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A Brillouin scattering investigation of relaxation versus crosslink density in glass- and gel-forming polymers

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Abstract. A Brillouin scattering study of the relaxational processes above the calorimetric glass transition temperature T_g (in the 1.2 – $1.6 T_g$ temperature range) on polyurethane gels is presented. The specificity of this work is to investigate several samples corresponding to various crosslink densities. The relaxational process observed by Brillouin scattering is compared to low-frequency measurements of the relaxational processes by other techniques: in contrast to low-frequency determinations, the Brillouin scattering relaxation time exhibits an Arrhenius behaviour for all the samples; however, the characteristic parameter of the time distribution width is the same for the two processes. The low-frequency relaxation and the high-frequency Brillouin scattering relaxation seem to merge for temperatures higher than $1.6 T_g$ and these data are discussed on the basis of different models for the glass transition. The influence of the crosslink density yields an increase of the mean relaxation time with increasing connectivity and small variations of the apparent activation energy. In contrast, the distribution time width is not composition dependent. Nevertheless, the most striking results are that a rescaling to T_g fully accounts for the variations of the mean relaxation time with the crosslink density and a correspondence between the crosslink density and the inverse of the temperature is suggested.

1. Introduction

The relaxational processes in glass-forming liquids are the subject of extensive studies. Many investigations have been devoted to fragile liquids in Angell's classification [1], in particular to polymers. In these glass-forming liquids the relaxational behaviour is quite universal. At a crossover temperature T_c located above the glass transition temperature (typically $T_c = 1.2$ – $1.5 T_g$), there is a splitting from a high-temperature regime with a single relaxational process to two separate processes: a slow (usually called α or structural) relaxation and a fast (β) relaxation. The α relaxation is cooperative and the characteristic relaxation time is well described by the Vogel–Fulcher–Tamman–Hesse equation:

$$\tau = \tau_0 \exp \frac{DT_0}{T - T_0} \quad (1)$$

where τ is the relaxation time, τ_0 is the relaxation time in the high-temperature limit and T_0 is the temperature where τ diverges. D is a coefficient related to the degree of fragility of the liquid. The so-called β relaxation time has an Arrhenius temperature dependence.

Depending on the experimental technique, the measurements can be sensitive to one or the other of the two processes (or to both). While this general behaviour is well established, the comparison of the times measured by different techniques as well as the interpretation and modelling of these relaxational processes are much debated.

On the one hand several authors among polymer scientists attribute the α relaxation to intermolecular interactions involving reorientations of several monomers whereas the β relaxation is considered to be due to the intramolecular (side-group or end-group) rotations [2, 3]. In other fragile liquids the bifurcation between the two relaxational processes has been attributed to decoupling between diffusion and vibration [4]. On the other hand several models have attempted to describe this universal behaviour in a more general framework. The most discussed models are some based on an analogy with spin-glasses [5, 6] and the so-called 'mode-coupling theory' [7]. Other approaches have been proposed introducing coupling between primary relaxing entities [8]. A review of the classical approaches in oxide glasses has been made by Scherer [9]. More specific models for organic and polymer glasses can be found in the article by Rössler and Sillescu [10].

The relaxational processes in glass-forming liquids have been investigated using numerous experimental techniques. Inelastic light scattering is a useful technique to probe these processes in the 10^{-8} – 10^{-12} s range. The first studies of structural relaxations on polymers in the liquid phase by Brillouin scattering made use of only the information contained in the position and width of the Brillouin component [11–16]. Moreover, most authors made the assumption that the Brillouin shift is large compared to the width of the Brillouin peak, which is correct only far from the coupling regions. More recent investigations in propylene carbonates have shown that more information can be deduced from a complete fit of the Brillouin profile [17]. However, in all these studies the longitudinal Brillouin line gives evidence of an Arrhenius process which deviates from the α relaxation related to the glass transition and measured at temperatures higher than T_g by very different techniques such as ultrasonic measurements, photon counting spectroscopy, dynamical mechanical thermal analysis, dielectric measurements or inelastic neutron scattering. Depending on the experimental technique, either the frequency space or the time space is probed. The description of these relaxations involves several models corresponding to time distributions or stretched exponentials. The characteristic parameter of the stretched exponential can be related to the parameter of the time distribution [18].

The aim of most of the studies of the relaxations is to test the variations with temperature of the parameters of the time distribution and to give a microscopic interpretation of the origin of the relaxational processes. The gel-forming polymers are of particular interest because changing the composition allows us to change the connectivity. Very few studies concern the light scattering in polymer gels [19, 14, 20]. None of these studies takes into account the full information contained in the spectra.

In this paper, we present a study on polyurethane gels by Brillouin scattering. The polyurethane networks were formed by condensation of polyoxypropylated triol and hexamethylene diisocyanate. The resulting population of molecules is widely polydisperse and has a mean average molecular weight which tends to infinity at a particular stage of the connectivity, i.e. the gel point. Further above this critical point, there exists a giant cluster called the gel fraction whose size is limited by the size of the container. With increasing reaction extent, the gel fraction continues to grow by reaction with molecules belonging to the sol phase. In addition, as in most polymers such a system exhibits a glass transition when the temperature decreases, and, of course, the glass transition temperature increases with the degree of crosslinking. Many papers have shown that the gelation transition is well described by a percolation model [21–24]. This model explains the behaviour only

very close to the gel point.

The study of the Brillouin spectra of these samples as a function of the temperature gives a determination of a relaxation time that we compare to measurements performed on the same materials in another frequency range. Polyurethane gels are good candidates to test the predictions of the models because they present the particular interest of being one of the most fragile glass-forming liquids in Angell's classification [25]. The study of the glass transition in a series of samples where the connectivity can be controlled by varying the ratio of the two components is particularly interesting for the future understanding of the microscopic origin of the relaxational processes.

The paper is organized as follows: experimental details are developed in section 2, section 3 presents a qualitative and quantitative analysis of the spectra, the influence of temperature is discussed in section 4 and section 5 examines the influence of the connectivity.

2. Experimental details

2.1. Samples

The polyurethane samples were formed by condensation of dried polyoxypropylene triol with hexamethylene diisocyanate [26] in various proportions defined by the stoichiometric ratio

$$r = [\text{NCO}]/[\text{OH}] \quad (2)$$

with [NCO] and [OH] the respective concentrations of NCO and OH groups. We studied samples where the OH groups are in excess, corresponding to $r \leq 1$.



The reaction was carried out at 313 K with a catalyst until there was complete consumption of the NCO groups. After about 2 days unreacted NCO groups cannot be detected by infrared spectroscopy. The fraction of OH groups which have reacted with NCO groups (which are involved in permanent urethane bonds) is then equal to r .

The critical value of r at which a gelation transition takes place is $r_c \approx 0.56$ [23].

2.2. Measurements

The Brillouin scattering measurements were performed with a six-pass tandem Fabry-Pérot interferometer constructed following Sandercock's design [27]. The light source was a Spectra-physics 2060 argon-ion laser operating at 514.5 nm. The power on the sample was about 100 mW. The free spectral range was adjusted by changing the thickness e of the Fabry-Pérot interferometer: $e = 7.5$ or 10 mm, corresponding to a free spectral range of 20 GHz or 15 GHz, respectively. The resolution was about 150 MHz or 100 MHz, respectively, and the contrast about 10^9 – 10^{10} . The advantage of the 'Sandercock interferometer' is that the spectra are undistorted by neighbouring interference orders. Spectra were recorded in the backscattering geometry and in the right-angle scattering geometry. In this latter configuration the aperture of the collection lens induces a broadening of the Brillouin line of the same order of magnitude as the resolution. The incident light was polarized perpendicular to the scattering plane (vertically). We measured the part of the spectra due to scattered light of the same polarization (VV):

$$I_{\text{VV}} = I_{\text{iso}} + \frac{4}{3} I_{\text{ani}} \quad (3)$$

where

$$I_{\text{ani}} = I_{\text{VH}}.$$

I_{ani} is the intensity of the light scattered from the anisotropic part of the polarizability tensor and I_{iso} the light scattered from the isotropic part. I_{ani} contains scattering-angle-independent contributions such as contributions from molecular orientational motions and second-order dipole–dipole induced scattering. It also contains a depolarized scattering-angle-dependent contribution arising from shear waves.

The anisotropic signal was found to be negligible in these samples in the temperature range of the investigations. The Brillouin component in the VV polarization is related to the elastic modulus:

$$M = K + \frac{4}{3}G \quad (4)$$

where M is the ‘longitudinal’ modulus, G the shear modulus and K the compressibility modulus.

The measurements were made at room temperature for eight samples with different stoichiometric ratios from $r = 0$ (triol) to $r = 1$.

Table 1. The calorimetric glass transition temperature T_g (K) determined by DSC for the four polyurethane samples studied as a function of temperature and characterized by their stoichiometric ratio r .

r	0	0.3	0.5	1
T_g (K)	213	232	238	257

The calorimetric glass transition temperature T_g is about 210–260 K (see table 1) [28]. T_g increases slightly with r . In order to investigate relaxations at temperatures higher than the glass transition, in the 1.2–1.6 T_g range, the measurements were performed from room temperature to about 373 K for four samples ($r = 0$, $r = 0.3$, $r = 0.5$ and $r = 1$) in a small oven with a proportional regulation. The range of investigated temperatures is limited due to a degradation of the samples at temperatures higher than 373 K.

3. Qualitative and quantitative analysis of the spectra

The longitudinal Brillouin component is due to the compressibility of the sample. As a matter of fact, the low-frequency data show that in these samples the shear modulus is much smaller than the compressibility modulus ($K/G > 30$) [25], so that $M \approx K$.

The profile of the Brillouin peaks of the spectra shown in figure 1(a) is clearly asymmetric, which is characteristic of relaxational processes. If the temperature is increased, the profile of the spectra becomes more asymmetric and the Brillouin shift decreases (figure 1(b)). In principle, an order of magnitude of the relaxation time can be deduced using

$$\tau = 1/\omega_{\text{max}} \quad (5)$$

where ω_{max} is the angular frequency of the Brillouin peak at the temperature for which the width of the Brillouin peak is maximum. The relaxation time τ obtained this way gives an order of magnitude for τ , useful for the fitting procedure (typically $\tau \approx 10^{-11}$ s). For most of the samples studied here, the maximum width is not reached in the investigated temperature range. However, the times deduced using the width at the highest investigated

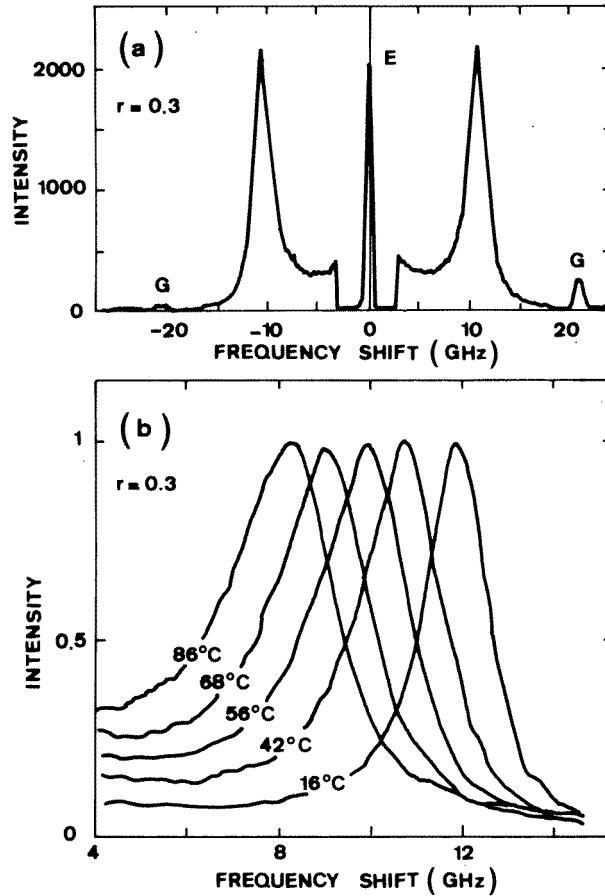


Figure 1. (a) An example of Brillouin spectra (the intensity is in arbitrary units) for sample $r = 0.3$ at 42°C in backscattering geometry (thickness of the interferometer $e = 7.5$ mm). The peaks labelled G are 'ghosts' due to the tandem interferometer. The ghosts G and the elastic signal E are attenuated by a factor of 10^5 . Moreover, in the figure, the elastic signal is also divided by 200. (b) The evolution with increasing temperature of the Brillouin signal for $r = 0.3$ from 16 to 86°C (in backscattering geometry). The spectra are normalized to their maximum intensity value.

temperature—which is not too far from the maximum width—are in good agreement with the values obtained from the fits and predict that τ increases with increasing stoichiometric ratio r .

The dynamical structure factor $S(q, \omega)$ of a general linearized hydrodynamic theory including non-exponential relaxation is fitted to the complete spectrum. Non-exponential relaxation is allowed through the introduction of a Cole–Davidson relaxation function using the relation

$$M^* = M_\infty - (M_\infty - M_0)/(1 + i\omega\tau_{\text{CD}})^{\beta_{\text{CD}}} \quad (6)$$

where M^* is the complex longitudinal modulus, M_∞ and M_0 are the limiting high- and low-frequency values of the longitudinal modulus, $M_\infty - M_0$ is characteristic of the amplitude of the relaxation, τ_{CD} is a relaxation time and β_{CD} is a parameter of the Cole–Davidson

distribution function.

The frequency-dependent Cole–Davidson relaxation function

$$\phi(\omega) = 1/[1 + i\omega\tau_{\text{CD}}]^{\beta_{\text{CD}}} \quad (7)$$

is identical to the more general Havriliak–Negami relaxation function [29]

$$\phi(\omega) = 1/[1 + (i\omega\tau_{\text{HN}})^{\alpha_{\text{HN}}}]^{\gamma_{\text{HN}}} \quad (8)$$

in the case of $\alpha_{\text{HN}} = 1$ and $\gamma_{\text{HN}} = \beta_{\text{CD}}$. This function is widely used for the analysis of dielectric measurements [30]. This relaxation function presents the drawback of introducing one more parameter, necessary if the frequency range of the study is wide. The extra parameter is not needed in the narrow frequency range studied here.

The Cole–Davidson distribution function can be related to the time-dependent stretched exponential (Williams–Watt) relaxation function:

$$\phi(t) = \exp[-(t/\tau_{\text{WW}})^{\beta_{\text{WW}}}] \quad (9)$$

through empirical relationships [18, 31].

We performed a conventional non-linear least-squares fitting procedure of the convolution of the experimentally determined instrumental function with the following theoretical expression, deduced from the hydrodynamics equations neglecting the thermal fluctuations [32, 33].

$$S(q, \omega) = (I_0/\omega)\text{Im}[(M^*q^2/\rho - \omega^2)^{-1}] \quad (10)$$

where ρ is the density of the sample and formula (6) is used for the complex longitudinal modulus. The adjustable parameters of this fitting procedure are the high-frequency limit sound velocity $V_\infty = \sqrt{M_\infty/\rho}$, the relaxation times τ_{CD} , the parameter β_{CD} characteristic of the width of the distribution, an arbitrary intensity scaling factor, a background parameter and the high- and low-frequency limit sound velocities V_∞ and V_0 . In order to reduce the number of parameters and to obtain a better determination of V_∞ , we used the value of V_0 determined independently: the ultrasonic measurements at a few megahertz show that $V_0 = \sqrt{M_0/\rho}$ follows a linear temperature dependence [34]. In the temperature range of investigation the relative variations of V_0 for one sample are of about 20%. The ultrasonic measurements for several samples show that V_0 at fixed temperature increases by about 15% with r increasing from zero to unity and the slope of V_0 does not change with the crosslink density. The value of V_∞ determined from the fitting procedure varies by about 30% in the whole temperature range for one sample. An example of variation of V_∞ with temperature is shown in figure 2 for sample $r = 1$ together with the sound wave velocity deduced from the position of the Brillouin line. A similar behaviour is obtained for all the samples.

The spectra for four temperatures in the range of investigation together with the best fit using formulas (6) and (10) are plotted in figure 3(a). Only some of the experimental data points are shown for clarity. The need for non-exponential relaxation ($\beta_{\text{CD}} < 1$) is evidenced in figure 3(b). Two fitting procedures were performed on the same experimental spectrum, one with five adjustable parameters as defined above and the other with only four free parameters and β_{CD} fixed equal to one (which corresponds to a single relaxation time or Debye behaviour). The profile of the spectrum is not well reproduced with a single relaxation time. The width of the peak is too small and the signal in the inner side of the Brillouin peak is not well reproduced. The same remark applies to all the asymmetric spectra.

As we carried out our measurements with two different scattering configurations, a comparison of the results deduced for the same sample using two series of fits is needed. Figure 4 shows the relaxation times deduced for the sample $r = 1$ for two

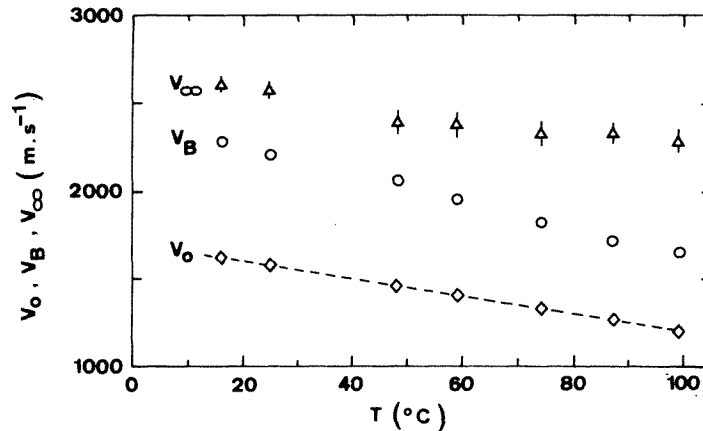


Figure 2. The evolution with increasing temperature of the sound velocity deduced from the Brillouin shift in backscattering geometry (\circ) together with the low- and high-frequency limit sound velocities V_0 (\diamond) and V_∞ (Δ) for sample $r = 1$. V_0 is determined from ultrasonic measurements and V_∞ is deduced from the fitting procedure of the Brillouin spectra. Error bars for V_∞ determinations correspond to the upper and lower limits of the 90% confidence interval deduced from the fitting procedure. This definition is also valid in the other figures for the quantities deduced from the fitting procedures.

different experimental configurations (right-angle scattering and backscattering geometries) represented in an Arrhenius plot. The two series of results are in good agreement in a large temperature interval. This confirms that the instrumental broadening of the Brillouin components (about 200 MHz) is negligible at high temperature when the relaxational process is strongly coupled to the acoustic waves. However, at low temperature, where the Brillouin linewidth is about 1 GHz, a departure between the two measurements shows that this approximation is no longer valid. The results for the two experimental configurations present a linear behaviour but the slope measured by right-angle scattering is slightly underestimated, so that the activation energy can only be deduced from backscattering measurements.

4. Results as a function of temperature

4.1. The nature of the relaxational process probed by Brillouin scattering

The relaxation times at lower frequencies in the polyurethane sample characterized by the stoichiometric ratio $r = 1$ have been measured by other techniques: ultrasonic measurements (US), dynamic light scattering (DLS) and dynamical mechanical thermal analysis (DMTA) [25]. As pointed out in section 1, the relaxation time observed corresponds to a ‘fragile’ behaviour: as a general rule the coefficient D of equation (1) ranges from three to 100, and it is equal to five for the polyurethane sample with $r = 1$, which means that this sample is very fragile glass [1].

Figure 5 shows a comparison of low-frequency measurements with our determination of τ . We plotted the average relaxation time deduced from the Cole–Davidson cut-off value τ_{CD} by [31]

$$\langle \tau \rangle_{CD} = \tau_{CD} \beta_{CD}. \quad (11)$$

Some difficulties arise when one compares relaxation times deduced from different

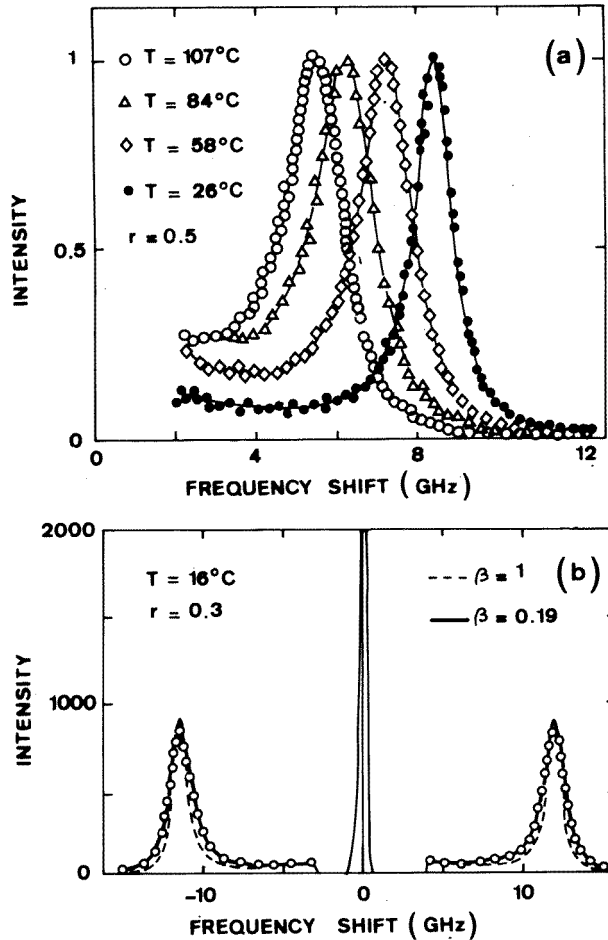


Figure 3. (a) Experimental spectra in right-angle geometry, normalized to the maximum intensity value, and best fits for the sample $r = 0.5$ at four different temperatures in the range of investigations. (b) One example of an experimental spectrum (in arbitrary units) for the sample $r = 0.3$ together with two fitting procedures: one with the parameter β_{CD} fixed equal to one and one with all the parameters being free. Only some data points are shown for clarity. The experimental spectra were recorded in backscattering configuration. The elastic signal attenuated by a factor of 10^7 is plotted with a thin solid line.

techniques: measurements can be sensitive to different quantities (frequency of maximum loss, half width at half maximum of the power spectra,...) and can be analysed using different distributions of relaxation time. The Cole–Davidson cut-off relaxation time deduced from the Brillouin scattering measurements can be converted to a stretched exponential time using the empirical relationship from Alvarez *et al* [18] or from Lindsey and Patterson [31]. Then, the empirical corrections from Patterson and Lindsey [35] can be used to compare this time to the low-frequency relaxation time τ_{max} (US measurements and DLS) corresponding to the frequency of the maximum loss. The use of both corrections leads to relaxation time values about two or three times smaller than the cut-off time τ_{CD} . Nevertheless, the use of τ_{CD} , $\langle\tau_{\text{CD}}\rangle$, τ_{WW} or τ_{max} can change the absolute value but not the

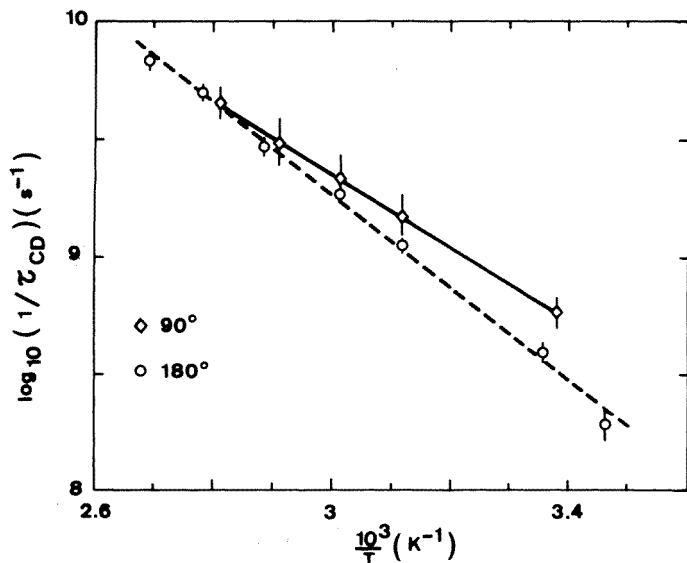


Figure 4. The evolution of the relaxation time τ_{CD} (cut-off value) with the temperature (Arrhenius plot) for the sample $r = 1$ in two experimental configurations: backscattering (\circ) and right-angle scattering (\diamond).

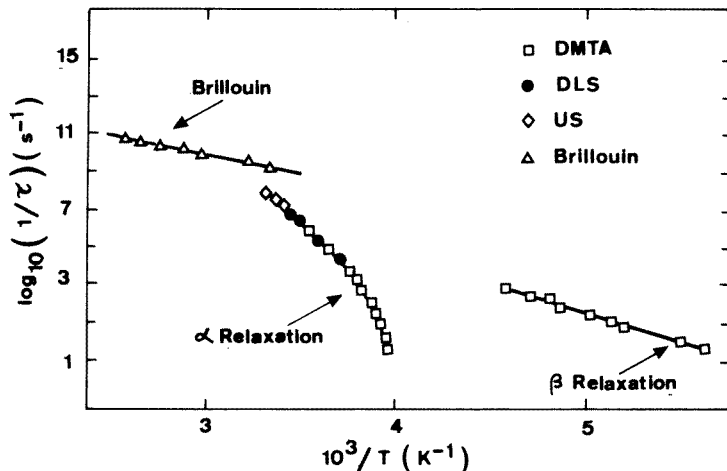


Figure 5. A comparison of the average relaxation time τ for the sample $r = 1$ determined by Brillouin scattering in backscattering geometry (Δ) with the relaxation time determined at lower frequencies by US measurements (\diamond), DLS (\bullet) and DMTA (\square) for α and β relaxations [25].

temperature dependence of the relaxation time measured by Brillouin scattering.

As in other Brillouin studies of polymers [36, 12, 37, 13], the longitudinal Brillouin scattering gives evidence of an Arrhenius process which deviates from the α relaxation measured at temperatures higher than T_g by US measurements, DLS and DMTA. The reasons for this deviation are not yet elucidated. They are discussed here by considering all the relaxations known in the polyurethane sample and by trying to relate them to the

high-frequency relaxation probed by Brillouin scattering (HFBR).

The so-called β relaxation observed at very low frequencies and at low temperatures has an activation energy of about 60 kJ mol^{-1} as evidenced by DMTA measurements whereas the activation energy measured from the Brillouin data is about 38 kJ mol^{-1} . Taking into account that these two measurements differ in frequency by a factor of 10^9 , the agreement is not too bad and the two processes could be related [38].

A third relaxation, called γ relaxation, has been evidenced in some of the polyurethane samples ($r \geq 0.8$) by low-frequency measurements [28]. The corresponding relaxation time is about 10^{-2} s at 150 K, about one order of magnitude lower than for the β relaxation at the same temperature. The values of the relaxation time deduced from the Brillouin scattering measurements could be in agreement with the expected values for the γ relaxation if one assumes an activation energy of about 36 kJ mol^{-1} for the γ process. Nevertheless, the amplitude of the γ relaxation should be smaller than the amplitude of the β relaxation, itself smaller than that of the α relaxation. The amplitude of the Brillouin and of the α relaxation as obtained from the US measurements can be deduced from the high- and low-frequency limit longitudinal modulus M_∞ and M_0 ; the two amplitude values are very close to each other. Moreover, the parameter β_{CD} can be converted to a stretched exponential parameter β_{WW} using the empirical relationship from Lindsey and Patterson or from Alvarez *et al* [18, 31] and the value of β_{WW} obtained is about 0.25–0.30, which is remarkably close to the one obtained by other techniques for the α relaxation ($\beta \approx 0.30$) [25].

These two arguments (the amplitude of the relaxation and the coincidence of the parameter characteristic of the distribution time) suggest that the relaxation evidenced by Brillouin scattering is an α relaxation disturbed by the β relaxation. Depolarized light scattering measurements show that in the Brillouin frequency range both α and β relaxations contribute as pointed out recently by Cummins *et al* [39]. These authors proposed a method using a memory function constructed from the depolarized light scattering spectra taking into account both α and β relaxations. The method was successfully used in the case of calcium potassium nitrate: this analysis allowed them to clarify the discrepancy between the relaxation time measured by Brillouin scattering and by the other methods. However, in this compound, the method is based on the fact that the relaxation time τ_α for the longitudinal density fluctuations (τ_α deduced from the Brillouin spectra) coincides with the structural relaxation time for the depolarized light scattering, and it is not clear how the method can be extended to other systems. The very low amplitude of the depolarized signal in polyurethane samples prevents us from performing the same data processing. Moreover, to take into account both α and β relaxations an extra fitting parameter is needed whose physical meaning is not obvious.

4.2. Parameter β of the time distribution—the non-ergodicity parameter

Assuming the HFBR is a structural relaxation, Brillouin scattering data can be used to test the predictions of several models.

The value of β_{CD} that we found does not vary too much with temperature (figure 6). The corresponding values of β_{WW} calculated using the empirical relationship from Lindsey and Patterson or from Alvarez *et al* [18, 31] are also plotted. The use of one relationship or the other does not change the results significantly. The numerical value for β_{CD} is in agreement with the value deduced from models which predict a transition from $\beta_{\text{WW}} = 1/3$ at low temperature to $\beta_{\text{WW}} = 1$ at high temperature [6]. This transition has been evidenced by Börjesson *et al* in $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ and $\text{Ca}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$ [40]. It is not observed for polyurethane samples in the investigated temperature range, which is in agreement with the

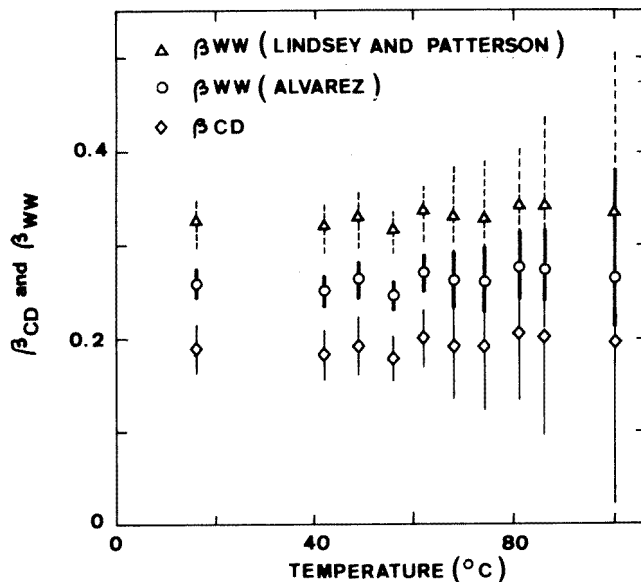


Figure 6. The evolution of the non-exponentiality parameter β_{CD} with the temperature for the sample defined by the stoichiometric ratio $r = 0.3$. The corresponding values of β_{WW} deduced from the empirical relationship of Alvarez *et al* or Lindsey and Patterson are also plotted.

behaviour of several other polymers [36] (though a Debye relaxation is also observable in some polymers such as *n*-lauryl methacrylate [41]). This can be related to the results of dielectric relaxation measurements performed by Schönhalz *et al* [42] on propylene glycol and poly(propylene glycol), showing that the relaxation function is Debye-like at high frequency for the monomer whereas, due to an increase of both intermolecular interactions and hindrance of conformational diffusion [30, 43], Debye behaviour is never reached for the corresponding polymer.

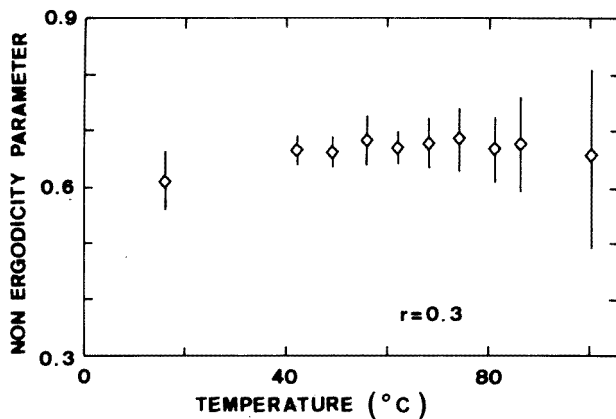


Figure 7. The non-ergodicity parameter $f(q \rightarrow 0) = 1 - V_0^2/V_\infty^2$ as a function of the temperature for sample $r = 0.3$.

The mode-coupling theory [7] predicts an ergodic-to-non-ergodic glass transition singularity at a crossover temperature T_c above the calorimetric glass transition temperature. The temperature dependence of the non-ergodicity parameter is predicted to be of the following form:

$$\begin{aligned} f_q(T) &= f_q^c & T > T_c \\ f_q(T) &= f_q^c + \sqrt{(T_c - T)/T_c} & T < T_c \end{aligned} \quad (12)$$

where f_q^c is a slowly varying function of T . The $q \rightarrow 0$ limit of f_q can be determined from Brillouin scattering or US measurements using [44]

$$f(q \rightarrow 0) = 1 - V_0^2/V_\infty^2. \quad (13)$$

The existence of a ‘cusp’ of f_q at T_c has been evidenced by Brillouin scattering in salol, although there is a discrepancy between the α relaxation time deduced from the low-frequency measurements and the relaxation time determined by Brillouin scattering [45]. In polyurethane samples, the value of f_q is nearly constant within experimental uncertainty and does not present a cusp (figure 7); it is quite high, suggesting that T_c is above the investigated temperature range. The glass transition temperature of these samples being around 210–260 K, the highest investigated temperature corresponds to $T \approx 1.6 T_g$. If the non-ergodicity parameter for these fragile samples presents a cusp as a function of temperature, in agreement with the prediction of mode-coupling theory, this is not at a temperature below $1.6 T_g$. Some authors have mentioned that the temperature T_c can be as high as $1.78 T_g$ [36]. In any case, as pointed out by Götze and Sjögren [7] one cannot reliably estimate the T_c analogue for polymers in the liquid state.

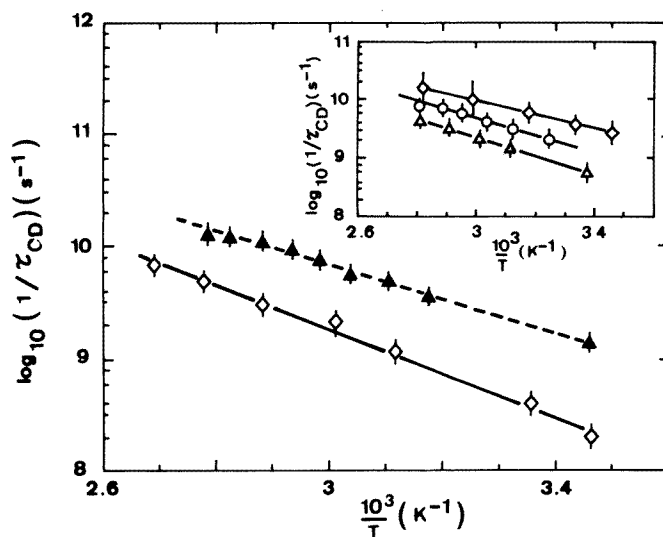


Figure 8. An Arrhenius plot ($\log \tau_{CD}$ versus $1/T$) for two polyurethane samples in backscattering geometry: $r = 0.3$ (\blacktriangle) and $r = 1$ (\diamond). In the inset are shown the apparent relaxation times versus $1/T$ in right-angle geometry for three samples: $r = 0$ (\diamond), $r = 0.5$ (\circ) and $r = 1$ (\triangle). The solid lines represent linear regressions.

5. The influence of the composition and of the crosslink density

The values of the relaxation times τ_{CD} measured in backscattering geometry for two samples ($r = 0.3$ and $r = 1$) at temperatures higher than room temperature are reported in an Arrhenius plot (figure 8). In the inset the relaxation time values measured in right-angle geometry for three samples are shown. The relaxation time in this temperature range has an Arrhenius behaviour for all samples. It can be noticed that the activation energy deduced from the measurements in backscattering geometry increases slightly with increasing r from 32 kJ mol^{-1} for $r = 0.3$ to 38 kJ mol^{-1} for $r = 1$. Even though the values of the activation energy cannot be accurately measured from the right-angle measurements, the slope is also increasing with increasing r in right-angle geometry (by about 30% from $r = 0$ to $r = 1$). The variations are slightly higher than the accuracy on the values of the slope. However, the order of magnitude is the same as the activation energy of polypropylene glycol [13] or $\text{Ca}(\text{NO}_3)_2\text{KNO}_3$ [46]. The values obtained from Brillouin scattering usually range from 8 kJ mol^{-1} [47] to 37 kJ mol^{-1} [46]. Small values have been attributed for example to conformational relaxation in n -alkanes [46]. Changing the crosslink density modifies the connectivity along with the chemical composition (r is changed) and the molecular weight. Nevertheless, it has been shown for several polymers [48, 10] that varying the molecular weight should not change the activation energy. The nearly constant value of E_a observed for various compositions demonstrates that the microscopic entities involved in the HFBR are slightly sensitive to the crosslink density.

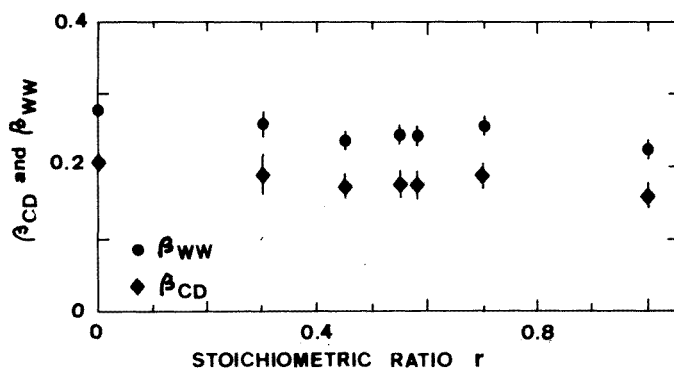


Figure 9. The evolution of the non-exponentiality parameter β_{CD} with the composition. The corresponding values of β_{WW} calculated using the relationship from Alvarez *et al* are also shown.

The variation of β_{CD} with the composition is plotted in figure 9. The corresponding values of β_{WW} deduced from the empirical relationship from Alvarez *et al* are also plotted [18]. The value of β_{WW} obtained is about 0.25–0.30 and is also independent of r .

The evolution of the spectra with the composition at one temperature ($T = 16^\circ\text{C}$) is shown in figure 10. The Brillouin shift and then the compressibility elastic modulus increase with increasing r . This variation can be related to variation of the glass transition temperature and can be due to changes of the crosslink density or of the chemical composition. It can also be pointed out that in figure 11 $\log \tau$ at room temperature appears proportional to r . Some analogy can be noticed between the inverse of the temperature and the stoichiometric ratio r .

The logarithm of the relaxation times is plotted in figure 12(a) for the sample $r = 0.3$

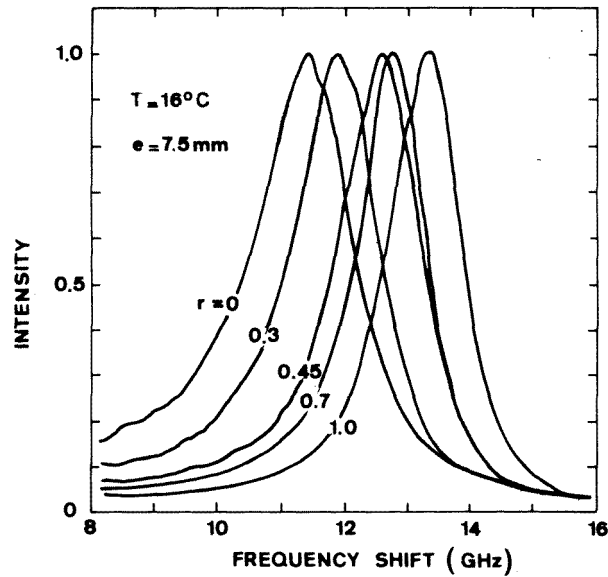


Figure 10. The evolution with the composition of the Brillouin signal at $T = 16^\circ\text{C}$ in right-angle scattering geometry. Only five spectra are shown for clarity. The intensities are normalized to their maximum value.

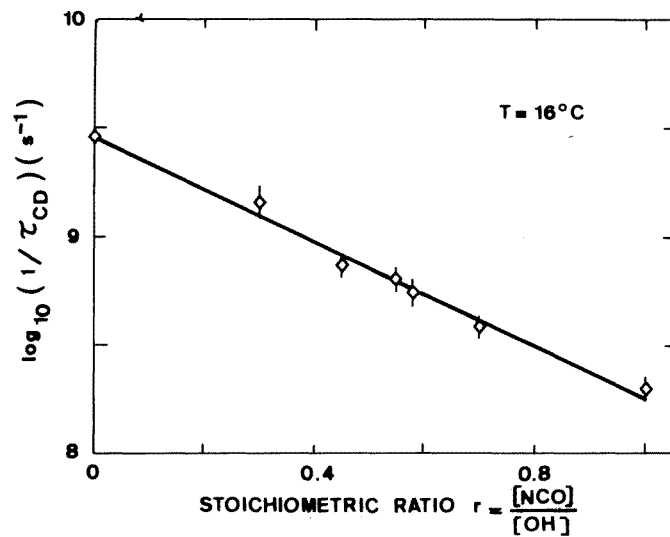


Figure 11. The evolution of $\log \tau_{\text{CD}}$ at room temperature with the stoichiometric ratio. The solid line represents a linear regression.

and the completely gelled sample ($r = 1$) versus T_g/T , corresponding to backscattering geometry measurements, and in figure 12(b) for the three samples studied in right-angle geometry. The relaxation times rescaled this way are superimposed. The differences in crosslink density are fully accounted for by the change of T_g . The temperature dependence

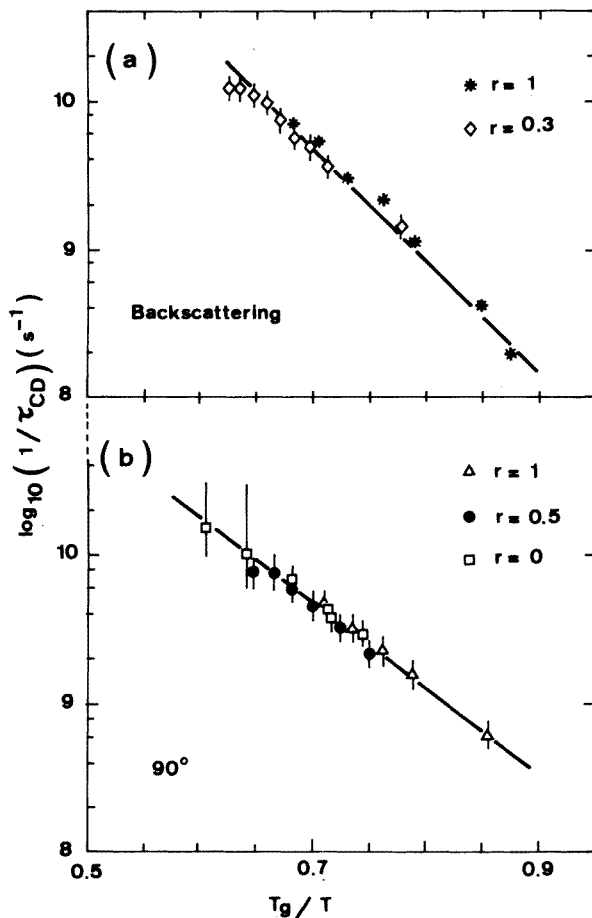


Figure 12. (a) A rescaled Arrhenius plot ($\log \tau_{CD}$ versus T_g/T) for the two polyurethane samples measured in backscattering geometry, corresponding to stoichiometric ratio $r = 0.3$ and $r = 1$. (b) The same plot for the three polyurethane samples measured in right-angle geometry, corresponding to stoichiometric ratio $r = 0$, $r = 0.5$ and $r = 1$.

for the relaxation time is described by the following expression:

$$\tau = \tau_0 \exp((E_a/kT_g)/(T/T_g)). \tag{14}$$

The rescaling shows that τ_0 is independent of the crosslink density and the activation energy is proportional to T_g . These results suggest that the relaxing entities are not affected by variations of the crosslink density whereas the energy barriers for the relaxation process are changed: the changes in crosslink density modify the spatial distribution of these entities or their interactions.

6. Summary and conclusion

In this paper we have presented a Brillouin scattering investigation on polyurethane glass-forming polymers. We have probed relaxations in the temperature range from $1.2-1.6 T_g$. The identification of the Brillouin-probed relaxation with one of the relaxations observed at

lower frequency remains a problem to elucidate in these polymers as well as in other polymers previously studied. Fitting procedures performed on the total inelastic light scattered allow us to determine the complex elastic modulus and the relaxational time which presents an Arrhenius behaviour with an activation energy comparable with that measured for a relaxational process observed in the solid phase at very low frequencies. We demonstrated that the relaxation does not follow a Debye behaviour and can be successfully accounted for by a Cole–Davidson distribution. By using empirical relationships between the parameter β_{CD} of the Cole–Davidson distribution and the parameter β_{WW} of a stretched exponential, we found that the relaxation distribution is nearly the same for the relaxation investigated by Brillouin scattering (HFBR) and the α relaxational process observed at a different frequency scale. Moreover, as β_{CD} is constant in the temperature range investigated, the two relaxations seem to collapse at very high temperature, higher than $1.6 T_g$. If this result is not strictly contradictory to the theoretical models such as the mode-coupling theory, it is yet in contrast with the behaviour of simple fragile liquids generally used for testing these models. The microscopic complexity of glass-forming polymers may be at the origin of these differences; this is in agreement with the description of Schönhalz *et al* [42] where hindrance persists in polymeric systems at high temperature. The influence of the stoichiometric ratio has shown that the relaxational time distribution remains unchanged with the crosslink density whereas the mean relaxation time increases and the activation energy slightly increases, too. These changes can be accounted for by rescaling with T_g . The results suggested the possibility of a time–stoichiometric ratio superposition principle analogous to the usual time–temperature superposition principle.

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