonic frequency. This broadening is due to the overlaping of the β relaxation in contrary to low frequency where the two relaxations are well separated.

A quantitative analysis of the evolution of the α relaxation with reaction extent is reported for polyurethanes of different prepolymer molar masses. The temperature dependence is found to be independent of connectivity and molar mass of the prepolymer and hence is described by the same TVHF law with the same parameters. The only effect of connectivity is the increase of T_g which is more pronounced for systems of lower prepolymer molar mass. In terms of relaxation time distribution, a broadening with increasing connectivity is observed which is also more pronounced for systems based on prepolymers of lower molar mass. This broadening is associated with a cross-link density effect which is higher for systems of low prepolymer molar mass at a given reaction extent.

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