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Spectroscopic Studies of
Poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide]. 1. Structures of
the Polyimide and Three Model Compounds

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ABSTRACT: Conformational changes of poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide] and its three model compounds *N*,*N*'-bis(phenoxyphenyl)pyromellitimide, *N*,*N*'-diphenylpyromellitimide, and *N*,*N*'-dicyclohexylpyromellitimide have been studied by UV resonance Raman spectroscopy, Fourier transform infrared spectroscopy, and UV–visible absorption spectroscopy. UV resonance Raman spectra of the polymer were obtained with excitation frequencies of 363.8 and 351.1 nm. Infrared frequency shifts between the difference spectra of crystalline and amorphous phases of the polyimide show that the phenoxyphenyl groups become more coplanar upon crystallization, increasing the conjugative interaction. The nitrogen atom also changes its hybridization state upon crystallization, showing the sensitivity of the lower electronic transition around 378 nm to conformational changes. The nature of this transition is that of a weak R band (n–π*), but intensification to a more K band (π–π*) nature occurs as conjugative interaction increases, providing a molecular probe of conformational changes for the application of UV resonance Raman spectroscopy.

Most molecular theories of yielding suggest that backbone conformational changes, activated by both temperature and the applied stress, contribute to the yielding process in polymer glasses.[1] However, these microscopic structural changes during yielding are quite difficult to characterize experimentally.

Since laser Raman spectroscopy is sensitive to the conformation of the polymer backbone, it has been used to study conformational changes occurring during deformation.[2,3] Conformational transformations and any attendant intermolecular changes that affect the electronic state of the polymer chains may be followed by resonance Raman spectroscopy (RRS). RRS benefits from the considerable enhancement of the Raman signals when the laser exciting line approaches an electronic transition of the molecule. RRS using visible excitation has been reviewed elsewhere.[4,5] Unfortunately, although many synthetic polymers show UV absorptions in the range 200–400 nm, few exhibit absorptions in the visible region where the visible laser lines with wide tunability can be used for RRS studies. In this paper we will use UV laser excitation. No literature is available on the UV resonance Raman spectroscopy of synthetic polymers; however, this technique has shown promise in a few initial studies on biopolymer systems.[6-8]

Poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide] (I) de-

I
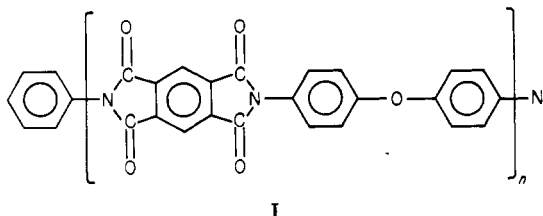
forms uniformly,[9] is thermally stable, and absorbs light in the near-UV range. Therefore, it represents a nearly ideal polymer for the RRS study of the yielding phenomena. Additionally, the stiffness of the pyromellitimide subunit suggests that conformational flexibility might be restricted to the phenoxy oxygen bond, which would obviously simplify the interpretation of the spectra. It is the purpose of this paper to report spectroscopic studies indicating the structural and UV transitional sensitivity to conformational changes; in the following paper this basic information will be used to explore stress-induced structural changes in poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide].

Experimental Section

The three model compounds *N*,*N*'-bis(phenoxyphenyl)pyromellitimide, *N*,*N*'-dicyclohexylpyromellitimide, and *N*,*N*'-diphenylpyromellitimide and the polyamic acid precursor to poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide] were prepared by condensing the respective amines with pyromellitic dianhydride.[10,16] 4-Aminophenyl ether and 4,4'-oxydianiline (Aldrich) were purified by preparing methanol solutions of the original compound and converting the amine to its hydrochloride salt. After the solutions were filtered through a column of activated charcoal to remove unconverted quinones, the amine was regenerated as a precipitate by the addition of NaOH and subsequent washing and drying under vacuum. The lack of substantial coloring in the aniline (Fisher) and the cyclohexylamine (Abbott Labs) allowed their direct use without further purification. Pyromellitic dianhydride (Eastman Kodak Co.) was used after vigorous vacuum drying.

After purification and drying, amine and anhydride were added to dry *N*-methylpyrrolidone (Fisher) in a 2:1 mole ratio to make a 10% by weight solution. Heating these solutions to 175 °C under flowing N$_2$ gas for 2 h and cooling to room temperature yielded crystalline precipitates which were then extensively washed with dimethylformamide (DMF), recrystallized from either dichloroacetic acid or a DMF–methanol mixture, and vacuum dried.

Following the experimental procedure of the original Du Pont work,[10] 4,4'-oxydianiline and pyromellitic dianhydride were first dissolved in dry dimethylacetamide. After the anhydride solution was slowly added to the amine solution and the mixture was stirred for 2 h under a N$_2$ atmosphere, a slightly cloudy, light amber-colored polyamic acid solution of approximately 10% solid content was formed. This solution was filtered and stored at –15 °C for further use.

UV–visible spectra were recorded with a Beckman UV–visible spectrophotometer (Beckman Acta MVI). The model compounds of the polyimide were dissolved either in trimethyl phosphate or dichloroacetic acid, and the spectra were recorded immediately after dissolution. Since SbCl$_3$, the only suitable solvent for the commercial polyimide film (Kapton H, Du Pont), chemically reacted with the polymer after a short time, films of polyamic acid which were 500–2000 Å thick were cast onto a fluorinated ethylene–propylene copolymer film substrate (FEP, Du Pont) after activation of the substrate surface tesla coil discharge. Heating for 1 h under vacuum at ca. 240 °C was sufficient to completely transform this film into an amorphous polyimide.

The infrared spectra were recorded as either KBr pellets or films on alkali halide substrates. The spectral resolution of the Fourier transform infrared spectrophotometer (Digilab FTS-14) was 2 cm^{-1} for all spectra throughout the frequency scale (3800–400 cm^{-1}), the wavenumber accuracy being better than 0.01 cm^{-1} as
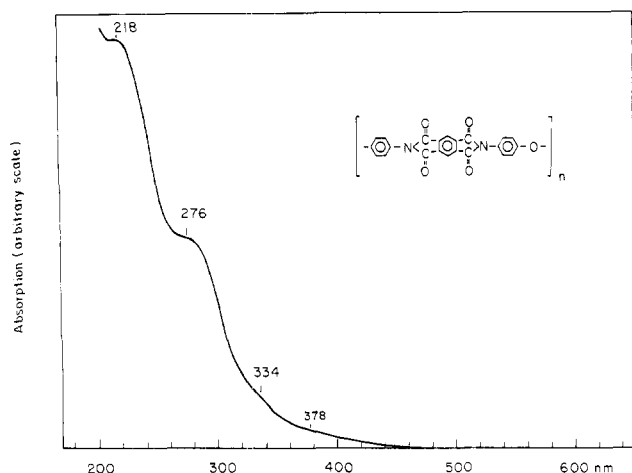
Figure 1. UV–visible absorption spectrum of poly[N,N'-bis-(phenoxyphenyl)pyromellitimide]. A very thin film of about 1000 Å was cast on an FEP substrate.

determined by the He–Ne laser monitoring system. All spectra are shown in absorbance mode.

An Ar^+ ion laser (Coherent Radiation CR-12) that was equipped with special dielectric coated mirrors of high reflectivity in the UV region was used as a source for RRS. In the near-UV region the 333.1-, 351.1-, and 363.8-nm lines can be isolated by interference filters. Although no ion discharge lines are observed with the 333.1-, 351.1-, and 363.8-nm lines, the strong laser lines appear in the RRS spectra. The 333.1-nm excitation interferes with the 351.1-nm line, and the 351.1-nm excitation is disturbed by the 363.8-nm line. The spectra were obtained with a holographic grating double monochromator (Spex 14018; blazed at 500 nm) coupled with a photomultiplier tube (RCA C-31034) and photon-counting electronics. The effective power on the sample is 1 mW for the 363.8-nm line and 4 mW for the 351.1-nm line, thus avoiding sample degradation and heating. The effective power of the 333.1-nm line is less than 1 mW. When the sample degrades, a fluorescence peak appears in the Raman spectrum which can be used as a measure of the degradation. A sample rotator is used throughout the experiments in order to minimize the heating problem. A commercial polyimide film of thickness 0.076 mm was used in our studies of the resonance Raman spectra of the polymer. Powders of the model compounds were mixed with $(NH_4)_2SO_4$ internal standard and KBr powder and pressed into pellets. Intensity measurements of the Raman signal were made by comparing the peak heights of the sample with the sulfur–oxygen stretching mode of the standard at 975 cm^{-1}.

Results

A. Ultraviolet Spectra of Polyimide and Model Compounds. A thin film cast from an $SbCl_3$ solution of the commercial grade film left $SbCl_3$ as an unwanted impurity; since this is the only solvent known to dissolve the polyimide,[11] we used the polyimide synthesized in our laboratory in order to avoid the use of $SbCl_3$. A very thin film of poly[N,N'-bis(phenoxyphenyl)pyromellitimide] (I) cast on an FEP film has absorption maxima at 218, 276, 334 nm and a very broad peak centered around 378 nm which extends as far as 500 nm (Figure 1). The FEP film used as a substrate has no transition in this frequency range. Since our ultimate concern is the yielding mechanism of the polyimide on the molecular level using resonance Raman spectroscopy with the UV laser line at 363.8 nm, an understanding of the nature of the very broad and weak transition around 378 nm is essential for the interpretation of the resonance Raman spectrum of the polyimide. This broad peak at 378 nm has been postulated to arise from an interaction, either inter- or intramolecular, between the pyromellitimide and phenoxyphenyl moieties since neither individually gives rise to a transition at such a low wavelength.[33] A determination of the inter- or in-
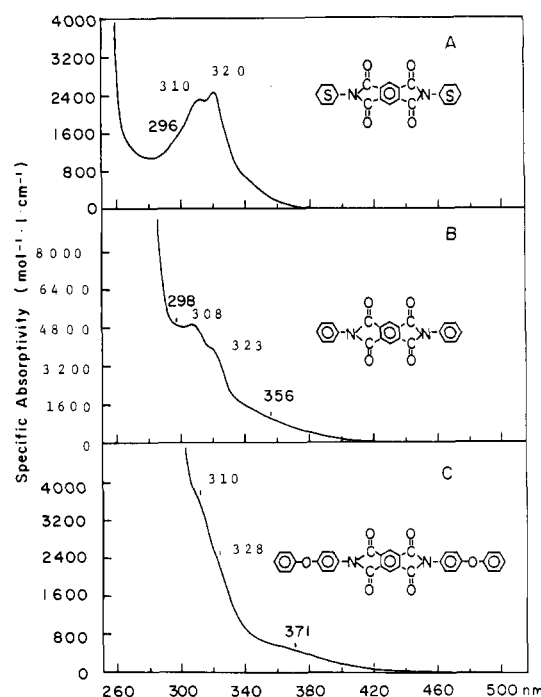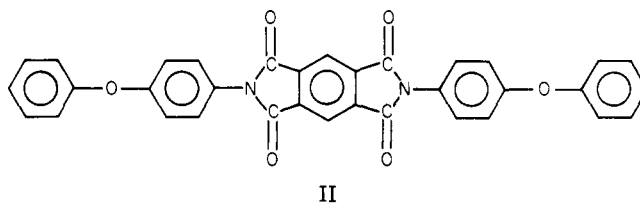

Figure 2. UV–visible absorption spectra of the model compounds of the polyimide as 1.5×10^{-4} M trimethyl phosphate solutions: (A) N,N'-dicyclohexylpyromellitimide; (B) N,N'-diphenylpyromellitimide; (C) N,N'-bis(phenoxyphenyl)pyromellitimide.

tramolecular nature of this transition can be made from the concentration dependence of the absorption intensity.

The complications of the $SbCl_3$–polymer system and insolubility of the polymer in all other solvents necessitated the synthesis of the model compound N,N'-bis(phenoxyphenyl)pyromellitimide (II), which has significant solu-

II

bility in dimethyl sulfoxide, trimethyl phosphate, and dichloroacetic acid. The UV–visible absorption spectrum of a trimethyl phosphate solution of II, shown in Figure 2, has absorption maxima at 310, 328, and 371 nm. Hypochromism, a red-shift in a more polar solution, was seen for the 371-nm transition which shifts to 385 nm in a dichloroacetic acid solution. The same trend was observed for the 310- and 328-nm transitions which merge and shift to 330 nm.

Dilute trimethyl phosphate and dichloroacetic acid solutions of II were made at concentrations ranging from 2.5 $\times 10^{-4}$ to 5.0×10^{-6} M and from 2.5×10^{-3} to 5.0×10^{-6} M, respectively. The intensity measurements at 320 and 360 nm for the trimethyl phosphate solutions and at 400 nm for the dichloroacetic acid solutions show that the intensities are a linear function of concentration, even at concentrations as low as 5.0×10^{-6} M (Figure 3). Thus the transition at 378 nm is associated with an intramolecular transition.

N,N'-Diphenylpyromellitimide (III) was synthesized to further study the effect of N-imide substitution on the spectrum. Pale yellow crystals (III) were obtained in contrast to the bright yellow color of the bis(phenoxyphenyl) model compound II. The broad absorption in the 330–400-nm region is blue-shifted relative to the bis-

III
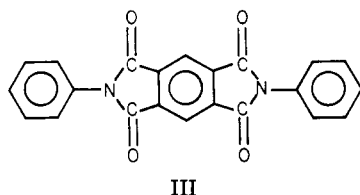
(phenoxyphenyl) compound II or the polyimide I, but the intensity seems to be slightly higher than the bis(phenoxyphenyl)-substituted compound; peak maxima are found at 298, 308, 323, and 356 nm (Figure 2).

Unlike the aromatic substituted compounds, N,N'-dicyclohexylpyromellitimide (IV) has no color; peak maxima

IV
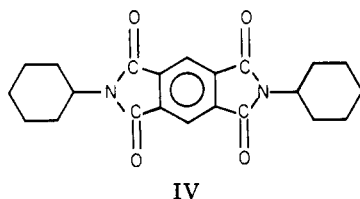
are found at 296, 310, and 320 nm (Figure 2). A shoulder at 345 nm which is probably related to the lowest frequency band of the other model compounds is also observed. In summary, the transition at 378 nm of the polymer I is associated with either the central phenyl group, the carbonyl groups, or the nitrogen atom but not entirely with the phenoxyphenyl group, as it occurs for the model compounds with no phenoxyphenyl.

B. Vibrational Spectra. The Raman spectrum of the poly[N,N'-bis(phenoxyphenyl)pyromellitimide] (I) (commercial grade) was recorded by using the laser exciting line at 363.8 nm (Figure 4). Due to the very weak Raman scattering of the polyimide, relatively low resolution (10 cm⁻¹) was used. However, the intrinsic line width, not the low resolution, is responsible for the broadness of the Raman lines. A high-resolution spectrum revealed that two strong lines centered at 1610 and 1394 cm⁻¹ were actually multiple lines which were still very broad. Detailed Raman and infrared frequencies are tabulated in Table I for the model compound as well as the polymer. The complicated molecular structure makes the assignments of vibrational modes very difficult; yet some tentative assignments are made and listed in Table I. Similar frequencies among the compounds originate in the pyromellitimide group, but attached substituents disturb the frequencies involving the nitrogen atom.

The biaxially oriented, highly crystalline commercial film[10] was too thick for infrared transmission studies and was not amenable to modification of its crystallinity. We could prepare isotropic thin films of variable crystallinity by casting the synthesized polyamic acid upon a suitable substrate. Figure 5 shows the FT IR difference spectra of spectroscopically purified amorphous (A) and crystalline (B) synthesized polyimides, using the spectral subtraction technique reported in the literature.[12] The infrared spectra before and after annealing were recorded and used to generate the difference spectra shown in Figure 5.

The Raman and FT IR spectra of the N,N'-bis(phenoxyphenyl)pyromellitimide (II) are illustrated in Figures 6 and 7, respectively. The major difference of the spectral features between the polyimide I and the model compound II arises, at least in part, from the terminal monosubstituted phenyl groups and large crystallinity differences. Some additional modes are observed in the spectrum of the model compound, probably due to the crystal field splitting. Nonetheless, the general spectral features are quite similar. Although the Raman spectra of the poly-
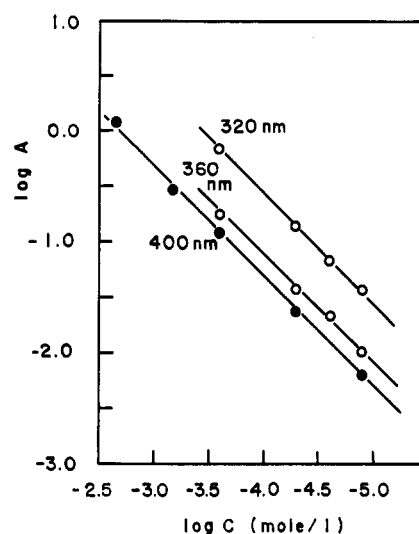

Figure 3. Intensity measurements of the UV absorptions of N,N'-bis(phenoxyphenyl)pyromellitimide at 320 and 360 nm for trimethyl phosphate solutions and at 400 nm for dichloroacetic acid solutions at various concentrations.
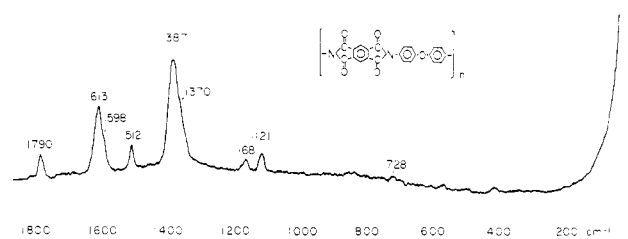

Figure 4. UV resonance Raman spectrum of commercial poly-[N,N'-bis(phenoxyphenyl)pyromellitimide] with the exciting laser line at 363.8 nm at 10-cm⁻¹ resolution and 30-mW laser output power (effective power at the sample is about 1–2 mW).
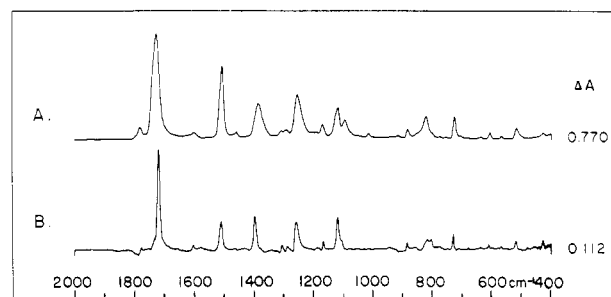
Figure 5. FT IR difference spectra of amorphous (A) and crystalline (B) poly[N,N'-bis(phenoxyphenyl)pyromellitimide] recorded at 2-cm⁻¹ resolution. A thin film was cast on a KBr plate. The polyimide was annealed at 400 °C for 3 h under N₂ gas in order to produce a crystalline phase rich sample.
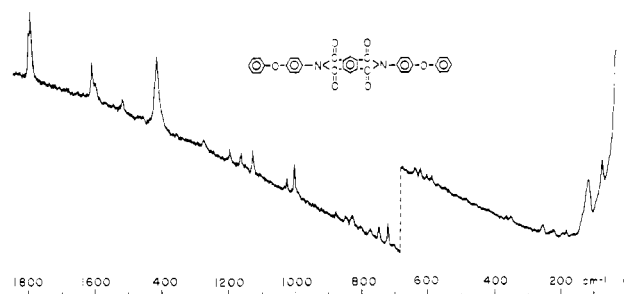

Figure 6. Raman spectrum of N,N'-bis(phenoxyphenyl)pyromellitimide excited at 488.0 nm with 4-cm⁻¹ resolution and 100-mW laser output power.
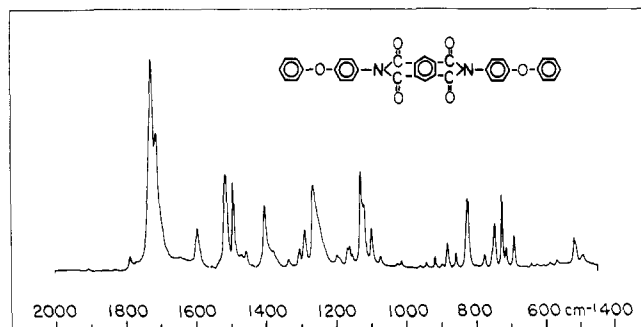
Figure 7. FT IR spectrum of *N,N'*-bis(phenoxyphenyl)pyro-mellitimide as a KBr pellet with 2-cm^{-1} resolution.
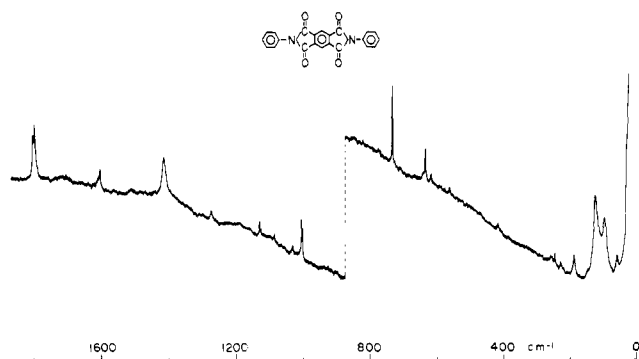

Figure 8. Raman spectrum of *N,N'*-diphenylpyromellitimide excited at 514.5 nm with 2-cm^{-1} resolution and 70-mW laser output power.
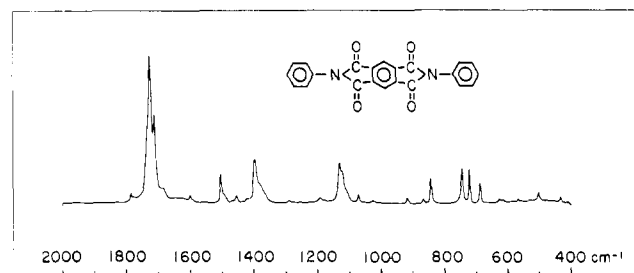

Figure 9. FT IR spectrum of *N,N'*-diphenylpyromellitimide as a KBr pellet with 2-cm^{-1} resolution.

imide and model compound show almost the same band-widths for the C=O stretching modes at 1789 cm^{-1}, there is remarkable narrowing of the lines of the bis(phenoxy-phenyl) model compound II at 1610 and 1414 cm^{-1}. Half-widths of the 1789-, 1610-, and 1414-cm^{-1} lines, re-corded at 4-cm^{-1} resolution with the 488.0-nm laser line, are 10, 31, and 35 ± 1 cm^{-1}, respectively, for the polyimide I and 10, 8, and 14 ± 1 cm^{-1}, respectively, for the bis-(phenoxyphenyl) model compound II. Conformational effects are probably responsible for this difference.

N,N'-Dicyclohexylpyromellitimide (IV) was synthesized to study the contribution of the central phenyl group to the spectrum of the polyimide. One of the striking aspects of this compound is that the C=C stretching modes at 1625 and 1615 cm^{-1} of the central phenyl are extremely weak in the infrared and Raman spectra as a consequence of the four strong electron-withdrawing C=O groups at-tached to this moiety[19] (Figures 10 and 11). The stronger bands observed in the region of 1615–1598 cm^{-1} in both the infrared and Raman spectra of the polyimide and aromatically substituted model compounds were therefore assigned to the C=C stretching modes of the aromatic substituents (Figures 4–9). The only C=C stretching mode in the Raman spectrum of *N,N'*-diphenylpyro-
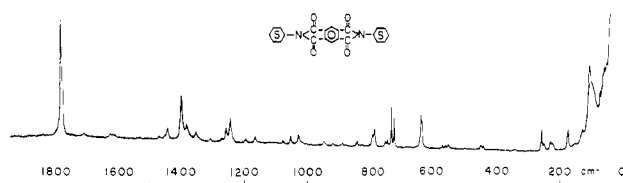

Figure 10. Raman spectrum of *N,N'*-dicyclohexylpyromellitimide excited at 514.5 nm with 4-cm^{-1} resolution and 100-mW laser output power.
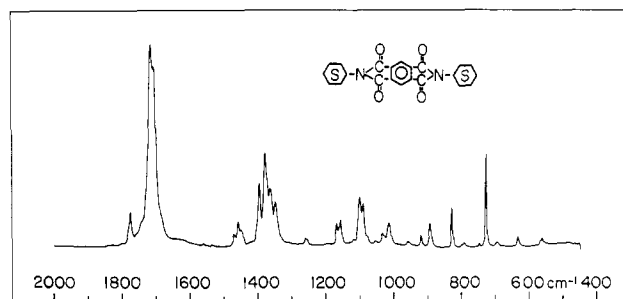

Figure 11. FT IR spectrum of *N,N'*-dicyclohexylpyromellitimide as a KBr pellet with 2-cm^{-1} resolution.

mellitimide (III) is found at 1602 cm^{-1} (Figures 8 and 9). Therefore, the Raman lines observed at 1608 and 1598 cm^{-1} in the bis(phenoxyphenyl) model compound II can be assigned to the disubstituted and monosubstituted phenyl groups, respectively.

The local symmetry around the central phenyl group of all the model compounds belongs to the point group D_{2h} which has a center of inversion. Therefore, to a first ap-proximation, the infrared and Raman intensities should obey a mutual exclusion principle. Although all the vi-brational modes appear in both infrared and Raman spectra due to the perturbation by the terminal substitu-ents, the strong modes in the infrared spectrum appear weakly in the Raman spectrum and vice versa. Even though the above intensity relationships between the in-frared and Raman spectra hold for most of the modes, there are strong multiple modes in three model com-pounds. Closer observation reveals slight frequency dif-ferences between the infrared and Raman spectra of these modes. Also, there are always weak counterparts at the same frequencies in the complementary spectrum, sug-gesting that these strong modes do not belong to the same vibrational modes.

C. Resonance Raman Spectra. Conformational perturbations induced by an applied stress may have a significant effect upon the electronic structure of the po-lyimide molecules and, thus, upon the resonance Raman spectrum. Therefore, it is essential to understand the origins of resonance enhancement. A useful method is to obtain Raman spectra at various excitation frequencies and plot excitation profiles, that is, intensity variations as a function of the excitation frequencies. The excitation profile is determined by the type of the electronic tran-sition. Those Raman lines arising from the structure giving rise to the electronic transition will be enhanced while others will not. Figure 12 shows the excitation profile of the resonance Raman spectra of *N,N'*-bis(phenoxyphenyl) pyromellitimide (II) where peak heights are measured relative to the peak of the internal standard, $(NH_4)_2SO_4$. Since the samples are made in KBr pellets, correction for the self-absorption is difficult. The intensity of the 1413-cm^{-1} line due to the CN stretching mode increases slowly as the excitation frequency approaches the UV re-gion while the 1625-cm^{-1} line which is assigned to the C=C stretching mode of the central phenyl group shows a more

Table I

imide								
I		**II**		**III**		**IV**		
IR		IR	Raman	IR	Raman	IR	Raman	tentative assignt
crystal	amorph							
		1797 sh	1796 sh	1787? w	1797 sh	1784 sh	1785 sh	}ν(C=O) in-phase
1779 w	1777 vw	1787 w	1791 vs	1779? vw	1793 vs	1779 w	1780 vs	
1725 vs	1717 vs	1725 vs		1726 vs		1714 vs	1710 vw	}ν(C=O) out-of-phase
		1712 s		1712 s		1706 s	1704 vw	
1625 vw			1626 m			1625 vw	1625 vw	ν_{16}, 1,2,4,5-C$_6$H$_2$
		1619 vw	1615 sh				1615 vw	ν_{16}
		1608 vw	1608 s					ν_{16} 1,4-C$_6$H$_4$
1600 vw	1602 vw	1599 sh	1598 sh	1601 w	1600 m			ν_{16} C$_6$H$_5$
1596 sh		1594 w						ν_{16}' 1,4-C$_6$H$_4$
		1586 sh	1587 sh	1592 vw				ν_{16}' C$_6$H$_5$
						1562 vw		
1555 vw		1554 vw		1552 vw				
						1536 vw		
1505 s	1508 m	1513 m	1517 w					ν_{13} 1,4-C$_6$H$_4$
		1492 m	1489 vw	1504 m	1507 w			ν_{13} C$_6$H$_5$
		1476 vw		1495 w		1480 vw		
1468 vw		1469 vw	1466 vw			1468 vw		ν_{13} 1,2,4,5-C$_6$H$_2$
1456 vw		1456 vw	1459 vw			1456 vw	1454 w	}δ(CH$_2$) C$_6$H$_{11}$
						1448 vw		
						1445 sh	1444 w	
1438 vw		1437 vw		1436 vw				ν_{13}' 1,4-C$_6$H$_4$
			1420 sh	1423 w				ν_{13}' C$_6$H$_5$
		1419 vw	1419 sh					
				1412 sh	1412 vs			
		1403 m	1402 sh	1400 sh	1400 sh	1401 sh	1401 m	
				1399 m				
						1395 m		
							1385 w	}ν(CN) (OC)$_2$NC
1383 m	1396 m	1379 vw		1381 sh		1379 m		
						1375 sh	1373 sh	
						1364 m		
							1356 vw	γ_w(CH$_2$) C$_6$H$_{11}$
						1348 m		
		1335 w		1321 vw				ν_9 C$_6$H$_5$
1307 w	1304 w	1304 w				1310 vw	1309 vw	
1290 w	1286 w	1289 w		1292 w				
			1275 w		1272 w		1273 vw	ν_{as}(COC)
1252 m	1257 m	1264 m						
						1262 vw	1260 w	
		1250 sh		1254 vw		1257 vw		γ_t(CH$_2$) C$_6$H$_{11}$
							1246 w	
1202 vw		1198 vw	1198 vw	1194 w		1195 vw	1198 vw	ν_{17}' 1,2,4,5-C$_6$H$_2$
1188 vw	1188 vw	1190 vw						ν_{17}' 1,4-C$_6$H$_4$
				1176 vw				ν_{17}' C$_6$H$_5$
1168 w	1166 w	1169 vw				1168 w	1167 w	
						1161 sh		
		1155 vw	1152? vw	1148 sh		1157 w		imide III (OC)$_2$NC
1117 m	1119 m	1129 m	1129 m	1131 m	1129 m			
		1121 w		1123 sh		1119 vw	1123 w	
				1110 sh				
						1100 m	1102? vw	
1095 w		1099 w				1080 sh	1079 vw	
1075 sh		1073 vw		1072 w				
						1055 vw	1056 w	
1051 vw								ν(C-C) C$_6$H$_{11}$
						1033 vw	1031 w	
		1025 vw	1028 w	1027 vw	1029 w			ν_{14} C$_6$H$_5$
		1013 vw		1015 vw		1014 w		ν_6 1,2,4,5-C$_6$H$_2$
			1004 m	1002 vw	1001 s			ν_6 C$_6$H$_5$
		960 vw				959 vw		
						952 sh	953 vw	
		943 vw						
916 vw		918 vw		919 w		922 w	922 vw	ν_{11}' 1,2,4,5-C$_6$H$_2$
		914 sh		915 sh				ν_{11}' C$_6$H$_5$
		896 vw				894 w	892 vw	
885 sh	885 w	882 w	880 vw					
		865 sh		869 w				
855 sh			852 vw					
				844 m			845 vw	
			833 vw					
821 m	818 w	824 m	821 vw	830 vw		829 m	830 vw	γ_w 1,2,4,5-C$_6$H$_2$
			805 vw					

Table I (*Continued*)

imide								
I		**II**		**III**		**IV**		
IR		IR	Raman	IR	Raman	IR	Raman	tentative assignt
crystal	amorph							
800 sh	804 w	797 vw		798 vw		799 vw	793 w	
						790 sh		
776 vw		774 w	777 vw					
752 vw		753 sh	751 w			749 vw	750 w	
		747 m		745 m				ν_4 C_6H_5
					733 vs		737 m	imide IV
726 m	729 w	726 m	725 m	723 m		728 m	728 m	
						724 sh		
		713 w						
705 vw			706 vw					
						698 vw		δ(CON)?
						693 vw		
		691 w		689 m				ν_8 C_6H_5
644 vw		643 vw	643 w				643 w	
					634 m	634 w		
630 vw		625 vw	629 vw					
				617 vw	616 w			ν_{18} C_6H_5
606 w	609 vw	608 vw	609 w					ν_{18} 1,4-C_6H_4
			593 w					
							578 vw	
568 vw		569 vw		569 vw		567 vw	567 vw	δ_{as}(C,C>NC)?
				562 w		562 vw		
			555 vw				556 vw	
518 w	520 w	518 w						
		514 sh						ν_{19}'? 1,4-C_6H_4
				505 w				ν_{19}' C_6H_5
500 sh		497 sh						δ_s(COC)
		492 vw						
							453 vw	ring def C_6H_{11}
							445 vw	
				435 w				
429 vw	427 vw	427 vw				419 w		
							398 vw	
		372 vw					374 vw	
		354 vw						
							345 vw	
							299 vw	
		260 w		259 w			260 w	
				248 w				
				231 w			231 vw	
		224 w					223 w	
		199 vw						
		186 w						
							177 w	
							153 vw	
		138 sh						
		124 vs					127 w	
		98 sh					103 s	
		80 s					65 sh	

abrupt increase. The intensity of the 1610-cm⁻¹ line due to the phenoxyphenyl carbons also increases with frequency but more slowly than the 1625-cm⁻¹ line. Exceptionally, the intensity of the 1794-cm⁻¹ line of the carbonyl groups decreases when the frequency of the exciting line increases. The resonance Raman behavior of the polyimide shows the same features of the model compound II. Unfortunately, the difficulty in introducing an internal standard into the polymer allowed only a relative comparison between the resonance enhancement of the lines. In summary, therefore, we have observed resonance enhancement of the vibrational modes of the central phenyl group, disubstituted phenyl group, and CN bonds using the 363.8-nm exciting line.

Discussion

A. Vibrational Spectra. The lack of crystal field splitting makes the vibrational spectrum of the polyimide much simpler than the spectra of its model compounds.

The degree of splitting among the model compounds depends upon the type of vibrational mode, with the modes related to the cyclohexyl group exhibiting the largest effect. Some additional spectral complications are observed because of the coexistence of the amorphous and crystalline phases of the polymer. The spectrum of each of these phases can be obtained by subtraction (Figure 5). The differences between the spectra of the polymer crystals and the crystalline model compounds could arise from differences in crystal structures and terminal effects. Kazaryan et al.[14] reported that poly[*N*,*N*'-bis(phenoxyphenyl)pyromellitimide] (I) has a planar zigzag conformation and one chemical repeat unit per unit cell. This crystal structure is consistent with the absence of crystal field splitting in the polymer.

In the absence of X-ray structural data on the model compounds, the strong, localized in-phase C=O stretching modes at 1730–1700 cm⁻¹ can be employed to gain insight into differences in intermolecular packing. Since the
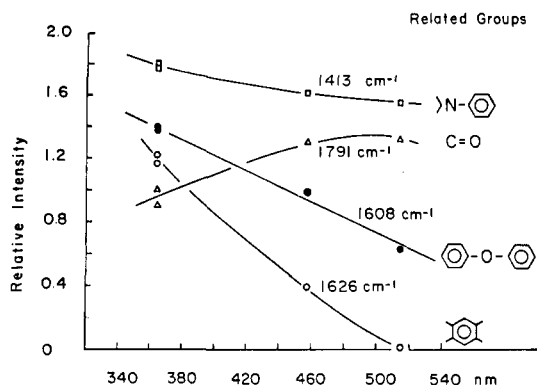
Figure 12. Excitation profile of N,N'-bis(phenoxyphenyl)pyromellitimide measured in a KBr pellet. Relative peak heights with respect to the peak height of an $(NH_4)_2SO_4$ internal standard are measured. The excitation frequencies are at 514.5, 457.9, and 363.8 nm. The resolution is adjusted at 10 cm^{-1} for all the spectra and the effective laser power at the sample is less than 5 mW at all the frequencies.

splitting of this mode is known to be a dipole–dipole coupling effect where $\Delta\nu$, the splitting frequency, increases as neighboring C=O groups approach each other,[15] the $\Delta\nu$'s observed for the dicyclohexyl, diphenyl, and bis(phenoxyphenyl) model compounds (8.9, 13.0, and 13.6 ± 0.1 cm^{-1}, respectively) indicate that the packing increases in this order. Judging from the packing differences of the cyclohexyl (IV) and phenyl (III) N,N'-disubstituted compounds, the coplanarity of the central phenyl ring with the substituted phenyl group is greater than for the cyclohexyl group. This result is in agreement with the reports[16,17] that a conjugation exists at the $>$N–C_6H_5 bond. An opposing force toward nonplanarity exists as a result of interaction between the oxygen lone-pair orbitals and the orbitals of the substituted phenyl groups when the planes of the C=O bonds and the phenyl groups are perpendicular to each other.[18] This interaction could stabilize the phenyl group in a skewed position at some angle between 0 and 90°. The similar $\Delta\nu$'s found for N,N'-diphenylpyromellitimide (III) and N,N'-bis(phenoxyphenyl)pyromellitimide (II) suggest that the rotation of the phenyl and phenoxyphenyl groups from the plane of the carbonyl group may be virtually the same. Close packing would also be promulgated if the phenoxyphenyl moiety retained the Morino structure.[19] The Morino structure exhibits a conformational energy minimum[20] where the phenyl rings bridged by the oxygen atom are skewed from coplanarity by ca. 35°.

Very strong Raman lines appear for all the materials studied around 1440–1370 cm^{-1}, a region where no phenyl or carbonyl modes are expected. These modes have been assigned as imide II bands where the stretching mode of the C,C$>$N– principally contributes.[16] The stretching mode of a CN group adjacent to a C=O group is known to appear around 1420–1300 cm^{-1},[21] and, thus, further supports this assignment. The frequency of the N–C_6H_5 stretching mode increases as the N atom is more highly substituted, as, for example, in aniline (1280 cm^{-1}), N-ethylaniline (1325 cm^{-1}), and N,N-diethylaniline (1365 cm^{-1}). Conjugation of the type

$$\text{C} \diagdown \atop \text{C} \diagup \text{N} \equiv \text{C}$$

stiffens the CN bonds and increases the CN stretching frequencies. This effect is seen in the model compounds where the imide II frequency increases in the order of cyclohexyl, diphenyl, and phenoxyphenyl substituents, implying that the electron-donating effect of the ether

linkage increases the conjugation in the bis(phenoxyphenyl) model compound II relative to the phenyl model compound III.
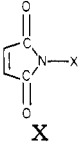
A question arises as to why the strong Raman lines and the medium infrared bands in this region differ in frequency by as much as 10–16 cm^{-1}. Although the mutual exclusion principle generally holds for most of the other modes, both these bands have weak counterparts. Different potential energy contributions from different CN groups could yield two distinguishable CN groups, namely, the C,C$>$N– group and the more substituent-sensitive $>$N–C group. In N,N'-dicyclohexylpyromellitimide (IV), all the vibrational modes related to the cyclohexyl substituents appear as two bands exhibiting a frequency difference between 8 and 36 cm^{-1}. The CN stretching mode of this compound also splits into two comparable medium-intensity bands at 1395 and 1379 cm^{-1} in the infrared spectrum while only one weak Raman counterpart is seen at 1385 cm^{-1}. The $>$N–C group, the immediate neighbor of the cyclohexyl group, probably most strongly contributes to the medium-intensity infrared bands at 1395 and 1379 cm^{-1} while the C,C$>$N– group is important for the Raman line at 1401 cm^{-1}. The strong Raman line increases in frequency by 11 cm^{-1} when cyclohexyl is replaced by phenyl. A negligible conjugation increase occurs at the C,C$>$N– bonds when phenyl is replaced by phenoxyphenyl, shifting the Raman line only by an additional 1 cm^{-1}. On the other hand, the medium-intensity infrared bands increase by 14 cm^{-1} and then by a further 4 cm^{-1} when compared in the same fashion. Even though these observations tend to support the simple substituent mechanism, the actual situation may be complicated by coupling between the two types of CN stretching modes.

According to the above discussion, the CN stretching mode of the polyimide is affected by changes in the bond order of the ether linkage. The infrared difference spectra of the crystalline and amorphous components show that the CN stretching mode increases by 13 cm^{-1} upon crystallization, suggesting that ordering increases the phenyl ether conjugation and coplanarity. However, the frequency increase seems slightly too high for a conjugation effect only, when compared with the diphenyl and bis(phenoxyphenyl) model compounds which show smaller differences.

Similarly, the COC antisymmetric stretching mode increases from 1252 to 1257 cm^{-1} as a result of the increased conjugation[21-23] accompanying crystallization. The opposite trend may be expected for the C=O stretching mode (imide I) since, if the conjugation at the C,C$>$N– bonds becomes stronger, the increased electron donation to the carbonyl oxygen will lower the carbonyl frequency. A frequency increase of the C=O stretching mode has been reported for disubstituted amides with strong electron-withdrawing groups substituted on the nitrogen atom.[24] As expected, the C=O stretching mode of the polyimide is reduced from 1725 to 1717 cm^{-1} upon crystallization. Suzuki has employed normal-coordinate analysis to show a 33% CN stretching mode contribution to the carbonyl band.[25] A contribution of the CN stretching mode to the C=O stretching mode has also been found for secondary amides[26-29] and tertiary amides.[30] Thus, increased conjugation at the C,C$>$N– group will increase the frequency of the CN stretching mode and enhance the contribution of the CN stretching to the imide I band, leading to a stronger coupling of the C=O and CN stretching mode and a lowering of the imide I frequency.

As described in the Results, the polymer and the bis-(phenoxyphenyl) model compound II show almost the

Table II

|	λ/nm	ε/(L·mol⁻¹·cm⁻¹)
Et	294	577
2,6-Et$_2$C$_6$H$_3$	290	460
C$_6$H$_5$	285	5200
C$_6$H$_5$OC$_6$H$_5$	295	7100
C$_6$H$_5$O-2-OMeC$_6$H$_4$	300	16600

same half line widths of the C=O stretching mode. However, unlike in the polymer, the C=C stretching modes of the disubstituted phenyl and the CN stretching modes are quite narrow in the crystalline model compound where the conformation of the phenoxyphenyl group is fixed. The multitude of possible conformations in the amorphous phase is responsible for the broadness of the polymer peaks.

B. UV–Visible Spectra and Resonance Raman Enhancement. Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] and its three model compounds possess a transition at 300–350 nm which is either a π–π* transition[31] or a n–π* transition.[18] Matsuo[18] reported that the transition in N-phenylmaleimide (V) around 300–350 nm showed a red-shift in a more polar solvent, while maleimide (VI) behaved in the opposite fashion. Hence, it was con-

V   VI
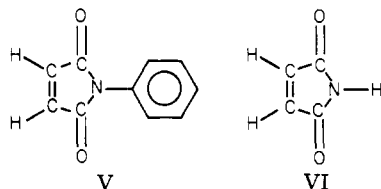
cluded that the n–π* transition predominates in maleimide (VI) in contrast to the N-phenylmaleimide (V) where the n–π* transition is strongly perturbed by a π–π* transition. Table II summarizes the intensity and frequency data for this transition in N-substituted maleimides.[32] Upon conjugation of an N-substituted aromatic group with the maleimide group, the transition shows the increase in intensity expected as the transition character changes from an allowed R band (n–π*) to an allowed K band (π–π*).[34] While ortho disubstitution of the phenyl group prevents conjugation and lowers the band intensity, substitution with electron-releasing, conjugating groups, such as phenoxy and methoxy, result in a large intensity increase. It is unclear whether the n–π* transition involves the oxygen lone pairs or the electrons of an sp³-hybridized N atom. However, maleic anhydride, which is isoelectronic with maleimide, does not show any significant transition in this frequency regime, suggesting that the N atom is involved. The transition from N sp³ to sp² hybridization upon conjugation with an aromatic substituent is also supported by dipole orientation measurements.[35]

Nurmukhametov[31] found that the fine structure of the phosphorescence spectrum of N-methylphthalimide (VII)

VII   VIII
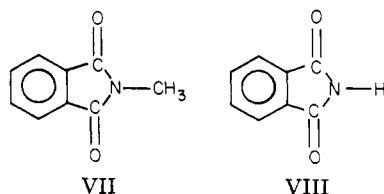
at liquid nitrogen temperature did not possess frequency

intervals that agreed with the vibrational modes of the carbonyl group, forcing them to conclude that the transition was π–π*. Even though no mention was made of the possibility of a nitrogen n–π* transition, this conclusion was also supported for both compounds by the observation of bathochromic shifts with increasing solvent polarity. In addition, the specific absorptivity of this band was too large for any n–π* transition. The most likely explanation is that a weak n–π* transition is present but heavily overshadowed by a π–π* transition of the disubstituted phenyl group.

Support for this assignment required careful examination of the excitation profile of N,N'-bis(phenoxyphenyl)pyromellitimide (II) (Figure 12). A steady increase in intensity is seen in the C=C stretching mode of the central phenyl group, which starts around 488.0 nm. The intensity increase of this mode seems to be too abrupt for the broad, weak transition centered around 380 nm. Consequently, we conclude that the transition around 330 nm is due to the π–π* transition of the central phenyl group.

In addition to the transition around 330 nm, there is at least one weak, broad transition around 380 nm. An intermolecular charge transfer was suggested as the source of this band.[33] However, Figure 4 shows this transition to be an intramolecular transition. Although the K band (π–π*) is submerged by the π–π* transition of the central phenyl in a compound where two phenylphthalimides are bridged by a nonconjugative hexafluoropropylene group,[16] replacement of this nucleus with a pyromellitic group, which allows conjugation between the two imide rings, causes a reemergence of this band at lower frequencies (350–370 nm) and, for some unknown reason, at a substantially lower intensity than for aromatically substituted maleimides. Since this band involves the N atom and the phenoxy group in the bis(phenoxyphenyl) model compound II, resonance Raman enhancement should be seen at the vibrational modes related to either the N atom or the phenoxy group. The excitation profile in Figure 12 confirms this prediction in that the intensity of both the C=C stretching mode of the phenyl rings of the phenoxyphenyl group and the CN stretching mode start to increase slowly around 500 nm in the fashion expected.

Conclusions

N-Substituted pyromellitimides, including the polymer poly[N,N'-bis(phenoxyphenyl)pyromellitimide], exhibit an intense π–π* transition of the central phenyl group at 300–330 nm and a weaker R band (n–π*) at lower frequency which red-shifts and intensifies to a K band (π–π*) upon the conjugation that attends aromatic substitution at the N atom. As a consequence of the sensitivity of the lower frequency transition to the hybridization state of the N atom, it is ideally suited as a probe of conformational changes at the N atom and, thus, any N-phenyl bond rotations induced by an applied stress.

The polyimide studied also has conformational flexibility around the phenoxyphenyl oxygen bridge. Frequency shifts in the C=O, CN, and COC stretching modes show that the two phenyl rings of the phenoxyphenyl group approach coplanarity and thus increase the conjugative interaction upon crystallization.

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Spectroscopic Studies of Poly[*N,N'*-bis(phenoxyphenyl)pyromellitimide]. 2. Structural Changes of Polyimide upon Yielding

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ABSTRACT: Resonance Raman, infrared, and ultraviolet spectroscopic studies of low-molecular-weight model compounds and polyimide film suggest that, when stress is applied to the polymer film, an sp^2 to sp^3 configurational change is activated at the imide nitrogen, adding an increment to the anelastic strain in the tensile direction. Yielding occurs in the polymer solid when a high enough concentration of high-energy, sp^3 configurations has accumulated in the solid. Permanent plastic deformation is thought to involve relaxation of high-energy configurations by an ether oxygen bond rotation to a state spectroscopically similar to the undeformed state.

Although small-amplitude molecular motion is first activated in polyimide at 60 K,[1] this polymer and the structurally related polyquinoxalines[2] are noteworthy for their lack of any significant relaxation peaks between 100 and 500 K. Motions released by the breakup of hydrogen bonding between absorbed water molecules and neighboring polyimide chains are activated at 200 and 353 K (1 Hz)[3,4] and are probably similar to those that would have been activated at 100 K in the absence of water. In the high-temperature regime two relaxations are present, one at 551 K and the other at 673 K, neither of which lead to any discontinuity in the heat capacity, and are, thus, not the T_g of the polyimide. The relative inflexibility of the aromatic units is thought to limit molecular motion at high temperatures to longitudinal slippage of parallel plates of adjacent aromatic chains between equivalent positions along the chain direction.[5] Motions activated at lower temperatures (ca. 100 K) could involve limited oscillations about the ether– and nitrogen–phenyl linkages or an out-of-plane inversion at the nitrogen–phenyl linkage, similar to that found in ammonia.

Striuk has recently demonstrated in an extensive review of aging in polymer glasses[6] that the large-amplitude main-chain motions necessary for volume or enthalpy relaxation or yielding and plastic deformation do not occur in a polymer glass below the β relaxation temperature, the temperature at which main chain oscillations are thermally activated. Typically the polymer glass is brittle below this