Effect of cure history on the morphology of polyimide: Fluorescence spectroscopy as a method for determining the degree of cure

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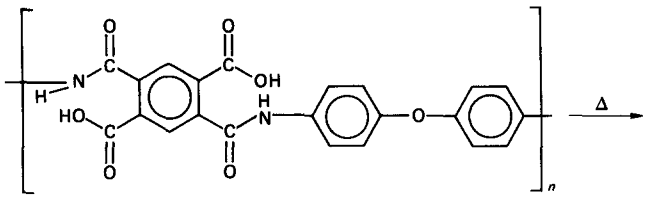
(Received 17 August 1987; accepted 4 December 1987)

Polyimides are widely used in a variety of technological applications, from interlayer dielectrics in multilevel very-large-scale integrated circuits to matrix resins in high-temperature composite materials. Although data are available from most polyimide manufacturers on the electrical and physical properties of fully cured polyimide, few data are available concerning the precured or undercured polymer. Moreover, there is currently no convenient method available to monitor the degree of cure, which is determined by the highest cure temperature used in the thermal treatment of the polyimide film. In the present studies the degree of cure of a poly(*N*,*N*′-bis(phenoxyphenyl)pyromellitimide)-type polyimide has been observed to have a profound influence on the fluorescence of films irradiated in the near-ultra-violet to visible regions. Excitation of two bands centred at 350 and 490 nm results in an emission band centred at 575 nm that undergoes a significant increase in intensity with cure temperature. We propose that this fluorescence behaviour is associated with an increase in local ordering or aggregation coincident with an increase in the final cure temperature, from 200 to 450°C. Conformational changes such as rotation around the *N*-phenyl bond are proposed to account for the change in morphology and fluorescence intensity with cure. In addition, the formation of a charge transfer complex between the dianhydride (acceptor) and diamine (donor) moieties is invoked to explain the low-energy absorption band that results in the observed fluorescence.

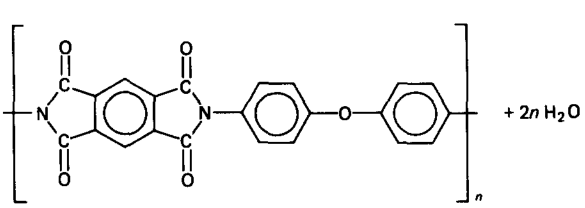
(Keywords: polyimide; spectra; ultra-violet; fluorescence; morphology; cure)

INTRODUCTION

Aromatic polyimides have gained wide popularity as high-performance materials in a variety of technological applications due to their thermal, mechanical and electrical properties. Most notable among these applications are as interlayer dielectrics in multilevel very-large-scale integrated (VLSI) circuits and as matrix resins in high-temperature composite structures. Aromatic polyimides can withstand thermal degradation up to 560°C in the absence of oxygen. They have excellent toughness and elongation properties and a glass transition temperature, T_g, in excess of 400°C. The dielectric constant of most polyimides is about 3.5, comparable to that of inorganic dielectrics. The processability of polyimide is enhanced by casting or extruding the soluble precursor, poly(amic acid). The subsequent intramolecular condensation reaction to form the heterocyclic imide, as shown below for the formation of poly(*N*,*N*′-bis(phenoxyphenyl)pyromellitimide) from its precursor, is typically a thermal process.



Poly(*N*,*N*′-bis(phenoxyphenyl)pyromellitamic acid)



Poly(*N*,*N*′-bis(phenoxyphenyl)pyromellitimide)

Such ‘curing’ not only drives the imidization reaction but is responsible for elimination of any solvents and the water condensation by-product, any thermally activated change in morphology and any associated change in material properties. The effect of curing on the material properties of polyimide can be seen in both the reduction in dielectric constant and the increase in T_g with degree of cure.

An essential prerequisite to obtaining the desired final properties is determination of the degree of cure. Methods previously used include Fourier-transform infra-red spectroscopy (*FT*i.r.) and X-ray diffraction. *FT*i.r. is used for determination of the extent of the imidization reaction through monitoring the reduction in absorption by the carboxyl groups in poly(amic acid) and the increase in absorption by the imide groups in polyimide. Since the imidization reaction is essentially complete for polyimide cured at temperatures less than 250°C, little additional structural information can be obtained from this technique in determining the degree of cure and material properties of polyimide subjected to higher temperatures. X-ray diffraction has been used to show that polyimide cured above 250°C undergoes molecular reorientation so

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0032-3861/88/071191-07$03.00

Table 1 Sample cure history

	Sample number					
Cure condition	1	2	3	4	5	6
200°C, 60 min	●	●	●	●	●	●
250°C, 60 min		●	●	●	●	●
300°C, 30 min			●	●	●	●
350°C, 30 min				●	●	●
400°C, 30 min					●	●
450°C, 30 min						●

as to obtain localized regions of ordered aggregates[1]; however, this technique does not lend itself to determination of the molecular groups involved in the aggregation. From a practical or processing view, neither of these methods would readily lend themselves to *in situ* measurement of the degree of cure.

The first objective of this investigation is to ascertain whether fluorescence spectroscopy can be utilized to determine the degree of cure of polyimide annealed at temperatures in excess of the point where the imidization reaction is essentially complete, about 200°C. For the purposes of this investigation, 'degree of cure' is loosely defined as the degree of aggregation associated with the final cure temperature. On a more fundamental level, we wish to learn whether fluorescence spectroscopy can provide insight into the molecular conformations necessary to produce highly ordered aggregated regions in polyimide films.

We will show that u.v. irradiation of polyimide results in an intrinsic fluorescence for which the intensity and emission wavelength depend strongly on the cure temperature. We propose that the change in the fluorescence is due to a change in the microenvironment of the chromophore associated with a higher degree of aggregation. This technique has the potential to assist in determining the molecular groups involved in the aggregation and as an *in situ* tool for determining the degree of cure.

EXPERIMENTAL

The samples used in this investigation were derived from the thermal imidization of one of the most common commercially available polyimide precursors, Du Pont PI-2555. The precursor is a poly(amic acid) formed from the polycondensation reaction of pyromellitic dianhydride (PMDA) and oxydianiline (ODA). Upon imidization, Du Pont PI-2555 forms a polyimide of the poly(*N*,*N*'-bis(phenoxyphenyl)pyromellitimide), or PMDA–ODA, type.

Six samples were prepared by spinning the poly(amic acid) precursor on 3 inch quartz wafers followed immediately by thermal imidization. A 19% solution of the poly(amic acid) in 1-methyl-2-pyrrolidinone was spun on at 3000 r.p.m. for 60 s; this results in ~3.5 μm thick films after imidization.

The samples all received initial thermal treatments of 142°C for 30 min followed by 200°C for 1 h to essentially complete the imidization reaction. They were then cured in successive 50°C increments, as specified by the full circles in *Table 1*. All of the thermal treatments were in an inert nitrogen atmosphere except for the first 142°C bake, which was in air. Thermal treatment up to 350°C was performed in a convection oven. The 400–450°C samples were prepared by subsequent heating in a Thermco Minibrute furnace.

A Spex Fluorolog 212 spectrophotometer was used for recording the emission and excitation spectra of each polyimide film lying along the diagonal in *Table 1*. The spectrum of each film was obtained at room temperature in air using 2 mm slit widths. Excitation spectra were subsequently normalized with respect to the lamp intensity fluctuations by dividing each spectrum by that obtained with a rhodamine-B standard solution.

RESULTS

A fluorescence excitation spectrum was measured for each sample by monitoring the emission intensity at 590 nm, one of the stronger emission peaks in the emission band, while scanning the excitation wavelength from 320 to 570 nm. The excitation spectra are shown in *Figure 1*. Several features of the spectra are observed to change with increasing cure temperature. The first of these is the intensity, which increases dramatically with cure temperature. This increase in intensity can be attributed primarily to two bands, one centred at about 350 nm and the other at about 490 nm. Another feature of interest is that, while the band at 350 nm remains broad and relatively featureless, the band at 490 nm becomes structured with increasing thermal treatment. The structured band is composed of several peaks at approximately 427, 465, 486, 509 and 532 nm. In addition, the intensity of the structured band increases relative to that of the unstructured band with cure.

The wavelengths corresponding to maximum emission, λ_{max}, of the 450°C cured sample in the excitation spectra are 352 nm for the unstructured region and 486 nm for the structured region. The positions of the excitation peaks in the structured region are constant, to within 0.5 nm, with respect to cure over the temperature range investigated. By contrast, λ_{max} in the unstructured region undergoes a 460 cm^{-1} blue shift with cure for samples cured between 200 and 300°C, while those samples cured between 300 and 450°C undergo an equivalent 460 cm^{-1} red shift with cure.

The emission spectra obtained with 352 and 486 nm

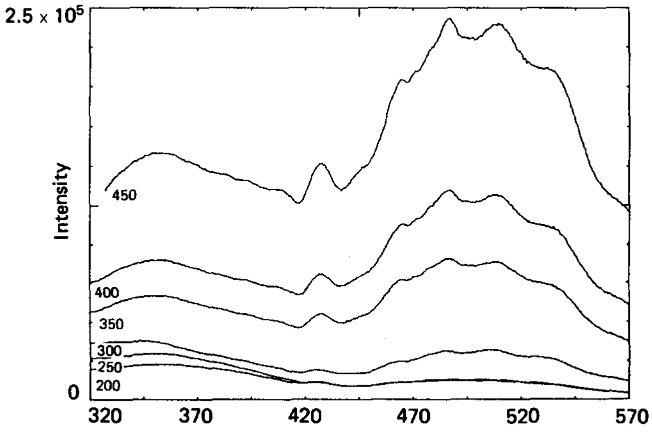

Figure 1 Excitation spectra: 590 nm emission intensity as a function of excitation wavelength and cure temperature (the numbers by the curves refer to the highest cure temperature (°C))

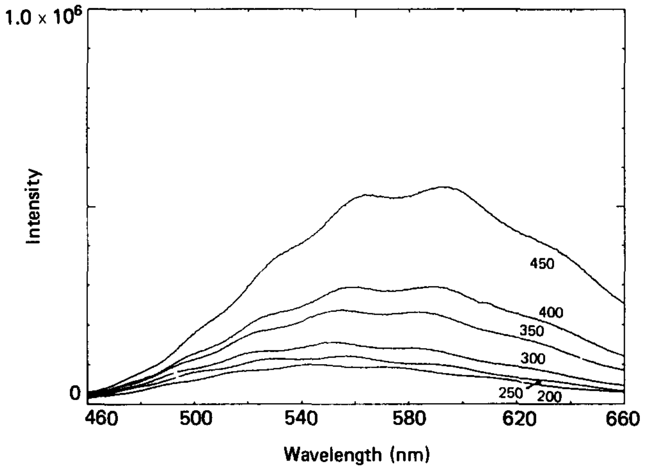

Figure 2 Emission spectra as a function of cure temperature for 352 nm excitation (the numbers by the curves refer to the highest cure temperature (°C))

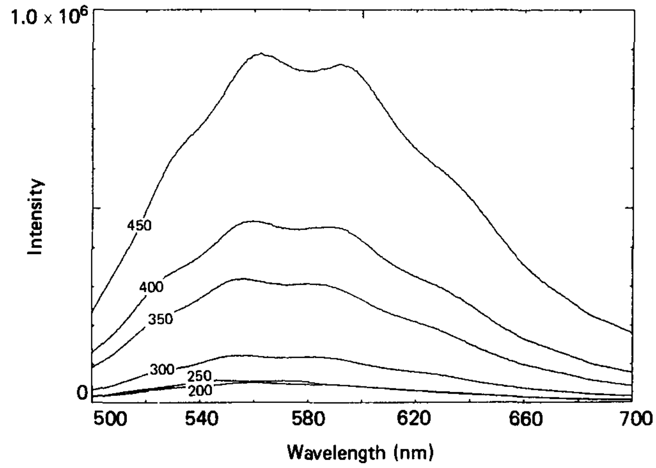

Figure 3 Emission spectra as a function of cure temperature for 486 nm excitation (the numbers by the curves refer to the highest cure temperature (°C))

excitation wavelengths are shown in *Figures 2* and *3*, respectively. The spectral shape is similar, with peaks around 560 and 590 nm and shoulders around 500, 530 and 630 nm. As expected from the excitation spectra, there is an increase in intensity with cure temperature for both sets of emission spectra, and the intensity increases faster with cure temperature for the structured (486 nm excitation) region. In general, for samples cured between 200 and 450°C, excitation at both 352 and 486 nm results in a red shift with cure of 630 $\mathrm{cm^{-1}}$ for the 560 nm emission peak and 590 $\mathrm{cm^{-1}}$ for the 590 nm emission peak. We have ignored the spectrum of the 250°C cured sample, which appears to be anomalously displaced relative to the spectra of the 200 and 300°C cured samples. Around 300–350°C there is a change in the relative intensities of the 560 and 590 nm emission peaks with cure. For 352 nm excitation the intensity of the 590 nm peak increases with cure relative to the intensity of the 560 nm peak, whereas for 486 nm excitation the 590 nm peak decreases with cure relative to the intensity of the 560 nm peak.

An Arrhenius plot of the 560 nm emission intensity for both excitation wavelengths is shown in *Figure 4*. The slope for the unstructured band gives an activation energy of 6.3 $\mathrm{kcal\,mol^{-1}}$ and the structured band results in an activation energy of 10.9 $\mathrm{kcal\,mol^{-1}}$. Both of these activation energies are relatively small, of the order of bond rotation energies.

DISCUSSION

The objective in the first part that follows is to identify the chromophores responsible for the fluorescence spectra. In the second part we will review the literature with respect to the aggregation and degree of ordering of polyimide with cure in order to interpret the change in fluorescence with respect to changes in the morphology of polyimide with cure. With an understanding of both the molecular groups responsible for polyimide fluorescence and the morphology of polyimide, we will propose a model for the change in conformation of the chain with cure.

Assignment of spectral features

Absorption spectra obtained from our polyimide samples compare favourably with the spectra available in the literature[2,3]. In comparing the absorption spectra of polyimide, described below, to the excitation spectra obtained in this investigation, it is apparent that fluorescence is obtained from excitation at the far red of the absorption spectrum.

Both Ishida *et al.*[2] and Barashkov *et al.*[3] have investigated the ultra-violet spectroscopic properties of PMDA–ODA. For the region less than 340 nm, their absorption spectra differ in that Ishida reports absorption peaks at 218, 276 and 334 nm, whereas Barashkov indicates broader peaks at about 230 and 280 nm with no peak at 334 nm. Direct comparison between Ishida's and

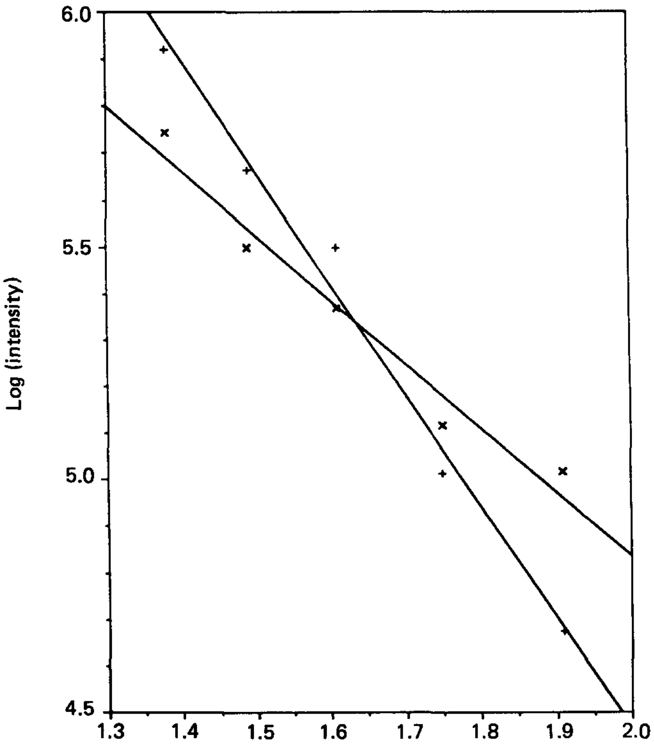

Figure 4 Arrhenius plots of the emission intensity as a function of cure temperature for 352 nm (×) and 486 nm (+) irradiation of polyimide films

Barashkov's results is not possible since the ordinate of Ishida's spectrum is in arbitrary units. Neither is it possible to compare our absorption spectra with the literature in the region less than 340 nm owing to the high absorptivity of our thick samples. However, the u.v. absorption results of Ishida and Barashkov concur for wavelengths greater than about 340 nm; in both there is a broad featureless absorption peak extending out as a 'tail' to around 500 nm. Ishida observes that this peak is centred at 378 nm. Since the absorption spectra of our samples are identical in the region of interest, greater than 340 nm, to that reported by the above authors, it is reasonable to conclude that our observed fluorescence is not due to any chromophore that is not intrinsic to PMDA–ODA type polyimide.

Barashkov *et al.*[3] observed fluorescence from the poly(amic acid) precursor and an *N*,*N*′-diphenyloxide pyromellitimide model compound, but did not observe polyimide fluorescence. They were surprised with this result and so are we, given the results in *Figures 1–3*. However, it is possible that in Barashkov's work they only illuminated their polyimide at wavelengths less than 340 nm where the fluorescent response is at a minimum, although the absorption is at a maximum.

Determination of the chromophores responsible for the long-wavelength absorption band of PMDA–ODA is of interest since this tail is in the region responsible for our observed fluorescence. In a study of model compounds Ishida[2] showed that the tail is intrinsic to the pyromellitimide moiety and that the centre of the peak associated with the tail became red-shifted with the degree of conjugation provided by the substituents at either end of the pyromellitimide group. An absorption spectrum of *N*,*N*′-dicyclohexylpyromellitimide produced a shoulder at 345 nm but not the extended tail apparent in the absorption spectrum of poly(*N*,*N*′-bis(phenoxyphenyl)pyromellitimide). A long-wavelength absorption tail was evident as a peak centred at 356 nm for *N*,*N*′-diphenylpyromellitimide and a peak centred at 371 nm for *N*,*N*′-bis(phenoxyphenyl)pyromellitimide.

This shift of the absorption to longer wavelength is consistent with the increase in conjugation and hence electron delocalization afforded the pyromellitimide moiety with aromatic substitution. Conjugation of this type is maximized when the aromatic rings are coplanar with the pyromellitimide structure, thus allowing π-orbital overlap from the aromatic substituent to the pyromellitimide group. In addition, such an aromatic-substituted pyromellitimide has the potential of forming a charge transfer complex between the aromatic substituent and the pyromellitimide. Thus the long-wavelength absorption tail might be a single broad band, indicative of the loose binding nature of the ground state in a charge transfer complex[4]. These two concepts will be expanded upon after discussion of the emission spectra.

The excitation spectra of PMDA–ODA indicate that more than one chromophore is responsible for the observed fluorescence. Our assignment of specific chromophoric groups to the excitation spectra will be limited to a review of some of the pertinent literature and a study of model compounds to be published[5]. We note first that transitions in the near-ultra-violet to visible range can only be accomplished with π-bonding and non-bonding electrons as transitions involving the σ-bond require vacuum- to far-ultra-violet radiation[4]. This leaves only $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions as being responsible for the structure of the excitation spectra. In fact, both such interpretations have been given. Matsuo[6] investigated the longest-wavelength (300–350 nm) absorption bands of a series of *N*-substituted maleimides and concluded that these bands were primarily due to the $n \rightarrow \pi^*$ transition of the carbonyl groups. Furthermore, increasing the electron-donating properties of the substituent, in going from hydrogen to an alkyl and finally to an aryl substituent, results in delocalization of the nitrogen lone-pair electrons to the carbonyl groups and a subsequent red shift of the longest-wavelength absorption bands. In contrast, Nurmukhametov *et al.*[7] investigated the long-wavelength absorption of phthalimide and *N*-methylphthalimide and assigned absorption in this region to $\pi \rightarrow \pi^*$ transitions. Something of a compromise was reached by Ishida *et al.*[2], who assigned the 300–330 nm absorption band of PMDA–ODA to a $\pi - \pi^*$ transition of the central phenyl ring and the long-wavelength absorption band to an $n \rightarrow \pi^*$ transition that red shifts and intensifies to a $\pi \rightarrow \pi^*$ transition upon conjugation of the nitrogen atom with aromatic substitution.

In a separate study of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) model compounds[5] we have found that the PMDA excitation λ_{max} occurs at 475 nm and the ODA λ_{max} occurs at 350 nm, consistent with assignment of the structured and unstructured bands of the excitation spectra of PMDA–ODA to the pyromellitic and diphenyl ether moieties, respectively. While PMDA is a dianhydride rather than a diimide, the $n \rightarrow \pi^*$ transition from delocalization of the nitrogen lone pair to the carbonyl in the diimide, as described by Matsuo[6] for the case of *N*-substituted maleimides, should be similar in nature to that of delocalization of the oxygen lone pair to the carbonyl in the dianhydride. In our study it was found that, while the absorption maxima of zone-refined PMDA in dioxane occurred at 304 and 314 nm, the excitation maximum was coincident with a minor absorption peak in the tail of the absorption spectrum at 475 nm. In our study of sublimed ODA, an interesting phenomenon with respect to ODA concentration in a variety of solvents was observed. For low concentrations of ODA, 10^{-6} mol l^{-1}, the excitation spectrum was consistent with the absorption spectrum, having absorption maxima at 250 and 305 nm. However, as the concentration was increased, the excitation spectrum both red-shifted and changed shape with concentration while the absorption spectrum was essentially invariant with concentration. At 10^{-2} mol l^{-1} the excitation spectrum of ODA in dioxane consisted of a single peak at 350 nm with total self-absorption for excitation at shorter wavelengths.

While the observed excitation spectra of PMDA and ODA are still under investigation, their individual spectra can be used to elucidate the PMDA–ODA polymer excitation spectra. The fact that the excitation λ_{max} of both PMDA and concentrated ODA are red-shifted with respect to the absorption maxima is consistent with the excitation spectra of PMDA–ODA. In addition, the total self-absorption of low-wavelength illumination in concentrated ODA might explain the lack of fluorescence from low-wavelength illuminated PMDA–ODA.

We believe, similar to Ishida[2], that the lower-wavelength excitation band of PMDA–ODA is a $\pi \rightarrow \pi^*$ transition and due to the model compound study believe

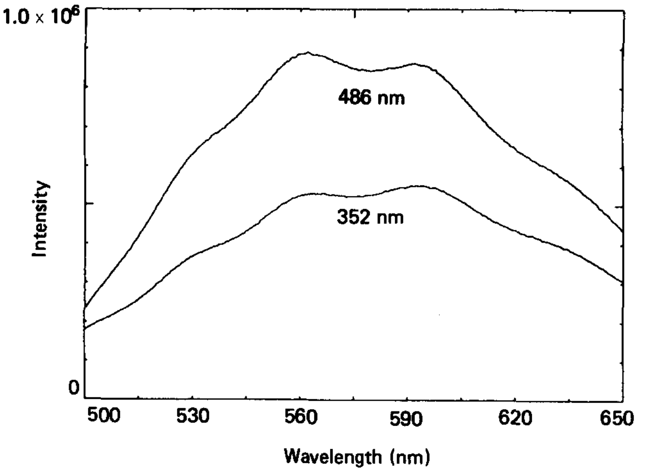

Figure 5 Emission spectra of a 450°C cured sample for 352 and 486 nm excitation

that the band originates at the diphenyl ether moiety. In addition, the longer-wavelength excitation band can be attributed to an $n \rightarrow \pi^*$ transition of the pyromellitimide moiety. It is not clear, however, why the red shift and intensification with conjugation requires that it should change to a $\pi \rightarrow \pi^*$ transition. Rather, we cite the work by Matsuo[6] to account for the red shift of the $n \rightarrow \pi^*$ transition with conjugation.

Excitation of either the broad or structured excitation bands results in a similar emission spectrum. *Figure 5* is an overlay of the emission bands from 352 and 486 nm excitation for the same 450°C cured sample. The positions of the peaks at 562 and 592 nm and the shoulders at 534 and 630 nm are identical and only the relative emission intensity varies. This similarity in emission spectra suggests that the emission chromophore is the same for both excitation wavelengths.

Evidence for the formation of a charge transfer complex (CTC) in aromatic polyimides has been presented by a number of authors[8–10]. Fainshtein *et al.*[8] investigated the conduction of a variety of polyimides and found it to be a function of the electron affinity of the dianhydride acceptor, providing evidence for the donor–acceptor property of CTC formation. Kotov *et al.*[9] investigated the absorption of a variety of individual dianhydride and diamine fragments, their complexes and the polyimides formed. They concluded that the long-wavelength absorption tail is due to the formation of a complex because the tail was only present in the presence of both donor and acceptor fragments. Fryd[10] investigated the effect of different diamines and dianhydrides on the T_g of the resulting polyimide and concluded that the ability of the polyimide to form a CTC played a major part in elevating the T_g.

In light of these literature results, we suggest that our fluorescence spectra are the result of excitation of either the diphenyl ether or pyromellitimide moieties followed by emission while in a CTC state. The CTC state occurs when the pyromellitimide and diphenyl ether groups are coplanar. This interpretation is similar to the previous discussion of the long-wavelength absorption tail of Ishida's[2] substituted pyromellitimides. In such a configuration, charge transfer can occur either intramolecularly from the donor to acceptor fragments across the conjugated π-orbital network or intermolecularly between adjacent coplanar fragments. If the fluorescence is an intramolecular process, then the increase in intensity with cure may be due to an increase in the population of the coplanar state. If the fluorescence is an intermolecular process between parallel planar structures, then the increase in intensity can still be related to an increase in the population of the coplanar state since the coplanar structure is necessary for the formation of the fluorescing sandwich structure.

This increase in emission intensity with population of the coplanar state provides a local torsional probe of rotation around the nitrogen–phenyl bond. Hence, one of the observed activation energies of the emission intensity can be assigned to rotation around the nitrogen–phenyl bond, either in terms of a rotational barrier to hindered rotation or as the exponential term in a Boltzmann distribution of quantized rotational states. Hayashi *et al.*[11] have shown that rotation of the amino–phenyl bond in *N,N*-dimethylaminobenzonitrile results in the formation of a twisted intramolecular charge transfer complex. This has been investigated using fluorescence spectroscopy and found to have an activation barrier of $\sim 7\ \mathrm{kcal\ mol^{-1}}$ in concentrated solution, comparable to that found in this investigation. This local torsional rotation around the amino–phenyl bond is analogous to what we believe occurs with cure in polyimide. Moreover, the reported activation energy is in line with our observed thermal activation energy as well as with the expected heat of formation of a charge transfer complex, which is of the order of $5\ \mathrm{kcal\ mol^{-1}}$ (ref. 4). As a separate activation energy was observed for each of the two excitation bands, we conclude that if the CTC is intramolecular then there is a second change in conformation with cure, such as bending of the nitrogen–phenyl or ether bonds or rotation round the ether bond. If the CTC is intermolecular then there might be two different morphologies. The increase in aggregation resulting in a decrease in the intermolecular distance between adjacent chromophores might then result in fluorescence of chromophores with orientational differences. Alternatively, there might be both intrachain and interchain CTCs and the dual excitation bands might be as a result of each. These points require further study.

Iida *et al.*[12] found that irradiation of polyimide at approximately 350 and 460 nm resulted in photoinduced current. Since these wavelengths correspond to the same excitation bands utilized in this investigation, it is quite possible that the fluorescence observed in the present study and the photogeneration of conduction electrons are related. Iida also found that the photocurrent depended strongly on the molecular ordering. Stretching of previously cured films at room temperature resulted in an increase in photocurrent and a reduction of molecular ordering, as determined by monitoring the intermolecular spacing with X-ray scattering. Wellinghoff *et al.*[13] have shown that the phenoxyphenyl group, incorporated in polyimide and lying outside the crystalline region, will rotate around the nitrogen–phenyl bond in response to a tensile stress along the film plane. This rotation results in a change in the electron hybridization of nitrogen from sp^2 in the planar structure to that of sp^3 in the rotated structure. These results indicate that a change in molecular ordering is accompanied by a rotation around the nitrogen–phenyl bond. A conformational probe of the rotational state of the nitrogen–phenyl bond can then be used to indicate the molecular ordering in polyimide.

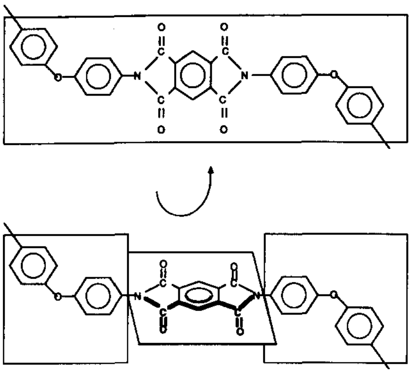

Figure 6 Rotation around the nitrogen–phenyl bond between the coplanar and perpendicular conformations

Molecular ordering

While it is generally accepted that the degree of aggregation increases with cure, the morphology of the aggregated region is currently still a subject of controversy. The most recent literature on the structure of polyimide has indicated that the molecular aggregation of polyimide results in only an amorphous or middle-ranged order[14–16] while some earlier authors cite the crystallizability of polyimide[17,18]. Another school of thought has been that cured polyimide is mesomorphic owing to its observed short-range order[19]. This short-range ordering is intermolecular and is caused by the parallel overlap of planar structures within the main chain. There is no long-range order in excess of about 100 Å because of the flexible linkages between the rigid aromatic groups of the main chain, such as the ether linkage in PMDA–ODA, preventing the formation of a truly crystalline polymer.

Part of the reason for this controversy lies in the method of sample preparation in that T_g changes with degree of cure, which itself changes with the cure temperature (T_c). The degree of cure is limited by the segmental mobility at any isotherm. In other words, quasi-equilibrium is obtained at any cure temperature, yet subsequent heating to a higher temperature will result in a greater degree of cure. It has been proposed that the glass transition temperature is approximately equal to the cure temperature for any specific cure[20]. Thus the polyimide must be heated above its previous T_c in order to allow sufficient segmental mobility so that a higher degree of cure can be obtained. Another consequence of sample preparation is that imposition of an external strain during cure can enhance the degree of ordering and impart a direction of orientation to the sample. Differing results may be obtained depending on whether the sample undergoes uniaxial strain (as in fibres), biaxial strain (from spinning on wafers) or if the sample is cured as a free-standing film.

Understanding the phenomenon of molecular ordering in polyimide is of significant interest regardless of whether the observed short-range order in polyimide is due to the formation of crystalline regions in an amorphous matrix or to the occurrence of mesomorphic behaviour. Some of the first authors to report on the crystalline structure of aromatic polyimides were Kazaryan *et al.*[17] Their data were gathered by X-ray diffraction studies of uniaxially oriented fibres and films. The results for PMDA–ODA indicate that crystallites of orthorhombic symmetry are formed with lattice parameters $a=6.31$, $b=3.97$ and $c=32$ Å, and that the molecule forms a second-order helix along the fibre axis (c). The chain conformation is that of a planar zig-zag structure, with the repeat unit consisting of two monomeric segments bent at alternating ether linkages.

Krasnov *et al.*[18] related their X-ray data to theoretical calculations and presented a theory for aromatic polyimide crystalline structures whereby the polyimide molecules orient themselves in parallel planar groups. Potential energy wells were calculated for rotation of main-chain phenyl rings in and out of parallel alignment. Their calculations indicated that, below a certain limit in oscillation amplitude, torsional oscillations of phenyl rings are mainly determined by the intramolecular barrier for hindered rotation. However, as the packing density increases, intermolecular repulsion between adjacent rings becomes the dominant force. They estimated that adjacent phenyl rings could undergo free rotation unhindered by intermolecular interactions if they were separated by an intermolecular distance of 6.6 Å or more. An intermolecular spacing of 5.2 Å would result in a barrier of 400 kcal mol^{-1} that would be prohibitive to phenyl rotation. These values for the effect of intermolecular spacing on phenyl rotation can be compared with the intermolecular spacing of 4.7–4.9 Å in the most highly ordered state[17]. This indicates that, for highly ordered polyimide, the rotational orientation of phenyl rings is fixed. The magnitude of the intermolecular spacing also requires that the adjacent phenyl rings associated with the diamine moiety be fixed coplanar with the imide moiety in highly ordered polyimide. However, there could be sufficient intermolecular spacing to allow rotation of phenyl rings around non-cyclic main-chain bonds in disordered polyimide in solution, in the partially cured (<200°C cure) condensed state or in the amorphous region of a fully cured film.

Changes in the morphology of PMDA–ODA either as an amorphous-to-crystalline phase transition or as an increase in the localized aggregation of a mesomorphic phase can be fully described by conformational changes associated with the nitrogen–phenyl and ether linkages. The structure of PMDA–ODA and the change in conformation with rotation around the nitrogen–phenyl bond are depicted in *Figure 6*. The increase in ordering of polyimide with cure has been associated with short-range changes in conformation. Owing to the 109° bond angle in the ether linkage, any rotation around the oxygen–phenyl bond would result in a change in the long-range ordering, unless cooperative rotation occurred along the chain. The pyromellitimide moiety, defined by the region across the acid dianhydride fragment from one nitrogen–phenyl bond to another, is a planar structure. Cooperative rotation of the nitrogen–phenyl bonds on either end of this moiety results in a short-range (single-segment) change in molecular ordering. The reduction in free energy of such a rotation to the planar conformation is twofold. First, the energy of conjugation, when the pyromellitimide moiety is coplanar with the phenyl rings on either side, is energetically favourable owing to the electron delocalization made available by the π-orbital overlap in the coplanar structure. Secondly, rotation around the nitrogen–phenyl bond to form the coplanar structure allows closer packing of adjacent chains oriented in the same direction, thereby obtaining a more ordered and lower-energy state. This lower-energy state is necessary in order to form the crystalline structure[17]. Thus the emission intensity can be used as a local torsional probe of the nitrogen–phenyl bond to determine the relative population of the coplanar structure and in so doing infer the relative degree of ordering.

CONCLUSIONS

Fluorescence spectroscopy can be used to monitor the degree of cure of polyimide. The observed increase in emission intensity with cure is caused either by an intramolecular rearrangement associated with coplanarization or by an intermolecular change in ordering associated with the increase in aggregation. Since both of these phenomena proceed concurrently, it is difficult to assign responsibility to either exclusively. The change in short-range order associated with an increase in aggregation or crystallinity with cure can be attributed to conformational changes such as the rotation of the nitrogen–phenyl bond, thus allowing denser packing of adjacent chains. We believe this type of rotation to the coplanar structure is responsible for the increase in emission intensity with cure.

ACKNOWLEDGEMENT

This work was partially supported by the Stanford Institute for Manufacturing and Automation at Stanford University.

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