

The Combined Effects of Temperature and Polymerization Rate Changes on the Real-Time Conduction and Relaxation of a Liquid, and the Evolution of Localized Motions

C. Cardelli and E. Tombari

Istituto di Fisica Atomica e Molecolare del CNR, via G. Moruzzi 1, 56124 Pisa, Italy

G. P. Johari*

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

Received: March 8, 2001; In Final Form: August 16, 2001

Simultaneous, real-time calorimetry and dielectric spectrometry were performed to study the manner in which molecular dynamics of a polymerizing liquid (stoichiometric amounts of 4,4'-diaminodicyclohexylamine and diglycidyl ether of bisphenol A) evolves during the thermal cycle which converts its initially (molecular) liquid to a vitrified solid of a cross-linked network structure without extraneous products and a loss of mass. As the extent of polymerization and temperature increase at a fixed heating rate, the dielectric relaxation spectra broadens, the characteristic relaxation time increases, and the equilibrium dielectric permittivity and dc conductivity decrease. An indication of the localized motions of the Johari-Goldstein relaxation was evident at high frequencies during the course of polymerization. The relaxation dynamics further evolves as further polymerization occurs on heating, and a new relaxation process develops in the partially polymerized state. Its spectra is described by a symmetric distribution of relaxation times, whose width increases on cooling and relaxation strength remains constant. Its relaxation rate follows the Arrhenius equation with an activation energy of 64 kJ/mol. There is also an indication of a further relaxation at high frequencies. The changes in the molecular dynamics observed as the liquid binary mixture at 298 K gradually became a vitrified solid at 393.2 K are expressed in terms of a decrease in the configurational entropy.

Introduction

Polymerization reactions occurring isothermally in a liquid decrease its absolute enthalpy, entropy, and volume, and increase its viscosity, dielectric and ultrasonic relaxation times, and shear and bulk moduli. The increase in viscosity, η , increases the vitrification temperature of a liquid irreversibly with time^{1–6} until the polymerization itself slows to a virtual halt. These irreversible changes are a consequence of an increase in the configurational restrictions as van der Waals' interaction are replaced by covalent bonds and the average interatomic distance decreases. When configurational restrictions become high enough that the liquid's η exceeds 10¹⁴ Poise, it is said to have vitrified. If the polymerization temperature is below the ceiling temperature, vitrification would occur before a chemical equilibrium is reached, and maximum polymerization may not occur. The process involves a negative feedback between chemical reactions and molecular diffusion, i.e., the occurrence of the polymerizing reactions slows the diffusion, which in turn slows the reaction itself.⁷ If the vitrified solid obtained by polymerization at a low temperature is subsequently heated, diffusivity of the reacting groups increases and polymerization occurs further. Thus the vitrification temperature increases further on heating a partially polymerized state.

As the density and viscosity of a diepoxide–diamine,^{1,2} diepoxide–monoamine,^{3,4,8,9} triepoxide–diamine,⁵ and triepoxide–monoamine⁴ increase on polymerizing spontaneously, a new relaxation process, which is termed the α -relaxation, evolves and rapidly dominates the dielectric relaxation behavior.

The dielectric strength of the α -process increases on further polymerization and its rate decreases, while the relaxation peak of the original relaxation process of the unreacted liquid remains in the GHz frequency range, but its relaxation strength decreases and becomes vanishingly small.^{1,9,10–13} Concurrently, a third relaxation process develops in the MHz frequency range.¹¹ Thus at a fixed high temperature in the unpolymerized state of an epoxide–amine mixture, only one fast relaxation process (in the GHz frequency range) occurs, in the intermediate state of polymerization, there are three processes, and in the finally polymerized state only two are discernible.^{12,13} Vitrification at a fixed temperature occurs when polymerization has reached an extent such that the rate of its α -relaxation process at that temperature decreases to a frequency of ~ 1 mHz.⁷ In contrast, vitrification of an unreacted or of a chemically stable liquid occurs on cooling at a temperature where the rate of its α -relaxation process, which evolves from the original GHz relaxation process, decreases to a frequency of ~ 1 mHz.

Polymerization may be carried out also by continuously heating the reacting liquid mixture. In this case, an increase in the temperature, T , has two effects: (i) the configurational entropy and volume increase and these in turn decrease the characteristic relaxation time, τ_0 , and η ; and (ii) the extent of polymerization, α , increases, and this decreases the configurational entropy and volume, which in turn increase τ_0 and η . The relative magnitudes of the two effects depend on α . In the initial stage of polymerization, the rate of increase in α with T , $(d\alpha/dT)_q$, at a given heating rate $q(= dT/dt)$, is small and the first effect dominates; in the intermediate state of polymerization, $(d\alpha/dT)_q$ is large and the second effect dominates, and in the

* Author to whom correspondence should be addressed.

high viscosity range, where $(d\alpha/dT)_q$ again becomes small, the second effect dominates. After α has reached its maximum value of one, $(d\alpha/dT)_q$ becomes zero, and the first effect dominates again.

For certain polymerization conditions, however, effect (ii) has been found to dominate with increase in T initially. Here τ_0 initially increases, reaches a maximum value when effect (ii) becomes comparable with effect (i), and finally τ_0 begins to decrease, thus showing a maximum value at a certain temperature as polymerization occurs on heating at a certain q .¹⁰ For certain other polymerization conditions the opposite is found,¹⁴ i.e., effect (i) dominates with initial increase in T , and τ_0 decreases initially, reaches a minimum value and then increases when polymerization continues and effect (ii) dominates with increase in T . Since the rate of polymerization depends on both the time and T , and the time determined by the heating rate q , there is a third effect, namely, that neither a maximum nor a minimum value of τ_0 may occur. Here we describe a simultaneous calorimetric and dielectric study in which this third effect is found.

Experimental Methods

4,4'-Diaminodicyclohexyl methane, also known as *p*-aminodicyclohexylmethane (PACM), of better than 98% purity was purchased from Fluka Chemicals and diglycidyl ether of bisphenol A (DGEBA) was a sample donated by Shell Chemicals. Both were used as such, as described in an earlier study, where citations to earlier work may be found.¹⁴ Stoichiometric mixtures (1 mole of PACM and 2 moles of DGEBA) were prepared by weighing and mechanically mixing at 300 K. The sample prepared was studied after 2–3 min of mixing in order to minimize polymerization during handling. The polymerization reactions between PACM and DGEBA lead to the formation of a network structure.

Thermal and dielectric measurements were made simultaneously on the same (one) sample both isothermally and during controlled heating and cooling according to a pre-programmed temperature–time profile. An instrument named SITA (Simultaneous Impedance and Thermal Analyzer), specially designed for real time, simultaneous calorimetry, and dielectric relaxation spectroscopy, was used for the study. Details of the equipment, procedure, and accuracy of the data have been given earlier.^{16–18}

Results and Data Analysis

The temperature–time profile for the polymerization of the PACM-DGEBA stoichiometric mixture, as performed by means of SITA, is summarized in Figure 1A. During heating from 308.2 to 393.2 K and subsequent thermal cycling from segment (1) through segment (6), various polymerization reactions occur at different rates in the liquid mixture. The NH_2 group of PACM first reacts with the epoxide group of DGEBA. In this addition reaction, the (cyclic) epoxide group opens, one H atom of the NH_2 group combines with the O atom of the now-open epoxide group, and an OH group is formed. The terminal C atom of the DGEBA becomes covalently bonded to the N atom of the diamine. This is the primary amine reaction. In the subsequent step, the second H atom of the NH_2 group, whose N atom is already covalently bonded to the terminal group of a diepoxide molecule after the primary amine reaction has occurred, combines with the O atom of the opened epoxide group of another DGEBA molecule, thus forming an OH group in the other molecule. Hence, the N atom of one NH_2 group becomes covalently linked to two DGEBA molecules. The latter reaction between the secondary amine and DGEBA is more sterically

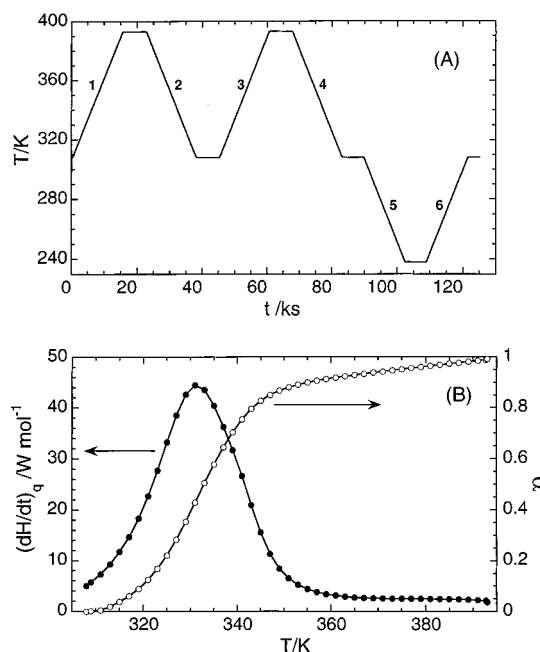


Figure 1. (A) The temperature–time profile used for the study of PACM-DGEBA mixture. The heating rate is 20 K/h. (B) The rate of heat released per mole of DGEBA and the extent of polymerization are plotted against the temperature while the liquid was heated from 308.2 to 393.2 K. Also plotted is the extent of reaction.

hindered than the first, and is therefore slower. A similar reaction with the second NH_2 group of the diamine connects the PACM molecule with four DGEBA molecules, each of which in turn is covalently bonded to two PACM molecules. There is also a third reaction known as etherification reaction,¹⁹ in which the OH group formed by the amine's reaction with the O atom of the epoxide group further reacts with the terminal epoxide group of another diepoxide molecule. This is the slowest reaction and becomes apparent only at high temperatures when its rate has increased substantially.

The heat evolved in these reactions was observed in the calorimetric part of the measurements made during heating at a rate of $q = 20$ K/h. It is shown in Figure 1B, where the rate of heat evolved during polymerization, $(dH/dt)_q$, is plotted against T . This plot corresponds to segment 1 of the plot in Figure 1A. It is evident that $(dH/dt)_q$ in Figure 1B does not reach zero when T reaches 393.2 K. This indicates that, (i) C_p of the polymerized state at 393.2 K is higher than that of the molecular state of the unreacted liquid at 293 K, and/or (ii) the polymerization is still occurring and its rate is relatively less T -dependent even though q of 20 K/h used in this study is 30-times slower than the rate of 10 K/min used generally in determining the total heat by differential scanning calorimetry. The total heat evolved was determined by adding the areas of all the exotherms observed for segments 1 to 4 of the plot in Figure 1A, and compared against the area under the remaining part of the curve by extrapolation to zero magnitude of $(dH/dt)_q$. The total area corresponded to 214 kJ/mol of DGEBA, and this remaining area corresponded to less than 0.2% of 214 kJ/mol (of DGEBA). This total heat of 214 kJ/mol was used in our calculation of α (= partial heat released up to T divided by 214). The plots of α against T from 308.2 to 393.2 K is also shown in Figure 1B (scale on the right). The plot corresponds to the measurements obtained for segment 1 in Figure 1A.

However, a DSC study²⁰ has shown that the ultimate glass softening temperature, T_g , of the polymer obtained by post-curing of PACM-DGEBA mixture is ~ 439 K, at which the

calorimetric relaxation time is 0.1–1 ks. Since the temperature to which the sample is heated here is ~ 46 K less than this T_g , it may be inferred that on heating to 393.2 K the sample in our study did not polymerize completely. Consequently, the total heat evolved may be more than 214 kJ/mol (of DGEBA), and hence our α values, as determined above, are overestimated. But as the sample had been kept for at least 16 ks at 393.2 K, and extrapolation of the exotherm to zero at T near 439 K in Figure 1B has indicated only a 0.2% increase, our neglect of the heat evolved on any further polymerization that may occur on heating to 439 K is within the experimental errors. Within that error plus the analytical errors, the heat of 214 kJ/mol (of DGEBA) evolved on heating to 393.2 K may be taken as corresponding to $\alpha = 1$, as had been considered in the earlier studies.^{10,14,18}

It should be pointed out that as increase in α brings a polymerizing sample close to its vitrification at a fixed T , an extremely small increase in α raises τ_0 by several orders of magnitude (see eq 12 later in this paper). Thus as $\alpha \rightarrow 1$, T_g becomes progressively more sensitive to increase in α . Therefore, the difference of 46 K between 393.2 and 439 K seems also qualitatively consistent with this sensitivity, i.e., that only a small increase in α is needed to raise an apparent T_g from 393.2 to 439 K. Nevertheless, if further long-time post-curing measurements to 439 K do show that the heat evolved is more than the above-given extrapolated value, then the values of α given here may be scaled with that new value. This scaling which may correspond to an overestimate of α by up to $\sim 1\%$, as before,^{10,14,18} has a negligible effect on our conclusions, and therefore, we discuss our results on the basis of our above calculated values obtained only by heating to 393.2 K.

The dielectric spectra were simultaneously measured for all segments (1) through (6) of the plot shown in Figure 1A, each spectra at 2 K intervals when the temperature was changed and or 360 s intervals, when the temperature was constant. The dielectric spectroscopy part of measurements during polymerization on heating the PACM-DGEBA mixture at 20 K/h from 308.2 to 393.2 K is shown in Figures 2 and 3. For convenience of expressing the main features, the plots of relative permittivity, ϵ' , dielectric loss, ϵ'' , and conductivity σ , are shown only for five fixed frequencies, 0.147, 1.0, 6.81, 46.4, and 464 kHz, in Figures 2A, 2B, and 2C, respectively. It is expected that polymerization occurs at all temperatures, but its rate, $(d\alpha/dT)_q$, is negligibly small at the lowest T of 303.2 K, and gradually increases as the temperature is increased initially. It becomes slower again at high temperatures, as the decrease in $(d\alpha/dT)_q$ in Figure 1B shows. The approximately linear initial decrease in ϵ' with increasing T is a combined effect of two processes, (i) the decrease in ϵ_s with increase in temperature according to the usual Curie law, and (ii) the decrease in ϵ_s with increase in polymerization.^{14,9} This is followed by a decrease in ϵ' corresponding to an inverted sigmoid-shape in Figure 2A. The sigmoid shape decrease is the consequence of increase in τ_0 when the effect of polymerization dominates the effect of heating such that τ_0 increases continuously with increasing temperature. Thus ϵ' decreases toward the limiting high-frequency permittivity, ϵ_∞ , of the polymer whose $\alpha \rightarrow 1$. At $T > 350$ K, and frequencies > 464 kHz, ϵ' of the polymerized state gradually increases on heating.

The plots in Figures 2B and 2C show the corresponding changes in ϵ'' and conductivity, σ , measured for the five frequencies. These show that ϵ'' and σ reach a peak at certain temperatures, which at first sight appear to be similar to those observed for a nonpolymerizing liquid. But here, these peaks

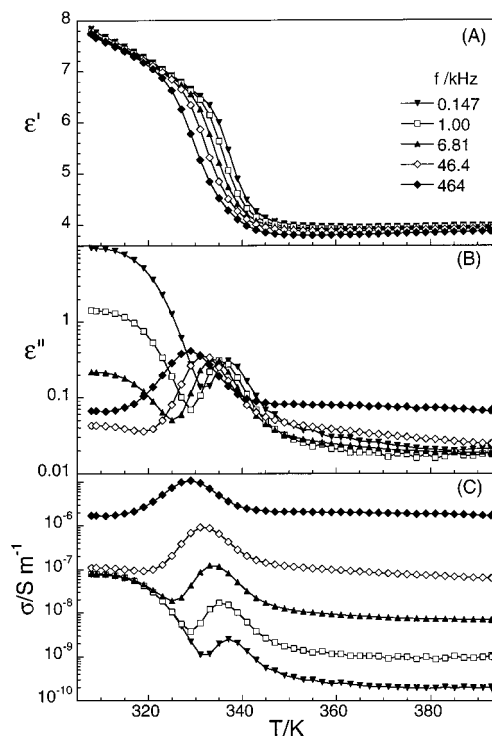


Figure 2. The ϵ' , ϵ'' , and σ of the PACM-DGEBA mixture measured at different fixed frequencies during heating at 20 K/h (segment 1 in Figure 1A) is plotted against the temperature in panels A, B, and C, respectively. The frequencies are indicated.

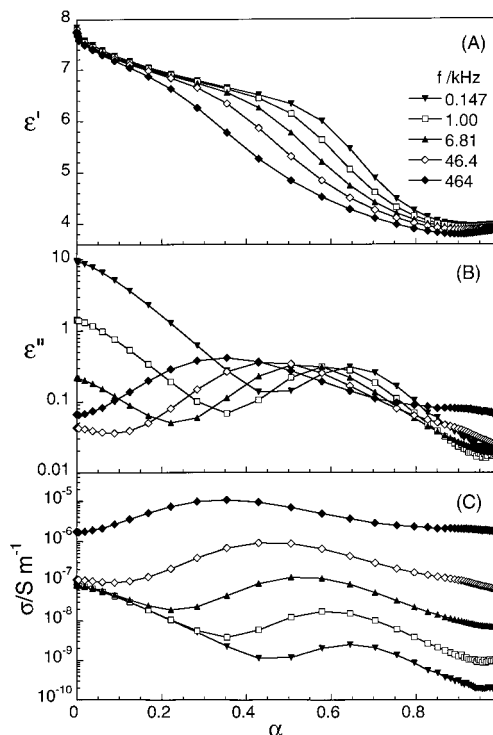


Figure 3. The ϵ' , ϵ'' , and σ of the PACM-DGEBA mixture measured during heating at 20 K/h (segment 1 in Figure 1A) at different fixed frequencies are plotted against the extent of polymerization, α . Each point corresponds to a different temperature which increases from left to right along the curves. For $\alpha = 0.1685$, $T = 323.0$ K; for $\alpha = 0.2214$, $T = 325$ K; $\alpha = 0.5786$, $T = 335.0$ K; and $\alpha = 0.8276$, $T = 345.0$ K. Each data point is for a temperature 2 K higher than the preceding one. Thus, the temperature for other data points may be determined.

shift to lower T on increase in the measurement frequency, which is the opposite of that found for a chemically stable liquid

for which the peaks shift toward higher T . The shift of the ϵ'' and the σ peaks to a lower T indicates that molecular relaxation time in the liquid is dominated by the increase in α and not increase in T . The partially polymerized state that shows a relaxation peak for 464 kHz is formed earlier, and therefore at a lower temperature for a fixed heating rate, than the partially polymerized state that relaxes at 0.147 kHz.

During the course of polymerization, the dc conductivity, σ_0 , decreases even though T continues to increase. The increase in ϵ' and decrease in ϵ'' seen at the high-temperature end of the plots for a fixed frequency measurement in Figures 2A and 2B is attributed to a predominant decrease in τ_0 due to increase in T of the sample's relaxation process whose maximum ϵ'' is reached at a frequency higher than the measurement frequencies. This is confirmed by the observed increase in ϵ'' with increasing frequency at a fixed temperature. Since T_g of the fully polymerized state of PACM-DGEBA is above 393.2 K, the changes in ϵ' and ϵ'' owing to a decrease in τ_0 of its α -relaxation process at these frequencies would be observed only at $T > 393.2$ K. The slow increase in ϵ' and decrease in ϵ'' at the high-temperature end in Figures 2A and 2B should therefore be seen as a part of a broad, Johari-Goldstein relaxation peak in the polymerized state.

The changes in ϵ' and ϵ'' plots of Figures 2A and 2B therefore contain effects of (i) increase in τ_0 and decrease in ϵ_s and σ , as α increases, and (ii) decrease in τ_0 and increase in ϵ_s and σ , as T increases. During heating at 20 K/min, the former effect dominates the relaxation behavior at relatively low temperatures, and the latter effect dominates at high temperatures where the polymerization rate has decreased to a minimum or is approaching zero. The same set of data are plotted against α in Figures 3A, 3B, and 3C, where each data point represents a different (T , α) pair and data points are separated by 2 K intervals. Here T increases from left to right and for $\alpha = 0.1685$, $T = 323.0$ K, for $\alpha = 0.2214$, $T = 325.0$ K, and for $\alpha = 0.8276$, $T = 334.5$ K. For other data points T may be determined by adding 2 K for each subsequent data point.

The spectra of ϵ' and ϵ'' at different T and α are shown in Figures 4A and 4B. For clarity, we have preferred this manner of plotting instead of the three-dimensional plots. Also, the spectra, which were measured every 360 s in this study or at 2 K interval, were many more than those shown here. In the partially polymerized state for $\alpha = 0.038$ at 315 K, the low-frequency plateau value of ϵ' (or ϵ_s) is observed. Here for the lowest T and low α values (shown by the upside-down filled triangle), ϵ'' decreases initially on increasing the frequency. This is the usual decrease associated with σ_0 . The ϵ'' value reaches a minimum and finally increases slightly at high frequencies. The relaxation features become clear at higher temperatures and both the ϵ' dispersion and the ϵ'' peak shift toward lower frequencies, finally moving out of our measurements range through the low-frequency side. In the spectra at 339.0 K ($\alpha = 0.704$), and at higher temperatures, ϵ' decreases and ϵ'' increases with the frequency above 10 kHz. This is an indication of a further relaxation process whose low-frequency end of the spectra is only partly observed here. The manner of ϵ' decrease and ϵ'' increase and their magnitudes, as determined here, are controlled by a combination of the increase in α and T .

The ϵ' and ϵ'' spectra were then measured when the sample was kept isothermally at 393.2 K for 6.25 ks between segments 3 and 4 in Figure 1A. The data at seven fixed frequencies are plotted against time in Figures 5A and 5B. These show that ϵ' decreases with time, and that the decrease is higher the lower

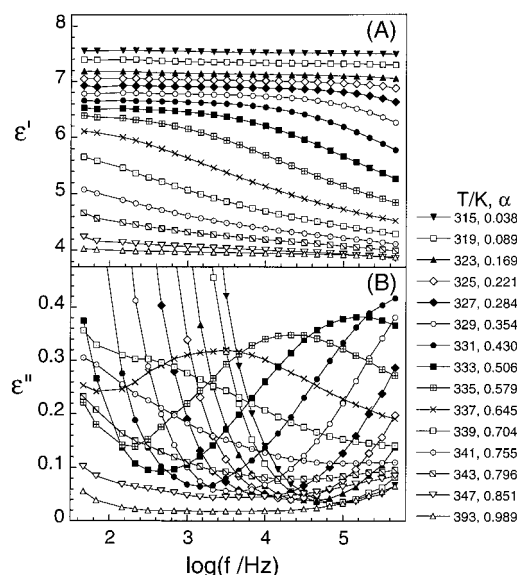


Figure 4. The ϵ' (panel A) and ϵ'' spectra (panel B) of the PACM-DGEBA mixture obtained at different T and α . Each spectrum measured at a certain temperature corresponds to a certain α , as listed.

the frequency. Correspondingly, ϵ'' decreases at low frequencies and increases for frequencies above 147 kHz. Both indicate that polymerization continues isothermally at 393.2 K, though extremely slowly, as $\sim 0.5\%$ decrease in ϵ' and at most 6% change in ϵ'' indicate. Evidently, the polymerization is incomplete, but it is not certain how close to its ultimate value of 1 has the α reached. This undoubtedly causes an uncertainty in our α values, but no more than $\sim 1\%$, as discussed earlier here. The ϵ' and ϵ'' spectra of the liquid kept isothermally at 393.2 K in segments 3 and 4 of Figure 1A were also plotted against time at a fixed frequency. The data showed a decrease of $\sim 0.25\%$ in ϵ' , and no decrease in ϵ'' within the experimental errors.

The sample was then cooled through segments 4 and 5 also at 20 K/h rate and its ϵ' and ϵ'' spectra obtained at 360 s intervals. Typical spectra obtained over the 377.5–239.0 K range are shown in Figures 6A and 6B. The decrease of ϵ' and the increase of ϵ'' at 377.5 K in Figures 6A and 6B correspond to the same feature that was observed in the dielectric spectra measured during polymerization at 393.0 K in Figures 4A and 4B, but for a state with α closer to 1, rather than α closer to 0.989 at 393.0. (Again, these α values are on a relative scale, and may need scaling if a substantial evolution of heat is measured on post-curing to 439 K, as discussed earlier here.) Therefore, the spectra in Figures 6A and 6B should correspond to the Johari-Goldstein relaxation, which has now been revealed also by physically aging a glass.²¹ These show clearly that the ϵ'' peak shifts to lower frequencies on cooling, and its height rapidly decreases, the latter being a characteristic of this relaxation process.^{22,23} Subsequent measurements at 360 s intervals were made on the sample kept at 239 K. These showed no change in the values of ϵ' and ϵ'' with time. The sample was heated again to 308.2 K as in segment 6 in Figure 1A, and its spectra measured in the same manner as done during the first heating. The spectra were found to be identical to those observed during the cooling of the sample in segment 5 of Figure 1A, and are therefore not included. Moreover, no indication of an exothermic feature was observed on thermal cycling. On that basis, we conclude that the spectra in Figure 6A are for an almost completely polymerized state of the network structure of PACM-DGEBA, as formed in the above-given thermal

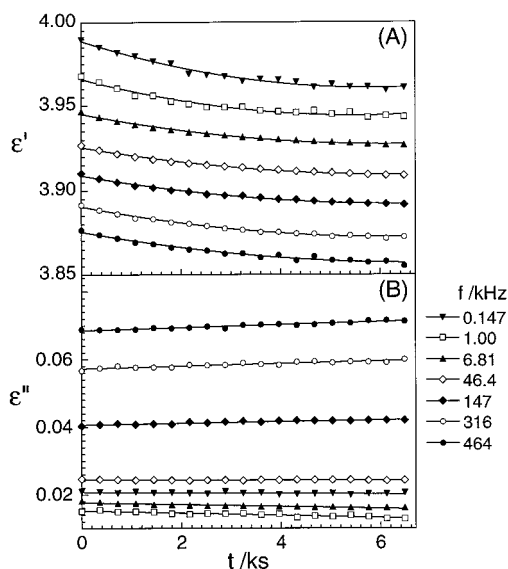


Figure 5. The ϵ' (panel A) and ϵ'' (panel B) of the PACM-DGEBA mixture are plotted against time when the polymerizing mixture was kept isothermally at 393.2 K between segments 1 and 2 in Figure 1A. The frequencies are indicated.

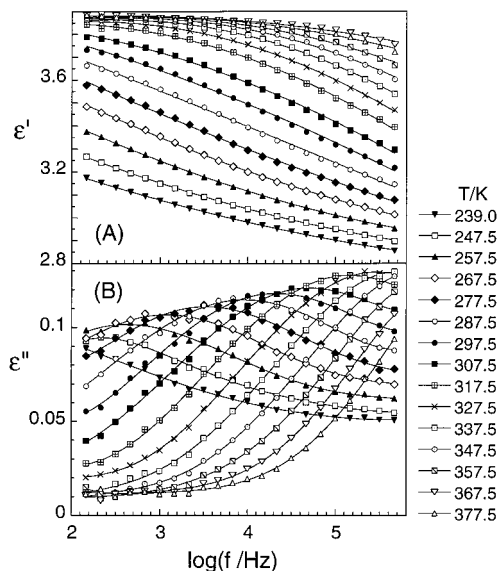


Figure 6. The ϵ' (panel A) and ϵ'' (panel B) spectra of the polymerized PACM-DGEBA mixture measured at different T values during the cooling of the sample from 393.2 to 238 K (segments 4 and 5 in Figure 1A). The spectra correspond to the sub- T_g or Johari-Goldstein relaxation. The temperatures are indicated.

history. The spectra were found to fit the Cole–Cole symmetric relaxation equation with the parameter $\alpha_{\text{Cole–Cole}}$ of 0.33 at 247.5 K linearly increasing with T to 0.44 at 337.5 K. The amplitude of the relaxation remained constant with changing T at 0.75 ± 0.05 . The data at $T < 300$ K indicated a contribution at high frequencies from a faster relaxation process. This process is the remnant of the gigahertz frequency relaxation process which has been observed in the unreacted liquid.¹¹ It was not investigated here further.

The normalized ϵ'' values were obtained from the data in Figure 6B. These are plotted against the normalized frequency in Figure 7A. The plots show the spectra broadening on cooling, as discussed above. Finally, Figure 7B shows a plot of the relaxation rate, $f_{\text{max}} (= \tau_0/2\pi)$, of the process in the glassy state against the reciprocal temperature. The data are described by the Arrhenius equation, $f_{\text{max}} = 10^{15.62} \exp(-E^*/RT)$, where E^*

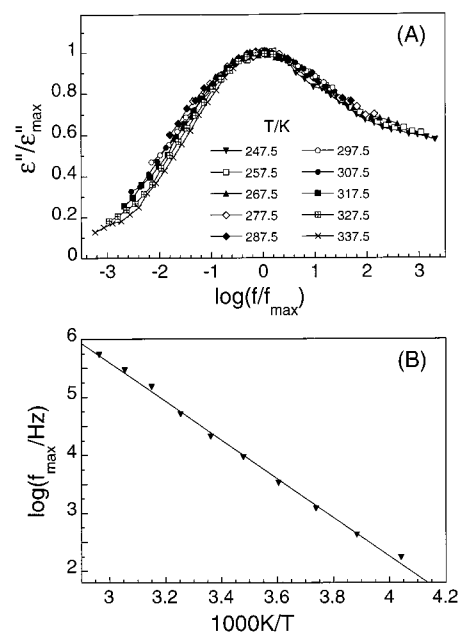


Figure 7. (A) The ϵ'' normalized by ϵ''_{max} is plotted against (f/f_{max}) . The temperatures are indicated. (B) The frequency of the ϵ'' peak is plotted against the reciprocal temperature. The line is the fit of the Arrhenius equation. Both (A) and (B) are for the polymerized PACM-DGEBA mixture in the glassy state. The data points noted as filled triangles in (B) are taken from ref 20.

is the activation energy and R the gas constant, with $E^* = 64.0$ kJ/mol.

The ϵ' and ϵ'' spectra shown in Figure 4 were analyzed in order to determine the dc conductivity, σ_0 , the stretched exponential parameter, β , and the characteristic relaxation time, τ_0 , of the relaxation function, $\phi = \exp[-(t/\tau_0)^\beta]$, where t is the microscopic time. The values of σ_0 are plotted against α in Figure 8A, those of β and ϵ_s against α in Figure 8B, and those of τ_0 against α in Figure 8C, where the temperatures are also indicated. Here, the first three data points from the extreme left are for $T = 321$, 323, and 325 K, respectively.

Figures 9A and 9B show the plots of ϵ' and ϵ'' against T , as measured for a fixed frequency of 1 kHz during first heating of the PACM-DGEBA mixture from 308.2 to 393.2 K and then cooling back to 308.2 K, heating again to 393.2 K, and finally cooling it to 238.2 K. The numbers in the figure refer to the segments of thermal history given in Figure 1A.

Discussion

a. Thermodynamic Changes during Polymerization. The plot in Figure 1B shows that α does not reach its limiting value asymptotically. At first sight this occurrence and the relatively large slope of the plot of α at $T > 350$ K would appear as a broadened out exotherm of the etherification reaction,¹⁹ as described earlier here. This is usually a high temperature reaction, which has also been observed in the isothermal polymerization of an excess-diepoxide-containing mixture at a relatively low temperature. In an earlier study of PACM-DGEBA' polymerization,¹⁸ a shoulder was found in the plot of $(dH/dT)_q$ against T above 345 K (Figure 1C in ref 18). But no shoulder in the plot of $(dH/dT)_q$ against T is observed here. Since sufficient amount of the diamine is already present for the stoichiometric reaction, it seems unlikely that the lack of asymptotic approach of α at high temperatures toward its value of 1 indicates the etherification reactions. We attribute, therefore, the broadened out exotherm at high temperatures, particularly

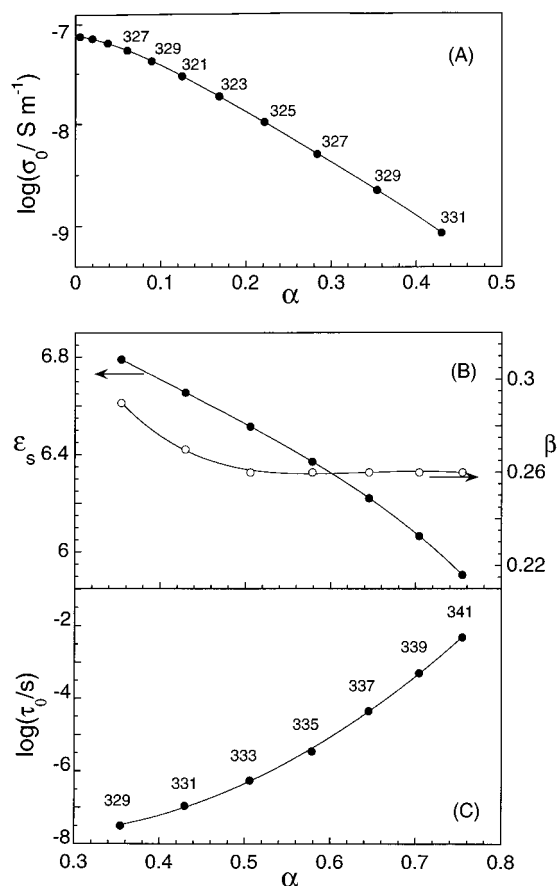


Figure 8. (A) The dc conductivity, σ_0 , is plotted against the extent of polymerization, α . (B) The corresponding plots of ϵ_s and β . (C) The corresponding plot of the characteristic relaxation time, τ_0 . All figures are for the polymerizing PACM-DGEBA mixture during its heating at 20 K/h in segment 1 of Figure 1A. The temperature is indicated next to the data points.

the slower than expected approach of α to the asymptotic limit, to a frustrated diffusion-control in the polymerization reaction. To elaborate, addition reactions approach the diffusion-control limit as η increases rapidly on initial heating, but after a certain rate of increase in α has been reached, an increase in T decreases η and this prevents the addition reactions from reaching diffusion control. (This is also observed when an incompletely polymerized state is heated beyond its T_g .) Hence, for a given q ($= dT/dt$), the polymerization rate $(d\alpha/dT)_q [= (d\alpha/dt)/q]$ would begin to rise again with increase in T , but only as long as decrease in η on heating dominates the increase in η on polymerization. Thus in the high-temperature limit where polymerization has occurred close to its maximum, the diffusion-control limit would not be reached and its (equilibrium) ceiling temperature may be found.

The above-discussed changes would cause (i) the dc conductivity, σ_0 , the static permittivity, ϵ_s , β , and τ_0 to vary in a manner that is determined by the more dominant of the two quantities, T or α , (i.e., the physical or the chemical states of the polymerizing liquid), and (ii) the evolution of the faster relaxation process observed in liquids and glasses, and change in its characteristics.

b. The Effects of Polymerization and Temperature on the ϵ_s , β , σ_0 , and τ_0 . Since both time and temperature continuously increase at a fixed q in our experiments, any observed effects are attributable to both. But since the time is not a control-variable, it is replaced by α and the state of a system is then defined precisely by only α and T at any instant during the

course of polymerization. Combined changes in ϵ_s , β , σ_0 , and τ_0 as a result of polymerization on heating at a fixed q are therefore written as follows:

$$d\epsilon_s = \left(\frac{\partial \epsilon_s}{\partial T}\right)_\alpha dT + \left(\frac{\partial \epsilon_s}{\partial \alpha}\right)_T d\alpha \quad (1)$$

$$d\beta = \left(\frac{\partial \beta}{\partial T}\right)_\alpha dT + \left(\frac{\partial \beta}{\partial \alpha}\right)_T d\alpha \quad (2)$$

$$d \ln \sigma_0 = \left(\frac{\partial \ln \sigma_0}{\partial T}\right)_\alpha dT + \left(\frac{\partial \ln \sigma_0}{\partial \alpha}\right)_T d\alpha \quad (3)$$

$$d \ln \tau_0 = \left(\frac{\partial \ln \tau_0}{\partial T}\right)_\alpha dT + \left(\frac{\partial \ln \tau_0}{\partial \alpha}\right)_T d\alpha, \quad (4)$$

where the first term on the right-hand side in eqs 1–4 represents the effect of T for a fixed α , and the second term, the effect of α at a fixed T . The first term in eqs 1–4 is for a chemically stable state, and the second for a chemically evolving state. The magnitude is generally negative for $(\partial \ln \sigma_0)/\partial T)_\alpha$ and positive for both $(\partial \beta/\partial T)_\alpha$ and $(\partial \ln \sigma_0/\partial T)_\alpha$. It is negative also for $(\partial \beta/\partial \alpha)_T$ and $(\partial \ln \sigma_0/\partial \alpha)_T$ and positive for $(\partial \ln \tau_0/\partial \alpha)_T$. The magnitude of $(\partial \epsilon_s/\partial T)_\alpha$ is usually negative, as given by the Curie law, but it can be positive or negative for $(\partial \epsilon_s/\partial \alpha)_T$, depending upon the change in the effective dipole moment on polymerization.

The slope of the plot of ϵ_s against α (as T also increases), as shown in Figure 8B, is negative. It is a reflection of the sum of two negative terms, and therefore the ϵ_s curve has a higher slope than it would have if T was to remain constant. In contrast, the corresponding plot of β also in Figure 8B shows a compensation of the two effects, and the change would be more if T was to remain constant. Even though T also increases as α increases, the plots of σ_0 in Figure 8A shows a monotonic decrease and that of τ_0 in Figure 8C shows a monotonic increase.

On the assumption that the predominant contribution to σ_0 is from the proton transfer along the H-bond network in the binary mixture, and not due to the ionic mobility, its magnitude is given by^{24–26}

$$\sigma_0 = \sigma_{0,0} \left(\frac{\alpha - \alpha_{\text{gel}}}{\alpha_{\text{gel}}} \right)^{p'} \quad (5)$$

where $\sigma_{0,0}$ is the dc conductivity at $\alpha = 0$, α_{gel} is the extrapolated gelation time, and p' is the critical exponent. For the condition that conduction via proton transfer along the H bonds dominates even at high temperatures where thermal energy is high and the ionic mobility (for the ionic conduction) large,

$$\left(\frac{\partial \ln \sigma_0}{\partial \alpha} \right)_T = \left(\frac{p'}{(\alpha - \alpha_{\text{gel}})} \right)_T \quad (6)$$

and using the Vogel-Fulcher-Tamman type^{27–29} temperature dependence of σ_0 ,

$$\sigma_0 = A_\sigma \exp \left(- \frac{B_\sigma}{RT_{0,\sigma}} \right) \quad (7)$$

where A_σ , B_σ , and $T_{0,\sigma}$ are empirical constants, we may write,

$$\left(\frac{\partial \ln \sigma_0}{\partial \alpha} \right)_\alpha = \left(\frac{B_\sigma}{(T - T_{0,\sigma})^2} \right)_\alpha \quad (8)$$

Thus,

$$d \ln \sigma_0 = \left(\frac{B_\sigma}{(T - T_{0,\sigma})^2} \right)_\alpha dT + \left(\frac{p}{(\alpha - \alpha_{\text{gel}})_T} \right) d\alpha \quad (9)$$

To obtain the corresponding conditions for τ_0 , we use its relation with α ,^{1,2,4-6,9}

$$\tau_0 = \tau_0(\alpha = 0) \exp[S(\alpha)^p] \quad (10)$$

or,

$$\ln \tau_0 = \ln \tau_0(\alpha = 0) + S(\alpha)^p \quad (11)$$

where S is a quantity equal to the normalized value of τ_0 at a fixed temperature, i.e., $S = \ln[\tau_0(\alpha = 1)/\tau_0(\alpha = 0)]$, and p is an empirical parameter. By differentiating eq 11 with respect to α ,

$$\left(\frac{\partial \ln \tau_0}{\partial \alpha} \right)_T = Sp\alpha^{p-1} \quad (12)$$

Since, both S and p depend on T and the nature of the polymerization reactions, the term $(\partial \ln \tau_0 / \partial \alpha)_T$ itself is a function of T here. On the assumption that τ_0 varies with T according to the Vogel-Fulcher-Tammann equation,²⁷⁻²⁹

$$\tau_0 = A \exp\left(\frac{B}{T - T_0}\right) \quad (13)$$

where A , B , and T_0 are empirical constants. The negative term $(\partial \ln \tau_0 / \partial T)_\alpha$, is given by

$$\left(\frac{d \ln \tau_0}{dT} \right)_\alpha = - \left(\frac{B}{(T - T_0)^2} \right)_\alpha \quad (14)$$

It is determined by both B and T_0 which themselves change with increase in α . Thus,

$$d \ln \tau_0 = - \left(\frac{B}{(T - T_0)^2} \right)_\alpha dT + Sp\alpha^{p-1} d\alpha \quad (15)$$

The change in B_σ , B , T_0 , and $T_{0,\sigma}$ with increase in α is not known. Therefore, it is difficult to determine the magnitudes of $(\partial \ln \sigma_0 / \partial T)_\alpha$ and $(\partial \ln \tau_0 / \partial T)_\alpha$ from eqs 9 and 15. Nevertheless, a qualitative consideration is still possible. When the second term on the right-hand side of eq 3 dominates, σ_0 decreases in our experiment, as seen in Figure 8B. Similarly, when the second term in eq 4 dominates, τ_0 increases, as seen in Figure 8C. Equations 9 and 15 also lead to conditions for a maximum and minimum values of both σ_0 and τ_0 . These maximum and minimum in both σ_0 and τ_0 have been observed in earlier studies.^{10,14}

The above discussion of τ_0 can be carried out also in terms of the configurational entropy theory.³⁰ In this theory, the configurational entropy, S_{conf} is related to τ_0 by

$$\tau_0 = \tau_0(\infty) \exp\left(\frac{\Delta\mu s_c^*}{S_{\text{conf}} k_B T}\right) \quad (16)$$

$$\ln \tau_0 = \ln \tau_0(\infty) + \left(\frac{\Delta\mu s_c^*}{S_{\text{conf}} k_B T} \right) \quad (16a)$$

where $\Delta\mu$ is the potential energy hindering the cooperative rearrangement of the molecules per repeat unit or monomer,

s_c^* is the critical entropy, k_B is the Boltzmann constant, and $\tau_0(\infty)$ is the relaxation time when TS_{conf} is formally infinity. Its magnitude is in the vibrational time range and is seen as invariant of α . In their interpretation of the various polymers and molecular liquids, Adam and Gibbs³⁰ had noted that $\Delta\mu s_c^*$ is constant for a material. We assume that $\Delta\mu s_c^*$ remains constant with increase in α (i.e., the macromolecule's size), and differentiate eq 16a with respect to α at a constant T to obtain

$$\left(\frac{\partial \ln \tau_0}{\partial \alpha} \right)_T = - \frac{\Delta\mu s_c^*}{k_B T S_{\text{conf}}^2} \left(\frac{\partial S_{\text{conf}}}{\partial \alpha} \right)_T \quad (17)$$

where the term $(\partial S_{\text{conf}} / \partial \alpha)_T$ is negative. It should be stressed that the use of the configurational entropy theory here does not imply that there is an underlying thermodynamic transition at a certain temperature above 0 K, only that S_{conf} decreases with decrease in T , and with increase in α . Arguments for the decrease of S_{conf} to zero at 0 K have been presented elsewhere,³¹ along with evidence from experiments in favor of those arguments.

The change in τ_0 with T is obtained by differentiating eq 16a with respect to T at a constant α ,

$$\left(\frac{\partial \ln \tau_0}{\partial T} \right)_\alpha = -\Delta\mu s_c^* \left[T \left(\frac{\partial S_{\text{conf}}}{\partial T} \right) + S_{\text{conf}} \right] \left(\frac{1}{k_B T^2 S_{\text{conf}}^2} \right)_\alpha \quad (18)$$

Equations 17 and 18 are then substituted in eq 4 to obtain,

$$d \ln \tau_0 = -\Delta\mu s_c^* \left[T \left(\frac{\partial S_{\text{conf}}}{\partial T} \right) + S_{\text{conf}} \right] \left(\frac{1}{k_B T^2 S_{\text{conf}}^2} \right)_\alpha dT - \left(\frac{\Delta\mu s_c^*}{k_B T S_{\text{conf}}^2} \right) \left(\frac{\partial S_{\text{conf}}}{\partial \alpha} \right)_T d\alpha \quad (19)$$

For τ_0 to increase in our experiment, as seen in Figure 8C, the second term on the right-hand side of eq 19, which is intrinsically negative (because $(\partial S_{\text{conf}} / \partial \alpha)_T < 0$), should exceed the first term. Equation 19 also indicates that τ_0 will be constant when the two terms compensate, or will become negative when the second term is lesser than the first (in which $(\partial S_{\text{conf}} / \partial T) > 0$), as has been already found by experiments.^{10,14} Since no independent means of determining $\Delta\mu$, s_c^* , and S_{conf} is currently available, predictions of these conditions have not yet been possible.

We finally discuss our observations of increase in τ_0 in terms of a temperature-variant Arrhenius energy, which has been recently expressed by Dyre et al.,³² and Dyre³³ and in terms of what was called the "shoving model".³³ They considered that molecular interactions are anharmonic at high viscosities, particularly near T_g , with strong short-range repulsion and weak long-range attraction, and that a certain amount of energy is spent in the shoving of the surrounding molecules in a local region before diffusion can occur at all. This increases the volume of the aggregate from V to $(V + \Delta V)$. In this manner, a critical volume may be defined as, $V_c = 2(\Delta V)^2/3V$. This consideration ultimately lead to the equation^{32,33}

$$\tau_0 = \tau_0(\infty) \exp(G_\infty V_c / k_B T) \quad (20)$$

where G_∞ is the temperature-dependent shear modulus of a liquid and k_B the Boltzmann constant. They^{32,33} argued that eq 20 resembles the expression obtained in the revised mode-coupling model,³⁴ when G_∞ is replaced by the zero-frequency bulk modulus. Although both G_∞ and V_c depend on T , they

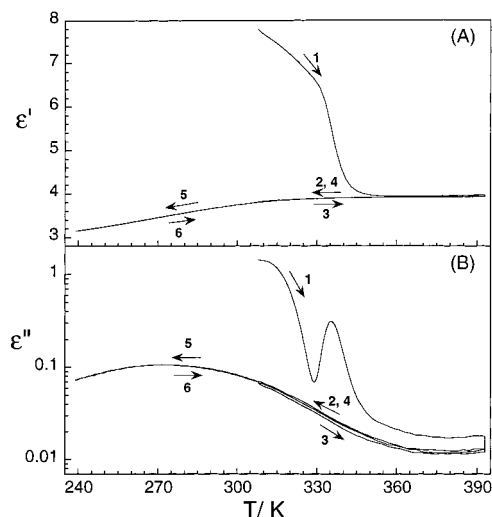


Figure 9. The ϵ' (panel A) and ϵ'' (panel B) measured at 1 kHz frequency are plotted against the temperature. The numbers refer to the segment of the temperature–time profile as shown in Figure 1A. The arrows indicate the direction of temperature change, heating or cooling at 20 K/h.

sumized that the temperature dependence of V_c is negligible in comparison with that of G_∞ . Thus the energy term, E , in the Arrhenius equation, $\tau_0 = \tau_0(\infty) \exp(E/RT)$ itself increases with decrease in T . Since the phonon-frequency values of the preexponential terms in eqs 16–20 are taken to be identical, a comparison of eqs 16 and 20 leads to $G_\infty V_c = z^* \Delta\mu$ when the quantities are represented in mole units. In relation to our experiments, it means that $G_\infty V_c$ increases rapidly on polymerization, i.e., the positive magnitude of $[d(G_\infty V_c)/d\alpha]$ is higher than that of $[d(G_\infty V_c)/dT]$.

c. The Localized Motions or the Johari-Goldstein Relaxation Process. We now consider the evolution of the localized relaxation, or the Johari-Goldstein process, with change in temperature, as is seen in the spectra in Figure 6A. As discussed earlier here, the Cole–Cole distribution parameter for these spectra increases with decrease in T , i.e., the spectra broadens, which is evident also from the normalized spectra in Figure 7A, its relaxation strength decreases and there is an indication of another relaxation process at higher frequencies. This relaxation is a new process that develops on polymerization⁷ and whose relaxation strength has been found to increase as α increases. The original relaxation peak in the unpolymerized liquid, which appears at gigahertz frequencies has been found to diminish rapidly^{11–13} on polymerization, and to become virtually extinct. Deviations from smooth decline in ϵ'' at the high-frequency end in the normalized spectra in Figure 7A indicates that this high-frequency relaxation process is still present, although its strength is small.

Evolution of this new relaxation process during the thermal cycling from 308.2 to 393.2 K may be seen more clearly in the plots of ϵ' and ϵ'' measured at a fixed frequency of 1 kHz in Figures 9A and 9B. Here ϵ' decreases from 7.8 at 307 K to 3.9 at 355 K, and then increases slightly on further heating to 393 K in segment (1) of Figure 1A, and a relatively narrow peak in ϵ'' appears, which is a result of dominating effect of polymerization, as discussed earlier here. On cooling from 393.2 to 238 K, ϵ' increases from 3.1 to 4.0 and remains within this range on thermal cycling. Correspondingly, a broad ϵ'' peak appears, as seen in Figure 9B. The low temperature beginning of this peak is not completely visible even over the broad temperature range of 155.2 K in Figure 9B. This is partially due to the contributions from the further relaxation process noted on the

high frequency side of the normalized spectra in Figure 7A which would appear at low temperatures, and partly due to the intrinsic width of the relaxation peak. It is remarkable here that heating of a molecular liquid leads to a vitrified polymer, with the characteristic features of the various molecular dipole and ion dynamics changing irreversibly.

The finding that the relaxation rate, f_m , of this process follows the Arrhenius equation in Figure 7B implies that its rate is independent of the overall S_{conf} of the partially polymerized states above and below their T_g s, i.e., S_{conf} in eq 16 remains constant with changing T , and E^* becomes equal to $(\Delta\mu_s^*/S_{\text{conf}})$. Strictly interpreted, this means that the rate of the Johari-Goldstein relaxation, is largely independent of a thermodynamic change in surrounding of the local regions caused by polymerization or temperature. As the volume also decreases on polymerization, it would be also independent of the change in the viscosity-determining free volume of a liquid in the current free volume theories.^{35,36} In terms of the Dyre et al. model,^{32,33} $[d(G_\infty V_c)/dT]$ in eq 20 becomes zero for the Johari-Goldstein relaxation. This also means that this relaxation may not involve anharmonic effect large enough to cause a significant deviation of $[d(G_\infty V_c)/dT]$ from zero. It should be mentioned that in another study of PACM-DGEBA mixture³⁷ the data analysis was empirical and led to different results from ours, as has been discussed in two earlier studies,^{18,38} where a list of references on studies of other thermosetting polymers has been provided.^{37,38} Williams et al.,³⁹ have also reviewed the dielectric relaxation studies on such time-variant process. These papers may be consulted for details of the earlier studies.

Conclusions

The dc conductivity decreases and the dielectric relaxation time increases on heating a liquid in which addition reactions polymerize it. This is the opposite of the usual finding that the dc conductivity increases and the dielectric relaxation time decreases on heating. Magnitude of the net effect varies with the temperature and the heating rate. Localized modes of the Johari-Goldstein relaxation become evident when polymerization approaches completion, the viscosity has reached a high value and the α -relaxation process has become substantially slow. There is evidence of a further relaxation at high frequencies. The Arrhenius energy of the localized motions is 64 kJ/mol, and its rate is independent of the overall configurational entropy of the liquid or the glassy state of the polymer formed. There is a remarkable change in the dielectric behavior on thermal cycling in which a molecular liquid becomes a glassy polymer with a new broad relaxation peak due to localized dipolar motions. Changes in the properties observed on increasing the temperature are predominantly due to the polymerization of the liquid mixture, and those observed on decreasing the temperature are attributable to the molecular motions in the vitrified polymer.

Acknowledgment. This work was partly supported by a Natural Sciences and Engineering Research Council of Canada's grant to G.P.J. for general research.

References and Notes

- (1) Tombari, E.; Johari, G. P. *J. Chem. Phys.* **1992**, *97*, 6677.
- (2) Parthun, M. G.; Johari, G. P. *Macromolecules* **1992**, *29*, 3254; *ibid.* **1993**, *26*, 2392; *J. Polym. Sci. B Polym. Phys.* **1992**, *30*, 655.
- (3) Johari, G. P.; Pascheto, W. J. *Chem. Soc., Faraday Trans.* **1995**, *91*, 345.
- (4) Parthun, M. G.; Wasylyshyn, D. A.; Johari, G. P. *J. Mol. Liq.* **1996**, *69*, 219; 283.
- (5) Wasylyshyn, D. A.; Johari, G. P. *J. Polym. Sci. Part B: Polym. Phys.* **1997**, *35*, 437.

- (6) Parthun, M. G.; Johari, G. P. *J. Chem. Phys.* **1995**, *97*, 6301.
- (7) Johari, G. P. Dynamics of Irreversibly forming Macromolecules. In *Disorder Effects in Relaxational Processes*; Richert, R., Blumen, A., Eds.; Springer: Berlin, 1994; p 627.
- (8) Parthun, M. G.; Johari, G. P. *J. Chem. Phys.* **1995**, *103*, 440. $TS_{\text{conf}} = 0$ on p 448 should read $TS_{\text{conf}} = \infty$ and the extreme rhs of eq 4 should be multiplied by the term $\{(\epsilon_{\infty} + 2)/3\}^2$.
- (9) Tombari, E.; Ferrari, C.; Salvetti, G.; Johari, G. P. *J. Phys. Condens. Matter* **1997**, *9*, 7017; *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1293.
- (10) Ferrari, C.; Tombari, E.; Salvetti, G.; Johari, G. P. *J. Chem. Phys.* **1999**, *110*, 10599.
- (11) Wasylyshyn, D. A.; Johari, G. P.; Tombari, E.; Salvetti, G. *Chem. Phys.* **1997**, *223*, 313; *J. Phys. Condens. Matter* **1997**, *9*, 10521.
- (12) Parthun, M. G.; Johari, G. P. *J. Chem. Phys.* **1995**, *103*, 7611.
- (13) Wasylyshyn, D. A.; Johari, G. P. *J. Chem. Phys.* **1996**, *104*, 5683.
- (14) Tombari, E.; Salvetti, G.; Johari, G. P. *J. Chem. Phys.* **2000**, *113*, 6957.
- (15) Johari, G. P.; Ferrari, C.; Salvetti, G.; Tombari, E. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2997.
- (16) Ferrari, C.; Salvetti, G.; Tombari, E.; Johari, G. P. *Il Nuovo Cimento* **1996**, *18D*, 1443.
- (17) Tombari, E.; Ferrari, C.; Salvetti, G.; Johari, G. P. *J. Polym. Sci. B, Polym. Phys.* **1998**, *36*, 303.
- (18) Tombari, E.; Ferrari, C.; Salvetti, G.; Johari, G. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1965. In Figure 4A, the peak is at zero on the log- (f/f_{max}) scale, and the correct labeling is the value given minus 4. The half-width of the relaxation peak in Figures 3A and 4A should be read as 3.3 decades and not 5 decades.
- (19) Schechter, L.; Wynstra, J.; Kurkjy, R. P. *Ind. Eng. Chem.* **1956**, *48*, 94.
- (20) Wissanrakkit, G.; Gilham, J. K.; Enns, J. B. *J. Appl. Polym. Sci.* **1990**, *41*, 1895.
- (21) Schneider, U.; Brand, R.; Lunkenheimer, P.; Loidl, A. *Phys. Rev. Lett.* **2000**, *84*, 5560.
- (22) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.
- (23) Johari, G. P. *J. Chem. Phys.* **1973**, *58*, 1766.
- (24) Parthun, M. G.; Johari, G. P. *Macromolecules* **1992**, *25*, 3149.
- (25) Zhou, J.-F.; Johari, G. P. *Macromolecules* **1997**, *30*, 8085.
- (26) Johari, G. P.; Wasylyshyn, D. A. *J. Polym. Sci. B, Polym. Phys.* **2000**, *38*, 122.
- (27) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
- (28) Tammann, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245.
- (29) Fulcher, G. *J. Am. Ceram. Soc.* **1925**, *77*, 3701.
- (30) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
- (31) Johari, G. P. *J. Chem. Phys.* **2000**, *113*, 751. *Chem. Phys.* **2001**, *265*, 217. *J. Phys. Chem. B.* **2001**, *105*, 3600. *J. Non-Cryst. Solids* **2001**, *288*, 148.
- (32) Dyre, J. C.; Olsen, N. B.; Christensen, T. *Phys. Rev. B* **1996**, *53*, 2171.
- (33) Dyre, J. C. *J. Non-Cryst. Solids* **1998**, *235–237*, 142.
- (34) Goetze, W.; Sjogren, L. *Rep. Prog. Phys.* **1992**, *55*, 241.
- (35) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1961**, *34*, 120.
- (36) Grest, G. S.; Cohen, M. H. *Adv. Chem. Phys.* **1981**, *48*, 455.
- (37) Fournier, J.; Williams, G.; Duch, C.; Aldridge, G. A. *Macromolecules* **1996**, *29*, 7097.
- (38) Wasylyshyn, D. A.; Johari, G. P. *J. Polym. Sci. B, Polym. Phys.* **1998**, *36*, 2703.
- (39) Williams, G.; Smith, I. K.; Holmes, P. A.; Varma, H. *J. Phys. Condens. Matter A* **1999**, *11*, 57.