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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 polyquinoxalines² 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 glasses⁶ 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

temperature and ductile above. The tensile stress-strain data obtained by Bessonov and Argon⁷ on polyimide and several other more flexible aromatic polyimides demonstrates that these materials shear yield and deform uniformly out to large strains over a wide temperature range, both above and below room temperature. The very broad, featureless, low-intensity loss that is observed in polyimide between 60 and 500 K, even in the absence of water, evidently serves the same purpose of enhancing the ductility as do the β relaxations in the substituted poly(phenylene oxides),⁸ polycarbonate of bisphenol A, and poly(ethylene terephthalate).⁹

When the yield stress vs. temperature data were analyzed according to Argon's molecular theory,¹⁰ very large yield activation volumes were found for polyimide, involving the cooperative motion of a parallel bundle of several adjacent polyimide chains over the monomer repeat distance along a chain. Of course, this large activation volume is consistent with the local liquid crystallike packing that would be expected for such a stiff planar molecule and, indeed, has been recently found by small-angle X-ray scattering experiments.¹¹ The stiffness of the molecule makes it likely that the large displacements necessary for plastic deformation are achieved at room temperature by the cooperative accumulation of many small displacements, perhaps similar to the inversion and oscillation processes discussed above.

The purpose of this paper is to elucidate the nature of these displacements in polyimide via vibrational and electronic spectroscopy. There have been many attempts, since Gubanov's original theoretical work in 1967¹² on the effect of stress on band anharmonicity, to use both infrared^{13–16} and Raman spectroscopy^{17–19} to study polymer molecules under stress. With the exception of a brief note by Evans et al.,²⁰ all the work so far has employed highly oriented fibers or films. The rationale for using highly oriented materials which deform relatively uniformly with little or no strain softening is as follows. Depending upon the rate at which the initial stress-activated conformation catalyzes conformational changes in neighboring chains, the plastic deformation may be either localized into sharp shear bands and crazes or distributed more uniformly into diffuse shear bands.²¹ Glasses which strain soften rapidly and only at high stress levels close to the yield stress deform by sharp shear bands and crazes.²¹ Examination of the conformational changes that attend strain softening by techniques such as infrared, ultraviolet, and Raman spectroscopy averages the changes occurring within the glass over relatively large sampling areas and times. Obviously, materials which strain soften more slowly by diffuse mechanisms will be more amenable to study by these techniques and will provide a more accurate correlation between microscopic spectroscopic characteristics and macroscopic stress-strain behavior. Consequently, we have made use of biaxially oriented polyimide film (Kapton H film, Du Pont) in this study with the knowledge that it deforms uniformly, at least on the macroscopic level. Its rather low crystallinity index of approximately 13%⁴ (because of very small crystallites and/or a very large density of defects) also ensures that the localized deformation processes commonly found in spherulitic materials will not develop.

The previous paper²² has shown that an increase in the sp^2 character of the nitrogen atoms of *N,N'*-disubstituted pyromellitimides increases the intensity and wavelength of their longest wavelength UV-visible transition. This same transition in polyimide would be significantly affected by the inversions at the nitrogen atom and/or os-

cillations about the nitrogen-phenyl bond which were mentioned as possible active mechanical relaxations. The conjugation between the π systems of the phenyl ether and the imide ring moieties would be changed by these motions. Obviously conformational changes in this polymer are amenable to study by techniques which are sensitive to the electronic state of the molecule, namely, UV-visible absorption spectroscopy and resonance Raman spectroscopy.

Experimental Section

Thin films of polyimide (ca. 1000 Å) were prepared for UV spectroscopy by doping the polyamic acid solution with about 0.1% by weight of a special phthalocyanine compound²³ which was soluble in the same *N*-methylpyrrolidone solvent and thermally stable up to the curing temperature of the polyamic acid ($\approx 240^\circ\text{C}$). The polyamic solution was cast onto a fluoroethylene-ethylene copolymer (FEP) substrate and cured to form the polyimide film. A detectable visible transition due to the phthalocyanine compound was found at 675 nm. Since this absorption peak was by far the strongest in the absorption spectrum of the phthalocyanine, none of its shorter wavelength absorptions significantly interfered with those of the polyimide in the region of interest (260–500 nm).

The doped polyimide film on the substrate was placed in a manual tensile stretcher which was subsequently clamped into the spectrophotometer. The sample was compensated by a reference channel which contained a piece of FEP film of the same thickness. The spectrum was recorded both before and after the application of a 13% strain. Since the band shape of the phthalocyanine was not noticeably affected by the imposed strain, it was used as an internal standard against which the strain-induced changes in the polyimide peak intensities could be measured. As an additional test, a sufficiently small area of polyimide was cast onto the FEP substrate so that it was completely contained within the beam incident upon it. In such a way the amount of material sampled by the beam did not change as a function of strain.

Electron micrographs of the deformed films were obtained first by shadowing the polyimide film in the strained condition on the FEP substrate with Pt-C at a 30° incident angle. After carbon coating the replica it was stripped from the substrate with a dried film of polyacrylic acid (PAA), a solution of which had been previously coated onto the replica. These layers were then floated onto a water surface, PAA side down, whereupon the PAA dissolved away, allowing the sample to be picked up with an electron microscope grid. The thicker commercial polyimide film was replicated in the same way after deformation.

Resonance Raman scattering from the commercial film sample (Kapton H film) was obtained by deforming the film in the stretcher up to a specified strain level and then sampling the scattered radiation at 90° to the incident laser beam at 363.8 nm. Sample degradation was avoided during the experiment by limiting the effective power on the sample to less than 1 mW and changing the beam position after an experiment at a given strain level. Of course, the fluorescence background, which is a measure of sample degradation,²² was monitored continuously. The strain was imposed on the same sample in the stepwise fashion while the beam power on the sample was maintained at a constant level throughout the series of scattering measurements at the different strain levels. The incident beam power was of consequence since the I_{1383}/I_{1610} ratio was found to decrease from 1.62 to 1.52 when a sample rotator was used instead of the stationary stretcher where the beam position was fixed on the sample, an effect undoubtedly due to different local sample temperatures. Therefore, the results with stretcher and sample rotator should not be directly compared. The data obtained with the same sampling technique is likely to be internally consistent. Relatively rapid scanning speeds prevented sample degradation and a good signal-to-noise ratio was achieved by employing a rather low 30-cm^{-1} resolution which still showed spectral features very similar to those of the 10-cm^{-1} resolution scan.

The stress-relaxation curves at each strain level were obtained with a minitensilon (Toyo Measuring Instrument Inc.). At a high strain level close to yield ($\approx 6\%$), the stress decayed quite rapidly

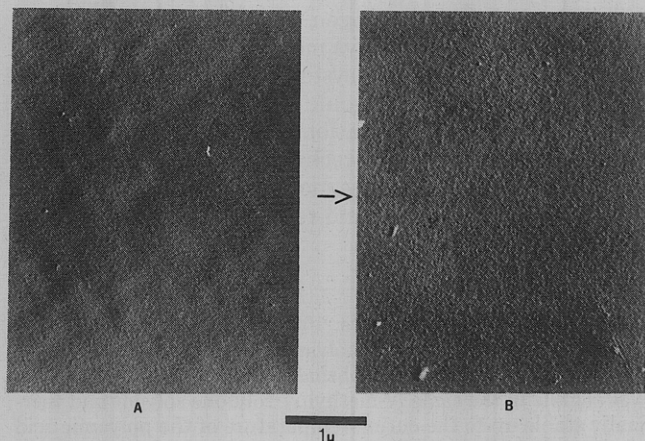


Figure 1. Electron micrographs showing (A) diffuse microshear banding in a thin polyimide film and (B) no noticeable local deformation in a thick polyimide film.

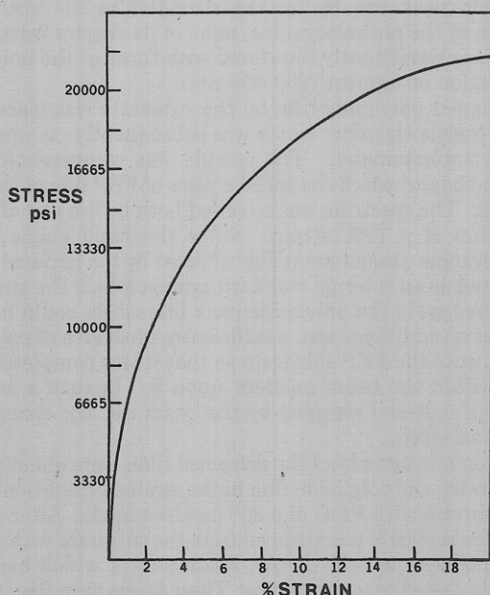


Figure 2. Engineering stress-strain curve of polyimide (Kapton H film).

for the first few minutes and then slowly varied. Raman spectra were obtained in the slow-relaxation region where the stress level did not change significantly over the time of the spectral collection ($\approx 75\%$ of the initial stress level).

Results and Discussion

A. Deformation Morphology and Stress-Strain Behavior. Diffuse microshear bands, similar to those found in ductile thermoplastics that display only limited strain softening, are seen in the thin polyimide film of Figure 1A. Previous experience²¹ leads us to the conclusion that the strain must be rather uniform throughout. In addition, due to the inflexibility of the polyimide chain, significant biaxial orientation must be also present within the plane of this thin film. The micrograph of the thicker polyimide film shows no evidence of localized deformation at all (Figure 1B). Of course, this result was anticipated from the very uniform macroscopic deformation of the thick film. It is thus safe to say that the spectroscopy is sampling the important deformation mechanism of the solid.

Figure 2 shows the partially relaxed engineering stress-strain curve of the commercial polyimide film used for the experiment. These stress levels are those which were maintained during the resonance Raman experiment at each strain level. The high stresses and lack of a yield

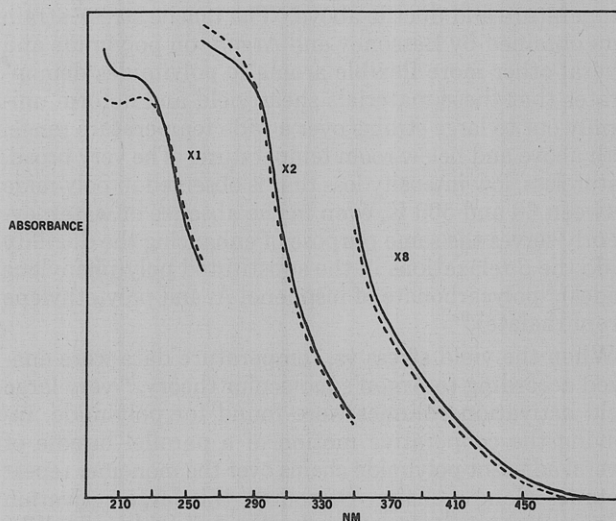


Figure 3. Effect of strain on the UV absorption of a thin polyimide film: (—) undeformed; (---) deformed 13%.

point are expected for a highly biaxially oriented film. Argon and Bessonov²⁴ found the same type of characteristics for their polyimide film (Kapton H film) which was deformed at a constant-strain rate. A further interesting feature is that strain softening starts at strain levels below 1%, a clear indication of anelastic behavior and the unequal distribution of stress across the molecules within this material.

B. UV-Visible Spectroscopy. The imposition of a 13% strain on the thin 1000-Å film leads to an increase in the intensity of the 276-nm peak and decreases in the 334- and 378-nm peaks (Figure 3) in three different doped samples and in one sample where the film size was smaller than the beam diameter.

The most significant change from our point of view is in the 378-nm band. As discussed in the previous paper,²² a change from sp^2 to sp^3 hybridization of the nitrogen atom decreases the intensity of this band. A decrease in the wavelength of the transition often attends this change in electronic structure which tends to submerge the band (now more $n \rightarrow \pi^*$) under the $\pi \rightarrow \pi^*$ of the central phenyl.

The long-wavelength peak of the central phenyl $\pi \rightarrow \pi^*$ shifts to shorter wavelength when the nitrogen conjugation changes from sp^2 in the phenoxy- and phenyl-substituted model imides (328 and 323 nm, respectively) to sp^3 in the cyclohexyl-substituted model compound (320 nm).²² Band overlap in this region makes it difficult to assign any band intensity changes for the series of model compounds, although it does appear that the band intensity is not changed substantially by differences in conjugation.

The net decrease in central phenyl $\pi \rightarrow \pi^*$ intensity under an applied stress could be caused by a decrease of the intensity of the overlapping 276- and 378-nm bands at 334 nm. Although the diphenyl ether $A_{1g} \rightarrow B_{2u}^*$ transition appears to intensify slightly upon stretching, it does so on its shorter wavelength side, most probably as a consequence of the wavelength increase of the band at 218–222 nm. The weakening of the longer wavelength side of the 276-nm band also suggests that it is moving to lower frequency upon stretching. A wavelength decrease and intensity decrease are expected for the $A_{1g} \rightarrow B_{2u}^*$ phenoxyphenyl band upon stretching ($sp^2 \rightarrow sp^3$ on N) since the imide nitrogen which weakly donates its electrons to the phenoxy ring in the sp^2 state²⁵ will be unable to do so in the sp^3 state and will actually become slightly electron withdrawing. The consequent reduction in the asymmetry of the phenoxy π cloud will reduce the transition proba-

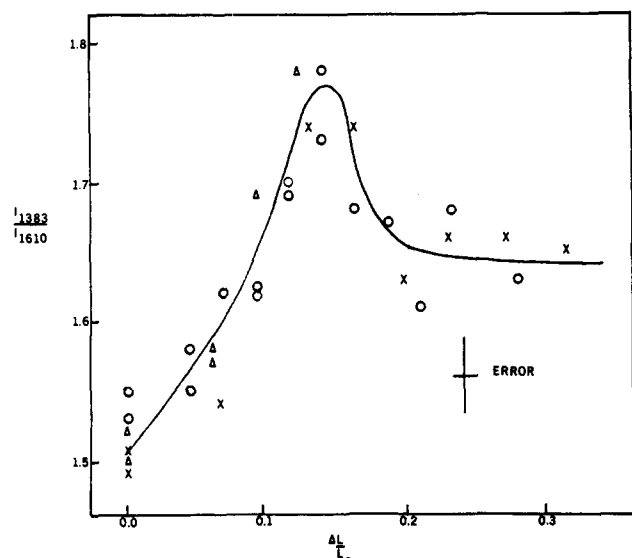


Figure 4. Peak ratio of the aromatic carbon stretching mode (1610 cm^{-1}) and N-C stretching mode (1383 cm^{-1}) vs. elongation: (Δ) first run; (\times) second run; (\circ) third run.

Table I^a

history ^b	I_{1383}/I_{1610}	average
(1) 0	1.63	1.62
(2) 0	1.62	
(3) 0	1.60	
(4) 0	1.64	
(5) 0	1.62	
(1) 0-8-0	1.62	1.60
(2) 0-8-0	1.59	
(3) 0-8-0	1.59	

^a The data in this table were obtained by using a sample rotator in order to minimize the heating effect of the laser radiation. Thus, the intensity ratio in this table is slightly different from the value in Table II, even for the same sample, and values should not be compared. ^b Percent stretch.

bility and, in most cases, will also reduce the wavelength of the transition.²⁶

C. Resonance Raman Spectroscopy. The ratio of the intensities of the Raman lines of the aromatic C=C stretching mode at 1610 cm^{-1} and the C,C>N-phenyl stretching mode at 1383 cm^{-1} was found to change significantly as a function of applied strain. The I_{1383}/I_{1610} ratio increased up to a maximum around 15% strain, whereafter it fell to an approximately constant value at 22% strain, maintaining this value up to 35% elongation (Figure 4). The ratio of the integrated peak area also behaves similarly (Table II), suggesting that the ratio change is not due to a peak shape change but arises from a change of resonance Raman enhancement. Clearly some form of molecular yielding is occurring which is not at all apparent from the stress-strain curve in Figure 2.

The UV results suggest that stress is inducing a configurational change from sp^2 to sp^3 at the nitrogen atom. Since conjugation energy is lost by this process, the unstable anelastic state would relax back into the sp^2 configuration when stress is released. Table I shows that the ratio of the unstrained sample is completely recovered when a film is stretched to 8% and returned back to 0%. The implication is that most of the strain up to 15% is either recoverable elastic or anelastic strain. The drop in the intensity ratio at 15% must be a consequence of plastic deformation where the unstable sp^3 state converts back into the stable sp^2 form with an increment in permanent strain. This mechanism is in line with that found for

Table II^a

history ^b	I_{1383}/I_{1610}	average
(1) 0	1.50	1.52
(2) 0	1.52	
(3) 0	1.52	
(4) 0	1.55	
(5) 0	1.52	
(1) 32.7 ^c	1.64	1.60
(2) 32.7 ^d	1.61	
(3) 32.7 ^d	1.57	
(4) 32.7 ^d	1.62	
(1) 0	1.99 ^e	
(2) 9.3	2.02 ^e	
(3) 14.0	2.14 ^e	
(4) 23.3	2.06 ^e	

^a The data in this table were obtained by using a stretcher with the same spot in the sample exposed during recording of the Raman spectrum. ^b Percent stretch.

^c Immediately after stretching. ^d Stress relaxed for 14 h.

^e These intensity ratios were obtained by measuring the peak area showing the true change of the intensities.

polycarbonate film by Robertson and Patel²⁷ and Kramer,²⁸ who found that most of the strain prior to 12% (yield) was elastic and anelastic, a rapid rise in plastic strain, at the expense of the elastic and anelastic parts, being seen only after 12%. Since the plastic strain does not support as much stress as the recoverable part, a drop in the true stress should be seen after the yield strain and is indeed often observed. However, many highly oriented films and fibers, including Kapton H film,²⁴ do not exhibit this yield drop. Unlike in unoriented films where the elastic strain level drops after yield,^{27,28} elastic bond angle deformations undoubtedly still make an increasing contribution to the stress level well after yield in oriented films made from inflexible molecules. The constantly increasing elastic strain could obscure the effect the large drop in anelastic strain would have on the stress-strain curve.

This mechanism has some similarity to that proposed by Wool and Statton¹⁵ for the stress-relaxation of polypropylene fibers. Their infrared experiments suggested that the initial homogeneous elastic strain funnels into a few overstressed bonds which then can nucleate conformational transitions. In our case the $sp^2 \rightarrow sp^3$ configurational change would be analogous to the overstressed bonds.

Applied stress can significantly reduce the vibrational frequency of backbone vibrations in single crystals of polydiacetylenes.^{17,18} In our experiment, however, the low resolution (30 cm^{-1}) and broadness of the Raman line of interest obscured somewhat the frequency shift in imide II mode around $1400\text{--}1380\text{ cm}^{-1}$ which is affected by the conjugation change at the N atom.²² Nevertheless, a stress-induced frequency decrease of $2.5 \pm 2.5\text{ cm}^{-1}$ was present at the molecular yield point in all our samples, supporting the view that stress decreased the conjugation at the nitrogen atom.

The excitation profile²² of the phenoxyphenyl model compound shows that the 1413 cm^{-1} line intensifies with increasing laser frequency much more slowly than either of the aromatic carbon stretching vibrations at 1608 cm^{-1} (phenoxyphenyl carbons) or 1628 cm^{-1} (central phenyl carbons). Therefore, the aromatic carbon vibrations should be more profoundly changed relative to the N-C vibrations by a stress-induced frequency shift or intensity change in the UV spectra. The increase in I_{1383}/I_{1610} ratio upon stressing thus could be a consequence of the decrease in both the phenoxy and central phenyl carbon resonance Raman enhancements by the frequency increase expected

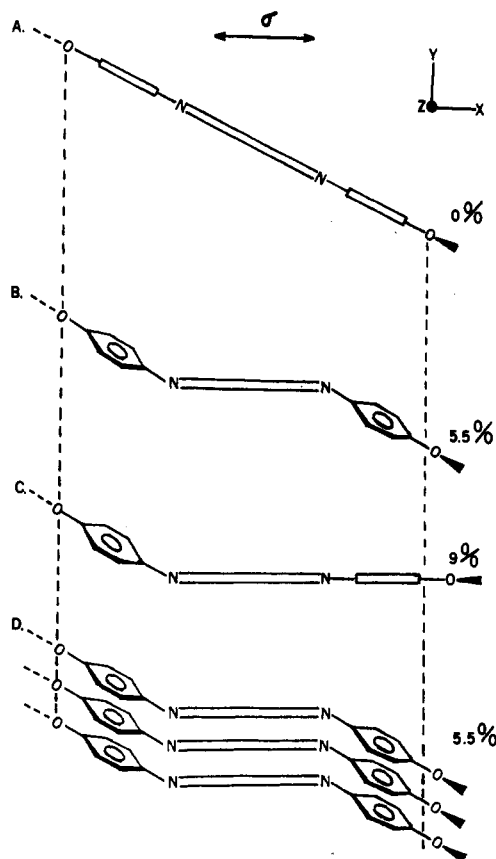


Figure 5. Configurational changes partially responsible for yielding of polyimide (Kapton H) film.

for the central phenyl and phenoxy UV transitions. The RR enhancement of the C–N band should be influenced mostly by changes in the 371-nm transition. However, both the breadth of the transition at 371 nm and the proximity of this peak maximum to the exciting laser frequency (363.8 nm) minimize the effect of frequency or intensity changes of this transition on the 1383-cm⁻¹ band.

A feature of additional interest is the relaxation of the I_{1383}/I_{1610} ratio to 1.60 upon stress-relaxation for 14 h at 32.7% strain (Table II). Apparently some of the activated configurations present at yield have converted, with an increment of plastic strain, to more stable configurations, spectroscopically similar to the undeformed material (undeformed ratio 1.52).

Cunningham and Ward^{16,31} have observed that plastic deformation in poly(ethylene terephthalate) (PET) requires a net conversion of gauche into trans conformations, a consequence of the greater extension of an all-trans chain. In polyimide, the only stable conformational changes involve rotation about the phenoxy oxygen; but since these do not necessitate a specified conjugation change of the phenoxy oxygen bond they might not be apparent spectroscopically.

Model and Conclusions

The crystal structure of polyimide dictates that the repeat unit have a planar zigzag structure where all of the phenyl groups are in approximately the same plane (Figure 5A).³⁴ However, outside the crystal, rotation of the phenoxyphenyl around the *N*-phenyl bond is possible, provided sufficient energy is available to overcome the energy of conjugation with the imide ring. Once conjugation of the ring systems is disrupted, the sp² state of N will no longer be stable and a transition to an sp³ state will occur since the N atom is known to be only very weakly

conjugated with the carbonyl groups.³⁰ A complete transition to an sp³ state would yield a bond angle of about 109° between the nitrogen–carbonyl bonds and the nitrogen–phenyl bond. Figure 5B shows a section of the original planar zigzag where only partial deconjugation of the aromatic system has occurred resulting in a bond angle of 153°. If, as in Figure 5B, the nitrogen atoms on either side of the pyromellitimide grouping invert in the opposite sense, a net molecular extension of between 5.5 and 4.7% will take place. This type of kinking would relieve a tensile stress directed along the *x* direction. Figure 5C shows a similar example where only one nitrogen has changed its configuration; a much larger extension of 9% is obtained. These kinking mechanisms require motion only in the *xy* plane, unlike rotations about the phenoxy oxygen bond which would involve motion in the *z* direction. In both thin films and uniplanar biaxially oriented thick films of polyimide the kinking mechanisms would make the predominant contribution to extension along the *x* axis and Poisson contraction along the *y* axis. It is easy to see how a bundle of parallel-packed polyimide chains could kink cooperatively to generate a net increment in tensile deformation (Figure 5D). A picture of this sort is similar to the macroscopic kink bands seen in poly(sulfur nitride) single crystals³⁰ and the microscopic kinks envisioned by Argon's model.¹⁰

The low-temperature dynamic mechanical loss at 60 K might signal the onset of limited oscillation of the 1,4-substituted phenyl about the phenyl nitrogen, leading of course to a small distortion of the planarity of the aromatic system and an extension in response to the stress. The magnitude of this same type of motion probably just grows larger with increasing temperature and/or applied stress in a continuous fashion. The featureless increase of the damping and heat capacity that is seen in the dry sample up to about 100 K agrees with the above mechanism.^{1,3}

Quantum mechanical calculations have revealed that the energy of conjugation between the phenyl ring and the pyromellitimide nucleus is approximately 18 kcal/mol.³² In the model presented in Figure 5, only partial disruption of the conjugation is necessary to yield the largest strain increment. If we assume the conjugation is proportional to $E_{\text{conj}} \cos \theta$,³³ where $E_{\text{conj}} = 18$ kcal/mol and $\cos \theta$ is the angle between the planes of the phenoxy ring and the central phenyl and, additionally, if we postulate that the twist about the *N*-phenyl bond necessary to achieve the 30° out-of-plane bend in Figure 5 is equal to 30°, then the total intramolecular activation energy for configuration 5B will be about 10 kcal/mol, on the same order of the activation energy expected for the onset of small-scale molecular motion in polyimide at 40 K. According to Bessonov and Argon,²⁴ the activation energy for yield in polyimide at room temperature is about 100 kcal/mol and the activation volume consists of roughly 6 repeat units acting cooperatively as a bundle. The intramolecular contribution to the activation energy, based on Figure 5B, D, could be about 60 kcal/mol, the remaining 40 kcal/mol being an intermolecular elastic strain energy stored in the surrounding matrix.

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Effect of Concentration on the Fluorescence Spectra and Lifetimes of Pyrene in Polystyrene Films[†]

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ABSTRACT: The emission spectra and lifetimes of pyrene-doped polystyrene films are investigated as a function of pyrene concentration. The excimer fluorescence observed in these films is shown to result from the formation of pyrene molecular pairs which satisfy the geometrical requirements for excimer formation. The predominant photophysical process leading to electronic excitation of these molecular pairs is shown to be dipole-dipole resonance transfer from pyrene monomers serving as energy donors. It is found that little or no energy migration between pyrene monomers occurs in these films.

Recently, the results of an investigation concerning the migration and transfer of singlet excitation in molecularly doped polymers were reported.¹ It was determined that the migration of the excitation among the system of like energy donors occurred by a series of random walk steps with each step occurring by dipole-dipole resonance transfer in the very weak coupling limit (Förster transfer).² These conclusions were based on measurements of the concentration dependence of the donor fluorescence lifetime in the presence of known concentrations of two types of fluorescence quenchers. An important distinction between those results and others concerning the migration and transfer in doped polymer films was the absence of self-quenching due to the formation of dimer or higher aggregate states which can serve as energy traps.³ The occurrence of fluorescence self-quenching, which in certain

cases is signaled by the presence of new emission such as excimer fluorescence, complicates interpretation of results since the concentration of the species responsible for the new emission is unknown.

The diffusion-limited formation of excited-state dimers in solution, resulting from the interaction of a ground-state molecule and an electronically excited molecule, was first observed by Förster and Kasper for the case of pyrene.⁴ These excited-state dimers were subsequently termed excimers, and the pyrene molecule has long served as the prototype for a great number of investigations concerning excimers and excimer emission as observed for a variety of compounds both in fluid solution and in the solid state.⁵ The observation of excimer emission from molecular crystals of a variety of compounds, again exemplified by pyrene, has been suggested as a diagnostic tool for determining the crystal structure since the translational freedom which allows the two molecules to achieve the proper orientation for excimer formation in solution is, of course, absent in the solid state and the two molecules

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