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Unocupied electronic states in polythiophen as probed by XAS and RAS

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ABSTRACT

Polythiophene is a typical conducting polymer. Unoccupied electronic states near the Fermi level of polythiophene polycrystalline powder were probed using S 1s X-ray absorption spectroscopy (XAS) and S *KL*2,3*L*2,3 resonant Auger spectroscopy (RAS). Its overall XAS spectral shape resembles those of 2,-2_-bithiophene and *α*-terthiophene polycrystalline powder. No energy shifts were observed in the *π*∗ and *σ*∗(S–C) states. In contrast, it was observed that the position of *σ*∗(C–C) resonance slightly shifts to lower energy concomitantly with the increase of thiophene repeating units. The normal Auger yield spectrum shows the lack of a delocalized peak, which suggests *π*∗-electrons remain localized at each thiophene unit during the S 1*s* core-hole lifetime of *ca* 1.1 femtoseconds. Although *π*∗ and *σ*∗(S–C) states in XAS are not resolved because of their overlap of electronic transitions, they were separated by plotting spectator Auger yields as a function of excitation energy. Such unresolved states in XAS are demonstrated to be distinguishable using RAS technique if the Auger spectator shifts of the corresponding states differ mutually. Results of this study underscore that excitation energy-dependent RAS can overcome the limitation of conventional XAS.

Keywords:
Polythiophene; bithiophene; terthiophene; X-ray absorption spectroscopy; Resonant Auger spectroscopy

INTRODUCTION

Organic electrically conducting polymers are widely regarded as promising materials for low-cost fabrication of photonic devices.[1] Such polymers are characterized by π-conjugated systems: long range delocalization of π-electrons governs their electrical and optical properties. The band structures of conjugated polymers originate from the interaction of the π-orbital of the repeating units along the chain.[2] However, it is difficult to determine whether low conducting properties are caused by intrinsic differences in electronic structure or by short conjugation lengths resulting from disorder. More information related to the electronic structure of conducting polymer is necessary to understand the conduction mechanism and to support future applications.

For probing unoccupied partial density of states (DOS), X-ray absorption spectroscopy (XAS) is commonly used.[3] However, XAS cannot distinguish localized and delocalized conduction band states without any theoretical approach. In a metal system, plotting the normal Auger yields around the XAS region exhibit an unoccupied conduction band state near the Fermi level (E_F).[4] More recently, we have demonstrated that the degree of delocalization of the unoccupied conduction band in a polymer system is obtainable by plotting the spectator (localization) and normal (delocalization) Auger intensities in resonant Auger spectroscopy (RAS) as a function of the photon energy.[5]

In a polymer system, RAS spectra can be interpreted on the basis of two competing decay channels: core-hole decay (e.g. S 1*s* core-hole lifetime is *ca* 1.1 femtoseconds[6]) and core-excited resonant electron delocalization. If the resonantly excited electron remains sufficiently long to be localized in the vicinity of a core hole site during the core-hole decay, the decay process results in final states of two holes with one electron (2h1e), known as 'spectator Auger'. Alternatively, if it delocalizes to the conduction band prior to the core-hole decay, the decay process results in final states of two holes (2h), known as 'normal Auger'. For that reason, if a polymer has a 'fast' delocalized conduction band state, an excited electron can delocalize along the polymer chain before core-hole decay. Consequently, the normal Auger yields exhibit the conduction band structure, similarly to the metal system.[4] Such 'fast' delocalization is comparable to the Fermi velocity of a typical metal.[5] Thus, delocalization of an initially localized core excited state around absorption atom as monitored by RAS is indicative of band conduction mechanism, where electrons are free to move in the conduction band.

Here, it is noteworthy that RAS includes time information, where the delocalization of a resonantly excited electron occurs on a comparable timescale as a core-hole lifetime. In the much slower electron delocalization compared to the core-hole lifetime, RAS spectra would indicate the electron localization on a monomer unit, even if ground-state unoccupied orbitals are delocalized along a polymer chain. Thus, RAS can monitor the electron delocalization through the conduction band on the time scale of core-hole lifetime[6] ranging from femtoseconds (10−15 s) to attoseconds (10−18 s).

In this study, we applied RAS to investigate partial DOS in the empty conduction band of polythiophene (PT). PT is a typical conducting polymer and it is interesting to note electron-transport behavior through $\pi*$-molecular orbitals delocalized along the polymer chain. The electron-transport property was monitored by Sulphur 1s core excitation in which the S 1*s* core-hole lifetime is *ca* 1.1 femtoseconds.[6] We have demonstrated that excitation energy-dependent RAS can overcome the limitations of conventional XAS.

EXPERIMENTAL

We used PT polycrystalline powder (Aldrich Chemical Co. Inc.) to investigate the electronic states of the conducting polymer. Oligothiophenes of 2,2-bithiophene (2T) and α-terthiophene (3T) (Tokyo Chemical Industry Co., Ltd.) were used to elucidate the propertiesofmore complex PT systems. The as-receivedpowdered samples were placed on conductive carbon tape. Experiments were performed at the beamline BL–27A of the Photon Factory, High Energy Accelerator Research Organization (KEK–PF) in Tsukuba. The BL–27A is equipped with an InSb(111) double-crystal monochromator with energy resolution of *ca* 0.8 eV around S *K*-edge. The Auger spectra were measured using a hemispherical analyzer [CLASS–100; Vacuum Science Workshop (VSW)] with a pass energy of 44 eV. The XAS spectra were measured using monitoring sample drain current near the S *K*-edge (2465–2500 eV). Such energies were chosen to excite the S 1*s* core electron to unoccupied orbitals of PT.

RESULTS AND DISCUSSION

Figure 1 shows the S *K*-edge XAS of PT compared to those of 2T and 3T. Peak 1 can be assigned to S 1*s* → $\pi*$ (4b1) and $\sigma*$(S–C) unoccupied states and peak 2 to $\sigma*$(C–C) based on the previous XAS studies of thiophene.[7,8] However, even for an isolated thiophene molecule, these states are not resolved in XAS because of closely located $\pi*$ and $\sigma*$ states. Since such $\pi*$ and $\sigma*$ orbitals are perpendicular and parallel to a thiophene ring, respectively, these states are resolved by polarization dependence in adsorbed thiophene systems.[8]

Although overall spectral shapes are very similar in PT, T2, and T3, the $\sigma*$(C–C) resonance slightly shifts to lower energy as increasing thiophene repeating units, which might be related to those in the ground state.[2] In contrast, no energy shift among them in the unoccupied states of $\pi*$(4b1) and $\sigma*$(S–C) was observed, where $\pi*$ (4b1) corresponds to the lowest unoccupied molecular orbital (LUMO).[9] One possible explanation for these differences could be discrepancy of these core-hole effects. The electrons in $\sigma*$(C–C) orbitals could be less affected by the core-hole potentials. Considering that the hybridization of energy levels occurs in PT, the equivalent spectral feature in different chain lengths (PT, T2, and T3) suggests insensitivity of XAS to $\pi*$ delocalization between adjacent molecules in the ground state as arising from the electron localization on the absorption site by the creation of the S 1*s* core hole. Such localization processes have been reported previously for phenyl and thiophene oligomers.[10,11] Similar localizations have also been reported in the gas phase.[12,13]

We measured RAS of PT as a function of photon energy to investigate more details of such delocalization. S *KL*2,3*L*2,3 RAS spectra of PT are shown at typical energies in Fig. 2. Interestingly, three Auger peaks are clearly observed at the $\pi*$(4b1) and the $\sigma*$(S–C) unoccupied states in XAS (peak 1 in Fig. 1). Peak 'C' is assigned to normal Auger by comparison with Auger spectra above the S 1*s* ionization potential. Peaks 'A' and 'B' are assigned to spectator Auger features, which are shifted to higher kinetic energy than the normal Auger, because of the screening interaction of a core hole with the localized spectator electron. This shift indicates that a spectator electron is caught in the localized empty state during Auger decay. The peak ‘B’ can be assigned to *KL*2,3*L*2,3($\pi*$) spectator Auger because peak ‘B’ appears at lower excitation energy than the peak ‘A’. Consequently, peak ‘A’ can be assigned to *KL*2,3*L*2,3 [$\sigma*$(S–C)] spectator Auger.

The 2100–2125 eV region of the S *KL*2,3*L*2,3 spectra were fitted with three Gaussian-shaped components. Figure 3 shows that partial yields for each Auger final state were obtained at each excitation energy from Gaussian peak areas. The normal Auger yield spectrum shows a step-like continuum, which is characteristic of free atoms.[14] In general, following Auger decay, the final state is reached, which is the same as that produced in the normal Auger, if the spectator electron delocalizes to an empty conduction band before the core-hole decay. The lack of a delocalized peak suggests $\pi*$-electrons remain localized at each thiophene unit during the core-hole decay.

The conduction band of conjugated polymer is attributed to delocalization via interaction of adjacent $\pi*$-orbitals of the repeating units along the chain. Nevertheless, no band-like state was observed in the normal Auger yield spectrum of PT, which suggests that ring–ring interactions between neighboring units would not be strong enough. This is in agreement with the previous results of gas-phase biphenyl.[13] In addition, PT is poorly conjugated[15] because thiophene rings are not aligned enough in parallel due to the rotation of interunit bond at room temperature. Such disorder also might affect the insufficient $\pi*$ delocalization along the chain in the ground state, which could disturb the ‘fast’ delocalization of a resonantly excited electron.

Figure 3 presents an interesting finding that the closely located $\pi*$ and $\sigma*$ states in XAS are separable using RAS technique. To date, such unresolved states have been probed only by polarization dependence for adsorption systems[8] or angle-resolved technique for isolated systems.[16] In disordered systems such as those of polymers and multilayers, however, the corresponding states are assigned based on the results of the other systems. Results of this study show that such unresolved states in XAS are separable by RAS when the spectator Auger shifts are different in each excited state.

CONCLUSIONS

PT is a typical conducting polymer. Unoccupied electronic states near the Fermi level of PT polycrystalline powder were probed using S 1*s* XAS and S $KL2,3L2,3$ RAS. Its overall XAS spectral shape resembles those of T2 and T3 polycrystalline powder. No energy shifts were observed in the $\pi*$ and $\sigma*$(S–C) states. In contrast, it was observed that the position of $\sigma*$(C–C) resonance slightly shifts to lower energy concomitantly with the increase of thiophene repeating units. The normal Auger yield spectrum shows the lack of a delocalized peak, which suggests $\pi*$-electrons remain localized at each thiophene unit during the S 1*s* core-hole lifetime of *ca* 1.1 femtoseconds. Although $\pi*$ and $\sigma*$(S–C) states in XAS are not resolved because of their overlap of electronic transitions, those were clearly separated by plotting spectator Auger yields as a function of excitation energy. Such unresolved states in XAS can be distinguished using RAS technique, if the Auger spectator shifts of the corresponding states differ mutually. Results of this study underscore that excitation energy-dependent RAS can overcome the limitation of conventional XAS.

Acknowledgments

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Figure Captions

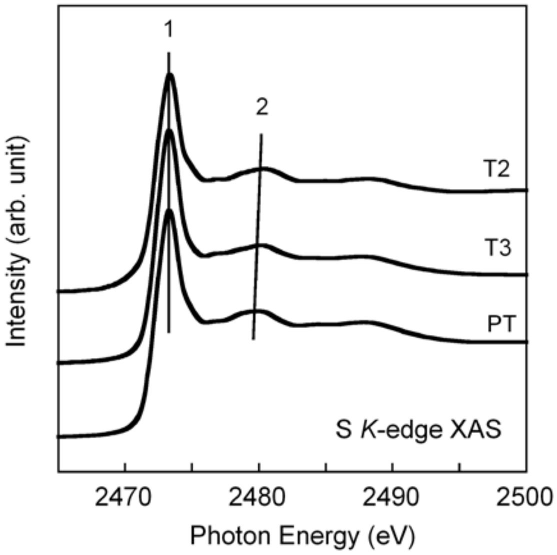

Fig. 1 S *K*-edge XAS spectra for T2, T3, and PT.

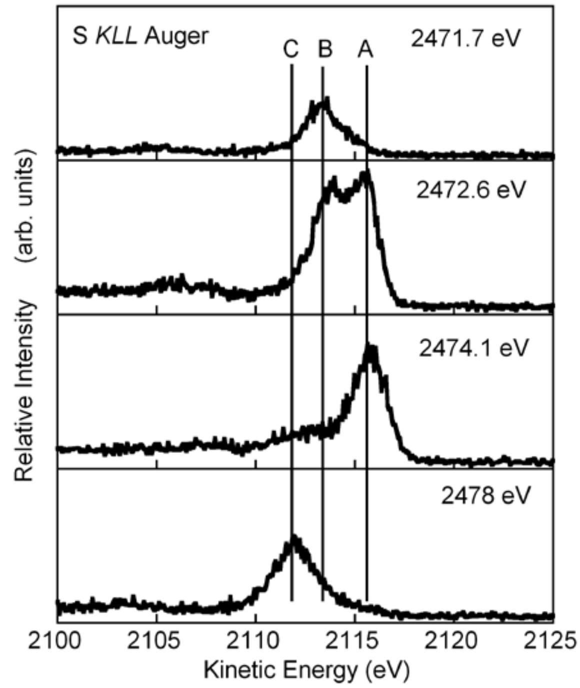

Fig. 2 S $KL_{2,3}L_{2,3}$ resonant Auger spectra for PT at the typical photon energies indicated. Three Auger peaks are visible. Peaks 'A' and 'B' are spectator Auger components, and peak 'C' is a normal Auger component.

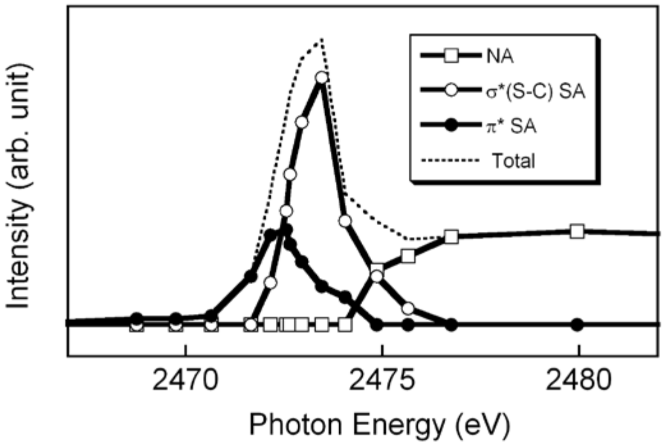

Fig.3 Integrated intensities of $KL_{2,3}L_{2,3}(\pi^*)$ spectator (closed circle), $KL_{2,3}L_{2,3}$ (σ^*(S-C)) spectator Auger (SA, open circle), and normal Auger (NA, open square) components near the S K-edge. The total of Auger yields is shown as doted line, which

is similar to S1s XAS.