Dielectric properties of the polymerization of an aromatic polyimide

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Dielectric measurements made over a wide range of frequency are shown to provide a sensitive means for observing the chemistry of the polymerization process of an aromatic polyimide continuously as the monomer mixture undergoes major changes in viscosity leading to a fully cured, insoluble, crosslinked thermoset. Dynamic dielectric measurements of the polymerization of the high temperature polyimide prepared from a mixture of BTDE, MDA, NE and designated LaRC-160 have been made at a series of frequencies from 5 to 5×10^6 Hz. The capacitance (C), dissipation (D), and the conductivity (G) together with time and temperature were recorded. The complex permittivity (ε^*) has been determined throughout the cure cycle. Using their frequency dependence, ε' and ε'' have been separated into their ionic and dipolar components. The time and temperature dependence of the dielectric data are correlated with the previously reported imidization cure chemistry of the LaRC-160 system (ref. 1). The high temperature crosslinking reaction has also been observed dielectrically and compared with published viscosity and reaction data. Changes in the time–temperature properties of this polyimide system as a function of resin age over a period of six months have also been studied. In addition, the effect of the resin's composition on the time–temperature cure properties of the polymer has been examined using dynamic dielectric measurements.

(Keywords: aromatic polyimide; LaRC-160; dielectric analysis; complex permittivity; specific conducitivity; ionic mobility)

INTRODUCTION

Most instrumental methods for analysing the polymerization process are limited to chemical characterization of the initial monomer mixture or destructive tests on the fully reacted polymer. A method which allows non-destructive, *in-situ*, characterization of the polymerization reaction is highly desirable. Dynamic dielectric measurements are potentially such a method.

Dynamic dielectric measurements made over a wide range of frequency have the potential to provide a sensitive and convenient technique for monitoring the cure process, the onset of flow, the onset of the reaction, and variations in the stoichiometry of the monomer mixture. In this paper, dynamic dielectric analysis is used to study the imidization and crosslinking addition reactions of an aromatic polyimide. The polymer is a crosslinked polyimide prepared from a solventless monomer mixture composed of diethyl-3,3′,4,4′-benzophenone tetracarboxylate (BTDE), ethyl-5-norbornene-2,3-dicarboxylate (NE), and a mixture of aromatic amines of which methylene dianiline is the primary component[2]. (This polymer has been named LaRC-160 after the NASA-Langley Research Center where it was originally formulated). In the initial reaction, the resin imidizes, forming short partially soluble polyimide chains endcapped by the unsaturated nadic groups[1]. Above 220°C these nadic groups begin to react through an addition reaction to form a crosslinked network[3–5].

This thermosetting aromatic polyimide is typical of many polymer systems in that it is extremely difficult to study the cure process continuously; that is, to examine the cure chemistry of going from a monomeric liquid of varying viscosity to a crosslinked insoluble high temperature solid. In this paper we show that DDA can monitor changes in the polymerization processes continuously from the soluble, unreacted mixture to a fully cured insoluble highly crosslinked thermoset. The resin's age and composition can also be observed electrically.

EXPERIMENTAL

The solventless LaRC-160 resin was prepared as prescribed by St. Clair and Jewell using 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 5-norbornene-2,3-dicarboxylic anhydride (NA) and a commercially available mixture of aromatic amines, Jeffamine AP-22, which is composed primarily of *p,p*-methylenedianiline (MDA)[2]. BTDE, the diethylester of BTDA, was prepared by dissolving the anhydride in a 5 M% excess of ethyl alcohol and refluxing for one hour. NE, the monoethyl ester of NA, was similarly prepared. These mixtures were cooled and mixed with the appropriate amine molar equivalent of Jeffamine AP-22. The resulting resin mixture was stored in a refrigerator at 12°C. The aromatic polyimide has a NE/BTDE molar ratio of 1.8[2]. Other monomer mixtures, with NE/BTDE molar ratios of 0.9, 3.7 and 8.5 were similarly prepared and stored as above.

Dynamic dielectric measurements were made using a Hewlett-Packard 4192A LF Impedance Analyzer controlled by a 9826 Hewlett-Packard computer. A diagram of the apparatus is shown in *Figure 1*. Experiments for the majority of the Figures and Tables were performed using an automated temperature ramp in which the time–temperature profile was controlled by the HP-9826 computer. The mould was inserted into a Carver Model C

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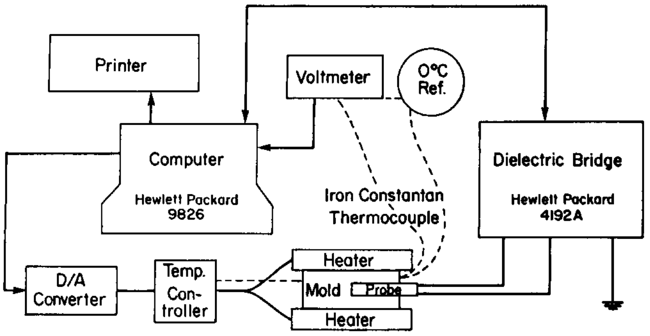


Figure 1 Diagram of the apparatus used for dynamic dielectric analysis

press, between two Carver heating platens. The temperature of the heating platens was controlled by a modified Model 76-1 RFL proportional temperature controller via a Kepco Model SN 488-122 D/A converter interfaced with the computer. The layup consisted of a number of layers of fibreglass cloth to insulate the capacitor from the metal mould, polymer resin or composite, a capacitor probe which can be inserted directly between layers of resin or composite and a further stack of insulating material between this and the mould top. An iron–Constantan thermocouple was attached directly to the mould and the temperature measured by a Kiethley 179 TRMS Digital Multimeter. All instruments were equipped with IEEE-488 bus lines to the computer. Instrument and lead contributions to the dielectric measurements were determined and subtracted from each measurement value. The time, frequency, capacitance (C), conductance (G) and temperature were measured at 2 min intervals at a number of frequencies over a frequency range of 5 to 5×10^6 Hz. Data was stored on a floppy disc for analysis after each run. Subsequent data manipulation was performed on a 9836 computer and plots were made on a 7475A Hewlett-Packard 6-pen plotter.

Dissipation, D, can be directly measured by the bridge up to a value of 20. During the imidization reaction, however, the ionic influence on the dielectric properties is so great that D exceeds 20 for significant portions of the reaction at the lower frequencies. Therefore D, as reported in this paper, has been calculated from the measured capacitance C, and conductance G at each frequency f (in Hz) and measurement cycle, m:

$$D(f,m) = \frac{G(f,m)(\text{mhos})}{2\pi f C(f,m)(\text{Hz}\cdot\text{Farads})} \tag{1}$$

The real and imaginary components of the complex permittivity are calculated from the following relationships:

$$\varepsilon' = \frac{C_{\text{material}}}{C_0}$$

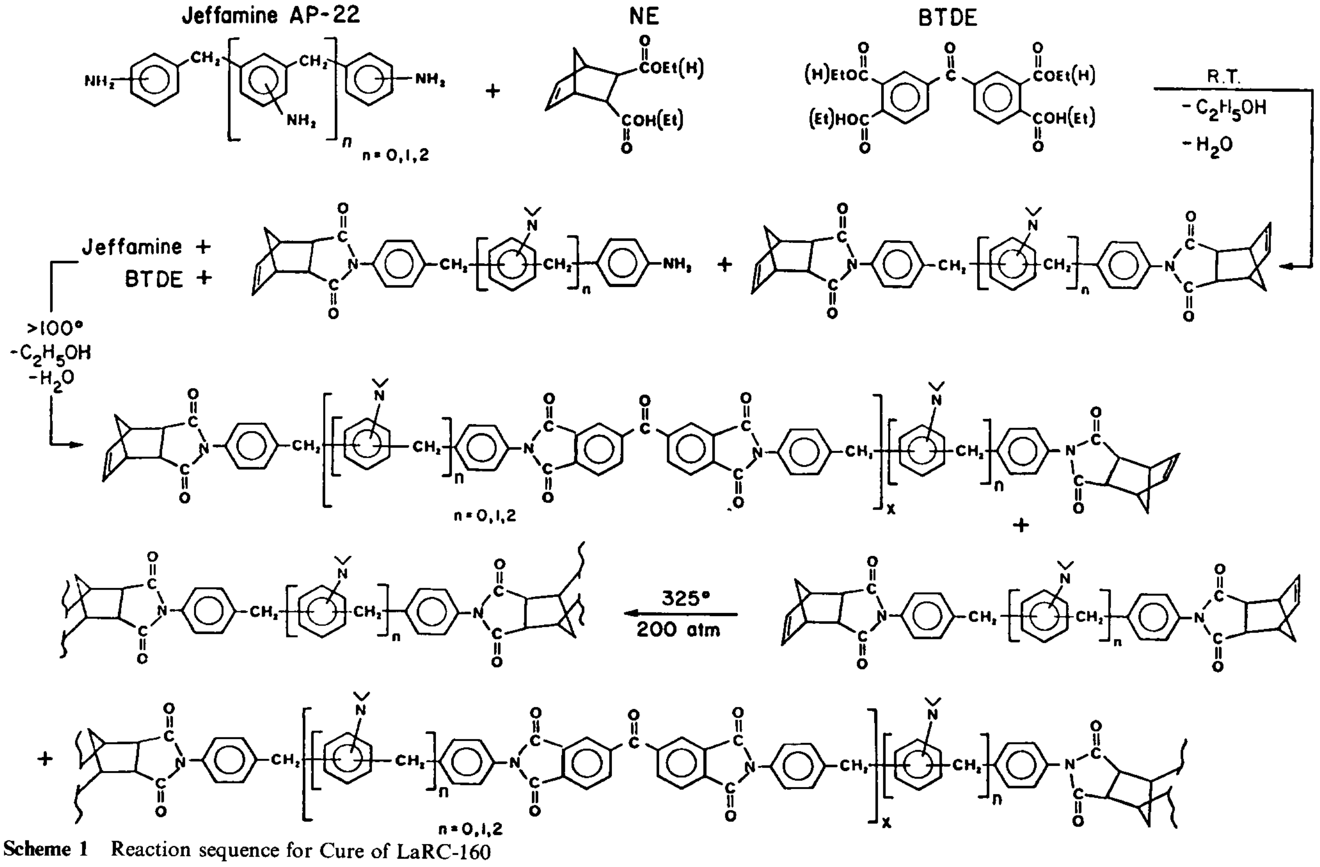
$$\varepsilon'' = \frac{G_{\text{material}}}{C_0 \cdot 2\pi f}$$

where C_0 is the air filled replaceable capacitance of the measuring cell.

Carbon 13 nuclear magnetic resonance (^{13}C n.m.r.) studies were done on Varian FT-80A NMR spectrometer. Samples were dissolved in DMSO-d_6 with TMS as an internal standard. A pectral width of 5000 Hz was used.

RESULTS AND DISCUSSION

The aromatic polyimide monomer mixture used in this study undergoes a two-step curing process involving first, polymerization (imidization) above 100°C, and second, a high-temperature crosslinking step above 220°C (*Scheme 1*).



Scheme 1 Reaction sequence for Cure of LaRC-160

The imidization reaction

The monomer mixture is highly viscous at room temperature. As heat is applied to initiate the imidization reaction, the monomer mixture melts and becomes increasingly fluid. This process continues until the growing polymer chains overcome the effect of increasing temperature. At this point the viscosity begins to rise. The viscosity then increases until flow is no longer observed. Capacitance C, and Conductance G, are dependent upon the ability of ions and dipoles to follow an applied oscillating field. They are therefore dependent upon the viscosity of the system. *Figure 2a* is a plot of C vs. time for the imidizing polyimide. *Figure 2b* is a plot of G vs. time for the same sample. The temperature ramp is also shown in each Figure. In a qualitative way, C and G reflect the viscosity of the dynamic resin system, first increasing (viscosity decreasing) with temperature until the effects of the molecular weight buildup dominate the viscosity. At this point, they decrease while viscosity increases. However, the chemistry and physics of the curing polyimide system are better understood in terms of the complex permittivity, ε^*, where $\varepsilon^* = \varepsilon' - i\varepsilon''$ since ε^* is a geometry independent property of the individual resin system.

The real and the imaginary components of ε^* can have both a dipolar and an ionic component.

$$\varepsilon' = \varepsilon'_d + \varepsilon'_i \qquad (3a)$$

$$\varepsilon'' = \varepsilon''_d + \varepsilon''_i \qquad (3b)$$

The dipolar component arises from rotational diffusion of molecular dipolar moments. One general form for the polar component's frequency dependence is

$$\varepsilon'_d - i\varepsilon''_d = \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + i\omega\tau)^\beta} + \varepsilon_\infty \qquad (4)$$

where ε_0 and ε_∞ are the limiting low and high frequency values of ε_d. The rotational diffusion rate of the polar moments is characterized by a relaxation time. β is the Cole–Davidson distribution parameter ($0 < = \beta < = 1$). It is a measure of the extent to which the motion of the dipoles are correlated with each other. For an ideal system $\beta = 1$.

Effects of ionic conduction in polymeric media subjected to an alternating electric field are a function of the mechanism for ion transport and as such reflect the viscosity of the medium, boundary conditions at the electrode surfaces, size of the ions involved, and heterogeneities in the system. In fluids, ions migrate to the electrodes and may form an electric double-layer at their surface causing electrode polarization. These ions may then diffuse through this layer and discharge at the electrode. As the viscosity increases, this motion is slowed, or sometimes blocked altogether.

Considerable research has focused on the effects of ionic conductivity on the frequency dependence of the dielectric constant ε' and the apparent conductivity, G_{app} or the dielectric loss term, ε'', (equation (2b)). Friauf concluded that for both + and − ions blocked, $\log \varepsilon'$ vs. $\log f$ would have a slope of −2.[6] However, if only one ion is blocked and the other free to translate, then the frequency dependence of ε' would vary as $f^{-3/2}$ while G would be proportional to $f^{-1/2}$ [7].

Uemura derived equations for diffusion controlled ionic translational motion in high molecular weight polymers. This model predicts $\varepsilon' \propto f^{-3/2}$ and $\varepsilon'' \propto f^{-1}$ [8]. However his treatment ignores both space charge effects and charge transfer at the electrodes.

Johnson and Cole derived an empirical formula for the behaviour of an ionic material (formic acid) in liquid and solid states[9]:

$$\varepsilon'_{app} = \varepsilon'_d + C_0 Z_0 \sin\left(\frac{n\pi}{2}\right) \omega^{-(n+1)} \left(\frac{\sigma}{8.85 \times 10^{-14}}\right)^2 \qquad (5a)$$

$$\varepsilon''_{app} = \varepsilon''_d + \frac{\sigma}{8.85 \times 10^{-14} \omega} - C_0 Z_0 \cos\left(\frac{n\pi}{2}\right) \omega^{-(n+1)} \left(\frac{\sigma}{8.85 \times 10^{-14}}\right)^2 \qquad (5b)$$

where C_0 is the replaceable capacitance in Farads, $Z = Z_0(i\omega)^{-n}$ is the electrode impedance induced by the ions, $\sigma(\text{ohm}^{-1}\ \text{cm}^{-1})$ is the specific conductivity and n is between 0 and 1. In their experiments the value of n for the liquid state was 1 and that for the solid formic acid was 0.5. At particular values of n, Johnson and Cole's equations correspond to various theoretical representations. $n = 1$

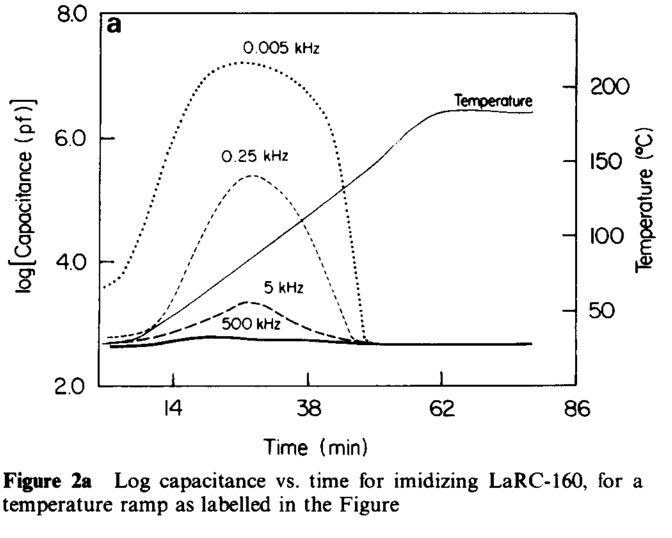


Figure 2a Log capacitance vs. time for imidizing LaRC-160, for a temperature ramp as labelled in the Figure

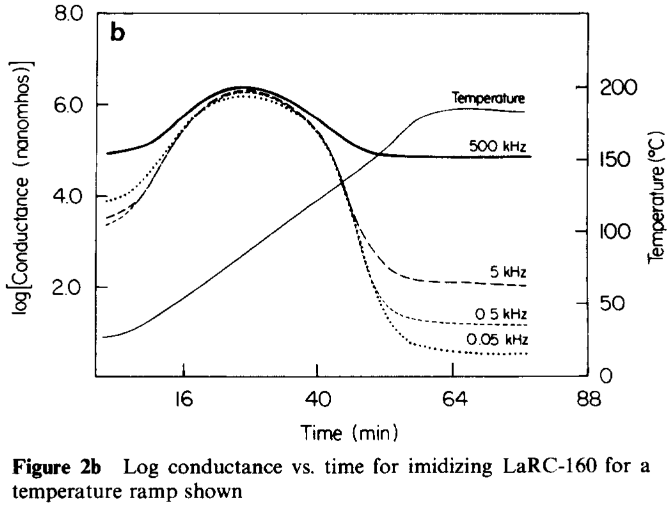


Figure 2b Log conductance vs. time for imidizing LaRC-160 for a temperature ramp shown

corresponds to the case when electrode polarization effects become dominant. When $n = 0.5$, equation (5) reduces to that of Uemura for diffusion controlled ionic effects. The boundary condition $n = 0$ is equivalent to pure d.c. conductance. A value of $0.5 < n < 1$ has been experimentally observed by Yanno *et al.*, in high polymers below their melt temperature and is attributed by them to interfacial polarization of ions about crystalline regions in the amorphous polymer[10].

The d.c. ionic component of ε'' is the term:

$$\frac{\sigma}{8.85 \times 10^{-14}\omega} \qquad (6)$$

where the specific conductivity $\sigma(\text{ohm}^{-1}\ \text{cm}^{-1})$ is an intensive variable, in contrast to conductance $G(\text{ohm}^{-1})$ which is dependent upon sample size. σ and G reflect primarily the translational motion of ions through the resin medium. ε', by contrast, is affected by electrode impedance and charge layer effects.

The frequency dependence of the complex permittivity of the aromatic polyimide through its polymerization phases will be reviewed and interpreted in terms of the above theoretical considerations.

Figure 3 is a plot of log ε' vs. time for imidizing LaRC-160. At the lower frequencies a single peak, large in magnitude, occurs, while at the higher frequencies the curve has two maxima corresponding to temperatures of ~80°C and ~130°C. These temperatures coincide with the temperatures at which the nadic group (~80°C) and the diethylbenzophenone tetracarboxylate (~130°C) begin to imidize[1]. This two-step change in ε', which is dominated by the dipolar component of ε' cannot be observed below 50 kHz. Here the dielectric response of ε' is dominated by ionic transport effects. This can best be illustrated by plotting log ε' vs. log f at specific times during the reaction as shown in *Figure 4*. Throughout the region of high fluidity (curves 2–4) the low frequency values of ε' are proportional to $f^{-3/2}$. This is equivalent to the boundary condition for equation (5) of $n = 0.5$, expected for diffusion controlled transport of ions through a viscous medium[8]. Only at frequencies above 5 kHz is the measurement time too fast to be governed by ionic phenomena.

The log ε'' vs. time plot (*Figure 5*) has a single maximum at all frequencies indicating that ionic effects dominate the region of high fluidity. Analysis of a plot of log ε'' vs. log f over this region (*Figure 6*) gives a slope of -1 for curves 2–4 throughout the frequency range. This is the result expected if ε'' is due to d.c. conductivity (equation (6)), i.e. diffusion controlled translation in ions[8].

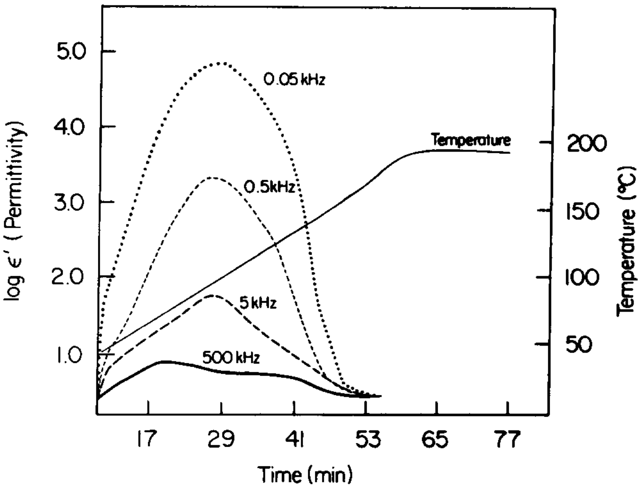


Figure 3 Log ε' vs. time for imidizing LaRC-160 for the temperature ramp shown

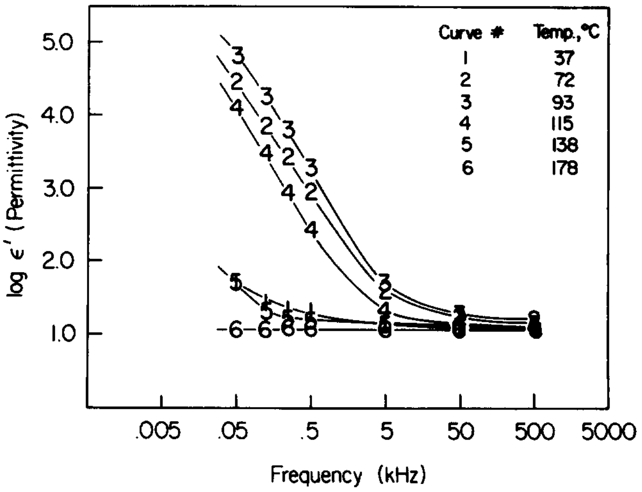


Figure 4 Log ε' vs. frequency for various time during the imidization of LaRC-160 for a temperature ramp as in *Figure 2*

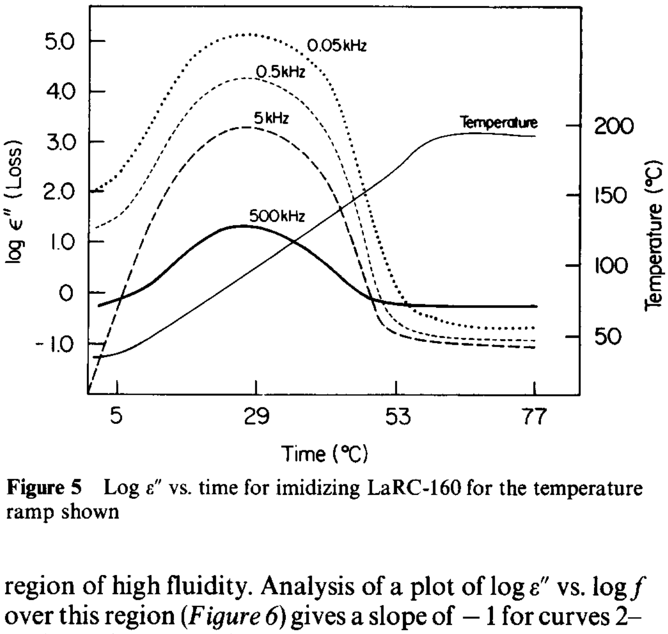


Figure 5 Log ε'' vs. time for imidizing LaRC-160 for the temperature ramp shown

A slight deviation from linearity for curve 3 (see both *Figures 4* and *6*) at the lowest frequency arises from the onset of blocking electrode polarization effects. As the temperature nears 180°C and the resin becomes hard, ionic translation is suppressed and dipolar phenomena are observed (curve 6).

When the ionic contribution to the dielectric loss term is due to d.c. conductivity, equation (6) can be used to calculate the specific conductivity, σ, of the bulk resin system. *Figure 7* shows the results of this calculation for the imidizing monomer mixture. To appreciate the magnitude of change observed in this quantity during the imidization reaction, one should note that 'pure' H_2O in equilibrium with atmospheric CO_2 has $\sigma = 1 \times 10^{-6}$ ohm^{-1} cm^{-1}, while good laboratory benzene has 1×10^{-12} ohm^{-1} cm^{-1}. For this polyimide system specific conductivity varies between 1×10^{-5} and 1×10^{-11} ohm^{-1} cm^{-1} during polymerization. When σ is due to the translational diffusion of ions through a viscous medium, it is directly dependent on viscosity and can be used to monitor the viscosity of the system. However, if

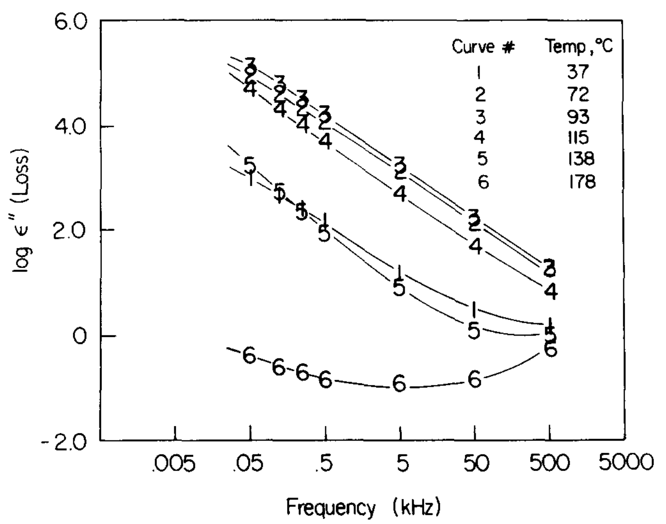


Figure 6 Log ε'' vs. frequency for times during the imidization LaRC-160 for a temperature ramp as in *Figure 2*

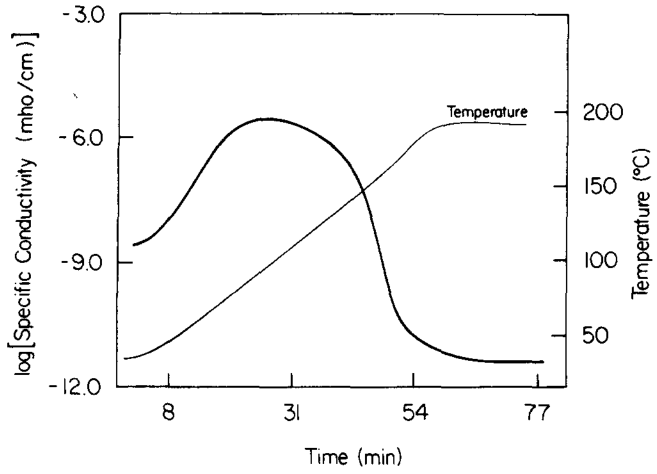


Figure 7 Log specific conductivity vs. time for imidizing LaRC-160

one goes to even lower frequencies (for example, 0.05 kHz, curve 3 of *Figures 4* and *6*) then the relationship of σ to viscosity is obscured by electrode polarization effects. Clearly an understanding of the frequency dependence of a dielectric signal is essential in determining whether one is monitoring dielectric, conductive or electrode polarization effects.

Based on ^{13}C n.m.r. data[1], the major portion of the imidization is complete within 10 min at the 180°C hold. However, as shown in *Figure 8*, one can continue to see a gradual drop in both ε' and ε'' at this temperature with time. This suggests that curing continues well past the point at which liquid-like translational diffusion of ions through the medium ceases.

The crosslinking reaction

Once the aromatic polyimide has been imidized, the resin is heated to above 280°C for about 1 h to crosslink the polymer chains. The process involves the unsaturated norborneyl end-groups in a complex rearrangement/elimination reaction. Several attempts have been made to study this reaction in model compounds[3-5].

The loss peak shown in *Figure 9* occurs in the region where crosslinking is known to occur. It has been attributed to crosslinking in LaRC-160 and in PMR-15. We find that Kapton film also gives a loss peak in this region (*Figure 10*). Kapton, like PMR and LaRC, is a polyimide. Unlike these resins, however, Kapton film does not undergo a crosslinking reaction. That it does undergo some sort of deformation at about 300°C is supported by the presence of flow lines in Kapton film heated to this temperature. Whether the observed loss peak for LaRC-160 is due to a deformation characteristic of polyimide chains or is due to the crosslinking reaction was tested by reheating the sample. Upon reheating LaRC-160, no loss

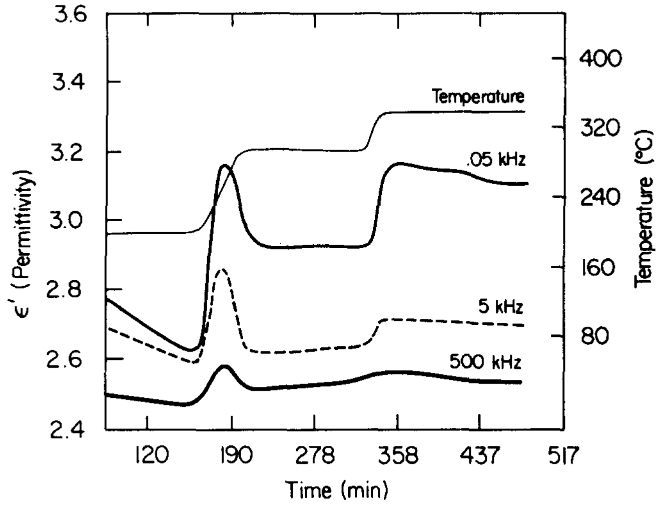


Figure 8 ε' vs. time for crosslinking LaRC-160

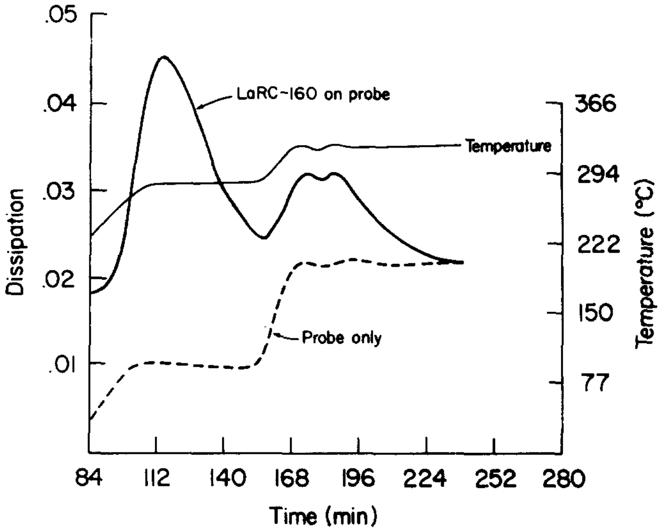


Figure 9 Comparison of dissipation for a probe coated with LaRC-160 vs. that for a probe alone for the temperature profile used to crosslink LaRC-160

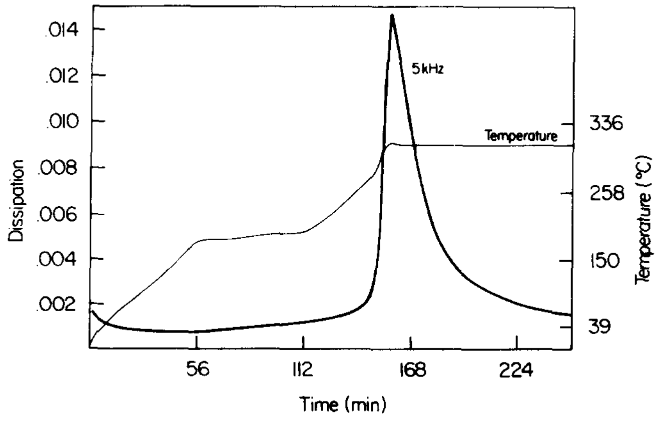


Figure 10 Dissipation vs. time for Kapton film for the temperature ramp shown in the Figure

peak in either the 260°C–300°C or 320°C–345°C region was observed (*Figure 11*). This fact supports the view that in the LaRC-160 system, the 300°C peak is indeed due to crosslinking. This observation also leads to a word of caution: in an early DDA study of LaRC-160, Whereta and Hadad used Kapton as a shield between the resin and the capacitor plate in their dielectric moulds[11]. We have shown that Kapton has a dissipation maximum in the temperature region of the crosslinking reaction (220°C–320°C) (*Figure 10*). Thus, we believe that the large amplitude in loss reported by Whereta and Hadad for the polyimide crosslinking reaction in relation to the low temperature dissipation during imidization is due in part to the presence of Kapton. In our experiments, where Kapton is not present, we see a very small loss at the crosslinking temperature relative to the value observed in the imidization reaction. Gluyas[12], in a study on the related polyimide, PMR, reported that he used Kapton as a shield to reduce the dissipation of imidizing PMR to amplitudes measurable on his instrumentation. When he used pre-imidized PMR, and monitored the crosslinking reaction, the Kapton shields were not necessary. He therefore also observed, as we do, a large dissipation in the imidization region as compared with the much smaller values in the crosslinking regions.

Plots of ε' and ε'' vs. time for crosslinking LaRC-160 suggest two distinct phenomena are contributing to the time dependence of the complex permittivity (*Figures 8* and *12*). The maximum in ε' occurs at 240°C, below the temperature of the reported minimum in viscosity (*Figure 8*)[13]. In experiments where we have held the resin at this temperature, we observe dynamic changes in the dielectric properties of the aromatic polyimide with time. Kumar *et al.*[14] have reported crosslinking of nadic end-capped bisaspartimides beginning at temperatures as low as 225°C. Endo–exo isomerization of the nadic group and cyclopentadiene evolution have also been observed to occur in this temperature region[3–5,15]. Thus, we attribute the cause of this dynamic change in the ε' vs. time plots at 240°C to the endo–exo isomerization, as well as the onset of crosslinking.

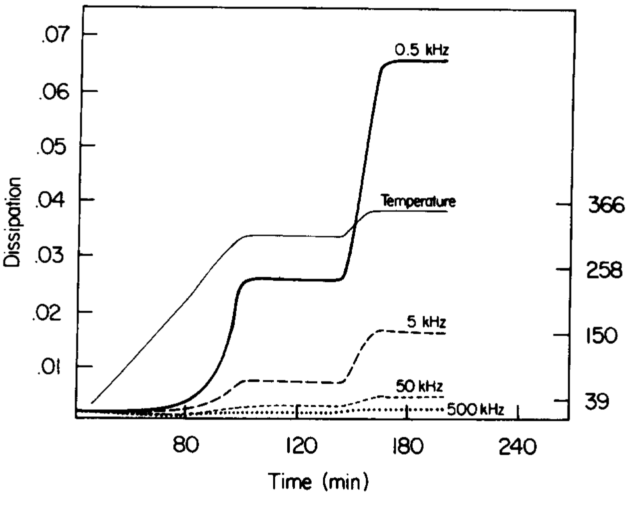


Figure 11 Dissipation vs. time for pre-cured LaRC-160 reheated to crosslinking temperatures

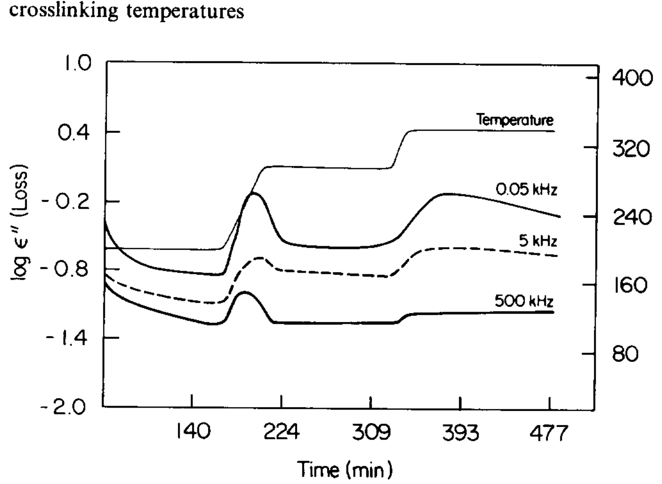


Figure 12 Log ε'' vs. time for crosslinking LaRC-160

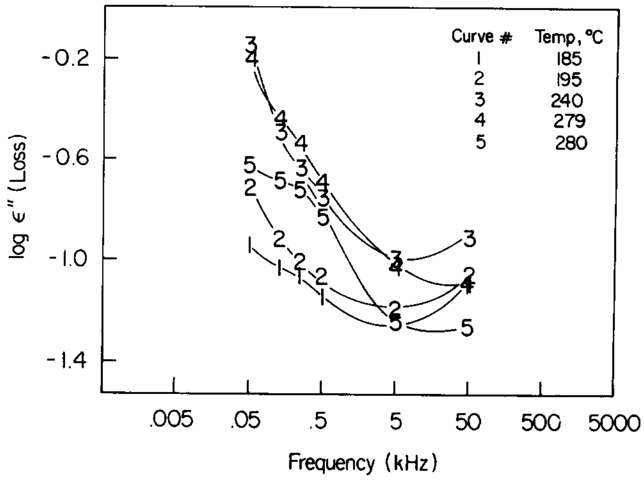


Figure 13 Log ε'' vs. frequency for LaRC-160 at various times during the ramp to and hold at 280°C. Curve 4 represents behaviour just as the hold is reached. Curve 5 is after 16 min at the 280°C hold. Curve 6 is after 112 min at the 280°C, when the electrical parameters have reached a steady state

The peak in ε'' for curing polyimide occurs in the 270°C–280°C region at frequencies $\leqslant 5$ kHz (*Figure 12*) when a heating rate of 2.5°C/min is used. To the extent that the magnitude of ε'' monitors the mobility of the ions and dipoles, ε'' monitors the viscosity of the system. The temperature of the maximum in ε'' corresponds well with the literature value for a viscosity minimum at 272°C during a 2°C/min heat ramp[13].

Plots of $\log \varepsilon''$ vs. $\log f$ help elucidate the ionic and dipolar contributions to the loss term. In *Figure 13* the region embracing the hold at 180°C to the end of the 280°C hold is plotted. At times during the high temperature cure where the viscosity is relatively high (curves 1 and 5) the high frequency portion of a dipolar-like dispersion with a maximum near 0.125 kHz is observed. This could be due to ions confined to localized 'hole-hopping' in the solid resin matrix. The true maximum of this dipole-like dispersion is obscured by electrical response of more mobile ions at lower frequencies. During the heating ramps of the high temperature cure cycle, the resin initially becomes more fluid. As a result, the mobility of the ions increases. Consequently, the electrical response of the more mobile ions extends to higher frequencies preventing observation of any of this 'dipolar-like' dispersion. As the resin crosslinks at the 280°C hold the viscosity of the system increases, contribution of the mobile ions decreases and the dipolar 'hole hopping' dispersion becomes again apparent. At the high temperature 320°C hold (*Figure 14*), the more mobile ionic contribution again partially masks this 'dipolar' dispersion. Both *Figures 13* and *14* show the low frequency end of a high frequency dispersion at the upper end of our measurement range.

The dielectric changes observed during heating to and the hold at 320°C reflect the temperature dependence of the dielectric response of a highly viscous polymer system. The magnitude of the ε'' is higher at each frequency than at 280°C due to the larger internal energy of the system at this high temperature which allows for greater mobility of the ions and dipoles with the electric field.

Lewis[16] has reviewed the dielectric behaviour of non-crystalline solids and found that the process of localized 'hole-hopping' which can occur in the solid state matrix results in a broad low frequency dispersion. This was shown to be mathematically equivalent to a Debye-type dielectric dispersion. The low frequency dielectric response of LaRC-160 is consistent with this view of the role of ions in the matrix. At very low viscosities these ions translate through the medium and build up at the electrodes. Initially, as the resin begins to harden, the translational motion of the ions is observed (*Figure 6*). As the resin continues to harden, the translational motion is confined to increasingly shorter distances, until only local 'hopping' is possible, and a Debye-type response is observed (*Figure 13*). If, however, the temperature of the resin matrix is increased, more energy is imparted to the system and the ions can once again travel farther (*Figure 14*).

Effects of resin composition on dielectric measurements

Differences in resin composition can also be observed by dielectric analysis. *Figure 15* shows the effect of resin composition on the log capacitance of imidizing LaRC. The point of maximum capacitance (minimum viscosity) occurs at increasingly lower temperatures as the relative amount of NE in the resin increases. The same shift in the point where the imidization reaction affects the dielectric dynamics of the resin system is observed when dissipation is plotted vs. temperature (*Figure 16*).

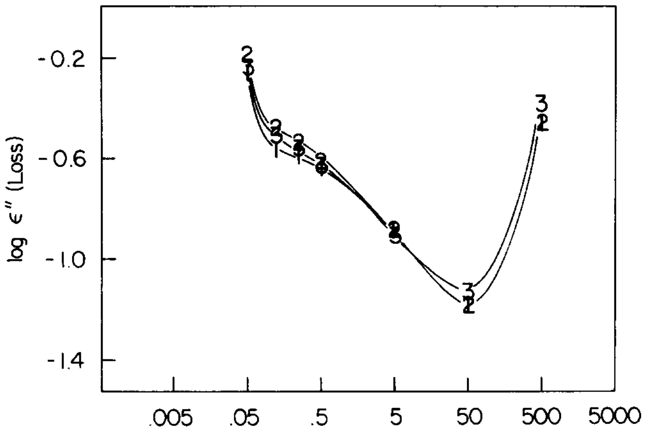


Figure 14 Log ε'' vs. frequency at various times during the 330°C hold. Curve 1, just as hold temperature is reached; Curve 2, 12 min at 330°C; Curve 3, 110 min at 330°C

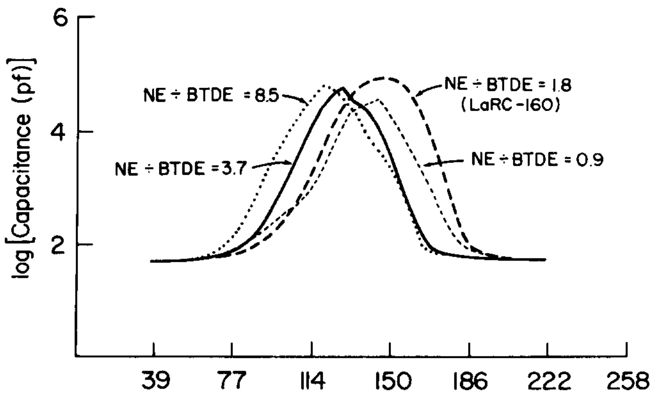


Figure 15 Capacitance vs. temperature at 500 Hz for LaRC of varying NE: BTDE ratios as labelled in Figure

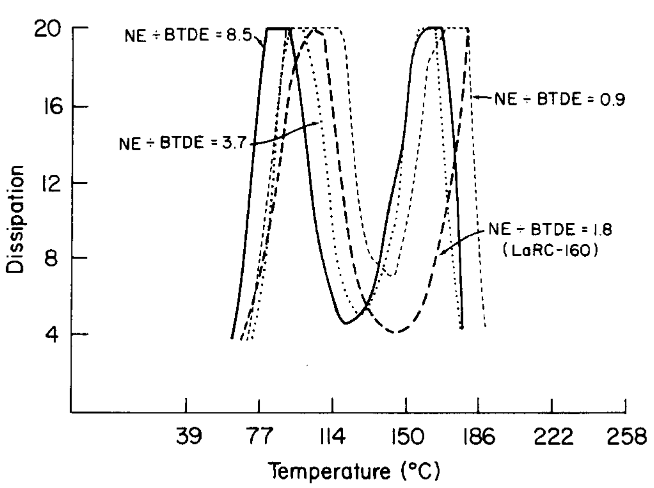


Figure 16 Dissipation vs. temperature at 500 Hz for LaRC of the same four compositions as in *Figure 15*

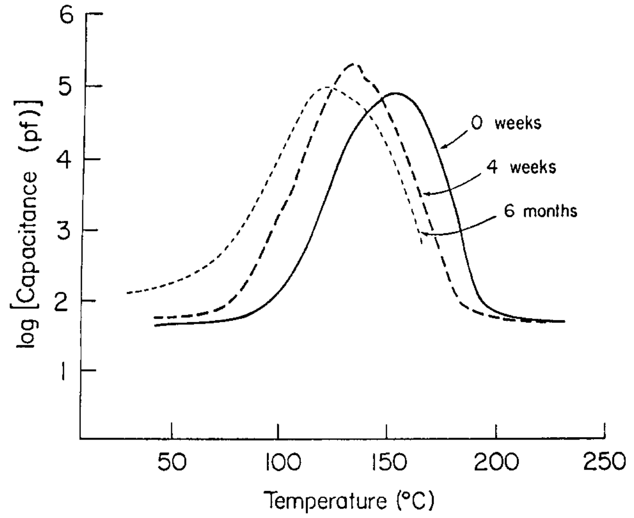


Figure 17 Log capacitance vs. temperature at 500 Hz for LaRC-160 for resin aged 0, 1 and 6 months at 5°C

Increasing [NE] decreases the temperature at which the effects of the imidization reaction overcome the effect of increasing temperature. NE imidization has been shown to begin at significantly lower temperatures than BTDE imidization[1]. The C and D vs. temperature results for varying resin compositions reflect this difference in the reactivity of the two esters.

Effects of resin age on dielectric measurements

Resin age affects the observed dielectric measurements of the imidization reaction of LaRC-160. *Figures 17* and *18* show the observed log capacitance and dissipation vs. temperature at 500 Hz of the imidizing resin freshly prepared and after one and six months storage at 12°C. Continued ageing of the resin further decreases the temperature at which the minimum viscosity of the imidizing monomer mixtures occurs as seen by comparing *Figure 2* with *Figure 17*.

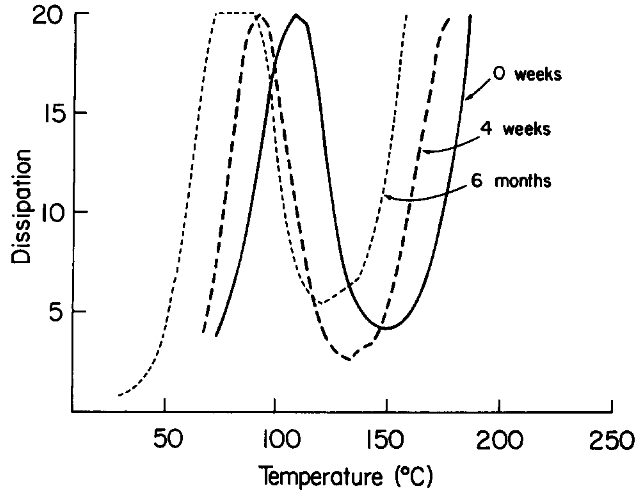


Figure 18 Dissipation vs. temperature at 500 Hz for the resin ages as in *Figure 17*

The shift in the viscosity minimum to shorter positions in the time–temperature profile with resin age reflects the amount of advancement that has taken place in the imidization reaction with storage time. ^{13}C n.m.r. data on ageing LaRC-160 stored at 5°C showed that even at this low temperature NE imidizes slowly[1]. Thus the curing 'old' resin starts from a more advanced state so that the energy required to achieve a given state of cure is much less than that required for 'fresh' resin and the observed changes occur at an earlier time on the time–temperature plot. While resin age affects the point of minimum viscosity in the imidization region of the curing LaRC-160 system, it does not affect the general shape of the dielectric profile.

The advancement of the imidization reaction with age does not appear to affect the high-temperature crosslinking reactions. This reaction does not take place during storage of uncured resin. Changes in the high-temperature dielectric profile have been found to be due to variations in the content of ions entrapped in the resin matrix[17].

CONCLUSIONS

Both the imidization and crosslinking reactions of an aromatic polyimide have been examined by dynamic dielectric analysis. The ionic and dipolar contributions to the complex permittivity ε^* have been separated. From the frequency dependence of the ionic portion of ε^*, the relative mobility of ions in the changing resin medium have been determined. In the early stages of the reaction, where viscosity is very low, d.c. conductivity dominates the electric signal and electrode polarization effects can be seen at the lowest frequencies being measured. As the viscosity increases with polymerization, the ionic mobility becomes increasingly hindered. In the solid, insoluble, crosslinked matrix the ions are confined to localized 'hole-hopping' mechanisms. The magnitude of this mobility is a function of the temperature at which the polymer matrix is studied.

Resin composition and age can affect the point of maximum value in the capacitance of the imidizing monomer mixture. The crosslinking reaction of the aromatic polyimide does not appear to be systematically affected by either of these variables.

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