Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

POLYMERIZATION, STRUCTURE AND THERMAL PROPERTIES OF ODPA-DMB POLYIMIDE FILMS

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Abstract

A new high molecular weight polyimide based on 4,4'-oxidiphthalic anhydride (ODPA) dian-hydride and 2,2'-dimethyl-4,4'-diaminobiphenyl (DMB) diamine has been synthesized *via* a one-step polymerization method. This polyimide is soluble in phenolic solvents. Films from 7 to 30 μm thick were cast from the polymer solution and show in-plane orientation on a molecular scale detected by Fourier transform infrared spectroscopy experiments. This anisotropic structure leads to anisotropic optical properties arising from two different refractive indices along the in-plane and out-of-plane directions. ODPA-DMB possesses high thermal and thermo-oxidative sta-bility. The glass transition temperature has been determined to be 298°C. Dynamic mechanical analyses show two relaxation processes appearing above room temperature: the β- and the α-re-laxation processes. The α-relaxation corresponds to the glass transition while the β-relaxation is a secondary relaxation process associated with the non-cooperative subsegmental motion.

Introduction

Aromatic polyimides possess high thermo-oxidative stability, high glass transition and/or melting temperatures, good hydrolytic and light stabilities, and they are insoluble in conventional organic solvents. These properties lead to wide applications in electronic parts, composite matrices, molding, adhesives, and wire coatings. Traditionally, aromatic polyimides have had to be synthe-sized *via* the conventional two-step polycondensation reaction and processed from the precursor poly(amic acid) forms due to the organo-insolubility of the polyimide. The polymers are then thermally or chemically imidized as the sec-

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ond step of polymerization. It is known that the by-product (usually water) is released during the imidization, and its presence drastically changes the material morphology as well as the ultimate mechanical properties.

Recently, organo-soluble aromatic polyimides have been synthesized *via* a one-step or single-stage polymerization method in which the dianhydrides and diamines are converted directly to polyimides in phenolic solvents such as *m*-cresol, *p*- or *o*-chlorophenol, *etc.*, in the presence of a tertiary amine catalyst at a high temperature [1, 2]. This provides an opportunity to obtain final products directly from the polyimide form and avoid the effect of a by-product.

Along this research line, a series of organo-soluble aromatic segmented rigid-rod polyimides synthesized from 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA) and various diamines *via* the one-step method have been developed. These polyimides show excellent mechanical properties and thermo-oxidative stability. Their structure-property relationships have also been extensively studied in the film and fiber forms [3–11].

We are continuing to extend our investigations to synthesize new organo-soluble aromatic polyimides as potential film and/or fiber resins for various applications and to understand the general roles that structure and morphology play in the ultimate properties. In this study, a new polyimide based on 4,4'-oxidiphthalic anhydride (ODPA) dianhydride and 2,2'-dimethyl-4,4'-diaminobiphenyl (DMB) diamine has been prepared. The chemical structure is
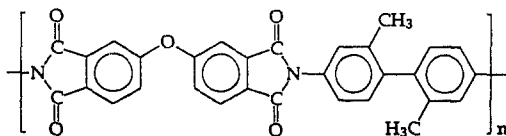
with the repeating unit weight of 486.5 g mol^{-1}. Because of the ether linkage in ODPA, this ODPA-DMB polyimide contains one flexible linkage in the main chain. When compared with other segmental rigid-rod polyimides reported earlier [3–11], one expects that the microscopic structure morphology and macroscopic properties may also differ from the others studied.

Experimental

Material and sample preparation

4,4'-Oxidiphthalic anhydride (ODPA) was purchased from Occidental Chemical Corp. and recrystallized from acetic anhydride. 2,2'-Dimethyl-4,4'-diaminobiphenyl (DMB) was synthesized from *m*-nitrotoluene *via* the benzidine arrangement reaction using the literature method [10]. The final product was recrystallized from ethanol and water three times to obtain pure DMB. The melting point range was 109~110°C.

The polymer was prepared by the one-step condensation polymerization from ODPA and DMB [1, 2]. Films were prepared by spreading a 1% (w/w, for Fourier transform infrared spectroscopy, FTIR, measurement) or 2–5% (w/w, for all the other measurements) ODPA-DMB/phenol solution on a glass plate at 60°C. The solvent was evaporated very slowly in a closed container at 60°C, followed by drying for 2 days at 150°C and another 24 hours at 250°C under reduced pressure in a vacuum oven. The films were heated an additional 1 hour at 300°C under vacuum in order to assure that any residual solvent had been removed. Precise control of the amount of the casting solution on the glass plate and maintaining horizontal level were necessary to obtain films of uniform thickness. The typical film thickness for FTIR measurements was 7 μm while for mechanical and dynamic mechanical measurements was 30 μm when the 5% solution was used.

Instrument and experiments

Relative thermal stability was determined *via* a TA Instruments TGA-2950 thermal gravimetric analyser (TGA). The powder samples of about 10 mg were heated to 700°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. To obtain the degradation activation energy, an isothermal mode was also used in the temperature range of 375~550°C. The temperature was driven from room temperature directly to the desired temperature, and the weight loss was monitored with respect to time at different isothermal temperatures under dry nitrogen.

A TA Instruments TMA 2940 thermomechanical analyzer (TMA) was used to determine the glass transition temperature (T_g) and linear coefficient of thermal expansion (CTE) of the ODPA-DMB polyimide films. Thin films with thicknesses of about 30 μm with a typical cross-sectional area of 0.10 mm^2 were mounted between two vertical clamps (tension mode). The samples were heated from 30 to 400°C at a heating rate of 5°C min^{-1} with different stresses. Both the T_g and CTE were measured as a function of the applied stress. The CTE in the solid state was calculated for the temperature range of 50~150°C.

Dynamic mechanical (DMA) measurements were conducted on a Seiko DMS 200 using the tension mode. The frequency was varied between 0.01 Hz and 10 Hz over a temperature range of 50~400°C with a heating rate of 1°C min^{-1}. Storage (E′) and loss (E″) moduli were measured and tan δ was calculated from the ratio E″/E′. Fourier transform infrared (FTIR) experiments were carried out on a Mattson Galaxy Model 5020 Spectrometer with the resolution of 4 cm^{-1}.

The in-plane and out-of-plane refractive indices for the free-standing films were determined by the optical wave-guide method using a Research Electro-Optics Model LSTP-1010.

Results and discussion

Polymerization

Equi-molar ODPA and DMB were dissolved in m-cresol to a total monomer concentration of 10% (w/w) with a small amount of isoquinoline catalyst. The resulting solution was heated under reflux in nitrogen for 12 hours following the one-step route [1, 2]. During the polymerization, no poly(amic acid) was isolated. The by-product (water) generated during imidization was continuously removed by distillation from the reaction mixture. The polymer does not precipitate and a clear solution is retained during the polymerization. This is a necessary condition to obtain high molecular weight polymers. After polymerization, the solution was cooled to about 100°C and was poured into methanol with vigorous stirring. The resulting polyimide powder was dried for several hours at 150°C, for 2 days at 250°C in a vacuum oven, and finally, for 1 hour under vacuum at 300°C.

This polyimide can be dissolved in several phenolic solvents such as phenol and m-cresol. However, it is only swollen in N-methyl pyrrolidone (NMP) even at its boiling temperature. The intrinsic viscosity (IV) determined at 60°C in phenol is 1.35 dL g^{-1}. This IV is lower than those of fluorinated aromatic polyimides such as 4.5 dL g^{-1} for BPDA-PFMB which was synthesized from 3,3'-diphenyl dianhydride (BPDA) and 2,2'-bis(trifluoromethyl)-4,4'diaminobiphenyl (PFMB)] [3] in m-cresol and 10 dL g^{-1} for BPDA-DMB in p-chlorophenol [10] prepared via the same synthetical route [1, 2]. It is known that IV data are closely associated with the equilibrium polymer conformations and are dominated by the interaction (solubility) parameters between the solvent molecules and the polymer segments. The low viscosity of ODPA-DMB in phenol may be explained by the different solubility parameters between the polymer and phenol solvent. However, polymer fractionation and solution properties have to be studied via gel permeation chromatography and light scattering experiments to reach a definitive conclusion. Another possible cause may be the different rigidities of the polyimide molecules. In ODPA-DMB, an ether linkage between the two imide rings may substantially affect the chain's flexibility compared with BPDA which possesses a direct linkage between these two imide rings.

In the polymerization process, specific efforts have been made to increase the IV of ODPA-DMB. However, it is difficult to obtain an IV greater than 1.4 dL g^{-1} even after prolonged polymerization at elevated temperature. Nevertheless, ODPA-DMB possessing this IV value was used to spin fibers from the solution. This indicates that the apparently low IV in ODPA-DMB seems to be due not to a low molecular weight but to greater molecular flexibility.

Molecular anisotropy in unoriented films

Segmented rigid-rod aromatic polyimides have been found to exhibit a preferential chain orientation direction parallel to the film surface if the thickness

of the unorientated films is less than 100 μm [3–6]. This kind of "in-plane ori-
entation" of the chain direction (molecular axis) can be characterized by FTIR
experiments for specific vibrational modes of the chain molecules in these
films. Figure 1 shows a FTIR spectrum of ODPA-DMB film having a thickness
of approximately 7 μm. The fingerprints of the vibration modes are the car-
bonyl absorption bands at 1777 cm^{-1} and 1723 cm^{-1}, which possess higher ab-
sorption frequencies than the imide absorption frequency range. The origin of
this doublet has been explained by Matsuo [11] in terms of in-phase and out-of-
phase coupled vibrations of the carbonyl groups, i.e., –C(=O)–NH and
–C(–O⁻)=NH–. The relative intensities of these two carbonyl absorptions can
be used to characterize the anisotropy of polyimide films. For the ODPA-DMB
film, the 1777 cm^{-1} absorbance, which possesses a transition moment vector
parallel to the imide plane, is the symmetrical stretching band of the carbonyl
groups (in-phase) and has an intensity of 0.47. The vibration at 1724 cm^{-1} is the
asymmetrical stretching band of the carbonyl groups (out-of-phase) and has an
intensity of 1.72. Dine-Hart and Wright [12] explained that such a weakening
of the in-phase carbonyl vibration is due to a tendency of a coaxial alignment in
these two carbonyl groups. Indeed, for many aromatic polyimides, we have
found that the comparison of these two band intensities is an accurate measure
of the structural anisotropy in the thin films [13].

On the other hand, the overall anisotropy within the unoriented film can also
be investigated via two absorptions: one at 1777 cm^{-1} band as used before (in-
plane), and the other at 744 cm^{-1} which represents the out-of-plane bending of
the carbonyl group and possesses a transition moment vector perpendicular to
the imide plane. Recently, it has been observed that the absorption of the IR
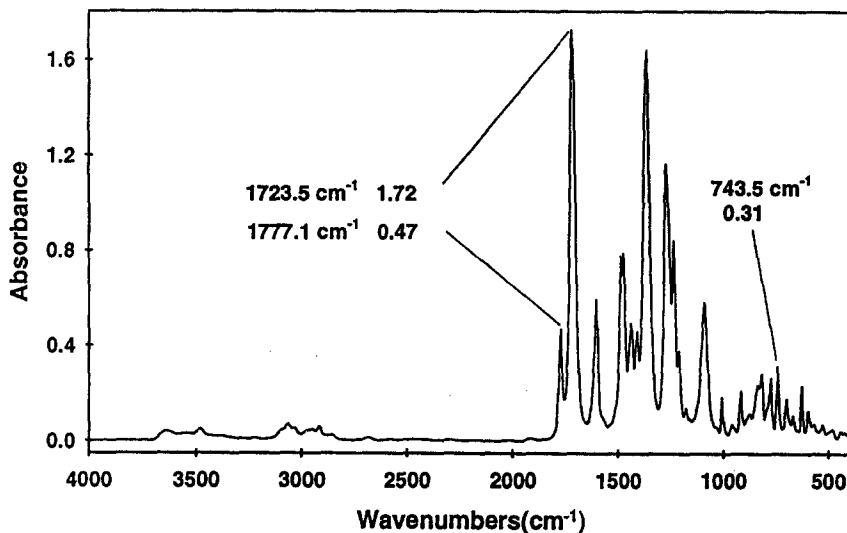beam yields different spectrum intensities at these two bands for other unori-

Fig. 1 FTIR spectrum of ODPA-DMB thin films

ented segmented rigid-rod polyimide films [7]. In ODPA-DMB films, the 1777 cm^{-1} absorption band intensity is relatively strong (0.47) compared to the 744 cm^{-1} band whose absorbance is 0.31. Since the absorption is stronger for the band having the transition moment vector parallel to the imide plane than for the band whose transition moment vector is perpendicular to the imide plane, the molecular axis must thus be more or less parallel to the imide plane. Therefore, an in-plane orientation can be derived.

This in-plane orientation can be further supported by the in-plane and out-of-plane refractive index data. The in-plane refractive index of the ODPA-DMB film is 1.6826 and the out-of-plane refractive index is 1.6377. The resultant birefringence is thus negative and it is –0.0449. In optical physics, this phenomenon is called as "uniaxial negative birefringence" [14]. Since the refractive index is reciprocally proportional to the light speed transmitted in the media, and along the chain direction the light speed is slower than that along the direction perpendicular to the chains. As a result, this negative birefringence is a clear indication that the chain direction is more or less parallel to the thin film surface and thus a molecular anisotropy exists in the thin film.

Thermal stability

In many applications the thermal stability of a polymer is critical. Figure 2 shows the TGA curve of ODPA-DMB powder samples under nitrogen atmosphere. The polymer displays good thermal stability up to at least 400°C (see below). The temperature at 5% weight loss is 503°C. At temperatures slightly higher than this temperature, a stepwise degradation of about 10% weight loss can be found. This may correspond to the loss of methyl groups at the 2- and 2'-positions of DMB which constitute 6.2% of total weight of the repeating unit.

In order to obtain the decomposition activation energy, the sample weight losses at different isothermal temperatures under nitrogen atmosphere for ODPA-DMB are recorded as shown in Fig. 3. From these isothermal degradation experiments, the activation energy of the thermal decomposition can be calculated from a relationship between logarithmic time *vs.* $1/T$ for each constant fractional weight loss [15]. Figure 4 is the calculated activation energy, E_a, for different fractional weight losses. The activation energy over a range of 1~10% weight loss is approximately 210~250 kJ mol^{-1}. This result is somewhat lower than those of other aromatic polyimides such as PMDA-ODA (around 280 kJ mol^{-1}) and BPDA-PFMB (around 300 kJ mol^{-1}) [10] presumably due to the presence of the ether linkage and the methyl groups in the polymer.

Glass transition temperature and coefficient of thermal expansion

Figure 5 shows the dimensional change of the OPDA-DMB films at different applied stresses in the TMA tensile mode. As the temperature increased the di-
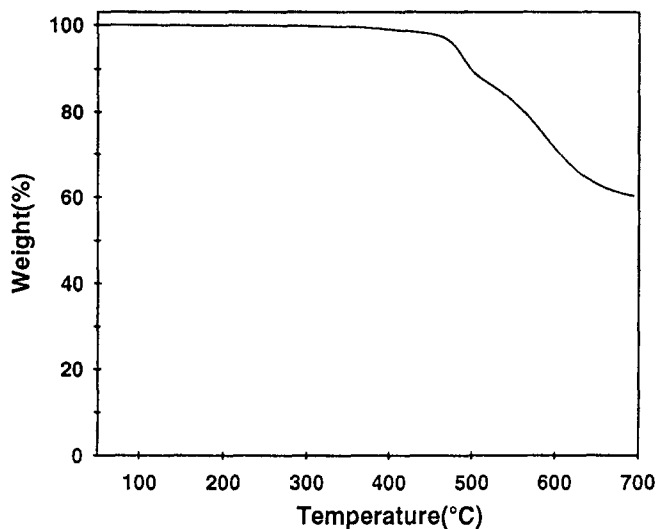
Fig. 2 TGA curve of ODPA-DMB at a heating rate of $10°C$ min^{-1} under dried nitrogen
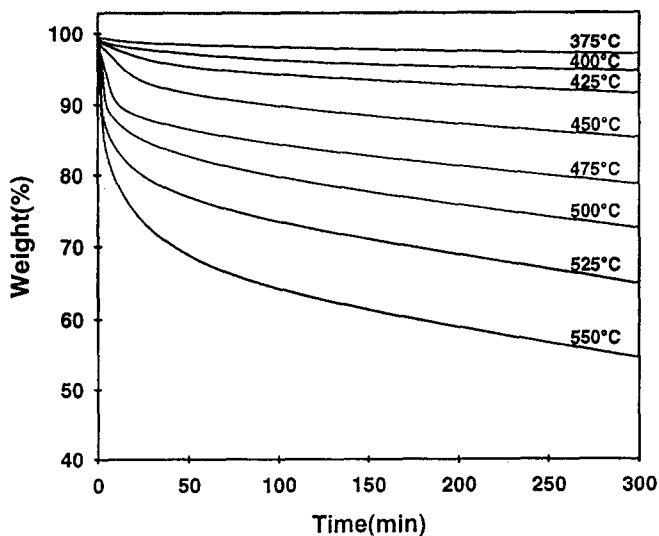

Fig. 3 Isothermal weight loss of ODPA-DMB with respect to time at different temperatures

mensional changes increase almost linearly until a sharp increase at temperatures above 250°C. The linear CTEs of the film at different applied stresses calculated from the slope in the temperature range between 50 and 150°C are shown in Fig. 6. The CTE value is about $50\times10^{-6}/°C$ at a stress of 0.44 MPa, and it increases to $66\times10^{-6}/°C$ at 4.4 MPa. Extrapolation of the CTE values to
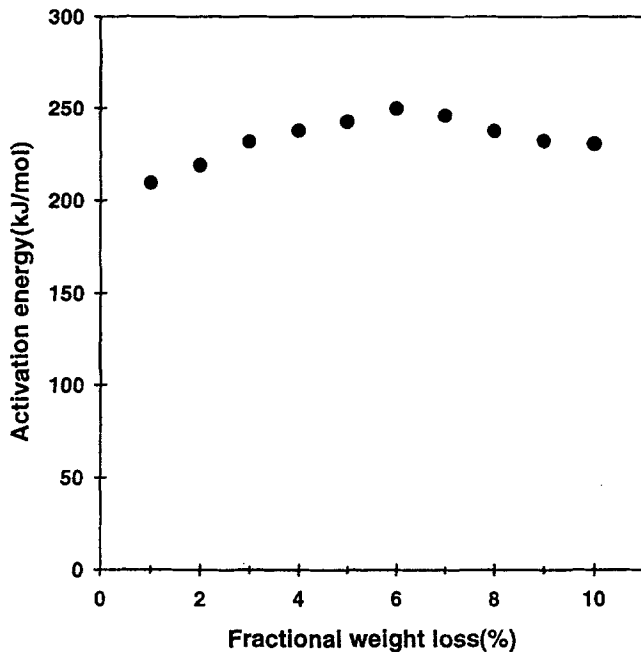
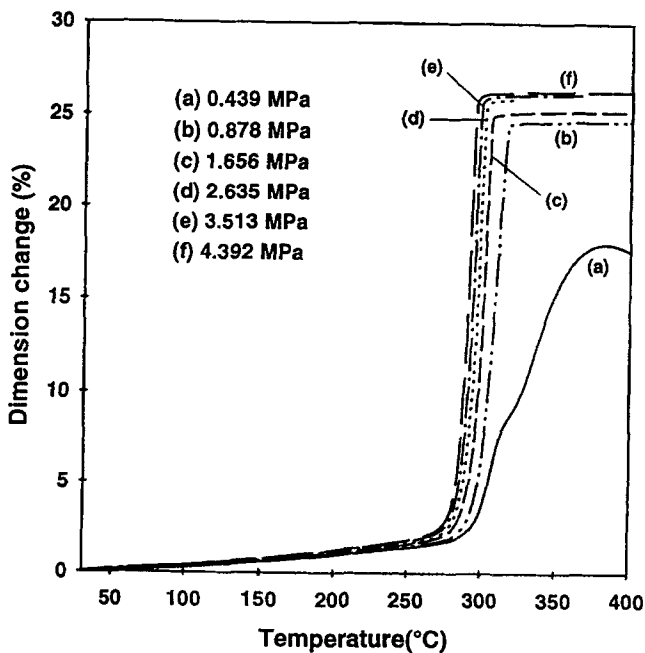Fig. 4 The decomposition activation energy change with the fractional weight loss

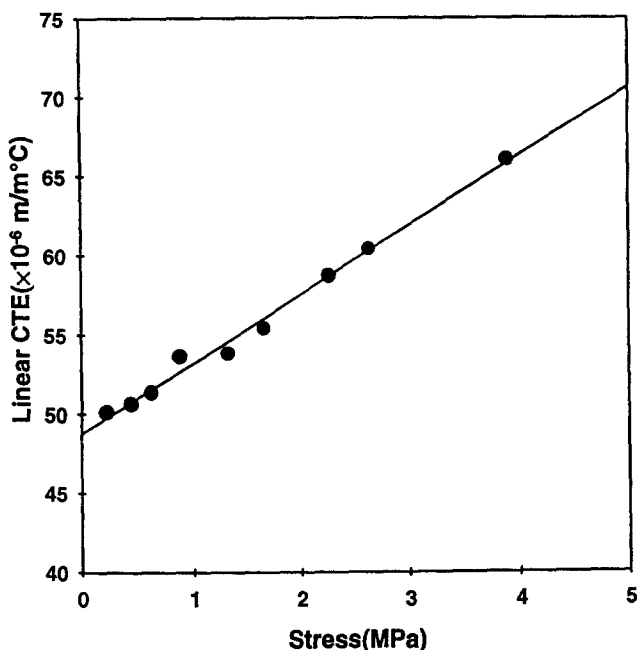Fig. 5 The dimensional change of ODPA-DMB films with temperature at different applied
stresses

Fig. 6 The coefficients of thermal expansion of ODPA-DMB films at different stresses and the extrapolation to obtain the CTE at zero stress

zero stress gives rise to the true CTE value of the film which is found to be $48.8 \times 10^{-6}/°C$.

When a system is under a uniformly applied tensile stress (σ) with a negligibly slow strain rate, the effect of stress on the glass transition temperature, T_g, can be expressed by the following equation [16–18]:

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

where, T_g^o is T_g at zero stress, ε 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 the applied tensile stress is sufficiently small, the exponential function can be expanded using a Tayler series to obtain a first order approximation of

$$T_g = T_g^o - K\sigma \tag{2}$$

where $K = (T_r V/\varepsilon)$ in a unit of °C/MPa. Therefore, there is a linear relationship between the applied tensile stress and the observed T_g as shown in Fig. 7, where T_g is defined as the onset temperature of the abrupt change of slope in the TMA measurements. Upon extrapolation, the T_g of the ODPA-DMB film at zero
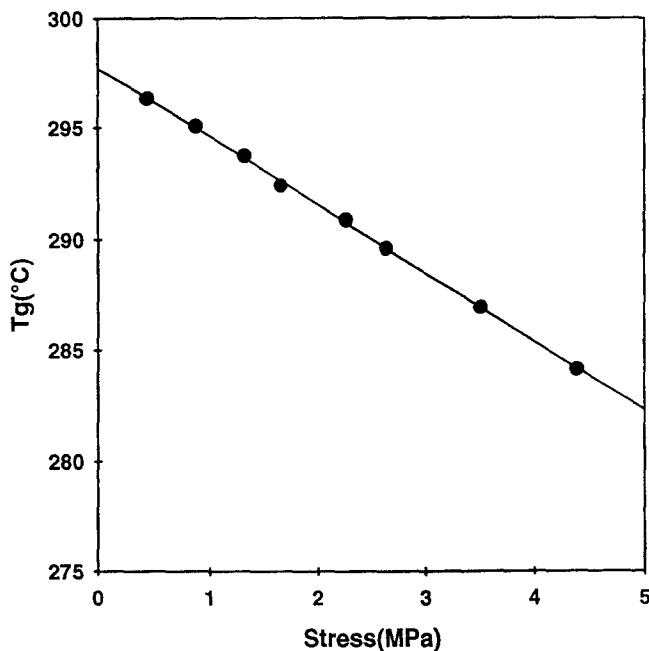
Fig. 7 The linear relationship between T_g and the applied stress. The extrapolation yields a T_g at zero stress of 298°C

stress can be found to be 298°C. This T_g determined from constant stress measurement is in good agreement with the α-relaxation peak (~301°C) observed by DMA analyses at a low frequency (0.1 Hz, see below).

Dynamic mechanical properties

Dynamic mechanical (DMA) data for the OPDA-DMB films (E', E'', tan δ) at several frequencies are shown in Fig. 8. It is obvious that two relaxation processes above room temperature can be identified: an α-relaxation which corresponds to the glass transition and a β-relaxation which is a secondary relaxation. The α-peak temperature is 301°C at 0.1 Hz and 330°C at 50 Hz, whereas the β-peak temperature is 116°C at 0.1 Hz and 185°C at 50 Hz. The peak temperature of the β-relaxation is more sensitive to frequency than that of the α-relaxation, corresponding to a lower activation energy. The origin of this β-relaxation process of aromatic polyimide films has been published before [19]. The observed magnitude of tan δ for the β-relaxation is about 0.1 in this frequency range. However, tan δ values for the α-relaxation shows a broader range of magnitude (0.27 at 50 Hz and 0.41 at 0.1 Hz). This suggests that the α-relaxation is more sensitive to low frequencies which reveals the relaxation time spectrum of the segmental motion occurred at T_g.
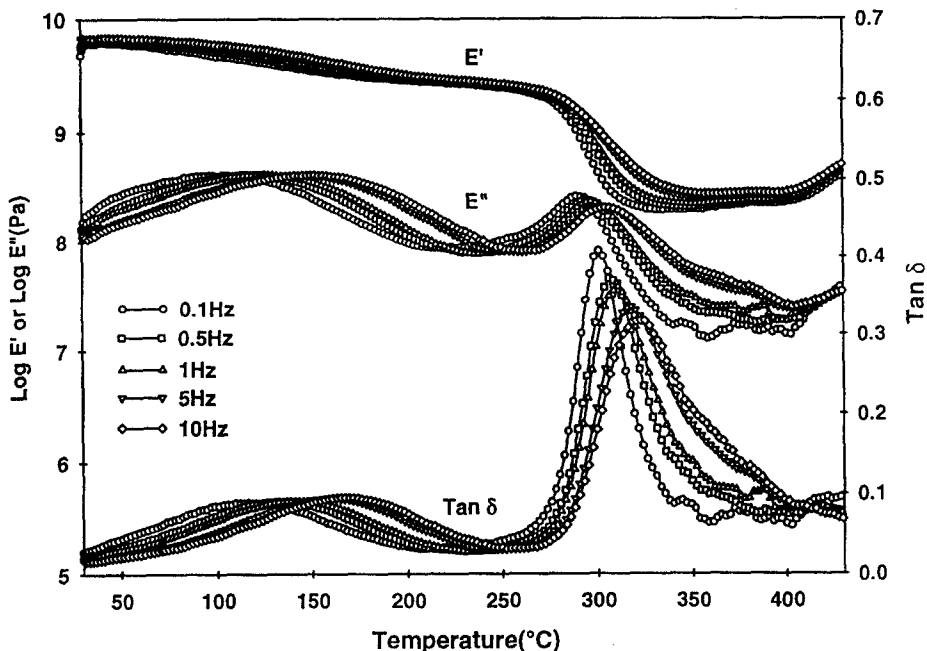
Fig. 8 DMA experimental results (E', E'' and tanδ) for ODPA-DMB films at different frequencies

The frequency dependence of the β-relaxation can be investigated using a simple Arrhenius equation:

$$f = A \exp[- E_a/RT] \qquad (3)$$

where f is the applied frequency, A is a pre-exponential factor, R is again, the universal gas constant, and E_a is the activation energy for the relaxation process. From this equation, we can determine the Arrhenius activation energy for the β-relaxation process by plotting the logarithmic of the frequency vs. the reciprocal of the peak temperature in Kelvin. For the OPDA-DMB films, the activation energy of the β-relaxation is 131 kJ mol^{-1} (Fig. 9). Based on the Erying absolute rate approach suggested by Starkweather [20, 21], an activation energy around 130 kJ mol^{-1} indicates a largely non-cooperative molecular relaxation at this temperature. We can thus conclude that the subsegmental motion responsible for the β-relaxation of as-cast ODPA-DMB is non-cooperative. On the other hand, this equation can also be applied to the α-relaxation to obtain an apparent activation energy of 604 kJ mol^{-1} (Fig. 9). However, it should be pointed out that application of Eq. (3) is not precise since a glass transition process possesses multiple relaxation times as a spectra, which should fit into the WLF
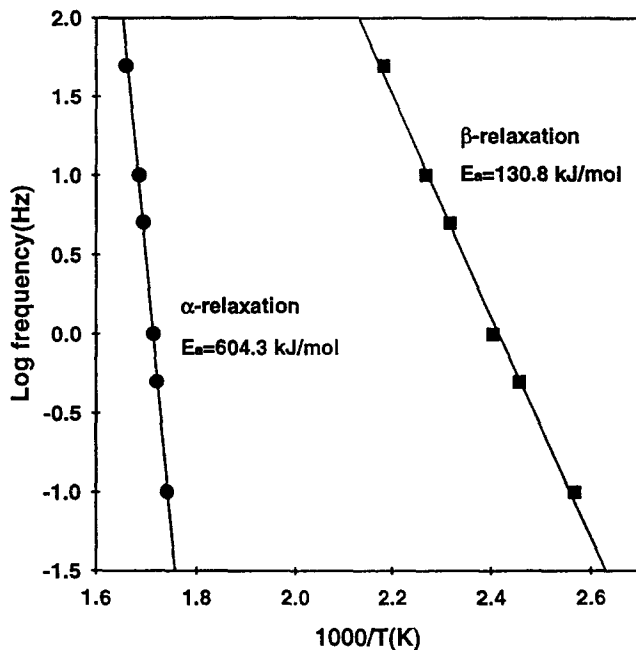
Fig. 9 Relationship between logarithmic frequency and reciprocal E'' peak temperature for both the α- and β-relaxation processes

equation. The apparent activation energy only holds in a limited frequency range such as in the case studied here (a three-order of magnitude range of frequencies).

Conclusion

The segmented rigid-rod polyimide ODPA-DMB has been synthesized *via* the one-step polymerization method. The ODPA-DMB films exhibit in-plane orientation in the molecular scale. This structural anisotropy leads to optical anisotropy with different refractive indices parallel and perpendicular to the film surface (uniaxial negative birefringence). This polyimide shows high thermal and dimensional stabilities and its glass transition temperature is around 300°C. Two molecular relaxation processes have been found above room temperature: the α- and β-relaxations. The α-relaxation corresponds to the glass transition while the β-relaxation is a secondary relaxation. The activation energy data of the β-relaxation indicates that this process is largely due to non-cooperative molecular motion in the solid state.

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