Synthetic Metals, 41–43 (1991) 1329–1332

PHOTOINDUCED ABSORPTION AND ERASABLE OPTICAL INFORMATION STORAGE IN POLYANILINES

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ABSTRACT

Photoinduced absorption spectroscopy has been used to study a variety of forms of polyaniline. Experiments on emeraldine base and leucoemeraldine base have led to a picture of the photoproduction and decay of massive, long-lived defect states that can be described in terms of conformational changes involving rotations of the C_6H_4 rings. Photoexcitation spectra of other polyanilines, such as pernigraniline base and poly(*o*-toluidine), exhibit similar features including relatively weak photoinduced infrared vibrations and a relatively strong photoinduced absorption peak near 1.4–1.5 eV. In several of these materials, the photoinduced changes are very long-lived, leading to an investigation of the polyanilines as media for erasable optical information storage.

DEFECT STATES IN POLYANILINE

Recent photoinduced absorption experiments [1] on the emeraldine base (EB) form of polyaniline (PAN) have shown that polarons are produced upon photoexcitation. These polarons are massive, as evidenced by the small photoinduced infrared active vibrational (IRAV) modes compared to higher-lying transitions, and are long-lived with lifetimes of several hours. Further experiments on emeraldine base and leucoemeraldine base (LEB) [2] have led to a picture of the photoproduction and decay of a variety of defect states, several of which can be interpreted in terms of conformational changes in the backbone of the polymer, in particular rotations of the phenyl (C_6H_4) rings.

The ground-state configuration of LEB consists of adjacent phenyl rings twisted out of the nitrogen-nitrogen plane by equal but opposite angles [3]. The removal of an electron

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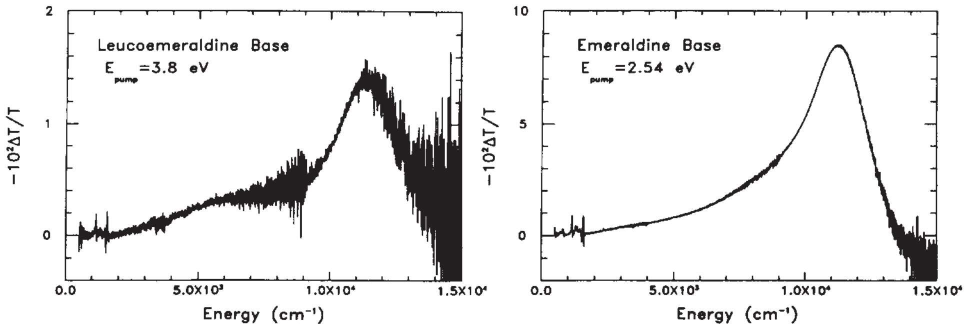

Fig. 1. Long-lived photoexcitation spectra of LEB and EB at 80 K.

from LEB results in the formation of a hole polaron, P_B^+, described as a ring-centered distortion in which the central and neighboring phenyl rings twist out of their ground-state configuration *toward* the nitrogen plane. This new conformation causes the energy levels of a P_B^+ to split off from the valence band by ~0.75 eV, with little or no splitting from the conduction band. The P_B^+ gives rise to new absorptions in the gap at ~0.75 and ~2.8 eV, but because of its large mass, induces relatively weak photoinduced IRAV modes [2].

Samples of LEB are known to contain a nonzero density of quinoid rings (~4%) whose neighboring nitrogen atoms have no hydrogens attached. The quinoid rings are planar (or nearly so) [4,5], with appropriate changes in bond lengths. A new localized energy level at ~2 eV above the valence band is formed, allowing the photoexcitation of excitons. If a P_B^+ is located near a planar quinoid ring, the gain in energy resulting from the delocalization of π holes over several lattice sites without having to drive additional rings toward planarity may be enough to bind or trap a P_B^+ near a quinoid site. This bound-state configuration, denoted P_{BQ}^+, is suggested to result in a new absorption level at ~1.4 eV [5] and is expected to be very long-lived because of the large inertial mass involved for relaxation (with rotation of the phenyl rings) to the ground state [2]. The P_{BQ}^+ is expected to be observed upon photoexcitation of LEB and, in addition, EB because of the higher concentration of quinoids. In Fig. 1, the long-time photoinduced absorption spectra of LEB and EB show the long-lived peak at ~1.4 eV (11,200 cm^{-1}) and the small photoinduced IRAV modes.

EFFECT OF OXIDATION STATE AND DERIVATIZATION ON DEFECT MASS

Photoexcitation spectroscopy of other forms of polyaniline has revealed a number of similarities and differences with that of LEB and EB [6,7]. The long-time photoinduced absorption spectra of the fully oxidized pernigraniline base (PNB) and the half-oxidized (EB) state of poly(*o*-toluidine) (POT-EB) are shown in Fig. 2. In both spectra, relatively weak photoinduced IRAV modes are present with a strong photoinduced absorption peak at ~1.5 eV. The defect states produced are very massive and have very long lifetimes (much greater than 24 h for samples at ~80 K). In both cases the defect states giving the 1.5-eV absorption are likely very similar to the P_{BQ}^+ discussed above.

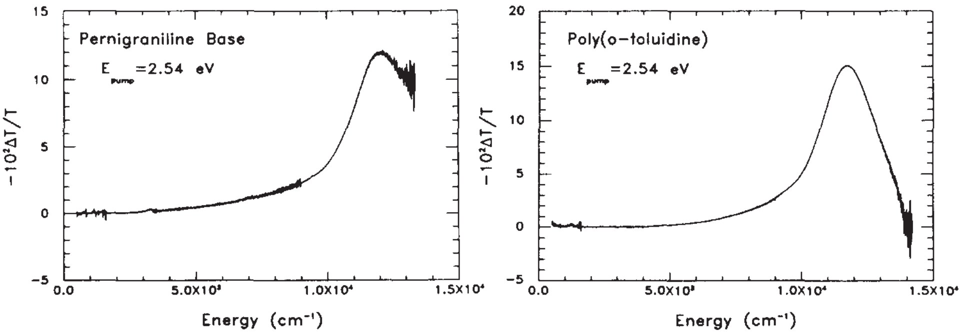

Fig. 2. Long-lived photoexcitation spectra of PNB and POT-EB at 80 K.

TABLE 1
Masses of long-lived defect states for various polyanilines.

Material	Defect mass
Leucoemeraldine base	$\sim 60\ m_e$
Emeraldine base	$\sim 60\ m_e$
Pernigraniline base	$\sim 300\ m_e$
Half-oxidized poly(*o*-toluidine)	$\sim 200\ m_e$

The masses of these long-lived defects in LEB, EB, PNB, and POT-EB, shown in Table 1, are determined from the band effective mass (assumed for convenience here to be the same for each of these materials [1]) and the ratio of the integrated intensities of the electronic and vibrational photoinduced absorptions (I_e/I_p). Because the masses in LEB and EB are similar, the spatial extent of the defects is likely confined to only 3–4 rings in both systems. However, in PNB the much larger mass is consistent with localization of the defect to 1–2 rings. An increase in the defect mass in POT-EB (~3 fold) is observed, which can only partly be explained by the increased moment of inertia from the methyl groups on the rings ($I_{POT}/I_{PAN} \simeq 1.56$). Further increases in the defect mass may result from interchain effects (due to increased interchain distances [8]) causing changes in the ground state and excited state ring angles, as well as an increase in the average ring angle resulting from the increased intrachain steric effects of the methyl groups. We note that an increased mass in EB for higher pump energies is observed, which may result from differing polaron environments (e.g., intra-/interchain effects) or the creation of additional defect species [2].

Our measurements have been made on materials whose crystallinity ranges from completely amorphous to ~50% crystalline [8,9]. For 100% crystalline materials, the long-lived effects may not be present, because in crystalline poly(paraphenylene sulfide) (PPS) we observe no long-lived signal. On the other hand, the observation of long-lived effects may require materials containing quinoid rings, which are found in all the base forms of polyaniline but are not found in PPS.

ERASABLE OPTICAL INFORMATION STORAGE

Because of the long lifetimes and strong intensities of the photoinduced absorption peak at 1.4–1.5 eV, we have investigated polyaniline for use as an erasable optical information storage medium [10]. Samples of numerous forms of polyaniline have been prepared as thin films or as powders dispersed in KBr pellets. Samples are first cooled to low temperatures, then illuminated with the 488-nm or 514-nm lines of an argon-ion laser. The magnitudes of the fractional change in transmission of the samples range from a few percent to greater than 30% depending on the particular sample studied, the concentration of the sample, and the temperature of the sample. The photoinduced signal can be erased by warming the sample to room temperature. The most promising materials have lifetimes of at least several days including PNB at ~80 K, half-oxidized POT at ~80 K, and fully-oxidized POT at 250 K. These results indicate that through molecular design a material *may* be synthesized that possesses long-lived effects at room temperature, which is necessary for practical devices.

An optical storage device would involve information being written on a thin film, composite, or blend of polyaniline using a visible or uv laser beam, with reading by a laser tuned near one of the peaks in the photoexcitation spectrum (e.g., 1.4–1.5 eV). The entire sample can be warmed for bulk erasure, or, potentially, a sufficiently intense laser operating near 1.4–1.5 eV can be used to heat the exposed portions of the sample to room temperature or higher for erasure of bit information. Other possible uses based on the photoinduced absorption phenomena include photorefractive devices and photoinduced gratings.

ACKNOWLEDGEMENTS

This work is supported in part by the Defense Advanced Research Projects Agency through a contract monitored by the U.S. Office of Naval Research.

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