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Dynamic t–T_{dyn}–T_{g} diagram analysis of thermal isomerization of polyisoimide using complex electric modulus properties

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Abstract

A time–temperature–glass transition temperature diagram under a dynamic-heating condition (dynamic t–T_{dyn}–T_{g} diagram) was developed to analyze physicochemical transitions of a reacting polyisoimide system using 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS) as a model system. Under the dynamic-heating condition, the complex electric modulus properties exhibited two transitions at high frequencies but three transitions at lower frequencies, due to the coupled phenomena of the viscoelastic glass–rubber transitions and the kinetic increment of the glass transition temperature of the isomerizing polyisoimide. The dynamic t–T_{dyn}–T_{g} diagram was proposed to analyze those multiple peaks to identify the material status and the transition temperatures corresponding to the initial glass transition (T_{g0}), vitrification (T_{vit}), and final glass transition ($T_{\mathrm{g}\infty}$) temperatures. Using the developed methodology, the isomerization of polyisoimide, which is usually difficult to analyze, was successfully investigated to identify the relationships among the thermodynamic, viscoelastic, and kinetic processes.

Keywords: Polyisoimide; Dielectric property; Complex electric modulus

1. Introduction

Polyimide materials have been widely used in the field of opto-electronic devices such as electric insulators, circuit boards, waveguides, and the alignment layers of liquid crystal displays, due to their excellent thermal and mechanical stabilities [1,2]. The polyimide systems used in the microelectronics industry need to have good processability and appropriate values of dielectric constant, which determine the signal propagation speed and wiring density in multichip packaging. Considerable effort has been made to design and synthesize new polyimides with appropriate dielectric constants [3–5]. Since most polyimides suffer from insolubility, opacity, and poor processability, the use of polyisoimide systems as a polyimide precursor has widely been investigated [6–10].

Polyisoimides are soluble and possess lower melt viscosities and lower glass transition temperatures than the corresponding polyimides, mainly because of their lower symmetry and structural irregularity arising from the *p*-and *m*-imino group linkages along the chain and possible *syn* and *anti* configurations [11]. However, after their shaping, the crosslinked polyisoimides can be converted thermally or photochemically to the corresponding polyimides with ease, without the formation of gaseous condensation by-products, thus desirably allowing for the generation of void-free products [12,13]. In particular, high optical transparency is

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important to expand the application of polyisoimides to optoelectric material systems, such as flexible solar radiation protectors, liquid crystal display (LCD) oriented films, or transparent high-temperature adhesives. For these applications, the use of a fluorinated polyisoimide has been investigated as a photosensitive polyimide precursor with high transparency and low dielectric constant for the production of a high-temperature adhesive system [14,15]. In addition, it has been reported that diamines containing sulfone groups are effective in preparing transparent polyisoimides, because they hinder the charge transfer interaction between the color-causing centers by reducing the electron density of the amine groups [16–18]. Accordingly, the model polyisoimide system used in this study was based on a fluorinated anhydride and sulfone-containing diamine for the applications requiring high optical transparency.

As with most cross-linking reactions of thermoset polymers, the isomerization of polyisoimides occurs during such chemical and physical changes as gelation, vitrification, glass transition, diffusion-limited cross-linking reactions, etc., in a coupled manner especially under the dynamic-heating condition. For polyisoimides to be widely used as potential precursors of polyimides, their thermal as well as photochemical isomerization kinetics should be controllable as a function of time and temperature in relation to these physicochemical changes. However, the exothermic energy of the isomerization reaction of polyisoimides is often so small that it can hardly be detected or analyzed as a function of time using typical thermal analysis techniques like DSC and TG/DTA [6]. Furthermore, the isomerization reaction of polyisoimides may take place in the middle of the glass transition in a mixed manner during dynamic-heating conditions and, thus, it is difficult to analyze the polyisoimide reaction kinetics and physicochemical transitions in a separate manner [8,14,16].

In this study, we investigated the isomerization process of polyisoimides using dielectric properties, which are probably one of the most sensitive material characteristics representing the structural changes of the reacting molecules and polymer backbones with respect to temperature and frequency. Using a model polyisoimide system based on 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS) [16], the dielectric properties were analyzed in an attempt to separate the multiple transitions of the reacting polyisoimide system. A dynamic t–T_{dyn}–T_{g} diagram was employed in this study, in order to interpret the multiple thermal transitions of the reacting polyisoimide under the dynamic-heating condition.

2. Experimental

2.1. Materials

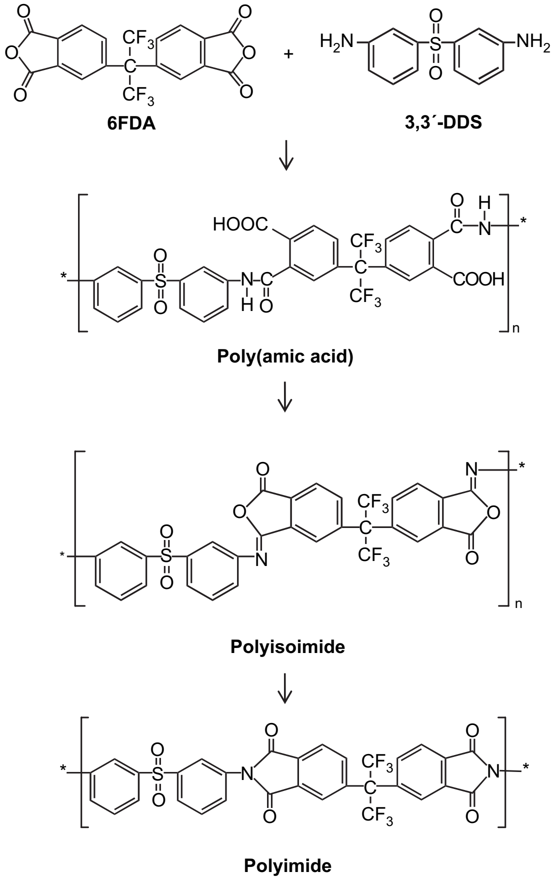
4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS) were purchased from Aldrich and vacuum dried before use. High purity triethylamine (TEA) and trifluoroacetic anhydride (TFAA) were purchased from Aldrich and used without further purification. *N*-Methyl-2-pyrrolidone and *N*,*N*-dimethylformamide were also purchased from Aldrich and purified by vacuum distillation.

2.2. Synthesis of polyisoimide

The polyisoimide system used in this study was synthesized using a similar method to one published previously [16]. In 10 ml of NMP, 1.24 g (5.0 mM) of 3,3′-DDS was completely dissolved and 2.22 g (5.0 mM) of 6FDA was added. The reaction was carried out for 6 h at room temperature under a nitrogen atmosphere. To the synthesized polyamic acid solution, 1.4 ml (10.0 mM) of TEA was added dropwise with mechanical stirring. The reaction mixture was cooled in an ice-water bath, and 2.1 ml (15.0 mM) of TFAA was added dropwise to the solution with mechanical stirring for 4 h at room temperature. The collected polyisoimide was washed with isopropanol, filtered and dried in vacuum at 70 °C for 60 h (Scheme 1). The average molecular weight of the synthesized polyisoimide was $\overline{M}_{\mathrm{W}} = 144{,}500$ and $\overline{M}_{\mathrm{n}} = 68{,}300$ (polydispersity at 2.1).

2.3. Measurement

A Bruker IFS-66 spectrometer was used to obtain the transmission spectra of the pristine polyisoimide and the



Scheme 1. Synthesis of polyisoimide model system.

partially isomerized polyimides after the thermal treatment at 230 and 260 °C for 30 min. DSC was used to measure the glass transition temperature and thermal reactions of polyisoimide and polyimide (Seiko Extar 6100 thermal analyzer) under a nitrogen atmosphere at a heating rate of 10 °C/min. The dielectric properties were measured by means of a Seiko Extar 6000 dielectric spectrometer (DES100) at five different frequencies of 10, 20, 10^2, 10^3 and 10^4 Hz from 30 to 280 °C at a heating rate of 3 °C/min in a nitrogen environment.

3. Results and discussion

Fig. 1 shows the transmittance FT-IR spectra of the pristine polyisoimide compared with those of the polyimides which were thermally imidized at 230 and 260 °C for 30 min. The IR spectrum of the pristine polyisoimide shows the characteristic bands at 1810 and 927 cm^{-1}, which correspond to the carbonyl stretching and the isoimide ring vibration, respectively. The thermal conversion from polyisoimide to polyimide can be confirmed by comparing IR spectrum (A) with spectra (B) and (C) in Fig. 1, in which the isoimide bands at 1810 and 927 cm^{-1} disappear along with the growth of the characteristic absorption peaks of the polyimide at 1786 and 1726 cm^{-1}, which are attributed to the asymmetric carbonyl and the symmetric carbonyl band of the polyimide, respectively.

As can be seen in Fig. 2, the glass transition temperature (T_g) of the pristine polyisoimide is measured to be 178 °C (Fig. 2A), and those of the thermally imidized polyimide are 235 and 255 °C at the isomerization temperatures of 230 and 260 °C (Fig. 2B and C), respectively. Apparently, the glass transition temperature of the reacting polyisoimide increases with the imidization temperature. Specifically in Fig. 2A, a small and broad peak of isomerization exotherm can be seen around 230 °C after the glass transition temperature. The isomerization exotherm of the polyisoimide is likely to occur right after and/or in the middle of the glass transition, but this peak is so small that it is impossible to analyze the peak to identify the physicochemical status of the reacting polyisoimide, due to instrumental limitations in resolution and the overlapped signals of the reactions and transitions. Accordingly, it is considered that those small and overlapped signals may be analyzed by the dielectric properties because the in-phase and out-of-phase electrical responses are so sensitive in a wide range of frequencies that the detailed physicochemical transitions may be detected in a separate manner.

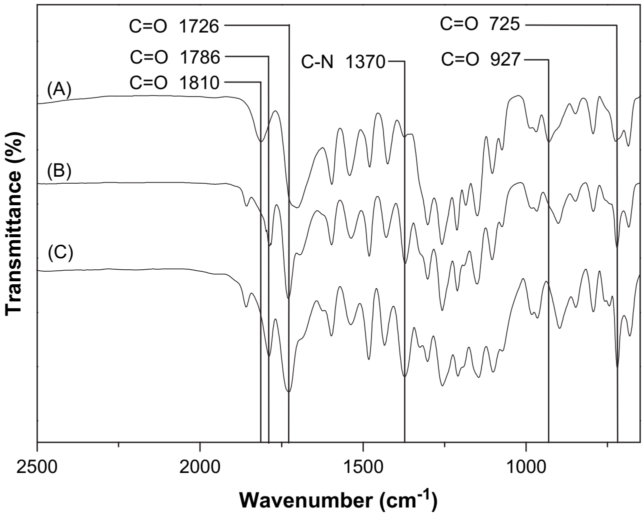


Fig. 1. FT-IR spectra of polyisoimide systems: (A) pristine polyisoimide, (B) polyisoimide partially imidized at 230 °C for 30 min, and (C) polyimide after complete isomerization at 260 °C for 30 min.

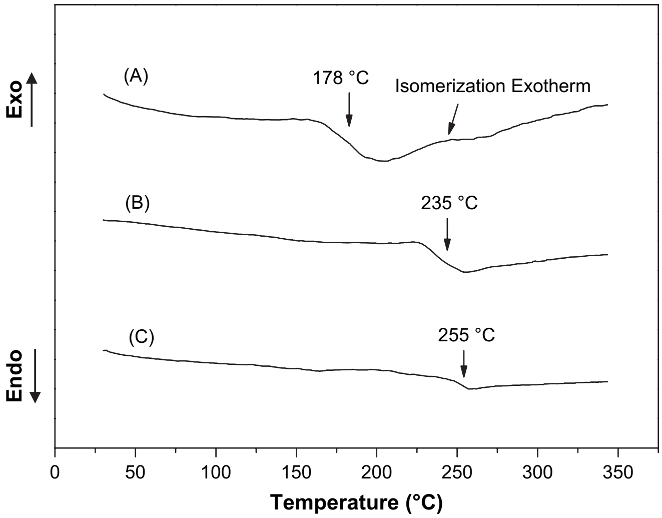


Fig. 2. DSC thermograms of polyisoimide systems: (A) pristine polyisoimide, (B) polyisoimide partially imidized at 230 °C for 30 min, and (C) polyimide after complete isomerization at 260 °C for 30 min.

In dielectric analysis, a sinusoidal voltage is applied to create an alternating electric field, and the measured current is expressed in a complex form (ε^*), which can be separated into capacitive and conductive components referred to as the permittivity (ε') and dielectric loss (ε''), respectively. According to the classic Debye equation, ε' represents the amount of alignment of the dipoles to the electric field and may be expressed as follows:

$$\varepsilon' = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{1 + 2\pi f \tau} \tag{1}$$

where ε_u and ε_r are the unrelaxed and relaxed permittivity, respectively, τ is the molecular relaxation time, and f is the frequency (Hz). ε'' refers to the amount of energy required to align the dipoles or move the ions, each corresponding to the dipole loss factor and the ionic conductance terms, respectively, viz.:

$$\varepsilon'' = \frac{(\varepsilon_r - \varepsilon_u) 2\pi f \tau}{1 + (2\pi f \tau)^2} + \frac{\sigma}{2\pi f \varepsilon_0} \tag{2}$$

where ε_0 is the absolute permittivity of free space (8.85×10^{-12} F/m), and σ is the bulk ionic conductivity. The ionic conduction term becomes significant when the polymer mobility is high or the experimental frequency is low [19]. For example, when a polymer is in the rubbery or liquid state due to its temperature being raised, the ionic conduction becomes dominant. Under this condition, the dipole term may be neglected and, thus, ε'' can be used to estimate the bulk ionic conductivity:

$$\sigma = 2\pi f \varepsilon'' \varepsilon_0 \tag{3}$$

The ionic conductivity is very useful for discriminating frequency-dependent dipolar phenomena such as the glass transition from frequency-independent phenomena such as the onset of flow and the viscosity minimum. For example, if the ionic conductivity converted by Eq. (3) is independent of frequency, we may suppose that the material is in the rubber or liquid state in which it has high molecular mobility.

The permittivity (ε') of the pristine polyisoimide can be seen in Fig. 3 as a function of temperature under the dynamic-heating condition at various frequencies. It increases with temperature between 150 and 190 °C, which corresponds to the glass transition temperature of the pristine polyisoimide, as measured by DSC to be 178 °C (Fig. 2A). In the temperature region between 190 and 240 °C, the permittivity decreases with temperature, which may be ascribed to the isomerization reaction of the polyisoimide making the polymer chains stiffer and the mobility lower. At temperatures above 250 °C, the thermal relaxation of the fully imidized specimens occurs with increasing temperature.

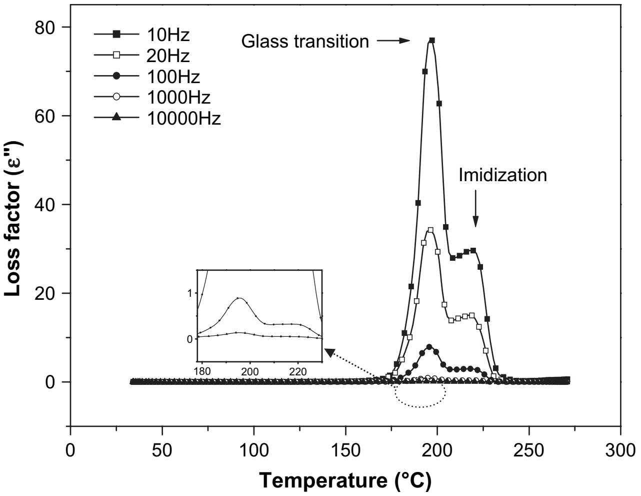


Fig. 4. Dielectric loss (ε'') of pristine polyisoimide measured at different frequencies as a function of temperature at a heating rate of 3 °C/min exhibiting two peaks representing the glass transition and isomerization of polyisoimide.

These two transitions, viz. the glass transition and isomerization reaction, can be more clearly seen in the plot of the dielectric loss (ε'') as a function of temperature in Fig. 4. The glass transition peak appears at around 190 °C and the isomerization peak at around 220 °C. It should be noticed that these peaks appear at similar temperatures for different frequencies, which is considered unusual because the glass transition of polymers is usually dependent on frequency due to the viscoelastic nature. In this sense, the glass transitions observed in the plot of ε'' versus temperature may be considered as being influenced by the following isomerization reactions. In the reacting polyisoimides, there is a great possibility that the isomerization reaction begins to proceed right after or in the middle of the glass transition because the carbonyl groups simply transform into imide rings within the main backbone chains, without bulk movement of the polymer chains. Therefore, it may be reasonable to suppose that the isomerization reaction takes place partially during the dynamic heating in the middle of the glass transition to provide the frequency-independent peaks of the glass transition.

The ionic conductivity in Eq. (3) is shown in Fig. 5 to exhibit the two frequency-dependent regions, $T < 185$ °C and $T > 230$ °C, where the dipole polarization is dominant and, thus, the reacting polymer system is considered to be in the glassy state. In the region where 185 °C $< T <$ 230 °C, however, the ionic conductivities are dominant and become frequency-independent due to the high mobility of the polymer, which demonstrates that the reacting polymer is in the rubbery or liquid state. In this rubbery (or liquid) region, the polyisomerization reaction rate becomes high, due to the high

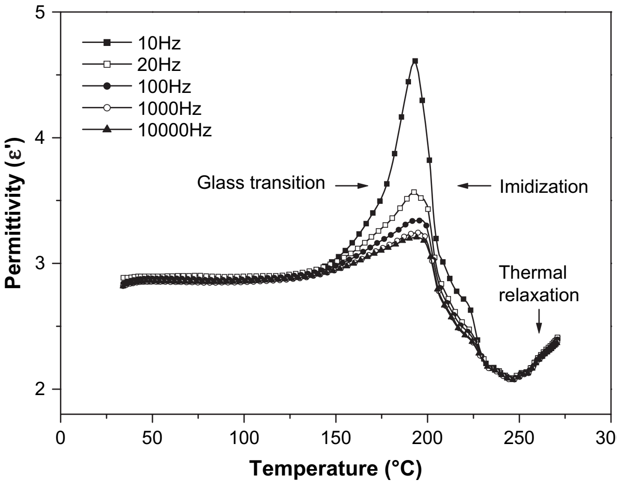


Fig. 3. Permittivity (ε') of pristine polyisoimide measured at different frequencies as a function of temperature at a heating rate of 3 °C/min exhibiting glass transition, isomerization, and thermal relaxation after complete isomerization.

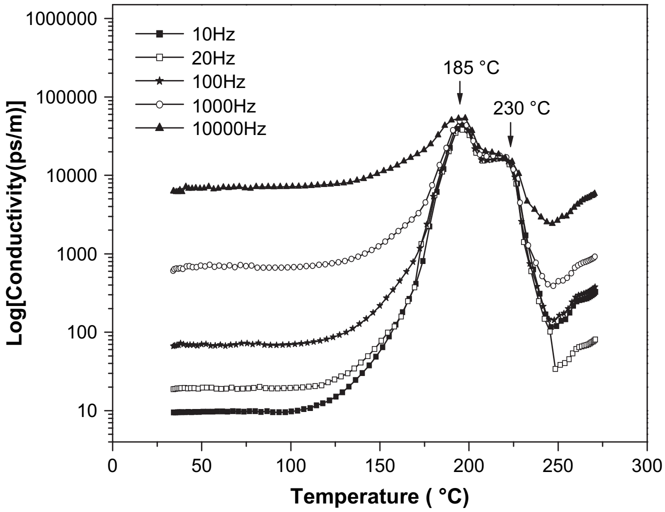


Fig. 5. Ionic conductivity of pristine polyisoimide measured at different frequencies as a function of temperature at a heating rate of 3 °C/min exhibiting two peaks representing the glass transition and imidization of polyisoimide.

mobility of the polymer, and consequently the glass transition temperature is considered to increase rapidly. After the polyisoimide is fully imidized, seemingly at temperatures above 230 °C in Fig. 5, the fully imidized polymer exhibits frequency-dependent dipole polarization.

In order to examine the details of the physicochemical changes, we used the complex electric modulus (CEM), which has been employed in the studies to investigate viscoelastic relaxation processes [20,21]. The advantage of adopting the CEM formalism is that it allows the electrode polarization and other grain boundary conductions to be discriminated, and is particularly effective in revealing high-frequency transitions, secondary relaxation, and overlapped thermal processes in a separate way [22]. The complex electric modulus (M^*) can be derived from the complex dielectric constant (ε^*) as

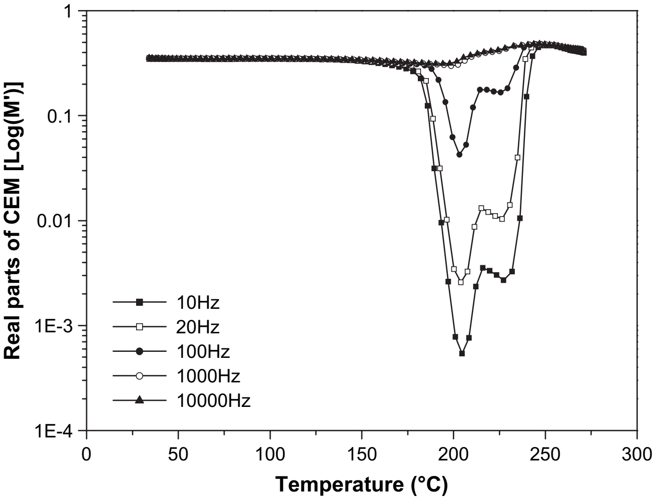


Fig. 6. Real parts of complex electric modulus (M') under the polyimide isomerization process.

$$\varepsilon^* = \varepsilon' + j\varepsilon'' \tag{4}$$

$$M^* = M' + jM'' = 1/\varepsilon^* \tag{5}$$

The real part (M') and the imaginary part of the complex electric modulus (M'') can be expressed as

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \tag{6}$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{7}$$

The real part of the CEM, (M'), behaves like a mechanical modulus as a function of temperature. Accordingly, M' usually decreases with increasing temperature in the typical glass–rubber transitions under the dynamic-heating condition. When it increases with increasing temperature in specific regions of temperature, it should be speculated that such reactions as cross-linking or polymerization occur and become dominant over the thermal relaxation process. As seen in Fig. 6, there are two decreasing and two increasing regions of M' as a function of temperature, corresponding to the regions where the thermal relaxations and isomerization reactions are dominant, respectively.

These complicated processes can be seen more clearly in the plot of the imaginary part of CEM, M'' versus temperature for various frequencies shown in Fig. 7. As can be seen, M'' is

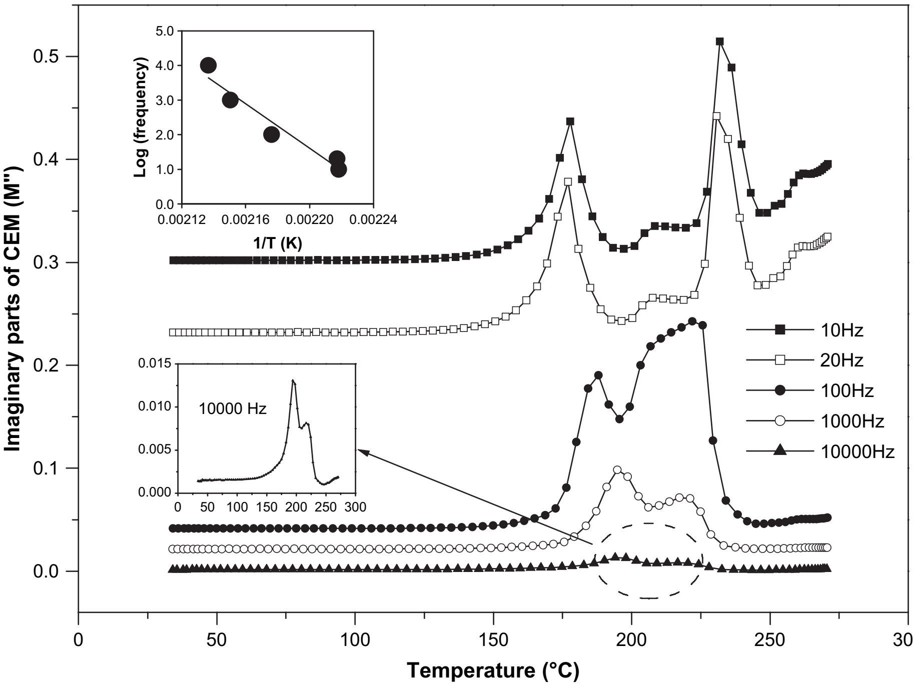


Fig. 7. Imaginary parts of complex electric modulus under the isomerization process exhibiting two peaks at higher frequencies and three peaks at lower frequencies. The peak temperatures specifically used for further analysis are 187 and 221 °C at 10^3 Hz, 194 and 217 °C at 10^4 Hz, and 177, 208, and 231 °C at 10 Hz. The inset shows Arrhenius plot of the first M'' peaks providing activation energy as 266.8 kJ/mol.

very efficient for separating those complex and overlapped transitions, especially in a narrow region of temperature. In Fig. 7A, three peaks are seen in the low frequency bands of 10 and 20 Hz, and two peaks can be seen in the high-frequency bands of 10^3 and 10^4 Hz. We believe that these complicated transitions observed in the plot of M'' versus temperature stem from two competing processes of the viscoelastic glass–rubber transitions and the isomerization kinetics occurring under the dynamic-heating conditions. The inset in Fig. 7 shows the Arrhenius plot of the first peak in the plot of M'' versus temperature, which can be ascribed to the temperature dependence of the viscoelastic relaxation rate of the pristine polyisoimide. The observed activation energy was 266.8 kJ/mol, which corresponds to the height of the energy barrier that has to be passed over during the transition. Here, as schematically shown in Fig. 8, we propose the use of a t–T_{dyn}–T_{g} diagram, in order to analyze the combined processes of the thermodynamic transitions and kinetic reactions under the dynamic-heating condition.

Previously, the isothermal t–T–T_{g} diagram was developed to describe the transformations of glass transition and vitrification as functions of time and temperature under isothermal conditions [24–26]. This diagram is a useful tool for the designing of thermoset curing cycles, because it can depict such physicochemical changes as gelation, glass transition, vitrification, and degradation as a function of time during polymerization reactions. Similar to the isothermal t–T–T_{g} diagram, the proposed dynamic t–T_{dyn}–T_{g} diagram in Fig. 8 shows three critical temperatures marked on the temperature axis: T_{g0}, the glass transition temperature of the initial material; T_{vit}, the vitrification temperature; and $T_{\mathrm{g}\infty}$, the glass transition temperature of the fully cured network. These temperatures appear (or are detected) at the time when the glass transition curve (T_{g} curve) crosses the dynamic-heating line (T_{dyn} line). The material status clearly depends on whether the T_{g} curve is above or below the T_{dyn} line belonging to the glassy or rubbery state, respectively.

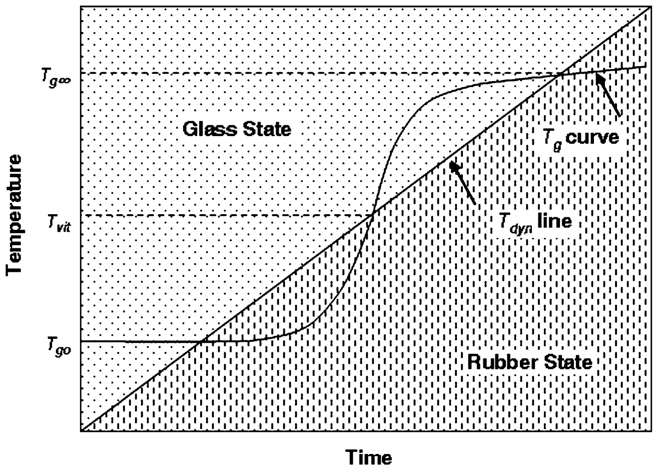


Fig. 8. Schematic representation of dynamic t–T_{dyn}–T_{g} diagram under the dynamic-heating condition. T_{g0}, $T_{\mathrm{g}\infty}$ and T_{vit} are the initial and final glass transition temperatures and vitrification temperature, respectively.

Assuming that the reacting polymer is initially in the glass state and heated as shown in Fig. 8, the T_{g} increment rate may be lower than a programmed heating rate of experiments, viz. the T_{dyn} line in Fig. 8, because the chain mobility in the glass state is low. Then, the T_{dyn} line (or dynamic-heating temperature) crosses the T_{g} curve. When it happens, the reacting polymer exhibits a glass-to-rubber transition at the point, where T_{g0} is detected, and the polymer is turned into rubber. Under the continuous heating, the T_{g} increment rate of the rubbery state polymer becomes high due to the high chain mobility and, therefore, the T_{g} curve crosses the T_{dyn} line secondarily to give T_{vit}. When it happens, the polymer is frozen (or vitrified) to be in the glass state. The reaction rate (or the T_{g} increment rate) of the vitrified polymer becomes low and, thus, the T_{dyn} line may cross the T_{g} curve thirdly to give $T_{\mathrm{g}\infty}$. Overall, these two dynamic processes of the T_{dyn} line and T_{g} curve proceed in a self-controlled and competing manner between the metastable glassy and supercooled liquid states to give three distinct transitions represented by T_{g0}, T_{vit} and $T_{\mathrm{g}\infty}$.

In the t–T_{dyn}–T_{g} diagram (Fig. 8), the T_{dyn} line and the T_{g} curve can be represented as a unique function of time as follows. First, the dynamic-heating temperature at a constant heating rate (T_{dyn} line) is represented by a unique function of time, viz.:

$$T_{\mathrm{dyn}} = T_0 + qt \tag{8}$$

where T_0 is the initial temperature and q is the heating rate. Second, there is a unique relationship between the glass transition temperature and the degree of conversion (α) in reacting polymer systems [23]: $T_{\mathrm{g}} = T_{\mathrm{g}}(\alpha)$. Subsequently, the degree of conversion, which is the degree of isomerization in this study, can be expressed as a function of time and temperature by various kinetic models [27,28] incorporating diffusion-limited as well as kinetic-controlled regimes [23,29]. Although the conversion is a function of time and temperature, the temperature is related to time by Eq. (8) in the dynamic-heating condition and, therefore, the conversion can simply be expressed as a function of time at a constant heating rate, viz.: $\alpha = \alpha_{\mathrm{q}}(t)$. As a result, the glass transition temperature can be expressed as a unique function of time under the condition of a constant heating rate, viz.:

$$T_{\mathrm{g}} = T_{\mathrm{g}}\left[\alpha_{\mathrm{q}}(t)\right] = T_{\mathrm{g,q}}(t) \tag{9}$$

Consequently, Eq. (9) gives the T_{g} curve represented as a unique function of time in the t–T_{dyn}–T_{g} diagram of Fig. 8. Typically, the T_{g} curve shows a sigmoidal shape as a function of time at a constant heating rate [23,29] as schematically expressed in Fig. 8. The sigmoidal shape of the T_{g} curve can also be understood by the phenomenological fact that the conversion, which is the integration of reaction rate, usually exhibits a sigmoidal shape with respect to time under the dynamic-heating condition. For example in DSC experiment, the reaction rate shows a maximum under the dynamic-heating condition and, thus, the integrated value of the reaction rate (i.e., conversion) may well give a sigmoidal shape of conversion. Since the T_g of thermoset polymers is approximately proportional to the conversion, it is reasonable to depict the sigmoidal feature of the T_g curve as a function of time in Fig. 8.

According to the time–temperature superposition principle [30,31], there is an equivalence between the experimental variables of temperature and frequency (or time). If the temperature is reduced, the relaxation process is slowed and the time scale of the relaxation process is shifted from higher to lower frequencies, and vice versa. As seen in Fig. 7, the initial glass transition temperatures (T_{g0}) measured at lower frequencies are lower than those at high frequencies: 177, 187, and 194 °C at 10, 10^3, and 10^4 Hz, respectively, which complies with the viscoelastic characteristics of the time–temperature superposition principle. In this study, the M'' peak temperatures measured at the frequencies of 10, 10^3, and 10^4 Hz (Fig. 7) were collectively depicted in the t–T_{dyn}–T_g diagram in Fig. 9. For example, three peak temperatures of M'' measured at 10 Hz in Fig. 7 are shown in Fig. 9 as three intersection points where $T_g = T_{dyn}$ at 177, 208, and 231 °C. Similarly, the two peaks measured at 10^3 Hz (187 and 221 °C) and 10^4 Hz (194 and 217 °C) in Fig. 7 are depicted in Fig. 9 at the intersection points at $T_g = T_{dyn}$.

As seen in the case of the 10 Hz curve in Fig. 9, after the T_{dyn} line reaches the initial glass transition temperature ($T_{g0} = 177$ °C), the polymer becomes rubbery. The isomerization reaction is so active in the rubbery state that the T_g curve increases fast and consequently crosses the T_{dyn} line causing the polymer to vitrify at $T_{vit} = 208$ °C. When the vitrification temperature is reached, the polymer enters into a metastable glassy state and, thus, the glass transition temperature increases so slowly with time that the T_{dyn} line crosses the T_g curve again to give $T_{g\infty} = 231$ °C. As a result, the three peaks represented in M'' can be clearly explained by this dynamic t–T_{dyn}–T_g diagram as T_{g0}, T_{vit}, and $T_{g\infty}$.

On the other hand, for the higher frequencies of 10^3 and 10^4 Hz, the T_{g0} of the reacting polymer shifts to higher temperatures due to the viscoelastic nature of the polymer. Similarly, the T_{vit} may well shift to higher temperatures at those higher frequencies and, thus, it may become too close to the T_g of the reacting polymer. In this case, the heating temperature (T_{dyn}) and the high-frequency T_g are similar to each other near the metastable glassy and supercooled liquid (or rubbery) states. Accordingly, the T_g curve, which is measured at high frequencies, may not clearly cross the T_{dyn} line to give a distinct T_{vit} peak, but a single and broad peak of $T_{g\infty}$ may be observed (see Fig. 7). This phenomenon can be schematically seen in Fig. 9 in the cases of higher frequencies at 10^3 and 10^4 Hz. It can also be confirmed by a monotonic increase in M' measured at high frequencies in Fig. 6.

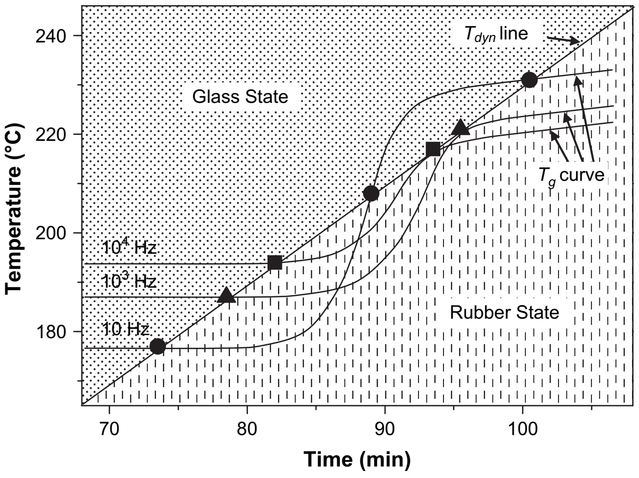


Fig. 9. Dynamic t–T_{dyn}–T_g diagram of polyisoimide isomerization for three different frequencies measured at a heating rate of 3 °C/min. The intersection points of T_{dyn} line and T_g curve correspond to the peak temperatures measured in Fig. 7.

Consequently, the proposed t–T_{dyn}–T_g diagram methodology is a useful analysis tool to identify different numbers of multiple transitions, which are often observed in reacting thermoset systems. According to this analysis, the multiple peaks stem from the coupled phenomena of the viscoelastic glass–rubber transitions and the kinetic increment of the glass transition temperature. The developed methodology makes it clear that the complex-transition behaviors observed in many reacting polymer systems under the dynamic-heating condition can be analyzed in a predictive manner for practical applications.

4. Conclusions

Using 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3′-diaminodiphenyl sulfone (3,3′-DDS) as a model polyisoimide system, a dynamic time–temperature–glass transition temperature (t–T_{dyn}–T_g) diagram was developed to analyze the isomerization reaction process. The multiple transitions of the reacting polyisoimide system observed in the electrical moduli properties were ascribed to the T_{g0}, T_{vit}, and $T_{g\infty}$, which were specifically determined by the viscoelastic nature of the polymer and the reaction kinetics.

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