Thermal dynamic relaxation and enthalpy distribution of an aromatic polyimide film: 6FDA-PFMB [1]

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Abstract

An aromatic polyimide, 6FDA-PFMB, was synthesized from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diamino biphenyl (PFMB), in refluxing *m*-cresol at high temperature. The polyimide film possesses two relaxation processes (α and β) above room temperature. The α-relaxation process is attributed to the glass transition, and the β-relaxation is the result of a sub-glass transition involving rotational motion in the PFMB diamine. An Arrhenius relation was utilized to investigate the β-relaxation and an activation energy E_a of 130 kJ mol^{-1} was determined. This value of the activation energy is close to the value calculated based on the relationship derived from absolute reaction-rate theory assuming a zero-entropy contribution to the relaxation process proposed by Starkweather. The distribution of relaxation times, or rather enthalpies, for the β-relaxation is obtained. The α-relaxation, however, obeys a WLF-type equation.

INTRODUCTION

Aromatic polyimide films exhibit excellent mechanical properties along with high thermal and thermo-oxidative stabilities. Most of the work carried out thus far has been concerned with the polyimide synthesized from pyrometallic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) [1–5], which is commercially available under the trade name of Kapton. It is widely used in electronic packaging applications. Recently, there has been considerable interest in the aromatic polyimide synthesized from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). This polyimide exhibits a high glass transition temperature, and a low dielectric constant compared to non-fluorinated polyimides such as PMDA-ODA [6, 7].

It has been reported that most aromatic polyimide and copolyimide films

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exhibit three relaxation processes (α, β and γ) in their dynamic mechanical and dielectric behaviors [8–23]. At very low temperatures (around $-80°C$), a γ-relaxation process can be observed. This process has been attributed to moisture absorption [8, 9, 11], and seems to be consistent with the results from dielectric relaxation studies [24, 25]. In this publication, the γ-relaxation will not be discussed further.

At high temperatures (usually $>300°C$), an α-relaxation process can be observed. This process is usually recognized as the glass transition. However, the temperature and magnitude of this relaxation is critically dependent upon the chain rigidity, linearity, ordered structure and cooperativity of segmental motion. In some cases, the magnitude of this relaxation is not prominent. For example, the glass transition of poly(4,4'-oxydiphenylenepyromellitimide) synthesized from PMDA and ODA [1, 2] is barely observable. This has led some investigators to conclude that this polyimide does not have an observable glass transition below $500°C$ [8]. Others have reluctantly described the softening at $400°C$ as the glass transition temperature of PMDA-ODA [9]. In a polyimide synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB), only a broad transition temperature range (over $200°C$) can be observed experimentally by heat capacity measurements by differential scanning calorimetry [26]. Within this temperature range, two relaxation processes (α and β) actually occur and overlap.

The first sub-glass β-relaxation process in polyimides is generally observed between 50 and $250°C$. An early report indicated that the β-relaxation in PMDA-ODA is attributed to crystalline interplane slippage which is the mechanism of loss behavior in graphite [8]. This mechanism was proposed because the β-relaxation process was observed in oriented films and not observed in essentially unoriented molded samples. This conclusion is, however, in conflict with the crystallinity dependence of the magnitude of the β-relaxation [27, 28]. Some researchers speculated that the β-relaxation must be caused by the mobility of residual poly(amic acids) which remain in the incompletely imidized sample [29–32]. However, later experimental results clearly showed that there is no direct correlation between amic acid content and the β-relaxation [33, 34]. Another explanation for the β-relaxation process was the so-called "rotational vibrations" [35–37]. It was proposed that the main type of motion is rotational vibration of small segments of a chain around quasi-equilibrium positions. Assignment of this vibration was to the motion of the phenylene and imide rings. Furthermore, it was suggested that the β-relaxation involves the mobility of phenylene groups in the diamines [9, 14]. However, the dianhydride portion of the polyimide can also affect the β-relaxation process. The transition temperature of the β-relaxation was reported to be remarkably constant for various flexible diamines in

polyimides, and decreased with the incorporation of flexible linkages in the dianhydrides [12].

These conclusions, based on the experimental observations for the β-relaxation process in various polyimides, are not consistent and sometimes conflicting. The complicated dynamic mechanical behavior observed in polyimides may arise from several factors. Because most polyimides have been synthesized through a two-step method where the poly(amic acids) were isolated, the imidization process (either thermal or chemical) and curing history may influence the β-relaxation process by inducing crosslinking and chain-stiffening side reactions [11]. In crystallizable polyimides such as PMDA-ODA [38], crystallinity and crystal morphology effects on the β-relaxation process should also be taken into account [28]. Structure anisotropy such as chain orientation (both in-plane and deformation orientation) may serve as another factor that influences the β-relaxation process [39]. In order to understand the origin of the β-relaxation, an amorphous, segmented rigid-rod polyimide, 6FDA-PFMB, was synthesized and characterized. In this way, one may avoid the crystal morphology effect on the β-relaxation. Furthermore, to fully characterize the relaxation behavior (dynamic stimuli) for the β-relaxation, it is often advantageous to investigate the distribution of relaxation times which reflects a distribution of relaxation enthalpies, as proposed by Starkweather [40].

EXPERIMENTAL

Materials and sample preparation

The polyimide studied in this publication was synthesized from 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB). The polymerization was conducted in refluxing *m*-cresol in a one-step process. Thus, the intermediate poly(amic acid) precursors were not isolated. The chemical structure of 6FDA-PFMB (Formula 1) has a molecular weight of the repeating unit of 728.5 g mol^{-1}. 6FDA-PFMB films were solution-cast from a 2% (w/w) solution on a glass plate. The films were dried at 150°C for five hours under reduced pressure and then heated for three hours at 250°C. The thickness of the films ranged from 10 to 20 μm. Precise control of the
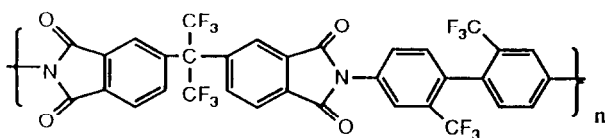
Formula 1. 6FDA-PFMB.

solution concentration is necessary in order to control the film's final thickness.

Equipment and experiments

Dynamic mechanical (DM) experiments were performed on a Rheometrics solid state RSA II analyzer. The films were clamped into the sample holder with a typical cross sectional area of 0.09 mm². An initial strain of 0.005% was chosen for the unoriented films. Different initial strains did not introduce a significant variation for DM data in our experimental strain range. However, a low strain could cause relatively larger data fluctuations due to a low signal:noise ratio, while a high strain could exceed the auto-controlled sample length or brake the sample. The temperature range was between 30 and 450°C with frequencies ranging from 0.005 to 15 Hz. When low frequencies were used, the heating rate had to be reduced in order to collect enough data for calculation.

RESULTS AND DISCUSSION

The sub-glass β-relaxation process

Figures 1 and 2 show the dynamic mechanical behavior for 6FDA-PFMB film at two different frequencies, 0.01 and 10.0 Hz. In a temperature range between 50 and 450°C, it is clear from both the loss modulus E'' and loss factor tan δ that two relaxation processes exist. The primary α-relaxation (attributed to T_g) occurs at around 321°C and 358°C for the two frequencies as shown in the two figures. The secondary, lower temperature β-relaxation occurs around 194°C and 290°C for the lower and higher
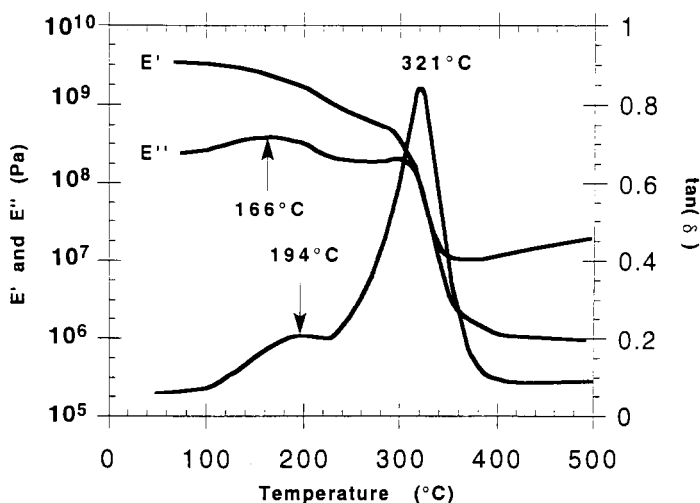

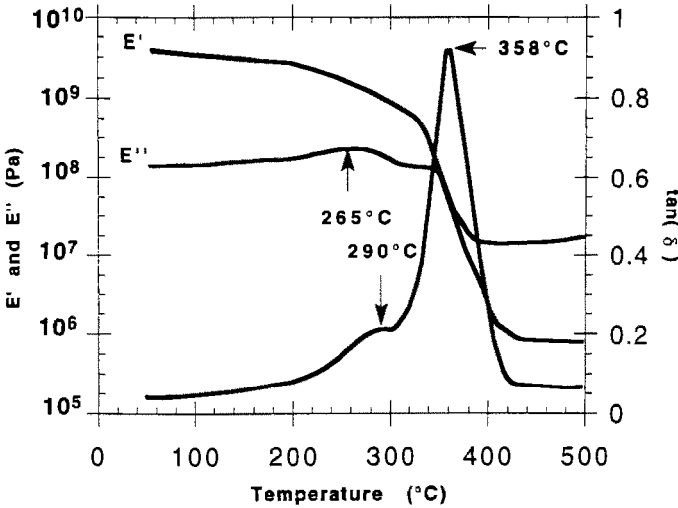Fig. 1. DM data of 6FDA-PFMB film (E', E'' and tan δ) at 0.01 Hz.

Fig. 2. DM data of 6FDA-PFMB film (E', E'' and tan δ) at 10 Hz.

frequencies, respectively. As the frequency increases, the lower temperature β-relaxation begins to overlap with the α-relaxation. The value of E' starts decreasing (Figs. 1 and 2) during the β-relaxation process. If one roughly estimates that E' decreases about one order of magnitude attributed to the β-relaxation, the α-relaxation is then responsible for about a 1.5 order of magnitude decrease in E'.

The relationship between the logarithmic frequency log f and the reciprocal transition temperature $1/T$ indicates an activation energy of 130 kJ mol^{-1} for the β-relaxation possess, as shown in Fig. 3. This
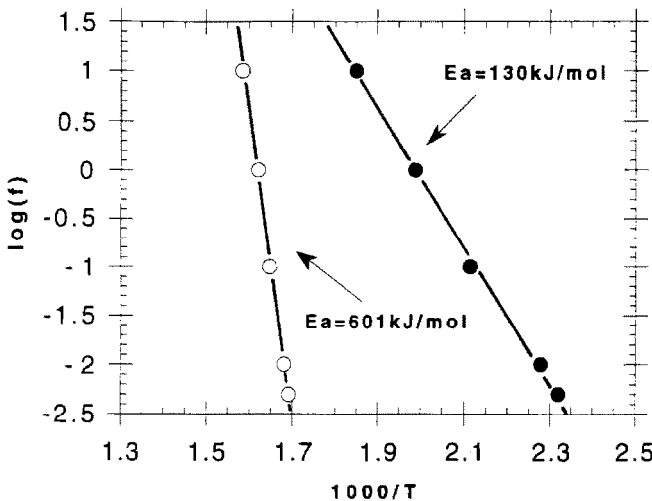

Fig. 3. Relationships between logarithmic frequency and reciprocal temperature (loss factor) for both α- and β-relaxations: O, α-relaxation; ●, β-relaxation.

activation energy is based on the frequency–temperature dependence as described by an empirical Arrenhius equation

$$f = A \exp[-E_a/RT] \tag{1}$$

If one follows the treatment proposed by Starkweather [40], utilizing the Eyring theory of absolute reaction rates, eqn. (1) can be expressed

$$f = (kT/2\pi h) \exp[-\Delta H/(RT)] \exp(\Delta S/R) \tag{2}$$

where h and k are the Planck and Boltzmann constants, respectively. The Eyring activation enthalpy ΔH [41] is

$$\Delta H = -R \; d \ln(f/T) \; d(1/T) \tag{3}$$

and the relationship between E_a and ΔH is thus

$$E_a = \Delta H + RT \tag{4}$$

Combining eqns. (2) and (4)

$$E_a = RT\{1 + \ln[k/(2\pi h)] + \ln(T/f)] + T\Delta S\} \tag{5}$$

Starkweather has proposed that for many relaxations, particularly those involving small sub-repeating unit groups which possess independent motion, the activation entropy ΔS should be close to zero [40]. Under this assumption for a relaxation at a frequency of 1 Hz, E_a follows a simple, almost linear, dependence on temperature

$$E_a = RT'\{1 + \ln[k/(2\pi h)] + \ln(T')\} \tag{6}$$

The extent to which the activation energy exceeds this value is equal to $T'\Delta S$. Equation (6) thus defines an effective lower limit for the activation energy of a viscoelastic response [40].

If we use eqn. (6) to calculate the activation energy E_a for the polyimide films (β-relaxation) with the assumption of $\Delta S = 0$, we obtain a value of 125 kJ mol^{-1}, which is close to the experimental value calculated from the Arrhenius equation (Fig. 3). This reveals that, for the β-relaxation, the assumption of $\Delta S = 0$ is probably correct and that the motion in this process must be largely non-cooperative in nature [40, 42].

The microscopic origin of this β-relaxation process is an interesting topic. Some reports have indicated that the β-relaxation process is associated with the motion involving the phenylene groups of the diamine [9, 14]. Our results, combined with our other studies [23, 28], support this explanation. No significant changes in this transition temperature and relaxation strength can be observed by introducing other types of dianhydrides such as PMDA, although it does significantly increase the chain rigidity, linearity and intermolecular packing [23, 28].

The detailed nature of this molecular motion in the β-relaxation has not been well characterized. From computer modeling and molecular dynamics, the two phenylene rings in PFMB may undergo a 180° rotation in

addition to small-angle fluctuations due to steric hindrance of the pendant trifluoromethyl groups [43]. However, this kind of motion must be proven by high temperature solid-state ^{13}C-NMR measurements.

Turning to the α-relaxation process which corresponds to the glass transition temperature, it is interesting that the apparent activation energies are close to 600 kJ mol^{-1}, obtained by an Arrhenius plot of log f versus $1/T$ (Fig. 3). This value is similar to those of previously studied polyimides [44]. Note that this apparent activation energy can only be approximated in a narrow frequency range. Non-linear behavior is observed if dielectric relaxation data are coupled with dynamic mechanical data [21]. Such large values of the apparent activation energies or enthalpies must go hand-in-hand with large activation entropies [40]. If one arranges eqn. (6) to give the activation free energy

$$\Delta F = \Delta H - T\Delta S = RT\{\ln[k/(2\pi h)] + \ln(T/f)\} \tag{7}$$

in the range of temperatures and frequencies of interest, this corresponds to activation free energies which should not be greater than about 200 kJ mol^{-1}. Therefore, a ΔH value of over 600 kJ mol^{-1} has to be balanced through a large apparent activation entropy of around 600–700 J K^{-1} mol^{-1}. The physical significance of a large positive apparent activation entropy is very hard to understand. This indicates that the activated segments are less ordered than the initial segments.

One possible explanation is that the glass transition temperature reflects a spectrum of internal motions having different activation energies involving molecular segments of varying sizes. As the frequency is increased, the absorption of energy is dominated by components having progressively smaller activation energies. This results in an apparent overall activation energy that is much larger than that of a single-component relaxation. This assumption that the activation energy is proportional to the size of the unit that must move cooperatively is, in fact, utilized in the theoretical treatment of the glass transition temperature [45, 46]. If one considers that the zero activation entropy condition serves as the non-cooperative motion of minimal sub-molecular units ($\approx$130 kJ mol^{-1}), the glass transition involves the cooperative motion of about five to six such units. At temperatures sufficiently far above the glass transition temperature, the motion again becomes non-cooperative [40].

A distribution of activation enthalpies

It is generally understood that viscoelastic relaxations in solids or liquids are always broader than a Debye relaxation. This broadening can be expressed as a distribution of relaxation times [40], which might in turn reflect a distribution of activation energies. The quantity $\Phi(\ln \tau)\,\mathrm{d}\ln \tau$ is the fraction of the relaxation process having relaxation times between $\ln \tau$

and $(\ln \tau + \mathrm{d} \ln \tau)$ [47]. Thus

$$\int_{-\infty}^{\infty} \Phi(\ln \tau)\, \mathrm{d} \ln \tau = 1 \tag{8}$$

During a dynamic mechanical experiment, the storage and loss moduli, E' are E'', are

$$E'(\omega) = E_r + (E_u - E_r) \int_{-\infty}^{\infty} \frac{\Phi_E(\ln \tau)\omega^2\tau^2\, \mathrm{d} \ln \tau}{1 + \omega^2\tau^2} \tag{9}$$

and

$$E''(\omega) = (E_u - E_r) \int_{-\infty}^{\infty} \frac{\Phi_E(\ln \tau)\omega\tau\, \mathrm{d} \ln \tau}{1 + \omega^2\tau^2} \tag{10}$$

where E_u and E_r are the limiting unrelaxed and relaxed moduli. The relaxation spectrum can thus be obtained from experimental data through the Alfrey approximation [48]

$$\Phi_E(1/\omega) = - \frac{\mathrm{d}E'(\omega)}{\mathrm{d} \ln \omega} \frac{1}{(E_u - E_r)} \tag{11}$$

and

$$\Phi_E(1/\omega) = \frac{2E''(\omega)}{\pi(E_u - E_r)} \tag{12}$$

Equation (7) is now used to characterize an entire loss peak. Dynamic mechanical data are taken over a range of temperature and frequency. The unrelaxed and relaxed moduli can, in principle, be obtained from a complex-plane plot of E'' versus E'. However, this plot needs data which cover a broader frequency range which is beyond the instrument limitation of dynamic mechanical experiments. We assume that the unrelaxed and relaxed moduli, E_u and E_r, can be approximated from values of the storage modulus obtained at low temperature and high frequency E_u, and at high temperature and low frequency E_r. For each combination of temperature and frequency, Φ is calculated from eqn. (11) or (12) and plotted against ΔF from eqn. (7). Figure 4 shows the relationships between Φ and ΔF for the β-relaxation of 6FDA-PFMB at different temperatures. It is evident that all the data points almost fall into a single master pattern. This indicates that the activation entropy is zero and, therefore, $\Delta F = \Delta H$. Thus, Fig. 4 represents the distribution of the activation enthalpy of the β-relaxation process for the polymer.

However, for the α-relaxation of the polymer, a single master pattern could only be achieved after shifting along the ΔF axis. From these shift factors, an apparent activation entropy of about 600–700 J K^{-1} mol^{-1} can be calculated [49]. One speculates that the large apparent activation
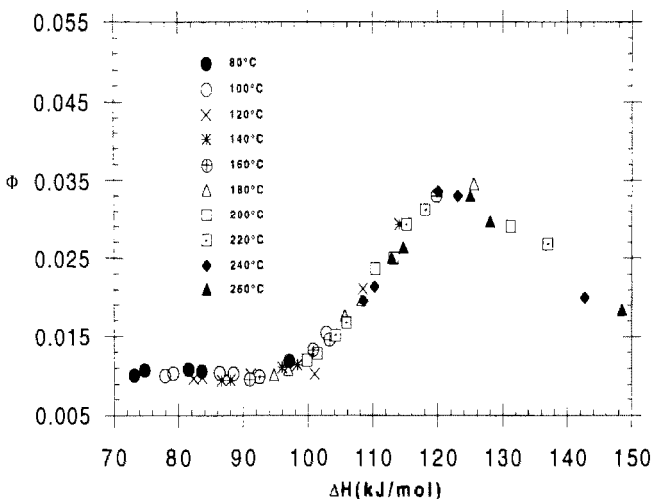
Fig. 4. Activation enthalpy distribution of the β-relaxation process.

entropy reflects the distribution of internal motions that are sampled differently at different temperatures.

CONCLUSIONS

Dynamic mechanical data indicate two relaxation processes (α and β). 6FDA-PFMB displays a β-relaxation process which is probably associated with the motion of the PFMB diamine. The activation energy for the β-relaxation is 130 kJ mol^{-1}. Because the activation entropy of this relaxation is very close to zero, a non-cooperative type of motion is expected. A distribution of activation enthalpies has been achieved for this process, and, in principle, this distribution represents the viscoelastic behavior of the relaxation process. However, the α-relaxation contributed from the glass transition temperature shows that its apparent activation energy and entropy are very large. This is attributed to a degree of cooperativity in the motion that is highly dependent upon the temperature.

ACKNOWLEDGMENT

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