ELSEVIER

Polymer 40 (1999) 4987–5002

polymer

Dianhydride architectural effects on the relaxation behaviors and thermal and optical properties of organo-soluble aromatic polyimide films

Fuming Li*, Jason J. Ge, Paul S. Honigfort, Shane Fang, Jyh-Chien Chen, Frank W. Harris, Stephen Z.D. Cheng

Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

Received 5 September 1998; received in revised form 3 October 1998; accepted 6 October 1998

Abstract

Dianhydrides of specific molecular architecture was designed and synthesized based on 2,2′-disubstituted 4,4′,5,5′-biphenyltetracarboxylic dianhydrides (2,2′-disubstituted BPDAs). Eight dianhydrides were polymerized with two 4,4′-diamino-2,2′-disubstituted biphenyl diamines (trifluoromethyl disubstituted groups, or PFMB, and methyl disubstituted groups, or DMB) to obtain two series of PFMB- and DMB-based aromatic polyimides. As the backbone structures of these two series of polyimides are unchanged throughout each series, the effects of the 2,2′-disubstituted groups of both the dianhydride and diamine constituents on the solubility and thermal and optical properties as well as the relaxation behavior of these polyimides can be identified. It was found that the PFMB-based polyimides with 2,2′-disubstituted BPDAs show excellent solubility while the DMB-based polyimides with the same dianhydrides are less soluble. The same trends can be found for both thermal and thermo-oxidative stability and optical transparency in the ultraviolet and visible light regions. These two series of polyimides exhibit glass transition temperatures (T_g) which show a competition between chain rigidity and linearity with regards to molecular packing. When the size of the 2,2′-disubstituted groups is small and their shape is close to spherical, the T_g initially increases with the size of these 2,2′-disubstituted groups. This is because of the fact that the steric hindrance of these groups prevents the appearance of a *cis*-conformation of BPDA. However, once these groups possess large size and exhibit anisotropic shapes, their effect on the molecular packing becomes dominant and the T_g starts to decrease. Further, this is the first time that three relaxation processes (the β_1, β_2, and α processes) were observed above room temperature in these aromatic polyimides. We have identified that the β_1 process is attributed to the local motion of the diamine constituents while the β_2 process is caused by the local motion of the dianhydride constituents. The α process is associated with the glass transition. The cooperativity of the molecular motion associated with the β_1 and β_2 processes are also discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dianhydrides; PFMB; DMB

1. Introduction

In a previous study, the effects of the addition of 2,2′-disubstituted pendant groups to main-chain 4,4′-diaminobiphenyls on the solubility, thermal and optical properties and transition and relaxation behaviors of organo-soluble aromatic polyimide films were investigated [1]. The study focused on a series of aromatic polyimides which were synthesized from twelve aromatic diamines (4,4′-diamino-2,2′-disubstituted biphenyls) and 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) via a one-step polycondensation method [2,3]. All of the resulting polyimides were amorphous and could be dissolved in common organic solvents. Moreover, the conjugation of the phenylene and imide groups in these polyimide films was interrupted, leading to blue shifts for light transmission. At the same time, the high thermal and thermo-oxidative stability of these polyimide films was retained. As this entire series of polyimides possessed the same backbone structure, the chain rigidity and linearity changed very little throughout the series. However, the molecular packing was affected because of the different sizes and anisotropic shapes of the 2,2′-disubstituted pendant groups that were introduced. Each polyimide film exhibited an α-relaxation process related to the glass transition, which significantly changed with the sizes and the shapes of the disubstituted groups. The films also displayed a sub-glass transition, or β-relaxation process, which was initiated by the motion of the 4,4′-diamino-2,2′-disubstituted biphenyls. This provided an opportunity to investigate how 2,2′-disubstituted groups affect the α- and β-relaxation behaviors of these polyimides. It was found that with an increase in the size and

---

* Corresponding author.

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.

PII: S0032-3861(98)00721-6

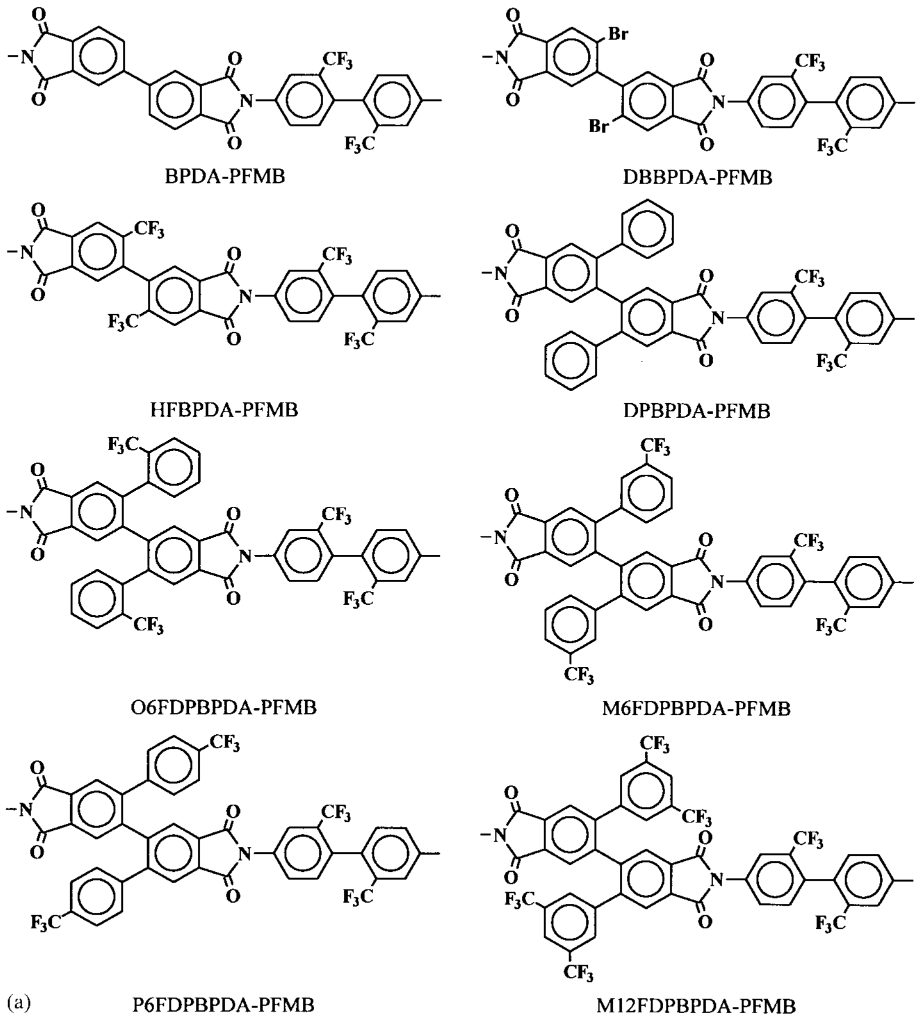
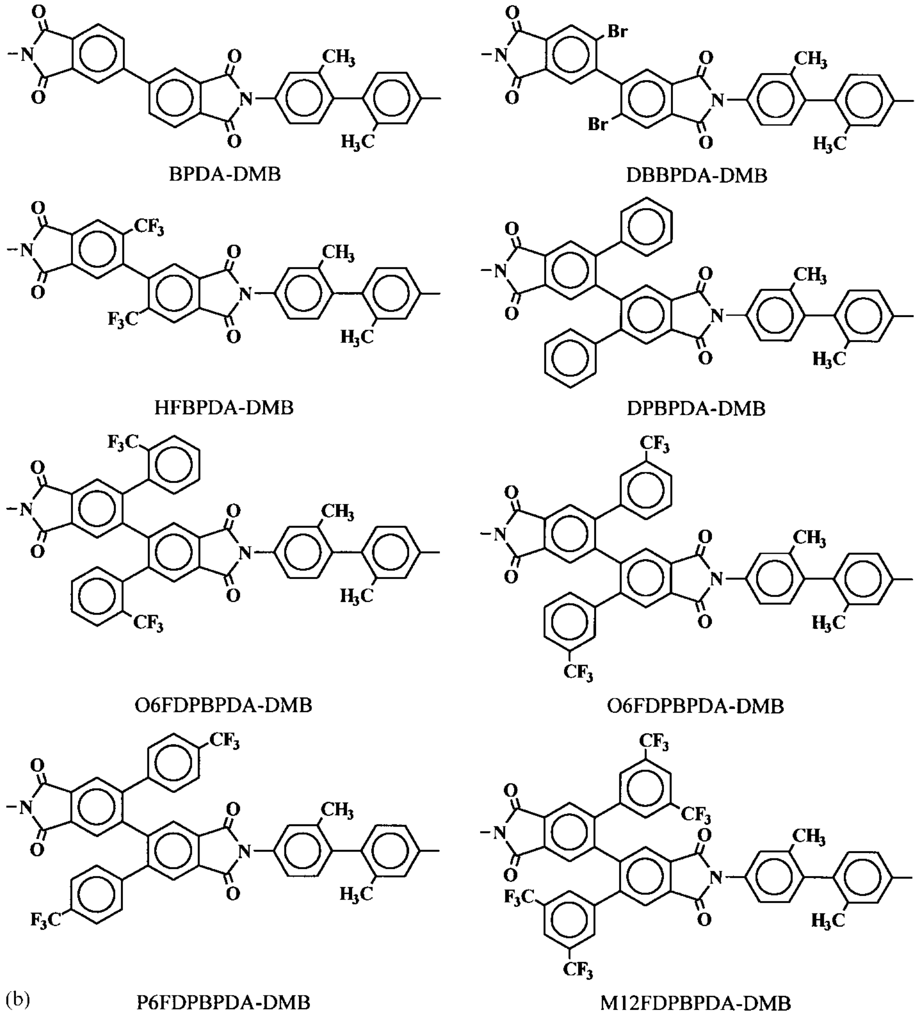


Fig. 1. Chemical structures of (a) eight PFMB- and (b) eight DMB-based aromatic polyimides.

shape anisotropy of the 2,2′-disubstituted groups of the diamine, the nature of the motion related to the β relaxation evolves from a non-cooperative process to a cooperative one, while the α-relaxation temperature (the glass transition temperature) is correspondingly decreased [1].

The development of this series of PFMB-based organo-soluble polyimides is particularly important for new and specific technologies such as linear and non-linear optical materials in addition to traditional applications in structural materials and integrated circuit insulators [4,5]. As these polyimides were synthesized in fully imidized forms, the direct processing technique used is superior in many aspects to the conventional two-step polymerization method in which poly(amic acid) precursors are first isolated prior to synthesizing the final material [6,7]. This is especially important in microelectronic and optical applications. In addition, linear optical anisotropy (difference in refractive indices) has recently been found in directions parallel (in-plane) and perpendicular (out-of-plane) to the film surface in these polyimide films. This optical anisotropy was utilized to design negative birefringent compensators, which are used to improve viewing angles in twisted and super-twisted nematic liquid crystal displays [8–12].

In order to further understand the mechanisms needed to control the optical properties of polyimide films, while yet retaining other excellent properties, two new series of polyimides were synthesized. The objective of this study is to design and synthesize seven new 2,2′-disubstituted pendant groups on 4,4′, 5,5′-biphenyltetracarboxylic dianhydride (2,2′-disubstituted BPDAs) and subsequently polymerize this with either a fluorinated diamine, 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl (PFMB) [3], or a non-fluorinated diamine, 2,27′-dimethyl-4,4′-diaminobiphenyl (DMB) [13]. Each of these two series of polyimides possesses chemical backbone structures which are unchanged throughout the series, but their 2,2′-disubstituted groups are different for each member of the series. Owing to this reason, by comparing the macroscopic responses of these two series of polyimides to the environment, the effects of these 2,2′-disubstituted groups on the polyimides' thermal and optical properties as well as their relaxation behaviors can be identified. This will also help to distinguish



BPDA-DMB DBBPDA-DMB

HFBPDA-DMB DPBPDA-DMB

O6FDPBPDA-DMB O6FDPBPDA-DMB

(b) P6FDPBPDA-DMB M12FDPBPDA-DMB

Fig. 1. (*continued*)

the difference between the effects of the steric repulsion of the 2,2′-disubstituted groups on the dianhydrides from the effects of the fluorine and non-fluorine diamines on the properties of these polyimides.

2. Experimental section

2.1. Materials and samples

A commercially available dianhydride, 4,4′, 5,5′-biphenyl-tetracarboxylic dianhydride (BPDA without disubstituted groups) and 2,2′-disubstituted BPDAs with pendant groups of bromine (DBBPDA), trifluoromethyl (HFBPDA), phenyl (DPBPDA) and trifluoromethyl substituted phenylenes at the *para-*, *meta-*, and *ortho*-positions (P6FDPBPDA, M6FDPBPDA, O6FDPBPDA, and M12FDPBPDA, respectively) were reacted with the PFMB diamine to form a series of aromatic polyimides. The resulting eight polyimides have the same backbone chemical structure but possess different pendant groups on the 2,2′-disubstituted BPDA dianhydrides (Fig. 1a). The above eight dianhydrides were also polymerized with the non-fluorinated diamine DMB in order to offer another series of eight polyimides (Fig. 1b) for the purpose of comparing their properties with the series of fluorinated PFMB-based polyimides.

The polyimides (Fig. 1a and b) were synthesized from the above dianhydrides and either the diamine PFMB or DMB via a one-step method [2,3,14–17]. The synthesis of HFBPDA-PFMB is used below as an example to illustrate the general synthetic route for the production of these polyimides. An amount of HFBPDA (1.50 mmol) was added to a stirred solution of 1.50 mmol of PFMB in *m*-cresol containing several drops of isoquinoline under nitrogen at ambient temperature. After being stirred for 3 h, the solution was heated to a reflux temperature of 200°C and held there for 3 h. During this polymerization process, the water generated from imidization was allowed to distill away from the reaction mixture together with 1–2 ml of *m*-cresol. Fresh *m*-cresol was continuously added in order to keep the total volume of the solution constant. After being allowed to

Table 1
Intrinsic viscosities of PFMB-based and DMB-based polyimides

PFMB-based Polyimides	$[\eta]$ (dl/g)	DMB-based Polyimides	$[\eta]$ (dl/g)
BPDA–PFMB	4.62[a]	BPDA–DMB	10.1[b]
DBBPDA–PFMB	1.85[c]	DBBPDA–DMB	1.76[c]
HFBPDA–PFMB	1.78[c]	HFBPDA–DMB	1.53[c]
DPBPDA–PFMB	1.58[c]	DPBPDA–DMB	1.45[c]
O6FDPBPDA–PFMB	1.47[c]	O6FDPBPDA–DMB	1.24[c]
M6FDPBPDA–PFMB	1.73[c]	M6FDPBPDA–DMB	1.52[c]
P6FDPBPDA–PFMB	1.18[c]	P6FDPBPDA–DMB	1.69[c]
M12FDPBPDA–PFMB	1.03[c]	M12FDPBPDA–DMB	1.14[c]

[a] Intrinsic viscosity determined in m-cresol at 60 ± 0.1°C.
[b] Intrinsic viscosity determined in p-cholorophenol at 60 ± 0.1°C.
[c] Intrinsic viscosity determined in THF at 30 ± 0.1°C.

cool to ambient temperature, the solution was diluted with 30 ml of *m*-cresol and then slowly added to a vigorously stirred solution of 95% ethanol. The precipitated polymer was collected via filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 h. The polymer was isolated with a 90%–95% yield. Following the same procedure, the other PFMB- and DMB-based polyimides with different 2,2′-disubstituted BPDAs were synthesized. Their intrinsic viscosities are listed in Table 1. Based on known molecular weight data with respect to the intrinsic viscosity, their molecular weights were high enough for polymeric study [18,19]. For example, an intrinsic viscosity of 1.78 dl/g in HFPBDA-PFMB corresponds to a weight average molecular weight of 58 000 g/mol.

Solutions of these polyimides in cyclopentanone (12% w/w) were filtered through 5 μm Whatman Teflon syringe filters (except for BPDA–PFMB and BPDA–DMB solutions, which were made in *m* cresol and *p*-chlorophenol). Films were made by solution casting onto clean glass substrates. The thickness of these films was controlled using a doctor knife and ranged between 30–40 μm. Wet films were placed in an oven at 60°C in order to slowly release the solvent. After 24 h, the samples were placed in a vacuum oven and dried at 180°C for 48 h. The resulting films were used for thermogravimetric (TG), thermal mechanical (TM) and dynamic mechanical (DM) experiments. Films used for obtaining UV–Visible (UV–VIS) spectra had a thickness of 6 μm. The preparation procedure for the films used in the UV–VIS measurements was the same as described previously but instead utilized a 5% (w/w) solution.

2.2. Equipment and experiments

Prior to TG experiments, all of the polyimide samples used were heated to 300°C, held there for 20 min, and cooled to 30°C. Samples were then heated in dry nitrogen or air to 650°C in a TA-2950 TG analyzer at a heating rate of 10°C/min. The two onset temperatures corresponding to 2% and 5% weight loss were used to evaluate the thermal and thermo-oxidative stability of these polyimides. The magnetic null method was used to calibrate the temperature of the TG instrument.

The T_gs of these polyimide films were determined using a TA-2940 TM analyzer 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 lengths of measurements were also calibrated. In order to precisely measure their T_gs, polyimide films were heated to 300°C in nitrogen 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 while they were simultaneously heated at 10°C/min. The T_g was taken as the onset temperature where the slope of dimensional change versus temperature exhibits 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 [20].

DM experiments were carried out in a Seiko DMS-200. The frequency range was set 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 from corresponding peak temperatures seen on the loss modulus (E'') curves. The activation energy of a single frequency relaxation can be calculated by plotting the natural logarithmic frequency, ln(f), versus the reciprocals of relaxation peak temperatures determined from the E'' curves. The slope of this Arrhenius linear relationship is proportional to the activation energy. If the molecular motion becomes cooperative, multiple relaxation frequencies are involved. However, 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 units. For this reason the Arrhenius equation is no longer adequate to describe the relaxation related to this type of cooperative molecular motion. Nevertheless, in a relatively narrow frequency region within three or four orders of magnitude, the above mentioned method remains satisfactory although the calculated activation energy only represents an apparent activation energy (E_a). In this study we

Table 2
The solubility of PFMB- and DMB-based polyimides with different dianhydrides. (+) Minimum solubility more than 5%(wt); (−) Maximum solubility less than 2%(wt); (*) Solubility of PFMB-based polyimide/solubility of DMB based-polyimide.

Dianhydride	Acetone	Cyclo-pentanone	THF	NMP	*m*-cresol	*p*-chloro-phenol
BPDA	− / −	− / −	− / −	− / −	+ / −	+ / + *
DBBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
HFBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
DPBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
O6FDPBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
M6FDPBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
P6FDPBPDA	+ / −	+ / +	+ / +	+ / +	+ / +	+ / +
M12FDPBPDA	+ / +	+ / +	+ / +	+ / +	+ / +	+ / +

applied the Arrhenius equation to determine the activation energies for both the sub-glass β-relaxation and the α-relaxation process. It should be kept in mind that these activation energies (E_β and E_α) become apparent activation energies if the relaxation involves segmental cooperative motion of the 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. Organo-solubility

As the aromatic polyimides synthesized from 6FDA and 2,2′-disubstituted biphenyl diamines show excellent solubility while BPDA–PFMB is only soluble in *m*-cresol and *p*-chlorophenol [1]. It is interesting to see whether the polyimides containing 2,2′-disubstituted BPDAs possess good organo-solubility. Further, comparison can also be made between PFMB- and DMB-based polyimides in order to obtain information regarding the effect of an incorporated fluorinated diamine on the solubility. Six solvents (acetone, cyclopentanone, tetrahydrofuran (THF), *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, and *p*-chlorophenol) were used to test the organo-solubility of the PFMB- and DMB-based polyimides at ambient temperature.

As shown in Table 2, except for BPDA–PFMB (of which the BPDA dianhydride does not possess 2,2′-disubstituted groups), the PFMB-based polyimides containing 2,2′-disubstituted BPDAs are soluble in all six of these common organic solvents. This surprising improvement in the organo-solubility of these polyimides can be attributed to the incorporation of twisted-biphenyl-imide structures in these 2,2′-disubstituted-BPDAs. In fact, the organo-solubility behavior of the polymers based on PFMB and the 2,2′-disubstituted-BPDAs is similar to that of previously reported analogous polymers based on 6FDA and 4,4′-diamino-2,2′-disubstituted biphenyls [1]. Thus, the introduction of 2,2′-disubstituted groups to BPDA is considerably effective in producing organo-soluble polyimides.

The solubility of the DMB-based polyimides under the same conditions is also shown in Table 2. As can be seen, BPDA–DMB is only soluble in *p*-chlorophenol. However, at the other side of the series spectrum, M12FDPBPDA–DMB is soluble in all six of the solvents used. The remaining DMB-based polyimides are insoluble in acetone but are soluble in all the other solvents studied. This indicates that 2,2′-disubstituted groups with larger steric volumes improve the polyimide’s solubility. This is similar to the fluorine effect, which is shown through the fact that each PFMB-based polyimide is more soluble compared to the corresponding DMB-based polyimide. For this reason, it

Table 3
Temperatures for 2% and 5% weight loss in air and nitrogen for PFMB- and DMB-based polyimides with different dianhydrides

Dianhydride	TGA (Air)[a] (°C) 2%/5%(wt)	TGA (N_2)[a] (°C) 2%/5%(wt)	TGA (Air)[b] (°C) 2%/5%(wt)	TGA (N_2) [b] (°C) 2%/5%(wt)
BPDA	531/564	530/565	468/509	489/515
DBBPDA	486/518	492/523	412/441	437/458
HFBPDA	530/549	537/566	464/498	460/503
DPBPDA	498/539	513/542	427/508	479/511
O6FDPBPDA	529/553	531/559	439/495	481/509
M6FDPBPDA	529/563	536/566	433/509	485/512
P6FDPBPDA	524/546	534/555	440/502	484/510
M12FDPBPDA	530/550	535/565	440/495	480/513

[a] PFMB-based polyimides.
[b] DMB-based polyimides.

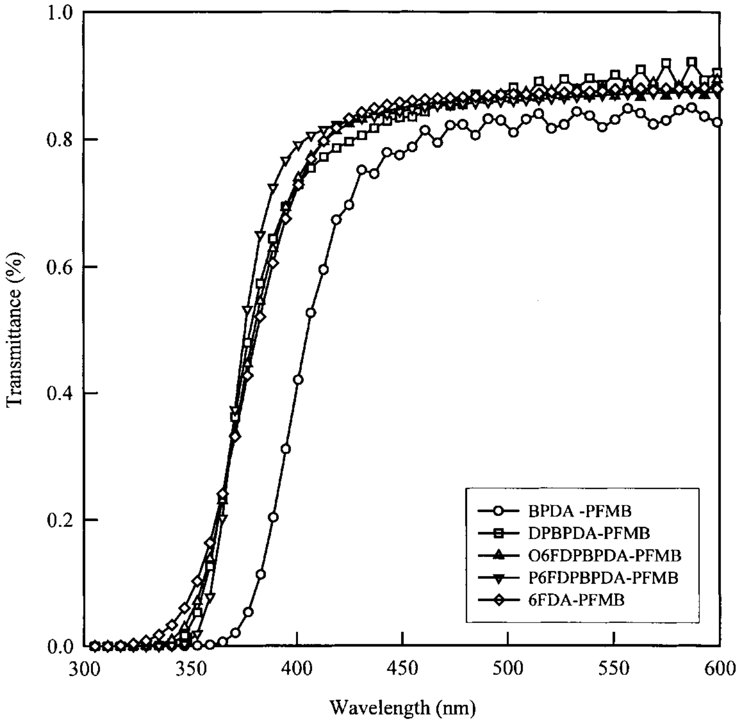


Fig. 2. A set of UV–VIS spectra of PFMB-based polyimide films (a UV–VIS spectrum of 6FDAPFMB is also included for comparison).

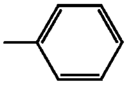
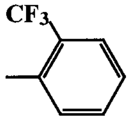
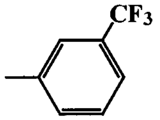
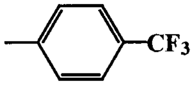
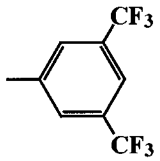
can be stipulated that, in addition to the size difference of the 2,2′-disubstituted groups, different electronic states exist when comparing the methyl groups of the DMB-based series with the trifluoromethyl groups of the PFMB-based series. This difference in electronic interactions between the substituent groups of the diamines and the dianhydrides of each series results in the improved solubility of PFMB-based polyimides compared to corresponding DMB based polyimides.

3.2. Thermal and thermo-oxidative stability

Thermal and thermo-oxidative stability can be roughly represented using the onset temperatures corresponding to 2% and 5% weight loss in both dry nitrogen and air atmospheres. This data is listed for PFMB- and DMB-based polyimide films in Table 3. In TG measurements with a heating rate of 10°C/min, PFMB-based films undergo 5% weight loss in a range of 523°C to 566°C in dry nitrogen and 518°C to 564°C in air. DBBPDA–PFMB, which consists of 2,2′-bromine disubstituted BPDA, shows the lowest onset temperatures for both weight loss amounts. DPBPDA–PFMB show slightly better thermal and thermo-oxidative stability compared to that of DBBPDA–PFMB. However, both polyimides are less stable then the other six fluorine-substituted BPDA polyimides. These fluorine-substituted PFMB-based polyimides exhibit almost the same onset weight loss temperatures as that of BPDA–PFMB. Previous studies on the thermal degradation mechanism for BPDA–PFMB have demonstrated that the thermal cracking temperature of trifluoromethyl groups attached onto the diamines is around 590°C, which is almost equal to that of the backbone chains [21,22]. Therefore, the thermal and thermo-oxidative stability of these PFMB-based polyimides is mainly determined by the stability of the 2,2′-disubstituted groups of the dianhydrides. Experimental results indicate that the fluorinated 2,2′-disubstituted BPDAs also possess almost the same stability as the backbone chains. From this evidence it can be stated that the weaker carbon-bromine bonds in DBBPDA decrease the stability of the corresponding polyimide, resulting in its lower weight loss temperatures.

The onset temperatures corresponding to 2% and 5% weight loss for DMB-based polyimides in both dry nitrogen and air atmospheres are also listed in Table 3. Film samples of these polyimides undergo 5% weight loss between 458°C and 515°C in nitrogen and between 441°C and 509°C in air at a heating rate of 10°C/min. The dependence of these polyimides' thermal and thermo-oxidative stability on their constituent 2,2′-disubstituted BPDAs shows the same trend as the PFMB-based polyimides. However, the onset weight loss temperatures for each of the DMB-based polyimides is almost 80°C lower than those of the corresponding PFMB-based polyimides. The thermal stability of these polyimide series depends on the electronic strength of the backbone and the 2,2′-disubstituted groups on the diamine and/or dianhydride. This is determined by the weakest bond among these structures. The methyl 2,2′-substituted groups (electron donating groups) of the DMB diamine are much less stable than the trifluoromethyl groups (electron with-

Table 4
The onset and 80% transmission wavelengths from UV–VIS spectra for both PFMB-based and DMB-based polyimide films

Dianhydride	2,2′-Disubstituted Groups	Onset / 80% Wavelength (nm) for PFMB-Based Films	Onset / 80% Wavelength (nm) for DMB-Based Films
BPDA	none	367/450	378/468
DBBPDA	—Br	343/409	338/424
HFBPDA	$-CF_3$	334/413	341/428
DPBPDA		339/420	347/435
O6FDPBPDA		341/415	352/426
M6FDPBPDA		347/411	350/439
P6FDPBPDA		346/405	352/432
M12FDPBPDA		342/408	346/428

drawing groups) of the PFMB diamine. This makes the DMB-based polyimides less stable than the PFMB-based polyimides. Further, this trend demonstrates that the effect of the 2,2′-disubstituted groups on the thermal and thermo-oxidative stability of the polyimide is more effective by changing the chemical structures in diamines than in dianhydrides.

3.3. Ultraviolet–visible transparency

Electron conjugation in polyimide films is studied using UV–VIS spectroscopy. Two quantities, the transmission onset and the 80% transmission wavelength, are used to evaluate the transparency of these films. The UV–VIS spectra of several PFMB-based polyimide films, which possessed a thickness 6 μm, are displayed in Fig. 2. The data for 6FDA-PFMB is also included in Fig. 2 for comparison. The onset and 80% transmission wavelengths for the PFMB-based polyimide films are listed in Table 4. They range from 334 to 367 nm for the onset wavelength and 405 to 450 nm for the 80% transmission wavelength. Introduction of the 2,2′-disubstituted groups to BPDA causes a reduction in the conjugation length of these dianhydrides and thus substantially decreases the color of these polyimide films. All of the PFMB-based polyimide films with 2,2′-disubstituted BPDAs exhibit a significant blue shift compared to the BPDA–PFMB film. These 2,2′-disubstituted BPDA films are transparent and clear in the UV–VIS wavelength region and exhibit almost identical UV–VIS absorption as that seen in the 6FDA-PFMB sample (Fig. 2).

The onset and 80% transmission wavelengths for the DMB-based polyimide films are also listed in Table 4. They range from 338 to 378 nm for the onset wavelength

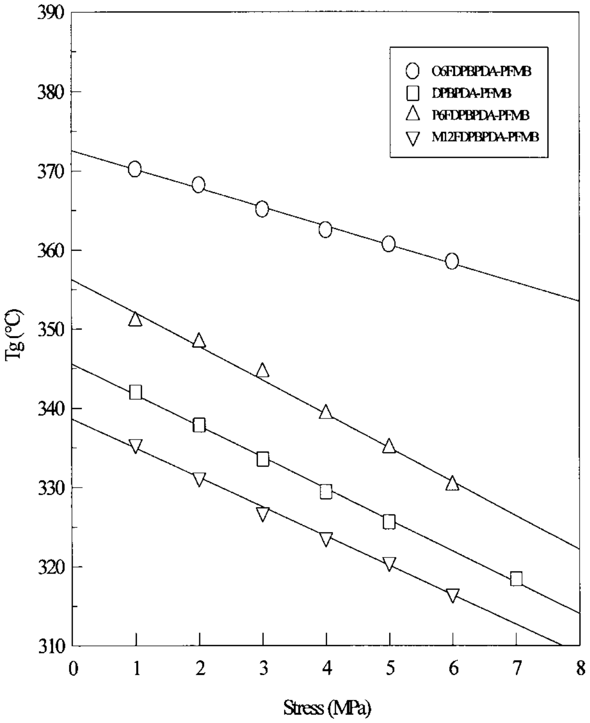


Fig. 3. Glass transition temperatures of PFMB-based polyimide films obtained using an extrapolation of the applied stress toward zero.

and 424–468 nm for the 80% transmission wavelength. The introduction of 2,2′-disubstituted groups to the dianhydride constituents of the DMB-based polyimide films also shows the same effect on the UV–VIS absorption as that for the PFMB-based polyimide films. However, the onset and 80% transmission wavelengths for each of the DMB-based polyimide films is about 10 nm longer than that of the corresponding PFMB-based polyimide films. This indicates that the methyl groups of DMB are not as efficient at breaking the conjugation length as the trifluoromethyl groups of PFMB. This is probably because of the differences in both the size and shape of the disubstituent groups and their electronic states in conjunction with the polymer backbone.

3.4. Glass transition temperatures

Figs. 3 and 4 show some examples of T_g measurements from TM experiments as a function of the applied stress for both the PFMB- and DMB-based polyimide films [1,20,21]. The T_g values are listed in Table 5 for these two series of films. The T_g ranges from 304°C to 372°C for the PFMB-based polyimide films and from 334°C to 369°C for the DMB-based polyimide films. The T_gs of these samples have also been measured using DSC. However, the heat capacity jump is less obvious in DSC heating diagrams owing to the broad T_g temperature ranges of these two series of polyimide films [23].

As the glass transition process is related to molecular motion at a structural level, which involves several molecular segments, T_gs are considered to be affected by both molecular packing and chain conformation (chain rigidity and linearity). It is interesting that BPDA–PFMB has the lowest T_g among the PFMB-based polyimide films. This is also true in the DMB-based polyimide series. BPDA (without 2,2′-disubstituted groups) may possess a *cis*- or a *trans*-

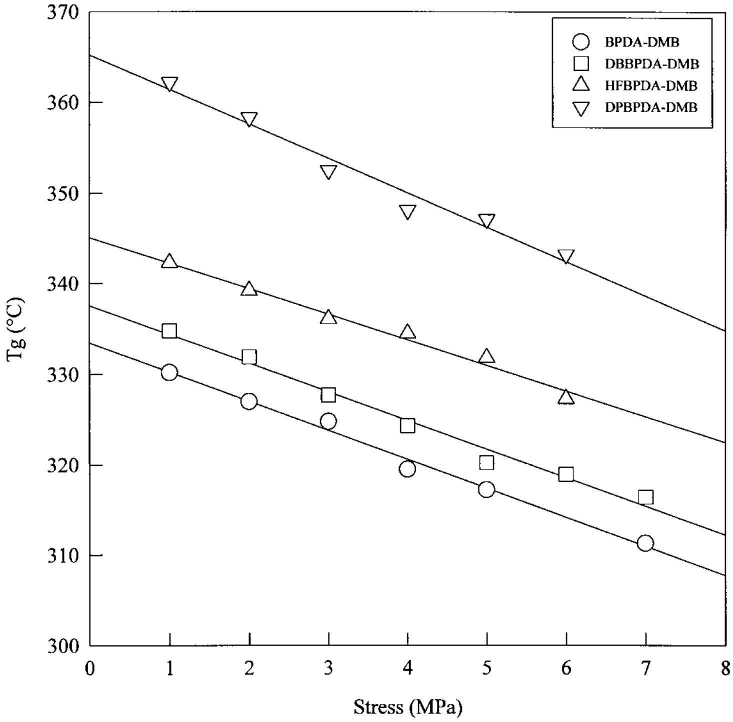
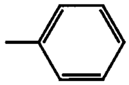
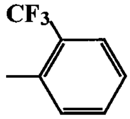
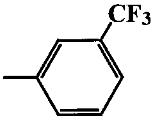
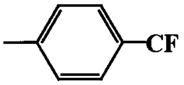
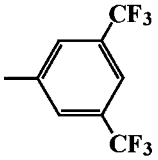


Fig. 4. Glass transition temperatures of DMB-based polyimide films obtained using an extrapolation of the applied stress toward zero.

Table 5
T_gs for both PFMB-based and DMB-based polyimide films

Dianhydride	2,2′-Disubstituted Groups in BPDA dianhydride	T_g (°C) (PFMB-based)	T_g (°C) (DMB-based)
BPDA	none	304	334
DBBPDA	—Br	330	337
HFBPDA	$—CF_3$	332	345
DPBPDA		346	364
O6FDPBPDA		372	369
M6FDPBPDA		342	346
P6FDPBPDA		356	367
M12FDPBPDA		339	342

conformation, both of which are illustrated in Fig. 5 (note that detailed torsion positions of the 2,2′-disubstituted groups may be different based on chemical structures which was illustrated in diamine crystals [24]). However, 2,2′-disubstituted BPDAs can only possess the *trans*-conformation owing to the steric repulsion of the 2,2′-disubstituted groups (Fig. 5). Therefore, the polyimides made from the 2,2′-disubstituted BPDAs adopt a more extended conformation. It is expected to take substantially more energy to motivate motions in these polyimides as compared with that of unsubstituted BPDA polyimides. This increases the chain rigidity and linearity of these polyimides and thus results in higher T_gs for these polyimide films as compared to BPDA-PFMB and BPDA-DMB.

The dependence of T_g on the size and anisotropic shape of the 2,2′-disubstituted groups of the dianhydrides for both of these series of samples is not the same as that of previously described 6FDA-based polyimide films [1]. Note that for 6FDA-based polyimides, the T_g decreases monotonically with increasing size and anisotropic shape of the 2,2′-disubstituted groups of the diamines [1]. As the size and, to a lesser extent, the anisotropic shape of the 2,2′-disubstituted groups of the dianhydrides increase, the molecular packing gradually loosens. This factor may become dominant in determining the T_gs for these series of samples. Hence, the T_g increases continuously until O6FDPBPDA-PFMB and O6FDPBPDA-DMB, which show the highest T_gs of their series. Finally, M12FDPBPDA-PFMB and M126FDPBPDA-DMB exhibit T_gs, which are significantly lower than the other 2,2′-disubstituted BPDA polyimides. For example, they are about 20°C lower than the P6FDPBPDA-polyimides. The T_g for each of the DMB-based polyimide films is several degrees higher than that of the corresponding PFMB-based polyimide films. This may be a size effect as a result of the smaller substituted group (methyl) on DMB compared to the larger one (trifluoromethyl) on PFMB.

Table 6
The β_1, β_2 and α relaxation peak temperatures for PFMB-based polyimide films with different dianhydrides as determined from E'' at 0.01 Hz and corresponding activation energies. (*) data cannot be obtained owing to overlapped relaxation processes

Diamine	0.01 Hz (°C), β_1	Activation energy, β_1 (kJ/mol)	0.01 Hz (°C), β_2	Activation energy, β_2 (kJ/mol)	0.01 Hz (°C), α	Activation energy, α (kJ/mol)
DBBPDA	183	*	235	*	381	*
DPBPDA	179	*	267	*	406	*
HFBPDA	180	146	293	189	393	*
O6FDPBPDA	182	*	200	*	391	731
M6FDPBPDA	179	136	260	*	372	967
M12FDPBPDA	179	144	266	*	364	1115
P6FDPBPDA	179	147	276	*	389	1015

Table 7
The β_1, β_2 and α relaxation peak temperatures for DMB-based polyimide films with different dianhydrides as determined from E'' at 0.01 Hz and corresponding activation energies. (*) data cannot be obtained owing to overlapped relaxation processes

Diamine	0.01 Hz (°C), β_1	Activation energy, β_1(kJ/mol)	0.01Hz (°C), β_2	Activation energy, β_2(kJ/mol)	0.01Hz (°C), α	Activation energy, α (kJ/mol)
DBBPDA	59	*	235	*	386	*
DPBPDA	61	100	265	*	385	*
HFBPDA	59	100	291	*	370	*
O6FDPBPDA	58	*	197	168	392	754
M6FDPBPDA	55	98	263	196	370	958
M12FDPBPDA	57	105	268	200	378	1031
P6FDPBPDA	58	96	278	*	376	1105

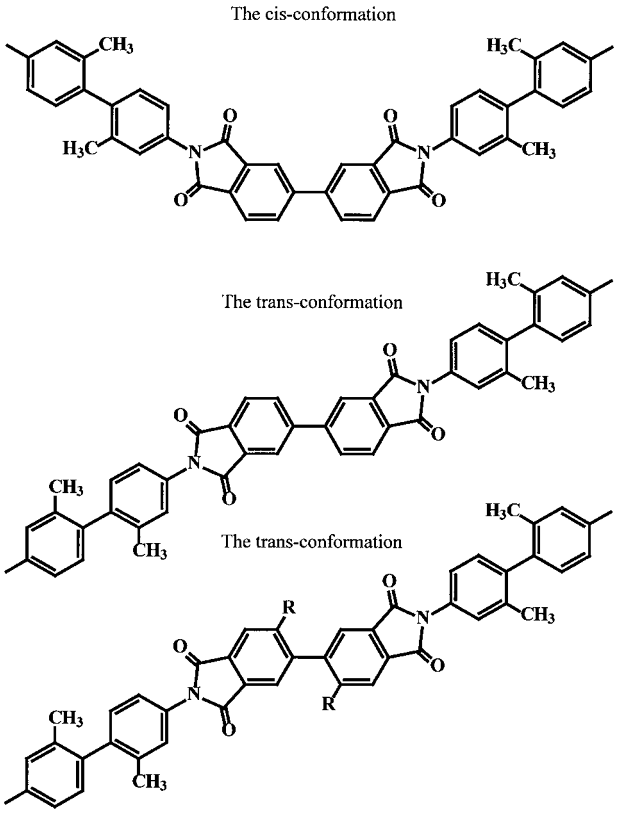


Fig. 5. Schematic illustrations of both the *cis*- and *trans*-conformations of BPDA–DMB and the *trans*-conformation of 2,2′-disubstituted BPDA–DMB.

3.5. Relaxation behaviors

Three relaxation processes can be observed above room temperature for both the PFMB- and DMB-based polyimide films. DM results of M12FDPBPDA-DMB are chosen as examples and are shown in Fig. 6. The low temperature and the medium temperature relaxation processes are defined as the β_1 and β_2 processes, respectively. The high temperature relaxation is an α-relaxation process. Based on DSC and TM results, the α relaxation corresponds to the glass transition temperature while the β_1- and β_2-relaxation processes are sub-glass transitions [23]. To our knowledge, this is the first report on aromatic polyimide systems, which possess three relaxation processes above room temperature.

As shown in Fig. 6, the β_1 relaxation is the most sensitive of these three processes with respect to frequency change. It is followed by the β_2 process, while the α relaxation is the least sensitive process with respect to frequency. This causes the β_1 relaxation to exhibit the lowest E_a while the α relaxation has the highest one. The Arrhenius equation can be used to obtain values for the E_as of these three relaxation processes. Table 6 contains the β_1-, β_2- and α-relaxation peak temperatures (obtained from E'' data) at 0.01 Hz for the PFMB-based polyimide films as well as E_as calculated from the Arrenhius equation. The experimental results for DMB-based polyimide films are listed in Table 7.

A constant β_1-relaxation temperature (around 180°C at 0.01 Hz) can be observed for all of the PFMB-based polyimide films (Fig. 7). In fact, the β_1-relaxation temperatures

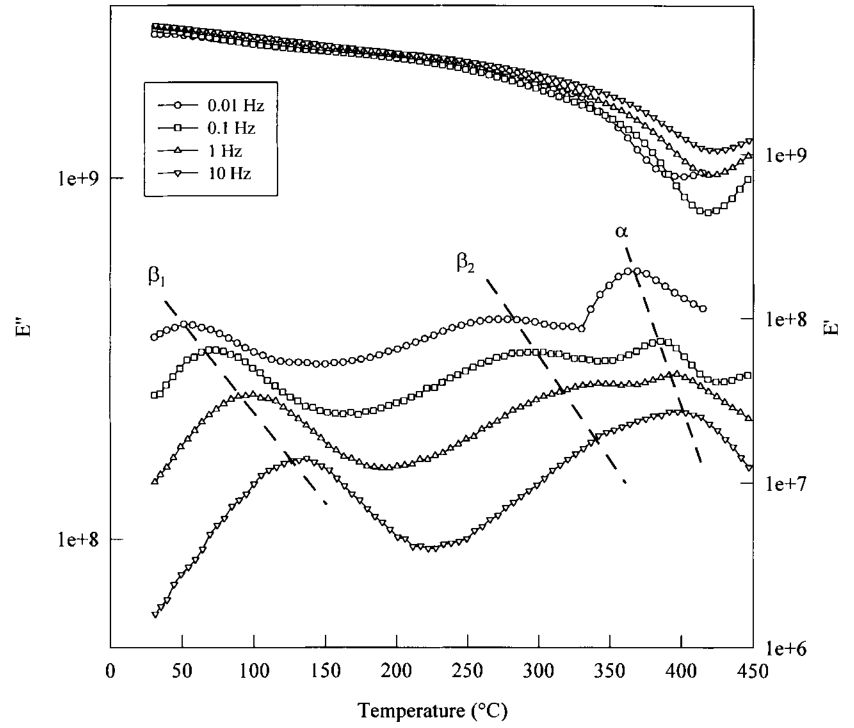


Fig. 6. DM results of the M12FDPBPDA–DMB films. E' and E'' changes with temperature at different frequencies and three relaxation processes can be seen.

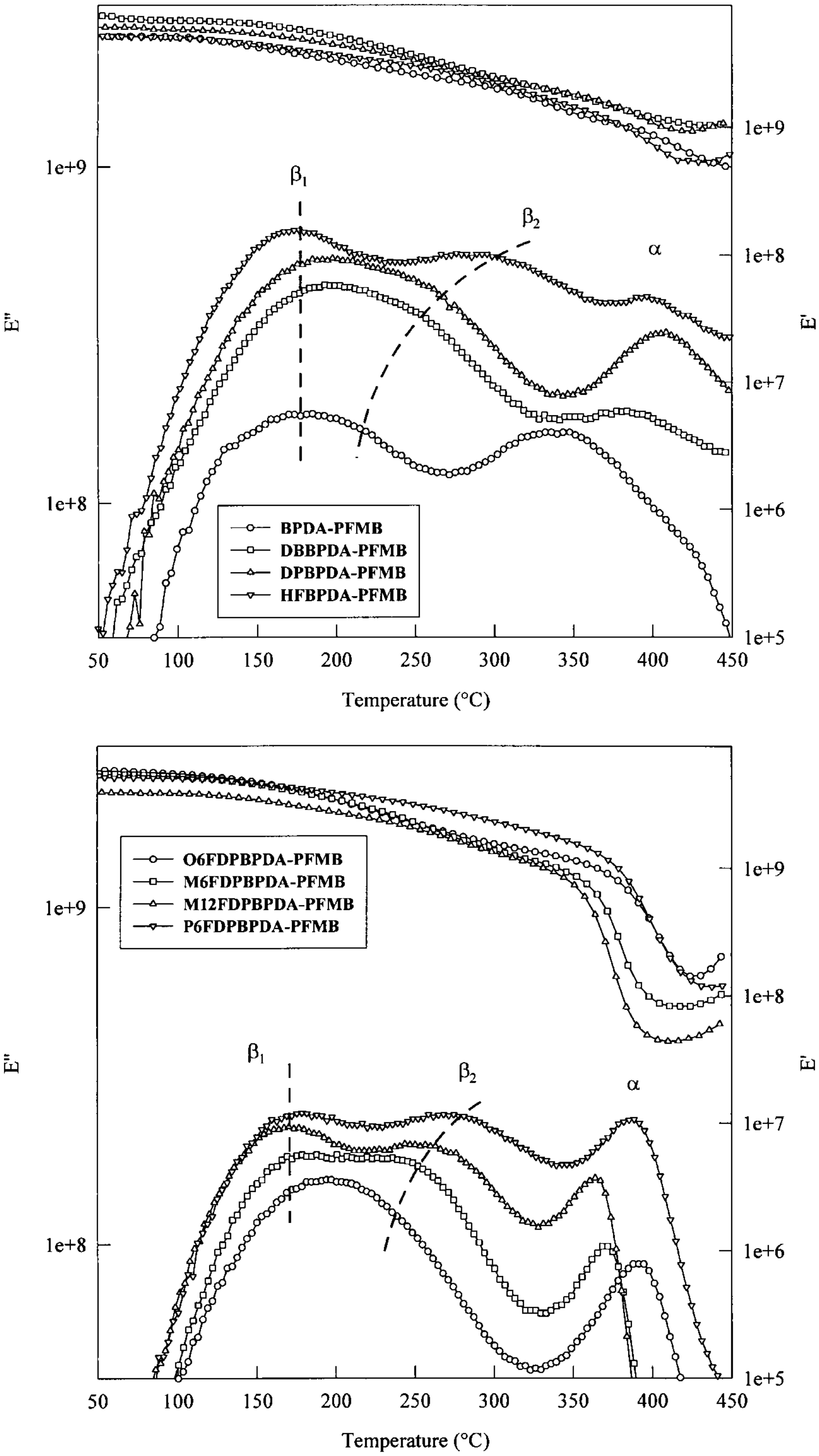


Fig. 7. DM results of the PFMB-based polyimide films with a constant β_1 relaxation temperature at 0.01 Hz.

are identical at all frequencies (from 0.01 to 10 Hz) in the PFMB-based polyimide films. It should also be noted that the PFMB-based polyimide films have a fixed diamine (PFMB). These results indicate that the β_1 relaxation is associated with a local motion related to the diamine constituent of this polyimide series. Therefore, polyimide films with a fixed diamine should exhibit the same β_1-relaxation behavior. This conclusion is further supported by the experimental results of the DMB-based polyimide films, which also have a fixed diamine (DMB). An identical β_1-relaxation temperature (around 58°C at 0.01 Hz) can be observed in all of the DMB-based polyimide films (Fig. 8). This β_1 relaxation also possesses the same frequency independence (from 0.01 to 10 Hz) as seen in the PFMB-based samples.

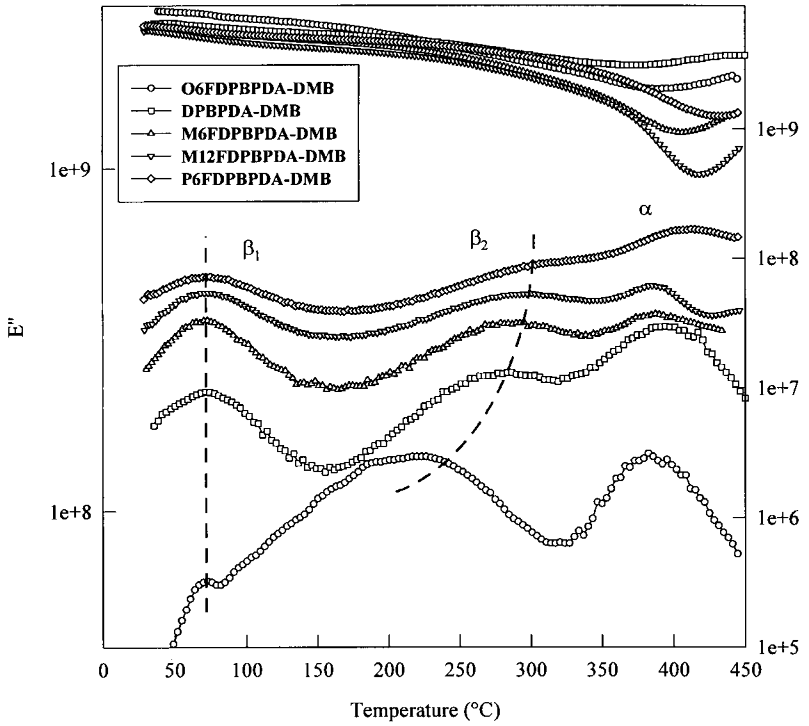


Fig. 8. DM results of the DMB-based polyimide films with a constant β_1 relaxation temperature at 0.01 Hz.

In Figs. 7 and 8, the β_2-relaxation temperature at 0.01 Hz increases from 200°C to 300°C with increasing size and anisotropic shape of the 2,2′-disubstituted groups of the BPDA dianhydrides in both the PFMB- and DMB-based polyimide films. Therefore, one speculates that the β_2-relaxation process must be associated with the local motion of the dianhydrides. If this is true then, when the dianhydride structure is fixed in polyimide films, the β_2-relaxation

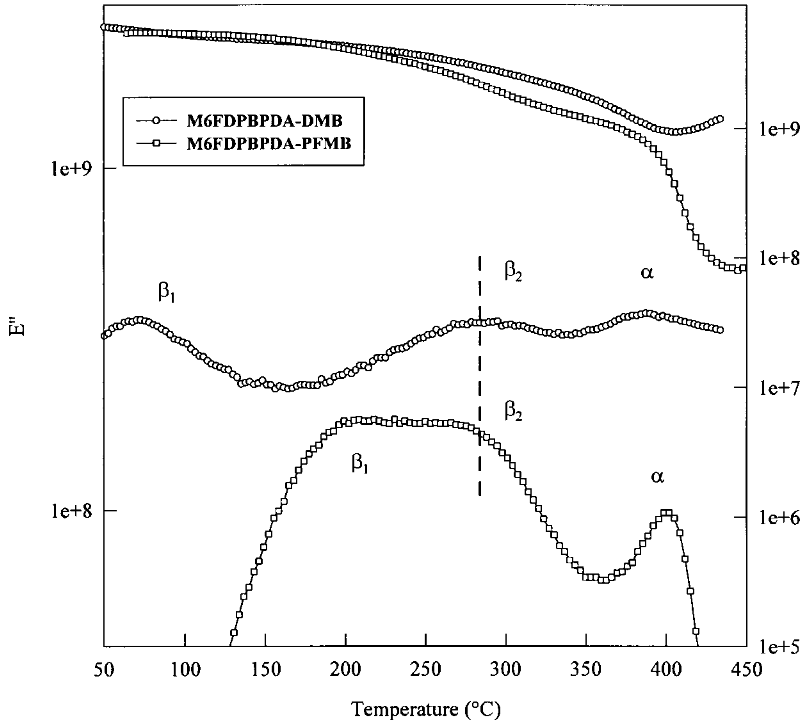


Fig. 9. DM results of M6FDPBPDA–PFMB and M6FDPBPDA–DMB films. E' and E'' data is shown with constant β_2-relaxation temperatures at 0.01 Hz.

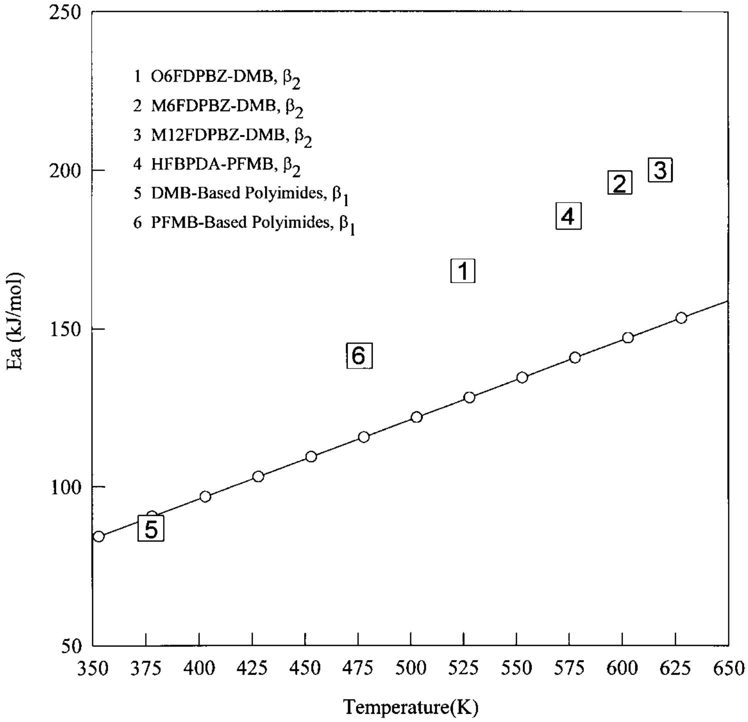


Fig. 10. Starkweather's plot of activation energies versus temperature. The solid linear line is the calculation based on Starkweather's theory [25,26] which serves as the lower limit of activation energies for non-cooperative motion. E_β for both the β_1- and β_2-relaxation processes of both series of polyimide films are included in this plot.

temperature should be constant, which was observed. As an example, Fig. 9 shows that both the M6FDPBPDA-DMB and M6FDPBPDA-PFMB polyimide films exhibit the same β_2-relaxation temperature (263°C at 0.01 Hz). A comparison of the β_2-relaxation temperatures can be made between all of the PFMB-based films and DMB-based polyimide films (Tables 6 and 7). There are seven pairs of samples, each of which contain a different dianhydride: DBBPDA–PFMB and DBBPDA–DMB, DPBPDA–PFMB and DPBPDA–DMB, M12FDPBPDA–PFMB and M12FDPBPDA–DMB, etc. The members of each separate pair contain the same dianhydride and show the same β_2-relaxation temperature at all frequencies in the range from 0.01 to 10 Hz. Based on these experimental results, we may conclude that the β_2-relaxation temperature is dependent upon the size and anisotropic shape of the 2,2′-disubstituted groups of the constituent dianhydrides. These substituent groups introduce steric hindrance which in turn hampers the local motion of the dianhydrides in these polyimides.

The highest temperature relaxation process, or α process, corresponds to the glass transition. The α-relaxation temperature obtained at 0.01 Hz ranges from 342°C to 406°C for the PFMB-based polyimides and from 357°C to 392°C for the DMB-based polyimides. DM results at 0.01 Hz (α-relaxation) and TM (T_g) results (Table 5) shows a consistent trend for these samples. The dependence of the α-relaxation temperature on the size and anisotropic shape of the 2,2′-disubstituted groups of the BPDAs is very similar to that of the T_g case discussed previously.

For DM data, plots of the logarithmic frequency versus the reciprocal relaxation peak temperature of the loss modulus yield the E_as for the β_1-, β_2- and α-relaxation processes. The E_βs for the β_1-relaxation of the PFMB-based samples are all 144 ± 5 kJ/mol and are independent of the dianhydride structure. This is consistent with our previous results, [1,25] that indicates that the origin of these β_1-relaxation is associated with the PFMB diamine. In the frequency region between 0.01 and 10 Hz only one β_2 relaxation can be completely separated from the other relaxation processes in this polyimide series (HFBPDA–PFMB) and its activation energy is 189 kJ/mol. Therefore, this β_2-relaxation process is caused by local motion of the dianhydrides, which is cooperative in nature. Lastly, the α-relaxation temperatures shift with changes in the size and anisotropic shape of the 2,2′-disubstituted groups of the BPDAs and the E_αs shift from 731 kJ/mol for O6FDPBPDA-PFMB to 1115 kJ/mol for M12FDPBPDA-PFMB (Table 6).

Similarly, for DMB-based polyimide films the E_as for the β_1-, β_2- and α-relaxation processes can also be calculated based on the slopes obtained from the linear relationships of the logarithmic frequency and the reciprocal relaxation peak temperature. The E_as for the β_1 relaxation of these samples are 100 ± 5 kJ/mol and are independent of the dianhydride structure (Table 7). This indicates that the origin of these β_1 relaxations can mainly be attributed to the diamine (DMB). The β_2-relaxation temperatures shift towards higher temperatures with increasing size and anisotropic shape of the 2,2′-disubstituted groups of the BPDAs (Table 7) and the E_βs increases from 168 kJ/mol for O6FDPBPDA-DMB to 200 kJ/mol for M12FDPBPDA-DMB (Table 7). The α-relaxation temperatures also shift with changes in the size and anisotropic shape of the 2,2′-disubstituted groups of the BPDAs and the resulting E_αs range from 754 kJ/mol for O6FDPBPDA-DMB to 1105 kJ/mol for M12FDPBPDA-DMB (Table 7).

The experimental activation energies for the β_1- and β_2-relaxation processes can also be compared to calculated values from the theory put forth by Starkweather, which represents non-cooperative motion [26,27]. Fig. 10 shows a relationship between the activation energies of the β_1 and β_2 processes and temperature at 1 Hz. The solid line with open circles in this figure is the calculated data based on the Starkweather theory [26,27]. For the β_1-relaxation process, which is attributed to the local motion of diamines, the experimental data falls right on or slightly above the solid line. This indicates that the local motion caused by the DMB diamine is non-cooperative while that of the PFMB diamine starts to deviate from the non-cooperative motion, as discussed in one of our previous publications [1]. Recently, a simple statistical model was also proposed in order to illustrate such types of local motion [28]. However, for the samples with relatively small 2,2′-disubstituted groups on the BPDA dianhydrides, the β_2 activation energies could not be separated experimentally as this process is overlapped by the β_1 relaxation. For samples with relatively large 2,2′-disubstituted groups on the dianhydrides, the experimentally observed activation energies for the β_2 processes exhibit positive deviations from Starkweather′s model (Fig. 10). Further increasing the size and anisotropic shape of the 2,2′-disubstituted groups of the BPDAs may make the β_2-relaxation processes deviate even farther from non-cooperative motion.

4. Conclusions

The introduction of seven different 2,2′-disubstituted groups to BPDA dianhydrides in these polyimide films results in dramatic changes in their glass transition and relaxation behaviors and thermal and optical properties. Polymers, which were soluble only in phenolic solvents without 2,2′-disubstituted groups become soluble in cyclopentanone, THF and other common organic solvents through the incorporation of 2,2′-disubstituents groups onto their BPDA constituents. However, the DMB-based polyimides are not soluble in acetone, while the PFMB-based polyimides are soluble in all the solvents used. This indicates that the trifluoromethyl groups of the PFMB diamine are more effective at enhancing the solubility of the polyimides. The dependence of the thermal and thermo-oxidative stability of the polyimides on the 2,2′-disubstituted groups of their constituent dianhydrides exhibits the same trend for both the series. However, the onset weight loss temperatures for each of the DMB-based polyimides is almost 80°C lower than that of the corresponding PFMB-based polyimides. The onset and 80% transmission wavelengths of these polyimide films are also lowered by the incorporation of 2,2′-disubstituted groups onto their BPDA dianhydride constituents. These two quantities are about 10 nm longer for each DMB-based polyimide film than that of the corresponding PFMB-based polyimide film.

BPDA–PFMB and BPDA–DMB possess the lowest T_gs for these two series of polyimides. The increase in T_g for polyimide films with 2,2′-disubstituted BPDAs can be attributed to an increase in chain rigidity and linearity via steric hindrance of the substituent groups of the dianhydride. This steric hindrance allows the dianhydrides to possess only the *trans*-conformation. When the size and anisotropic shape of the 2,2′-disubstituted groups of the dianhydrides further increases, the resulting looser molecular packing becomes the dominant factor and results in the reduction of the T_g.

It is particularly interesting that three relaxation processes (the β_1, β_2 and α) can be found above room temperature in both of these series of polyimide films. The β_1 and β_2 processes are found to be associated with local sub-group motions of the diamine and the dianhydride portions in the polyimides, respectively. When the size and anisotropic shape of the 2,2′-disubstituted BPDAs increase, the β_2-relaxation temperature increases and this motion becomes cooperative in nature. However, further investigations are necessary to determine the details of these types of motions.

Acknowledgements

This work was supported by the NSF Science and Technology Center of ALCOM at Kent State University, Case Western Reserve University and The University of Akron, the NSF DMR (96-17030) and the Federal Aviation Administration (FAA 94-G-026).

References

[1] Li F, Fang S, Honigfort PS, Chen JC, Harris FW, Cheng SZD. Polymer (in press).
[2] Harris FW. In: Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides, ch. 1. New York: Chapman and Hall, 1990.
[3] Harris FW, Hsu SL-C. High Perform Polym 1989;1:1.
[4] Sroog CE, Andrey AL, Abramo SV, Berr CE, Edwards WM, Olivier KL. J Polym Sci 1965;A3:1373.
[5] Sroog CEJ. Polym Sci Macromol Rev 1976;11:161.
[6] Franke H, Knabke G, Reute R. Molecular and Polymeric Optoelectronic Materials SPIE 1986;682:191.
[7] Reuter R, Franke H, Feger C. Appl Opt 1988;27:4565.
[8] Li F, Harris FW, Cheng SZD. Polymer 1996;37:5321.
[9] Cheng SZD, Li F, Savitski EP, Harris FW. Trends in Polym Sci 1997;5:51.
[10] Harris FW, Li F, Cheng SZD. In: Hougham G, editor. Fluoropolymers: syntheses and properties. ACS Symposium Series Book, 1999, in press.

[11] Li F, Kim K-H, Savitski EP, Chen J-C, Harris FW, Cheng SZD. Polymer 1997;38:3223.
[12] Li F, Savitski EP, Chen J-C, Yoon Y, Harris FW, Cheng SZD. In: Jenekhe S, Wynne K, editors. Photonic and optoelectronic polymers. ACS Symposium Series, vol. 672, 1997:2.
[13] Eashoo M, Wu Z, Zhang A, Shen D, Wu C, Harris FW, Cheng SZD, Gardner KH, Hsiao BS. Macromol Chem Phys 1994;195: 2207.
[14] Harris FW, Lin S-H, Li F, Cheng SZD. Polymer 1996;37:5321.
[15] Lin S-H, Li F, Cheng SZD, Harris FW. Macromolecule 1998;31:2080.
[16] Lin S-H. Ph.D. Thesis, Department of Polymer Science, The University of Akron, Akron, OH, 1995.
[17] Chen C-C. Ph.D. Thesis, Department of Polymer Science, The University of Akron, Akron, OH, 1996.
[18] Kwan SCM, Wu C, Li F, Savitski EP, Harris FW. Cheng SZD. 1997;Macromol Chem Phys 198:3605.
[19] Savitski EP, Li F, Lin SH, McCreight KW, Wu WE, Hsieh RFR, Leland ME, McIntyre DM, Harris FW, Cheng SZD. Int J Poly Anal Charact 1997;4:153.
[20] Arnold Jr FE, Cheng SZD, Harris FW. Thermochimica Acta 1992;212:189.
[21] Arnold Jr FE, Cheng SZD, Hsu SL-C, Lee CJ, Harris FW. Polymer 1992;24:5179.
[22] Li F, Huang L, Shi Y, Jin X, Wu Z, Shen Z, Chung C, Lyon RE, Harris FW, Cheng SZD. J Macromol Sci Phys 1999;B38:107.
[23] Li F. Ph.D. Dissertation, Department of Polymer Science, The University of Akron, Akron, OH, 1998.
[24] Chuang KC, Kinder JD, Hull DL, McConville DB, Youngs W. J Macromolecules 1997;30:7183.
[25] Arnold Jr FE, Bruno KR, Shen D, Eashoo M, Lee CJ, Harris FW, Cheng SZD. Polym Engng Sci 1993;33:1373.
[26] Starkweather Jr. HW. Macromolecules 1990;23:328.
[27] Starkweather Jr HW. Polymer 1991;32:2443.
[28] Hougham G, Jackman T. Polym Preprints (Polym Chem Div American Chemical Society) 1996;37:162.