Evolution of the Molecular Organization in Bis(*n*-propylimido)perylene Films under Thermal Annealing

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Submicron thin solid films of bis(*n*-propylimido)perylene have been fabricated on several substrates by vacuum evaporation. The effect of postdeposition thermal annealing on the molecular orientation was examined using in situ reflection absorption infrared spectroscopy. The interpretation of the vibrational infrared and Raman spectra of the neat material and films was first undertaken to provide the vibrational backgrounds for the interpretation of changes observed on thermal annealing by reflectance spectroscopy. The spectroscopic characterization include FT Raman, electronic, and emission spectra of solutions, bulk solid, and nanometric films.

Introduction

Organic photoconductive materials have, in the past 30 years, enjoyed much scientific attention. This interest comes on the heels of the quest for and harnessing of alternative sources of clean energies, such as solar energy. Though initial attention was focused on inorganic photoconductive materials for solar energy conversion, the advantages of organic materials have been recognized.[1] Solar energy conversion, however, is just one of many potential uses of organic photoconductive materials, others include electrophotography and xerography. Moreover, the vast availability of molecular photoconductive materials, low production costs, immense diversity, lower toxicity as compared to their inorganic counterparts, and the ability to synthetically optimize these materials for a specific set of desired properties has fuelled this interest.[2] Perylenebis(dicarboximides) are a type of such organic materials that are also distinguished by a high quantum yield of fluorescence, that makes them highly promising materials for dye lasers.[3]

The study of the photophysical and electrical properties of organic photoconductors is essential to determining important chemical and physical factors that influence, and in some cases govern, the characteristics of these materials. These factors include molecular structure and solid state morphology, and it has been generally assumed that the structural order of the material is a determinant factor in the understanding and control of their inherent photophysical and electrical properties.[4] In many cases correlations have been established between the value of a certain property as a function of the degree of molecular orientation, such as the change in photoconduction.[1] The attempt to investigate the solid-state morphology of molecular photoconductors is clouded by the fact that for a single material, polymorphism often occurs. Polymorphism in perylene pigments has been reported[2] and, as with phthalocyanines, is thought to be due to the intermolecular forces between the perylene molecules such that a variety of molecular stacking arrangements of similar interaction energies are possible.[5] This phenomenon alludes to the fact that for a thin film, not only does phase heterogeneity influence its properties but in addition consequent phase transformations, degree of crystallinity, and the various types of crystal structures a polymorph may assume must be taken into consideration.

In the thin-film technique used here, the perylenebis(dicarboximide) material is physically deposited by vacuum evaporation. The advantages of the technique are the applicability to any material, wide adjustability in substrate temperature, access to surface during deposition, and lower contamination. In vapor-phase techniques, the deposition is determined by the source, the transport factors, and three principle surface factors: substrate surface condition; reactivity of the arrival material, and the energy input. The energy input is possibly the most important influencing surface factor and may be applied in situ or postdeposition. These

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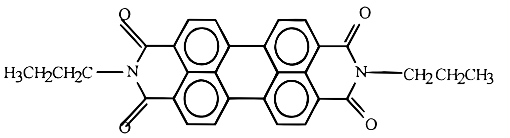
factors determine the structure and composition of the deposited film and in turn the various film properties: optical, electrical, magnetic, chemical, mechanical, and thermal.[6]

Vibrational spectroscopy provides four observables that may be used to extract physical information from thin solid films: the resonance band position, the band shape, the selection rules, and the band intensity. It is this wealth of information that makes vibrational spectroscopy a unique optical probe for determination of the overall structure, chemical, mechanical, and localized intermolecular interactions in thick and submicron thin solid films.[7] In particular, the simple polarization selection rules operating in the specular reflection absorption infrared spectroscopy (RAIRS) have been extensively used to determine the orientation of nanometric organic films thermally deposited on a reflecting metal surface. Transmission and reflection spectroscopic techniques can be used complementary to enable a definitive account of the molecular orientation of perylene molecules.[8,9] In the present work these tools are used to investigate the evolution in the solid-state molecular organization of PTDIPr films as revealed by the change in the degree of molecular orientation after thermal annealing.

Experimental Section

Bis(*n*-propylimido)perylene. This perylene pigment was prepared by condensing perylene-3,4,9,10-tetracarboxylic acid dianhydride with propylamine in an appropriate solvent.[10] The product was purified by temperature gradient sublimation.



Thin-Film Preparation. The substrates used were transparent and precleaned Borosilicate slides (Baxter Cat. M6145). They were cleaned by rubbing with absolute ethanol and subsequent drying under a continuous flow of dry nitrogen gas. Metal deposition was performed in a Balzers vacuum system evaporator equipped with an Edwards E2M2 rotary vacuum pump, which function as precursor to the Edwards diffusion pump. Silver shots (Aldrich 20,436-6) were thermally evaporated from a cupped tungsten boat, using a Balzers BSV 080 glow discharge/evaporation unit. The background pressure was nominally 10^{-6} Torr, as measured by the Balzers IKR 020 cold cathode gauge. On a substrate preheated to 200 °C, silver was deposited at a rate of 0.5 nm/s to a total mass thickness of 100 nm. This deposition rate was allowed to stabilize before the shutter was opened. Film thickness and deposition rate were monitored using a quartz crystal oscillator. The bulk density of silver employed was 10.5 g/cm^3, the tooling factor 105%, and the *Z* ratio 0.529. The PTDIPr was deposited onto continuous silver films (mass thickness, 100 nm) and silver island films (mass thickness of 6 nm), in turn supported on a glass substrate. The evaporation system used was of the same setup aforementioned, with the exception that the substrate was not heated. The perylene pigment was evaporated from tantalum boats at room temperature and the deposition rate for PTDIPr was 0.2 nm/s. The bulk density employed for PTDIPr material was 1 g/cm^3, the tooling factor 92%, and the *Z* ratio 1.

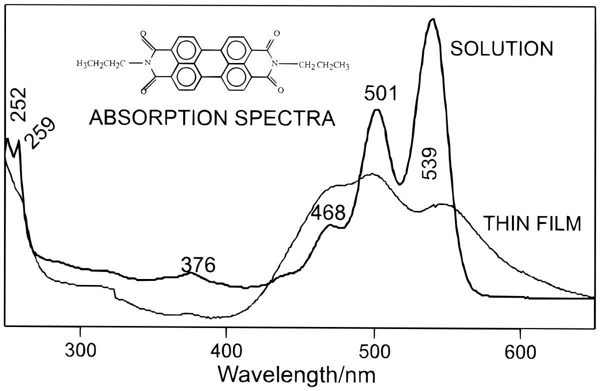


Figure 1. Absorption spectra of PTDIPr in solution and of a thin solid film.

Film Characterization. The main reference in the infrared spectra is the transmission spectrum of the isotropically dispersed PTDIPr in KBr. Infrared spectra were routinely recorded in the region of 400−4000 cm^{-1} on the Bomem DA3 FTIR spectrometer with a 1 cm^{-1} resolution. The reflection absorption infrared spectra were recorded on an in-house-modified Bomem 110-E equipped with a Judson midrange (650 cm^{-1}) 1 mm × 1 mm MCT detector.[11] The entire system was purged and maintained under a closed cell of dry air. The sample holder was adapted to include four concave mirrors which focused the IR beam onto the substrate at an 80° angle of incidence.[12] The substrate holder consisted of a flat aluminum heating element, which was thermally controlled by a 100 V variastat. The temperature of the substrate was monitored using a thermocouple. Annealing of the sample during the RAIRS measurements was performed in situ on the heating plate.

The FT Raman spectrum of PTDIPr was recorded with a Bruker RFS100. The surface-enhanced Raman spectrum was recorded with a THR 1000, using the backscattering geometry of a microscope attachment with a ×100 objective, and a liquid nitrogen cooled CCD detector.

Model Calculations. Geometry optimization and vibrational calculations performed to help the assignment were executed on Hyperchem 4.5. Calculations for the perylene tetracarboxylic acid dianhydride (PTCDI) moiety were carried out using the semiempirical AM1 and PM3 methods.

Results and Discussion

Spectroscopic Characterization of the Material. The electronic absorption spectra of PTDIPr in solution and that of a thin solid film evaporated onto KBr substrate is shown in Figure 1. The characteristic vibronic progression of PTCD molecules is clearly observed in the dilute solution spectrum.[13] It should be pointed out that the vibronic structure corresponds to a constant wavenumber of 1407 cm^{-1}. This is the difference between the 0,0 band at 539 nm and the 501 nm maximum, and the difference between the 0,1 band at 501 nm and the 468 nm band. The same components are seen in the electronic spectrum of the film; however,

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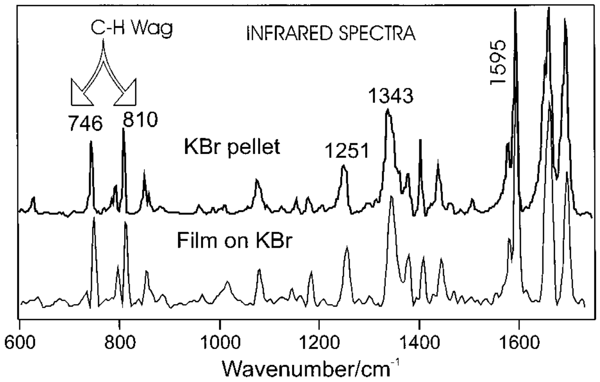

Figure 2. FTIR transmission spectra of an isotropic sample and a thin solid film of PTDIPr on KBr.

the effect of band broadening in the solid produces an overlapping as shown in Figure 1. The broadening observed in the film's spectrum is even more pronounced in the electronic absorption spectrum of the isotropic sample (KBr pellet). A characteristic broad excimer emission was observed for the evaporated film at 686 nm and for the KBr pellet at 696 nm. The steady-state fluorescence spectrum in solution was identical with that of other members of the series.[4]

Vibrational Spectra. The 168 fundamental vibrational modes of bis(*n*-proplylimido)perylene were calculated using semiempirical AM1 and PM3 methods, but only the assignment of characteristic fundamental vibrational wavenumbers is discussed. For large molecules the local symmetry arguments may be used to find the directionality of the dipole moment derivatives that may allow molecular orientation determination. Therefore, the goal here is the identification of normal modes and local symmetry assignments, i.e., the identification of the molecular group largely responsible for the change in the dipole moment as well as the directionality of the dynamical dipole. For instance, the infrared active vibrations of the PTCD moiety may be classified into in-plane and out-of-perylene-plane fundamental vibrational modes. Further, the normal modes of PTDIPr are expected to correlate with the vibrational spectra of *N*-pentyl-*N'*-propylperylenebis(dicarboximide) (PPTCDPr) that has been previously reported.[4]

The most significant and relevant group frequencies for molecular orientation considerations in PTDIPr films are the carbonyl stretching vibrations, the in-plane C=C and ring stretching vibrations of perylene, and the out-of-perylene-plane C−H wagging vibrations. The antisymmetric and symmetric in plane C=O stretching vibrations for PTDIPr are observed at 1662 cm^{-1} and 1697 cm^{-1}, respectively, while the C=C stretches are at 1595 and 1580 cm^{-1}. The two out-of-plane vibrational modes with a dynamic dipole moment perpendicular to the perylene plane, the C−H wags, are observed at 810 cm^{-1} and 746 cm^{-1}.[9] The infrared spectrum of the isotropic sample and that of the thin solid film on KBr are shown in Figure 2. The transmission spectra of the evaporated film of the PTDIPr, shown in Figure 2, reveals that the out-of-plane C−H wagging bands at 746 and 810 cm^{-1}, and the carbonyl stretchings observed at 1662 and 1697 cm^{-1} have the same relative intensity as found in the isotropic sample. The differences in relative intensities between the infrared spectra of bis-PTDIPr dispersed in KBr (isotropic reference sample), and the evaporated thin film are minimal, indicating that anisotropies in the thin-film structure are not detectable. It may be concluded that the film formed on KBr does not present any large degree of molecular organization. The full bandwidths at half-maximum (fwhm) are also very similar for the two samples. Since fwhm are sensitive to changes in the intermolecular interactions due to molecular alignment, it is a confirmation of minimal organization in the evaporated film. Relative intensities, fwhm, and the corresponding wavenumbers for all the infrared spectra are listed in Table 1.

FT Raman and SERRS. The selection rules for infrared and Raman are extracted from a comparison of the FT Raman and FT-IR spectra of PTDIPr presented in Figure 3. It can be seen that although the relative intensities are very different, the Raman-active bands are also observed in the FTIR spectrum. The off-resonance FT Raman excited at 1064.1 nm shows the main peaks of the chromophore that are also seen in resonance Raman effect and surface-enhanced resonance Raman scattering (SERRS) as shown in Figure 4. Two important differences between the FT Raman and SERRS: first, the carbonyl stretching vibrations are not seen in SERRS. Second, the SERRS spectrum shows very clearly the presence of combinations and overtones in the 3000 cm^{-1} region. Since the problem of overtone intensities is particularly interesting in resonance Raman spectroscopy, a separate study of overtones in RRS and SERRS for a series perylene derivatives is underway. In conclusion, the observation of vibrational modes in both the infrared and Raman spectra defines a low-symmetry point group (Cs or C_1) for this symmetrically substituted PTCD molecule. The relative intensities, fwhm, and the corresponding wavenumbers are listed in Table 2.

RAIRS and Thermal Annealing of Thin Films

For polarized radiation, the absorption by infrared active modes depends on the square of the cosine of the angle between the electric vector **E** and the dynamic dipole μ. In reflectance spectroscopy, the reflectivity of the metal fixes the polarization of the light. At the appropriate angle of incidence, the p-polarized ($\mathbf{E}\perp$, perpendicular to the metal surface) component of the electromagnetic wave is the main source for signal detection and the intensities are completely determined by the directionality of μ at the surface. The prediction of intensities for a well-defined molecular orientation is what is termed "surface selection rule".[14] Simply, this implies that the vibrational modes that have a dynamic dipole moment perpendicular to the metal surface will be enhanced, while those parallel to the surface would be suppressed. The RAIRS spectra of PTDIPr deposited onto a smooth 100 nm silver surface are shown in Figure 5. The vibrational probes used here for molecular orientation on the surface are the C−H wags at 810 and 746 cm^{-1} and the in-plane C=O stretching vibrations. The reference spectrum is the KBr spectrum given in Figure 2. The spectrum label before annealing is the

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Table 1. Observed Infrared Wavenumbers for PTDIPr[a]

	KBr pellet		film		RAIRS-1		RAIRS-2		
cm^{-1}	RI	fwhm	RI	fwhm	RI	fwhm	RI	fwhm	assignment
746	16	6	33	6	16	6	100	6	C−H wagging
810	13	5	28	5	17	5	78	5	C−H wagging
850	4	5	4	5	7	5	24	5	C−H wagging
1077	15	9	14	9	12	8	15	8	C−H bend
1083	20	11	3	9			5	7	C−H bend
1251	24	12	25	12	15	11	19	10	C−H bend
1343	61	14	57	16	6	12	20	10	C−N stretch
1404	13	6	15	6	7	6	5	6	ring stretch
1440	24	9	21	7	6	10	5	9	ring stretch
1580	6	11	12	8	2	8	2	7	C=C stretch
1595	38	8	50	8	21	8	25	7	C=C stretch
1652	62	12	30	10	10	9	18	9	C=O stretch
1662	100	9	100	9	84	10	30	7	C=O stretch
1688	60	8	7	11	30	8	7	8	C=O stretch
1697	66	11	51	11	100	11	25	8	C=O stretch

[a] Relative intensity (RI) and the full width at half-maximum (fwhm in cm^{-1}) are given for each spectrum. RAIRS-1: room temperature. RAIRS-2: spectrum at 200 °C.

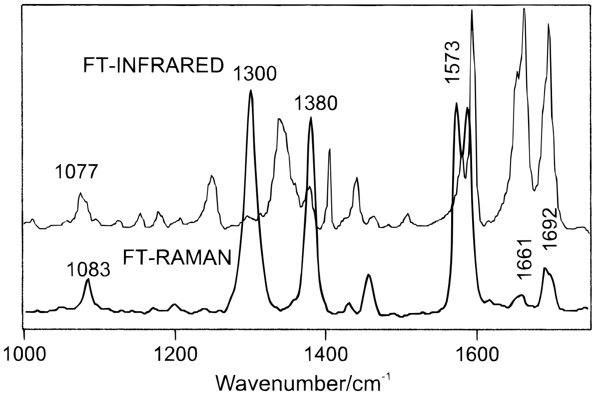

Figure 3. FT-Raman and FTIR spectra of the isotropic PTDIPr sample.

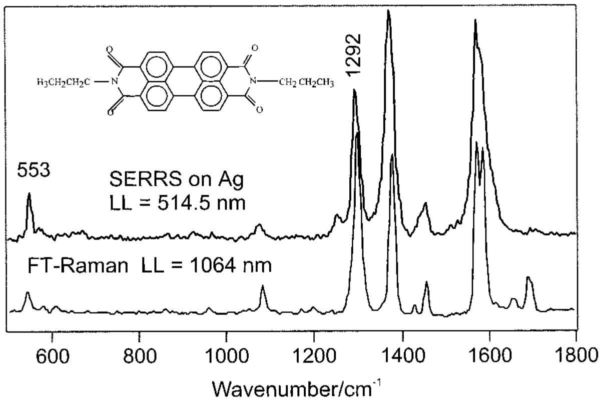

Figure 4. Enhanced inelastic light scattering in resonance with the electronic transition (SERRS) at 514.5 nm and the off resonance spectrum at 1064.1 nm.

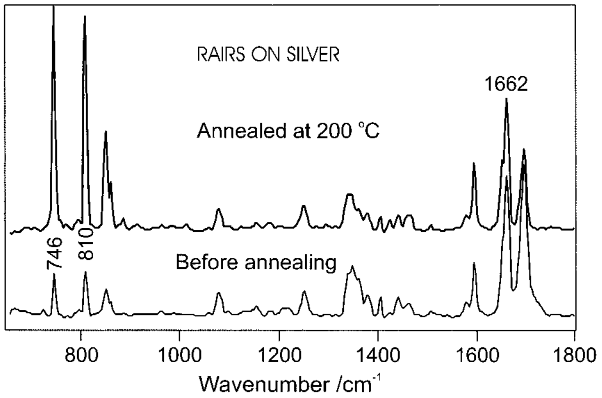

Figure 5. Reflection absorption spectra of PTDIPr film at room temperature and after annealing at 200 °C.

Table 2. Raman Wavenumbers, Relative Intensities (RI), and fwhm (in cm^{-1}) for PTDIPr

FT Raman (1064 nm)			SERRS (514.5 nm)			
cm^{-1}	RI	fwhm	cm^{-1}	RI	fwhm	assignment
545	6	12	553	9	12	per ring def
1083	10	12	1076	2	12	C−H bendings
			1255	8	16	C−H bend
			1292	34	11	C−H bend
1300	100	19	1300	27	11	per ring stretch
			1372	100	17	per ring stretch
1380	63	15	1381	17	10	per ring stretch
1431	1	10	1442	7	15	per ring stretch
1456	10	12	1456	10	13	per ring stretch
1573	47	11	1572	60	11	C=C stretch
			1581	41	11	C=C stretch
1588	60	14	1590	30	17	C=C stretch
1653	1	9				C=O stretch
1661	3	11				C=O stretch
1692	8	10				C=O stretch
1701	6	9				C=O stretch

original film evaporated onto the silver surface held at room temperature. The C−H wagging modes have a dynamic dipole perpendicular to the plane of the chromophore, while the C=O modes have a μ in the plane of the perylene moiety. Therefore, as the molecule becomes oriented with the perylene ring flat-on the silver surface, the dynamic dipole of the C−H wagging bands becomes more parallel with the electric field component, which results in the enhancement of these C−H bands, as observed.

The correlation between thermal annealing and molecular orientation in PTCD derivatives has not yet been investigated to date. There are many consequences of thermal annealing, and they include reevaporation of the dye from the substrate, decomposition, oxidation of the metal substrate, and polymorphism. Experimentally, to guard against extensive oxidation, the thermal annealing of the thin films was performed in a dry air-purged cell. The perylene studied was established to be thermally stable within the temperature range employed for annealing, with decomposition temperatures above 450 °C. The decomposition temperatures were verified by performing DSC measurements.

A study of bis-PTDIPr spectra, indicated that the overall intensity of the vibrational bands has not decreased on annealing, therefore ruling out the possibility of reevaporation. A close inspection, reveals that there are four carbonyl components at 1652 and 1662 cm^{-1}, 1688 and 1697 cm^{-1}. The high-wavenumber bands are the locally symmetric stretches (μ along the long perylene axis) and the middle are the locally antisymmetric vibrations. Thus, the strong absorption at 1697 cm^{-1} points to a certain degree of head-on molecular orientation of the perylene moiety on the surface of the substrate. On thermal annealing the relative intensity of the 1662 cm^{-1} is the strongest in the group. Since the effective dynamic dipole of this C═O modes is along the short perylene axis, it indicates an edge-on molecular orientation of the perylene chromophore. In summary, the RAIRS spectra of the annealed bis-PTDIPr film reveals a large increase in relative intensity for the C−H out-of-plane wagging that is consistent with a predominant perylene flat-on molecular orientation. The analysis of the C═O bands further points out an intensity contribution from a fraction of molecules with an edge-on orientation. Furthermore, as can be seen in Table 1, annealing is characterized by a smaller fwhm in some bands. This provides evidence for a reduction in the amorphous content of the sample as the sample adopts a more crystalline configuration.

Conclusion

In conclusion, it is shown that thermal annealing of physisorbed molecules, such as bis-PTDIPr, can effect a change in the molecular orientation and increase molecular organization in the evaporated film. Harnessing this tool to produce films of a certain molecular architecture is industrially important. In the xerographic industry molecular architecture, as defined by polymorphism and molecular orientation of the dyes on a substrate, strongly influences the photogeneration efficiency of a photoconductor and hence photoconductivity. A spectroscopic characterization of the new material has been carried out to determine molecular symmetry and fundamental vibrations of the chromophore. The chromophore was also characterized by the absorption and emission electronic spectra, and its surface-enhanced resonance Raman scattering.

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