Organo-Soluble Segmented Rigid-Rod Polyimide Films Part 3: Effects of Copolymer Composition on Thermal Expansivity and on Relaxation Processes

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A series of copolyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), pyromellitic dianhydride (PMDA) (1,2,4,5-benzenetetracarboxylic dianhydride) and 2,2'-bis(trifluoromethyl) benzidine (PFMB) have been synthesized with varying BPDA-PFMB and PMDA-PFMB compositions. A systematic change in the linear coefficient of thermal expansion (CTE) and the glass-transition temperature \( T_g \) is observed by changing the ratios of the BPDA-PFMB and PMDA-PFMB compositions. Both the CTEs and \( T_g \) have been found to follow the molar-additivity rules. Dynamic mechanical experiments manifest two relaxation processes above room temperature. A subglass \( \beta \) relaxation, which is independent of the copolymer composition relative to the varying dianhydride composition, is found in the copolyimides studied. This \( \beta \) transition exhibits the same temperature and frequency dependence in all the copolyimides. An \( \alpha \) transition (corresponding to the glass-transition temperature) is observed and is dependent on the PMDA-PFMB composition within the system. The possible molecular origin of the \( \beta \) relaxation is also discussed.

**Keywords:** Copolyimide; Glass-transition temperature; Thermal expansion; Relaxation

In the first two publications of this series, we reported a detailed study of the structure formation and macroscopic properties of the polyimide film synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,2'-bis(trifluoromethyl) benzidine (PFMB) in refluxing m-cresol via a one-step process where the poly(amic acid) precursors were not isolated. Similar to other segmented rigid-rod polyimides, BPDA–PFMB thin films with a thickness ranging from 10 to 30 \( \mu \)m exhibit an in-plane orientation of the crystals. Namely, the \( c \) axis of the crystals are oriented parallel to the film surface determined through both transmission and reflection modes of wide-angle X-ray diffraction (WAXD) experiments. It has been speculated that owing to the chain rigidity the whole chain may also lie parallel to the film surface. This anisotropic structure can be enhanced through an annealing process. Traditionally, polyimides were synthesized through a two-step polymerization. The conditions of an imidization process of poly(amic acid)s, as a second step of the polymerization, often affects the ultimate structure and morphology of the fully imidized films. A film-thickness effect on the structure and morphology has also been investigated. It is commonly understood that an anisotropic structure will lead to differences in thermal, mechanical, dielectric and optical properties parallel and perpendicular to the film surface. These anisotropic properties have not only been observed in BPDA–PFMB and its copolyimides but also in other aromatic polyimide films.

In this paper we focus on the effect of copolymer composition on the thermal and dynamic mechanical properties of BPDA–PFMB-based copolyimides. The chemical structures are expressed in Scheme 1 and designated as (BPDA–PFMB)_x(PMDA–PFMB)_y. It can be further simplified to CPI(x/y), where \( x \) and \( y \) are the molar percentages of the comonomers ranging from 0 to 100. CPI(100/0) represents the homopolyimide BPDA–PFMB which has been studied previously. This family of copolyimides is also organo-soluble and was prepared in refluxing m-cresol in a one-step process. The PMDA–PFMB composition ranges from 0 to 50%. From computer modelling, it has been found that the dianhydride BPDA in the polymers possesses two conformational isomers, gauche and trans. Even in the case of...
the *trans* conformation, BPDA introduces a kink along the chain direction, and PFMB is a linear portion of the chain molecules. On the other hand, the dianhydride PMDA attributes to the linear portion in the copolymers. With increasing the PMDA–PFMB composition in the copolymides, the length of this linear portion of the chain molecules is increased, as well as the chain rigidity of the copolymides. This can be illustrated in Fig. 1 where homopolymer CPI(100/0) and copolymer CPI(50/50) are shown as examples.

At high temperatures above 140 °C, the copolyimides show a homogeneous solution state below a concentration of ca. 15%. On cooling, the copolyimide solutions undergo a sol–gel transition to form gel-like structures. The transition temperatures and kinetics depend upon the concentration, molecular weight and chain rigidity of the copolyimides.

**Experimental**

**Materials**

The copolyimides were synthesized from BPDA, PMDA, and PFMB diamine. The diamine monomer synthesis was first reported by Rogers *et al.* Since the chemical reactivities of BPDA and PMDA are different and PMDA–PFMB polymer is insoluble in *m*-cresol, a macromonomer was first synthesized from 1 mol of BPDA and 2 mol of PFMB to form the soluble blocks. For CPI(50/50) a further 1 mol of PMDA was added to the polymerizing solution, and statistically an alternating copolyimide of BPDA–PFMB and PMDA–PFMB is obtained. For other compositions a certain molar percentage of PMDA is added into solution first and then the rest of the BPDA dianhydride is added to finish the polymerization. Following this procedure random copolyimides are obtained. If both BPDA and PMDA are added at the same time the copolymides exhibit phase separation observed optically and through dynamic mechanical experiments (two glass-transition temperatures). Detailed polymerization procedures are discussed in another publication.

In this study three different compositions were studied, CPI(100/0), CPI(70/30) and CPI(50/50). Their statistical molecular weights are 570, 548 and 533 g mol⁻¹, respectively (496 g mol⁻¹ for the PMDA–PFMB segment). Their intrinsic viscosities range from 0.35 to 0.45 dm³ g⁻¹ at 60 °C in *m*-cresol. Films of these copolyimides were prepared by spreading a 2% (m/m) *m*-cresol solution on a glass plate with a doctor knife followed by drying at 150 °C for 5 h and 250 °C for 3 h under reduced pressure in a vacuum oven (VWR-1410D). In this manner the thickness of the films was controlled between 10 and 30 μm. Before thermal mechanical or dynamic experiments were performed, the free-standing films were preheated under initial stresses ranging from 0.5 to 2.0 MPa up to 300 °C at a heating rate of 20 °C min⁻¹ and held there isothermally for 5 min under a dry nitrogen atmosphere. The films were cooled at a rate approximately equal to the initial heating rate. Quantitative experiments were carried out immediately after the preheating.

**Equipment and Experiments**

Thermal mechanical analysis was used to study the in-plane linear coefficient of thermal expansion (CTE) and the glass-transition (Tg) behaviour of the copolyimide films. Our experiments were carried out on a TA TMA 2940 thermal
mechanical analyser under a dry nitrogen atmosphere. The ribbon-shaped samples were mounted between two vertical clamps and a stress of 1–10 MPa was applied (the cross-sectional area of the film samples was ca. 0.09 mm²). The heating rate used was 15°C min⁻¹ in a temperature range of 30–450°C. In each experiment a linear relationship between the percentage of elongation (strain) and temperature was observed below 200°C. The slope of the percentage of elongation versus temperature in the temperature range 50–200°C is taken to be the CTE of the solid state. As the temperature approaches Tg we observe a dramatic increase in the CTE. The onset temperature of this change is recognized as Tg which is obtained for a particular applied stress with a preheat treatment history.

Dynamic mechanical measurements were carried out on a Rheometrics solid-state analyser (RSA II). The frequency range used was 0.001–15 Hz with a heating rate of 10°C min⁻¹. At very low frequencies (<0.005 Hz) the heating rate was reduced in order to have enough time to accumulate the data. A strain of 0.05% was used in the dynamic measurements under normal atmospheric conditions from room temperature to 450°C.

Results and Discussion

Coefficients of Thermal Expansion

Fig. 2 shows the CTEs measured at different applied stresses for three polyimides [CPI(100/0), CPI(70/30) and CPI(50/50)] under an initial annealing stress of 0.5 MPa. CPI(100/0) which is the homopolyimide BPDA–PFMB shows the highest CTE measured under the same thermal conditions. For example, the CTE measured at 2.0 MPa is 11.5×10⁻⁶°C⁻¹ while the CTEs are 8.0×10⁻⁶°C⁻¹ and 3.2×10⁻⁶°C⁻¹ for CPI(70/30) and CPI(50/50), respectively. Since the CTEs are dependent upon the initial stress during the preheat treatment and the applied stress during the measurements (the higher the applied stress is, the higher the measured CTE will be), it is necessary to employ a double extrapolation method.¹⁹ Since the measured CTE is dependent on the applied stress in a linear relationship under the applied stress below 10 MPa, the CTE is measured at different applied stresses and extrapolated to zero stress. A second extrapolation is necessary owing to the introduction of some orientation into the films during the preheat treatment process. The doubly extrapolated values of the CTEs are 6.98×10⁻⁶, 2.62×10⁻⁶, and 1.38×10⁻⁶°C⁻¹ for CPI(100/0), CPI(70/30) and CPI(50/50), respectively. It is observed that on increasing the PMDA composition the CTE decreases. This indicates that the chain rigidity and linearity play an important role in the thermal expansion behaviour. Other possible effects on the CTEs may involve chain packing and molecular motion. A systematic study of the thermal expansion of aromatic polyimides has been carried out by Numata et al.²⁰,²¹ However, quantitative correlation between CTE and microscopic structural parameters has not been achieved. In particular, the anisotropic structure (in-plane orientation) in the films may further complicate any type of correlation. It should also be noted that the CTE parallel to (in-plane) and perpendicular to (out-plane) the film surface must be different.

It is generally understood that stresses may be frozen into the films during the film processing. For example, the stress induced through the film casting and solvent evaporation as well as preheat treatment. In many cases, they affect the CTE data measured. In our experiments, the free-standing films were uniformly annealed at 300°C for 5 min before the CTE measurements. The frozen stress introduced during film casting and solvent evaporation should be largely released. However, a small initial stress applied during preheat treatment (0.5–2.0 MPa) may also cause some degree of structure anisotropy, and therefore, affect the CTE data obtained experimentally. In Fig. 3, a negative CTE extrapolated for CPI(50/50) when the initial stress during the preheat treatment is relatively high is an illustration of this effect. Note that a negative CTE with temperature in polymeric materials has no theoretical base unless specific packing interactions among chain molecules are introduced. This is because of the anharmonic vibrational nature of the molecular motion in the solid state. It is thus necessary to utilize a double-extrapolation method in the solid state in which the extrapolated CTE at zero applied stress is plotted against initial annealing stress and extrapolated to zero initial annealing stress.¹⁹ Therefore, we conclude that the differences among the double-extrapolated CTEs for this series of copolymides should reflect the difference in the polymer structures. With the CTEs and compositions of the copolymides in hand, one can design a material with a specific CTE by adjusting the molar percentage of PMDA–PFMB in the (BPDA–PFMB)ₙ–(PMDA–PFMB)ₙ copolyimide system.

We expect that the CTE should obey the additivity rules based on either the weight fraction or molar fraction of the random copolyimide compositions, similar to those observed for their Tg (see below). With the three copolymides studied it has been observed that there is a linear composition dependence on the CTE based on the molar percentage of PMDA. The adherence to the additivity rules is expected since we are examining random copolymers as opposed to a block copolymer or polymer blend. Block copolymers and blends will possess some degree of aggregation resulting in

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**Fig. 2** Relationship between CTE and stress for (○) CPI(100/0), (●) CPI(70/30) and (▲) CPI(50/50) under 0.5 MPa initial stress during preheat treatment.

**Fig. 3** Relationship between CTE and stress for CPI(50/50) under an initial stress of (○) 0.5, (●) 1.0 and (▲) 2.0 MPa during preheat treatment.
Glass-transition Temperatures

Thermomechanical measurements provide the linear expansion as a function of temperature. ($T_g$ is taken to be the temperature at which a dramatic increase in CTE occurs). Fig. 4 shows the relationship between $T_g$ and the applied stress for CPI(100/0), CPI(70/30), and CPI(50/50), respectively. $T_g$ decreases in a linear relationship with increasing applied tensile stress in a range below 10 MPa. The extrapolated values of $T_g$ were obtained from films that were annealed at 300 °C for 5 min under a tensile stress of 0.5 MPa. A double extrapolation is not necessary since $T_g$ shows a negligible dependence on the initial stress used during the preheat treatment process. From this observation we may speculate that during the preheat treatment process we are introducing some orientation but not enough to restrict segmental motion. The slope of $T_g$ vs. applied tensile stress (Fig. 4) reveals the sensitivity of $T_g$ towards an applied stress. Interestingly, the CPI(100/0) shows the most sensitivity to the tensile stress among the three copolymers studied. This may be an indication of the effect of increasing chain rigidity and linearity by increasing the amount of PMDA–PFMB.

There are a number of semi-empirical predictions of the change of $T_g$ with composition in random copolymers. We can start with the DiMarzio–Gibbs equation

$$T_g = m_1 T_{g1} + m_2 T_{g2}$$

(1)

where $T_g$ is the glass-transition temperature of a copolymer composed of two monomer units 1 and 2 with mole fractions $m_1$ and $m_2$ and $T_{g1}$ and $T_{g2}$ are the glass-transition temperatures of homopolymers 1 and 2, respectively. On the other hand the Fox equation uses weight fractions:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

(2)

Here $w_1$ and $w_2$ are the corresponding weight fractions of monomer units 1 and 2. These two equations possess different theoretical aspects, namely conformational entropy and free volume, but both are based on additivity rules. We obtained a better fit using molar fractions rather than the Fox equation which makes use of weight fractions (Fig. 5).

Another important feature shown in Fig. 4 is the decrease of $T_g$ with increasing applied tensile stress in the range 1–10 MPa. An earlier study found that the cause of decreasing $T_g$ with increasing applied tensile stress was an increase in free volume$^{24}$ as opposed to the decrease in the free volume expected when considering a hydrostatic pressure. During the 1980s, Chow proposed a theoretical prediction of stress-induced $T_g$. When a system is under a uniform tensile stress ($\sigma$) with a negligible strain rate, the effect on $T_g$ can be described by$^{25-27}$

$$T_g = T_g^0 + \frac{(RT_g^0/\varepsilon)(1 - \exp[\sigma V/(RT_g^0)])}{\varepsilon}$$

(3)

Here $\varepsilon$ is the average energy of hole formation and $T_g^0$ is a reference temperature, $V$ is the tensile-activation volume and $R$ is the universal gas constant. If $\sigma = 0$, eqn. (3) reduces to $T_g = T_g^0$, and if the applied stress is sufficiently small and approaches zero, eqn. (3) becomes:

$$T_g \approx T_g^0 - (T_g^0/\varepsilon)\sigma = T_g^0 - K\sigma$$

(4)

where the slope $K$ has the units of temperature/stress. The generation of eqn. (4) involves the expansion of the exponential term into a series when the external work is sufficiently small, i.e. $\sigma V \ll 1$. Eqn. (3) gives rise to a molecular explanation of the linear relationship between $T_g$ and an applied tensile stress ($\sigma$) as shown in Fig. 4. This stress dependency of $T_g$ (as well as that of the CTE) in the thin films may be practically significant for microelectronic applications since spin-coated films usually have a certain degree of frozen-in stress.

Relaxation Processes

Fig. 6 and 7 show dynamic mechanical behaviour for the CPI(50/50) film at two different frequencies of 0.005 and 10.0 Hz. In the temperature range 50–450 °C it is clear that from both the loss modulus ($E''$) and loss factor (tan $\delta$) two relaxation processes exist. The primary $x$ relaxation (attributed to $T_g$) occurs at ca. 345 and 385 °C for the lower and higher frequencies, respectively. As the frequency increases the lower temperature $R$ relaxation begins to merge with the $x$ relaxation.

Fig. 8–10 show dynamic results measured at 1.0 Hz for the CPI(100/0), CPI(70/30), and CPI(50/50) films. Of particular interest are the changes occurring in the storage modulus and the loss modulus during the $x$ and $R$ relaxations. It is evident that $E''$ starts decreasing in all cases (Fig. 8–10) during the $R$ relaxation process. For CPI(100/0) a more-or-less continuous decrease in $E''$ is observed owing to the overlap of the $x$ and $R$ relaxations. The increase of the PMDA–PFMB leads to a separation of the two relaxations due to the effect of increasing the $x$ relaxation temperature. This is also manifested in the $E''$ data in which a loss-modulus peak at higher temperature ($x$ relaxation) becomes more evident.
Fig. 6 Dynamic mechanical data for CPI(50/50). (a) $E'$, 10.0 Hz; (b) $E'$, 0.005 Hz; (c) $E''$, 0.005 Hz; (d) $E''$, 10.0 Hz. Temperature range 50–450 °C.

Fig. 7 Dynamic tan δ data for CPI(50/50) at (a) 0.005 and (b) 10.0 Hz. Temperature range 50–450 °C.

Fig. 8 Dynamic mechanical data for CPI(100/0) at a frequency of 1.0 Hz. (a) $E'$, storage modulus; (b) $E''$, loss modulus

Fig. 9 Dynamic mechanical data for CPI(50/50) at a frequency of 1.0 Hz. (a) $E'$, storage modulus; (b) $E''$, loss modulus

Fig. 10 Dynamic mechanical data for CPI(70/30) at a frequency of 1.0 Hz. (a) $E'$, storage modulus; (b) $E''$, loss modulus

It has been reported that a second subglass transition (γ) relaxation process occurs at ca. −80 °C for many polyimide films and it has been attributed to moisture effects. A low-temperature relaxation of this type was not observed in this case because our measurements were made at, or above, room temperature, and our samples were preheated to 300 °C. The β-relaxation temperatures for the polyimide films are constant and occur at the same temperature (possess same magnitude) and exhibit the same frequency dependence regardless of the percentage of PMDA–PFMB. The relationship between logarithmic frequency ($\log f$) versus reciprocal transition temperature ($1/T$) indicates that the β relaxation processes for the three polymers studied exhibit ca. the same activation energies ($E_a \approx 130$ kJ mol$^{-1}$), as shown in Fig. 11. This activation energy is based on an empirical Arrhenius equation of

$$f = A \exp(-E_a/RT)$$  \hspace{1cm} (5)

If the treatment proposed by Starkweather is followed, utilizing the Eyring theory of absolute reaction rates, eqn. (5) can be expressed as

$$f = (k_B T/2\pi h) \exp[(-\Delta H/(RT))] \exp(\Delta S/R)$$  \hspace{1cm} (6)

The Eyring activation enthalpy $\Delta H^{33}$ is

$$\Delta H = -R \ln (f)/(d/1/T)$$  \hspace{1cm} (7)

and the relationship between $E_a$ and $\Delta H$ is

$$E_a = \Delta H + RT$$  \hspace{1cm} (8)

with increasing PMDA–PFMB composition. If it is estimated that $E'$ decreases ca. one-half an order of magnitude attributed to the β relaxation, the α relaxation is then responsible for ca. one order of magnitude decrease in $E'$. Another interesting observation is the increase in $E'$ above 400 °C for all of the polyimides studied. This is related to a crystallization process. In PMDA–ODA films (Kapton) similar observations have been reported and attributed to both a crystallization process and crosslinking. In this case the crosslinking is not important since these films possess a very high thermal and thermo-oxidative stability up to 500 °C.
Combining eqn. (6) and (8) gives
\[ E_a = RT \left[ 1 + \ln\left(\frac{k_B}{2\pi h}\right) + \ln(T/T_f) \right] + T\Delta S \] (9)

Starkweather has reported that for many relaxations, particularly those involving small submolecular fragments moving independently of one another, the activation entropy \(\Delta S\) is close to zero.\(^{32}\) If this is the case, and \(T\) is the temperature at which the frequency of the relaxation is 1 Hz, \(E_a\) follows a simple, almost linear dependence on temperature:
\[ E_a = RT \left[ 1 + \ln\left(\frac{k_B}{2\pi h}\right) + \ln(T) \right] \] (10)
The extent to which the activation energy exceeds this value is equal to \(T\Delta S\). Eqn. (10) thus defines an effective lower limit for the activation energies of a viscoelastic response.\(^{32}\) Very few, if any, relaxations have significantly negative activation entropies.

If we use eqn. (10) to calculate the activation energy, \(E_a\), for these copolyimide films (\(\beta\) relaxation) under the assumption of \(\Delta S = 0\), we obtain a value of 124–126 kJ mol\(^{-1}\), which is close to the experimental value calculated from the Arrhenius equation (Fig. 11). This reveals that for the \(\beta\) relaxation the assumption of \(\Delta S = 0\) is probably correct and the motion in this process must be largely non-cooperative in nature.\(^{32,34}\)

The microscopic origin of this \(\beta\)-relaxation process is interesting. For PMDA–ODA film (Kapton), it was attributed to interplane slippage because this process was observed in oriented films and not observed in an essentially unoriented molded sample.\(^5\) However, we have observed that the \(\beta\) relaxation can also be seen in the unoriented films studied here. Some reports indicate that the \(\beta\) relaxation process is associated with the motion involving the phenylene groups of the diamine.\(^{30,35}\) Our results support this explanation since as shown in Fig. 11, no significant changes in the transition temperatures and relaxation strength can be observed. This indicates that the introduction of PMDA does not affect the \(\beta\)-relaxation process although it has significantly increased the chain rigidity and linearity and intermolecular packing. However, in this series of copolyimide films, the diamine composition (PFMB) does not change owing to the one-to-one correspondence with the BPDA and PMDA dianhydrides.

The detailed nature of this molecular motion in the \(\beta\) relaxation has not been well characterized. It has been speculated that this process should be associated with so-called rotational vibrations of the phenylene rings.\(^{36–38}\) From computer modelling and molecular dynamics the two phenylene rings in PFMB may undergo a 180\(^\circ\) rotation in addition to small-angle fluctuations due to steric hindrance of the pendant trifluoromethyl groups.\(^{39}\) However, this kind of motion must be proven by high-temperature \(^{1}^2\)C solid-state NMR measurements.

Turning to the \(\alpha\)-relaxation process which corresponds to \(T_g\), it is interesting that the apparent activation energies are also close to one another at ca. 800 kJ mol\(^{-1}\) obtained by an Arrhenius plot of \(\log f vs. 1/T\) (Fig. 12). These values are higher than previously studied polyimides.\(^{40}\) Note that this apparent activation energy can only be approximated in a narrow frequency range. Non-linear behaviour is observed if dielectric relaxation data is coupled with dynamic mechanical data.\(^2\) Such large values of the apparent activation energies or enthalpies must go hand-in-hand with large activation entropies.\(^{32}\) If eqn. (6) is rearranged to give the activation free energy,
\[ \Delta F = \Delta H - T\Delta S = RT \left[ \ln\left(\frac{k_B}{2\pi h}\right) + \ln(T/f) \right] \] (11)
The range of temperature and frequency of interest corresponds to activation free energies no greater than ca. 200 kJ mol\(^{-1}\). Therefore, a \(\Delta H\) of over 800 kJ mol\(^{-1}\) has to be balanced through a large apparent activation entropy of ca. 900–1000 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 \(T_g\) reflects a spectrum of internal motions having different \(E_a\) involving molecular segments of varying sizes. As the frequency is increased, the absorption of energy is dominated by components having progressively smaller values of \(E_a\). This results in an apparent overall \(E_a\) that is much larger than that of a single-component relaxation. This assumption that \(E_a\) is proportional to the size of the unit that must move cooperatively, is used in the theoretical treatment of \(T_g\).\(^{41–42}\) If one considers that the zero activation entropy condition serves to be the non-cooperative motion of minimal submolecular units (ca. 130 kJ mol\(^{-1}\)), the glass transition involves the cooperative motion of ca. five to six such units. At temperatures sufficiently far above \(T_g\), the motion again becomes non-cooperative.\(^{32}\)

It is also interesting that with increasing chain rigidity (increasing the PMDA–PFMB composition) \(T_g\) shifts to higher temperatures, but the magnitude of the loss factor (\(\alpha\) relaxation) remains almost constant. The magnitude of tan \(\delta\) for these copolyimides is lower (only ca. 1/3–1/2) compared with those of other polyimides with the same diamine (PFMB), but different dianhydrides.\(^{43}\) This reveals that the relatively weak tan \(\delta\) is attributed mainly to the BPDA and PMDA dianhydrides. Again, detailed types of molecular

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**Fig. 11** Relationship between log \(f\) and reciprocal temperature for the \(\beta\)-relaxation peak temperatures for (○) CPI(100/0), (△) CPI(70/30) and (●) CPI(50/50)

**Fig. 12** Relationship between log \(f\) and reciprocal temperature for the \(\alpha\)-relaxation peak temperatures for (○) CPI(100/0), (△) CPI(70/30) and (●) CPI 50/50
Distributions 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, which might in turn reflect a distribution of activation energies. The quantity \( \Phi(\ln \tau) \) is the fraction of the relaxation process having relaxation times between \( \ln \tau \) and \( \ln (\tau + \ln \tau) \). Thus:

\[
\int_{-\infty}^{\infty} \Phi(\ln \tau) d\ln \tau = 1
\]

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

\[
E'(\omega) = E_u + (E_a - E_u) \int_{-\infty}^{\infty} \frac{\Phi(\ln \tau) \omega^2 \tau^2 d\ln \tau}{1 + \omega^2 \tau^2}
\]

and

\[
E''(\omega) = (E_a - E_u) \int_{-\infty}^{\infty} \frac{\Phi(\ln \tau) \omega d\ln \tau}{1 + \omega^2 \tau^2}
\]

Where \( E_u \) and \( E_a \) are the limiting unrelaxed and relaxed moduli. The relaxation spectrum can thus be obtained from experimental data through the Alfrey approximation.45

\[
\Phi(1/\omega) = -\frac{dE'(\omega)}{d\ln \omega} (E_u - E_a)
\]

and

\[
\Phi(1/\omega) = 2E'(\omega) \frac{1}{\tau(E_u - E_a)}
\]

Eqn. (11) 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 be, in principle, obtained from a complex-plane plot of \( E'' \) vs. \( E' \). However, this plot needs data that cover a broader frequency range beyond the instrument limitation of dynamic mechanical experiments. We thus assume that moduli at low and high temperatures may serve as approximations of the limiting unrelaxed and relaxed moduli, \( E_u \) and \( E_a \), at different frequencies. For each combination of temperature and frequency, \( \phi \) is calculated from eqn. (15) or (16) and plotted against \( \Delta F \) from eqn. (11). Fig. 13(a) and (b) show the relationships between \( \phi \) and \( \Delta F \) for the \( \beta \) relaxation of the CPI(100/0) and CPI(50/50) at different temperatures. It is evident that all the data points fall into a single master pattern. This indicates that the activation entropy is zero and therefore \( \Delta F = \Delta H \). The figures then represent the distributions of activation enthalpies of the \( \beta \)-relaxation process for these two polymers.

However, for the \( \alpha \) relaxation of the polymers, a single master pattern could be achieved only after shifting along the \( \Delta F \) axis. From these shift factors, apparent activation entropies of ca. 900–1000 J K\(^{-1}\) mol\(^{-1}\) can be calculated.46 It could be speculated that the large apparent activation entropies reflect the distribution of internal motions that are sampled differently at different temperatures.

Conclusions

A set of thin-film copolyimides with different molar percentages of BPDA–PFMB and PMDA–PFMB comonomers show the composition dependence of thermal mechanical and thermal dynamic properties. With increasing PMDA–PFMB composition the CTE decreases and the \( T_g \) increases, both following the molar-additivity rules. These relationships provide an opportunity for designing accurately the properties needed in specific applications. Dynamic mechanical data indicate two relaxation processes (\( \alpha \) and \( \beta \) relaxations). The copolyimides display a \( \beta \)-relaxation process independent of composition revealing that the process must be attributed to the PFMB diamine. The activation energy for the \( \beta \) relaxation is 130 kJ mol\(^{-1}\) for all the copolyimide films studied. Since the activation entropy of this relaxation is very close to zero, a non-cooperative type of motion is expected. On the other hand, the \( \alpha \) relaxations attributed to the glass-transition temperatures are composition dependent. The apparent activation energies and entropies are very large. This is attributed to a degree of cooperation in the motion that is highly dependent upon the temperature.

This work was supported by the Materials Research Division of the National Science Foundation Science and Technology Center of Advanced Liquid Crystal Optical Materials (ALCOM) at Kent State University, Case Western University and the University of Akron (DMR-892047). SZDC gratefully acknowledges the support of the Presidential Young Investigator Award (DMR-9157738) from NSF and the industrial matching funding provided by Hercules Inc. The synthesis of the copolyimides was supported by a NASA-Langley Research Center Grant (NAG-1-448).
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