Charge-Induced Relaxation in Polymers

C. B. Duke and T. J. Fabish
Xerox Webster Research Center, Rochester, New York 14644
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The interpretation of contact-charge-exchange experiments using polymers requires the existence of electronic states contiguous to the Fermi energies of contacting metals. The atomic and electronic relaxations, both of the molecular moiety on which the charge is localized and of the surrounding polymer matrix, combine to provide suitable localized intrinsic electronic states.

Our purpose to this Letter is to indicate, within the context of examining the specific example of polystyrene, how several experimental observations which are inexplicable within the framework of traditional one-electron models of the electronic structure of polymers admit a simple interpretation when considered in the light of a model in which atomic and electronic relaxation processes associated with the injected charges are considered explicitly. Specifically, contact-charge-exchange experiments between metals and polystyrene have revealed the existence of electronic acceptor states in the (bulk) polymer at energies contiguous to the work function of a variety of metals.[1] Since traditional (one-electron) models[2,3] of the electronic structure of polymers predict that polystyrene is a wide-band-gap insulator, these acceptor states must exist at energies deep within the one-electron optical energy gap. The invariance of these states for differing polymer preparative methods[1] and their systematic variation with the molecular structure of the monomeric units[4] seem to preclude their association with the morphological defects[5] or impurities[3] invoked to interpret transport experiments. Consequently, their nature has remained a mystery.[1,4]

We demonstrate herein how such deep acceptor (or donor) states may arise as a consequence of atomic[6] and electronic[7] relaxation processes induced by the injected charges. The body of our analysis consists of the determination of the various contributions to the relaxation energy, E_p, in terms of directly measurable physical quantities, and their numerical evaluation for polystyrene. We conclude with a discussion of contact-charge-exchange measurements which substantiate the predictions of our model.

Polystyrene was selected as the model polymer for initial study both because of ease in purification and film preparation,[1] and because many of the parameters describing its electronic structure may be determined independently. The first strong singlet optical transition in polystyrene ($E \cong 4.7$ eV) arises from particle-hole (molecular exciton) states constructed from the $e_{1g}(\pi)$ and $e_{2u}(\pi^*)$ molecular orbitals in the benzene moiety.[8] Thus, to a first approximation, in a one-electron model electrons are injected into the $e_{2u}(\pi^*)$ orbital ($E_a = +1.14$ eV relative to vacuum[9]) and holes are injected into the $e_{1g}(\pi)$ orbital ($E_d = -9.24$ eV[10]).

Turning first to our assessment of intramolecular relaxations, we recall that polystyrene acts as an electron acceptor relative to all the metals used in the contact experiments.[1] Consequently, we must assess the energies of $e_{2u}(\pi^*)$-derived acceptor states. Electron impact measurements[11] of resonant electron scattering from the vacant $e_{2u}(\pi^*)$-derived orbitals in gas-phase alkyl-substituted benzenes reveal that alkyl substitution shifts the lowest-energy empty orbital relative to benzene by $\Delta E = -0.1 \pm 0.05$ eV. Thus, we adopt $E_a = 1.0$ eV as the rigid-matrix one-electron energy of this orbital in the (neutral) ethylbenzene molecular moiety characteristic of polystyrene. This energy is not that of a negative anion of the ethylbenzene moiety, however, because the presence of an additional electron induces both nuclear and electronic relaxations relative to neutral ethylbenzene.

The nuclear relaxations cause an atomic intramolecular contribution, E_{pa}(intra), to the relaxation energy. We have shown elsewhere[10] that this contribution to E_p may be evaluated directly by analysis of vibrational progressions in electron-impact spectra (acceptor state) and photoemission spectra (donor state) of the appropriate gas-phase molecules. In the case of benzene, the electron-impact cross sections[12] and calculations of the appropriate coupling constants[10] predict a value of $E_{pa}(\text{intra}) = 0.25 \pm 0.1$ eV for this quantity.

The intramolecular electronic contributions, E_{pe}(intra), to the relaxation energy can be obtained experimentally by recognizing that the photodetachment threshold of a gas-phase ethylbenzene anion measures the energy of a fully relaxed negative moiety.[13] Thus, comparison of the photodetachment spectra of the anion and electron-impact spectra of the neutral species yields directly the total intramolecular contribution, $E_p(\text{intra}) = E_{pa}(\text{intra}) + E_{pe}(\text{intra})$, to the relaxation energy. Since photodetachment spectra are not available for ethylbenzene anions, however, we must turn to model calculations for $E_{pe}(\text{intra})$. A crude estimate is obtained by utilizing assessments of corrections to the $e_{2u}(\pi^*)$ Hartree-Fock eigenvalue as a measure of the electron affinity of benzene. The calculations of Hoyland and Goodman[14] yield $E_{pe}(\text{intra}) \sim 1.9$ eV. We obtain for the sum of the electronic and atomic contributions $E_p(\text{intra}) = 2.15 \pm 1$ eV, with the large uncertainty emanating from our use of theoretical estimates for $E_{pe}(\text{intra})$.

The intermolecular contributions, $E_p(\text{inter}) = E_{pa}(\text{inter}) + E_{pe}(\text{inter})$, to the relaxation energy of an acceptor (donor) state in a polymer are caused by the nuclear and electronic relaxation of the polymer matrix surrounding the charged radical anion (cation). Such electronic relaxations have been considered extensively in discussions of ionic states in molecular crystals,[15] in which case an injected charge is considered to reside in a dielectric medium of polarizable molecules. Calculations for typical aromatic hydrocarbon crystals yield[15] $E_{pe}(\text{inter}) = 1.5 \pm 0.5$ eV. Recognizing that the relaxation of a dielectric medium is the same for positive and negative injected charges, both the donor and acceptor intermolecular relaxation energies can be evaluated by comparing photoemission spectra from molecules in the gas phase with comparable spectra associated with these molecules in a condensed (polymeric, crystalline, or amorphous) phase.[16] Such experiments yield[16-18] $E_{pe}(\text{inter}) = 1.25 \pm 0.25$ eV for a variety of molecular solids. Estimation of the intermolecular atomic relaxation contributions, $E_{pa}(\text{inter})$, is less certain because neither the nature nor the magnitude of the electron-vibration coupling is well established.[19] Presuming that the predominant coupling mechanism is the induction of dipoles on surrounding phenyl groups by the injected charge on one,[19] we estimate that $E_{pa}(\text{inter}) \sim 0.1$ eV—a value which, in principle, is verifiable by observation of the detailed shift and change in line shape of the zero-molecular-vi-bration ionization peak of the $e_{1g}(\pi)$-derived orbitals in polystyrene relative to gas-phase ethylbenzene.[20]

A numerical estimate of $E_p(\text{inter})$ for polystyrene can be obtained from existing photoemission data. The solid-state ionization potential of polystyrene is 7 eV,[21] whereas gas-phase values for alkyl-substituted benzenes are about 9 eV.[22] We obtain $E_p(\text{inter}) \cong 2$ eV, the bulk of which is attributed to electronic intermolecular relaxation.

In the case of polystyrene, the numerical estimates indicated above lead to a total relaxation energy for the $e_{2u}(\pi^*)$-derived acceptor state of $E_p = E_{pa}(\text{intra}) + E_{pe}(\text{intra}) + E_{pa}(\text{inter}) + E_{pe}(\text{inter}) = 4.2$ eV. The resulting energetics for both acceptor and donor states are shown schematically in Fig. 1 for a metal/polymer contact configuration. Since in a polymer the local configuration around a particular ethylbenzene moiety can vary substantially, we anticipate local fluctuations of about ± 20% in the intermolecular contributions to E_p. Therefore the acceptor and donor states should exist as distributions of width about 0.4 eV—an expectation in accord with the measured width of 0.5 eV (Fig. 2) obtained from the charge-exchange experiments.

Let us now turn to the interpretation of the ex-

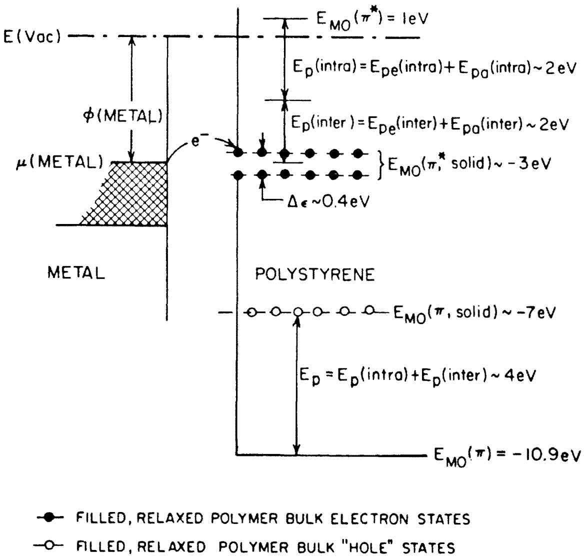

FIG. 1. Schematic indication of charge-exchange energetics in a metal-polystyrene contact. φ designates the metallic work function, μ the Fermi energy of the metal, and $\Delta\epsilon$ the width of the energy states accessible to a particular metal in a contact. Thus, relaxation effects in the polymer shift the lowest-energy virtual $e_{2u}(\pi^*)$-derived acceptor orbital to the immediate vicinity of the Fermi energy of the electrode, rendering thermal electron injection probable at room temperature. Similarly, relaxation effects shift the smallest Koopman ionization potential of styrene (Ref. 14) to its observed (Ref. 21) value in polystyrene.

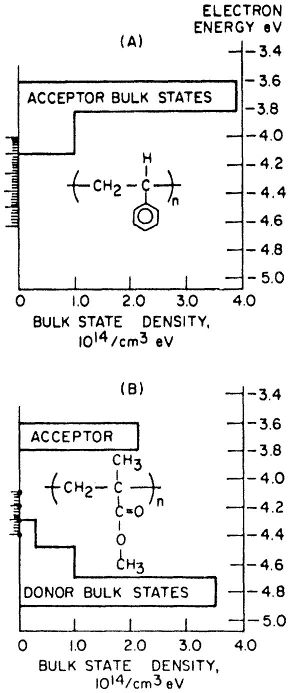

FIG. 2. The distribution of filled, fully relaxed bulk electronic states sampled by the contacting metal for (a) atactic polystyrene (Ref. 1; the density of electron-acceptor surface states is 7.5×10^{10} cm^{-2} eV^{-1}), and for (b) poly(methyl methacrylate) (the density of electron donor surface states is 4.2×10^{10} cm^{-2} eV^{-1}).

periments that motivated this analysis: the injection of electrons from metal contacts into polystyrene. Without consideration of the complete array of polymer relaxation processes [electronic and atomic, intramolecular and intermolecular], no empty intrinsic polymer electronic states occur sufficiently close to the metallic Fermi energies to achieve the observed levels of charge injection at room temperature.[1] Once the polymer relaxation processes are considered, however, the lowest-energy virtual ethylbenzene orbital is shifted from $\sim +1$ eV to -3.2 eV, well within the range accessible to electron injection from In ($\varphi = 3.8$ eV) and Pb ($\varphi = 4.0$ eV), marginally assessible to Au ($\varphi = 4.3$ eV) and Ni ($\varphi = 4.5$ eV), and inaccessible to Pt ($\varphi = 5.3$ eV). The measured densities of bulk electronic charge injected by these metals contacted to polystyrene, shown in Fig. 2(a), are in surprisingly good correspondence with the predictions of our relaxation-model analysis.

Having recognized the large relaxation energy shifts of localized electronic states in polymers, we can utilize contact-charge-exchange experiments to examine the density of these states. An example of this new perspective is illustrated in Fig. 2(b) in which we present the measured state density for poly(methyl methacrylate) which acts as both a donor and acceptor of charge from the various metal contacts. These results, considered in light of existing calculations and photoemission data for acetic acid derivatives,[23] reveal the anticipated stronger relaxation effects for the more polar ester groups of poly(methyl methacrylate) than for styrene. They also demonstrate that not only the magnitude of the charge exchange[4] but also the donor and acceptor density of states are intimately related to the electronic structure of the molecular constituents of the polymer.

In summary, we are suggesting that charges injected into polymers form localized states characterized by large relaxation energies, E_p ~ 4 eV, which admit evaluation solely in terms of independently measurable quantities. This relaxation model leads to an immediate interpretation of charge-exchange spectra which were inexplicable[1] in terms of the traditional view[2,3] of polymers as organic semiconductors with traps, and hence provides a viable and useful alternative to this view.

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Optical Free-Induction Decay in $LaF_3:Pr^{3+}$†

Azriel Z. Genack, Roger M. Macfarlane, and Richard G. Brewer
IBM Research Laboratory, San Jose, California 95193

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The dephasing time of coherently prepared Pr^{3+} impurity ions in a LaF_3 crystal is measured by optical free-induction decay. Above 4°K, phonon processes severely shorten the decay time. Below 4°K, we observe a temperature-independent decay time of 0.38 μsec. This is surprisingly short considering that there are no contributions from first-order hyperfine, phonon, or Pr^{3+}-Pr^{3+} interactions.

Dynamic interactions in solids have been studied in the past by a variety of coherent pulse and steady-state techniques which extract a narrow homogeneous line shape from a broad inhomogeneous profile. Within the last few years, rf pulse methods have been extended to the optical region where photon echo studies have uncovered new aspects of relaxation behavior, particularly in ruby.[1] This Letter describes a related technique, that of optical free-induction decay (FID),[2] which has some unique advantages over the echo and steady-state methods and is well suited to examining interactions in optically excited solids. In optical free induction, the entire decay behavior is obtained in a single burst, as in NMR. Furthermore, because of the sensitivity afforded by optical heterodyne detection, weak transitions can be studied and the laser power may be low, avoiding the complications of power and inhomogeneous broadening present in the previous observation of FID in a solid.[3] Here we report the dephasing characteristics of coherently prepared trivalent praseodymium impurity ions in a lanthanum trifluoride crystal at low temperature. This system, unlike ruby,[1] exhibits no first-order hyperfine interaction and allows the study of other optical dephasing mechanisms.

The Pr^{3+} transition examined is between the lowest crystal-field components of ${}^1D_2 \rightarrow {}^3H_4$ (5925.2 Å), and the linewidth has been studied previously at lower spectral resolution[4] by the steady-state technique of fluorescence line narrowing.[5] FID signals of the type shown in Fig. 1 for $LaF_3:Pr^{3+}$ display dephasing times that correspond to an extremely narrow optical linewidth of 830 kHz (full width at half-maximum) and a

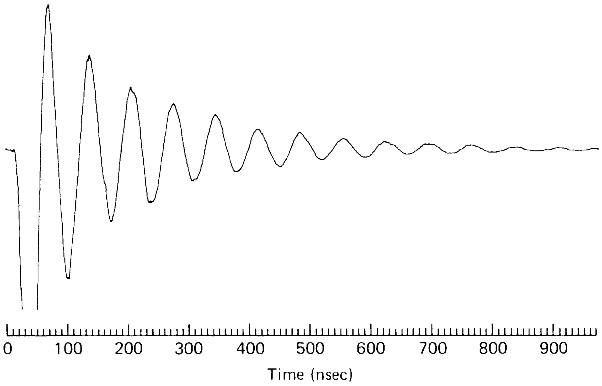

Fig. 1. Optical free-induction decay in $LaF_3:Pr^{3+}$ (0.1%) at 1.5°K. The tracing was obtained with a Tektronix 7904 sampling oscilloscope and an X-Y recorder in an 8-min interval.