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Gigahertz dielectric and dynamic heat capacity relaxation during polymerization and configurational entropy-independent relaxation

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Abstract. The relaxation dynamics of a catalytically polymerizing, initially molecular liquid was studied by dielectric spectroscopy in the 1 MHz–10 GHz frequency range until a macromolecular network structure formed and the liquid became a solid isothermally. Further, its dynamic heat capacity for a fixed 5 mHz frequency, and the heat evolved during the growth of the molecular network, were measured. These are related to the number of new covalent links or bonds, n , formed. In the molecular liquid at 335.4 K, one relaxation peak with a spectral half-width of 2.4 decades appears at 0.8 GHz frequency. All polarization of the liquid at 335.4 K relaxes by this relatively broad relaxation process. As the liquid's viscosity increases and the volume and configurational entropy, S_{conf} , decrease isothermally with increase in n in the macromolecule, the strength of this relaxation decreases, but its characteristic time does not change. Both effects are analogous to the effects of the increase in viscosity and density, and decrease in S_{conf} , on the Johari–Goldstein relaxation during supercooling a chemically stable liquid and physically ageing a glass. The rate of orientational diffusion observed in the GHz range is not affected by a decrease in S_{conf} or increase in the density.

1. Introduction

For gaining insight into the molecular dynamics during the polymerization process, dielectric measurements are used mainly in two ranges of frequencies. One is the GHz range in which the spectrum of a chemically stable liquid shows at high temperatures only one, although in several cases a broad, peak in the relaxation spectrum [1–3]. In a plot against the reciprocal temperature, its rate linearly connects with that of the Johari–Goldstein relaxation (we use this term to distinguish it from the β -relaxation of the mode-coupling theory, as suggested in several reviews on the subject [2–6]) observed in rigid molecular and polymeric glasses according to an Arrhenius equation and its strength decreases rapidly with the temperature. All orientation polarization of the liquid at high temperatures relaxes by this dynamics of hindered dipolar rotation, without the requirement of cooperativity [1, 7]. On supercooling the liquid, the slower dynamics of the α -relaxation evolves and separates from that of the original relaxation process in a time–temperature plane and, after it has separated, the orientational polarization associated with it grows rapidly [7]. Its relaxation rate decreases progressively more rapidly on further supercooling until the liquid transforms to a rigid glass [1, 7] and becomes kinetically metastable. The decrease in the relaxation rate occurs usually according to the Vogel–Fulcher–Tamman equation [8–10], and is interpreted in terms

of a decrease in the liquid's free volume or configurational entropy in a manner that differs from that in the mode-coupling theory [11], mainly because the latter leads to a structural freezing at a temperature much higher than the usual glass transition temperature, T_g [12]. Concurrently, the contribution to orientational polarization from the faster relaxation process decreases and its rate continues to decrease relatively slowly with temperature, according to the Arrhenius equation, without a discontinuity at T_g [1, 7].

Phenomenologically similar changes occur during the isothermal polymerization of a molecular liquid, where an increase in the size of the diffusing entity decreases the configurational enthalpy, entropy and volume. Studies of the dielectric spectra in the kHz–MHz frequency range [13, 14] have shown that as the number of covalent bonds in the liquid's structure increases on polymerization, a new, slower mode of molecular motions evolves, its strength increases and both its dielectric strength and rate decrease progressively rapidly with increase of the macromolecule's size, the latter according to an equation whose parameters are temperature dependent [13]. These observations have been confirmed from studies over the 0.1 kHz to 10 GHz range, which showed the evolution of the slower relaxation more clearly [15–17]. However, none of these studies revealed how the strength and the rate of the fastest relaxation process changes *during* the course of a liquid's polymerization.

We report a study of the changes in; (i) the dynamics and strength of the fastest, GHz frequency dipolar relaxations in a molecular liquid *during* the growth of a molecular network, (ii) the dynamic heat capacity and (iii) the heat evolved as the macromolecule in the structure grows. We then relate the observations to the number of covalent bonds formed rather than the period of reaction. From this and an earlier, 1 kHz frequency study [18], we conclude that polymerization of a liquid has the same consequences for its molecular dynamics as decrease in volume, V , and configurational entropy, S_{conf} , and increase in viscosity, on cooling a chemically stable liquid. The results also show that spontaneous decrease in V and S_{conf} on polymerization has no effect on the average rate of its GHz relaxation dynamics, just as a decrease in S_{conf} on spontaneous structural relaxation of a chemically stable glass has no effect [1, 7] on the rate of its Johari–Goldstein relaxation.

2. Experimental details

Diglycidyl ether of bisphenol-A (DGEBA), molecular weight 380, was obtained from Shell Chemicals under its trade name EPON 828 EL. Dimethylbenzylamine (DMBA, 98% purity) which acts as a catalyst, was purchased from Aldrich Chemicals. Both chemicals were used as supplied. All mixtures were prepared by weighing in amounts of 4–5 g, and mechanically mixing for 1 min at 298 K. These were used within 2–3 min of mixing.

The mechanism of this catalytic polymerization has been discussed before [18–21]. Briefly, the sequence of polymerization reactions below 363 K [21] is that the first reaction is an addition reaction between $C_6H_5CH_2N(CH_3)_2$ and one epoxide group of one DGEBA molecule which forms a zwitterion. In the second reaction the zwitterion reacts with one epoxide group of another DGEBA molecule. This increases the chain length and further separates the negatively and positively charged atoms of the zwitterion along the chain. In the third reaction, the zwitterion dissociates into a chain with a $CH_2 = C(R_1)O$ -group (R_1 being the first reacting DGEBA molecule without one epoxide group) at one end and $-CH(R'_1)OH$ at the other end (R'_1 being the second reacting DGEBA molecule without one epoxide group). This double-bonded group further reacts to produce a crosslinked network and the original amount of the tertiary amine, DMBA, remains in the molecular network. A fraction of this amine may remain H-bonded to the protons of the $-OH$ groups in the

polymerized DGEBA network structure in which the distance between two crosslinks is on average the same as the length of the crosslink itself, after complete polymerization.

Two sets of equipment were used for the dielectric measurements: (i) frequency domain spectroscopy (FDS) and (ii) time domain reflectometry (TDR). Measurements in the 1 MHz–20 MHz range were made by FDS for which the assembly was built around a capacitance bridge, and was also used in an earlier study [13]. The capacitance and conductance were determined from the phase shift and the relative amplitude of the sinusoidal voltages measured on the sample arm and on the reference arm. The assembly consisted of a radio-frequency circuit, a sinusoidal voltage generator, and a computer-controlled digitizing oscilloscope. The entire assembly including the dielectric cells was calibrated with air, chloroform, heptane and methylene chloride as dielectric standards at 298 K, as described before [13]. The measured dielectric permittivity and loss are accurate to within 1%. The data acquisition at a given frequency, which was done by a computer, took 1 s. TDR measurements were made by means of a dual-channel assembly similar to that used by Cole *et al* [22]. The principal part of the assembly consisted of a Tektronix WPO 7854 waveform processing oscilloscope, a 7S12 TDR/sampler, a 7S11 sampling unit, a S52 pulse generator and two S6 feed through sampling heads. The details of this assembly have been described by Bertolini *et al* [23], where the details of the dielectric cell's design and the measurement procedure have also been given. The assembly was calibrated with the same standards as the FDS assembly. The measured ϵ' and ϵ'' are accurate to within 3%. The temperature of the liquid contained in the dielectric cell was automatically controlled to within 0.1 K. Both FDS and TDR assemblies were computer interfaced for automatic data acquisition.

The dynamic heat capacity was measured by an instrument designed for the purpose and described elsewhere [24]. The heat evolved during the polymerization reaction was measured by Perkin Elmer's DSC 4 interfaced to a standard PC using a data acquisition program written by us, and by a procedure described earlier [25, 26].

3. Results

130 spectra of permittivity, ϵ' , and loss, ϵ'' , of the liquid DGEBA containing 10 mol% DMBA as a catalyst were obtained during the progress of its polymerization at 335.4 K. To relate the spectra to the number of covalent bonds formed on polymerization, rather than the polymerization reaction time, the heat evolved during the polymerization of the DMBA–DGEBA liquid mixture was measured at 335.4 K at different times by DSC as described earlier [25, 26]. This DSC isotherm is shown in figure 1(a). After polymerization at 335.4 K for 20 h, the sample was cooled to 293 K and scanned during rate heating from 293 K to ~ 430 K at a rate of 10 K min^{-1} . This scan is shown in figure 1(b). It shows a glass transition endotherm beginning at 353 K, and an exotherm resulting from further reaction. The total heat evolved on polymerization, ΔH^0 , was obtained by adding the heat evolved isothermally and the heat evolved on heating at 10 K min^{-1} . This was equal to 113 kJ mol^{-1} of DGEBA, and it was assumed to remain constant with changing temperature. The number of covalent bonds formed, n , in the liquid at an instant, t , was determined from the equation:

$$n(t) = bN_A \Delta H(t) / \Delta H^0 \quad (1)$$

where N_A is the Avogadro number, $\Delta H(t)$ is the heat evolved during the isothermal polymerization at a time t , and ΔH^0 is the total heat of polymerization as described before here. The quantity b is determined by the functionality of the reacting molecules. The

network structure that forms on polymerization by this catalytic reaction has each DGEBA molecule linked to four other DGEBA molecules according to the reaction described before [18]. Hence, b is equal to 2. $\Delta H(t)$ was calculated by dividing the partial area of the plot in figure 1(b) by ΔH^0 . The value of n thus calculated is plotted against time in figure 1(c).

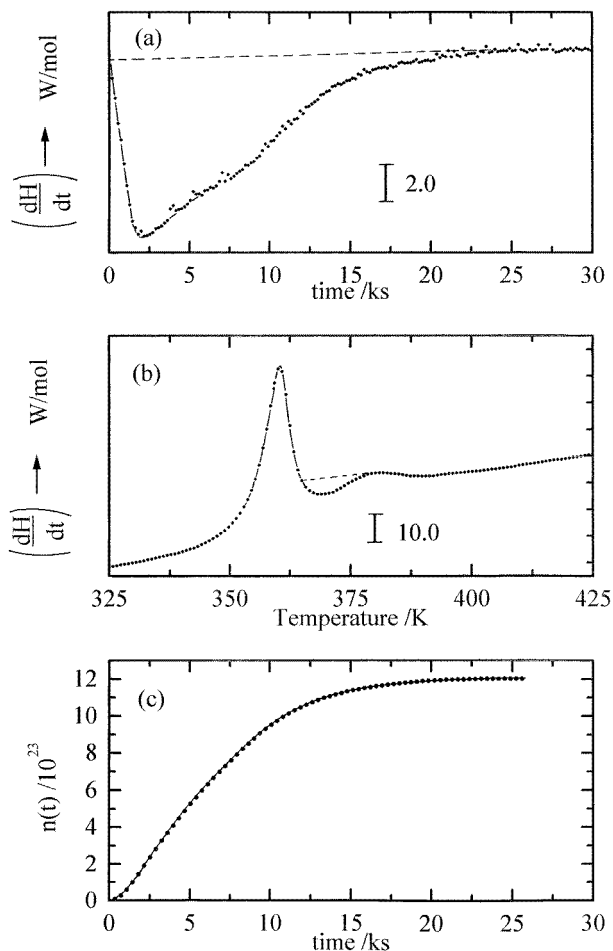


Figure 1. (a) The heat evolved measured during the network structure formation is plotted against the polymerization time at 335.4 K, (b) the DSC scan of the isothermally polymerized sample obtained by heating at a rate of 10 K min⁻¹, and (c) n plotted against the polymerization time.

The dynamic heat capacity of the mixture was measured for a frequency of 5 mHz in a separate experiment [24]. This gave accurate values of the real part of the heat capacity, C'_p , but not an accurate value of the imaginary part, C''_p , because of the relatively large amount of heat evolved during the polymerization which interfered with the measurements of the small C''_p . C'_p is plotted against the reaction time in figure 2(a). The variation of C'_p with polymerization time was converted to its variation with n , and the plot of C'_p against n is shown in figure 2(b).

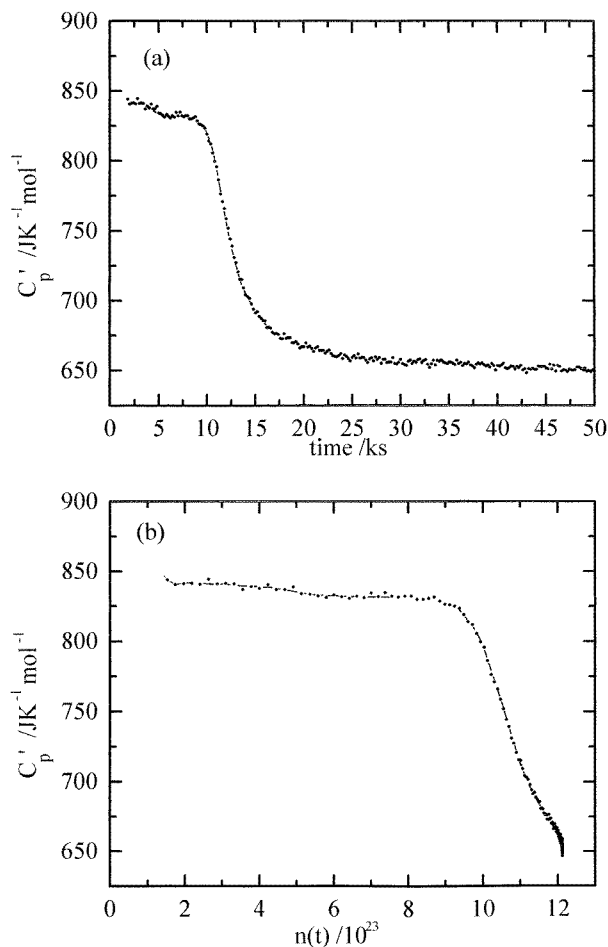


Figure 2. (a) The real component of the dynamic heat capacity plotted against the polymerization reaction time of the liquid at 335.4 K; (b) the real component of heat capacity is plotted against the number of covalent bonds formed. The sinusoidal frequency of the heat pulse was 5 mHz (time period 200 s).

Selected spectra for different times during the network's growth are shown in figure 3. Here, the ε'' peak is broad and, so, only partially complete. Part of the low-frequency side of the peak is not observable in the 1 MHz–10 GHz range. The ε' spectra do not show a low-frequency plateau to yield the static permittivity value, but the value can be estimated from the small region where the slope of ε' reaches a minimum value in the low-frequency side of the spectrum.

The spectra could not be fitted with a stretched exponential relaxation function, $\phi = \exp[-(t/\tau_0)^\beta]$, where τ_0 is the characteristic relaxation time and β the stretching parameter, partly because of the poor definition of the low-frequency side of the spectrum. The width of the peak is 2.4 decades, which is broader than that for a single relaxation process (1.14 decades) and further broadens on polymerization, mainly because of the contribution to ε'' from another relaxation process that evolves and moves towards the low-frequency side of the spectrum. The height of the ε'' peak seen in figure 3 is plotted in figure 4, against the number of covalent bonds formed in the liquid.

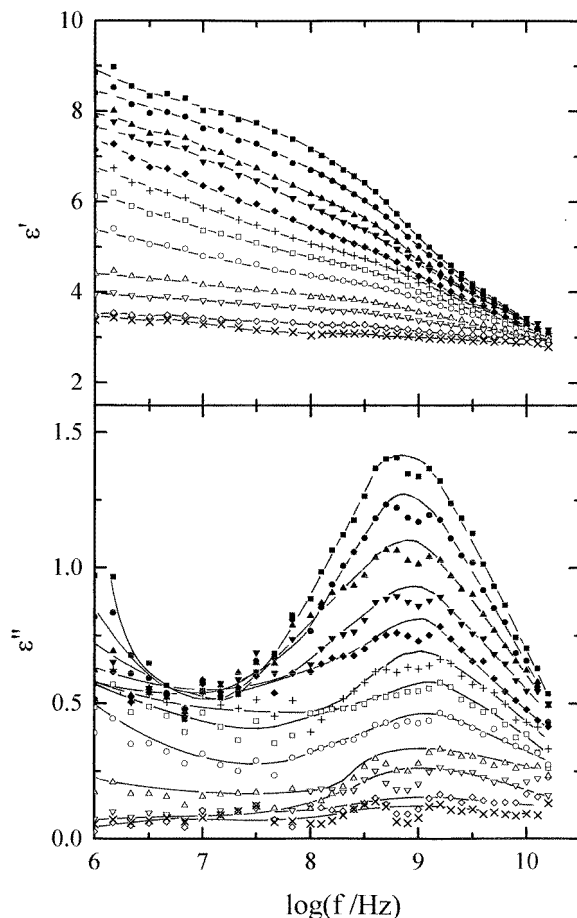


Figure 3. The ϵ' and ϵ'' spectra of the liquid mixture at several stages during the course of its polymerization at 335.4 K. The notations are for different values of n (to be multiplied by 10^{23}), as follows: (■) 0.092; (●) 0.89; (▲) 1.75; (▼) 2.19; (◆) 3.09; (+) 4.01; (□) 4.91; (○) 6.21; (◇) 8.07; (▽) 9.49; (◇) 12.01; (×) 12.04.

4. Discussion

4.1. The dynamic heat capacity

We first consider the change in C'_p as the network structure formed on polymerization. The shape of this plot in figure 2 resembles the shape of the ϵ' plot against t and n of polymerizing materials [13, 14, 25]. The low- n limit of C'_p , i.e. $833 \text{ J mol}^{-1} \text{ K}^{-1}$, in figure 2(a) and (b) represents the C_p of the liquid when the characteristic time of its intra- and intermolecular modes is much shorter than the experimental time window, 200 s, corresponding to 5 mHz. This is the usual thermodynamic C_p measured when enough time is taken to allow all dynamic modes to contribute. The limiting low value of C'_p , i.e. as $n \rightarrow bN_A$, is about $650 \text{ J mol}^{-1} \text{ K}^{-1}$. This value contains no contributions from modes that became kinetically frozen in over this time scale and hence make no contribution to C_p . As discussed earlier [24], the decrease in C_p on increasing n is a result of at least five occurrences during

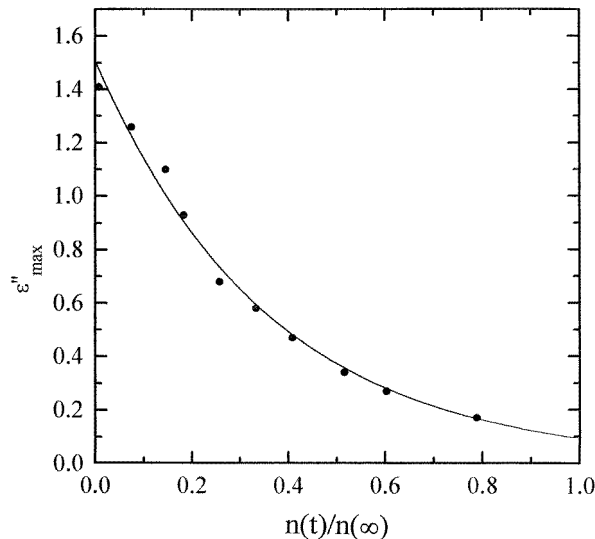


Figure 4. The ϵ'' peak height from figure 3 is plotted against $n(t)/n(\infty)$ for the liquid mixture during its polymerization at 335.4 K.

polymerization, namely, (i) a decrease in the concentration of the impurity ions as they associate to form ion-pairs, and decrease C'_p from 842 to 833 J mol⁻¹ K⁻¹ because of a decreased extent of ion-solvent interaction, (ii) an increase in the molecular diffusion time which causes C'_p to decrease from 833 to 652 J mol⁻¹ K⁻¹ with the rate of polymerization from a state with $n = 0$ to a macromolecular state with $n \rightarrow bN_A$, the lower value representing the contributions from all the modes with characteristic frequencies much lower than that used in the experiment, (iii) a concomitant increase of the contribution to C_p (by at most a few %) from the high-frequency modes as the vibrational frequencies increase and new vibrational modes with a new density distribution become important, (iv) a change in the relaxation function as the liquid's chemical and physical structure changes, and (v) a splitting of the unimodal relaxation function into a bimodal relaxation function as the α -process evolves. The most important of these effects, which can be described entirely in terms of hydrodynamics, is the increase in the structural relaxation time or progressively increasing viscosity with increase in n . Unfortunately, our inability to extract C''_p data from this experiment prevents us from obtaining the data for structural relaxation time in the manner done before [24], but it is clear that the S_{conf} of the liquid, which is equal to the integral of C_p in a $\ln(T)$ plane, decreases as the molecular network structure forms in it.

4.2. The dielectric spectrum

The spectra in figure 3 show that for the molecular state of the liquid, there is only one relaxation peak at 0.8 GHz and spectral half width of 2.4 decades at 335.4 K. The broadness of the peak is not necessarily an indication of the reorientation of a multiplicity of dipoles of discrete relaxation times, for similar broadness of the spectra appears also in pure rigid molecular liquids [1, 7]. Rather, it is seen as a distribution of the environment for the dipolar orientation or a hierarchy of molecular dynamics [27]. The 0.8 GHz peak frequency corresponds to a characteristic relaxation time, τ_0 , of 0.2 ns. The liquid's viscosity, η , at

this temperature is of the order of a few poise. On the assumption that τ_0 is proportional to η at such low viscosities, this gives an average relaxation time of a few tenths of 1 ns according to the Maxwell equation, $\tau_0 = \eta/G_\infty$, where G_∞ is the limiting high-frequency shear modulus of the liquid, typically 10^{10} dynes cm^{-2} . Also, since no other relaxation has been observed at lower frequencies, it is evident that all polarization in the liquid relaxes by this dynamics at 335.4 K, and the estimated static dielectric permittivity of 8.5 ± 0.3 of the molecular liquid in figure 3 is the same as that deduced from the 1 kHz frequency measurements (see figure 7 in [18]).

The height of the ε'' peak in figure 3 decreases with increase in n . Its height, ε''_{max} , plotted against n in figure 4, shows that the decrease occurs according to an equation,

$$\varepsilon''_{max} = 1.51 \exp[-2.794n(t)/n(\infty)] \quad (2)$$

where $n(\infty)$ is equal to the number of bonds formed as $t \rightarrow \infty$. $n(\infty)$ is equal to bN_A . This decrease is significant in two ways: firstly, it indicates that part of the dynamics of dipolar relaxation is becoming separated from the GHz relaxation, and secondly, that the decrease is remarkably similar to that which occurs on densification and decrease in the configurational entropy, S_{conf} , during the spontaneous structural relaxation of a vitrified state.

For the first, we recall the results of the fixed 1 kHz frequency dielectric studies [18] as a function of temperature, which showed that in the supercooled state of the liquid, there are two relaxation processes, one the Johari–Goldstein relaxation, whose ε'' peak appears at 145.4 K ($\varepsilon''_{max} = 0.077$) in the glassy state, and the second the α -relaxation, whose peak appears at 264 K ($\varepsilon''_{max} = 2.08$), in the liquid state. The studies [18] also showed that as n increased on polymerization, the low-temperature peak remained at 145–146 K, but the α -relaxation peak shifted to higher temperatures from 264 K up to 325 K (figure 7 in [18]), as T_g of the liquid increased and approached the experiment's temperature. Concomitantly, the height of the smaller peak at 145–146 K decreased and became indiscernible. The vanishing of this relaxation peak corresponds to the decrease of the GHz frequency relaxation peak in figure 3. Thus, when the liquid is partially polymerized isothermally, or $n > 0$, the temperature for the 0.8 GHz peak remains at 335.4 K and that of the Johari–Goldstein relaxation for the 1 kHz peak remains at 145–146 K, but the relaxation strength decreases in both cases.

For the second, we recall the effects of structural relaxation on physical ageing of vitrified molecular liquids and polymers. Studies have shown that the ε''_{peak} of the Johari–Goldstein relaxation decreases on structural relaxation of a glass, as the state densifies and its S_{conf} decreases [1, 7] under isothermal conditions. The decrease in the ε''_{peak} on increase in n seen in figure 3 is remarkably similar to that effect. Although the essential change here is in the chemical structure, its consequences for thermodynamics are manifestly similar to that of structural relaxation of a chemically stable glass. The results here show that the effect on the dynamics of at least the fastest relaxation is also manifestly similar in the two cases.

4.3. Configurational entropy-independent relaxation.

Finally, we consider the sensitivity of the relaxation dynamics to S_{conf} , both chemical and physical. As is seen in figure 3, the characteristic relaxation rate ($=\omega_{peak}$) of the process does not change as n increases spontaneously and the enthalpy, entropy ($=S_{conf} + S_{vibrational}$), and V of the liquid decrease. This has been observed also in studies where the Johari–Goldstein relaxation was investigated in the glassy state for a fixed, 1 kHz measurements and the ε''

peak was observed at about 146 K [18, 25, 26, 28]. In the Adam–Gibbs description of the relaxation time in terms of the configurational entropy [29],

$$\tau = \tau_{\infty} \exp(\Delta\mu s_c^* / k_B T S_{conf}) \quad (3)$$

where $\Delta\mu$ is the potential energy hindering the cooperative rearrangement per monomer segment of the molecule, s_c^* is the critical entropy, k_B the Boltzmann constant, and τ_{∞} is the relaxation time when the term $T S_{conf}$ approaches infinity. Accordingly, for a fixed T , $\log \tau$ is proportional to the inverse of S_{conf} . The relaxation peak at the GHz frequency in figure 3 does not change when S_{conf} decreases on the macromolecules' growth. This means that this relaxation's dynamics is determined entirely by the thermal energy, while that of the α -relaxation is determined additionally by the S_{conf} . We interpret that as evidence for the view that hindered reorientation of molecules is at the origin of the dynamics that leads to the evolution of the α -relaxation process in a liquid [30, 31] near and above T_g , and that the role of S_{conf} becomes important only when the hydrodynamics of a liquid has slowed to a point where the rate of the α -relaxation separates, or bifurcation of the relaxation rates occurs in the reciprocal temperature plane.

There are two further aspects of this relaxation dynamics that need be discussed. Studies of physical ageing of glasses [1, 7, 32–34] and of liquids cooled at different rates [32, 33], which causes their fictive temperature, T_f , to change, have shown that the height of the relaxation peak observed at a temperature below T_g decreases as T_f of the glass is decreased. The height of the ϵ'' peak at GHz frequency decreases as n increases and H , S , V , and S_{conf} decrease. In this sense, the dependence of the magnitude of this process on S_{conf} during a chemical reaction seems to be analogous to the dependence of its magnitude on S_{conf} during physical ageing.

Second, the same studies showed that the temperature of the Johari–Goldstein relaxation peak for 1 kHz and 10 kHz frequency dielectric measurements does not change on lowering T_f by physical ageing of a glass, or on raising T_f by rapidly quenching the liquid to obtain its glassy state. Since ageing decreases the configurational contribution to H , S , and V , and quenching increases it, the observations made here and the earlier observations [1, 7, 32–34] demonstrate that the rate of the Johari–Goldstein relaxation is not affected by a decrease in S_{conf} or in free volume. This is remarkable, particularly in view of the theory [30, 35] that the dynamics of this process be seen as fundamental to the existence of the α -relaxation of a glass, and that the α -relaxation evolves from this primary, localized dynamics in the low- and high-density sites in the structure of a liquid or glass.

5. Conclusions

The gradual extinction of the relaxation process in the GHz frequency spectra during a macromolecular network growth is remarkably similar to that observed during physical ageing of a chemically stable glass where the strength of the Johari–Goldstein relaxation decreases. The free volume, configurational enthalpy, and entropy decrease spontaneously during both occurrences: (i) polymerization in which the chemical structure of the liquid state changes irreversibly and (ii) physical ageing of glasses where no chemical change occurs. The decrease is accompanied by a decrease in the height or strength of the relaxation peak without significant change in its frequency or temperature. In its dielectric consequences, a polymer network's growth mimics the spontaneous structural relaxation on physical ageing.

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