

High Pressure Visible Spectroscopy of Polyimide Film

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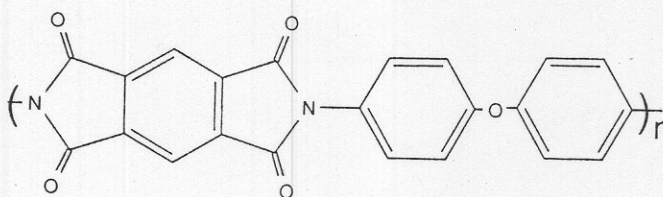
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INTRODUCTION

The origin of the color of polyimide films has been a mystery for some time. Initial studies suggested that interactions between the aromatic backbone moieties and the imides might lead to a low energy charge transfer transition in the absorption spectrum. Studies of low molecular weight model imides supported this assumption,¹ and spectroscopic examination of a series of polyimides indicated the presence of a low energy transition which was dependent upon the ionization potential of the diamine segment in the polymer backbone.^{2,3} One of the more interesting ramifications of this work has been the use of the charge transfer complex hypothesis to explain and predict structure-property relationships of polyimides.^{4,5} In this paper, we present data on the high pressure electronic spectroscopy of Kapton[®] polyimide film and show how these spectra provide direct evidence of intermolecular charge transfer complex formation in polyimide films.

EXPERIMENTAL

Kapton[®] polyimide film samples were commercial material 0.3 mil in thickness and 150 × 150 micron square. Kapton[®] type H polyimide film is composed of the chemical structure shown below.



Hydrostatic pressure was applied to the Kapton[®] polyimide film sample with a diamond anvil cell (DAC) constructed after the NBS design. The film was placed inside a 300 micron hole drilled in the center of a steel gasket pre-indented by the diamond

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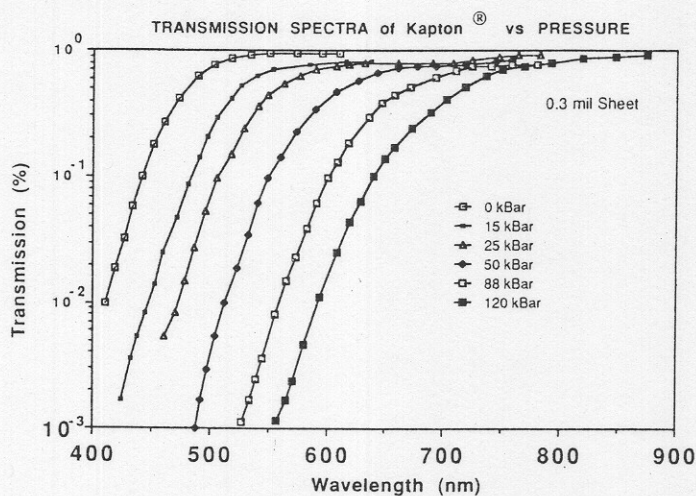


Fig. 1. Transmission spectra of 0.3 mil thick Kapton® film measured as a function of pressure at room temperature.

anvils. The hole was then filled with a 1:4 ratio of ethanol:methanol mixture as the pressure medium. A small ruby chip was placed in the compartment near the film for determination of the pressure through the use of the ruby fluorescence method.⁶ After loading of the sample, the DAC was pressurized with a hydraulic press to the desired pressure and the pressure retained in the cell with a lock ring. The pressurized cell containing the film sample was then placed in the optical line for transmission measurements.

The pressurized Kapton® polyimide film was illuminated with light from a tungsten-halogen lamp. Light transmitted through the film was imaged onto an aperture and then into a 1/3 meter grating spectrometer (Instrument SA Inc. Model HR320). The aperture size was smaller than the image of the sample so that only light transmitted through the sample entered the spectrometer. The light dispersed by the spectrometer was detected by a photomultiplier with a GaAs photocathode. The intensities of light transmitted through the sample and through a spot immediately adjacent to the sample were recorded on successive scans. The transmission coefficient of the sample was computed from the ratio of these two intensities. This procedure was repeated for each pressure increment up to 120 kBar.

RESULTS AND DISCUSSION

The high pressure transmission spectra of Kapton® polyimide film band edge in the visible are shown in Figure 1 as a function of pressure. Because of the high absorption coefficient and the thickness of the film, the techniques employed could not be used to monitor the absorption maxima. Figure 2 shows the variation of the absorption edge of Kapton® polyimide film with pressure, where the absorption edge has been arbitrarily defined as the wavelength at which the transmission coefficient drops to 1% of the maximum value. Although the absorption edges broaden slightly with increase in pressure, as is evident in Figure 1, this does not have a serious effect on the steepness of the absorption edge, so the slope of the absorption edge versus pressure curve in Figure 2 should not be dependent upon the definition of the absorption edge. At pressures below 120 kBar, the spectroscopically observed changes were strictly reversible.

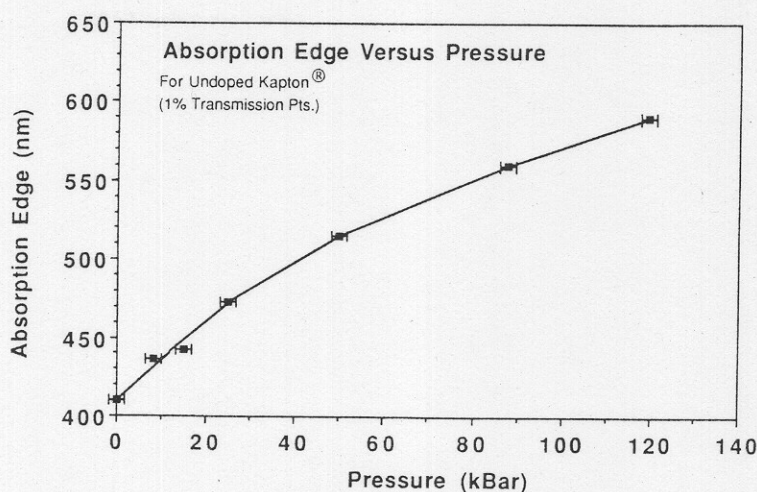


Fig. 2. The shift of the absorption edge of 0.3 mil thick Kapton® film as a function of pressure deduced from the transmission curves in Figure 1. The absorption edge has been defined as the wavelength at which the transmission coefficient decreases to 1% of the maximum value.

The apparent red shift of the absorption band edge in Kapton® polyimide film is consistent with an assignment of this low energy transition as charge transfer in nature. The pressure dependence of organic charge transfer complexes has been studied in the solid state, solution, and in polymer matrices.⁷⁻¹² These studies demonstrate that the charge transfer transitions in organic species show a pressure dependence which is characterized by an increase in intensity, an invariance of the absorption band width, a change in the complex equilibrium constant, and an energy shift which is variable in magnitude and direction, depending upon the composition, with increasing pressure. All of these changes can be understood in terms of Mulliken charge transfer theory,¹³ and have been outlined by Offen¹¹ and Sawamura.⁸ In this analysis, the energy of the charge transfer transition, $h\nu_{ct}$, is given by^{13,8}:

$$h\nu_{ct} = (4\beta_0\beta_1 + E^2)^{1/2}(1 - S_{01})^{-1} \quad (1)$$

$$E = W_1 - W_0 \cong I_p - E_a - (e^2/r_{DA}) \quad (2)$$

$$\beta_0 = W_{01} - W_0S_{01} \quad (3)$$

$$\beta_1 = W_{01} - W_1S_{01} \quad (4)$$

where W_0 is the energy of the no-bond structure, W_1 is the energy of the "dative" structure, and W_{01} is the interaction matrix, which is approximately proportional to the overlap integral S_{01} . For a weak charge transfer complex, $S_{01} < 1$. I_p and E_a are the ionization potential of the donor and the electron affinity of the acceptor respectively, while e and r_{DA} represent the charge on an electron and the intermolecular spacing, respectively. For a weak charge transfer complex $4\beta_0\beta_1 \ll E^2$.¹³ As pressure is increased, r_{DA} decreases and S_{01} increases, resulting in an overall decrease in the energy of the charge transfer transition and a red shift of the absorption maximum; such a shift is found in the data shown in Figures 1 and 2.

The data presented in Figures 1 and 2 show only the band edge of the spectrum. As the data do not show a true shift in the absorption maximum, additional factors,

which may lead to the observed red shift, need to be considered. With increasing pressure and decreasing r_{DA} , the increase in S_{01} increases the magnitude of charge transfer, and thus the intensity of the charge transfer band is amplified.¹³ Although the width of the transition is invariant with pressure, the band edge will appear to shift to lower energy with an increase in the intensity, over and above the intrinsic red shift of the absorption maximum. This result is also an implication of the charge transfer nature of the band edge. In addition to electronic considerations, the equilibrium constant for complex formation is expected to increase with increasing pressure.^{10,14} A larger equilibrium constant results in an increase in the intensity of the charge transfer absorption and will be apparent as a red shift in the band edge.

In summary the observed pressure-induced red shift of the absorption band edge can best be understood by application of Mulliken theory for intermolecular charge transfer transitions. These data and interpretations provide convincing evidence that the lowest energy transition in Kapton[®] polyimide film is the result of an intermolecular charge transfer complex between the imide and diphenyl ether portions of the polymer backbone.

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