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Contribution of the Dynamic Mechanical Spectroscopy for Studying the Microstructure of Polyimides

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Summary: Different polyimide films based on various aromatic diamines and dianhydrides have been studied by dynamic mechanical thermal analysis. Polyimides exhibit three mechanical relaxations related to specific molecular motions. We have analyzed the sub-glass gamma relaxation which appears at 1Hz in –140°C to –50°C temperature range. This relaxation originates from water molecules in polyimides. Its temperature location strongly depends on the chemical structure of polyimides. Then, the temperature of this relaxation process was correlated to microstructural parameters. It was found that the gamma relaxation shifts towards higher temperatures with: (i) decreasing the free volume; (ii) decreasing the intersegmental distance determined X-ray diffraction; (iii) increasing the wavelengths of 50% transmission determined by UV-visible spectroscopy.

Introduction

The molecular motions of polyimides have been characterized by different techniques including dielectric relaxation,[1-4] nuclear magnetic resonance spectroscopy[1, 5-7] and dynamic mechanical analysis.[4, 8-12] Three relaxations, designed α, β and γ at decreasing temperature, have been detected by Dynamic Mechanical Thermal Analysis (DMTA). The α relaxation related to the glass transition and the sub-glass β processes originate from molecular motions of polyimide sequences. Temperature (or frequency) locations of these relaxation processes strongly depend on the chemical structure of polyimides.[8, 10] In contrast, the γ mechanical relaxation detected in –140°C to –50°C[12] is attributed to the presence of water molecules in polyimides.[1, 13, 14] This transition obeys an Arrhenius law and the activation energy is about 50 kJ/mol.[1, 15]

In this paper, we investigate the correlation of mechanical γ relaxation temperature with microstructural parameters of polyimide, as suggested by a preliminary study focused on three ODA-based polyimides.[12]

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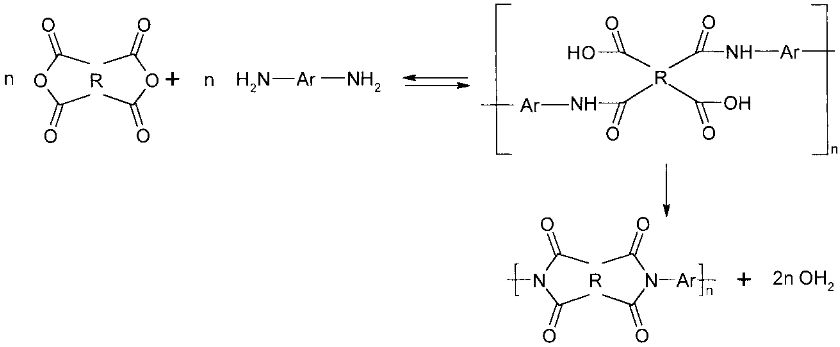
Experimental section

A series of 11 polyimides composed of 4 dianhydrides and 4 diamines were synthesized via a two-step process by thermal imidization method as follows.



Their molecular structures are summarized in Figure 1. All the monomers are commercially available, except for the 2,6-bis-(3'aminophenox)-benzonitrile (BACN) and for the 2-trifluoromethyl-4,4'-diaminodiphenyl ether (ODACF$_3$) which syntheses have been described respectively by Pascal et al.[16] and Pinel.[17] The polyimide syntheses are detailed in a previously reported procedure.[17-19]

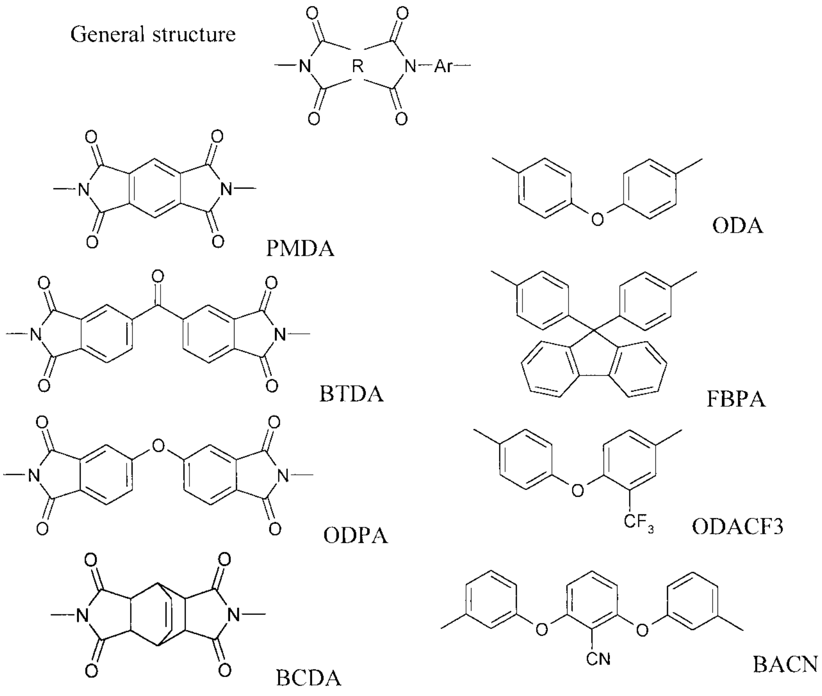


Figure 1. Repeat unit structures of polyimides used in this study.

Films were prepared by casting polyimide solution onto glass plate and then dried in an oven to evaporate solvent. The thickness of the polyimide films peeled from substrates ranged from 10 to 35 μm. Films were maintained under room atmosphere before analysis. Water content was determined by thermogravimetric analysis using a TA2050 – TGA at a heating rate of 5°C/min under air.

Dynamic mechanical thermal analyses (DMTA) were performed using a Rheometrics MKIII at 10Hz. Samples were $(10x5)mm^2$ films at a heating rate of 1°C/min from –150°C to 500°C under dry nitrogen flow. Dynamic strain amplitude of 10μm was superimposed on a static deformation of about 50μm. Densities of the polyimide films were determined at 20°C by the floating method using a mixed solvent of n-hexane and carbon tetrachloride. The free volume fraction (FVF) of the polyimide were calculated by the following equation (1):

$$FVF = 1 - \frac{1.3V_w\rho}{M} \qquad (1)$$

where ρ is the density of the polyimide, M is the molecular weight of the repeating unit, and V_w is the Van der Waals volume calculated using the group contribution method of Bondi.[20-22] Wide-Angle X-ray Diffraction (WAXD) measurements were undertaken on a Siemens D500 X-ray diffractometer with at least 0.05°(2θ) scan increments. The broadness of the diffraction peak obtained for amorphous polymers can be an indicator of the chain spacing. The corresponding d-spacing (d) was calculated from the diffraction peak maximum using the Bragg law, $\lambda = 2\ d \sin\theta$. UV-Visible absorption of polyimide films was measured with a Perkin Elmer Lambda 11 spectrophotometer at room temperature. The color indices of the polyimides were estimated from the wavelengths of 50% transmission for 20μm thick film, $\lambda_{50\%}$.

The microstructural parameters of polyimide films are listed in Table 1.

Results and discussion

Figure 2 displays tanδ versus temperature at 10Hz for ODA-based polyimides. The temperatures (Tγ) at which the γ relaxation maximum occurs are listed in Table 1. It can be observed that the height and location temperature of the gamma relaxation strongly depend on both dianhydride and diamine structures. The tanδ amplitude of the gamma relaxation is related to the water content (Table 1). It is to note that the gamma relaxation disappears by drying the sample in the apparatus[23] but Tγ does not depend on the water content.[1] For each diamine, the dianhydride can be classified as follows according to $T\gamma$.

BCDA < ODPA < BTDA < PMDA.

The influence of the diamine structure is not so clear. Nevertheless, it can be noted that the γ relaxation of FBPA-based polyimides is located at temperature lower than that of other polyimides.

Table 1. Physical properties of polyimide films.

Polyimide	ρ (g/cm^3)	FVF	d (Å)	$\lambda_{50\%}$ (nm)	$T\gamma$ (°C) at 10Hz	Water content (w.t.%)
PMDA-ODA	1.412	0.115	4.23	495	-60	0.3
BTDA-FBPA	1.278	0.146	3.95	490	-90	0.4
BTDA-ODA	1.372	0.122	4.04	490	-80	0.2
BTDA-BACN	1.359	0.121	4.15	525	-80	0.0
ODPA-ODA	1.368	0.134	4.69	455	-100	0.2
ODPA-BACN	1.356	0.142	5.24	385	-90	0.0
ODPA-ODACF3	1.414	0.153	4.37	420	-90	0.5
BCDA-FBPA	1.250	0.157	6.28	320	-125	3.1
BCDA-ODA [12]	1.335	0.136	4.55	320	-115	3.0
BCDA-ODA [23]	1.326	0.150	5.43	430	-120	2.4
BCDA-BACN	1.329	0.132	5.26	355	-100	0.2
BCDA-ODACF3	1.418	0.147	5.57		-110	1.8

Moreover, based on results published by Hirayama et al.[24], we can distinguish two kinds of polyimides: (i) polyimides which $T\gamma$ is located below 115°C at 1Hz (class I) and (ii) polyimides which γ relaxation appears above –80°C (class II). Some of those polyimides are listed in Table 2.

It appears that structures that give rise to polyimides belonging to class I are the dianhydrides, BCDA and 6FDA, and the diamines, TSN, MDX and FBPA. The common point of such chemical structures (Figures 1 and 3) is that they are quite voluminous and induce steric hindrance, which disturbs the chain packing. Moreover, for BCDA, the alicyclic group induces a break in the conjugative structure, resulting in a decrease of the electron affinity of the diimide. In contrast, the dianhydrides PMDA and BPDA have a high electron affinity, 1.9eV[25, 26] and 1.38-1.40eV[25, 26], respectively and have the ability to form charge complex transfer with aromatic ring of diamine moieties. Moreover, the structures of these two dianhydrides and both diamines, HAB and TEPQ, favor chain packing. Indeed, BPDA-TPEQ is a semicrystalline polyimide[24] and PMDA-ODA could exhibit chain ordering.[27]

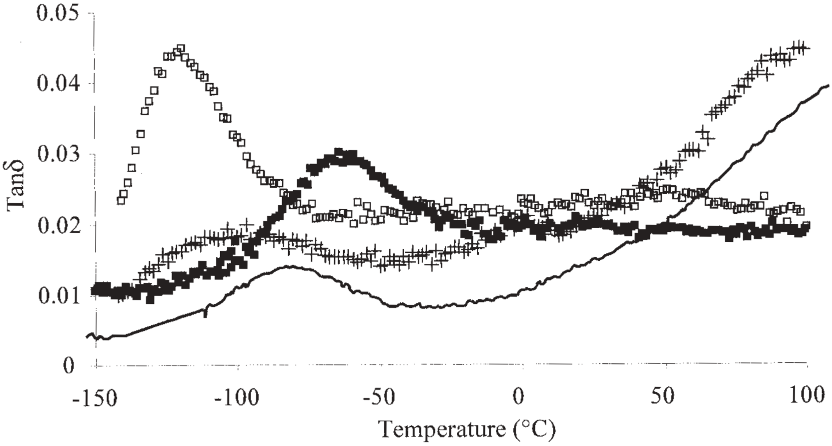


Figure 2. Tanδ at 10Hz as a function of temperature for PMDA-ODA (■), BTDA-ODA (〰), ODPA-ODA (+) and BCDA-ODA (□).

Table 2. γ relaxation temperature of some polyimides reported by Hirayama et al.[24]

Polyimides	Tγ (°C) at 1Hz	Polyimides	Tγ (°C) at 1Hz
6FDA-TSN	-125	PMDA-ODA	-78
BPDA-TSN	-122	BPDA-HAB	-63
6FDA-MDX	-117	BPDA-TPEQ	-78
BPDA-MDX	-124		
PMDA-MDX	-122		
6FDA-ODA	-116		
Class I		Class II	

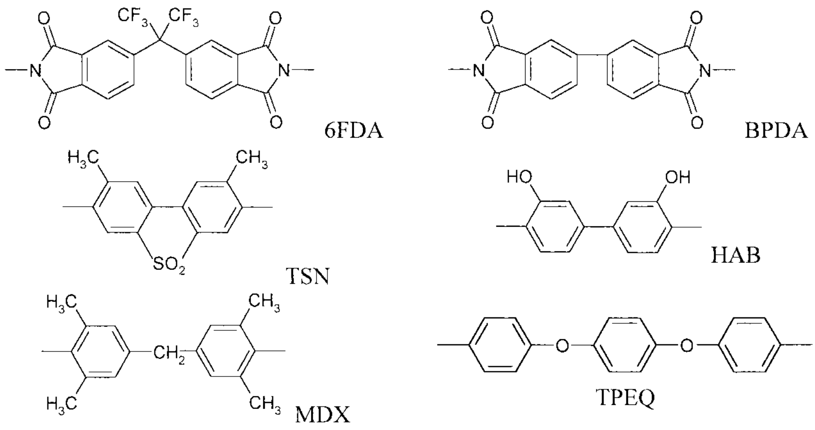


Figure 3. Chemical structure of diimide and diamine moieties previously mentioned.

In such a condition, we can suppose that the gamma relaxation temperature of polyimides could be related to the chain packing. To confirm such a hypothesis, the plots of microstructural parameters versus $T\gamma$ for the studied polyimides are shown in Figure 4. Results reported elsewhere[24] are also plotted in Figure 5. Our experiments show that the gamma relaxation shifts towards higher temperatures by decreasing the interchain distance (Figure 4a). This correlation is confirmed by the analysis of literature results (Figure 5a). This implies that the increase in the chain packing seems to make the water motion at the origin of the sub-glass gamma relaxation more difficult and, in turn, results in a shift of the relaxation towards higher temperatures.

The increase of $T\gamma$ with decreasing the free volume fraction (Figure 4b) is consistent with such an explanation. Nevertheless, results of Hirayama et al.[24] do not give evidence for the FVF/$T\gamma$ correlation (Figure 5b) while these relationship have been observed for polysulfones.[28] The color index ($\lambda_{50\%}$) determined for polyimides films is also a microstructural parameter, as it is mainly due to formation of charge transfer complex.[26] The shift of the gamma relaxation towards higher temperatures is correlated to the increase of $\lambda_{50\%}$ (Figure 5b). So, the increase in the magnitude of interchain interaction suggested by the orange shift of the polyimide coloration results in an improvement of chain packing and, thus, affects the molecular motions, which give rise to the gamma relaxation.

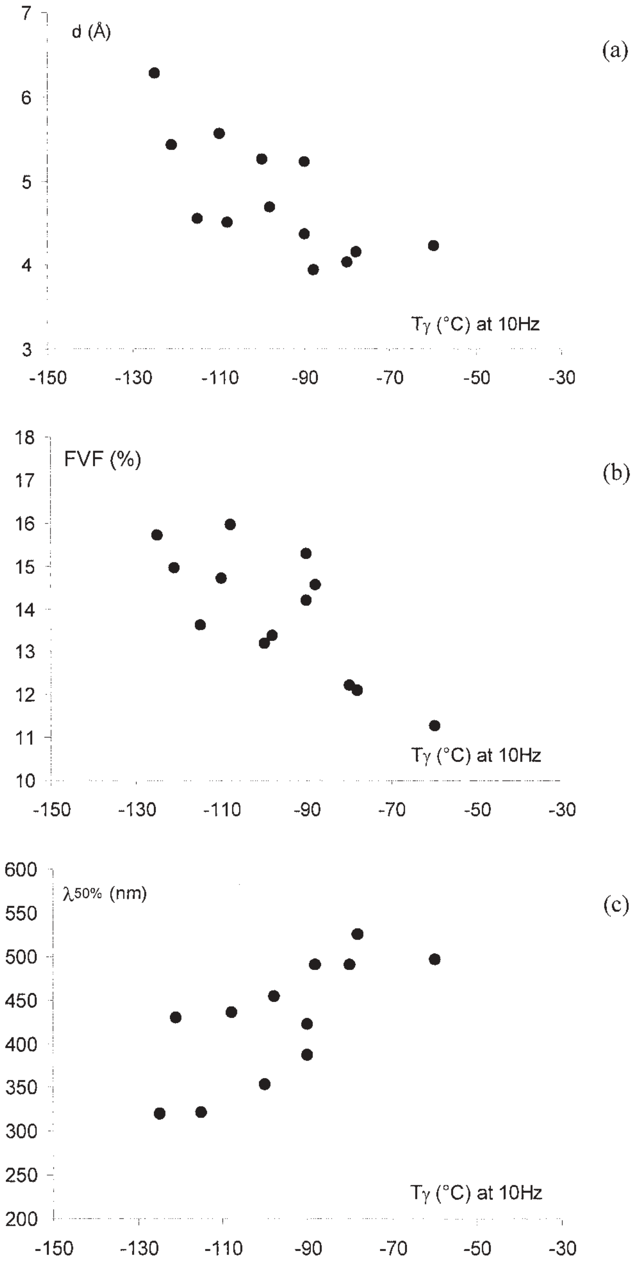


Figure 4. Relationship between the gamma relaxation temperature recorded at 10Hz and microstructural parameters: d-spacing (a), free volume fraction (b) and color index (c).

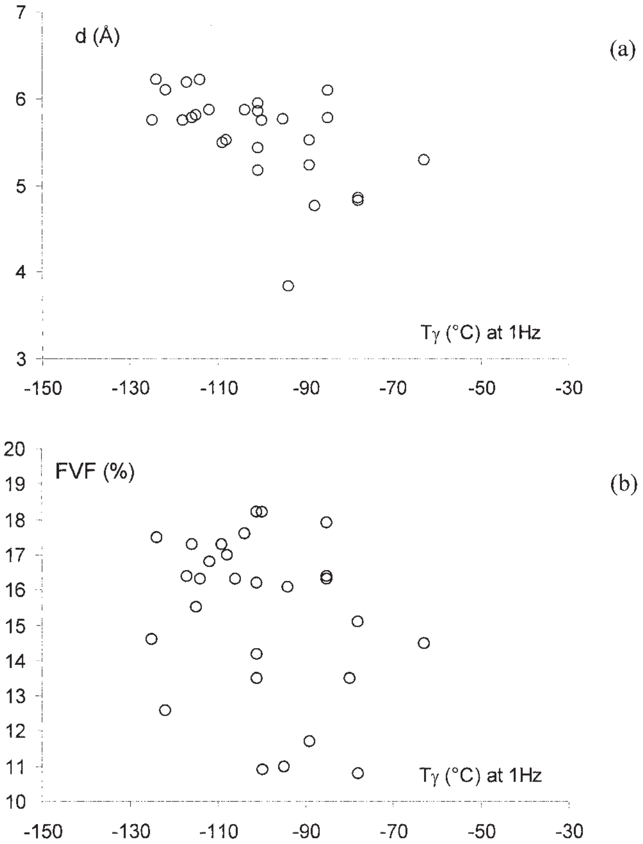


Figure 5. Plot of Tγ versus d-spacing (a) and FVF (b) for Hirayama et al. results.

Acknowledgments

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