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Diamine architecture effects on glass transitions, relaxation processes and other material properties in organo-soluble aromatic polyimide films

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

A series of twelve aromatic diamines, 4,4′-diamino-2,2′-disubstitutedbiphenyls, has been designed and synthesized. These diamines were reacted with 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) to form polyimides via a one-step polycondensation method. All of the resulting polyimides could be dissolved in common organic solvents and exhibited excellent film forming ability. At the same time, their inherent high thermal and thermo-oxidative stability of these polyimides was retained in the films. Because of the incorporation of disubstituted groups at the 2- and 2′-positions of these biphenyl diamines, their crystallinity was suppressed to the level that they were in complete amorphous state. Further, the conjugation of the phenylene and imide groups in these polyimide films was interrupted, leading to clear blue shifts during light transmission. As this series of polyimides possessed the same backbone, the chain rigidity and linearity changed very little throughout the series. However, the molecular packing was affected by the introduction of different disubstituted pendant groups. Each polyimide film exhibited an α relaxation process related to the glass transition. This relaxation changed significantly with the size and the shape of the disubstituted pendant groups. In addition to this process, each of these polyimide films displayed a sub-glass transition, the β relaxation process, which was initiated by motion of the 4,4′-diamino-2,2′-disubstituted biphenyls. This study provided an opportunity to investigate how disubstituted pendant groups affected the α and β relaxation behaviors of these polyimides. With an increase of the sizes and the shape anisotropy of the disubstituted pendant groups at the 2- and 2′-position, the nature of the motion regarding to the β relaxation was found to evolve from a non-cooperative process to a cooperative one, while the glass transition temperature (the α relaxation temperature) correspondingly decreased.

Keywords: Glass transition; Aromatic polyimide film; Disubstituted pendant groups

1. Introduction

Aromatic polyimides possess many useful properties such as high transition temperatures, excellent dimensional stability, low dielectric constants, and outstanding thermal and thermo-oxidative stability. Some of these materials have been widely used in industry as structural materials and integrated circuit insulators [1,2]. It is also well-known that aromatic polyimides are usually insoluble in most organic solvents due to their highly conjugated, rigid-rod-like chemical structures. This makes it impossible for most polyimides to be directly processed in their imidized forms. Therefore, a two-step polymerization has been commonly used. In this two-step process poly(amic acid) precursors are formed first while chemical, or thermal imidization takes place in the second step [3]. However, the poly(amic acid)s (PAA)s synthesized in the first step of this process are unstable under normal environmental conditions and depolymerization is more likely to take place with increasing storage time. Complicated imidization chemistry via both chemical and thermal processes leads to changes in the material's structure, morphology, and proterties [4,5]. In order to avoid many problems associated with handling (PAA)s, a one-step polymerization route has been proposed [3]. A necessary condition of the success of this synthetic route is the organo-solubility of the resulting polyimides.

This direct processing technique to the polyimide form is especially important in microelectronics and optical applications. Recently, linear optical anisotropy in directions parallel (in-plane) and perpendicular (out-of-plane) to the film surface has been found in many aromatic polyimide films. This optical anisotropy has been utilized to design negative birefringent compensators, which are used to improve viewing angles in twisted nematic or super twisted nematic liquid crystal displays [6,7]. In the past, some structural modifications have been performed to improve the

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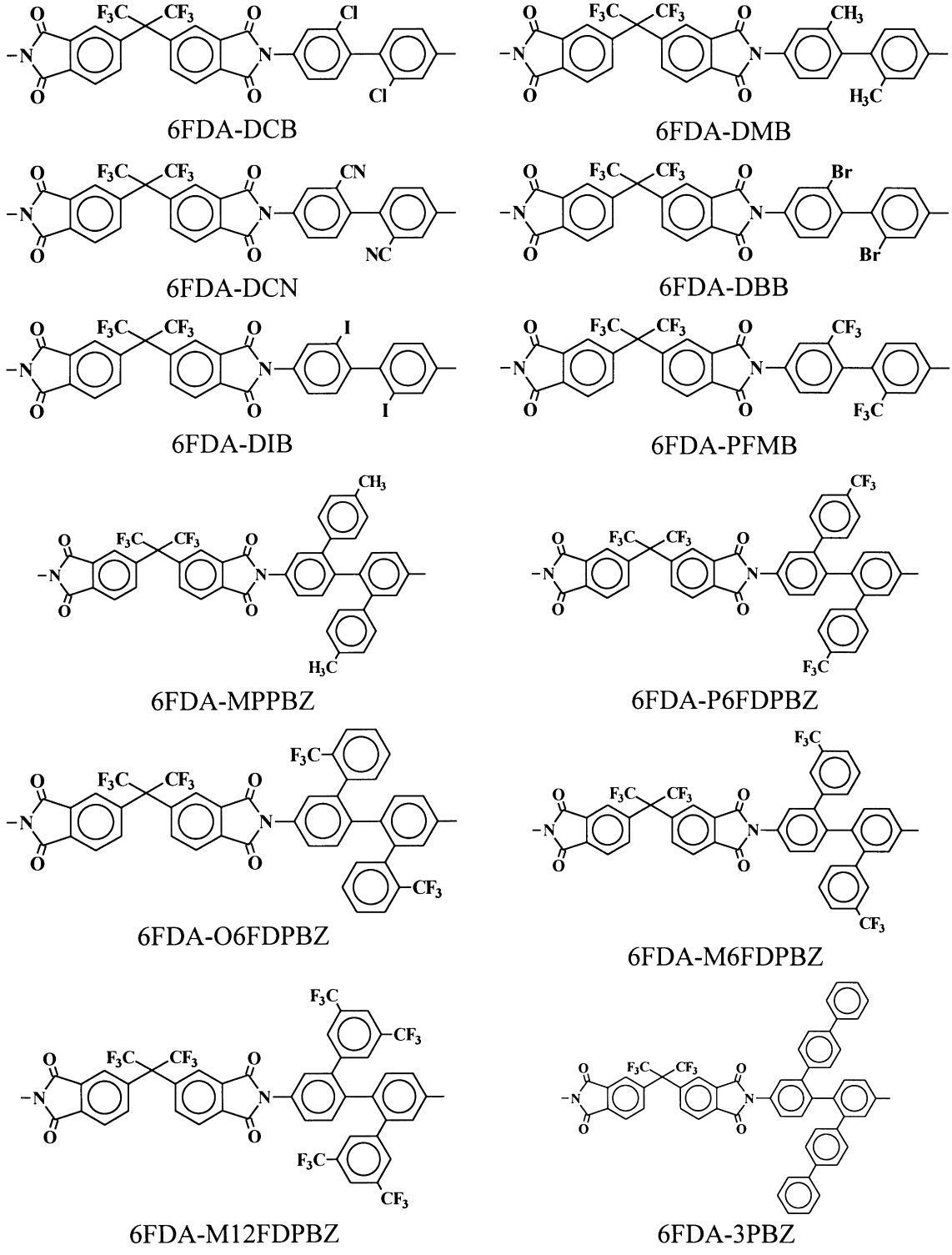


Fig. 1. Set of 6FDA-based aromatic polyimides synthesized from 6FDA dianhydride with different 4,4′-diamino-2,2′-disubstituted biphenyls.

solubility of the polyimides, all of which involved an increase in the chain flexibility. As a result, the properties associated with the rigid-rod-like parent polymers were forfeited.

Designing the molecular architecture of aromatic polyimides is crucial in developing the desirable film (and material) properties needed for specific applications. In our case, maintaining the rigidity and linearity of the backbone is advantageous because it minimizes and even avoids the weakening of polyimides' inherent thermal, dimensional and mechanical properties as well as maintaining the optical anisotropy in polyimide films. Our approach towards

maintaining the rigidity and linearity of the polyimide backbone is to incorporate disubstituted pendant groups at the 2- and 2′-positions of the biphenyl diamine. A series of new polyimides can be obtained when a fixed fluorinated dianhydride, 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), is reacted with a series of 4,4′-diamino-2,2′-disubstituted biphenyls. The resulting twelve polyimides possess identical backbones but different disubstituted groups at the 2,2′-positions of the biphenyl diamines. These substituents include halogens, methyl, cyano, trifluromethyl groups, methyl substituted phenyl groups, trifluromethyl phenyl groups and biphenyl groups substituted at the *para*-, *meta*-, and *ortho*-positions.

This publication focuses on the study of the effects of disubstituted pendant groups on the glass transition temperature and relaxation processes of these 6FDA-based polyimides along with other material characteristics such as solubility, thermal stability, and optical properties.

2. Experimental section

2.1. Materials and film samples

The twelve newly designed aromatic diamines used in this research were synthesized in our laboratories as shown in Fig. 1 with the appropriate nomenclature for each molecule [8–12]. Samples shown in Fig. 1 include 4,4′-diamino-2,2′-dichlorobiphenyl (DCB), 4,4′-diamino-2,2′-dibromobiphenyl(DBB), 4,4′-diamino-2,2′-diiodobiphenyl (DIB), 4,4′-diamino-2,2′-dimethylbiphenyl (DMB), 4,4′-diamino-2,2′-dicyanobiphenyl (DCN), 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl (PFMB), 4,4′-diamino-2,2′-bis(*p*-methylphenyl)biphenyl (MPPBZ), 4,4′-diamino-2,2′-bis(4-phenylphenyl)biphenyl (3PBZ), 4,4′-diamino-2,2′-bis(*p*-trifluoromethyl-phenyl)biphenyl (P6FDPBZ), 4,4′-diamino-2,2′-bis(*o*-trifluoromethylphenyl) biphenyl (O6FDPBZ), 4,4′-diamino-2,2′-bis(*m*-trifluoro-methylphenyl)biphenyl (M6FDPBZ), and 4,4′-diamino-2,2′-bis[3,5-bis (trifluoromethyl)phenyl] biphenyl (M12FDPBZ). All of these diamines can be catalogued as 4,4′-diamino-2,2′-disubstituted biphenyls.

Polyimides were synthesized from these diamines (Fig. 1) and the dianhydride of 6FDA via a one-step method [3,8–12]. The 6FDA was purchased from Chriskev Co. It was dried at 150°C under reduced pressure and sublimated prior to use. The synthesis of 6FDA-PFMB is used as an example to illustrate the general synthetic route used to create the polyimides studied. An amount of 6FDA (1.70 mmol) was added to a stirred solution of 1.70 mmol of PFMB in *m*-cresol containing five drops of isoquinoline under nitrogen at ambient temperature. After being stirred for 3 h, the solution was heated to reflux and held there for 3 h. During this time, the water evolved from imidization was allowed to distill away from the reaction mixture together with 1–2 ml of *m*-cresol. The *m*-cresol was continuously replaced in order to keep the total volume of the solution constant. After being cooled to ambient temperature, the solution was diluted with 30 ml of *m*-cresol and then slowly added to a solution of vigorous stirred 95% ethanol. The precipitated polymer was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 h. Polymer was isolated from this processed with a 91–95% yield. Following this procedure, other 6FDA-based polyimides with different 4,4′-diamino-2,2′-disubstituted biphenyls were synthesized by replacing PFMB with other diamines. The intrinsic viscosities of these polyimides ranged between 1.1–2.6 dl/g, which, based on known molecular weight data with respect to the intrinsic viscosity [13,14], indicates that their molecular weights were high enough to be useful.

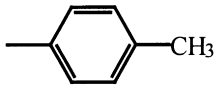
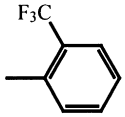
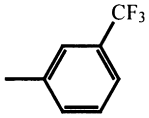
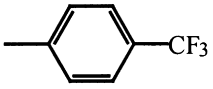
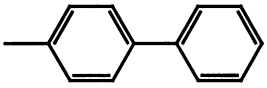
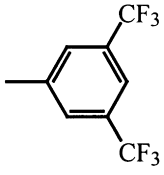
Solutions of these polyimides in cyclopentanone 12%(w/w) were filtered through 5 μm Whatman Teflon syringe filters. Films were made by solution casting on clear glass substrates. The thickness of these films was controlled using a doctor knife. Wet films were placed in an oven at 60°C in order to release the solvent slowly. After 24 h, the samples were placed in a vacuum oven and dried at 180°C for 48 h. The resulting controlled film thickness from this procedure was around 30 μm. These films were used for thermogravimetric (TG), thermal mechanical (TM) and dynamic mechanical (DM) experiments. Films used to obtain UV-Visible (UV-VIS) spectra had a thickness between 8–10 μm. The preparation procedure for forming these films was the same as described previously except for the use of a 5%(w/w) solution. Samples for dielectric (DE) experiments were prepared by solution casting directly onto single plate sensors purchased from TA Instruments. These samples were dried continuously in a vacuum oven at 150°C overnight and annealed above their glass transition temperatures (T_gs) before each measurement.

2.2. Equipment and experiments

All of the polyimide samples used for TG measurements were heated to 300°C, held for 20 min, and cooled to 30°C prior to experimental measurements. Samples were then heated in nitrogen or air to 650°C in a TA-2950 TG using a heating rate of 10°C/min. The magnetic null method was used to calibrate the temperature of the TG. Two onset temperatures at 2% and 5% weight loss were used to evaluate the thermal and thermal-oxidative stability of these polyimides.

The T_gs of these polyimide films were determined using a TA-2940 TM in tension mode. The temperature of the TM was calibrated using standard Indium and Zinc samples measured in penetration mode according to the standard procedure. The force and gage length of each measurement were also calibrated. In order to precisely measure their T_gs, polyimide films were heated to 300°C in a nitrogen atmosphere while under 1.0 MPa of annealing stress and held there for 20 min. After cooling to 30°C at −10°C/min, these films were subjected to several stresses and heated

Table 1
Temperatures for 2% and 5% weight loss in air and nitrogen for 6FDA-based polyimides with different diamines

Diamine	2,2′-disubstituted groups	TGA (air) (°C) 2%/5%(wt)	TGA (N_2) (°C) 2%/5%(wt)
DCB	–Cl	458/497	486/513
DMB	$-CH_3$	480/503	488/505
DCN	–CN	475/513	500/528
DBB	–Br	434/472	457/504
DIB	–I	341/413	375/467
PFMB	$-CF_3$	490/518	505/530
MPPBZ		425/471	440/480
O6FDPBZ		493/517	507/523
M6FDPBZ		488/508	506/525
P6FDPBZ		487/513	506/523
3PBZ		485/513	501/521
M12FDPBZ		482/509	505/525

at 10°C/min. The T_g was taken as the onset temperature where the slope of dimensional change versus temperature has a second-order-like transition. T_gs obtained at each stress level were then extrapolated to zero stress in order to determine the real T_g.

DM experiments were carried out on a Seiko DMS-200. The frequency range used was between 0.01 and 100 Hz, and the heating rate was 1°C/min. The modulus was calibrated using a standard steel strip sample. The temperature was calibrated using a standard PMMA sample. Relaxation temperatures were determined via the corresponding peak temperatures on the loss modulus (E'') curves. In general, the Arrhenius equation can only be used to calculate the activation energies of relaxation processes that are associated with the independent motions of small groups and fragments of the repeating unit. TA DEA 2970 was used to investigate the in-plane DE relaxation in a frequency range of 0.1–100 kHz using the single plate sensor. The heating rate used in this DE analysis was 1°C/min. As the dielectric loss (ε'') increases rapidly at high temperature as a result of ionic conductivity, electric loss modulus $M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$ was used to describe the dielectric relaxation in order to suppress the contribution of ionic conductivity to the dielectric loss [15]. Changes in the electric loss modulus (M'') with temperature and frequency present a similar picture of DE relaxation to that of E'' as determined via DM relaxation. The relaxation temperatures at different frequencies were determined via the maxima of the M'' curves. The relaxation map in the frequency range from 0.01 to 100 kHz was obtained by combining DM and DE analysis results.

The activation energy of a single frequency relaxation

can be calculated by plotting the natural logarithmic frequency, ln(f), versus the reciprocals of the relaxation peak temperatures as determined from the E'' and M'' curves. The slope of this Arrhenius curve is proportional to the activation energy. However, if the molecular motion becomes cooperative, multiple relaxation frequencies are involved. In principle, the Arrhenius equation is no longer adequate to describe relaxations related to this type of molecular motion. Nevertheless, in a relatively narrow frequency region within three or four orders of magnitude, the above method remains satisfactory though the calculated activation energy only represents an apparent activation energy. In this study we applied the Arrhenius equation to determine the activation energies for both the sub-glass β relaxation and the α relaxation. It should be kept in mind that these activation energies ($E\beta$ and $E\alpha$) become apparent activation energies if the relaxation involves the cooperative motion of several of polymeric molecules.

Transmission UV-VIS spectra were obtained using a Perkin Elmer Lambda 4B spectrometer in transmittance mode. The examined wavelength regions scanned ranged from 200 to 900 nm.

3. Results and discussion

3.1. General characterization of the polyimide films

In order to examine the solubility of the 6FDA-based polyimides, six solvents were used to dissolve these polyimides at ambient temperature: acetone, cyclopentanone, tetrahydrofuran (THF), dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), and dimethylacetamide (DMAc). The polyimides were considered to be soluble in a solvent if a solution of 5%(w/w) concentration could be prepared. Our observations show that the 6FDA-based polyimides studied are soluble in all of these common organic solvents. The surprising solubility of these polyimides can be partially attributed to the incorporation of twisted-biphenyl diamines. These non-coplanar diamines disrupt chain packing, eliminating crystallinity and interrupting conjugations along the chain backbones. The resulting relatively loose packing of these polyimides permits solvent molecules to penetrate through the polymeric chains better. Another important factor towards increasing the solubility comes from the asymmetric linkage in those 6FDA dianhydrides. For example, 6FDA–PFMB can quickly dissolve in many common organic solvents. However, the analogous BPDA–PFMB (BPDA stands for 3,3′,4,4′-biphenyl-tetracarboxylic dianhydride) is soluble only in *m*-cresol [16,17]. It is clear that the fluorinated isopropylidene group on the 6FDA moiety dramatically enhances the solubility of the related polyimides. Further, the higher solubility of 6FDA–PFMB is considered due mainly to the differences in chain packing caused by the sp^3-hybridized carbon and attached trifluoromethyl groups. It has been found that 6FDA–PFMB does not pack as close as the semicrystalline BPDA–PFMB analogue [16,17]. However, it is difficult to distinguish how the size effect of the 2,2′-disubstituted groups on the diamine moiety improve the solubility because both dianhydride and diamine moieties play roles in improving the solubility. If a relatively linear dianhydride is used to replace 6FDA, the effect of the diamine on the solubility may become more apparent [18].

The thermal and thermo-oxidative stability of these materials can be estimated via non-isothermal TG experiments in dry nitrogen or air. Onset temperatures for 2% and 5% weight losses in both environments are listed in Table 1. These polyimide film samples underwent 5% weight losses between 467 and 530°C in nitrogen and between 413 and 518°C in air when a heating rate of 10°C/min was used. Polyimides with halogen-disubstitued groups display relatively lower weight loss onset temperatures with a sequence from low to high temperatures of I to Br to Cl. Polyimides containing methyl disubstituted groups display better thermal and thermo-oxidative stability compared with those having halogen disubstituted groups. Further improved thermal and thermo-oxidative stability can be found in polyimides containing fluorine-disubstituted groups. This is possibly attributed to the higher carbon–fluorine bond energies in these polyimides. The chemical bond energies of carbon–iodine, carbon–bromine, carbon–chlorine, carbon–hydrogen and carbon–fluorine bonds are 240, 276, 328, 413 and 441 kJ/mol, respectively [19].

In principle, the thermal and thermo-oxidative stability of polyimides is determined by the electronic strength of the weakest chemical bond in the polymeric molecules. It has been found that the incorporation of 6FDA containing a hexafluoropropane linkage leads the polyimide to a small decrease in the thermal and thermo-oxidative stability as a result of the interruption of the aromaticity [20]. The temperatures for the thermal cracking of simple aromatic backbones are usually higher than those of backbones with attached disubstituted groups [21,22]. Therefore, the thermal and thermal-oxidative stability of our 6FDA-based polyimides may mainly depend on the stability of the 2,2′-disubstituted groups on the diamine moiety. However, non-isothermal TG experiments present only a partial image of the thermal degradation behavior. More precise measurements involve studies of the thermal degradation kinetics and detailed thermal degradation mechanisms. These can be carried out with isothermal TG and TG-mass spectroscopy experiments [23].

Electron conjugation in polyimide films can be investigated using UV-VIS spectroscopy. Stronger electron conjugation leads to a higher absorption wavelength (red shift). The wavelengths of transmission onset and 80% transmission are used to evaluate the transparency of the films. If these two wavelengths shift to lower values (blue shift), the polyimide film is believed to be more optically transparent. The UV-VIS spectra of several 6FDA-based polyimide

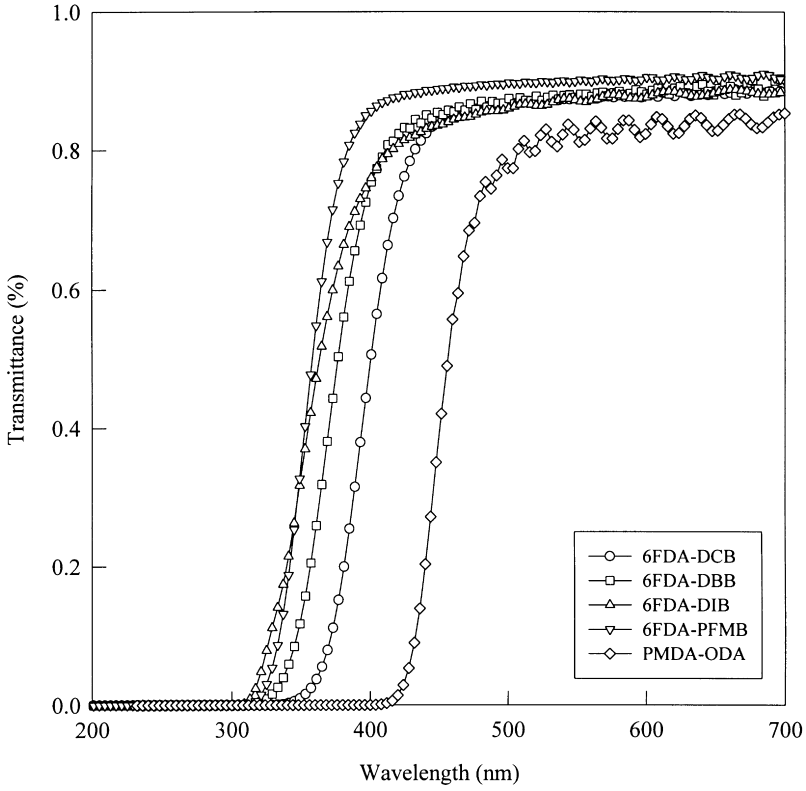


Fig. 2. A set of UV-VIS spectra of 6FDA-based polyimide films (a UV-VIS spectrum of PMDA–ODA is also included for comparison).

films are displayed in Fig. 2. Data of Kapton® films synthesized from pyromellitic dianhydride (PMDA) and 4,4′diaminodiphenyl ether (ODA) via a two-step method are also included in Fig. 2 for comparison. The wavelengths of the onset transmission and the 80% transmission for these polyimide films are given in Table 2, ranging from 315 to 349 nm and 384 to 433 nm, respectively. Thus, these polyimide films are found to be transparent in the UV-VIS wavelength region. These results clearly show more significant blue shifts in these polyimide films as compared to the Kapton® film.

In principle, the wavelengths of the onset transmission and the 80% transmission are qualitatively associated with the electron conjugation length of the polymeric chain backbones. A longer conjugation length leads to a higher transmission wavenumber. As determined via their wavelengths, these 6FDA-based polyimide films are more transparent than many polyimide films prepared based on other dianhydrides [24,25]. The superior transparency may be attributed to the limited electronic conjugation along the chain backbones of these 6FDA-based polyimides. The introduction of the 2,2′-disubstituted biphenyl diamines causes significant reductions in the conjugation lengths of these diamines. As a result, the color of these polyimide films is substantially diminished. The efficiency in breaking the conjugation length also depends upon the size and the shape of disubstituted groups. Arranging the size and the shape anisotropy of these groups from the smallest (DCB) to the largest (M12FDPBZ) leads to significant blue shifts of in the 80% transmission wavelength from 433 to 384 nm (Table 2).

3.2. Glass transition behaviors

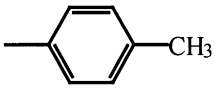
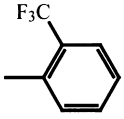
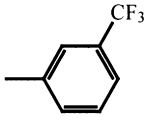
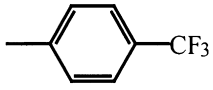
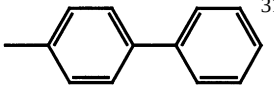
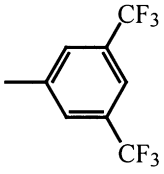
TM measurements were used to determine the T_gs of the film samples. It should be noted that T_gs acquired from TM measurements depend upon the stress applied during the measurements, as shown in Fig. 3. A true T_g value can be obtained via a linear extrapolation of the applied stress to zero [26,27]. This theoretical treatment is based on the microscopic explanation that the T_g decreases linearly with the increase of applied tensile stress σ. Based on the multiple-hole energy model [28], the kinetics of the glass transition [29], the volume relaxation memory behavior [30], and the equation of state for polymeric liquid and glassy states [31], Chow proposed that for a system under a uniform σ with negligible strain rate, the effect of an applied stress on T_g is given by [32]

$$T_g = T_g^0 + (RT_r^2/\bar{\varepsilon})[1 - \exp\{(\sigma V)/(RT_g^0)\}] \quad (1)$$

where $\bar{\varepsilon}$ is the average energy of hole formation, T_r is a reference temperature, V is the tensile activation volume, and R is the universal gas constant. If $\sigma = 0$, the equation reduces to $T_g = T_g^0$. If σ is in the vicinity of but slightly larger than zero, Eq. 1 becomes

$$T_g = T_g^0 - (\sigma T_r V)/\bar{\varepsilon} = T_g^0 - K\sigma \quad (2)$$

Table 2
The onset and 80% transmission wavelengths of UV-VIS spectra for 6FDA-based polyimide films

Diamine	Substituted groups	Onset/80% optical transparency wavelength (nm)
DCB	–Cl	349/433
DMB	$-CH_3$	341/425
DCN	–CN	344/433
DBB	–Br	316/417
DIB	–I	326/412
PFMB	$-CF_3$	319/388
MPPBZ		317/394
O6FDPBZ		316/393
M6FDPBZ		318/390
P6FDPBZ		321/397
3PBZ		315/391
M12FDPBZ		316/384

where $K = T_r V/\bar{\varepsilon}$. This slope reflects the sensitivity of the films with respect to the stress applied. Detailed derivation requires the exponential term in Eq. 1 to be expanded into a series when $\sigma V \ll 1$. Eq. 2 gives a molecular explanation of the linear relationship between T_g and σ.

Fig. 4 shows T_g values as functions of applied stress for several 6FDA-based polyimide films. Table 3 lists the T_g values determined using TM experiments. Two chemical structural factors should be considered for the T_g variation seen in this series of samples: the size and the anisotropic shape of the disubstituted groups. T_gs of these polyimides lie in the range from 315 to 336°C when the sizes of the disubstituted groups is smaller than 0.03 nm^3 and the shapes of these groups are close to that of a sphere (polyimides containing the first six diamines). Despite hampering with the coplanarity of the two backbone phenylene rings, the disubstituted groups at the 2- and 2′-positions in the aromatic diamine moieties are not large enough to sufficiently disrupt the neighboring molecular chain packing. However, T_g decreases with a further increase in the size and the shape anisotropy of the disubstituted groups. For 6FDA–PFMB the T_g is 315°C, while for 6FDA–M12FDPBZ T_g becomes 263°C. This indicates that, when their sizes exceed 0.03 nm^3, and their shape deviates from spherical, these substituted groups start to weaken the molecular packing. Consequently, the T_g value, which is the macroscopic index of the onset of cooperative segmental motion, starts to decrease. Moreover, it is interesting to find that there are two groups of slopes in Fig. 4. The first six polyimides, which possess disubstituted groups smaller than the CF_3 group (0.03 nm^3 in volume) and are spherical in shape, show similar and relatively steep slopes, while the other six polyimides (with larger and unisotropic disubstituted groups) have similar but relatively shallow slopes. This indicates that the polyimide films with smaller and isotropic disubstituted groups exhibit more sensitivity towards the applied stress than those with larger and unisotropic disubstituted groups. This must be associated with the difference of molecular packing in these two groups of polyimide films. However, mechanisms which explain the cause of this response difference with respect to applied stress are still not complete.

The T_gs of the polyimide samples have also been measured using differential scanning calorimety (DSC) [18]. The trend of T_g variation with disubstituted group is the same as that seen in the TM experiments. However, T_gs measured by DSC are slightly different from those determined by TM experiments. This difference may be attributed to different heating rates, and more fundamentally, the distinctive nature of the testing methods (calorimetric versus thermo-mechanical responses).

3.3. α and β relaxation processes

It is qualitatively known that molecular packing and chain motions are closely associated with each other. DM experiments at various frequencies can be employed to study this correlation. Above room temperature, the polyimide film samples have shown two relaxation processes whose origins are similar to those discovered in a series of PFMB-based aromatic polyimides containing different commercial dianhydrides [33]. The DM result of 6FDA–PFMB at several frequencies is chosen as an example and shown in Fig. 5. The low-temperature relaxation process is defined as the β relaxation and the high-temperature one is defined as the α relaxation. The α relaxation corresponds to the glass transition while the β relaxation is a sub-glass transition process. As shown in Fig. 5, it is clear that the β relaxation is more sensitive to changes in frequency as

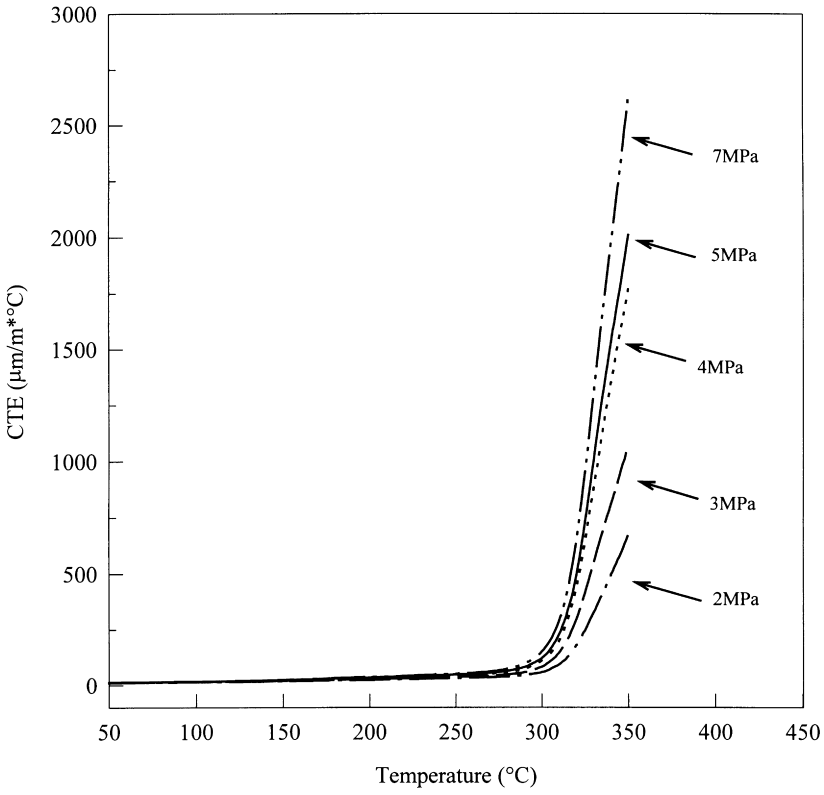


Fig. 3. TM results of 6FDA–DBB films at different stresses during heating at 10°C/min.

compared to the α relaxation. This indicates that the β relaxation has a relatively lower $E\beta$. Recent work has shown that this β relaxation is attributed to the motion of disubstituted biphenyl diamines [33]. A simple statistical thermodynamics model has also been tried in order to elucidate the molecular origin of this β relaxation [34].

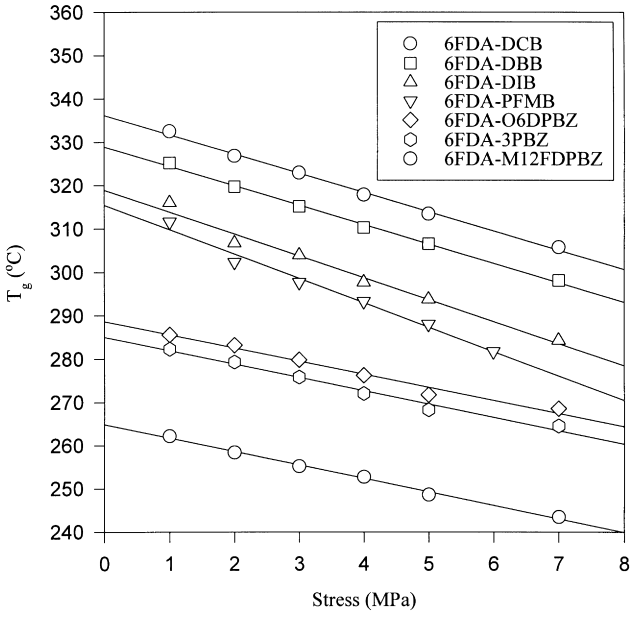
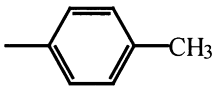
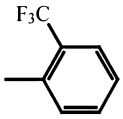
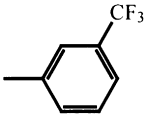
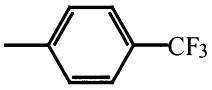
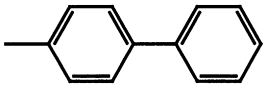
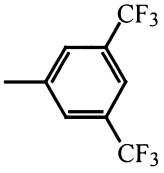


Fig. 4. Glass transition temperatures of several 6FDA-based polyimides obtained via plots of T_g versus stresses applied during the measurements.

As DM experiments cover only a relatively narrow frequency region (0.01 to 100 Hz, five orders of magnitude), DE experiments have also been performed in order to study the relaxation behaviors of these polyimide films over a wider frequency region which extends into 0.1 MHz (seven orders of magnitude). Fig. 6 shows electric loss modulus changes at different frequencies for 6FDA–PFMB. Based on both the DM and DE experimental results shown in Fig. 7, linearity is found in the β relaxation map of 6FDA–PFMB from 0.01 Hz to 1 kHz. The $E\beta$ is calculated to equal 144 kJ/mol. As the α relaxation is not a single relaxation process and it obeys the WLF equation, the α relaxation map deviates from linearity at high frequencies when relaxation maxima shift towards higher temperatures. However, a linear relationship is retained over a limited frequency range from 0.01 Hz to 1 kHz. Thus, an apparent $E\alpha$ value of 963 kJ/mol can still be calculated from the slope of the linear portion of the α relaxation.

Table 4 lists both the β and α relaxation temperatures at 1 Hz for polyimide films as well as their $E\beta$'s and apparent $E\alpha$'s. Surprisingly enough, an increase in the size and the shape anisotropy of disubstituted groups leads to a decrease in the α relaxation temperature (from 373 to 282°C at 1 Hz) while simultaneously resulting in an increase in the β relaxation temperature (from 112 to 261°C at 1 Hz). This implies that the sizes and the shape anisotropy of

Table 3
T_gs of 6FDA-based polyimide films measured using TM experiments

Diamine	2,2′-disubstituted groups	T_g (°C)
DCB	–Cl	336
DMB	$-CH_3$	325
DCN	–CN	331
DBB	–Br	329
DIB	–I	319
PFMB	$-CF_3$	315
MPPBZ		286
O6FDPBZ		289
M6FDPBZ		278
P6FDPBZ		283
3PBZ		285
M12FDPBZ		263

disubstituted groups may affect these two relaxation processes in a different manner. For the β relaxation, the substituted groups introduce steric hindrance, hampering the local motion of small groups and fragments on the repeating unit. For the α relaxation, the introduced steric hindrance is the source of looser molecular packing, and thus it enhances the segmental motion (Fig. 8).

Table 4 also shows that the $E\beta$s for the β relaxation process increase with the enlargement of the size and anisotropic shape of the disubstituted groups (e.g. for 6FDA–DCB $E\beta$ is 97 kJ/mol while for 6FDA–M12FDPBZ $E\beta$ is 270 kJ/mol). If we use the method proposed by Starkweather [35,36], a calculation can be carried out to identify the type of molecular motions involved in this process. The Eyring theory of absolute reaction rate is utilized in this calculation if the frequency–temperature dependence is of an Arrenhius type. The activation energy E_a can be written as

$$E_a = RT\{1 + \ln[k/(2\pi h)] + \ln(T/f) + T\Delta S^+\} \quad (3)$$

where ΔS^+ is the activation entropy, f is the frequency, and h and k are Plank and Boltzman constants. Starkweather proposed that for many relaxation processes, particularly for those involving independent motions of small sub-chemical repeating unit groups, the activation entropy ΔS^+ should be close to zero [36]. Under this assumption, for a relaxation at a frequency of 1 Hz, E_a shows a simple, almost linear dependence on temperature:

$$E_a = RT'\{1 + \ln[k/(2\pi h)] + \ln(T')\}. \quad (4)$$

The difference between the experimental E_a and this value equals to $T'\Delta S^+$. Therefore Eq. 4 defines the effective lower limit of E_a for a viscoelastic response.

Fig. 9 shows the relationship between the $E\beta$ values of these aromatic polyimide films and temperature. The solid line is the calculation based on Eq. 4. It is evident that for polyimides with disubstituted groups smaller than a CF_3 group (0.03 nm^3 in volume), the experimental $E\beta$ values fall either on the solid line or slightly above this line. This implies that the origin of the β relaxation in these six polyimide films is mainly attributed to the non-cooperative motion of diamines in the solid state. However, the experimental $E\beta$s start to deviate away from the Starckwhether's solid line with increasing shape anisotropy and size larger than a CF_3 group. The molecular motion related to these β relaxations is no longer non-cooperative, but instead, has evolved into a cooperative process. This trend can be further correlated in the β relaxation peak temperature of these samples, which deviates from the linear Arrenhnius line at high frequencies towards higher temperatures. All of these observations indicate that, for these polyimide films, their β relaxation is no longer a single relaxation process but involves multiple relaxations and multiple frequencies.

The apparent $E\alpha$ data listed in Table 4 indicate that, for polyimides containing disubstituted groups with increasing size and anisotropy, their apparent $E\alpha$s are likely to increase. These α relaxation processes are associated with the cooperative motion involving a few segments.

4. Conclusions

A specific diamine architecture has been designed in order to develop aromatic polyimides with the desirable organo-solubility, thermal and thermo-oxidative stability, and optical transparency, and at the same time, to maintain excellent mechanical, dielectric, and optical properties in films of these polyimides. The approach we used was to introduce disubstituted groups at the 2- and 2′-positions of 4,4′-diaminobiphenyl. As a result, the conjugation of the phenylene and imide rings was interrupted, yet the linearity and the rigidity of the polyimides was retained. 6FDA was

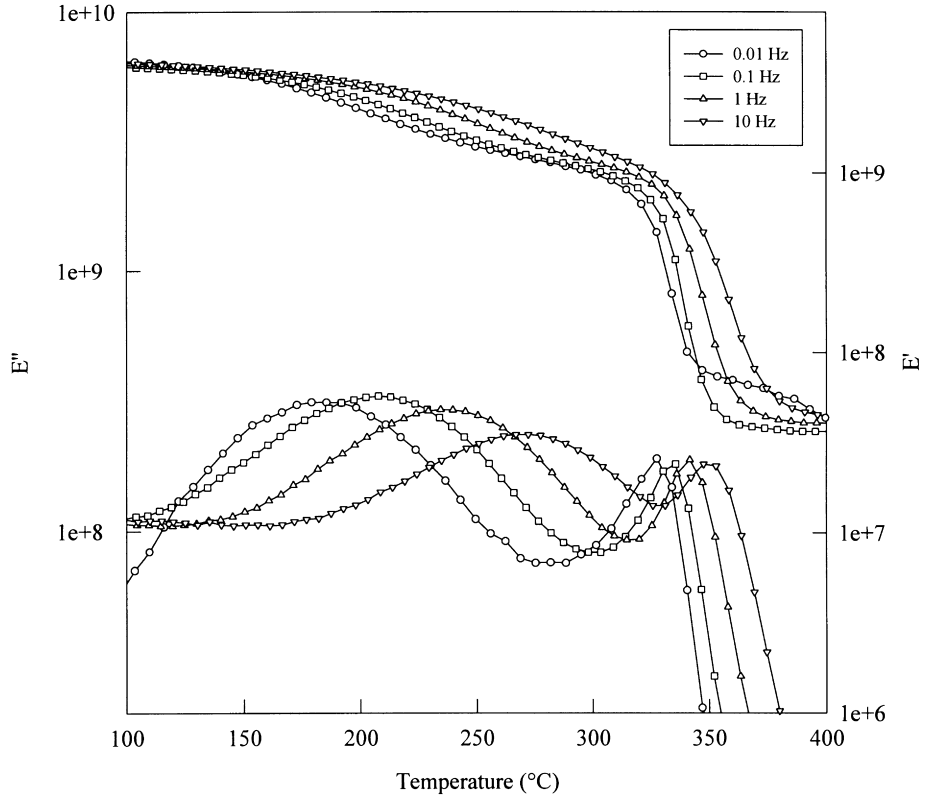


Fig. 5. DM results of 6FDA–PFMB polyimide films at different frequencies.

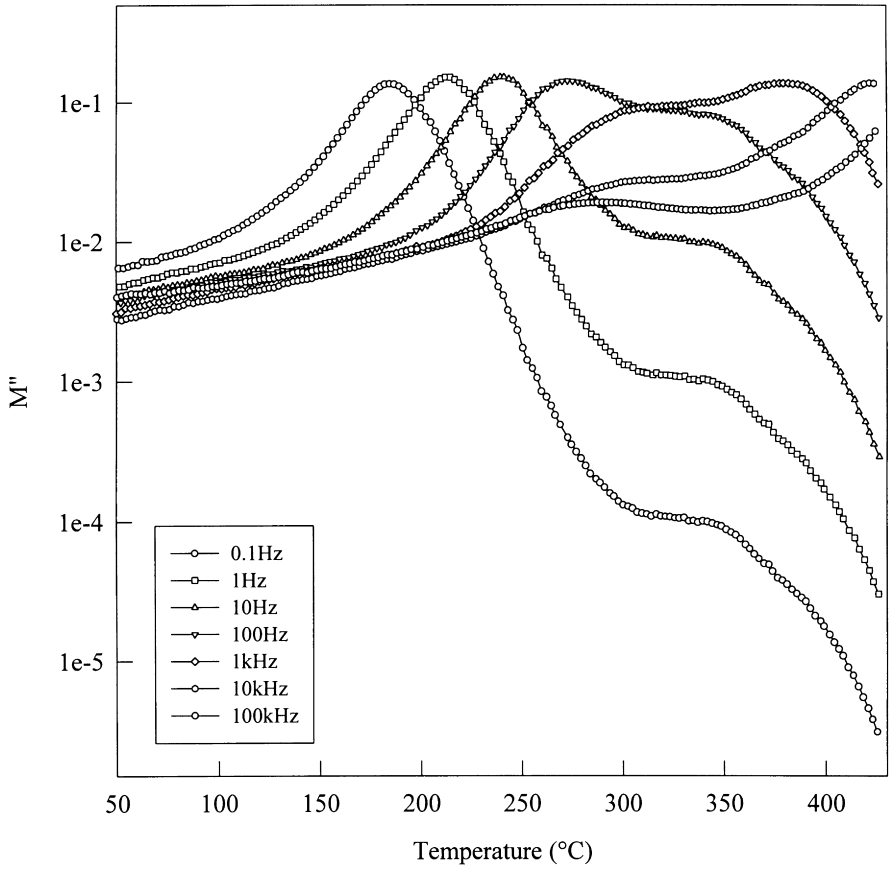


Fig. 6. Dielectric results (M'') of 6FDA–PFMB films at different frequencies.

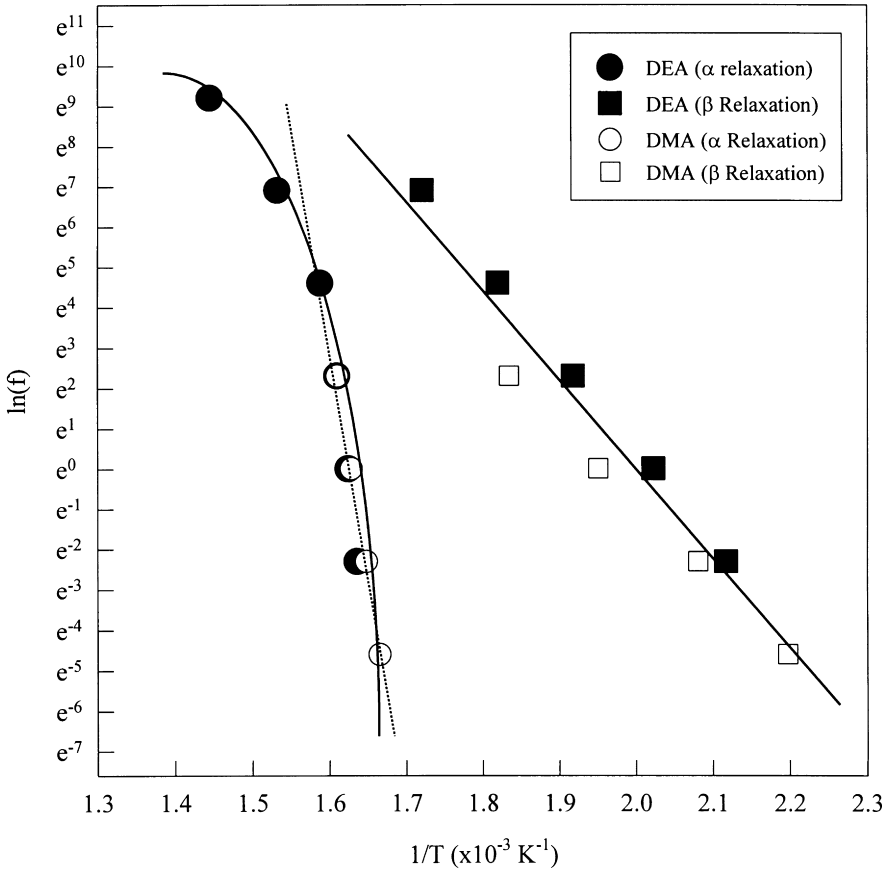


Fig. 7. Relationships between ln(*f*) and the reciprocal relaxation peak temperature obtained from E'' for both the β and α relaxation processes on 6FDA–PFMB films.

polymerized with twelve different 4,4′-diamino-2,2′-disubstituted biphenyls to create a series of fluorinated aromatic polyimides. The glass transition temperatures of these polyimide films were found to decrease with the enlargement of the size and the anisotropy of the disubstituted groups at the 2- and 2′-positions on the biphenyl diamine moieties. This process is further correlated by their α relaxation behaviors as determined from DM and DE experiments. The β relaxation process that relates to the sub-group motion of the diamines in polyimides can be found in all of these polyimide films. Of particular interest, the β relaxation temperature increases with the enlargement of the size and the shape anisotropy of the disubstituted groups. In addition, the local motion type related to the β relaxation changes

Table 4
The α and β relaxation temperatures and activation energies as determined from E'' different frequencies for 6FDA-based polyimide films with different diamines

Diamine	1 Hz (°C)	β activation energy (kJ/mol)	1 Hz (°C)	α activation energy (kJ/mol)
DCB	111.8	97	372.7	656
DMB	124.4	97	367.7	635
DCN	122.2	103	364.3	702
DBB	151.2	115	371.7	650
DIB	203.8	133	364.1	713
PFMB	239.6	144	341.2	963
MPPBZ	232.9	180	301.0	947
O6FDPBZ	207.1	158	317.0	731
M6FDPBZ	227.5	217	288.8	801
P6FDPBZ	258.1	255	294.1	1130
3PBZ	—[a]	—[a]	294.2	1085
M12FDPBZ	261.1	270	282.1	933

[a] The data are overlapped with the α relaxation.

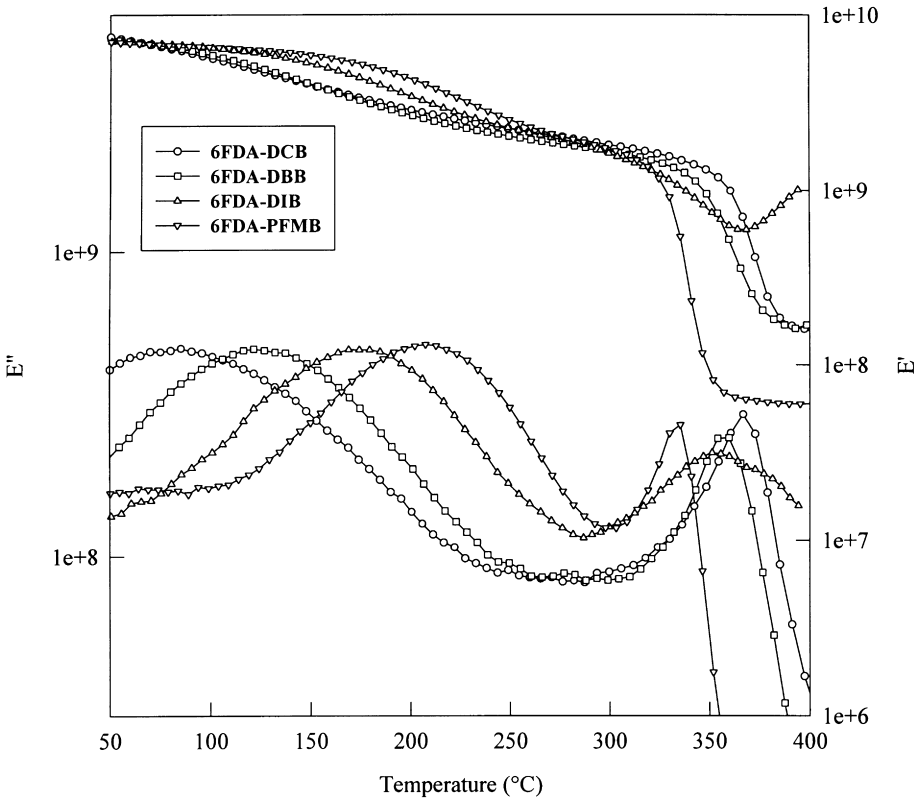


Fig. 8. E' and E'' versus temperature at 0.1 Hz for 6FDA-based polyimide films.

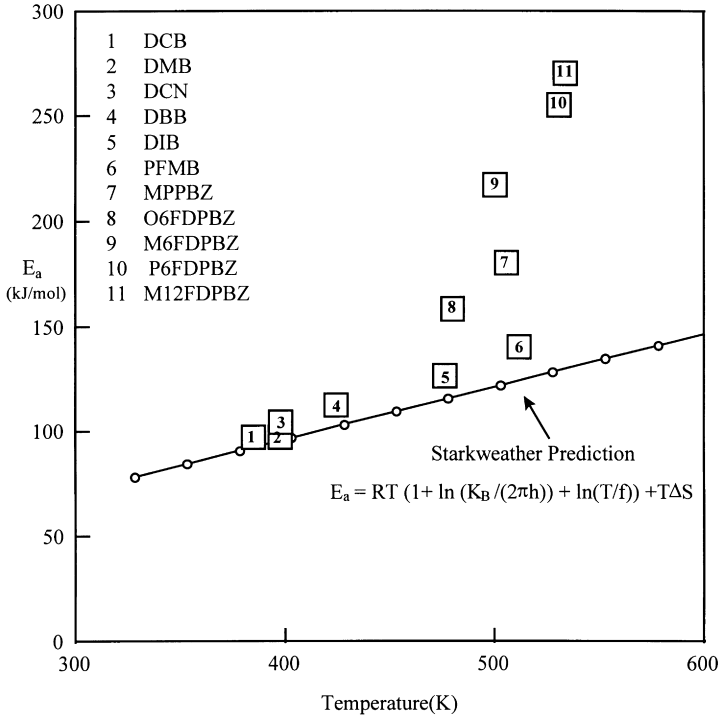


Fig. 9. Non-cooperative versus cooperative motion in the β relaxation of 6FDA-based polyimide films.

from a non-cooperative to a cooperative process based upon Starkweather's treatment.

Acknowledgements

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