X-ray Photoelectron Spectroscopy of Iodine-Doped Nonconjugated Polymers

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The effects of iodine doping on poly(*cis*-butadiene) and the cis and trans isomers of polyisoprene were examined by core-level X-ray photoelectron spectroscopy (XPS). The XPS results for iodine-doped poly(*cis*-butadiene) are similar to that for polyisoprene, suggesting that both polymers are doped by a similar mechanism. Core-level XPS of the iodine-doped polymers suggests that the direction of charge transfer is from the backbone carbon to the iodine species. The binding energies of the iodine species in the I_{3d} spectra of the doped polymers indicate the presence of molecular iodine and I_3^- (and/or I_5^-) species and the absence of a significant concentration of cationic iodonium-π complex. In conjunction with conductivity measurements, XPS analysis of cryogenically cooled (−80 °C) iodine-doped poly(*cis*-isoprene) and poly(*trans*-isoprene) provides direct spectroscopic evidence that the conductivity of the doped polymers is due to excess iodine, present in the form of polyiodide chains.

Introduction

Electronically conducting organic polymers have, until recently, been observed to contain one key structural element in common, notably the presence of conjugated double bonds.[1] Delocalization of the radical ions (polarons) and diions (bipolarons) created upon doping with an appropriate electron acceptor or donor is believed to be a prerequisite to the attainment of high electronic conductivity ($\geq 10^{-1}$ S cm^{-1}) in these systems.[2] Thakur challenged this idea a few years ago, by demonstrating that hydrocarbon polymers containing isolated double bonds display conductivity's of up to $\sim 10^{-1}$ S cm^{-1} upon doping with iodine.[3] The results of this[3] and subsequent studies[4,5] suggested that the conductivity of iodine-doped polyisoprene is electronic in nature. Furthermore, Thakur and co-workers postulated that the mechanism of charge transport is through the intersite hopping of radical cations.[3–5] Since these results contradict a large body of experimental evidence that conjugation is necessary for electronic conductivity, they have been greeted with some skepticism.[6–8]

There are several reasons that have prompted the present investigation. The first reason relates to the contradictions between the experimental results of Thakur and co-workers and other investigators who have attempted to duplicate these results. We cite two examples: one, the contradictory results regarding the lack of doping of poly(*cis*-butadiene) (PcB) reported by Thakur[3] and contradicted by Suh and Wnek[7] and Shang et al.,[8] and second, the differing levels of conductivity attained for the same polymers in different studies. For example, in comparison with the maximum conductivity of 10^{-1} S cm^{-1} for iodine-doped polyisoprene reported in the original study by Thakur,[3] subsequent studies have reported only modest conductivity's of up to 10^{-4} S cm^{-1}.[7,8] While this discrepancy may be related to the packing of the polymer in the solid state (which may be a function of film preparation, as suggested by Shang et al.,[8] rather than a function of unimolecular properties), the 3 orders of magnitude discrepancy between the conductivity observed in these studies is of some concern.

The second reason relates to the mechanism of charge transport, which is subject to considerable controversy. Thakur et al. observed that the charge carriers in iodine-doped polyisoprene appeared to be p-type and that the conductivity did not decrease after ion bleaching, thus suggesting that the ionic contribution to the overall conductivity is negligible.[3] The observation of unpaired spins in iodine-doped polyisoprene was also cited in support of a radical cationic mechanism of carrier transport.[4] Suh and Wnek have, however, suggested that these results can be adequately explained by charge transport along anionic polyiodide chains.[7] Shang et al. have also disputed the mechanism of charge transport as being due to radical cations in view of the extremely low value of unpaired spins observed by them for iodine-doped polyisoprene; instead they believe that π-complex formation of iodine with the polymer double bonds is responsible for the conductivity of the iodine-doped polymers.[8]

We wish to note that the first study to investigate the doping of poly(butadiene) derivatives was not by Thakur et al. In 1987, Petit et al. investigated the iodine doping of PcB as part of a study on the conductivity mechanism in monosubstituted polyacetylenes.[9] The results of that

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study, relevant to the doping and conduction mechanisms for iodine-doped nonconjugated polymers, are as follows: after doping with iodine, PcB was found to be conductive (2×10^{-4} S cm^{-1}) only when excess molecular iodine was present. However, when the doped polymer films were kept under vacuum, the conductivity dropped to $<10^{-15}$ S cm^{-1}). These conductivity values were similar to those of iodine-doped films where only I_3^- was known to be present. The authors suggested that the observed conductivity could only be due to the presence of excess iodine, present in the form of polyiodide anions. We find it interesting that this study has received little mention in the literature,[10] despite its obvious relevance.

Photoelectron spectroscopies are extremely useful probes of the chemical and electronic structure of solids. Since X-ray photoelectron spectroscopy (XPS) does not require long-range order to be analytically useful, it can be used to interrogate structurally disordered solids such as polymers. Core-level XPS provides precise elemental quantitation and local bonding information. Details of electronic structure are accessible by valence-band XPS or ultraviolet photoelectron spectroscopy (UPS). Consequently, core-level XPS and valence-band XPS/UPS have provided many insights for a variety of conducting polymers.[11] Photoelectron spectroscopies have heretofore not been used to investigate the doping of nonconjugated polymers. In this study, we investigate the iodine doping of nonconjugated hydrocarbon polymers by core-level XPS with the intent of resolving the discrepancies observed in previous studies and clarifying the underlying mechanism by which charge transport occurs in this system.

Experimental Section

Polymer Preparation. Poly(*cis*-butadiene) (95.3% cis, 1.4% trans, and 3.3% vinyl as specified by manufacturer) (PcB), poly(*cis*-isoprene) (97% cis: vide supra) (PcIP), and poly(*trans*-isoprene) (PtIP) were acquired from Scientific Polymer Products and were used as received. The purity of the polymers was checked by transmission FTIR (FTS-60, Bio-Rad Instruments, Cambridge, MA) of the cast films on KBr plates. Tetra-*n*-butylammonium triiodide [$(CH_3(CH_2)_3)_4N{\cdot}I_3$] was acquired from American Tokyo Kasei Inc. (Portland, OR) and analyzed as received.

The substrates used to cast the films were either Si wafers or glass disks. Samples for conductivity measurements were prepared on 12- or 25-mm-diameter glass disks. Prior to casting the films, the Si wafers were cleaned by ultrasonication in methylene chloride, acetone, and methanol, respectively, while the glass disks were cleaned by ultrasonication in a 1.5% (v/v) solution of Isopanasol (C. R. Callen Co. Seattle, WA) in deionized/reverse osmosis-purified water followed by repeated rinses in deionized/reverse osmosis-purified water. All the polymers were dissolved as 2–4% (w/v) solutions in toluene; typically 100 μL of the polymer solution were pipetted onto the substrates and allowed to dry in air. This procedure was repeated several times and led to the formation of films a few hundred micrometers thick, ascertained gravimetrically.

Doping and Conductivity Measurements. Doping of samples with iodine vapor was carried out in a glovebox under an argon atmosphere. Polymer-coated glass disks were placed onto a glass slide which was then placed in a glass tube. The glovebox was evacuated and purged with argon (to positive pressure) several times to eliminate air from the glovebox. Iodine crystals were then introduced into the glass tube, below the glass slide on which the samples were placed. The glass tube was then sealed with a Teflon-lined rubber stopper, and the iodine sublimated by mild heating of the glass tube. After doping, the glass tube was allowed to cool to ambient temperature and removed to a fume hood, where the samples were recovered from the glass tube. The samples were then weighed in air to gravimetrically determine the extent of doping, following which their conductivities were measured in air with a commercially available four-point-probe apparatus (Alessi Inc.). The approximation of Valdes for an infinitely thin film was used to compute the film conductivity.[12] The thickness of the doped polymer films were computed gravimetrically.

X-ray Photoelectron Spectroscopy. XPS analyses were performed on a S-Probe spectrometer (Surface Science Instruments, Mountain View, CA), which includes a monochromatized Al Kα X-ray source, a hemispherical analyzer, and a position-sensitive detector. All polymers were analyzed at 35° takeoff angle. The takeoff angle is defined as the angle between the sample plane and the axis of the analyzer. Survey scans (0–1000 eV) were run at 150-eV analyzer pass energy and 1000-μm X-ray spot size to determine the elemental composition of each polymer. The experimental peak areas were numerically integrated and normalized to account for the number of scans, the number of channels per electronvolt, the Scofield photoionization cross section,[13] and the sampling depth. The S-Probe transmission function for a pass energy of 150 eV was assumed to be constant over the appropriate range of photoelectron kinetic energies.[14] The sampling depth was assumed to vary as KE$^{0.7}$, where KE is the kinetic energy of the photoelectrons.[14] High-resolution C_{1s} and I_{3d} spectra were obtained at a pass energy of 25 eV. The C_{1s} and I_{3d} spectra were resolved into individual peaks using a least-squares fitting program. A mixed Gaussian–Lorentzian line shape was used to fit the spectra. In all cases except for the pristine polymers, the C_{1s} spectra were fit with $\leq 10\%$ Lorentzian contribution to the line shape; the primary hydrocarbon peak in the C_{1s} spectra of the pristine polymers was curve-fit with a mixed Gaussian–Lorentzian line shape (90:10) and up to 10% asymmetry, in accordance with a recent report in the literature.[15] The Lorentzian contribution to the I_{3d} line shape was up to 30%. A combination of a low-energy flood gun, set at 5 eV, and a metal screen placed on the sample holder was used to minimize sample charging. All polymer binding energies (BEs) were referenced by setting the CH_x peak maximum in the resolved C_{1s} spectra to 285.0 eV.

The protocol for the XPS analysis of iodine-doped polymers at cryogenic temperatures was as follows: immediately after doping a polymer with iodine vapor in the glovebox, the sample was removed from the glovebox, weighed (the weight of the doped sample was used to compute the film thickness), and its conductivity measured in air with a four-point-probe apparatus. The sample was then mounted on a sample holder and introduced into the preparation chamber of the spectrometer where it was cooled to −80 °C under a nitrogen atmosphere. After the sample reached a steady-state temperature of −80 °C in the preparation chamber, it was introduced into the analysis chamber. The temperature of the sample was also maintained at −80 °C in the analysis chamber for the duration of the experiment. Cooling of the sample holder in the preparation and analysis chambers is achieved by liquid nitrogen flow through a cold stub in thermal contact with the sample holder. The temperature is maintained at a set point (−80 °C in these experiments) by heating coils in the cold stub which are connected in a feedback loop with a

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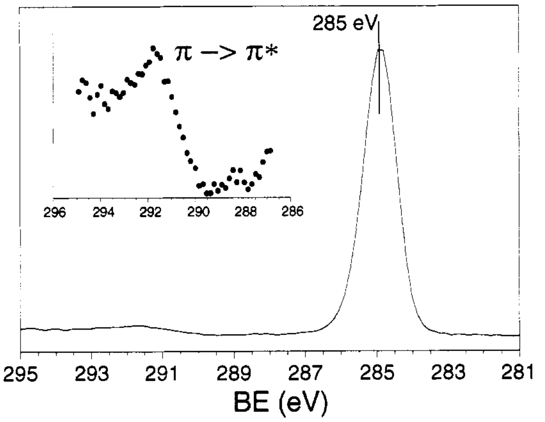

Figure 1. High-resolution XPS C_{1s} spectrum of pristine PcB.

Table I. Least-Squares Curve-Fitting Results of the C_{1s} Spectra of the Polymers before Iodine Doping

	% peak area of C_{1s} spectral envelope	
polymer	CH_x[a]	$\pi \rightarrow \pi^*$
poly(*cis*-butadiene) (PcB)	96.6	3.4
poly(*cis*-isoprene) (PcIP)	97.5	2.5
poly(*trans*-isoprene) (PtIP)	97.2	2.8

[a] Referenced to 285 eV.

thermocouple. The time elapsed between removal of the sample from the glovebox after conclusion of doping and cooling of the sample to -80 °C in the preparation chamber of the spectrometer was minimized to prevent desorption of iodine from the sample; typically, the elapsed time was ~10 min. After XPS analysis at -80 °C, the sample was kept under vacuum ($\leq 10^{-5}$ Torr) in the preparation chamber of the spectrometer for >12 h at 25 °C to desorb excess iodine, reanalyzed by XPS, and then removed from the spectrometer to determine its conductivity.

Results

Prior to iodine doping, poly(*cis*-butadiene) (PcB), poly(*cis*-isoprene) (PcIP), and poly(*trans*-isoprene) (PtIP) were analyzed by core-level XPS to verify polymer purity. In all cases, survey spectra (0–1000 eV) showed the absence of oxygen contamination in the outer 50 Å of the polymer films. High-resolution C_{1s} spectra of the three polymers revealed the presence of a primary peak at 285 eV and a secondary peak at 291.3–291.5 eV, which can be attributed to a $\pi \rightarrow \pi^*$ shakeup satellite.[16] A representative C_{1s} spectrum of pristine PcB is shown in Figure 1, and the least-squares results for the C_{1s} spectra of the three polymers are shown in Table I. We found that the peak centered at 285 eV was best fit with a mixed Gaussian–Lorentzian line shape with a small asymmetric component on the higher BE side, in accordance with a recent report in the literature.[15] The observed asymmetry has been assigned to vibrational effects in the different C–H bonds.

The doping of PcB, PcIP, and PtIP with iodine vapor in an argon atmosphere led to the incorporation of iodine in all three cases. The color of the polymer films also changed from transparent to black. These results contradict those observed by Thakur, wherein they found that iodine vapor does not dope PcB.[3] Table II summarizes the XPS results for iodine-doped PcB. We first focus attention on the results of the survey scan spectra with the exception of the XPS results for the iodine-doped polymers analyzed at -80 °C. The iodine incorporation of ~3 at. % for iodine-doped PcB translates into a molar doping level of 0.12 (i.e., $(C_4H_6I_{0.12})_m$), assuming uniform doping throughout the outermost 50 Å. Similarly, molar doping levels ranging from 0.09 to 0.15 are obtained for iodine-doped PcIP and PtIP. The maximum iodine incorporation for the polyisoprene polymers of 0.15 (mole basis) is low when compared with the results reported by Thakur.[3] There are at least two reasons for this discrepancy: First, we have used XPS to calculate the I:C ratios, whereas Thakur calculated these values gravimetrically, a method we believe to be much less precise than XPS. Second, the excess iodine in these experiments was removed under vacuum. We believe that the iodine concentration reported by Thakur is largely due to the presence of excess iodine; results reported later in this paper support this contention.

The high-resolution C_{1s} and I_{3d} spectra of iodine-doped PcB are shown in Figure 2. In general, interpretation of the C_{1s} spectrum of iodine-doped PcB is complicated by the oxygen incorporation in iodine-doped PcB (compared with the iodine-doped polyisoprene polymers which typically show ≤1 at. % oxygen after doping; refer to Table II). This is because the binding energy shifts induced by oxygen-containing moieties may overlap with those induced by the interaction of iodine with the carbon atoms in the polymer. Note that the sample corresponding to the C_{1s} spectrum in Figure 2a contains <1% oxygen; the low oxygen concentration in this iodine-doped PcB sample allows easier identification of spectral features related to iodine doping as compared to iodine-doped PcB samples with substantially greater oxygen incorporation. The $\pi \rightarrow \pi^*$ shakeup satellite at 291.5 eV, observed in the C_{1s} spectrum of pristine PcB (Figure 1), is lost upon iodine doping (Figure 2a). The weakening of the double bonds in the polymer repeat unit suggested by this result is in agreement with the IR results of Thakur[3] and Shang et al.[8] The C_{1s} spectrum of iodine-doped PcB is somewhat broadened on the high-BE side in comparison with the pristine polymer (see Figure 1 for comparison). Least-squares curve-fitting of the C_{1s} spectrum of iodine-doped PcB reveals the presence of a peak centered at 285.8–286 eV. The fact that this peak is observed even when no oxygen is detected and its BE suggest the presence of electropositive carbon atoms. Furthermore, the intensity of this peak (typically a few percent of the total peak area) is consistent with the overall doping level and may indicate the presence of a radical cationic species.

The I_{3d} spectrum of iodine-doped PcB is shown in Figure 2b. The I_{3d} spectral line shape for iodine-doped PcB is similar to that for PcIP and PtIP; the least-squares curve-fit results of the I_{3d} spectra of the doped polymers in Table II reveal the presence of four peaks. We note that these spectra are similar to those observed by Salaneck et al. for iodine-doped polyacetylene.[17] Specifically, peaks are observed at 619.2 and 620.6 eV along with two shakeup satellites at higher BE. The peak at 619.2 eV was assigned by Salaneck et al. to be due to I_3^-, while the peak at 620.6 eV was assigned to molecular I_2. We discuss these assignments in greater detail elsewhere in this paper, though we draw attention to the fact that the XPS results

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Table II. XPS Results of Iodine-Doped Nonconjugated Polymers

		survey spectrum		$I_{3d5/2}$ spectrum	
polymer	doping time (min)	at. % I	at. % O	% I_2 (eV)	% I_3^- or % I_5^- (eV)
PcB	30[a]	2.9 ± 0.7	5.1 ± 3.1	41.5 ± 5.5	53.0 ± 8.8
	120[a]	3.0	8.2	(619.2 ± 0.1)	(620.7 ± 0.1)
PcIP	60[b]	8.3	0.3	42.1 (619.6)	45.6 (620.6)
	60[a]	1.7	1.4	39.4 (619.2)	56.6 (620.6)
PtIP	60[b]	10.5 ± 0.6	0.6 ± 1.0	23.8 (619.5)	63.2 (620.5)
	60[a]	2.6	0	40.2 (619.2)	53.6 (620.6)
$(C_4H_9)_4N{\cdot}I_3$	c	13.9 (15.0)	at. % N = 4.6 (5.0)	70.6 (619.0)	23.0 (620.5)

[a] Samples were outgassed under a pressure of ≤10^{-5} Torr for ≥12 h before XPS analysis at 25 °C. [b] Samples were cooled to −80 °C in the preparation chamber of the spectrometer immediately after doping, transferred to the analysis chamber, and kept at −80 °C for the duration of XPS analysis. [c] Values in parentheses in survey scan results correspond to stoichiometry of compound. The resolved C_{1s} spectrum (results not shown) shows two peaks (285 and 286.3 eV) with a peak area ratio of 2.3 (stoichiometric ratio = 3).

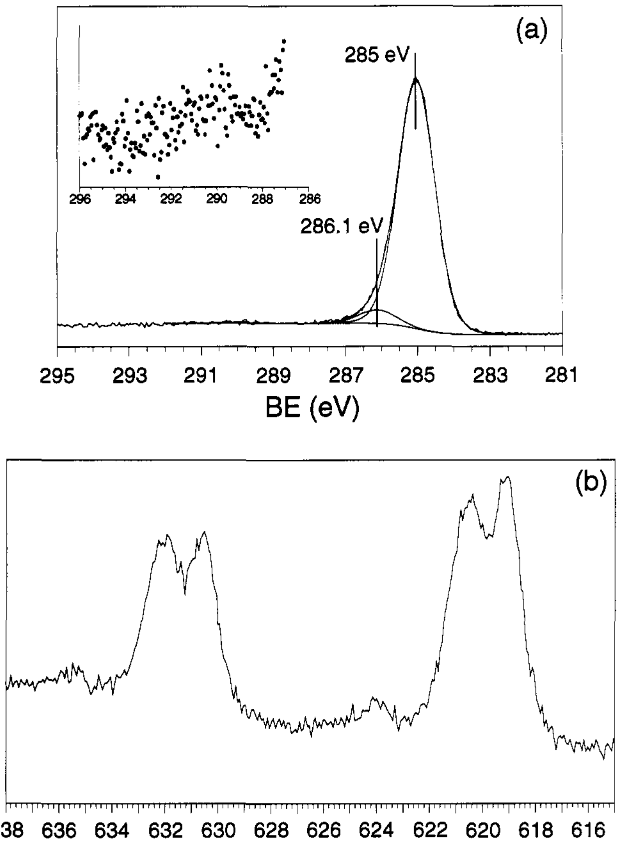

Figure 2. High-resolution (a) C_{1s} and (b) I_{3d} XPS spectra of iodine-doped PcB. PcB was doped with iodine vapor for 30 min. Details of the degree of iodine incorporation and the least-sqaures curve-fitting results for the $I_{3d5/2}$ spectrum of iodine-doped PcB are in Table II.

unambiguously demonstrate that PcB is doped by iodine similarly to polyisoprene in all except one respect; PcB shows a greater reactivity toward oxygen upon doping. It is not clear whether this occurs during doping (due to reaction with the residual air in the glovebox) or as a consequence of exposure of the doped polymer to atmosphere during sample transfer to the spectrometer.

The conductivity of the iodine-doped polymers before introduction into the spectrometer was ~10^{-5} S cm^{-1} for PcIP and PtIP and ~10^{-6} S cm^{-1} for PcB. After XPS analysis, the conductivity of the doped films was too low to be measured with our experimental setup. Upon being exposed to iodine vapor after XPS analysis, the polymers regained their original levels of conductivity. These results are consistent with the previously reported loss of conductivity of iodine-doped PcB upon storage in air or vacuum.[9] We followed the loss in conductivity of iodine-doped PcIP as a function of storage in air and vacuum. These results are shown in Figure 3. The maximum conductivity for PcIP agrees with those reported by other authors,[7-9] with the sole exception of Thakur.[3] Loss of conductivity is faster in vacuum than in air, which is consistent with the absorption of excess iodine by diffusion during doping. The loss of conductivity upon storage in air or vacuum observed in this study and by Petit et al.[9] suggests that excess iodine (i.e., not present simply as a counterion to the carbocationic species) is implicated in the observed conductivity. This is further suggested by the fact that these conductivity values are typical for ionically doped polymer systems[19] and iodine crystals.[20]

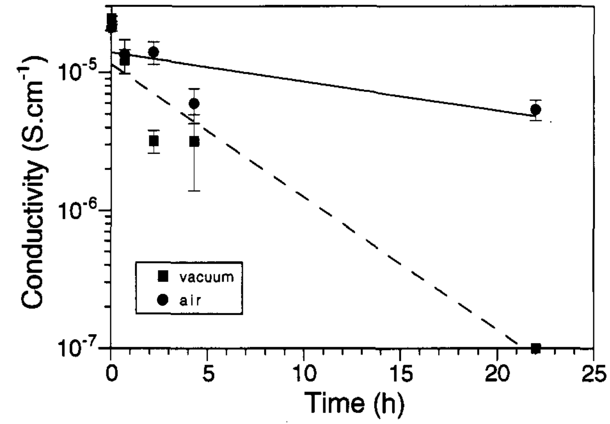

Figure 3. Loss of conductivity as a function of storage time in air (filled squares) and in vacuum (filled circles) for PcB and PcIP. Polymers were doped for 1 h.

To investigate the role of excess iodine in the conductivity of iodine-doped PcB and polyisoprene, polymer films were doped with iodine, immediately cooled to −80 °C in the preparation chamber of the spectrometer to freeze excess iodine, and analyzed by XPS. The sample conductivity was also measured, before and after XPS analysis. We note that the XPS results for iodine-doped PcIP and PtIP at −80 °C are essentially identical (see Table II). The XPS survey spectrum of iodine-doped PcIP analyzed at −80 °C is shown in Figure 4a; the survey spectrum of the same sample analyzed after storage at a pressure of ≤10^{-5} Torr for ≥12 h at 25 °C is shown in Figure 4b. The samples maintained at −80 °C during pumpdown and XPS analysis are effectively frozen and should retain excess iodine, while the samples exposed to a prolonged pumpdown under

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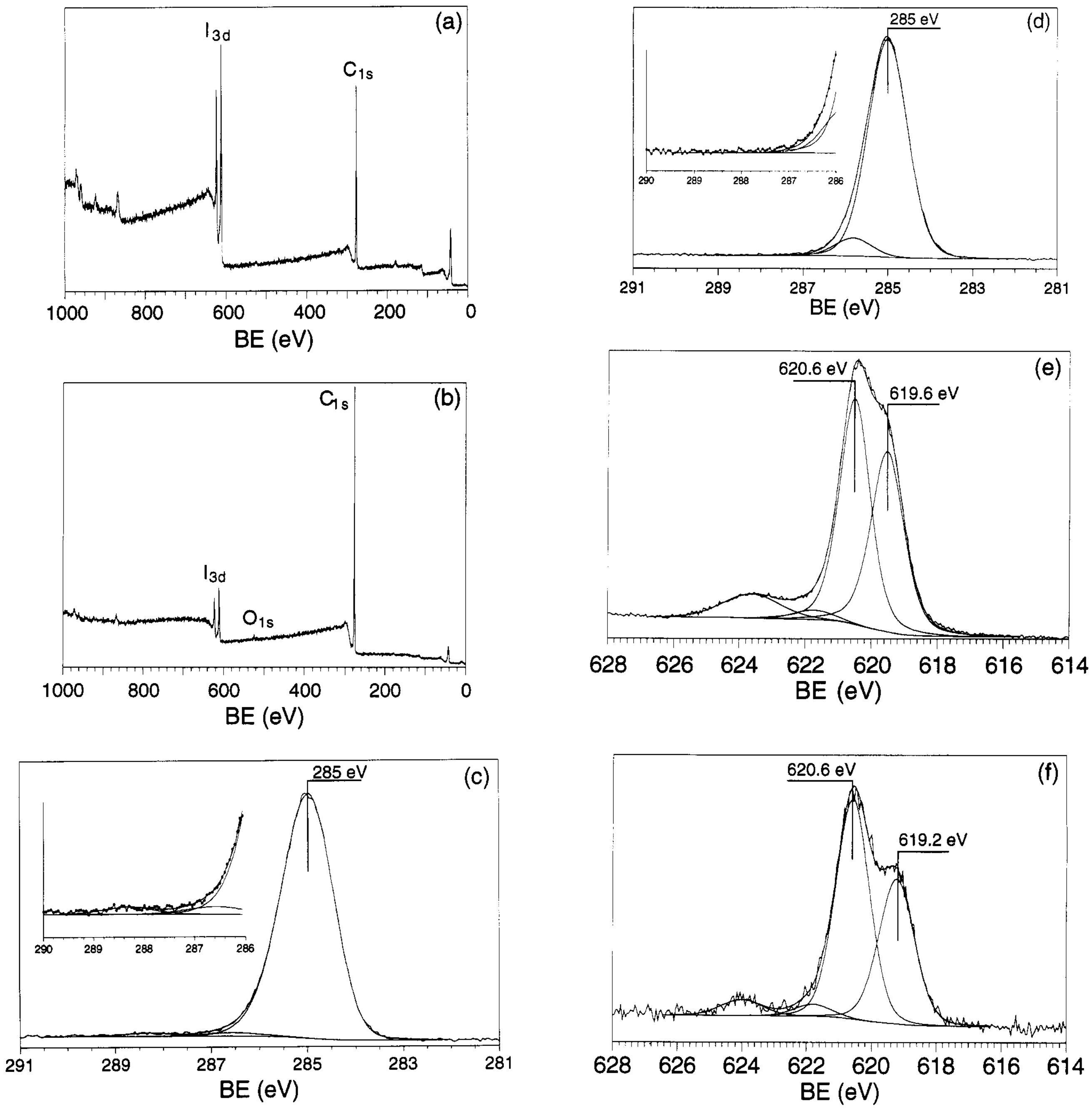

Figure 4. XPS results of iodine-doped PcIP: (a, c, and e) immediately following doping, while maintaining the sample at −80 °C during analysis; (b, d, and f) the same sample, after analysis at −80 °C, was stored at $\leq 10^{-5}$ Torr for ≥ 12 h at 25 °C and then reanalyzed by XPS. Spectra in panels (a) and (b) are survey scan spectra; (c) and (d) are high-resolution C_{1s} spectra; (e) and (f) are $I_{3d5/2}$ spectra. The sample was doped with iodine vapor for 1 h in an argon atmosphere.

vacuum would be expected to lose weakly absorbed iodine. This is indeed the case, as shown by comparing the I:C ratio for iodine-doped PcIP maintained at −80 °C for the duration of the XPS analysis (Figure 4c) with a sample that was stored under vacuum at ambient temperature before XPS analysis (Figure 4d); the I:C ratio decreases five-fold when the sample is maintained at 25 °C at a pressure of $<10^{-5}$ Torr (see Table II for details). We also note that the conductivity of the sample whose spectrum is shown in Figure 4c is $\sim 10^{-5}$ S cm^{-1}, while samples stored under vacuum typically have a conductivity of $<10^{-7}$ S cm^{-1}.

Relatively subtle differences are observed between the C_{1s} spectrum of iodine-doped PcIP maintained at −80 °C (Figure 4c) and the sample exposed to prolonged vacuum at 25 °C (Figure 4d). In both cases, a minor peak centered ~0.8–1.0 eV higher than the primary hydrocarbon peak (285 eV) is observed. We note that the BE shift of this peak is somewhat higher than that reported by Salaneck et al. for iodine-doped polyacetylene.[17] As we have noted earlier, the position of this peak is consistent with a electropositive carbon atom, and may be due to a radical cation.

The I_{3d} spectra of iodine-doped PcIP (and PtIP) frozen at −80 °C clearly differ from that of a doped sample that has been exposed to prolonged vacuum. The survey spectra show that upon exposure of a freshly doped sample to prolonged vacuum, the iodine incorporation decreases five fold from ~10 at. % to ~2 at. %. In addition to the decrease in intensity of the I_{3d} photoemission line (relative to the C_{1s} line), the I_{3d} spectral line shape also changes dramatically. Detailed results of peak fits of the $I_{3d5/2}$

spectra for PcIP and PtIP are in Table II. We note that the results for PcIP and PtIP are identical; the $I_{3d5/2}$ spectra of PcIP analyzed at −80 °C and after exposure to prolonged vacuum are shown in Figures 4e,f, respectively.

The $I_{3d5/2}$ spectrum of the sample frozen at −80 °C immediately after iodine doping can be resolved with peaks at 619.6, 620.6, 622.4, and 624 eV. The intensities and peak centers of the latter two peaks suggest that they are shakeup satellites associated with the two major peaks.[17] Upon prolonged exposure to vacuum (Figure 4f), the peak at 619.6-eV shifts 0.4 eV lower and is observed at 619.2 eV. Similarly, the shakeup satellite associated with this peak also shifts 0.4 eV lower to 622 eV. We make the following assignments to account for these peaks: at high iodine concentration, the primary iodine species present are molecular iodine (I_2) and I_2 complexed with I_3^- to form I_5^-. The former species appears at 620.6 eV, while the latter species appears at 619.6 eV. Upon loss of excess iodine, the I_5^- species is converted to I_3^-, which appears as a peak at 619.2 eV (Figure 4f). The assignment of the peak at 619.2 eV to an I_3^- species is based upon the XPS analysis of tetrabutylammonium triiodide (see Table II for summarized XPS results). While the compound, as received, was not purely triiodide, the dominant peak (~70% peak intensity in the resolved $I_{3d5/2}$ spectrum) was centered at 619 eV. We further note that the BEs of I_2, I_5^-, and I_3^- would be expected to follow $BE(I_2) > BE(I_5^-) > BE(I_3^-)$.

The presence of I_5^- in samples that display conductivities of $\sim 10^{-5}$ S cm^{-1} suggests that the iodine is present in the form of anionic polyiodide chains of I_2 and I_5^- species. Prolonged exposure of iodine-doped PcIP (and PtIP) to a vacuum of $\geq 10^{-5}$ Torr does not result in a complete loss of the I_2 species. The intensity of the I_{3d} line decreases with respect to the C_{1s} line, but even after 15-h exposure to vacuum, the relative intensity of I_2 is ~50% of the peak corresponding to I_3^-. The total concentration of iodine drops sufficiently so that the primary species present, i.e., I_3^- and I_2, cannot interact to form polyiodide chains of sufficient length to confer substantial conductivity to the doped samples. The I_{3d} spectra of the doped polymers also rules out the presence of a significant concentration of iodonium π-complex. This is because such a cationic species would be present as a peak with a BE of ≥622 eV. Though curve resolution of the $I_{3d5/2}$ spectra of the doped polymers reveals the presence of two peaks at 622 and 624 eV, the intensities and positions of these peaks suggest that they are shakeup satellites associated with the two major peaks in the spectra.

Discussion

There are three possible mechanisms for the observed conductivity of iodine-doped nonconjugated hydrocarbon polymers: an electronic, ionic, or a mixed ionic–electronic mechanism. We first review the available evidence from previous studies and then discuss our results within the context of these mechanisms.

There are (at least) three possible mechanisms by which iodine-doped nonconjugated polymers may be electronic conductors. The first, proposed by Thakur, is by the creation of radical cations.[3-5] Evidence in support of this mechanism rests in part on the weakening of bands corresponding to double bonds at 836 and 1673 cm^{-1} and the observation of a new peak at 1545 cm^{-1} in the IR spectrum of iodine-doped PcIP. This latter band was assigned to a radical cationic species by Thakur.[3] We note that Shang et al. did not observe the band at 1545 cm^{-1} and report only a modest weakening of bands corresponding to the double bond in the mid-IR spectrum of iodine-doped PcB.[8] Though the NMR and electron spin resonance results of doped PcIP have been touted by Thakur as supportive of a radical cationic mechanism,[5] these results have been disputed by Shang et al.[8] Furthermore, we note that recent valence-effective Hamiltonian (VEH) band structure calculations by Shuai and Bredas indicate that the formation of radical cations by oxidation with iodine is unlikely, based on the solid-state ionization potentials calculated for the cis and trans isomers of polybutadiene and polyisoprene,[21] a possibility that was previously suggested by Suh and Wnek.[7] Our C_{1s} XPS results indicate that electropositive carbon species are present in the doped polymers. These species may be the radical cationic species proposed by Thakur et al. However, we do not believe that this species is the charge carrier. This is because the XPS and conductivity measurements strongly implicate excess iodine as the charge carrier; pertinent results are discussed later in this section.

The second mechanism by which charge transport could be electronic in nature is by the intersite hopping of iodonium π-complexes. This mechanism has been postulated by Shang et al.,[8] based on the similarities in the visible, near-IR, and far-IR results of iodine-doped PcB with those of π-bridged complexes observed elsewhere. We note that Shang et al. observed that the far-IR and UV results indicate the presence of I_3^- species. It is, therefore, curious that they believe the iodonium π-complex to be the charge carrier rather than a polyiodide species. Orlandi and Zerbetto have performed semiempirical MNDO normal-mode analyses for a butadiene dimer and its doped derivatives, namely, the radical cation, the iodonium π-complex, and the iodo cation (σ-complex).[22] Their results were ambiguous in terms of supporting either of these mechanisms. On the basis of their calculations, they concluded that the changes in the mid-IR region of doped PcB could only be explained by the formation of radical cations, while those observed in the far-IR region were explained by iodonium π-complex formation. Our XPS results suggest that iodonium π-complexes are not present in significant concentration in the doped polymers and are thus unlikely to be the primary charge carrier.

The third mechanism by which charge transport could be electronic in nature is by the iodine-catalyzed isomerization of nonconjugated polybutadiene and polyisoprene to conjugated polyacetylene, originally suggested by Suh and Wnek.[7] The changes in the resonance Raman spectrum of PcIP upon iodine doping have been attributed to such an isomerization.[23] We, however, note that I_3^- species were also observed in these spectra,[23] but that no attempt was made to delineate between the effect of polyiodides and "polyacetylene" units on the conductivity of iodine-doped PcIP. Definitive proof that iodine catalyzes isomerization of PcIP to polyacetylene by the mechanism postulated by Williams and Gerard[23] would require the direct observation of loss of HI from the halogenated intermediate in the isomerization of polyisoprene to polyacetylene. Our results argue against this mechanism for the following reasons: first, we note that the shakeup satellites in the C_{1s} spectra of iodine-doped

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(21) Shuai, Z.; Bredas, J. L. *Macromolecules* **1991**, *24*, 3724.
(22) Orlandi, G.; Zerbetto, F. *Chem. Phys. Lett.* **1991**, *187*, 641.
(23) Williams, K. P. J.; Gerard, D. L. *Polym. Commun.* **1990**, *31*, 290.

poly(acetylene)[17] do not appear to be present in the C_{1s} spectra of the iodine-doped nonconjugated polymers; second, the radical cations responsible for carrier transport should be unaffected by vacuum. The observation that conductivity is lost upon storage of doped samples in vacuum and subsequently regained upon exposure to iodine vapor strongly precludes this mechanism.

We believe that the conductivity of iodine-doped polybutadiene and polyisoprene is caused by excess iodine present in these systems. We have clearly established, through XPS analysis of cryogenically cooled, doped polymers, that excess iodine is associated with conductivity; the loss of conductivity in this system upon storage in vacuum (or air) is directly correlated with the loss of iodine. The presence of an initial five-fold excess of iodine, observed spectroscopically, is associated with a conductivity of 10^{-4}–10^{-5} S cm^{-1} in these polymers. With prolonged storage under vacuum, excess iodine is lost and the conductivity drops to $<10^{-7}$ S cm^{-1}. Subsequent exposure of these films to iodine vapor results in a rise in the conductivity to their original values (i.e., prior to prolonged pumpdown under high vacuum). These results strongly indicate that excess iodine is the charge carrier. We also note that the observed conductivity in the range of 10^{-4}–10^{-5} S cm^{-1} is consistent with the conductivity levels observed in ionically conducting systems.[19,20] This process is also accompanied by clear and reproducible changes in the core-level spectral line shape of iodine. High-resolution XPS reveals that immediately following doping, iodine is present as a mixture of I_2 and, we postulate, I_5^- moieties. We suggest that polyiodide chains comprising I_5^- and I_2 moieties are responsible for charge transport in the doped polymers. Storage under vacuum results in loss of a substantial fraction of molecular iodine; the BE shift in the I_{3d} spectrum to lower BE (a shift of 0.4 eV in the resolved $I_{3d5/2}$ spectrum in comparison with samples with excess iodine) is consistent with the BE of I_3^-. Thus, the residual iodine in the samples that have been stored under vacuum is present as a mixture of I_2 and I_3^-. The formation of polyiodide chains of I_2 and I_3^- is hindered by the low overall iodine concentration, resulting in loss of conductivity. The actual mechanism by which conductivity occurs in polyiodide anions appears to be unclear, though "superionic-like" conductivity[24] based on the virtual movement of anions and little displacement of nuclei may well account for the conduction mechanism in these and related systems (e.g., polyiodide salt complexes of polymers).[19]

Finally, we note that it is not possible to exclude a minor contribution to the observed conductivity from one of the electronic mechanisms that have been postulated, though the loss of conductivity after storage of the iodine-doped polymers under vacuum, and the reversibility of this process after reexposure to iodine is incompatible with charge transport being primarily through the partcipation of radical cations or iodonium ions. The contribution to the overall conductivity by one of these mechanisms is likely to be less than 1% of the total conductivity, simply based upon the observed loss of conductivity in this system as a function of loss of excess iodine.

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